

МЕХАНИКА ЖИДКОСТИ, ГАЗА И ПЛАЗМЫ

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MATHEMATICAL MODELING OF THE EQUILIBRIUM COMPLETE REPLACEMENT OF METHANE BY CARBON DIOXIDE IN A GAS HYDRATE RESERVOIR AT NEGATIVE TEMPERATURES*

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Abstract

Gas hydrates, which contain the largest amount of methane on our planet, are a promising source of natural gas after the depletion of traditional gas fields, the reserves of which are estimated to last about 50 years. Therefore, it is necessary to study the methods for extracting gas from gas hydrates in order to select the best of them and make reasoned technological and engineering decisions in the future.

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One of these methods is the replacement of methane in its hydrate with carbon dioxide. This work studies the construction of a mathematical model to observe this method. The following process is considered in this article: on one side of a porous reservoir, initially saturated with methane and its hydrate, carbon dioxide is injected; on the opposite side of this reservoir, methane and/or carbon dioxide are extracted. In this case, both the decomposition of methane hydrate and the formation of carbon dioxide hydrate can occur.

This problem is stated in a one-dimensional linear formulation for the case of negative temperatures and gaseous carbon dioxide, which means that methane, carbon dioxide, ice, methane, and carbon dioxide hydrates may be present in the reservoir. A mathematical model is built based on the following: the laws of conservation of masses of methane, carbon dioxide, and ice; Darcy's law for the gas phase motion; equation of state of real gas; energy equation taking into account thermal conductivity, convection, adiabatic cooling, the Joule — Thomson effect, and the release or absorption of latent heat of hydrate formation. The modelling assumes that phase transitions occur in an equilibrium mode and that methane can be completely replaced by carbon dioxide. The results of numerical experiments are presented.

Keywords

Mathematical modeling, gas hydrates, methane, carbon dioxide, porous medium, gas filtration, replacement, equilibrium phase transition.

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Introduction

According to the British Petroleum Statistical Review of World Energy 2019, the total proved reserves of natural gas (196.9 trln m³) will last for about 50 years at the current production level (3.9 trln m³) [3]. However, a significant amount of gas (mainly methane) on our planet is part of gas hydrates, the reserves of which (1,000-20,000 trln m³) can last hundreds of years after the depletion of traditional gas fields [6]. Currently, the model calculations of the price of gas production from hydrates show \$420 per 1,000 m³ [7], while the cost of traditional gas production for Gazprom was about \$15 per 1,000 m³ in 2017 [10], i. e., the industrial development of gas hydrate deposits is significantly more expensive than the industrial development of traditional gas fields. The ongoing research aims at determining the most effective technological and engineering solutions for the cost-effective development of gas hydrate deposits in the future [2].

This work studies one of the promising methods of gas production from gas hydrates — the replacement of methane in hydrate with carbon dioxide [2, 5, 13]. During the replacement, the carbon dioxide is injected into a porous medium, and its molecules replace the methane molecules in a gas hydrate and remain in the reservoir. The methane is released in a free form, which allows its extraction (Fig. 1). Thus, the replacement method allows not only the production of methane, but also the disposal of carbon dioxide.

The following sections of the article include the statement of the problem of filtering methane and carbon dioxide (taking into account the formation or decomposition of their hydrates, for the case of negative temperatures), a mathematical model, as well as the results of the numerical experiments.

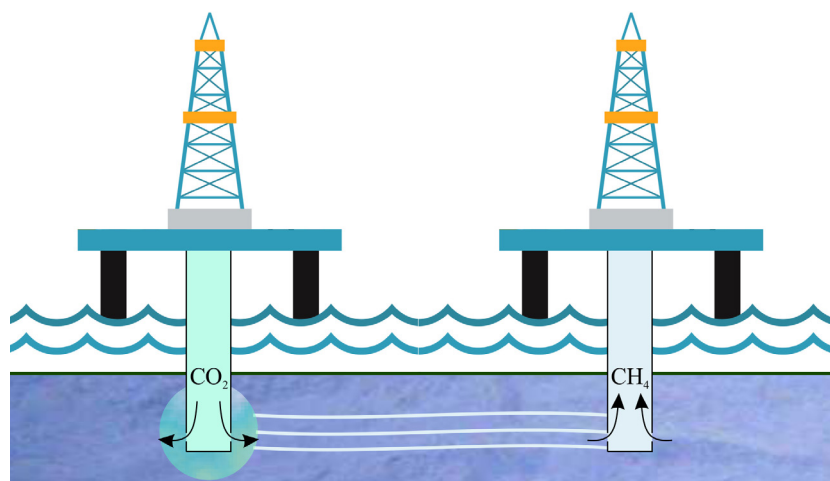


Fig. 1. Production of methane from a gas hydrate field using the replacement method by carbon dioxide

Рис. 1. Добыча метана из газогидратного месторождения путем замещения углекислым газом

Problem statement

In a one-dimensional linear formulation, we consider a porous reservoir, initially saturated with methane and its hydrate (Fig. 2, Initial state). There, 0 corresponds to the left reservoir boundary, L is the reservoir length and the coordinate of its right boundary, x is the linear coordinate. The initial pressure p_0 and the temperature T_0 correspond to the thermodynamic conditions for the existence of methane hydrate in a stable state. The process is considered at negative temperatures, i. e. $T_0 < 0$ °C. At the left boundary, the carbon dioxide injection begins with the pressure $p_{inj} > p_0$ and the temperature $T_{inj} < 0$ °C, which correspond to the thermodynamic conditions for the existence of both CO_2 in the gaseous state and stable CO_2 hydrate. Under these conditions, decomposition of methane hydrate, formation of carbon dioxide hydrate and displacement of gaseous methane to the reservoir right boundary will occur. Simultaneously with the injection, the methane extraction begins at the right boundary with pressure $p_{extr} < p_0$. The extraction pressure p_{extr} must be such as to provide thermodynamic conditions for the decomposition of CH_4 hydrate and the stable existence of CO_2 hydrate. Under these conditions, the methane hydrate will decompose in to free methane and ice. The free methane will be extracted at the right boundary, and the ice will form the carbon dioxide hydrate when it comes from the left boundary, on which it is injected. Thus, a region with carbon dioxide and its hydrate will form from the left boundary and methane and ice from at the right boundary (Fig. 2, Intermediate state). What will happen between these two

areas, and how these areas will evolve, will be shown later in the calculations. Ultimately, all the methane will be displaced, and only the carbon dioxide and its hydrate will remain in the porous medium (Fig. 2, Final state).

