Regimes of Decomposition of Clathrate in Natural Strata Purged by Methane

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Abstract. The process of decomposition of a methane clathrate in a finite-length stratum initially saturated with methane clathrate and methane, which is purged by warm methane, is studied. The influence of the initial parameters of the stratum and purging conditions on the evolution of methane clathrate temperature and saturation is examined. The existence of solutions is demonstrated, which predict methane clathrate decomposition both on the frontal surface and in the volume zone.

1. Introduction
In the current paper we consider the features of methane clathrate decomposition at warm methane injection into a stratum of a finite length, saturated initially with methane clathrate and methane. The self-similar solution to the problem on cold methane injection into a stratum, saturated with water and methane, was obtained in [1–4].

2. Basic Equations
Let’s consider a stratum, saturated initially with methane clathrate and methane, whose temperature $T_0$ and pressure $p_0$ meet the condition of stable existence of methane clathrate and methane. Let injection of methane with pressure $p_w$ and temperature $T_w$ ($T_w > T_0$) is started through the left surface of a stratum ($x = 0$). These parameters meet the conditions of joint existence of water and methane, and they are kept constant during the entire process of methane clathrate decomposition into the water and gas. We will assume that there are three zones formed in the porous medium, where water, methane clathrate and methane are in different states. Hence, the pores of the first (nearest) zone are filled with water and methane, and the pores of the third (distant) zone are filled with methane clathrate and methane. The second (transition) zone contains methane clathrate and products of its decomposition (water and methane) in the state of phase equilibrium. At that, there are two moving surfaces $x = x_{i(i)}$ ($i = n, d$), which separate the said zones: surface $x = x_{d(d)}$ separates the third and transition zones and surface $x = x_{n(n)}$ separates the first and transition zones.

To describe the processes of filtration and heat transfer at methane injection into the porous medium, accompanied by methane clathrate decomposition, let’s assume the unitemperature model of stratum, i.e., the temperature of contained substance (water, methane, and methane clathrate) and temperature of the stratum coincide at every point. Let’s also assume that bed porosity is constant; its water, skeleton of the porous medium, and methane clathrate are incompressible, and methane is calorically perfect gas:
Here \( m \) is porosity of the stratum, \( \rho_j \) (\( j = g, h, sk, \) and \( l \)) are true phase densities (subscripts \( g, h, sk, \)) are attributed to the parameters of gas, methane clathrate, skeleton of the porous medium, and water, respectively), \( T \) is temperature of the stratum, \( p \) is pressure of the stratum, \( R_g \) is reduced methane constant. Methane clathrate is the two-species system with mass concentration of methane \( G \).

The conditions of mass conservation for methane and water in the one dimensional statement can be presented as [1, 2]:

\[
\frac{\partial}{\partial t} (m S_g \rho_g) + \frac{\partial}{\partial x} (m S_g v_g \rho_g) = -mG \rho_h \frac{\partial S_h}{\partial t},
\]

\[
\frac{\partial}{\partial t} (m S_l) = -m (1 - G) \rho_h \frac{\partial S_h}{\partial t},
\]

\[ S_g + S_h + S_l = 1, \]

where \( v_g \) is gas phase velocity, \( t \) is time, \( S_j \) is saturation of pores by the \( j \)th phase.

For methane filtration lets’ assume Darcy law:

\[
m S_g \rho_g = -\frac{k_g}{\mu_g} \frac{\partial p}{\partial x},
\]

where \( \mu_g \) is dynamic viscosity methane, \( k_g \) is gas phase permeability:

\[
k_g = k_0 \frac{(m S_g)^3}{(1 - m S_g)^2} \approx k_0 S_g^2, \quad (k_0 = k_o m^3).
\]

Here \( k_0 \) is absolute permeability of the porous medium.

The energy equation can be written as:

\[
\rho c \frac{\partial T}{\partial t} + c_g \rho_g m S_g v_g \frac{\partial T}{\partial x} = \frac{\partial}{\partial x} \left( \lambda \frac{\partial T}{\partial x} \right) + m \rho_h L_h \frac{\partial S_h}{\partial t},
\]

\[ \lambda = (1 - m) \lambda_{sk} + m \sum_{j=g,h} S_j \lambda_j, \]

where \( T \) is temperature of the stratum, \( \lambda_j \) (\( j = sk, g, h, l \)) and \( c_j \) are coefficient of heat conductivity and specific heat capacity of skeleton, methane, methane clathrate and water, values \( \lambda \) and \( \rho c \) are coefficient of heat conductivity and specific volumetric heat capacity of “porous stratum - methane clathrate” system, and \( L_h \) is specific heat of methane clathrate decomposition into the water and gas.

