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Formation of carbon dioxide hydrate in a closed volume of a water-saturated porous medium

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Abstract. In the present work, a mathematical model is constructed for the formation of carbon dioxide hydrate in a closed volume of a porous medium saturated with water and carbon dioxide. The thermobaric parameters of the system correspond to the conditions for the existence of gaseous carbon dioxide and CO_2 hydrate at positive temperatures. The system of basic equations includes mass conservation equations for phase components, energy and state equations. An analysis was made of the influence of the initial parameters of the system (water saturation, pressure, temperature, porosity) on the intensity of hydrate formation. A decision map has been constructed illustrating the possible modes of hydrate formation, in particular, when water completely or partially passes into the composition of the gas hydrate._

Keywords: formation of carbon dioxide hydrate, porous medium, water saturation

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Образование гидрата углекислого газа в замкнутом объеме водонасыщенной пористой среды

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Аннотация. В настоящей работе построена математическая модель образования гидрата углекислого газа в замкнутом объеме, заполненном пористой средой, насыщенной водой и диоксидом углерода. Термобарические условия системы соответствуют условиям существования газообразного диоксида углерода и гидрата CO_2 при положительных температурах. Система основных уравнений состоит из уравнений сохранения массы для всех компонентов, уравнения энергии и уравнения состояния газа. Проведен анализ влияния начальных параметров системы (водонасыщенности, давления, температуры, пористости) на интенсивность гидратообразования.

Ключевые слова: образование газогидрата углекислого газа, пористая среда, водонасыщенность

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Introduction

In the past few decades, much attention has been paid around the world to the problem of excessive carbon dioxide emissions as a result of the work of a large number of enterprises that contribute to the pollution of the Earth's atmosphere. Sufficiently safe and reliable way to store greenhouse gases is their storage in the gas hydrate state, since the method of such conservation will save not only large volumes of carbon dioxide, but also a fairly large amount of fresh water [1, 2]. In this connection, the study of the theoretical foundations of underground utilization of carbon dioxide by converting it into a gas hydrate state is an important and urgent task.

Mathematical modeling of carbon dioxide hydrate formation in a porous formation saturated with methane and water is considered in [3, 4]. Experimental work on the study of the formation of carbon dioxide hydrate in rocks was carried out in [5]. The influence of temperature, water and ice saturation, and the composition of soil samples on the kinetics of hydrate formation was assessed, and the course of the process at positive and negative temperatures was compared. The effect of surfactants and porous material on the intensity of CO_2 hydrate formation was studied in [6–8].

In the present work, the process of formation of carbon dioxide hydrate in an isolated porous medium saturated with water and carbon dioxide is studied.

Problem statement

We consider a porous medium that is in a sealed and thermally insulated container and in its initial state is saturated with water and carbon dioxide. The initial pressure and temperature correspond to the thermobaric conditions for the formation of a hydrate and the existence of gaseous carbon dioxide. Let us assume that at will be the formation of CO_2 hydrate at positive temperatures, and taking into account the homogeneity of the initial thermobaric conditions and the tightness of the container, the filtration flow of gas in a porous medium will be neglected. The porous medium, water and gas hydrate will be assumed to be incompressible and motionless. The accepted statement of the problem means that during the characteristic time of filling the container until the pressure value is reached, hydrate formation in a porous medium can be neglected. For this, it is necessary that the porous medium has a sufficiently high permeability, and the characteristic dimensions of the container must be small. This statement of the problem is the theoretical basis of one of the methods for experimental study of the kinetics of hydrate formation.

Let us write the mass conservation equations for water, hydrate and gas, taking into account the above assumptions:

$$\frac{d\left(mS_w\rho_w\right)}{dt}=-J_w,\ \frac{d\left(mS_h\rho_h\right)}{dt}=J_h,\ \frac{d\left(mS_g\rho_g\right)}{dt}=-J_g. \tag{1}$$

Here m and S_i are, respectively, the porosity of the skeleton and the volume saturation of pores with water, hydrate, and gas, J_w and J_g are the intensities of water and gas consumption for hydrate formation with the intensity J_h per unit volume of the porous medium. Here and in what follows, the subscripts w, h, g, correspond to the parameters related to water, carbon dioxide gas hydrate, and carbon dioxide.