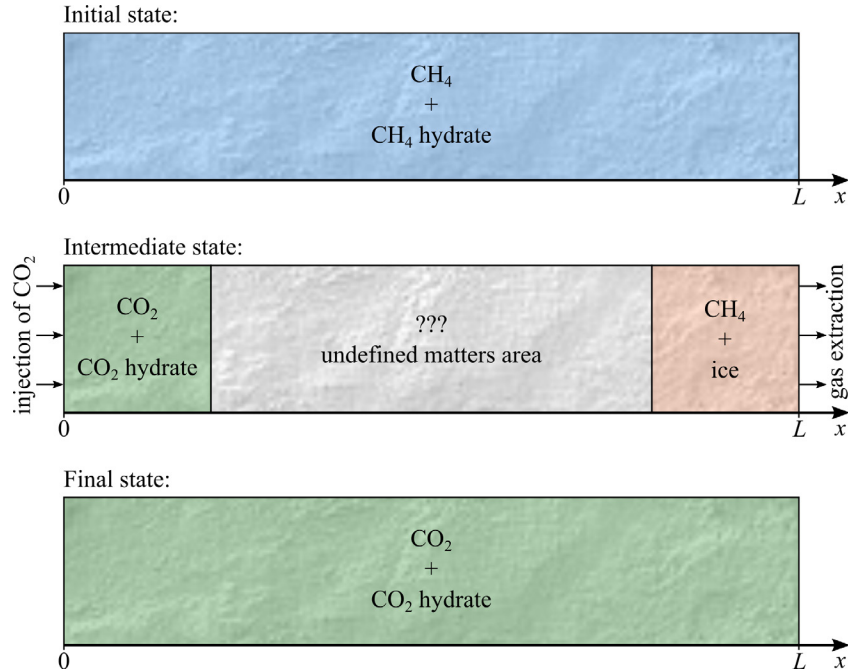


Fig. 2. Schematic representation of matters saturating a porous medium

Рис. 2. Схематичное представление насыщающих пористую среду веществ

Mathematical model

When modeling, we will accept the following assumptions: at each separate point in space, the temperature of the porous medium skeleton, gas phase, ice, and hydrates coincide; mass concentrations of gases in their hydrates are constant ($G_{\text{CH}_4} = \text{const}$, $G_{\text{CO}_2} = \text{const}$); the porous medium skeleton, ice, and hydrates are incompressible and immobile; reservoir porosity is constant ($m = \text{const}$); the formation and decomposition of gas hydrates occur in an equilibrium mode; carbon dioxide can completely replace methane in its hydrate. The following scheme has been adopted for the replacement process:

“CH₄-CO₂ replacement can only occur under such operating pressures that the CH₄ partial pressure is lower than the pure CH₄ hydrate formation equilibrium pressure and the CO₂ partial pressure is higher than the pure CO₂ hydrate formation equilibrium pressure” [4].

Thus, we will assume that methane hydrate decomposes when the partial pressure of methane in a gas mixture is lower than the equilibrium pressure of methane hydrate for reservoir temperature; and carbon dioxide hydrate is formed when the partial pressure of carbon dioxide in the gas mixture is higher than the equilibrium pressure of carbon dioxide hydrate for the reservoir temperature and ice is present.

The conservation equations for the masses of methane, carbon dioxide and ice are as follows:

$$m \frac{\partial}{\partial t} (k_{\text{CH}_4} \rho_g S_g) + m \frac{\partial}{\partial x} (k_{\text{CH}_4} \rho_g S_g v_g) = -m \rho_{h\text{CH}_4} G_{\text{CH}_4} \frac{\partial S_{h\text{CH}_4}}{\partial t}, \quad (1)$$

$$m \frac{\partial}{\partial t} (k_{\text{CO}_2} \rho_g S_g) + m \frac{\partial}{\partial x} (k_{\text{CO}_2} \rho_g S_g v_g) = -m \rho_{h\text{CO}_2} G_{\text{CO}_2} \frac{\partial S_{h\text{CO}_2}}{\partial t}, \quad (2)$$

$$m \frac{\partial}{\partial t} (\rho_{\text{ice}} S_{\text{ice}}) = -m \rho_{h\text{CH}_4} (1 - G_{\text{CH}_4}) \frac{\partial S_{h\text{CH}_4}}{\partial t} - m \rho_{h\text{CO}_2} (1 - G_{\text{CO}_2}) \frac{\partial S_{h\text{CO}_2}}{\partial t}, \quad (3)$$

$$S_g + S_{\text{ice}} + S_{h\text{CH}_4} + S_{h\text{CO}_2} = 1, \quad (4)$$

$$k_{\text{CH}_4} + k_{\text{CO}_2} = 1, \quad (5)$$

where t is time; x is the linear coordinate; m is the reservoir porosity; k_{CH_4} and k_{CO_2} are the mass concentrations of methane and carbon dioxide in the gas phase; ρ_g , ρ_{ice} , $\rho_{h\text{CH}_4}$, and $\rho_{h\text{CO}_2}$ are the densities of the gas phase, ice, methane, and carbon dioxide hydrates; S_g , S_{ice} , $S_{h\text{CH}_4}$, and $S_{h\text{CO}_2}$ are the saturations of the porous medium with gas, ice, methane, and carbon dioxide hydrates; v_g is the gas velocity; G_{CH_4} and G_{CO_2} are the mass content of methane and carbon dioxide in their hydrates.

