Mathematical model of liquid sulfur dioxide injection into layer saturated with water and methane

M K Khasanov
Sterlitamak branch of Bashkir state University, Lenin Avenue 49, Sterlitamak, Russia
E-mail: hasanovmk@mail.ru

Abstract. The mathematical model of sulfur dioxide solution injection into the layer saturated with the water and methane accompanied by formation of sulfur gas hydrate is presented. For the axisymmetric problem, self-similar solutions describing the distribution of temperature and pressure in the layer are constructed. It is established that depending on the mass flow rate of sulfur dioxide injection, the formation of sulfur dioxide gas hydrate can occur both on the front surface and in the extended region. There are determined the limit values of the mass flow rate of sulfur dioxide injection separating different modes of sulfur dioxide gas hydrate formation. It is established that the mode with the gas hydrate formation of sulfur dioxide in an extended region is realized at high values of mass injection flow rate of sulfur dioxide and of the initial temperature of the layer.

1. Introduction
Currently, one of the emission reducing methods of sulfur dioxide produced by industrial facilities into the atmosphere is its underground disposal in depleted hydrocarbon deposits [1-3]. One of the ways to reduce the risk of gases utilized outlet to the surface is their transfer to the gas hydrate state, which, compared to the free state, allows one to store the same amount of gas at much lower pressures [4-8].

Any relevant technological schemes should be accompanied by calculations according to theoretical models that adequately reflect the real conditions. In this regard, the construction of adequate mathematical models of gas hydrates formation in the natural layer is relevant. Mathematical models of gas hydrate formation in extended porous layers during gas injection are formulated, in particular, in [9-10]. However, in this paper we investigate the case with the same pumped gas that saturates the layer in the initial state. A mathematical model of SO$_2$ gas hydrate formation during injection of sulfur dioxide solution into a layer saturated with methane and water is constructed in this paper.

2. Mathematical model
The existence conditions of sulfur dioxide gas hydrate are shown in the phase diagram (Figure 1) [4]. In this diagram, curve $J$ determines the three – phase equilibrium between water, sulfur dioxide gas and its gas hydrate, curve 2 – the equilibrium between water, sulfur dioxide solution and its gas hydrate, and curve 3 – the two-phase equilibrium between liquid and gaseous sulfur dioxide. Accordingly, sulfur dioxide gas hydrate exists to the left of curves $J$ and 3. All four phases are in equilibrium at the quadrupole point $Q_2$ ($T_{Q_2}$=285.1 K и $p_{Q_2}$=0.233 MPa).

Let’s assume that the horizontal porous layer at the initial moment is saturated with water and methane, their pressure $p_0$ and the temperature $T_0$ in the initial state lie above the curve 2 and to the left
of the curve 3 in the phase diagram (i.e., in the existence region of a mixture of sulfur dioxide solution and its gas hydrate):

\[ t = 0: \ T = T_0, \ p = p_0, \ S_w = S_{w0}, \ S_l = 1 - S_{w0}, \ S_h = 0, \ S_s = 0 \]

where \( S_j \) (\( j = w, g, h, s \)) is the pore’s saturation of the \( j \)-th phase (\( w \) – water, \( g \) – methane, \( h \) – gas hydrate, \( s \) – sulfur dioxide).

\( \text{Figure 1. Phase diagram of "SO}_2\text{-H}_2\text{O" system.} \)

Let’s assume that the liquid sulfur dioxide is pumped through the well, having opened the layer for its entire thickness. In this paper we consider a model with piston displacement of methane by sulfur dioxide, as well as the case when the process of hydrate formation is limited not by kinetic mechanisms, but by the rate of filtration mass transfer in a porous medium. This is true for time scales greatly exceeding the typical time of the process kinetics. Then it can be assumed that hydrate formation occurs at the methane displacement border by sulfur dioxide. Consequently, in the case under consideration, two typical areas are formed in the layer. In the first (nearest) zone, the pores are saturated with liquid sulfur dioxide and its gas hydrate, and in the second (remote) zone – with water and methane. Thus, taking into account these assumptions, the formation of sulfur dioxide gas hydrate completely occurs on the mobile front surface separating these two areas.

