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Mathematical Model of Carbon Dioxide Injection into a Porous Reservoir Saturated with Methane and Its Gas Hydrate

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Abstract: In this paper, the process of methane replacement in gas hydrate with carbon dioxide during CO₂ injection into a porous medium is studied. A model that takes into account both the heat and mass transfer in a porous medium and the diffusion kinetics of the replacement process is constructed. The influences of the diffusion coefficient, the permeability and extent of a reservoir on the time of full gas replacement in the hydrate are analyzed. It was established that at high values of the diffusion coefficient in hydrate, low values of the reservoir permeability, and with the growth of the reservoir length, the process of the CH₄-CO₂ replacement in CH₄ hydrate will take place in the frontal regime and be limited, generally, by the filtration mass transfer. Otherwise, the replacement will be limited by the diffusion of gas in the hydrate.

Keywords: gas hydrates; carbon dioxide; replacement CH₄-CO₂; porous medium; diffusion

1. Introduction

Recently, special attention has been paid to the problem of developing natural gas hydrate deposits due to their wide spread in nature and the large reserves of hydrocarbons contained in such deposits. There are several main methods of methane recovery from a methane hydrate deposit: lowering the pressure and increasing the temperature of the deposit to the point of the hydrate decomposition, and injecting organic or brine solutions that promote the gas hydrate dissociation [1–4]. The mathematical modeling of the development of gas hydrate deposits using these methods is considered in [5–11]. The reduction of atmospheric emissions of carbon dioxide is very important in reducing the anthropogenic impact on climate. One way to solve this problem is the capture of industrial carbon dioxide gas and its further injection into geological formations for long-term storage. Mathematical models of the processes of heat and mass transfer in extended porous reservoirs upon carbon dioxide injection have been formulated; in particular, in [12–14].

One of the important environmental problems that needs to be addressed is the reduction of carbon dioxide emissions into the atmosphere. One of the methods of CO₂ utilization is its underground conservation in the gas hydrate state [15]. The numerical study of the processes of heat and mass transfer, accompanied by hydrate formation, when injecting gas into a porous reservoir, is carried out, for example, in [16–19].

The above problems can be resolved in one way: by injecting carbon dioxide into the methane hydrate reservoir, followed by the exchange of methane with CO_2 in the gas hydrate. This method allows the simultaneous conservation of CO_2 and production of CH_4 [20–22]. As a result of the above process, methane hydrate is replaced by CO_2 hydrate without the release of free water, which contributes to maintaining the mechanical strength of the rock [23]. Also, in contrast to the decomposition of the gas hydrate under depression or heating to gas and water, in this case the process will be realized with little heat release [24].

Ohgaki K., Takano K. et al. [25] were one the first teams to investigate the recovery of CH_4 with CO_2 in the gas hydrate. In their work, the process of hydrate formation in water saturated with methane was experimentally studied when CO_2 was injected into the solution. It was found that the stability region of CO_2 hydrate is wider and the heat of hydrate formation is higher than that of methane hydrate. Also, during the experiments, it was revealed that, at the end of the process, the concentration of carbon dioxide hydrate was significantly higher than that of methane hydrate. The work from M. Ota [26] experimentally studied the process of the substitution of CH_4 molecules by CO_2 molecules in hydrate using laser spectroscopy methods. The influence of pressure and fugacity on the process was analyzed. Falenty A., Salamatina A.N., Kuhs W.F. et al. have experimentally investigated the process of replacing CH_4 molecules by CO_2 molecules in methane hydrate, obtained from ice powder [25,27]. It was established that, at the initial stage, a more intensive formation of CO_2 hydrate occurs; then, the process slows down due to the formation of a CO_2 hydrate film, which prevents the contact of carbon dioxide and methane hydrate, and the process is further determined by the diffusion mechanism.

The results of studies [25–28] successfully describe the features of the process kinetics but do not take into account the effect of heat and mass transfer in extended natural reservoirs. In addition, in [25–28] and other similar experimental studies, the results of studies of the replacement process in samples containing only the gas hydrate phase are described. However, a study of this process in porous media is also of great interest, since the high specific contact surfaces of gas, liquid and hydrate are realized in such media, which are necessary for the intensification of the replacement process. In addition, most natural gas hydrates are contained in porous media.

In the work of G. Tegze et al. [29], a theoretical description of the replacement process of methane by liquid carbon dioxide in gas hydrate in the porous medium sample is presented. The kinetics of the process are described using the phase-field model and the diffusion model. The results of the numerical simulation and experimental data are compared. It is worth noting that the mathematical model in [29] and other similar theoretical studies take into account only the kinetics of the process, but not the filtration and heat transfer in a reservoir. However, in the development of real extended gas hydrate reservoirs, filtration and heat transfer in the reservoir have a significant effect on the process features.