The following equation of state for real gas is accepted, in which the supercompressibility coefficient is calculated according to the Latonov — Gurevich equation [8]:

$$p = z_g \rho_g R_g T, \quad (6)$$

$$z_g = (0.4 \cdot \lg(T/T_c) + 0.73)^{p/p_c} + 0.1 p/p_c, \quad (7)$$

$$R_g = R \left/ \left(\frac{k_{\text{CO}_2}}{M_{\text{CO}_2}} + \frac{k_{\text{CH}_4}}{M_{\text{CH}_4}} \right) \right.^{-1}, \quad (8)$$

$$\varphi_{\text{CH}_4} = \frac{k_{\text{CH}_4}}{M_{\text{CH}_4}} \left/ \left(\frac{k_{\text{CO}_2}}{M_{\text{CO}_2}} + \frac{k_{\text{CH}_4}}{M_{\text{CH}_4}} \right) \right., \quad \varphi_{\text{CO}_2} = 1 - \varphi_{\text{CH}_4},$$

$$T_c = \varphi_{\text{CH}_4} T_{c\text{CH}_4} + \varphi_{\text{CO}_2} T_{c\text{CO}_2}, \quad p_c = \varphi_{\text{CH}_4} p_{c\text{CH}_4} + \varphi_{\text{CO}_2} p_{c\text{CO}_2},$$

where p is the pressure; z_g is the supercompressibility coefficient of real gas; ρ_g is the gas phase density; R and R_g are the universal and specific gas constants; T is the temperature; T_c and p_c , $T_{c\text{CH}_4}$ and $p_{c\text{CH}_4}$, as well as $T_{c\text{CO}_2}$ and $p_{c\text{CO}_2}$ are the critical temperatures and pressures of the gas phase, pure methane, and pure carbon dioxide; M_{CH_4} and M_{CO_2} are the molar masses of the methane and carbon dioxide; φ_{CH_4} and φ_{CO_2} are the mole fractions of the methane and carbon dioxide in the gas phase.

For the gas phase filtration, we have enacted Darcy's law:

$$mS_g v_g = -\frac{k_g}{\mu_g} \frac{\partial p}{\partial x}, \quad (9)$$

$$k_g = k_0 S_g^3, \quad \mu_g = \varphi_{\text{CH}_4} \mu_{\text{CH}_4} + \varphi_{\text{CO}_2} \mu_{\text{CO}_2},$$

where k_0 and k_g are the absolute reservoir permeability and permeability for gas; μ_g , μ_{CH_4} , and μ_{CO_2} are the dynamic viscosities of the gas phase, pure methane and pure carbon dioxide.

The heat transfer equation in a porous medium [1], taking into account the formation and decomposition of hydrates, takes the following form:

$$\begin{aligned} \rho c \frac{\partial T}{\partial t} + m \rho_g c_g S_g v_g \left(\frac{\partial T}{\partial x} + \varepsilon \frac{\partial p}{\partial x} \right) - m \rho_g c_g S_g \eta \frac{\partial p}{\partial t} - \frac{\partial}{\partial x} \left(\lambda \frac{\partial T}{\partial x} \right) = \\ = m \rho_{h\text{CH}_4} L_{\text{CH}_4} \frac{\partial S_{h\text{CH}_4}}{\partial t} + m \rho_{h\text{CO}_2} L_{\text{CO}_2} \frac{\partial S_{h\text{CO}_2}}{\partial t}, \\ \rho c = (1-m) \rho_{sk} c_{sk} + m \sum_{j=g, ice, h\text{CH}_4, h\text{CO}_2} S_j \rho_j c_j, \quad \lambda = (1-m) \lambda_{sk} + m \sum_{j=g, ice, h\text{CH}_4, h\text{CO}_2} S_j \lambda_j \quad (10) \\ c_g = k_{\text{CH}_4} c_{\text{CH}_4} + k_{\text{CO}_2} c_{\text{CO}_2}, \quad \lambda_g = \varphi_{\text{CH}_4} \lambda_{\text{CH}_4} + \varphi_{\text{CO}_2} \lambda_{\text{CO}_2}, \\ \varepsilon = -\frac{1}{\rho_g c_g} \frac{T}{z_g} \left(\frac{\partial z_g}{\partial T} \right)_p, \quad \eta = \frac{1}{\rho_g c_g} - \varepsilon. \end{aligned}$$

Here, ρc and λ are the volumetric heat capacity and thermal conductivity of the saturated porous medium; ρ_j , c_j and λ_j ($j = sk, g, ice, h\text{CH}_4, h\text{CO}_2$) are the densities, heat capacities and thermal conductivities of the porous medium skeleton, gas, ice, methane, and carbon dioxide hydrates; c_j and λ_j ($j = \text{CH}_4, \text{CO}_2$) are the heat capacities and thermal conductivities of the pure methane and carbon dioxide; ε and η are the Joule — Thomson and adiabatic cooling coefficients; L_{CH_4} and L_{CO_2} are the specific heats of formation/decomposition of methane and carbon dioxide hydrates to gas and ice.

The phase transitions occur in the equilibrium mode, the pressure and temperature on the equilibrium curve of phase transitions for methane hydrate (11) and carbon dioxide hydrate (12) are related at negative temperatures by the following equations [9]:

$$\ln(p_{eqh\text{CH}_4}) = \ln(2.6) + \frac{2,768}{273} - \frac{69,900}{273^2} - \frac{2,768}{T} + \frac{69,900}{T^2}, \quad (11)$$

$$\ln(p_{eqh\text{CO}_2}) = \ln(1.2) + \frac{13,854}{273} - \frac{1,351,500}{273^2} - \frac{13,854}{T} + \frac{1,351,500}{T^2}. \quad (12)$$

Next, we transform the basic equations to obtain the system of equations for calculations.

From the equations (1), (5), (6), and (9), we obtain an equation for calculating the mass concentration of carbon dioxide in the gas phase:

$$\begin{aligned} \frac{\partial k_{\text{CO}_2}}{\partial t} + \frac{\partial p}{\partial t} \frac{k_{\text{CO}_2}}{p} - \frac{\partial z_g}{\partial t} \frac{k_{\text{CO}_2}}{z_g} - \frac{\partial R_g}{\partial t} \frac{k_{\text{CO}_2}}{R_g} - \frac{\partial T}{\partial t} \frac{k_{\text{CO}_2}}{T} + \\ + \frac{\partial S_g}{\partial t} \frac{k_{\text{CO}_2}}{S_g} + \frac{\partial S_{h\text{CO}_2}}{\partial t} \frac{\rho_{h\text{CO}_2} G_{\text{CO}_2}}{\rho_g S_g} - \frac{1}{m \rho_g S_g} \frac{\partial}{\partial x} \left(k_{\text{CO}_2} \rho_g \frac{k_g}{\mu_g} \frac{\partial p}{\partial x} \right) = 0. \end{aligned} \quad (13)$$

