Analytical solution of the problem of hydrate formation in a porous medium with a temperature jump at the phase transition front

N G Musakaev\textsuperscript{1,2} and M K Khasanov\textsuperscript{3}

\textsuperscript{1}Tyumen Branch of Khrustianovich Institute of Theoretical and Applied Mechanics of SB RAS, Tyumen, Russia
\textsuperscript{2}Industrial University of Tyumen, Volodarskogo Str. 38, Tyumen 625000, Russia
\textsuperscript{3}Sterlitamak Branch of Bashkir State University, Sterlitamak, Russia

E-mail: musakaev@ikz.ru

Abstract. The results of theoretical study of the methane hydrate formation during the hydrocarbon gas injection into a porous reservoir initially saturated with methane and water are presented. In the axisymmetric approximation, mathematical model with a stepwise temperature distribution in the reservoir is considered. For this case, an approximate analytical solution is constructed with a temperature jump at the gas hydrate formation front in the form of an explicit functional dependence of the self-similar coordinate of this boundary on the parameters of a porous medium and an injected gas.

1. Introduction

At the present time, natural gas (mainly contains methane, in most cases about 90\% and more) is one of the main sources of raw materials for the energy and chemical industries [1–4]. Natural gas consumption is projected to grow at least over the next twenty years [4]. Therefore, there is a need to develop efficient technologies for this gas storage.

Natural gas can be stored in porous reservoirs, and a number of researchers have proposed to organize the storage of this hydrocarbon raw material in gas hydrate form [5–7]. The advantages of such organization of storage are the ability of gas hydrates to bind a significant amount of gas in a small volume with a relatively small pressure, and the non-explosive nature of this storage form [4, 8]. It is also worth noting that the guest gas (methane) is stored in the molecular form, so it is possible to extract gas from such reservoir due to pressure drop or thermal effects on the reservoir (theoretical study of these methods for gas extraction is presented in a number of works, including ours, for example, [3, 9–12]).

In [13–16], numerical solutions of the problem of the cold gas injection (with a temperature below the initial reservoir temperature) saturated with methane and water are presented. In this work, analytical solution of this problem is constructed in axisymmetric formulation, which is a functional dependence of the gas hydrate formation boundary coordinate on the mass flow rate and temperature of an injected gas and the parameters of a porous medium. Comparison of numerical and analytical solutions is carried out.
2. Problem statement and main equations

For considered model problem we assume that a horizontal porous reservoir of a constant thickness with impermeable top and bottom boundaries at the initial time moment is saturated with methane and water. The pressure $p_0$ and temperature $T_0$ of the reservoir in the initial state correspond to the thermodynamic conditions for the existence of methane and water in free state (non-gas hydrate) and they are the same in the whole reservoir.

Suppose that a gas with a constant mass flow rate $Q$ (per unit height of a well) and at a constant temperature $T_w < T_0$ is pumped through a well with a radius $r_w$. As a result of gas injection near the well a region saturated with methane and its hydrate can form. We will assume that the gas hydrate formation occurs completely on a circular frontal surface. In this case, two zones appear in a porous medium. In the area (hereinafter, the parameters of this zone will be indicated by the subscript in brackets $i = 1$), which is located near the well, water has completely passed to the gas hydrate state, therefore, only methane and its hydrate are present in the pores of this zone. In second zone ($i = 2$), the porous medium is saturated only with gas and water.

For this problem statement, the following system of nonlinear differential equations, which is based on the methods and approaches of mechanics of multiphase media [18], describing non-isothermal gas flow in a porous medium was proposed in [14–17]:

$$
\frac{\partial p_i(t)}{\partial t} = \frac{k_i}{mS_g(r)\mu_g} \frac{1}{r} \frac{\partial}{\partial r} \left( \rho p_i \frac{\partial p_i}{\partial r} \right), \quad \frac{\partial T_i(t)}{\partial t} = \lambda \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T_i}{\partial r} \right) + \frac{c_g k_i P_i(t)}{R_g \mu_g} \frac{\partial p_i}{\partial r} \frac{\partial T_i}{\partial r}.
$$

Here $m$ is the porosity; $S_g$ is the gas saturation; $R_g$ is the specific gas constant; $k_i$ is the coefficient of phase permeability for gas; $c_g$ and $\mu_g$ are the specific heat capacity and dynamic viscosity of the gas phase; $\rho c$ and $\lambda$ are the specific volumetric heat capacity and thermal conductivity coefficient of the system "porous reservoir – fluid".