At present, there are only a few works on the mathematical modeling of the methane replacement processes with carbon dioxide taking into account heat and mass transfer in the reservoir. Thus, the mathematical models of the replacement of CH_4 by CO_2 when carbon dioxide is injected into the gas hydrate reservoir are presented in [30,31]. However, these studies do not take into account the diffusion kinetics of the substitution process.

Theoretical studies of the replacement process when injecting CO_2 into a reservoir saturated with CH_4 hydrate were carried out by White M.D., McGrail B.P. et al. [32–34]. In these works, a mathematical model is presented, used simulators are described, and numerical solutions are obtained for the process of methane extraction from the reservoir saturated with hydrate when carbon dioxide is injected in different phase states. In these works, mathematical models take into account both the kinetics of the replacement process and the heat and mass transfer in the reservoir. The description of the kinetics is based on the Kim–Bishna model [35,36]. This model assumes that the rate of the replacement process is related with the diffusion mass transfer of carbon dioxide and methane in a gas hydrate. The rate of hydrate formation directly depends on the difference between the pressure in gas phase and the equilibrium pressure of hydrate formation. The proportionality coefficient, called

the kinetic parameter, is independent of time. Therefore, the model of Kim–Bishna does not take into account the deceleration of the driving force of the substitution process with the increasing thickness of the carbon dioxide layer over time.

In this paper, we present a mathematical model for the exchange of CH_4 with CO_2 in gas hydrate, taking into account both the kinetics and heat and mass transfer in a natural reservoir. At the same time, when describing the kinetics of the replacement process, the dependence of the rate of diffusion mass transfer of carbon dioxide in the gas hydrate on the growth of the thickness of the carbon dioxide gas monohydrate layer is taken into account. Mainly, attention is paid to the study of the degree of influence of the replacement kinetics and heat and mass transfer in the reservoir on the intensity of the methane recovery process from the gas hydrate at different parameters of the reservoir.

2. Mathematical Model

2.1. Problem Statement

The continuous process of CO_2 injection into a porous medium is studied in a one-dimensional linear approximation [37]. The problem is considered in a one-dimensional approximation; i.e., the presented mathematical model has a limited area of applicability. It is valid only for reservoirs with a sufficiently large thickness and width. In addition, the presented model corresponds to the simplest case of carbon dioxide injection, when injection occurs continuously for a long time and with a constant pressure. This choice is due to the fact that the present work aims to identify only the most important, general and universal laws of the process of replacement of methane in CH_4 hydrate with carbon dioxide, which are independent of the specific method of the carbon dioxide injection into a gas hydrate deposit. Figure 1 shows the temperature and pressure conditions for the existence of hydrates CH_4 and CO_2 . The ranges of pressures and temperatures corresponding to the stable existence of CO_2 and CH_4 hydrates are below curves 1 and 2, respectively. In this paper, it is supposed that the substitution process will be realized under thermobaric conditions corresponding to the existence of CH_4 hydrate and CO_2 hydrate, as well as the existence of carbon dioxide in the gaseous state (darkened area in the phase diagram).

Figure 1. Curve of phase equilibrium CO_2 + water (1), CH_4 + water (2), gas CO_2 + liquid CO_2 (3).

As methane hydrate is less stable than carbon dioxide hydrate, under certain conditions, carbon dioxide molecules will replace methane molecules in gas hydrate without releasing free water [14,15].

Let the hydrate deposit at the initial moment of time consist of three components, namely the skeleton of a porous medium, methane and its hydrate.

Let us write the mass conservation equations for CO₂ and CH₄ [38–42]:

$$\begin{aligned} \frac{\partial}{\partial t}(mS_g\rho_{g(dc)}^0) + \frac{\partial}{\partial x}(mS_gv_{g(dc)}\rho_{g(dc)}^0) &= -J_{g(dc)} \\ \frac{\partial}{\partial t}(mS_g\rho_{g(mt)}^0) + \frac{\partial}{\partial x}(mS_gv_{g(mt)}\rho_{g(mt)}^0) &= J_{g(mt)} \end{aligned} \quad (1)$$

For the skeleton, hydrate and gas, the subscripts *sk*, *h* and *g* are used, respectively; the subscripts *i* = *dc*, *mt* refer to the parameters of CO₂ and CH₄; *S_g* is the gas saturation; *m* is the reservoir porosity; *v_{g(i)}* and *ρ_{g(i)}* (*i* = *dc*, *mt*) are the partial velocities and densities of the components of mixture carbon dioxide and methane; and *J_{g(mt)}* and *J_{g(dc)}* are the intensities of the CH₄ release from hydrate and the CO₂ transition to hydrate.