From the equations (1), (2), (5), (6), and (9), we obtain an equation for calculating the pressure:

$$\begin{aligned} \frac{\partial p}{\partial t} - \frac{\partial z_g}{\partial t} \frac{p}{z_g} - \frac{\partial R_g}{\partial t} \frac{p}{R_g} - \frac{\partial T}{\partial t} \frac{p}{T} + \frac{\partial S_g}{\partial t} \frac{p}{S_g} + \\ + \frac{p}{\rho_g S_g} \left(\frac{\partial S_{h\text{CH}_4}}{\partial t} \rho_{h\text{CH}_4} G_{\text{CH}_4} + \frac{\partial S_{h\text{CO}_2}}{\partial t} \rho_{h\text{CO}_2} G_{\text{CO}_2} \right) - \frac{z_g R_g T}{m S_g} \frac{\partial}{\partial x} \left(\rho_g \frac{k_g}{\mu_g} \frac{\partial p}{\partial x} \right) = 0. \end{aligned} \quad (14)$$

We transform the heat transfer equation (10) taking into account Darcy's law (9), which results in an equation for calculating the temperature:

$$\begin{aligned} \rho c \frac{\partial T}{\partial t} - \rho_g c_g \frac{k_g}{\mu_g} \frac{\partial p}{\partial x} \frac{\partial T}{\partial x} - \rho_g c_g \frac{k_g}{\mu_g} \varepsilon \left(\frac{\partial p}{\partial x} \right)^2 - m \rho_g c_g S_g \eta \frac{\partial p}{\partial t} - \frac{\partial}{\partial x} \left(\lambda \frac{\partial T}{\partial x} \right) = \\ = m \rho_{h\text{CH}_4} L_{\text{CH}_4} \frac{\partial S_{h\text{CH}_4}}{\partial t} + m \rho_{h\text{CO}_2} L_{\text{CO}_2} \frac{\partial S_{h\text{CO}_2}}{\partial t}. \end{aligned} \quad (15)$$

Solving the differential equation (3), taking into account the initial conditions (18), we obtain an equation for calculating the ice content:

$$S_{\text{ice}} = \frac{\rho_{h\text{CH}_4}}{\rho_{\text{ice}}} (1 - G_{\text{CH}_4}) (S_{h\text{CH}_4} - S_{h\text{CH}_4}) - \frac{\rho_{h\text{CO}_2}}{\rho_{\text{ice}}} (1 - G_{\text{CO}_2}) S_{h\text{CO}_2}. \quad (16)$$

The gas saturation is expressed from equation (4):

$$S_g = 1 - S_{\text{ice}} - S_{h\text{CH}_4} - S_{h\text{CO}_2}. \quad (17)$$

Next, we write down the initial and boundary conditions.

Initially, the reservoir contains only methane and its hydrate (Fig. 2, Initial state):

$$\begin{aligned} t = 0, x \in [0; L]: \quad k_{\text{CO}_2} = 0, \quad p = p_0, \quad T = T_0, \quad S_g = S_{g0}, \quad S_{\text{ice}} = 0, \\ S_{h\text{CH}_4} = S_{h\text{CH}_4} = 1 - S_{g0}, \quad S_{h\text{CO}_2} = 0. \end{aligned} \quad (18)$$

Carbon dioxide is injected at the left boundary:

$$t > 0, x = 0: \quad k_{\text{CO}_2} = 1, \quad p = p_{\text{inj}} > p_0, \quad T = T_{\text{inj}}. \quad (19)$$

At the right boundary, gas is extracted:

$$t > 0, x = L: \quad \frac{\partial k_{\text{CO}_2}}{\partial x} = 0, \quad p = p_{\text{extr}} < p_0, \quad \frac{\partial T}{\partial x} = 0. \quad (20)$$

The system of equations (7), (8), and (13)-(17), taking into account the initial and boundary conditions (18)-(20), is solved numerically by the method of simple iterations. The partial differential equations (13)-(15) are solved using the implicit scheme and the tridiagonal matrix algorithm. A feature of the proposed model is the lack of explicit equations for finding hydrates saturations — a special iterative procedure has been developed for their calculation. All together, they form a closed system, which allows numerical experiments to research the replacement method.

The limits of applicability of this model in stated formulation are shown on Fig. 3.

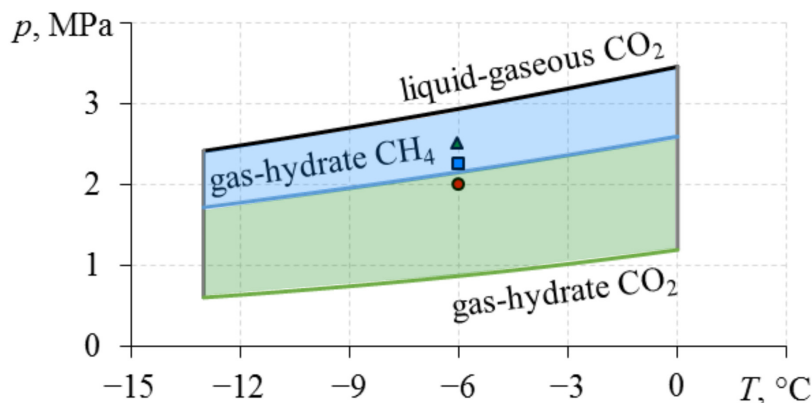


Fig. 3. The limits of applicability of purposed model in stated formulation

Notes: the shapes indicate the parameters for calculations: the green triangle is the CO_2 injection, the blue square — the initial state in the porous medium, the red circle — the extraction pressure at the right boundary.

Рис. 3. Границы применимости модели в указанной постановке

Примечания: фигурами отмечены параметры для тестовых расчетов: зеленый треугольник — закачка CO_2 , синий квадрат — начальное состояние в пористой среде, красная окружность — давление откачки с правой границы.