In [16, 17] self-similar solutions of this problem were constructed. These solutions allow to find the pressure and temperature in selected areas of a porous reservoir. In the aforementioned papers, these solutions are substituted into relations at the phase transition boundary. These relations are obtained from the conditions of the mass and heat balance, as well as the condition of the temperature continuity at the phase transition boundary. In this case, a system of transcendental equations arises, which in the general case can only be solved using numerical methods.

However, it is of fundamental interest to obtain an analytical solution that establishes a certain type of functional dependence between the phase transition boundary coordinate, and the parameters of an injected gas and a porous medium. This solution can be used in the analysis of the mathematical model of studied process. The main difficulty in constructing this analytical solution is related to the features of the equation describing the heat balance at the phase transition boundary. Therefore, we will study the temperature field in a reservoir with various parameters.

In the considered problem, the gas hydrate formation is accompanied by the release of the phase transitions latent heat and leads to an increase in the reservoir temperature. However, to continue the process of the methane hydrate formation, the temperature at the phase transition boundary should not be higher than the equilibrium temperature of hydrate formation, which is ensured by heat transfer in a reservoir. Therefore, the rate of movement of the boundary of the gas hydrate formation is limited by the heat transfer in a reservoir. In the general case, heat transfer in a reservoir is provided by two mechanisms: convective and conductive.

Figure 1 shows the temperature and pressure distributions in a reservoir, based on the self-similar solutions obtained in [16, 17]. For the parameters characterizing the system “porous reservoir – fluid”, the following values are taken: $m = 0.1$, $S_h = 0.2$, $k_0 = 10^{-12}$ m$^2$, $T_w = 273$ K, $Q = 0.3$ kg/(m·s), $T_0 = 280$ K, $p_0 = 4$ MPa, $G = 0.12$, $T_s = 10$ K, $p_{s0} = 5.5$ MPa, $R_g = 520$ J/(K·kg), $\rho_g = 2500$ kg/m$^3$, $p_h = 900$ kg/m$^3$, $\rho_l = 1000$ J/(K·kg), $c_{sk} = 1560$ J/(K·kg), $\mu_g = 10^5$ Pa·s, $\lambda_i = 2$ W/(m·K), $\lambda_h = 2.11$ W/(m·K), $\lambda_l = 0.58$ W/(m·K), $L_h = 5 \cdot 10^7$ J/kg. Here the subscripts $sk$, $h$, $l$ and $g$ are referred to the parameters of the porous skeleton,
hydrate, water, and gas, respectively; $\rho_j$, $c_j$ and $\lambda_j$ ($j = sk, h, l$ and $g$) are the true density, specific heat capacity and thermal conductivity coefficient of the $j$-th phase; $G$ is the mass concentration of gas in methane hydrate; $S_j$ ($j = g, l, h$) is the saturation of pores with the $j$-th phase; $k_0$ is the absolute reservoir permeability; $L_h$ is the specific heat of the methane hydrate formation; $p_{e0}$ is the equilibrium pressure corresponding to the initial temperature $T_0$; $T^*$ is the empirical parameter that has the dimension of temperature and depends on the composition of natural gas. The self-similar variable has the form

$$\tilde{\chi} = \sqrt{\chi^T} \tilde{t}$$

where $\chi^T = \lambda(\rho c)$ is the coefficient of the reservoir thermal diffusivity.

![Figure 1](image_url)

**Figure 1.** Distributions of temperature and pressure on the self-similar coordinate $\tilde{\xi}$. $\tilde{\xi}(s)$ is the self-similar coordinate of the gas hydrate formation boundary.

