Gas hydrate formation of sulfur dioxide by injection of liquid carbon dioxide into a natural layer saturated with methane and ice

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Abstract. A mathematical model of injection of liquid sulfur dioxide into a natural layer saturated with ice and methane, accompanied by the formation of SO$_2$ gas hydrate on the front surface is presented. The case when the initial state of the system, as well as the pressure and temperature of the injected liquid sulfur dioxide correspond to the thermobaric conditions of the existence of sulfur dioxide gas hydrate is considered. That, the formation of sulfur dioxide gas hydrate occurs on the front surface, coinciding with the surface of methane displacement by sulfur dioxide. In this case, two characteristic zones are formed in the layer. In the first (near) zone the pores are saturated with sulfur dioxide and its gas hydrate, in the second (far) zone it is saturated with ice and methane. The dependences of the temperature and the coordinates of the formation border of sulfur dioxide gas hydrate on the injection pressure are explored. It is established that the injection pressure increase causes the rise in temperature and movement speed of the surface of the formation of sulfur dioxide gas hydrate. It is shown that at sufficiently high values of injection pressure and initial layer temperature, the temperature rises above the ice melting temperature at the formation border of sulfur dioxide gas hydrate. This corresponds to the formation of an intermediate region saturated with a mixture of water and methane. It is determined the dependence of the limit value of the sulfur dioxide injection pressure, above which an intermediate region saturated with a mixture of water and methane appears on the initial layer temperature.

1. Introduction.
One of the ways to reduce the emission of sulfur dioxide into the atmosphere is the utilization of sulfur dioxide produced by industrial plants in depleted gas deposits [1, 2]. However, long-term underground storage of gas or liquid in the form of a fluid risks its entry to the surface.

In this regard, the theoretical possibility of underground gas storage in the gas hydrate state is considered [3-8]. Herewith the particular interest is the study of the possibility of underground disposal of sulfur dioxide in the cryolithozone conditions. There are suitable geological objects, namely collectors, covered with a continuous layer of permafrost. Frozen rocks will shield the burial, and low temperatures will contribute to hydrate formation. Due to the effect of slow decomposition of gas hydrates (up to a complete stop) with a decrease in pressure below the pressure of the gas hydrate existence at negative temperatures (the effect of self-preservation of gas hydrates), solid gas hydrate can be stored for a very long time even at pressures and temperatures not corresponding to thermo baric conditions of its existence. In view of the above, gas storage in the gas hydrate state in the
cryolithozone conditions will significantly reduce the probability of trans boundary transfers of sulfur dioxide or its leakage to the surface.

Any relevant technological schemes should be accompanied by calculations according to theoretical models that adequately reflect the real conditions. Mathematical models describing the formation of methane gas hydrates in porous layers accompanied by methane injection are formulated, in particular, in papers [8-10]. In this paper, a mathematical model of the formation of sulfur dioxide gas hydrate during the injection of liquid sulfur dioxide into a layer saturated with ice and methane is investigated. The conditions under which the existence of a zone saturated with a mixture of water and methane is possible are investigated.

2. Problem statement.
In the phase diagram (Figure 1) thermo baric conditions for the stable existence of SO\(_2\) gas hydrate are presented. Here curve 1 corresponds to the three-phase equilibrium between gaseous sulfur dioxide, its gas hydrate and water (ice), curve 2 is the two-phase equilibrium between gaseous and liquid sulfur dioxide, and curve 3 presents the equilibrium between liquid sulfur dioxide, its gas hydrate and water. SO\(_2\) gas hydrate exists above curve 1 and to the left of curve 3, i.e. at sufficiently high pressures and low temperatures. At the upper quadrupole point \(Q_2\) (\(T_Q=285.1\) K and \(p_Q=0.233\) MPa) gaseous and liquid sulfur dioxide, as well as its gas hydrate and water are in equilibrium.

