

*GAS HYDRATE FORMATION*

**GAS HYDRATE FORMATION IN POROUS ICE-RICH METHANE RESERVOIRS  
UPON INJECTION OF CARBON DIOXIDE: FORWARD MODELING**

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Formation of CO<sub>2</sub> hydrate during injection of carbon dioxide into porous ice-rich methane reservoirs is studied using forward modeling in terms of heat and mass transfer. The obtained solutions describe the temperature and pressure patterns in the sediments and show that gas hydrate forms at three different regimes depending on the injected gas pressure and reservoir permeability. The results have implications for strategies of subsurface CO<sub>2</sub> sequestration and safe disposal as gas hydrate in porous reservoirs, as well as for the conditions of CO<sub>2</sub> hydrate stability.

*Carbon dioxide sequestration, gas hydrate, porous reservoirs, permafrost, methane*

**INTRODUCTION**

Rapid growth of atmospheric carbon dioxide (CO<sub>2</sub>) responsible for the greenhouse effect has been a focus of major recent concern. It was suggested to reduce greenhouse emissions by capture and sequestration of CO<sub>2</sub> in deep sedimentary formations [Oldenburg *et al.*, 2001; Benson and Cole, 2008]. As an alternative to long-term fluid carbon dioxide storage fraught with emission risks, permanent underground CO<sub>2</sub> disposal is possible by solid clathrate hydrate formation [Jadhawar *et al.*, 2006], in unfrozen sediments, as well as in permafrost [Chuvilin and Guryeva, 2009; Duchkov *et al.*, 2009]. Frozen and ice-rich rocks are commonly poorly permeable for gas though may contain zones of high permeability [Olovin, 1993]. Low permeability of the frozen cap and stability of gas hydrates at low temperatures secure sequestration of CO<sub>2</sub> in permafrost [Duchkov *et al.*, 2009]. Formation of gas hydrates actually increases the capacity of CO<sub>2</sub> reservoirs because, at the same conditions, the amount of gas in a unit volume of hydrate far exceeds that of free gas [Makogon, 1974]. On the other hand, gas hydrate formation produces hydrate plugs around boreholes and impedes further gas flow, which poses engineering problems. In this respect, formation of gas hydrates in ice-rich rocks requires a special study.

Modeling gas hydrate formation is additionally motivated by poor understanding of deposition mechanisms of hydrate-bearing sediments in permafrost and on the Arctic shelf [Yakushev *et al.*, 2003].

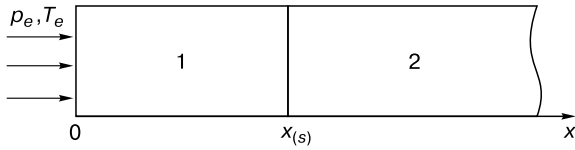
Mathematical modeling of the injection of gas into porous reservoirs and its conversion to hydrates can shed light on some deposition patterns of continental hydrate-bearing sediments.

Experiments on CO<sub>2</sub> hydrate formation in porous media containing ice and water [Chuvilin *et al.*, 2007; Chuvilin and Guryeva, 2008, 2009; Komai *et al.*, 2008] show that gas hydrates can accumulate in water-saturated rocks, as well as in those partly saturated with ice, while the process decays more rapidly in the former case. Note that those and other similar experiments were applied to small samples under isothermal and isobaric conditions. Meanwhile, gas hydrate formation in small samples is constrained by the kinetics of the process, unlike the natural reservoirs where it depends more on heat and mass transfer in the porous medium itself.

Gas hydrate formation in water-bearing reservoirs of methane (CH<sub>4</sub>) was modeled previously [Shagapov *et al.*, 2008, 2011, 2015; Khasanov *et al.*, 2010] assuming injection of the same gas. The model of Tsyppkin [2014] simulated injection of CO<sub>2</sub> into methane reservoirs. We now investigate injection of free CO<sub>2</sub> into a frozen methane reservoir and the ensuing formation of gas hydrates.

**Heat and mass transfer in a porous ice-rich methane reservoir upon injection of CO<sub>2</sub>**

We obtain a 1D forward model for CO<sub>2</sub> injection into a porous ice-rich (with the initial saturation  $S_{i0}$ )



**Fig. 1. Model of carbon dioxide injection.**

1 – saturation with CO<sub>2</sub> hydrate and free carbon dioxide; 2 – saturation with ice and methane;  $x_{(s)}$  is phase boundary;  $p_e$  and  $T_e$  are, respectively, pressure and temperature of injected carbon dioxide.

methane reservoir impermeable from above and from below, which occupies the halfspace  $x > 0$ . Let the initial pressure ( $p_0$ ) and temperature ( $T_0$ ) be constant throughout the reservoir and thermodynamically allow coexistence of methane and ice in the pore space. Assume that gaseous CO<sub>2</sub> is injected from the left-hand reservoir edge ( $x = 0$ ) where constant pressure and temperature ( $p_e$  and  $T_e$ , respectively) are maintained such to allow free CO<sub>2</sub> to be mixed with its hydrate (Fig. 1).