From the data presented in figure 1 it can be seen that the temperature distribution has a stepped character with a temperature jump at the gas hydrate formation front. This is due to the release of latent heat of hydrate formation at the front of phase transitions, as well as to the fact that at the considered parameters the heat transfer in the reservoir occurs to a greater extent due to the convective mechanism. Thus, for an approximate description of the process of formation of gas hydrate, can be used the model with a stepwise temperature distribution in a reservoir. This allows to modify the conditions at the boundary of the gas hydrate formation in order to build analytical solutions that describe the movement of the phase transitions boundary.
3. Mathematical model with the stepwise temperature distribution in a reservoir

Let us consider the solution with a temperature jump at the gas hydrate formation front \( r = r_{(o)} \) from the value of \( T_r \) to the value of the equilibrium hydrate formation temperature \( T_{(o)} \). Since a gas is continuously injected into a reservoir, the process of gas absorption due to the hydrate formation has little effect on the pressure change in the reservoir. Therefore, in the mass balance equation at the phase transition boundary \( r = r_{(o)} \), we can neglect the corresponding term. Then, taking the stepwise temperature distribution in the reservoir, the conditions of mass and heat balance at the hydrate formation front, taking into account the Darcy law and the equation of state of the calorically perfect gas, can be presented for the self-similar variable \( \xi \) in the form:

\[
\frac{k(2)}{T(s)} \frac{dp_{(2)}}{d\xi} - \frac{k(1)}{T_w} \frac{dp_{(1)}}{d\xi} = m \mu_g \left( \frac{S_{g(1)}}{T_w} \frac{p_{(s)}}{T_w} - \frac{S_{g(2)}}{T_{(s)}} \frac{p_{(s)}}{T_{(s)}} \right) \chi^{(T)}(\xi_{(s)}),
\]

\[
\frac{k(1)}{T_w} \frac{dp_{(1)}}{d\xi} - \frac{k(2)}{T_w} \frac{dp_{(2)}}{d\xi} = \mu_g \left( \frac{R_g \rho c_s}{c_g} (T_{(s)} - T_w) + m S_{h(1)} \rho_h L_h \frac{R_g}{c_g} + m p_{(s)} (S_{g(2)} - S_{g(1)}) \right) \chi^{(T)}(\xi_{(s)}),
\]

where \( k(i) = k_0 S^3_{g(i)} \) (\( i = 1, 2 \)).

From the piezoconductivity equation we can get, by ignoring the difference in the permeability of selected zones and the gas absorption at the phase transition boundary due to hydrate formation, the following expression for finding the pressure at \( \xi = \xi_{(o)} \):

\[
\frac{dp^2}{d\xi^2} = \frac{Q \mu_g R_g T_w}{\pi k(1)} \frac{1}{\xi_{(s)}} \exp \left( \frac{\xi_{(s)}^2}{4 \eta(1)} \right).
\]

\[
\eta(1) = \frac{\chi^{(P)}(\xi)}{\chi^{(T)}(\xi)}, \quad \chi^{(P)}(\xi) = \frac{k(1) p_0}{m S_{g(1)} \mu_g}.
\]

Since the propagation velocity of pressure perturbations in a reservoir significantly exceeds the movement speed of the phase transition boundary (\( \eta(1) >> \xi_{(s)}^2 \)), from equations (1) and (2) we can get the following relation for finding the self-similar coordinate of the gas hydrate formation boundary:

\[
\xi_{(s)} = \frac{QT_w}{\pi^2 \chi^{(T)}(\xi)} \left( \frac{\rho c_T}{c_g} - m S_{h(1)} \rho_h L_h \frac{R_g}{c_g} (T_w - T_{(s)}) + m S_{g(1)} \frac{p_{(s)}}{R_g} \right).
\]

At high permeability values, the pressure value at the boundary of gas hydrate formation approaches to the initial reservoir pressure value, and the temperature value at this boundary approaches to the equilibrium hydrate formation temperature value corresponding to the initial reservoir pressure [16, 17]:

\[
p_{(s)} = p_0, \quad T_{(s)} = T_0 + T_e \ln \left( p_0 / p_{(s)} \right).
\]

Substituting these relations into (3), we can write the following relation for the self-similar coordinate of the gas hydrate formation boundary:
\[
\xi_{(s)} = \frac{QT_w}{\sqrt{\frac{\pi k}{c_g} \left[ \frac{\rho c_T}{c_g} - \frac{m S_{h(1)} p_h T_h L_h}{c_g (T_w - T_0 - T_s \ln (p_0 / p_{s0}))} + \frac{m S_{g(1)} p_0}{R_g} \right]}}.
\] (5)

Figure 2 shows the dependences of the self-similar coordinate of the phase transition boundary on the permeability with the parameters corresponding to figure 1. The solid curve corresponds to the solution with a continuous temperature distribution at the boundary of the gas hydrate formation. This solution takes into account convective and conductive mechanisms of heat transfer. The dashed curve corresponds to the solution with a temperature jump at the hydrate formation boundary (5). This solution takes into account only the convective mechanism of heat transfer.

