Injection of hydrogen sulfide into a porous medium partially saturated with water

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Abstract. In the basis of equations of the mechanics of multiphase media a mathematical model of injection of hydrogen sulfide in liquid state into a porous medium saturated with water and oil is constructed. The dependence of the coordinate and temperature of the front of formation of hydrogen sulfide hydrate on the flow rate of hydrogen sulfide injection was studied. It is established that at rather high intensity of injection of hydrogen sulfide temperature on border of phase transitions can rise above the equilibrium temperature of dissociation of hydrogen sulfide hydrate.

1. Introduction

One of methods of decrease in emission in the atmosphere of the hydrogen sulfide produced by the oil processing enterprises is its burial in the exhausted oil and gas collectors [1, 2]. For the purpose of decrease in risk of leak of recyclable gases on a surface the possibility of their transfer in a gas hydrate state which allows to store identical volumes of gas with smaller pressure [3-6] is considered now. The mathematical models of a heat and mass transfer in the porous medium considering hydrate formation processes are necessary for creation of technologies of underground utilization of hydrogen sulfide in a hydrate state. Mathematical models of formation of gas hydrates when injection gas on the porous medium which is partially saturated with water are formulated, in particular, in works [7-9]. However in these works it is injected, the same gas which saturates the porous medium in an initial state. Mathematical model of injection carbon dioxide are provided to the layer saturated with water and methane in work [10]. In the real work the mathematical model of formation of H2S hydrate at injection of hydrogen sulfide in liquid state on the porous medium saturated with water and oil is provided.

2. Mathematical model

Let a pore of natural layer in initial time be saturated with water with an initial water saturation of $S_{w0}$ and oil, pressure of $p_0$ and $T_0$ temperature in which initial state formations of H2S hydrate meet conditions. Let's believe that through the well which has opened layer on all thickness hydrogen sulfide in liquid state is injected.

Conditions of formation of H2S hydrate are given in the phase diagram (fig. 1) [5]. On this chart curve $gh$ corresponds to three-phase balance between gaseous hydrogen sulfide, H2S gas hydrate and water, curve $lh$ – to balance between liquid hydrogen sulfide, H2S gas hydrate and water, and curve $lg$ – to two-phase balance between gaseous and liquid hydrogen sulfide. Respectively H2S gas hydrate
stable exists in the field of more to the left curve \(lh\) and \(gh\).

![Figure 1. Phase diagram of the H\(_2\)S-H\(_2\)O system.](image)

In this work we will neglect water filtration (since the case when initial value the water saturation of the porous medium does not exceed 0.2 is considered). Also we will neglect kinetics of process of hydrate formation and to consider that oil displacement by liquid hydrogen sulfide happens in the piston mode. Then it is possible to consider that H\(_2\)S gas hydrate is formed on frontal border of displacement of oil by hydrogen sulfide. In this case in the porous medium two zones are formed. In the first (near) zone of a pore are saturated with hydrogen sulfide and H\(_2\)S gas hydrate, and in the second (distant) zone of a pore are saturated with water and oil.

At the mathematical description of processes of a heat and mass transfer at injection of liquid hydrogen sulfide on porous medium we will believe: water and H\(_2\)S gas hydrate are not mobile and are not squeezed, oil and hydrogen sulfide are elastic liquids, and the porosity is constant.

The system of the main equations describing processes of heat transfer and filtrations of oil and water in natural layer consists equations of continuity, inflow of heat and state, and also Darcy’s law [8]:

\[
\begin{align*}
\frac{\partial}{\partial t} (\rho_i m_{Si}) + \frac{1}{r} \frac{\partial}{\partial r} (r \rho_i m_{Si} \nu_i) &= 0, \\
\rho_i \frac{\partial \theta_i}{\partial t} + \rho_i c_i m_{Si} \nu_i \frac{\partial \theta_i}{\partial r} &= \frac{1}{r} \frac{\partial}{\partial r} \left( r \lambda_i \frac{\partial \theta_i}{\partial r} \right), \\
m_{Si} \nu_i &= \frac{k_i}{\mu_i} \frac{\partial p_i}{\partial r}, \\
\rho_s &= \rho_{oi} \exp(\beta_s (p - p_{oi})), \\
\rho_i &= \rho_{oi} \left(1 + \beta_i (p - p_{oi})\right).
\end{align*}
\]