For the intensities J_w, J_g and J_h we write the stoichiometry conditions [9]:

$$J_w=\left(1-G\right)J_h,\ J_g=GJ_h. \tag{2}$$

Taking into account Eqs. (1) and relations (2), we obtain expressions for determining the saturation of hydrate, water and gas:

$$S_h = \frac{\left(1 - S_{w0} - S_g\right)}{\left(1 - \rho_h\left(1-G\right)/\rho_w\right)},\ S_w = S_{w0} - \frac{\rho_h}{\rho_w}\left(1-G\right)S_h. \tag{3}$$

Assuming that the temperature for all components of the system is the same, we write the heat balance equation:

$$\rho c\frac{dT}{dt} = J_h l,\ \rho c = \left(1-m\right)\rho_{sk}c_{sk} + m\sum_{j=w,g,h}\rho_j S_j c_j. \tag{4}$$

Here c_j and ρc are the specific heat capacity of the phases and l is the specific volumetric heat capacity of the system, and is the specific heat per unit mass of the hydrate released during its formation. Due to the fact that the largest contribution to the value of the volumetric heat capacity is made by the corresponding parameters of the skeleton of the porous medium, we will consider them to be constant values.

For carbon dioxide, we write the equation of state of the gas:

$$p = \rho_g R_g T. \tag{5}$$

For the kinetics of the formation of carbon dioxide hydrate, we accept the scheme of phase transitions considered in [9, 10]. According to this scheme, we consider a porous medium as a system of porous micro channels with radius a, water covers the walls of these channels ($a < r < a_w$), carbon dioxide hydrate will form on top of this layer ($a_w < r < a_h$), and in the remaining annular layer ($r > a_g$)) the gas mixture will flow. The rate of hydrate formation will be determined by the diffusion of carbon dioxide through the CO_2 hydrate layer formed between the gas and water.

For the intensity of formation of carbon dioxide hydrate, we write the expression:

$$J_h = \frac{4m\rho_g D}{aG\ln\left(1 + S_h/S_g\right)}, \tag{6}$$

where a is the microchannel radius in a porous medium, D is the diffusion coefficient of carbon dioxide through the CO_2 hydrate layer.

The permeability of a porous medium is related to the radius of the channels by the following relation:

$$a = \left(k/m\right)^{1/2}. \tag{7}$$

The system of Eqs. (1–5), taking into account (6, 7), is reduced to a system of ordinary differential equations for changing pressure, temperature and hydrate saturation:

$$\frac{d\left(pS_g\right)}{dt} = -\frac{GJ_hR_gT}{m},\frac{dT}{dt} = \frac{J_h l}{\rho c},\frac{dS_h}{dt} = \frac{J_h}{m\rho_h}.$$

Result of calculation

For the parameters characterizing the system porous medium - gas hydrate CO_2 - carbon dioxide, the following values are taken [11]: $m = 0.1$, $k = 10^{-11}$ m, $\rho c = 2.5\cdot10^6$ J/(m$^3\cdot$K), $l = 10\cdot4.8^5$ J/kg, $\rho_h^0 = 1117$ kg/m^3, $\rho_w^0 = 1000$ kg/m^3, $G = 0.29$, $R_g = 189$ J/(kg$\cdot$K), $D = 10^{-16}$ m^2/s.

For determination of the equilibrium temperature for system "CO_2 + water + gas hydrate" for the current pressure during the hydrate formation process, we write the phase equilibrium condition for temperature and pressure [9]:

$$T_s(p) = T_{s0} + T_* \ln(p/p_{s0}),$$

where T_{s0} is the equilibrium temperature at pressure value p_{s0}, T_* is an empirical parameter having the dimension of temperature. These parameters are defined for carbon dioxide as T_{s0}=280 K, p_{s0}= 2.88 MPa, T_*= 7.1 K [11].

Fig. 1 shows the dynamics of pressure (*a*), temperature (*b*), and hydrate and water saturation (*c*) at different values of the initial water saturation S_{w0} = 0.3 (line 1) and 0.05 (line 2). The initial values of pressure and temperature are taken respectively p_0= 3 MPa, T_0=274 K. The dotted line corresponds to the water saturation value. Here and below, the dashed line corresponds to the equilibrium temperature for the current pressure values.

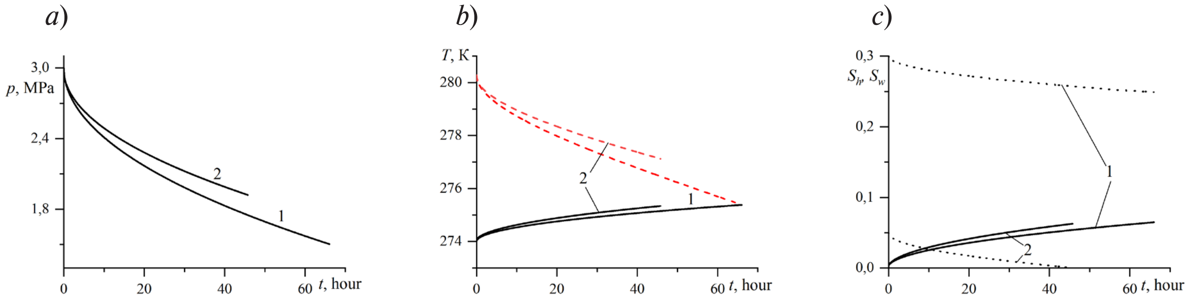

Fig. 1. Dynamics of pressure p (*a*), temperature T (*b*), hydrate and water saturations S_h, S_w (*c*) versus time at different values of initial water saturation (1 – S_{w0} = 0.3, 2–0.05)

It is shown that due to the consumption of gas for the formation of hydrate and the release of energy due to the phase transition, the pressure of the system decreases and the temperature rises. The end of the process of hydrate formation is either the complete transition of water into the composition of the hydrate (line *1*), or the achievement of an equilibrium temperature of the system (line *2*), corresponding to the current pressure in the porous medium. A higher intensity of hydrate formation is observed at lower values of the initial water saturation, which is associated with a higher specific contact surface between the hydrate and water.