Depending on various factors, such as the composition and state of the gas, the pressure and temperature of the medium, the gas hydrate can have a diverse structure: from solid (ice-like) to porous (snow-like). In the case of the hydrate porous structure, during the replacement process, a mixed gas hydrate can be formed with a continuous distribution of the concentrations of CH₄ and CO₂ in the volume of the hydrate. However, in our work, we will consider the case when the hydrate has a continuous (ice-like) structure, so there is a clear boundary between CO₂ and CH₄ hydrates. Then, the value of volume hydrate saturation will be equal to

$$S_h = S_{h(dc)} + S_{h(mt)}$$

where *S_{h(i)}* is used for the saturation of pores with methane hydrate (*i* = *mt*) and the carbon dioxide hydrate (*i* = *dc*), where *S_g* + *S_h* = 1.

As the gas hydrate is immovable, we obtain

$$\frac{\partial}{\partial t}(mS_{h(dc)}G_{(dc)}\rho_{h(dc)}^0) = J_{g(dc)}, \quad \frac{\partial}{\partial t}(mS_{h(mt)}G_{(mt)}\rho_{h(mt)}^0) = -J_{g(mt)} \quad (2)$$

where *G_(i)* and *ρ_{h(i)}* (*i* = *dc*, *mt*) are the relative mass of gas in the hydrate and the hydrate density, respectively.

We write the equation of H₂O mass conservation in the hydrate in the following form:

$$\frac{\partial}{\partial t}m(S_{hd}(1 - G_d)\rho_{hd}^0 + S_{hm}(1 - G_m)\rho_{hm}^0) = 0$$

Considering the initial state (*S_{hd}* = 0, *S_{hm}* = *S_{hm0}*) in integrating this equation, we find the dependence of the phase saturation of CH₄ hydrate and CO₂ hydrate:

$$S_{hm} = S_{hm0} - S_{hd} \frac{(1 - G_d)\rho_{hd}^0}{(1 - G_m)\rho_{hm}^0}$$

Note that the density of carbon dioxide hydrate is greater than the density of methane hydrate: *ρ_{h(dc)}*⁰ = 1115 kg/m³, *ρ_{h(mt)}*⁰ = 910 kg/m³ [2]. In the hydrates of CO₂ and CH₄ in the equilibrium state, there are about six molecules of H₂O per gas molecule. It is considered that the average mass fraction of CO₂ and CH₄ in the hydrate are equal to *G_(dc)* = 0.28 and *G_(mt)* = 0.12, respectively. Therefore, the following relation is performed with good accuracy:

$$(1 - G_{(dc)})\rho_{h(dc)}^0 = (1 - G_{(mt)})\rho_{h(mt)}^0 \quad (3)$$

There is no release of H_2O from the gas hydrate composition in the process of the CH_4 - CO_2 exchange [20,21]. Hence, taking into account Equation (3), the following relation is valid for the intensities $J_{g(dc)}$ and $J_{g(mt)}$:

$$\frac{J_{g(dc)}}{M_{(dc)}} = \frac{J_{g(mt)}}{M_{(mt)}} \quad (4)$$

where $M_{(dc)}$ and $M_{(mt)}$ are the molar mass of carbon dioxide and methane.

For the gas mixture as a whole, we introduce the mass-average velocity:

$$\rho_g^0 v_g = \rho_{gd}^0 v_{gd} + \rho_{gm}^0 v_{gm}, \quad \rho_g^0 = \rho_{gd}^0 + \rho_{gm}^0 \quad (5)$$

Adding up the Equation (1), and then taking into account Equations (4) and (5), we obtain

$$\frac{\partial(mS_g \rho_g^0)}{\partial t} + \frac{\partial(mS_g \rho_g^0 v_g)}{\partial x} = J_{gd} \left(\frac{M_m}{M_d} - 1 \right) \quad (6)$$

To describe the mixture filtration and the diffusion mixing of its components, we will use the Darcy law and Fick's law, respectively:

$$mS_g v_g = -\frac{k_g}{\mu_g} \frac{\partial p}{\partial x} \quad (7)$$

$$\begin{aligned} \rho_{g(dc)}^0 w_{g(dc)} &= -\rho_{g(mt)}^0 w_{g(mt)} = D_g \frac{\partial \rho_{g(mt)}^0}{\partial x} \\ w_{g(dc)} &= v_{g(dc)} - v_g, \quad w_{g(mt)} = v_{g(mt)} - v_g \end{aligned} \quad (8)$$

where D_g is the diffusion mixing coefficient of the components of gas mixture; and $w_{g(i)}$ ($i = dc, mt$) is the diffusion rate of the components of the methane and carbon dioxide mixture.

We assume that the mixture of methane and carbon dioxide is a calorically perfect gas and obeys the Dalton law:

$$p_{g(dc)} = \rho_{g(dc)}^0 R_{(dc)} T, \quad p_{g(mt)} = \rho_{g(mt)}^0 R_{(mt)} T, \quad p = p_{g(dc)} + p_{g(mt)} \quad (9)$$

where $R_{(dc)}$ and $R_{(mt)}$ are the specific gas constant of carbon dioxide and methane.