Here \(r\) – radial coordinate; \(t\) – time; \(m\) – porosity; \(T\) – temperature; \(p\) – pressure; the lower indexes \(i = l, s\) belong respectively to parameters of oil and liquid hydrogen sulfide; \(k_i\) – phase permeability; \(\mu_i\) – dynamic viscosity; \(\nu_i\) – the actual average speed; \(\rho_i\) – density; \(c_i\) – specific heat; \(\rho c\) and \(\lambda\) – effective values of heat capacity per unit volume and coefficient of heat conductivity of saturated stratum. As in values \(\rho c\) and \(\lambda\) the main contribution is made by parameters of oil stratum, will consider further them constants.
We will set dependence of coefficient of phase permeability of \( k_i \) on absolute permeability of \( k_0 \) and saturation of \( S_i \) as follows:

\[
k_i = k_0 S_i^3 \quad (i = s, l).
\]

On frontal border between zones the ratios following from conditions of balance of heat and mass are carried out:

\[
\frac{k_i}{\mu_i} \frac{\partial p_{(i)}}{\partial r} = m \left( \frac{\rho_h}{\rho_s} S_i G + S_i \right) V_n,
\]

\[
-\frac{k_i}{\mu_i} \frac{\partial p_{(1)}}{\partial r} = m S_n V_n,
\]

\[
m S_n \rho_h (1 - G) V_n = m S_{w0} \rho_n V_n,
\]

where \( \rho_h, S_h \) and \( L_h \) – density, a saturation and specific mass heat of formation of \( \text{H}_2\text{S} \) hydrate, \( S_{w0} \) and \( \rho_n \) – initial water saturation of the porous medium and density of water, \( V_n \) – the speed of a frontal surface of hydrate formation. The lower indexes \( j = l, 2 \) correspond to the parameters of the near and distant zones, respectively. The lower index \( n \) belongs to parameters on a frontal surface between zones.

Let’s consider that hydrogen sulfide in liquid state is injected on porous Medium with the fixed mass flow rate of \( Q \) (on well height unit) and the continuous temperature of \( T_e \). Let’s consider rather great values of time after the beginning of injection of hydrogen sulfide. Then the radius of the first \( r_{(n)} \) area will exceed considerably the well radius of \( r_e \) and the size of the well will practically not exert impact on features of course of process. In this case conditions on well border taking into account Darcy’s law have an appearance:

\[
r = r_e \rightarrow 0, \quad t > 0: \quad -\frac{2k_e \pi}{\mu_i} \left( r \rho_s \frac{\partial p}{\partial r} \right) = Q, \quad T = T_e.
\]

3. Self-similar solution

Let’s enter a self-similar variable:

\[
\xi = t / \sqrt{\lambda^{(s)} t},
\]

where \( \lambda^{(s)} = \lambda / \rho c \).

Then from (1) we will receive the following decisions for temperature and pressure in each of layer zones:

\[
P_{(1)} = P_{(n)} + \frac{Q \mu_i \beta_i}{2 \rho_{(0)} k_e} \int \xi \exp \left( -\frac{\xi^2}{4 \eta_{(1)}} \right) d\xi,
\]

\[
T_{(1)} = T_e - \frac{\int \xi \exp \left( -\frac{\xi^2}{4 \eta_{(1)}} \right) P_{(1)} d\xi}{\int \xi \exp \left( -\frac{\xi^2}{4 \eta_{(1)}} \right) P_{(1)} d\xi}, \quad 0 < \xi < \xi_{(n)},
\]

\[
0 < \xi < \xi_{(n)},
\]
\[ p_{(2)} = p_0 + \left( p_{(\alpha)} - p_0 \right) \int_{\xi_0}^{\xi} \exp \left( -\frac{\xi^2}{4n_{(2)}} \right) d\xi, \]

\[ T_{(2)} = T_0 + \left( T_{(\alpha)} - T_0 \right) \int_{\xi_0}^{\xi} \exp \left( -\frac{\xi^2}{4n_{(2)}} \right) d\xi, \]

where \( p_{(\alpha)} = \exp \left( \beta \left( p_{(\alpha)} - p_0 \right) \right) \), \( n_{(\alpha)} = k_s / \mu mS_0 \beta_s \chi^{(T)}(\xi_{(\alpha)}), \) and \( n_{(2)} = k_i / \mu mS_0 \beta_i \chi^{(T)}(\xi_{(2)}). \)