Let us take the following simplifying assumptions. Liquid sulfur dioxide we consider as an elastic liquid, and methane as a calorically perfect gas. We will consider the case when the value of the initial water saturation of the layer doesn’t exceed 0.2, then the water can be considered immobile.

The system of basic equations describing the filtration and heat transfer processes in a porous medium and representing the mass and energy conservation laws to Darcy’s one and the equation of state, in the axisymmetric case with the above assumptions in each of the areas has the form [10]:

\[
\frac{\partial}{\partial t} \left( \rho_i mS_i \right) + \frac{1}{r} \frac{\partial}{\partial r} \left( r \rho_i mS_i \nu_i \right) = 0,
\]

\[
\rho \xi \frac{\partial T}{\partial t} + \rho_i c_i mS_i \nu_i \frac{\partial T}{\partial r} = \frac{1}{r} \frac{\partial}{\partial r} \left( r \lambda_i \frac{\partial T}{\partial r} \right),
\]

\[
mS_i \nu_i = -k_i \frac{\partial p}{\mu_i \partial r},
\]

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

where \( t \) is the time; \( r \) is a radial coordinate; \( m \) is the porosity; \( p \) is the pressure; \( T \) is the temperature; low indexes \( i = s, g \) refer respectively to the parameters of sulfur dioxide and methane; \( \rho_i \) is the density; \( k_i \) is the phase permeability; \( \nu_i \) is the actual average speed; \( c_i \) is the specific heat capacity; \( \mu_i \) is the
dynamic viscosity; $\beta_i$ is the compressibility factor; $\rho_c$ and $\lambda$ are the effective values of the volumetric heat capacity and thermal conductivity of the layer saturated. Since the corresponding parameters of the rock include the main contribution to the value $\rho_c$ and $\lambda$ we assume them as the constant values.

The phase coefficient dependence of the $k_i$ permeability on the $S_i$ saturation and absolute permeability $k_0$ can be defined as follows:

$$k_i = k_0 S_i^3 \quad (i=s, g).$$

At the border between the regions, the relations following from the conditions of mass and heat balance are performed:

$$-\frac{k_s}{\mu_s} \frac{\partial p_s}{\partial r} = m \left( \frac{\rho_h}{\rho_s} S_h G + S_s \right) V_n, \quad -\frac{k_t}{\mu_t} \frac{\partial p_t}{\partial r} = mS V_n,$$

$$mS_h \rho_h (1 - G) V_n = mS_w \rho_w V_n, \quad \lambda \frac{\partial T_t}{\partial r} - \lambda \frac{\partial T_s}{\partial r} = m \rho_h L_b S_h V_n. \quad (3)$$

Here, $L_b$ is the specific heat of gas hydrate formation from liquid sulfur dioxide and water; the lower index $j=1,2$ refers, respectively, to the parameters in the first and second regions; $G$ is the relative mass concentration of sulfur dioxide in the gas hydrate; $S_w$ is the initial water saturation of the layer; $V_n$ is the velocity of the hydrate formation border. The temperature and pressure at this border will be considered continuous. Here and further, the index $n$ refers to the parameters on the border between the regions.

The value of the hydrate saturation in the first area can be found from the third equation (3):

$$S_h = \frac{\rho_h S_w}{\rho_h (1 - G)}.$$

We introduce a dimensionless value $P_{(1)}$ equal to the given density of liquid sulfur dioxide, respectively:

$$P_{(1)} = \frac{\rho_s}{\rho_h} = \exp \left( \beta_i \left( P_{(1)} - P_h \right) \right).$$

On basis of the system (2) the equations for the piezoconductivity and temperature conductivity will take the form in every area:

$$\frac{\partial P_{(1)}}{\partial t} = \chi_i^{(p)} \frac{1}{r} \frac{\partial P_{(1)}}{\partial r}, \quad \frac{\partial T_{(1)}}{\partial t} = \chi_i^{(T)} \frac{1}{r} \frac{\partial T_{(1)}}{\partial r} + \chi_i^{(T)} \frac{1}{r} \frac{\partial \left( \frac{r}{p_{(1)}} \right)}{\partial r}, \quad (4)$$

$$\frac{\partial P_{(2)}}{\partial t} = \chi_2^{(p)} \frac{1}{r} \frac{\partial P_{(2)}}{\partial r}, \quad \frac{\partial T_{(2)}}{\partial t} = \chi_2^{(T)} \frac{1}{r} \frac{\partial T_{(2)}}{\partial r} + \chi_2^{(T)} \frac{1}{r} \frac{\partial \left( \frac{r}{p_{(2)}} \right)}{\partial r}, \quad (5)$$