The equation for the internal energy of the system has the following form:

$$\rho c \frac{\partial T}{\partial t} + mS_g \rho_g^0 c_g v_g \frac{\partial T}{\partial x} = \frac{\partial}{\partial x} \left(\lambda \frac{\partial T}{\partial x} \right) + m \left(\rho_{h(dc)}^0 l_{h(dc)} \frac{\partial S_{h(dc)}}{\partial t} + \rho_{h(mt)}^0 l_{h(mt)} \frac{\partial S_{h(mt)}}{\partial t} \right) \quad (10)$$

$$\begin{aligned} \rho c &= (1-m) \rho_{sk}^0 c_{sk} + m \left(S_g \rho_g^0 c_g + S_{h(dc)} \rho_{h(dc)}^0 c_{h(dc)} + S_{h(mt)} \rho_{h(mt)}^0 c_{h(mt)} \right) \\ \rho_g^0 c_g &= \rho_{g(dc)}^0 c_{g(dc)} + \rho_{g(mt)}^0 c_{g(mt)}, \\ \lambda &= (1-m) \lambda_{sk} + m \left(S_g \lambda_g + S_{h(dc)} \lambda_{h(dc)} + S_{h(mt)} \lambda_{h(mt)} \right) \end{aligned}$$

Here, the designation of the specific thermal conductivity and heat of the j -th phase are λ_j and c_j ($j = g, h$) respectively; the designation of the specific heat of CH_4 hydrate decomposition and CO_2 hydrate formation are $l_{h(mt)}$ and $l_{h(dc)}$; the designations λ and ρc are used for the thermal conductivity and specific volume heat capacity.

The system of relations is supplemented by the following conditions:

$$x = 0, t > 0: \quad T = T_e, \quad p = p_e, \quad p_{g(dc)} = p_{g(dc)e} \quad (11)$$

$$x = L, t > 0 : \quad \frac{\partial T}{\partial x} = 0, \quad p = p_0$$

$$0 < x < L, t = 0 : \quad T = T_0, \quad p = p_0, \quad p_{g(dc)} = 0$$

where L is the linear reservoir size; T_0 and p_0 are the initial reservoir temperature and pressure; and T_e and p_e are the temperature and pressure of the CO_2 injected into the layer.

2.2. Description of the CH_4 - CO_2 Replacement Kinetics in the Hydrate

We accept that the rate of substitution of methane in the composition of gas hydrate with CO_2 is limited by the diffusion of gas through the layer of CO_2 hydrate formed between the gas phase and CH_4 hydrate. The diffusing carbon dioxide with an average density of $\rho_{g(dc)}$ in the hydrate will be called mobile, and the gas in the hydrate with a mass concentration G_i is immobile. Note that in connection with the adopted Equation (4), it becomes unnecessary to solve the inverse diffusion problem for the methane transfer through the hydrate layer of carbon dioxide.

We consider the following limiting scheme. We will assume that the skeleton of a porous medium is a set of channels with a cylindrical shape of radius a . In the presented model, it is assumed that CH_4 hydrate completely covers the channel walls. For this case, CH_4 hydrate will be located in the ring-shaped layer between $r = a$ and $r = a_{(dc)}$, and CO_2 hydrate in the layer between $r = a_{(dc)}$ and $r = a_g$. Then, we obtain

$$S_{h(mt)} = 1 - \left(\frac{a_{(dc)}}{a}\right)^2, \quad S_{h(dc)} = \left(\frac{a_{(dc)}}{a}\right)^2 - \left(\frac{a_g}{a}\right)^2, \quad S_g = \left(\frac{a_g}{a}\right)^2 \quad (12)$$

For the process of the transfer of a diffusing gas through a layer of CO_2 hydrate, we will use the diffusion equation [43,44]:

$$\frac{\partial \rho_{g(dc)}}{\partial t} = D_{h(dc)} \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial \rho_{g(dc)}}{\partial r} \right), \quad a_g < r < a_{(dc)} \quad (13)$$

where $D_{h(dc)}$ is the diffusion coefficient of CO_2 in its hydrate; $\rho_{g(dc)}$ is the average carbon dioxide density, which is dissolved in its hydrate.

Under the boundary conditions,

$$r = a_g : \quad \rho_{g(dc)} = \rho_{g(dc)s}, \quad r = a_{(dc)} : \quad \rho_{g(dc)} = 0 \quad (14)$$

the quasi-stationary solution of Equation (13) is as follows:

$$\rho_{g(dc)} = \rho_{g(dc)s} \frac{\ln(r/a_{(dc)})}{\ln(a_g/a_{(dc)})}, \quad a_g < r < a_{(dc)} \quad (15)$$

where $\rho_{g(dc)s}$ is the mobile carbon dioxide density in the CO_2 hydrate for a saturated state.