On the basis of relations (2) - (4) we obtain equations for finding the coordinate of the formation boundary of hydrogen sulfide hydrate \( \xi_{(\alpha)} \) and the values of the parameters \( p_{(\alpha)} \) and \( T_{(\alpha)} \) on it:

\[ \frac{Q \mu \beta_i \exp \left( -\frac{\xi^2}{4n_{(1)}} \right)}{n_0 \lambda \beta_i} = A_1 \left( p_{(\alpha)} \xi_{(\alpha)} \right), \]

\[ \frac{1}{\xi_{(\alpha)}} \int_{\xi_0}^{\xi} \exp \left( -\frac{\xi^2}{4n_{(2)}} \right) d\xi = A_2 \xi_{(\alpha)}, \]

\[ \left( T_{(\alpha)} - T_0 \right) \exp \left( -\frac{\xi^2}{4n_{(2)}} \right) = B \xi_{(\alpha)}, \]

where \( A_1 = \frac{m \mu \beta_i \chi^{(T)}}{k_i} \left( \frac{\rho \rho S_g}{\rho \rho S} + 1 - S_0 \right), \) \( A_2 = \frac{m \mu \beta_i \chi^{(T)}}{k_i} (1 - S_v), \) and \( B = \frac{m \rho \rho L S}{2 \rho \rho L} \).

4. Calculations results

Dependences of coordinate and temperature of the front of phase transitions (full curve) and the equilibrium temperature of dissociation of H₂S hydrate (dotted curve) from a mass flow rate of injection hydrogen sulfide are given in Fig. 2. For system parameters adopted values: \( S_{v0} = 0.12, \) \( m = 0.3, \) \( p_0 = 6 \text{ MPa}, \) \( T_w = 292 \text{ K}, \) \( T_0 = 294 \text{ K}, \) \( k_0 = 2 \cdot 10^{-11} \text{ m}^2, \) \( G = 0.24, \) \( \lambda = 2 \text{ W/(m·K)}, \) \( \rho_c = 2 \cdot 10^6 \text{ J/(K·kg)}, \) \( L_0 = 4.1 \cdot 10^5 \text{ J/kg}, \) \( \beta_s = 3 \cdot 10^9 \text{ Pa}^{-1}, \) \( \beta_i = 1 \cdot 10^9 \text{ Pa}^{-1}, \) \( \rho_h = 1003 \text{ kg/m}^3, \) \( \rho_{\alpha c} = 890 \text{ kg/m}^3, \) \( \rho_{\alpha h} = 900 \text{ kg/m}^3, \) \( \mu_c = 2 \cdot 10^{-4} \text{ Pa·s}, \) \( \mu_i = 2 \cdot 10^{-3} \text{ Pa·s}, c_1 = 1800 \text{ J/(K·kg)}, c_i = 1900 \text{ J/(K·kg)}. \)

According to Fig. 2 with increase in a mass flow rate of injection hydrogen sulfide the speed of the front of hydrate formation increases. It is caused by the fact that in this task the movement of a phase boundary is defined by the oil displacement speed by liquid hydrogen sulfide which increases with increase in intensity of injection.

From Fig. 2 it is visible that temperature at the front of formation of H₂S hydrate increases with in a mass flow rate of injection hydrogen sulfide. From Fig. 2 that the temperature at the formation front of the H₂S hydrate increases with the mass flow of injected hydrogen sulphide. It is caused by the fact that with increase in a mass flow rate of injection hydrogen sulfide the speed of the front of hydrate formation increases and respectively intensity of allocation of the latent heat of phase transitions increases. As temperature on the well is lower than the temperature at the formation front of H₂S
hydrate, the part of heat which is marked out on it is taken away through well walls. On the other hand with increase in speed of border of phase transitions intensity of heat extraction through walls of the well decreases that leads to increase in temperature H$_2$S gas hydrate formations at the front. As a result at rather high values of a mass flow rate and according to the high speed of the movement of border of phase transitions temperature on this border can exceed the equilibrium temperature of dissociation of H$_2$S hydrate. This case corresponds to incomplete transition of water to a condition of gas hydrate.

![Figure 2. Dependence of coordinate and temperature of the front of phase transitions on a mass flow rate of injection H$_2$S.](image)

5. Conclusions
Specific features of formation of H$_2$S hydrate due to injection of a liquid hydrogen sulfide into a natural layer initially filled with oil and water are considered. It is found that, depending on the mass flow rate of hydrogen sulfide injection, the H$_2$S hydrate forms either at a frontal surface or in an extended zone.

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