The initial thermodynamic conditions in the reservoir should ensure the stable existence of methane hydrate, i. e. they lie above the “gas-hydrate CH_4 ” curve on Fig. 3. Gaseous CO_2 is injected into the reservoir, i. e. its pressure and temperature should be below the “liquid-gaseous CO_2 ” curve. The injection pressure should exceed the initial reservoir pressure. Therefore, in the aggregate, the initial conditions and conditions for the injection of carbon dioxide should lie in the blue zone. To ensure the decomposition of methane hydrate and the stable existence of carbon dioxide hydrate, the parameters at the right boundary (extraction parameters) should lie in the green zone. It should also be ensured that throughout the calculation, the pressure and temperature in whole reservoir do not exceed the “liquid-gaseous CO_2 ” boundary, since only the gaseous CO_2 is considered. The shapes on the graph indicate the parameters for numerical experiments.

Numerical experiments

For the numerical experiments, the following parameters have been adopted: $t = 365$ days; $\Delta t = 600$ s; $L = 100$ m; $\Delta x = 0.01$ m; $p_0 = 2.25$ MPa; $T_0 = -6$ °C; $m = 0.2$; $k_0 = 5 \cdot 10^{-14}$ m²; $S_g = 0.8$; $S_{hCH_4} = 0.2$; $p_{inj} = 2.5$ MPa; $T_{inj} = -6$ °C; $p_{extr} = 2$ MPa; $\rho_{sk} = 2,000$ kg/m³; $c_{sk} = 1,000$ J/(kg · K); $\lambda_{sk} = 1.5$ W/(m · K); $\rho_{ice} = 900$ kg/m³; $c_{ice} = 2,000$ J/(kg · K); $\lambda_{ice} = 2.2$ W/(m · K); $\rho_{hCH_4} = 900$ kg/m³; $c_{hCH_4} = 2,000$ J/(kg · K); $\lambda_{hCH_4} = 0.5$ W/(m · K); $G_{CH_4} = 0.12$; $L_{CH_4} = 120$ kJ/kg; $\rho_{hCO_2} = 1,100$ kg/m³; $c_{hCO_2} = 2,000$ J/(kg · K); $\lambda_{hCO_2} = 0.5$ W/(m · K); $G_{CO_2} = 0.28$; $L_{CO_2} = 70$ kJ/kg; $R = 8.3145$ J/(mol · K); $M_{CH_4} = 16.042$ g/mol; $p_{cCH_4} = 4.641$ MPa; $T_{cCH_4} = 190.55$ K; $M_{CO_2} = 44.011$ g/mol; $p_{cCO_2} = 7.382$ MPa; $T_{cCO_2} = 304.19$ K; the values of dynamic viscosity, thermal conductivity, as well as heat capacity of pure methane and carbon dioxide have been determined by interpolating tabular data [11, 12].

Fig. 4 shows a schematic representation of the matters saturating the porous medium after 5 days.

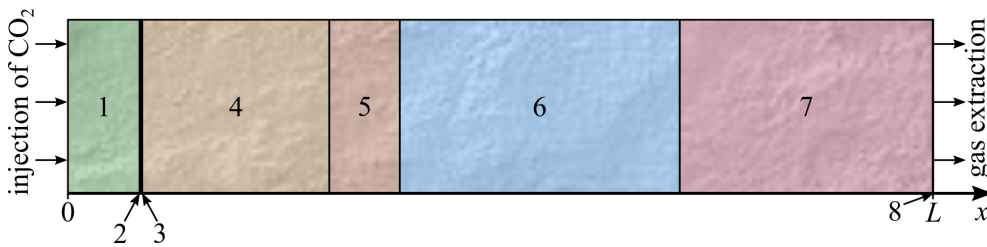


Fig. 4. Schematic representation of matters saturating the porous medium after 5 days

Рис. 4. Схематичное представление насыщающих пористую среду веществ через 5 суток

After 5 days in the porous medium, 8 extended areas with various sets of saturating matters were observed, namely:

1. CO₂ + hydrate CO₂ (8.4 m). Only carbon dioxide and its hydrate are observed.
2. CH₄ + CO₂ + ice + hydrate CO₂ (0.07 m). Both gases are observed, all methane hydrate decomposes, and carbon dioxide hydrate forms in the extended area.
3. CH₄ + CO₂ + ice (0.02 m). Both gases are observed, all methane hydrate is decomposed, carbon dioxide hydrate is not formed.
4. CH₄ + CO₂ + ice + hydrate CH₄ (21.6 m). Both gases are observed, decomposition of methane hydrate occurs in extended area, carbon dioxide hydrate is not formed.
5. CH₄ + CO₂ + hydrate CH₄ (8.26 m). Both gases are observed, methane hydrate does not decompose, carbon dioxide hydrate is not formed.
6. CH₄ + hydrate CH₄ (32.24 m). In the porous medium, only methane and its hydrate are present, which corresponds to the initial state.
7. CH₄ + ice + hydrate CH₄ (29.16 m). The decomposition of methane hydrate in extended area occurs due to a decrease in pressure at the right boundary.
8. CH₄ + ice (0.25 m). Near the extraction boundary, all methane hydrate decomposed.

Consider the distributions of pressure, temperature and hydrate saturation after 5 days (Fig. 5).