The value of the mass of mobile carbon dioxide passing per unit of time through a unit contact surface area between CO_2 and CH_4 hydrates is equal to

$$j_{g(dc)} = -D_{h(dc)} \left(\frac{\partial \rho_{g(dc)}}{\partial r} \right)_{a_{(dc)}} \quad (16)$$

Substituting Equation (15) into Equation (16), we obtain

$$j_{g(dc)} = \frac{\rho_{g(dc)s} D_{h(dc)}}{a_{(dc)} \ln(a_{(dc)}/a_g)} \quad (17)$$

The CO_2 consumption intensity $J_{g(dc)}$ is associated to the flow $j_{g(dc)}$: $J_{g(dc)} = A_h j_{g(dc)}$, where A_h is the total specific surface area of contact between CO_2 and CH_4 hydrates (i.e., the surface area of contact

between the hydrates per unit volume of a reservoir). For this value in the framework of the adopted scheme, we obtain

$$A_h = 2\pi a_{(dc)} n_{(dc)}, \quad n_{(dc)} = \frac{m(1 - S_{h(mt)})}{\pi a_{(dc)}^2} \quad (18)$$

where $n_{(dc)}$ is the number of channels with a diameter of $2a_{(dc)}$ in the volume unit.

Using the analogy with Henry's law, we will assume that the saturated concentration of free carbon dioxide in the composition of carbon dioxide hydrate is proportional to the partial pressure of carbon dioxide in the gas phase; i.e.,

$$\rho_{g(dc)s} = \Gamma_{(dc)} p_{g(dc)} \quad (19)$$

where $\Gamma_{(dc)}$ is Henry's parameter.

Then, for the intensity $J_{g(dc)}$ of the carbon dioxide consumption for the formation of its hydrate per volume unit of porous medium, using Equations (17) and (18), we can write

$$J_{g(dc)} = 2m(1 - S_{h(mt)}) \frac{\rho_{g(dc)s} D_{h(dc)}}{a_{(dc)}^2 \ln(a_{(dc)}/a_g)} \quad (20)$$

We introduce a new empirical parameter, which will be called the reduced diffusion coefficient for carbon dioxide in a gas hydrate:

$$D = \frac{\rho_{g(dc)s} D_{h(dc)}}{\rho_{g(dc)}^0} \quad (21)$$

Substituting Equation (19) and the first equation from Equation (9) into the last formula, we obtain

$$D = D_{h(dc)} \Gamma_{(dc)} R_{(dc)} T \quad (22)$$

In [45], based on the experimental data processing, the values of the methane diffusion coefficient through the gas hydrate layer were found to be of the order of 10^{-13} m²/s at the temperature of 274 K. By analogy with liquids, the diffusion coefficient $D_{h(dc)}$ and Henry's parameter $\Gamma_{(dc)}$ can be regarded as sufficiently conservative values (for example, weakly dependent on the value $p_{g(dc)}$). Since the relative change in temperature for the processes under consideration is small, the reduced diffusion coefficient D will be considered constant. It should be mentioned that many factors can influence the intensity of the hydrate decomposition and formation, such as the introduction of various surfactants, the exposure of the shock and electromagnetic waves [46–53], etc. The empirical parameter D depends both on the hydrate structure and on the porous medium skeleton features.

We transform the above equations, using the independent variables $\rho_{g(dc)}^0$, ρ_g^0 , T and $S_{h(dc)}$. The first equation from Equation (1), taking into account Equations (7) and (8), can be written as

$$mS_g \frac{\partial \rho_{g(dc)}^0}{\partial t} = \frac{\partial}{\partial x} \left(\rho_{g(dc)}^0 \frac{k_g}{\mu_g} \frac{\partial p}{\partial x} \right) + mS_g D_g \frac{\partial^2 \rho_{g(dc)}^0}{\partial x^2} - J_{g(dc)} \quad (23)$$

As the second equation, we use Equation (6), which, taking into account Equation (7), will take the form

$$mS_g \frac{\partial \rho_g^0}{\partial t} = \frac{\partial}{\partial x} \left(\rho_g^0 \frac{k_g}{\mu_g} \frac{\partial p}{\partial x} \right) + J_{gd} \left(\frac{M_{(mt)}}{M_{(dc)}} - 1 \right) \quad (24)$$

The heat influx in Equation (10), taking into account Equations (4) and (7), can be written in the form

$$\rho c \frac{\partial T}{\partial t} = \rho_g^0 c_g \frac{k_g}{m\mu_g} \frac{\partial p}{\partial x} \frac{\partial T}{\partial x} + \lambda \frac{\partial^2 T}{\partial x^2} + \left(\frac{l_{h(dc)}}{G_{(dc)}} - \frac{M_{(mt)}}{M_{(dc)}} \frac{l_{h(mt)}}{G_{(mt)}} \right) J_{gd} \quad (25)$$

To close this system, it is enough to add one more differential equation following from the first equation in Equation (2):

$$mG_{(dc)}\rho_{h(dc)}^0 \frac{\partial S_{h(dc)}}{\partial t} = J_{g(dc)} \quad (26)$$