Let the semi-infinite horizontal layer in its initial state be saturated with ice with initial saturation \(S_w\) and methane. We assume that the initial temperature of the formation \(T_0\) is lower than the temperature \(T_Q\) corresponding to the quadrupole point. Therefore, in this case the initial state of the system corresponds to the thermo baric conditions of SO\(_2\) gas hydrate existence. Let us assume that liquid sulfur dioxide is injected through the boundary \((x=0)\), its pressure \(p_e\) and temperature \(T_e\) correspond to the existence conditions of sulfur dioxide gas hydrate.

\[
\begin{align*}
t & = 0: & S_w &= S_{w0}, & T &= T_0, & p &= p_0, & (x \geq 0) \\
x & = 0: & T &= T_e, & p &= p_e, & (t > 0)
\end{align*}
\]

In this paper we consider a model with piston displacement of methane by liquid sulfur dioxide. Then it can be assumed that the formation of sulfur dioxide gas hydrate occurs on the front surface coinciding with the surface of methane displacement by sulfur dioxide. In this case, two characteristic zones are formed in the layer. In the first (near) zone pores are saturated with sulfur dioxide and its gas

![Fig.1. Phase diagram of system «SO2-H2O»](image)
hydrate, in the second (far) zone they are saturated with ice and methane. Such characteristics provoke the appearance of a mobile interfacial surface between the regions, the peculiarity of which is the complete transition of ice to the gas hydrate state (hydrate formation front).

3. Basic equations.

The system of basic equations describing the processes of heat and mass transfer in the layer during injection of liquid sulfur dioxide in the rectilinear-parallel case has the form [8-10]:

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

\[
\rho c \frac{\partial T}{\partial t} + \rho_i c_i m_{S_i} \nu_i \frac{\partial T}{\partial x} = \frac{\partial}{\partial x} \left( r \lambda \frac{\partial T}{\partial x} \right),
\]

\[
m_{S_i} \nu_i = -\frac{k_i}{\mu_i} \frac{\partial p}{\partial x}, \quad k_i = k_0 S_i^3,
\]

\[
\rho_s = \rho_{0_i} \exp(\beta_s (p - p_0)), \quad p = \rho_g R_g T.
\]

There are here: \(x\) - coordinate; \(t\) - time; \(T\) - temperature; \(p\) - pressure; \(m\) - porosity; the subscripts \(i=s, g\) refer respectively to the settings of sulfur dioxide and methane; \(S_i\) - saturation of the pores; \(\rho_i\) is the density; \(\nu_i\) - the actual average speed; \(k_0\) is the absolute permeability of the porous medium; \(k_i\) – phase permeability; \(\beta_s\) - the coefficient of compressibility of liquid sulphur dioxide; \(c_i\) - specific heat capacity; \(\mu_i\) - the dynamic viscosity; \(R_g\) - the gas constant of methane; \(\rho c\) and \(\lambda\) are the effective values of the volumetric heat capacity and heat capacity for a saturated layer.

The relations arising from the conditions of the ice mass balance, sulfur dioxide and methane, as well as the balance of heat are performed at the border between the zones:

\[
-k_s \frac{\partial p}{\partial x} = m \rho_{S_i} S_i G + S_i V_n,
\]

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

\[
m_{S_0} \rho_h (1-G)V_n = m_{S_{w0}} \rho_w V_n,
\]

\[
\lambda \frac{\partial T}{\partial x} - \lambda \frac{\partial T}{\partial x} = m \rho L_h S_n V_n.
\]

\(G\) presents the relative mass concentration of sulfur dioxide in the gas hydrate; \(S_{w0}\) is the initial water saturation of the layer; \(L_h\) presents the specific heat of \(SO_2\) gas hydrate formation from liquid sulfur dioxide and water; the subscripts \(j=1,2\) refer respectively to the parameters in the regions 1 and 2; \(V_n\) is the speed of the formation border of sulfur dioxide gas hydrate. Here and further, the subscript \(n\) refers to the parameters on the surface between the zones, and the subscripts \(h\) and \(w\) refer respectively, to the parameters of gas hydrate and ice.