The regions, where methane, water and methane clathrate can be in different states, are formed in the stratum at methane clathrate decomposition. On the surfaces between these regions, where phase saturations, heat and mass flows undergo jumps, the relationships following from the equations of energy balance and mass balance are satisfied [5]:

\[
\left[ m \left( \rho h S_h (1 - G) \right) \dot{x}_{(i)} \right] = 0, \quad \left[ m \left( \rho_g S_g \left( v_g - \dot{x}_{(i)} \right) - \rho_h S_h G \dot{x}_{(i)} \right) \right] = 0,
\]

\[
\left[ \lambda \frac{\partial T}{\partial x} \right] = \left[ m \rho_h L_h S_h \dot{x}_{(i)} \right].
\]
Here \( \psi' - \psi^- \) is the surge of parameter \( \psi \) on surface \( x = x_i \), \( \dot{x}_i \) is velocity of this surface motion, subscripts \( i = d, n \) correspond to values on the distant and nearest surfaces, respectively. The pressure \( p \) and temperature \( T \) on both surfaces are assumed to be continuous.

In the second zone containing water, methane clathrate and methane where methane clathrate decomposition occurs, the equation of phase equilibrium is accepted [6]:

\[
T = T_0 + T_\ast \ln \left( \frac{p}{p_{s0}} \right),
\]

(8)

where \( T_0 \) is temperature of the porous medium in the initial state, \( p_{s0} \) is equilibrium pressure, corresponding to the temperature \( T_0 \), and \( T_\ast \) is empirical parameter that depends on the form of clathrate.

Let the porous medium is initially saturated with methane clathrate and methane, whose temperature and pressure correspond to conditions of stable existence of methane clathrate and methane and they are the same in the whole porous medium:

\[
p = p_0, \quad T = T_0, \quad S_h = \nu \quad (0 \leq x \leq L, \quad t = 0).
\]

(9)

Injection of warm methane is started through the left surface of the porous medium under temperature \( T_w \) and pressure \( p_w \), its values meet the conditions of joint existence of water and methane:

\[
p = p_w, \quad T = T_w \quad (x = 0, \quad t > 0).
\]

(10)

On the right surface of the porous medium, we impose conditions modeling the absence of the heat flow and constant pressure:

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

(11)

Applying the equation of the methane state and Darcy law to relations (2) and (6) and assuming that the characteristic temperature drops in the porous stratum are insignificant, we can get the equations of thermal conductivity and piezoconductivity, total for all porous medium regions:

\[
\frac{\partial p}{\partial t} = \frac{k_g}{m \mu_g S_g} \frac{\partial}{\partial x} \left( p \frac{\partial p}{\partial x} \right) - \gamma R \frac{\partial S_h}{\partial t},
\]

(12)

\[
\frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left( \kappa^{(T)} \frac{\partial T}{\partial x} \right) + \frac{c_g k_g}{\mu_g \rho c} \frac{\partial p}{\partial x} \frac{\partial T}{\partial x} + \Delta T \frac{\partial S_h}{\partial t},
\]

(13)

where \( \gamma R = \frac{G \rho h R_g}{1 - S_{10}}, \quad \Delta T = m \frac{\theta h L_i}{\rho c}, \quad \kappa^{(T)} = \lambda / \rho c \).

In the transition zone, where the temperature \( T \) and pressure \( p \) of the stratum are connected by the conditions (8):

\[
\frac{\partial T}{\partial x} = \frac{T_\ast}{p} \frac{\partial p}{\partial x}, \quad \frac{\partial^2 T}{\partial x^2} = \frac{T_\ast}{p} \frac{\partial^2 p}{\partial x^2} \quad \frac{T_\ast}{p^2} \left( \frac{\partial p}{\partial x} \right)^2.
\]

Using the last relationships, from the conditions (12) and (13) we obtain the equations describing distributions of methane clathrate saturation and pressure in the transition zone of the porous medium:
\[
\frac{\partial p}{\partial t} = \frac{k_g}{m \mu_g S_g} \frac{\partial}{\partial x} \left( p \frac{\partial p}{\partial x} \right) - \frac{RT}{\Delta T} \frac{\partial^2 T}{\partial x^2} + \frac{c_g k_g R}{\mu_g \rho c} \frac{p}{\Delta T \cdot R_g} \frac{\partial p}{\partial x} \frac{\partial T}{\partial x}, \quad (14)
\]

\[
\frac{\partial S_h}{\partial t} = \frac{1}{\Delta T} \left[ \frac{\partial T}{\partial t} - \frac{\partial}{\partial x} \left( \kappa(T) \frac{\partial T}{\partial x} \right) - \frac{c_g k_g p}{\mu_g \rho c \cdot R_g} \frac{\partial p}{\partial x} \frac{\partial T}{\partial x} \right]. \quad (15)
\]