For other variable parameters included in Equations (23)–(26), taking into account Equations (12), (20) and (22), we obtain

$$J_{g(dc)} = \frac{4m\rho_{g(dc)}^0 D}{a^2 \ln(1 + S_{h(dc)}/S_g)} \quad (27)$$

$$S_{h(mt)} = S_h - S_{h(dc)}, \quad S_g = 1 - S_h \quad (S_h = \text{const})$$

Based on Equation (9) for pressure, we can get

$$p = \left(\rho_{g(dc)}^0 (R_{(dc)} - R_{(mt)}) + \rho_{g(dc)}^0 R_{(mt)} \right) T \quad (28)$$

In accordance with the above assumptions, the permeability of the gas mixture and the radius of porous tubules will be specified as

$$k_g = k(a_g/a)^2, \quad a = \sqrt{k/m} \quad (29)$$

where k is the absolute permeability coefficient of the porous skeleton.

We supplement the system of Equations (23)–(29) with the boundary and initial conditions:

$$\begin{aligned} t > 0, \quad \begin{cases} x = 0: & \rho_g = \rho_{ge}, \quad \rho_{g(dc)} = \rho_{ge}, \quad T = T_e, \\ x = L: & \rho_g = \rho_{g0}, \quad \partial T / \partial x = 0, \end{cases} \\ t = 0, \quad 0 > x > x_0: & \quad \rho_g = \rho_{g0}, \quad \rho_{g(dc)} = 0, \quad T = T_0. \end{aligned} \quad (30)$$

The system of Equations (23)–(29) with the boundary and initial conditions in Equation (30) was solved by the finite difference method.

3. Calculation Results

Figure 2 shows the distributions of the partial pressures and hydrate saturations of carbon dioxide and methane at $k_0 = 5 \times 10^{-12} \text{ m}^2$, $p_0 = 3.1 \text{ MPa}$, $D = 5 \times 10^{-15} \text{ m}^2/\text{s}$, $T_0 = 273 \text{ K}$. The original parameters used in the model are shown in Table 1 [11,16,19,39,54]. Note that the temperature fields in a reservoir will largely depend on the porous reservoir material, since it affects the values of thermal conductivity and specific volumetric heat capacity. The averaged values of the coefficients of thermal conductivity and specific volumetric heat capacity, characteristic of most reservoirs, are used in the work. The process will approach the frontal mode of hydrate substitution in the reservoir with a decrease in permeability. When implementing this mode, the reservoir is conventionally divided into two zones: the near one, containing carbon dioxide hydrate and the gas mixture $\text{CO}_2\text{-CH}_4$, and the far one, containing methane and its hydrate. In Figure 2, we can observe that the frontal mode is limited primarily by filtration mass transfer, and the role of diffusive mass transfer weakens.

We used the approximate analytical solutions presented in [31] to test the mathematical model. In [31], approximate analytical solutions were obtained for the problem of decomposition of methane gas hydrate during the injection of gaseous CO_2 into a gas-hydrated formation based on the method of converting to a self-similar variable.

Figure 3 presents the dependence of the coordinates of the hydrate substitution boundary in time. The solid line corresponds to the numerical solution obtained in our work with $D = 10^{-16} \text{ m}^2/\text{s}$, while the dashed line corresponds to the analytical solution obtained in [31]. The figure shows that these

solutions show a fairly good agreement, which indicates the reliability of the mathematical model presented in our work.

Figure 2. The distributions of partial pressures ($p_{g(dc)}$, $p_{g(mt)}$) and hydrate saturations of carbon dioxide and methane. Lines 1, 2 and 3 correspond to $t = 0.27, 2$ and 5 h.

Table 1. Basic parameters for the model.

Variables	Symbol	Value	Unit
Porosity	m	0.1	-
Initial hydrate saturation	$S_{h(mt)0}$	0.2	-
Reservoir length	L	10	m
Injection temperature	T_e	273	K
Injection pressure	p_e	3.4	MPa
Specific volumetric heat capacity	ρC	$2.5 \cdot 10^6$	J/(K·m ³)
System thermal conductivity coefficient	λ	2	W/(m·K)
Mass concentrations of carbon dioxide in hydrate	$G_{(dc)}$	0.28	-
Mass concentrations of methane in hydrate	$G_{(mt)}$	0.12	-
Gas constant of methane	$R_{(mt)}$	520	J/(kg·K)
Gas constant of carbon dioxide	$R_{(dc)}$	189	J/(kg·K)
Density of carbon dioxide hydrate	$\rho_{h(dc)}$	1115	kg/m ³
Density of methane hydrate	$\rho_{h(mt)}$	910	kg/m ³
Dynamic viscosity of carbon dioxide	$\mu_{g(dc)}$	$1.5 \cdot 10^{-5}$	Pa·s
Dynamic viscosity of methane	$\mu_{g(mt)}$	$1.12 \cdot 10^{-5}$	Pa·s
Heat of the formation of CO ₂ hydrate	$l_{h(dc)}$	$4.8 \cdot 10^5$	J/kg
Heat of the formation of methane hydrate	$l_{h(mt)}$	$4.37 \cdot 10^5$	J/kg
Specific heat capacity of CO ₂	$c_{g(dc)}$	731	J/(kg·K)
Specific heat capacity of methane	$c_{g(mt)}$	1560	J/(kg·K)
Diffusion mixing coefficient of the components of gas mixture	D_g	10^{-5}	m ² /s