According to the water mass balance state (the third ratio of the system (3)) for the value of hydrate saturation in the first zone we have:

\[
S_h = \frac{\rho_{w0} S_{w0}}{\rho_h (1-G)}.
\]

On the basis (2) the equations of piezoconductivity and temperature conductivity in each layer zone will be written in the form:
\begin{align}
\frac{\partial p(t)}{\partial t} &= \chi^{(p)}(t) \frac{\partial}{\partial x} \left( \frac{\partial p(t)}{\partial x} \right), \\
\frac{\partial T(t)}{\partial t} &= \chi^{(T)}(t) \frac{\partial}{\partial x} \left( \frac{\partial T(t)}{\partial x} \right) + \chi^{(T)}(t) X(t) \frac{\partial p(t)}{\partial x} \frac{\partial p(t)}{\partial x}, \\
\frac{\partial p_2(t)}{\partial t} &= \chi^{(p)}(t) \frac{\partial}{\partial x} \left( \frac{\partial p_2(t)}{\partial x} \right), \\
\frac{\partial T_2(t)}{\partial t} &= \chi^{(T)}(t) \frac{\partial}{\partial x} \left( \frac{\partial T_2(t)}{\partial x} \right) + \chi^{(T)}(t) X_2(t) \frac{\partial p_2(t)}{\partial x} \frac{\partial T_2(t)}{\partial x},
\end{align}

где 
\[ \chi^{(p)}(t) = \frac{k_s}{\mu_m (1 - S_h) \beta_s}, \quad \chi^{(p)}(t) = \frac{k_s p_0}{\mu_m (1 - S_{w_0})}, \quad \chi^{(T)} = \frac{\lambda}{\rho c}, \quad X(t) = \frac{p_0 c_s k_s}{\lambda \mu \beta_s}, \]
\[ X_2(t) = \frac{c_s k_s}{2 \lambda R_2 T_0 \mu_t}. \]

4. Self-similar solution.

Let’s introduce self-similar variable: 
\( \xi = \sqrt[4]{\chi^{(T)} \tau} \). For this variable based on (4) and (5) we get solutions for pressure and temperature distribution in each layer zone:
\begin{align}
p(t) &= p_n + \left( p_e - p_n \right) I(\xi, \xi_n; \eta_1), \\
T(t) &= T_n + \left( T_e - T_n \right) I(\xi, \xi_n; \eta_1) \frac{1}{J(0, \xi_n)}, \\
p_2(t) &= p_n^2 + \left( p_n^2 - p_0^2 \right) I(\xi, \xi_0; \eta_2) \frac{1}{J(\xi_0, \infty; \eta_2)}, \\
T_2(t) &= T_0 + \left( T_e - T_0 \right) I(\xi, \xi_0; \eta_2) \frac{1}{J(\xi_0, \infty; \eta_2)},
\end{align}

where \( \eta_j = \chi^{(p)}(1) / \chi^{(T)}(1) (j=1, 2) \) and these integrals are introduced: 
\[ I(a, b; c) = \int_a^b \exp \left( -\frac{\xi^2}{4c} \right) d\xi, \]
\[ J_1(a, b) = \int_a^b \exp \left( -\frac{\xi^2}{4} - X_1 p_1 \right) d\xi, \quad J_2(a, b) = \int_a^b \exp \left( -\frac{\xi^2}{4} - X_2 p_2 \right) d\xi. \]

Based on the relations (3) taking into account the distributions for pressure and temperature (6) and (7), we obtain the relations to determine the self-similar coordinate of the hydrate formation surface \( \xi_n \) and the pressure and temperature values on it:
\[
\left( p_e - p_0 \right) \exp \left( -\frac{\xi^2}{4\eta_{(1)}} \right) \frac{1}{I\left(0, \xi_{(1)}, \eta_{(1)}\right)} = A_{(1)} \xi_{(1)},
\]
(8)

\[
\left( p_0^2 - p_0^2 \right) \exp \left( -\frac{\xi^2}{4\eta_{(2)}} \right) \frac{1}{I\left(\xi_{(2)}, \infty; \eta_{(2)}\right)} = A_{(2)} p_{(0)} \xi_{(2)},
\]
(9)

\[
\left( T_{(1)} - T_e \right) \exp \left( -\frac{\xi^2}{4} - X_{(1)} p_{(0)} \right) J_{(1)}\left(0, \xi_{(1)}\right) - \left( T_0 - T_e \right) \exp \left( -\frac{\xi^2}{4} - X_{(2)} p_{(0)}^2 \right) J_{(2)}\left(\xi_{(2)}, \infty\right) = B \xi_{(1)},
\]
(10)

where \( A_{(1)} = \frac{m \mu \chi^{(T)}_{h}}{2k_{s}} \left( \rho_{h} G S_{h} + \rho_{s} \right), A_{(2)} = \frac{m \mu \chi^{(T)}_{h}}{k_{s}} (1 - S_{s0}), B = \frac{m \rho_{h} L_{h} S_{h}}{2 \rho c} \).