Figure 2. Dependence of the self-similar coordinate of the phase transition boundary on permeability.

Figure 2 shows that smaller values of the reservoir permeability correspond to larger values of the coordinate of the gas hydrate formation boundary, found from the solution that takes into account convective and conductive mechanisms of heat transfer. This is due to the fact that a decrease in the porous medium permeability at a constant given mass flow rate of the injected gas requires an increase in injection pressure (pressure at the well bottom) and leads to an increase in pressure at the phase transition boundary. And this increase in pressure contributes to the acceleration of the gas hydrate formation.

Also from the data presented in figure 2 follows that the reduction in permeability does not affect the value of the gas hydrate formation boundary coordinate, found from the approximate analytical solution (5). This is due to the fact that when obtaining solution (5), assumption (4) on the constancy of pressure at the phase transition boundary was used.

The approximate analytical solution (5) adequately describes the position of the gas hydrate formation boundary at sufficiently high permeability values, \( k_0 > 10^{-13} \) m\(^2\) (figure 2). With a decrease in permeability, the value of thehydrate formation boundary coordinate, calculated from solution (5), increasingly differs (becomes smaller) from the value of the hydrate formation boundary coordinate found from the solution, which takes into account the convective and conductive mechanisms of heat transfer.

4. Conclusions
Approximate analytical solution was constructed with a temperature jump at the gas hydrate formation front in the form of an explicit functional dependence of the hydrate formation boundary coordinate on the parameters of an injected gas and a porous medium. It is established that this solution describes well the movement of the phase transition boundary at sufficiently high values of the absolute reservoir permeability. With a decrease in permeability, the value of the hydrate formation boundary
coordinate, calculated from the approximate analytical solution, increasingly differs (becomes smaller) from the value of the hydrate formation coordinate, which is found on the basis of the solution with a continuous temperature distribution at the phase transition boundary.

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References
[1] Makogon Y F 2010 J. of Natural Gas Science and Engineering 2(1) 49–59
[2] Demirbas A 2010 Methane gas hydrate (London: Springer)
[3] Musakaev N G, Borodin S L and Khasanov M K 2018 Int. J. of Heat and Mass Transfer 118 455–61
[4] Veluswamy H P, Kumar A, Seo Y, Lee J D and Linga P 2018 Applied Energy 216 262–85
[5] Benson S M and Cole D R 2008 Elements 4 325–31
[6] Bondarev E A, Rozhin I I, Popov V V and Argunova K K 2015 Earth’s Cryosphere 19(4) 64–74
[7] Oldenburg C M, Pruess R and Benson S M 2001 Energy and Fuel 15 293–8
[8] Byk S Sh, Makogon Y F and Fomina V I 1980 Gas Hydrates (Moscow: Khimiya)
[9] Shagapov V Sh, Chiglintseva A S and Syrtlanov V R 2009 J. of Applied Mechanics and Technical Physics 50(4) 628–37
[10] Musakaev N G, Khasanov M K, Borodin S L and Belskikh D S 2018 Vestnik Tomskogo Gosudarstvennogo Universiteta - Matematika i Mekhanika 56 88–101
[11] Shagapov V Sh, Khasanov M K, Gimaltdinov I K and Stolpovsky M V 2013 Thermophysics and Aeromechanics 20(3) 339–46
[12] Khabibullin I L, Khamitov A T and Nazmutdinov F F 2014 High Temperature 52(5) 697–702
[13] Shagapov V Sh, Musakaev N G and Khasanov M K 2005 Thermophysics and Aeromechanics 12(4) 605–16
[14] Nurislamov O R and Shagapov V Sh 2009 J. of Applied Mathematics and Mechanics 73(5) 581–91
[15] Shagapov V Sh, Khasanov M K, Gimaltdinov I K and Stolpovsky M V 2011 J. of Applied Mechanics and Technical Physics 52(4) 599–607
[16] Shagapov V Sh, Musakaev N G and Khasanov M K 2015 Int. J. of Heat and Mass Transfer 84 1030–9
[17] Shagapov V Sh, Khasanov M K and Musakaev N G 2008 J. of Applied Mechanics and Technical Physics 49(3) 462–72
[18] Nigmatulin R I 1991 Dynamics of Multiphase Media (New York: Hemisphere Publ. Corp.)