Fig. 2 shows the dependences of pressure, temperature and hydrate saturation of the system on time. Lines 1 and 2 correspond to the values of the skeleton porosity m = 0.1 and 0.2. The intensity of hydrate formation increases approximately 2 times with growing porosity. This effect is explained by an increase in the specific area of the porous medium, which contributes to the intensification of the process.

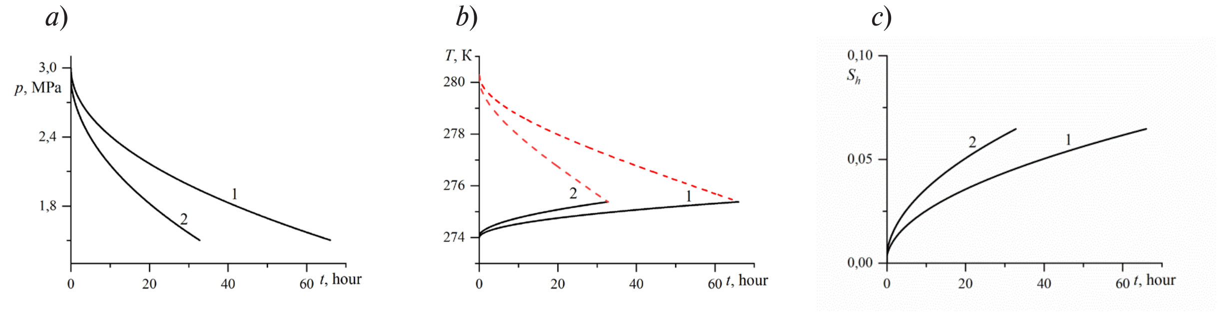

Fig. 2. Dynamics of pressure p (a), temperature T (*b*), hydrate saturation S_h (*c*) versus time at different values of porosity (1 – m = 0.1, 2–0.2)

Fig. 3 illustrates the dependences of the relative hydrate saturation after the termination of the hydrate formation process on the initial static pressure (*a*) at S_{w0} = 0.3, and on the initial water saturation at T_0 = 273 K (*b*). In Fig. 3,*a*, lines *1* and *2* correspond to the temperature values T_0 = 273 K and 277 K. In Fig. 3,*b*, lines *1* and *2* correspond to pressure values p_0= 2 and 3.5 MPa.

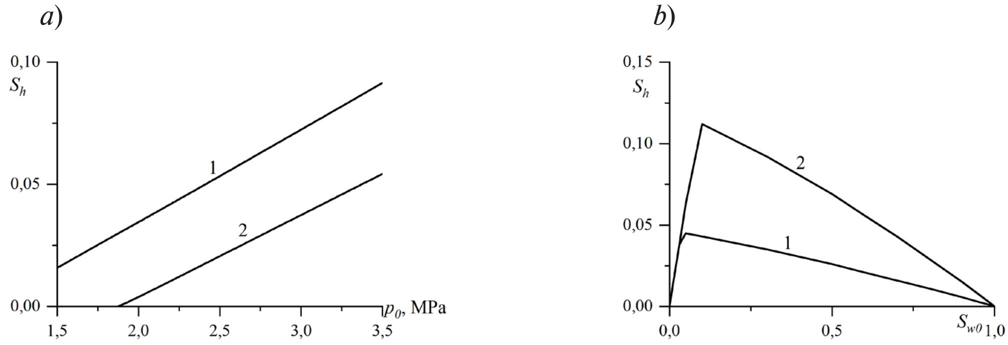

Fig. 3. Influence of initial pressure values (*a*), initial water saturation (*b*) on the final value of hydrate saturation S_h

It is established that the higher the initial pressure and the lower the initial temperature, the greater the proportion of water passes into the gas hydrate state (Fig. 3, *a*). It is revealed that there is a certain value of the initial water saturation, which depends on the initial pressure and the initial temperature at which the greatest hydration saturation is achieved by the end of the process (Fig. 3,*b*). At low values of the initial water saturation, a complete transition of water into the hydrate occurs, and at high values of the initial water saturation, the temperature of the equilibrium value is reached and the water does not completely enter the hydrate state.

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