5. Results of calculation.

The Figure 2 shows the dependence of coordinate and border temperature for gas hydrate formation on the injection pressure. For other parameters the following values are accepted:

- \( m = 0.2, S_{s0} = 0.2, T_0 = 272 \text{ K}, T_e = 270 \text{ K}, \rho_0 = 3 \text{ MPa}, k_0 = 5 \times 10^{-15} \text{ m}^2, G = 0.372, \mu_s = 3.68 \times 10^{-4} \text{ Pa} \cdot \text{s}, \mu_e = 1 \times 10^{-4} \text{ Pa} \cdot \text{s}, \beta_s = 1.35 \times 10^{-9} \text{ Pa}^{-1}, \lambda = 2 \text{ W/(m-K)}, \rho c = 2 \times 10^8 \text{ J/(K-kg)}, \rho_h = 1390 \text{ kg/m}^3, \rho_s = 900 \text{ kg/m}^3, \rho_{s0} = 1434 \text{ kg/m}^3, c_s = 1350 \text{ J/(K-kg)}, L_h = 5.5 \times 10^4 \text{ J/kg}.

According to the Figure 2 the movement rate of the hydrate formation surface increases with injection pressure increasing. This is due to the fact that the movement of this surface is limited by the flow rate of liquid sulfur dioxide, which increases with the injection pressure rise in the layer. Also Fig. 2 shows that as the injection pressure increases, the temperature on the phase transition surface increases. This is due to the release of the latent heat of phase transitions in the formation of hydrate, and increasing injection pressure occurs an increase in the surface speed of the phase transitions (i.e., the intensity of hydrate formation). In addition, part of the heat released on the surface of the phase transitions is discharged through the colder left formation border, so with the increase in the coordinate of the hydrate formation surface, the intensity of heat removal through the left formation border of the decreases. According to the above, as the injection pressure increases, the temperature rises.

As a result, at sufficiently large injection pressure values, the temperature at the hydrate formation boundary can exceed the melting temperature of ice (273 K) that corresponds to the appearance of an intermediate region saturated with a mixture of water and methane.

Calculations were carried out to find the limit value of the injection pressure of sulfur dioxide \( p_{pe} \), above which an intermediate region saturated with a mixture of water and methane arises.
Figure 2. Dependence of coordinate and border temperature for gas hydrate formation on the injection pressure.

The Figure 3 shows the dependence of the limit pressure value on the initial one \( a \) with \( T_0 = 280 \) K as well as on the initial temperature \( b \) with \( p_0 = 4 \) MPa. According to the Figure 3 as the initial pressure increases and the initial layer temperature decreases, the injection limit pressure value increases. This is due to the fact that with an increase in the initial pressure and a decrease in the initial temperature, the temperature on the formation surface of sulfur dioxide gas hydrate decreases. A low intensity of heat removal through the left formation border and a high intensity of the latent heat of hydrate formation realized at large values of the injection pressure and, accordingly, the velocity of the boundary of phase transitions are required to exceed the equilibrium decomposition temperature of the gas hydrate on this surface. Thus, the intermediate region saturated with a mixture of water, sulfur dioxide and its gas hydrate in their phase equilibrium state occurs at high values of injection pressure, and the initial layer temperature, as well as at low initial pressure values.
Fig. 3. Dependence of the limit pressure value on the initial temperature $p_0 = 2.8$ (curve 1) and $p_0 = 3.0$ (curve 2) MPa.

6. Conclusions
It was constructed a mathematical model of injection of liquid sulfur dioxide into a porous medium saturated with ice and methane, accompanied by the formation of sulfur dioxide gas hydrate. It was found that with increasing injection pressure an increase in temperature at the formation border of sulfur dioxide gas hydrate arises. It is shown that a zone saturated with a mixture of water and methane arises at high values of injection pressure and initial layer temperature, as well as at low values of initial pressure in the porous medium.

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