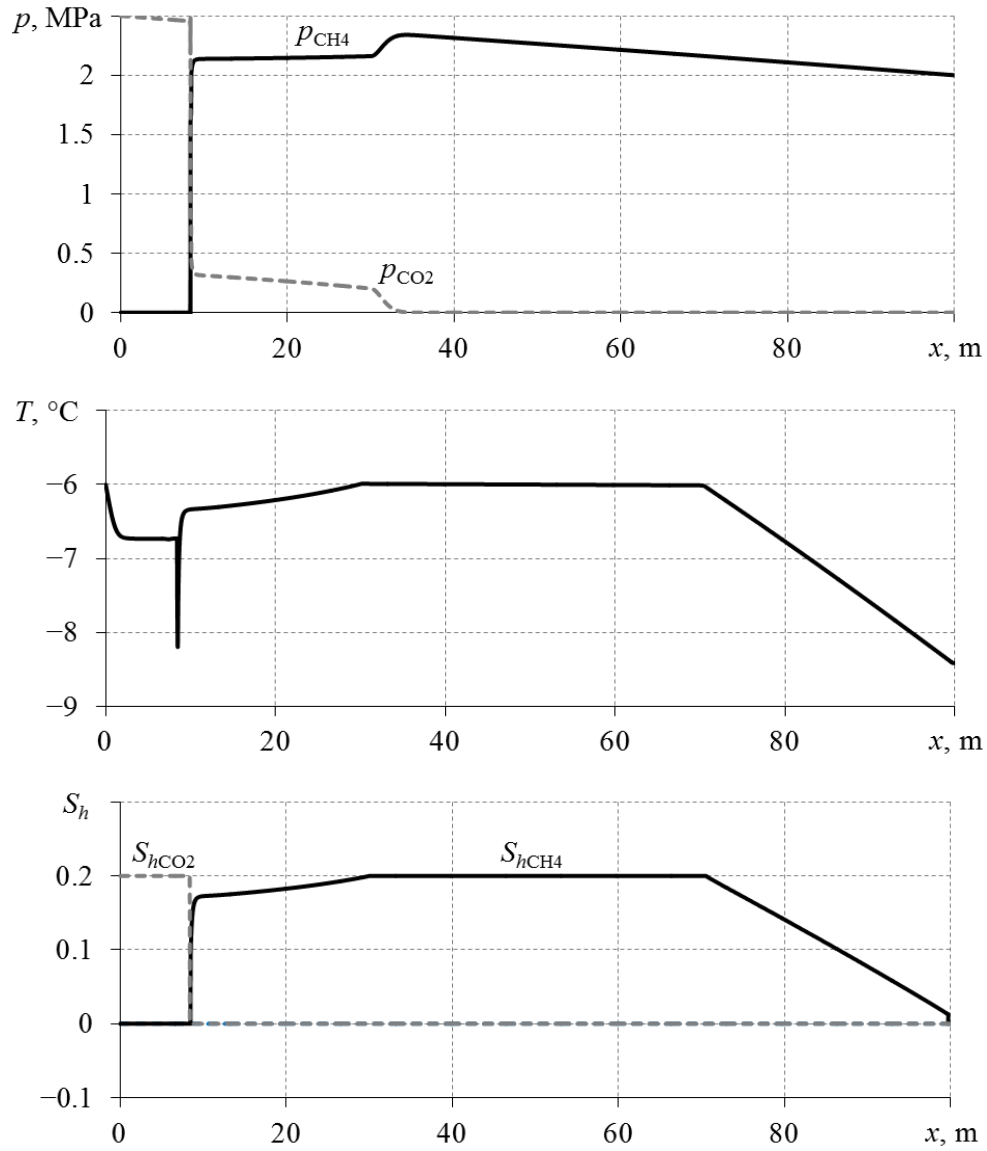


Fig. 5. The distributions of partial pressure of methane (p_{CH_4}), partial pressure of carbon dioxide (p_{CO_2}), temperature (T), saturations of methane hydrate (S_{hCH_4}), and carbon dioxide hydrate (S_{hCO_2}) along the porous medium length after 5 days

Рис. 5. Распределения парциальных давлений метана (p_{CH_4}), углекислого газа (p_{CO_2}), температуры (T), гидратонасыщенностей метана (S_{hCH_4}) и углекислого газа (S_{hCO_2}) по длине пористой среды через 5 суток

Fig. 5 shows that carbon dioxide mixes with methane (the areas in which both partial pressures are nonzero) and displaces it to the right boundary. At the same time, there is a decrease in pressure near the right boundary due to gas extraction. With a decrease in the partial pressure of methane below equilibrium ($p_{\text{CH}_4} < p_{\text{eqhCH}_4}$), its hydrate decomposes and the temperature in the reservoir decreases due to absorption of latent heat of phase transition. An increase in the partial pressure of carbon dioxide above equilibrium ($p_{\text{CO}_2} > p_{\text{eqhCO}_2}$) leads to the formation of carbon dioxide hydrate with increasing temperature in the reservoir due to the release of latent heat of phase transition. With the complete decomposition of methane hydrate, the temperature drops to ≈ -8.2 °C. With the further formation of carbon dioxide hydrate at this point, the temperature rises to ≈ -6.7 °C. The initial temperature is -6 °C. Thus, the replacement process is endothermic. This is due to the higher latent heat of formation/decomposition of methane hydrate ($L_{\text{CH}_4} = 120$ kJ/kg) compared to carbon dioxide hydrate ($L_{\text{CO}_2} = 70$ kJ/kg). It can be noted that with complete replacement, the hydrate saturation of CO_2 is equal to the initial hydrate saturation of CH_4 . We verify this by nullifying the left side of equation (3) and substituting the parameter values used in the calculations:

$$\begin{aligned} \rho_{\text{hCH}_4} (1 - G_{\text{CH}_4}) \frac{\partial S_{\text{hCH}_4}}{\partial t} &= -\rho_{\text{hCO}_2} (1 - G_{\text{CO}_2}) \frac{\partial S_{\text{hCO}_2}}{\partial t}, \\ 900 \cdot (1 - 0.12) \cdot (-0.2) &= -1,100 \cdot (1 - 0.28) \cdot 0.2, \\ -158.4 &= -158.4. \end{aligned}$$

Thus, the volume of methane hydrate and the volume of carbon dioxide hydrate formed after the replacement are the same, which ensures the mechanical stability of a porous medium after replacement.

Let us consider further how the matters saturating the porous medium change with time (Fig. 6). As observed, initially (after 5 days), 8 regions with various combinations of saturating matters are formed in the porous medium (these regions are described in detail above). After 25 days, the carbon dioxide already reaches the right reservoir boundary, and only 5 areas remain, in each of which the carbon dioxide is present in free form. In this case, from the injection boundary, the carbon dioxide hydrate is formed, and then the methane hydrate decomposes. From the side of the extraction boundary, methane hydrate decomposes. This happens until all methane hydrate in the porous medium decomposes.

After 50 days, only 3 areas remain in the reservoir: in the first one, carbon dioxide hydrate is already fully formed; in the second, carbon dioxide hydrate is being formed; and the third area contains free methane, carbon dioxide and ice. The last two areas are gradually pushed to the boundary of extraction, and ultimately only carbon dioxide and its hydrate remain in the reservoir. Full replacement for this set of parameters occurred at about 60 days.

Fig. 6 also shows that for the replacement scheme adopted in this work and for the parameters values considered, the formation of carbon dioxide hydrate at some point in the porous medium occurs only after the complete decomposition of methane hydrate.