Figure 3. Dynamics of phase transition front coordinate. The solid line corresponds to the solutions obtained in this work, the dashed line in work [31].

We also performed a comparison with the experimental data presented in [55]. In this work, the process of the replacement of methane in CH_4 hydrate with CO_2 in a dispersed medium is considered, and the dynamics of temperature changes for this process is presented. The experiment was carried out in two stages. The first stage was a test study of the methane hydrate formation in a quartz sand sample partially saturated with water. At the second stage of the experiment, the process of methane replacement with carbon dioxide in the hydrate saturated sand sample was studied. The initial methane hydrate saturation was 10%, the sample porosity was 34%, and the initial temperature in the reactor was 275 K.

Figure 4 shows a comparison of the results of numerical study and experimental data, given in [55], for changes in temperature over time. As can be seen from Figure 4, energy is released due to the replacement; after the completion of the CH_4 - CO_2 replacement process, the sample temperature returns to the initial one. It is worth noting the satisfactory agreement between the experimental data and the calculation results using the proposed model.

Figure 4. Comparison of calculated temperature with experimental data from [55]. The solid line is the numerical study results according to the proposed model, while the points are the experimental data.

Figure 5 represents the parameter distributions along the length of the reservoir at different of time instants at $k_0 = 10^{-16} \text{ m}^2$, $D = 10^{-16} \text{ m}^2/\text{s}$, $T_0 = 274 \text{ K}$, $p_0 = 3 \text{ MPa}$; $T_s(p)$ is the equilibrium temperature of phase transitions at the current pressure in the reservoir. It is shown that the injection of the CO_2 into the reservoir leads to the increase of carbon dioxide partial pressure in the porous medium and to the initiation of the CH_4 hydrate to CO_2 hydrate transition process. The surface of the methane displacement by CO_2 reaches the right border of porous medium in a time of about 1 min. Subsequently,

methane is displaced, which was recovered from the gas hydrate as a result of the replacement process. The process of CH₄-CO₂ exchange in the methane hydrate occurs with the reservoir heating.

Figure 5. The distributions along the coordinate x of the partial pressures of CO₂ $p_{g(dc)}$ and CH₄ $p_{g(mt)}$, the reservoir temperature, the hydrate saturation S_h at various times moments. Curves 1, 2, 3, 4 correspond to $t = 10, 30, 70$ and 440 s. On the bottom right of the figure, solid lines correspond to $S_{h(dc)}$, and dashed lines correspond to $S_{h(mt)}$.

The mass flow rate of the gas passing through a unit cross-sectional area of the reservoir is equal to

$$q_{g(dc)e} = \rho_{g(dc)e}^0 m S_g v_{ge}, \quad q_{g(dc)} = \rho_{g(dc)}^0 m S_g v_g, \quad q_{g(mt)} = \rho_{g(mt)}^0 m S_g v_g$$

where $q_{g(dc)e}$ is the specific mass flow rate of the injected CO₂; and $q_{g(dc)}$ and $q_{g(mt)}$ are the specific mass flow rates of CO₂ and CH₄ at the reservoir outlet.

The specific (expressed per unit of the reservoir cross-sectional area) mass of the conserved CO₂ $Q_{g(dc)}$ and the specific mass of the CH₄ extracted from the reservoir $Q_{g(mt)}$ over a period of time T can be determined as follows:

$$Q_{g(dc)} = \int_0^T (q_{g(dc)e} - q_{g(dc)}) dt, \quad Q_{g(mt)} = \int_0^T q_{g(mt)} dt \quad (31)$$

Figure 6 shows the time dependences of the specific mass flow rates of the injected and extracted carbon dioxide, the mass flow rate of the extracted methane, the specific mass of carbon dioxide buried in the reservoir in the gas hydrate state, and the specific mass of the produced methane. It is evident that, at the initial stage, free methane is displaced from the reservoir. In the second stage, CH₄ in the hydrate is replaced by CO₂. As a result of the process of CO₂ injection into the reservoir, about 35 kg/m² of methane is extracted and about 115 kg/m² of CO₂ is stored.

Figure 6. Evolution with time of the specific mass flow rates of the CO₂ injected into the layer $q_{g(dc)}$ and produced from the reservoir $q_{g(mt)}$, the produced methane $q_{g(mt)}$, the specific mass of the conserved CO₂ $Q_{g(dc)}$ and the specific mass of the produced CH₄ $Q_{g(mt)}$.