Since, methane clathrate decomposition occurs within the transition zone, we will assume that on the nearest surface of clathrate decomposition \( x = x_{(n)} \) there is the surge of methane clathrate saturation from \( S_{h(n)}^- = 0 \) to \( S_{h(n)}^+ > 0 \). Using relationships (7), we obtain the balance equations the energy and methane mass:

\[
\frac{k_g^+}{\mu_g} \left( \frac{\partial p}{\partial x} \right)_{(n)}^+ - \frac{k_g}{\mu_g} \left( \frac{\partial p}{\partial x} \right)_{(n)}^- = m \dot{x}_{(n)} \left[ S_{g(n)}^- - S_{g(n)}^+ - \frac{\rho_h G S_{h(n)}^+}{\rho_g(n)} \right], \quad (16)
\]

\[
\lambda \left( \frac{\partial T}{\partial x} \right)_{(n)}^+ - \lambda \left( \frac{\partial T}{\partial x} \right)_{(n)}^- = m \rho_h L_h S_{h(n)}^+ \dot{x}_{(n)}. \quad (17)
\]

Hereinafter the subscripts “plus” and “minus” are attributed to the values before and after the surface, respectively.

On the distant surface of clathrate decomposition \( x = x_{(d)} \) the value of methane clathrate saturation \( S_h \) is assumed continuous and equal to initial methane clathrate saturation of the porous medium. Then, on the basis of equations (7) the balance equations for the heat and methane mass on this surface take form:

\[
\left( \frac{\partial p}{\partial x} \right)_{(d)}^- = \left( \frac{\partial p}{\partial x} \right)_{(d)}^+, \quad \left( \frac{\partial T}{\partial x} \right)_{(d)}^- = \left( \frac{\partial T}{\partial x} \right)_{(d)}^+. \quad (17)
\]

The method of front capture by nodes of the spatial grid was used for solution to problem (12)–(15) with initial and surface Equations (9)–(11) and equations on moving surfaces of clathrate decomposition (16) and (17).

### 3. Results

For parameters describing the “porous stratum - methane clathrate” system, the following values were adopted: \( L = 1 \text{ m}, \ k_0 = 10^{-14} \text{ m}^2, \ v = 0.2, \ T_0 = 280 \text{ K}, \ p_0 = 4 \text{ MPa}, \ T_w = 290 \text{ K}, \ p_w = 7 \cdot 10^6 \text{ Pa}, \ G = 0.13, \rho_{da} = 5.45 \cdot 10^6 \text{ Pa}, \ T_* = 10 \text{ K}, \ R_g = 530 \text{ J/(K·kg)}, \ c_g = 1560 \text{ J/(K·kg)}, \rho_h = 900 \text{ kg/m}^3, \ \lambda_h = 2.2 \text{ W/(m·K)}, \ c_h = 2000 \text{ J/(K·kg)}, \rho_l = 1000 \text{ kg/m}^3, c_l = 4000 \text{ J/(K·kg)}, \dot{\lambda}_t = 0.6 \text{ W/(m·K)}, \rho_{sk} = 2.1 \cdot 10^3 \text{ kg/m}^3, \ c_{sk} = 900 \text{ J/(K·kg)}, \mu_g = 10^{-3} \text{ kg/(m·sec)}, \ \lambda = 2 \text{ W/(m·K)}, \rho_c = 2.5 \cdot 10^6 \text{ J/(K·m}^3), \ L_h = 4.5 \cdot 10^7 \text{ J/kg} [7–8].

Distributions of methane clathrate saturation and temperature of the system (solid lines) are shown in figure 1. The initial value of pressure in the reservoir was taken \( p_0 = 6 \cdot 10^6 \text{ Pa}. \) The dashed line is the equilibrium temperature of the stratum. According to the figure, at above listed values temperature and pressure of injected methane clathrate decomposition until \( t \approx 4 \cdot 10^5 \text{ sec} \) occurs on the frontal boundary.

However, formation of the volume zone of methane clathrate decomposition is observed then. This is due to the fact that at injection there is a heat flow from the left surface deep into the porous medium, which causes a temperature increase in the zone saturated with methane clathrate and...
methane and formation of the volume zone of methane clathrate decomposition. At that, two moving surfaces are formed; one of these surfaces by moment \( t \approx 5 \times 10^4 \) sec reaches the right surface of the porous medium. Then, two zones exist in the porous medium: the first (nearest) one saturated with water and methane and the distant (second) one containing methane clathrate and products of its decomposition (water and methane); they are separated by the only moving surface. Thus, at methane purging of the porous medium clathrate decomposition occurs firstly on the frontal boundary and then, in the volume zone of methane clathrate decomposition.

![Figure 1](image)

**Figure 1.** Distributions of methane clathrate saturation and temperature (numbers on curves – time in hours).

4. Conclusion
The process of methane clathrate decomposition in a porous medium, initially saturated with methane and methane clathrate, was studied for the case of warm methane purging of the stratum. It is shown that methane clathrate decomposition occurs firstly on the frontal boundary and then in the volume zone.

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