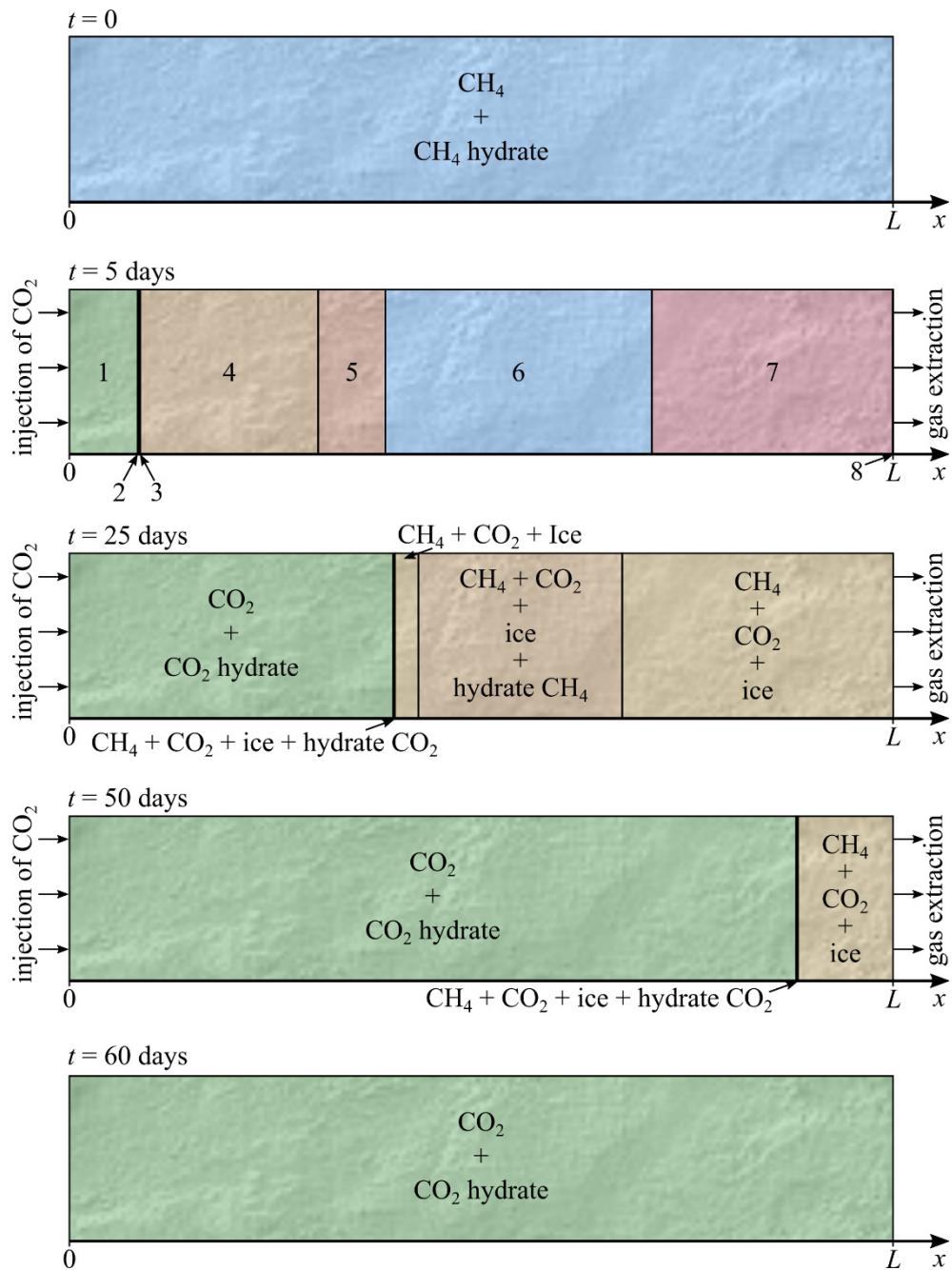


Fig. 6. Schematic representation of matters saturating the porous medium at different time points

Рис. 6. Схематичное представление насыщающих пористую среду веществ в различные моменты времени

Fig. 7 shows the change in time of accumulated methane production mass (Q_{extr}) and the residual mass of methane in the reservoir (Q_{resid}), if only gas extraction occurs at the right boundary (only the depression method). Hereinafter, the masses are presented per unit cross-sectional area of a porous medium.

Fig. 8 shows the change in time of accumulated methane production mass (Q_{extr}) and the residual mass of methane in the reservoir (Q_{resid}) if the gas is extracted at the right boundary and the carbon dioxide is injected at the left boundary. The same parameters are presented on Fig. 9 for the carbon dioxide.

Fig. 7 shows that about 2,000 kg of methane have been produced from 1 m² of the reservoir cross section by the depression method in 100 days, while about 1,500 kg still remain in the porous medium. Thanks to the additional use of the carbon dioxide injection, in 60 days, it is possible to produce all methane weighing about 3,500 kg (Fig. 8). This method also ensures the disposal of about 9,900 kg of carbon dioxide (Fig. 9). Thus, the use of the replacement method in addition to the depression method allows accelerating the production of methane from a gas hydrate deposit, producing a large mass of methane and burying a significant amount of carbon dioxide.

Conclusion

In a one-dimensional linear formulation, we have considered the problem of combining the depression and replacement methods for gas production from a porous medium, initially saturated with methane and its hydrate, at negative temperatures. The replacement scheme is presented, in which the phase transitions occur in an equilibrium mode, and the methane can be completely replaced in hydrate by the carbon dioxide. A mathematical model has been developed based on the equations of conservation of masses of methane, carbon dioxide, ice and hydrates, the equation of state of real gas, Darcy's law, and the heat transfer equation. Thermal conductivity, convection, non-isothermal effects during gas filtration, as well as absorption or release of latent heat of hydrate formation/decomposition have been taken into account. The system of equations of the mathematical model has been solved numerically using the simple iteration method, the implicit scheme, and the tridiagonal matrix algorithm, as well as the original authors' algorithm for calculating hydrates saturations. This required creating a calculation program to perform the numerical experiments. The calculations show that with a combination of the depression and replacement methods, the formation of 8 extended areas with various sets of saturating matters is possible in a porous medium.