The influence of various parameters on the time t_{rep} of the complete replacement of CH₄ in hydrate with CO₂ was studied.

Figure 7 shows the dependence of the time t_{rep} of complete replacement on the absolute reservoir permeability k ; the dependence is constructed for two values of the reduced diffusion coefficient D . It can be seen that, at low values of the reservoir permeability, the reduced diffusion coefficient has little effect on the time of transition of CH₄ hydrate in CO₂ hydrate in the entire reservoir. This is due to the fact that, in the case with low values of the porous medium permeability k , the CH₄-CO₂ replacement process is limited by the mass transfer due to filtration. At high values of the reservoir permeability, the rate of the methane replacement in the CH₄ hydrate with carbon dioxide significantly depends on the reduced diffusion coefficient magnitude D (Figure 7). We note that the increase in the replacement time, in the case of the growth in the porous media permeability k at the high values of the reservoir permeability, is due to the decrease in the specific contact surface between the CO₂ hydrate and CH₄ hydrate with an increased value of k .

Figure 7. Change of the time t_{rep} of the total methane replacement in CH_4 hydrate with CO_2 in the entire reservoir as a function of the reservoir permeability k at different values of the reduced diffusion coefficient D . Lines 1 and 2 correspond to $D = 5 \times 10^{-16}$ and $5 \times 10^{-15} \text{ m}^2/\text{s}$.

The dependence of the time t_{rep} of the total substitution of CH_4 by CO_2 in the CH_4 hydrate on the hydrate saturated reservoir length is shown in Figure 8. It can be seen that, for short-length reservoirs with a decrease in permeability, the rate of hydrate of CH_4 methane to the hydrate of CO_2 transfer increases. This is due to the fact that, in this case, the process of the CH_4 - CO_2 replacement is limited by diffusion, and a decrease in permeability corresponds to an increase in the specific contact surface between the hydrate and the gas. It is also worth noting that, in the case of a short-length reservoir, the complete CH_4 - CO_2 replacement occurs at relatively short time intervals (Figure 8). As the length of the reservoir increases, the process of transition of CH_4 hydrate to CO_2 hydrate in the reservoir becomes increasingly dependent on the filtration mass transfer, which, in turn, depends significantly on the porous medium permeability. Therefore, in the case of long reservoirs, the time for the complete replacement of methane in the CH_4 hydrate with carbon dioxide decreases with increasing the reservoir permeability.

Figure 8. Change of the time t_{rep} of the total methane replacement in methane hydrate with carbon dioxide depending on the reservoir length. Curves 1 and 2 correspond to $k = 5 \times 10^{-12}$ and $5 \times 10^{-13} \text{ m}^2$.

Figure 9 shows the dependence of the time of full replacement t_{rep} on the reservoir length; the dependence is constructed for two values of the reduced diffusion coefficient D . It is evident that, as the reservoir length increases, the influence of the kinetics on the time of full transition of CH_4 hydrate to CO_2 hydrate decreases, and the role of the filtration mass transfer increases.

Figure 9. Change of the time t_{rep} of the total methane replacement in methane hydrate with carbon dioxide depending on the reservoir length at different values of the reduced diffusion coefficient D . Lines 1 and 2 correspond to $D = 4 \times 10^{-15} \text{ m}^2/\text{s}$ and $4 \times 10^{-16} \text{ m}^2/\text{s}$.

4. Conclusions

The process of methane replacement in gas hydrate with carbon dioxide during CO_2 injection into a porous medium was studied. The calculations show that, for the process of CO_2 injection into the gas hydrate reservoir, two stages can be distinguished. The first stage is specified by the beginning of the CH_4 - CO_2 replacement process; in the second stage, methane, formed as a result of replacement, is extracted from the hydrate saturated reservoir.

It was established that at high values of the reduced diffusion coefficient of carbon dioxide in its hydrate, low values of the reservoir permeability, and with the growth of the reservoir length, the process of the CH_4 - CO_2 replacement in CH_4 hydrate will take place in the frontal regime. In this regime, the replacement process is determined primarily by the intensity of filtration mass transfer in the reservoir. Otherwise, the process of the CH_4 - CO_2 replacement will occur in the volume area of the reservoir. In this case, the process is determined by the intensity of gas diffusion in hydrate. For the case of highly permeable porous media (the hydrate formation process is limited by the diffusion of gas in the hydrate), an increase in the methane replacement time in the CH_4 hydrate with carbon dioxide is shown, which is caused by a decrease in the specific surface of contact between CH_4 hydrate and CO_2 hydrate with increasing reservoir permeability.

The presented mathematical model is more universal and allows us to consider the simultaneous influence of two factors (diffusion mechanism, filtration mass transfer) on the process under study.

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