где $\chi_i^{(T)} = \frac{\lambda}{\rho C}, \chi_i^{(p)} = \frac{k_s}{\mu_s m (1-S_h) \beta_s}, \chi_2^{(p)} = \frac{k_g p_0}{\mu_g m (1-S_w0)}, X_{(1)} = \frac{\rho_0 \epsilon c_s k_s}{\lambda \mu_s \beta_s}, X_{(2)} = \frac{\rho \epsilon c_g k_g}{2 \lambda \mu_g \beta_g}.$

We assume that liquid sulfur dioxide with a given mass flow rate $Q$ and the temperature $T_r$ is injected through the well, which opened the layer for its entire thickness. As a result of its injection, an area saturated with sulfur dioxide and its gas hydrate is formed. In this paper, we consider sufficiently large time values after the start of sulfur dioxide injection, where the radius of the first area $r_{(0)}$ significantly exceeds the radius of the well $r_e$. Then we can assume that the value $r_e$ hasn’t any virtually effect on the characteristics of the hydrate formation process in the layer. Then the conditions in the well, taking into account the Darcy’s law will take the form:

$$r = r_e: \quad \frac{2 k_s \pi p_0 k_s}{\mu_s \beta_s} \left( r \frac{\partial P_{(1)}}{\partial r} \right) = Q, \quad T = T_e \quad (r_e \to 0, \ t > 0).$$

We introduce a self-similar variable: $\xi = r / \sqrt{\chi^{(T)} r}$. For this variable, from (4) and (5) we obtain
solutions for pressure and temperature in each area:

\[ P_{(1)} = P_{(n)} + \frac{Q \mu_s \beta_s}{2 \pi \rho s k_s} \int_{\xi}^{\xi_{(n)}} \frac{1}{\xi} \exp \left( -\frac{\xi^2}{4 \eta_{(1)}} \right) d\xi, \]

\[ T_0 = \frac{\int_{0}^{\xi_{(n)}} \frac{1}{\xi} \exp \left( -\frac{\xi^2}{4 \eta_{(1)}} \right) d\xi}{\int_{0}^{\xi_{(n)}} \frac{1}{\xi} \exp \left( -\frac{\xi^2}{4 \eta_{(1)}} \right) d\xi}, \]

\[ T_{(2)} = T_0 + \frac{\int_{0}^{\xi_{(n)}} \frac{1}{\xi} \exp \left( -\frac{\xi^2}{4 \eta_{(2)}} \right) d\xi}{\int_{0}^{\xi_{(n)}} \frac{1}{\xi} \exp \left( -\frac{\xi^2}{4 \eta_{(2)}} \right) d\xi}, \]

where \( \eta_{(j)} = \chi_{(j)}^{(p)} / \chi_{(j)}^{(T)} \) for \( j=1, 2 \).

On the basis of relations (3), taking into account solutions for pressure and temperature (6) and (7), we obtain equations to find the coordinate of the hydrate formation border \( \xi_{(n)} \) and the parameters values \( p_{(a)} \) and \( T_{(a)} \) on it:

\[ \frac{Q \mu_s \beta_s}{\pi k_s \rho_s \alpha} \exp \left( -\frac{\xi^2_{(n)}}{4 \eta_1} \right) = A_{(1)} P_{(n)} \xi^2_{(n)}, \]

\[ \frac{\int_{0}^{\xi_{(n)}} \frac{1}{\xi} \exp \left( -\frac{\xi^2}{4 \eta_{(1)}} \right) d\xi}{\int_{0}^{\xi_{(n)}} \frac{1}{\xi} \exp \left( -\frac{\xi^2}{4 \eta_{(1)}} \right) d\xi} \]

where \( A_{(1)} = -\frac{m \mu_s \beta_s \chi^{(T)} \rho_s GS_h}{k_s} \left( \rho_s GS_h + 1 - S_h \right), \)

\( A_{(2)} = -\frac{m \mu_s \beta_s \chi^{(T)} \rho_s GS_h}{k_s} \left( 1 - S_w \right), \)