The calculations have also shown that the replacement process is endothermic, and that the average temperature in a reservoir decreases. The results have revealed that the volume of methane hydrate and the volume of carbon dioxide hydrate, formed after the replacement, coincide, which ensures the mechanical stability of the porous medium after the replacement. The comparison has been made only for the depression method for methane extraction from gas hydrates and the combination of the depression and replacement methods. This comparison has shown that the additional use of the replacement method allows the extraction of a greater amount of methane in a shorter time. In addition, a significant amount of carbon dioxide can be buried.

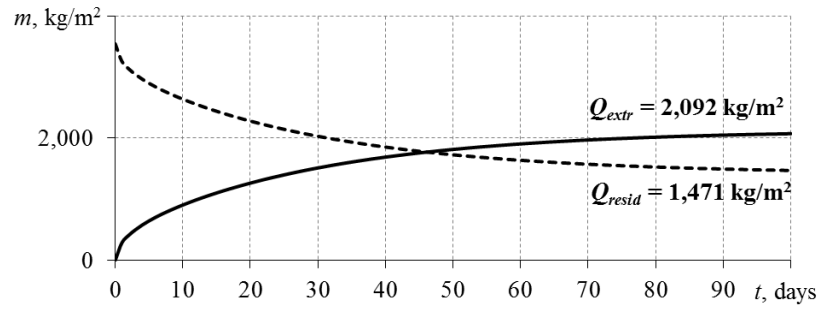


Fig. 7. Change in time of the extracted (Q_{extr}) and residual (Q_{resid}) specific masses of methane when using only the depression method

Рис. 7. Изменение со временем добытой (Q_{extr}) и остаточной (Q_{resid}) удельных масс метана при депрессионном методе добычи

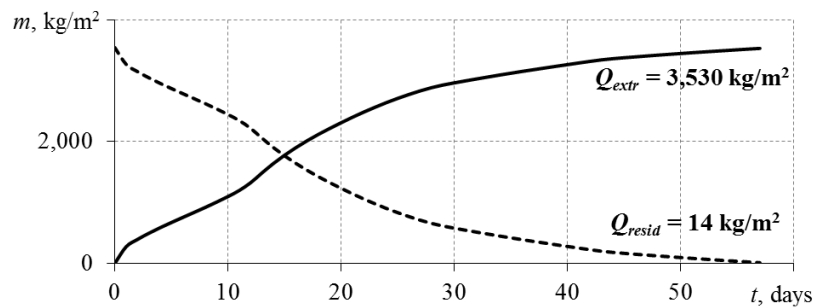


Fig. 8. Change in time of the extracted (Q_{extr}) and residual (Q_{resid}) specific masses of methane with a combination of the depression and replacement methods

Рис. 8. Изменение со временем добытой (Q_{extr}) и остаточной (Q_{resid}) удельных масс метана при комбинации депрессионного и замещения методов добычи

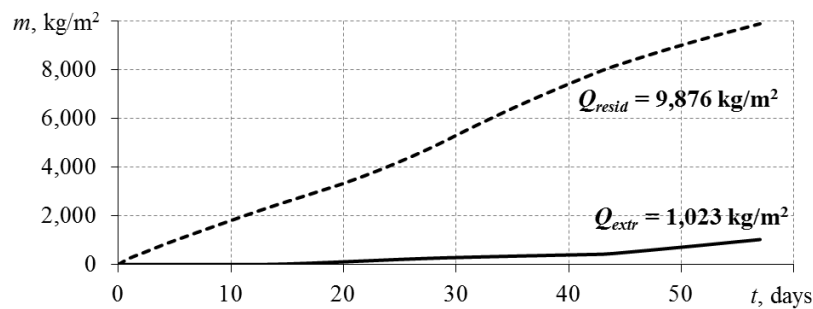


Fig. 9. Change in time of the extracted (Q_{extr}) and residual (Q_{resid}) specific masses of carbon dioxide with a combination of the depression and replacement methods

Рис. 9. Изменение со временем добытой (Q_{extr}) и остаточной (Q_{resid}) удельных масс углекислого газа при комбинации депрессионного и замещения методов добычи

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МАТЕМАТИЧЕСКОЕ МОДЕЛИРОВАНИЕ РАВНОВЕСНОГО ПОЛНОГО ЗАМЕЩЕНИЯ МЕТАНА УГЛЕКИСЛЫМ ГАЗОМ В ГАЗОГИДРАТНОМ ПЛАСТЕ ПРИ ОТРИЦАТЕЛЬНЫХ ТЕМПЕРАТУРАХ*

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Аннотация

Газовые гидраты, в которых содержится наибольшее количество метана на нашей планете, являются перспективным источником природного газа, особенно после истощения традиционных газовых месторождений, запасы в которых оцениваются примерно на 50 лет. Поэтому уже сегодня необходимо проводить исследования методов добычи газа из газовых гидратов для выбора наилучших из них и принятия в будущем обоснованных технологических и инженерных решений.

Одним из таких методов является замещение метана в гидрате углекислым газом. Данная работа посвящена построению математической модели для исследования этого метода. В работе рассматривается следующий процесс: с одной стороны пористого

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пласта, изначально насыщенного метаном и его гидратом, закачивается углекислый газ, с противоположной стороны этого пласта происходит откачка метана и/или углекислого газа. При этом может происходить как разложение гидрата метана, так и образование гидрата углекислого газа.

Данная задача рассмотрена в одномерной линейной постановке для случая отрицательных температур и газообразного диоксида углерода, т. е. в пласте могут присутствовать метан, углекислый газ, лед, гидраты метана и углекислого газа. Построена математическая модель, в основе которой лежат: законы сохранения масс метана, углекислого газа и льда; закон Дарси для движения газовой фазы; уравнение состояния реального газа; уравнение энергии с учетом теплопроводности, конвекции, адиабатического охлаждения, эффекта Джоуля — Томсона и выделения или поглощения скрытой теплоты гидратообразования. При моделировании принято, что фазовые переходы происходят в равновесном режиме и возможно полное замещение метана углекислым газом. В статье приведены результаты численных экспериментов.

Ключевые слова

Математическое моделирование, газовые гидраты, метан, углекислый газ, пористая среда, фильтрация газа, замещение, равновесный фазовый переход.

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