\( B = \frac{m \rho_s L_h S_h}{2 \rho c}. \)

3. Calculations results

Figure 2 shows the temperature distribution in the layer at various values of pressure of sulfur dioxide injection \( Q = 0.01 \) (a) and 0.05 (b) kg/(m²·c). The dashed line is the temperature of the upper quadrupole point. For other parameters the following values are accepted: \( m = 0.2, S_{w0} = 0.2, p_0 = 4 \) MPa, \( T_0 = 278 \) K, \( T_e = 275 \) K, \( k_0 = 1 \times 10^{-13} \) m², \( G = 0.372, \mu_r = 3.68 \times 10^{-4} \) Pa·s, \( \mu_g = 1 \times 10^{-4} \) Pa·s, \( \beta_s = 1.35 \times 10^{-9} \) Pa⁻¹.
\[ \lambda = 2 \text{ W/(m·K)}, \quad \rho c = 2 \cdot 10^6 \text{ J/(K·kg)}, \quad \rho_l = 1390 \text{ kg/m}^3, \quad \rho_w = 1000 \text{ kg/m}^3, \quad \rho_{0s} = 1434 \text{ kg/m}^3, \]

\[ c_s = 1350 \text{ J/(K·kg)}, \quad L_h = 2.62 \cdot 10^5 \text{ J/kg}. \]

Figure 2. Temperature distribution in the layer at different mass flow rates of sulfur dioxide injection \( Q = 0.01 \) (a) and 0.05 (b) kg/(m·c). The dashed line is the temperature of the upper quadrupole point.

Figure 2 shows that the layer temperature is below the equilibrium decomposition temperature of gas hydrate in the area saturated with sulfur dioxide and its gas hydrate at low mass flow rates (case a). Therefore, in this case the solution with the frontal border of gas hydrate formation gives an adequate mathematical description of the process. At a higher mass flow rate of injected sulfur dioxide (case b), the layer temperature rises above the equilibrium decomposition temperature of \( \text{SO}_2 \) gas hydrate in some part of the first area. Therefore, in this case, an extended area of \( \text{SO}_2 \) gas hydrate formation appears where water, liquid sulfur dioxide and its gas hydrate are in equilibrium.

According to Figure 2 the appearance of an extended area of sulfur dioxide gas hydrate formation at sufficiently high mass flow rates of sulfur dioxide injection is due to the fact that with the increase in flow rate the layer temperature at the border of gas hydrate formation increases. This temperature increase can be explained by the fact that the movement speed of the phase transitions border increases with increasing flow rate and accordingly the intensity of the latent heat of hydrate formation increases. At the same time, since the temperature in the well is lower than the temperature at the hydrate formation border, part of the heat released at this border is removed through the well walls. However, by increasing the coordinate of the hydrate formation border (i.e. its distance from the well) the intensity of heat removal through the well walls decreases, which leads to a temperature increase at this border. As a consequence, for sufficiently large values of the mass flow and accordingly for a movement high speed of the hydrate formation front the temperature can exceed the equilibrium temperature of decomposition of the of sulfur dioxide hydrate at this front.

Calculations were carried out to determine the limit value of the injection flow rate of sulfur dioxide \( Q^* \), above which the mode is implemented with an extended area of hydrate formation.

The Figure 3 shows the dependence of the mass flow rate limit value of sulfur dioxide injection on the initial layer temperature. We can see that with the initial temperature decreasing the limit value of the mass flow increases. This is due to the fact that the formation temperature at the border of sulfur dioxide gas hydrate formation decreases in this case. Therefore, to exceed the layer temperature at this border of the equilibrium decomposition temperature of sulfur dioxide gas hydrate, we need a high release intensity of latent heat of hydrate formation and a low intensity of heat removal through the well walls. It is realized at large values of mass flow and, accordingly, of the velocity of the phase transitions border.
4. Conclusions
The self-similar solutions of the problem for gas hydrate formation SO₂ are obtained by liquid sulfur dioxide injection into the layer saturated with methane and water. It is established that the formation of sulfur dioxide gas hydrate in the layer can occur both on the front surface and in the extended area. It is determined that the mode with an extended area of the gas hydrate formation is realized at high values of mass injection flow rate and the initial temperature of the layer.

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