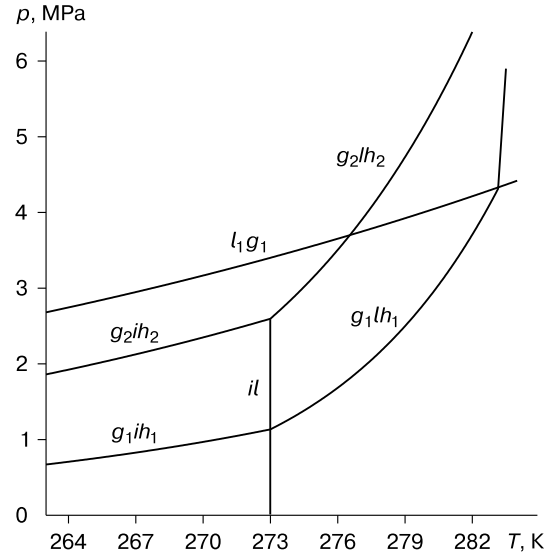
The conditions at which gas hydrates (of carbon dioxide and methane) can exist are shown in the phase diagram of Fig. 2 [Istomin and Yakushev, 1992] where the curves  $glh$  and  $gih$  refer to three-phase equilibrium “gas–liquid–hydrate” and “gas–ice–hydrate” and the curves  $il$  and  $lg$  refer to two-phase equilibrium “ice–water” and “liquid–gas”, respectively. The subscripts 1 and 2 refer, respectively, to CO<sub>2</sub> and CH<sub>4</sub> in the gas, liquid, and hydrate forms. Thus, the initial pressure and temperature values are below the  $g_2ih_2$  curve (in the field of the ice-methane mixture) while the values for the injected CO<sub>2</sub> lie between the curves  $g_1ih_1$  and  $l_1g_1$  (in the field of mixed gaseous and hydrate CO<sub>2</sub>).

The temperatures and pressures for the three-phase equilibrium “gas–liquid–hydrate” are related as [Byk et al., 1980]:

$$T = T_0 + T_* \ln \left( \frac{p}{p_{s0}} \right), \quad (1)$$

where  $p_{s0}$  is the equilibrium pressure corresponding to the temperature  $T_0$ ;  $T_*$  is the empirical parameter depending on the gas hydrate composition and on the H<sub>2</sub>O state.

Mass and heat transfer by infiltration is much more rapid than that by diffusion. In this respect, we assume, like Tsyphkin [2014], that the two gases do not mix and that the front of methane expulsion by carbon dioxide is stable, proceeding from the mostly laminar flow behavior in porous media and greater viscosity of CO<sub>2</sub> than CH<sub>4</sub>. Then, CO<sub>2</sub> injection into a methane reservoir (Fig. 1) produces two domains in which the pores are filled with free CO<sub>2</sub> + CO<sub>2</sub> hydrate (proximal domain 1) and methane + ice (dis-



**Fig. 2. Phase diagrams of CO<sub>2</sub>–H<sub>2</sub>O and CH<sub>4</sub>–H<sub>2</sub>O systems.**

$glh$  and  $gih$  are curves of three-phase equilibrium “gas–liquid–hydrate” and “gas–ice–hydrate”;  $il$  and  $lg$  are curves of two-phase equilibrium “ice–water” and “liquid–gas”; subscripts 1 and 2 refer to CO<sub>2</sub> and CH<sub>4</sub>, respectively (free gas and its hydrate).

tant domain 2). With these assumptions, all CO<sub>2</sub> hydrate forms at the moving front between the two domains under the control of mass transfer in a porous medium.

The suggested model is valid for the case when gas hydrate formation is constrained by heat and mass transfer in porous media rather than by the kinetics of the process as it has long characteristic times corresponding to a large size of the reservoir. Note that the mole H<sub>2</sub>O content in a unit volume of ice is about 15 % higher than in a unit volume of CO<sub>2</sub> hydrate, i.e., the volume changes when gas hydrate forms. This change produces pores and cracks in the gas-hydrate zone between gas and ice which thus come again into immediate contact.

The heat and mass transfer during CO<sub>2</sub> injection into a porous bed is modeled with the following assumptions: (1) the porous rocks and the saturating material (gas and hydrate) have the same temperature; (2) CO<sub>2</sub> hydrate is a two-component system with the CO<sub>2</sub> weight fraction  $G$ ; (3) the rock skeleton and the gas hydrate are incompressible, and the porosity  $m$  is constant.

The system of equations describing infiltration and heat transfer in a porous medium includes the conservation equations and Darcy’s law. In the 1D case, with the above assumptions, this system for each domain is [Khasanov et al., 2010; Shagapov et al., 2015]

$$\begin{aligned} \frac{\partial}{\partial t}(\rho_{g(j)} m S_{g(j)}) + \frac{\partial}{\partial x}(\rho_{g(j)} m S_{g(j)} v_{g(j)}) &= 0, j = 1, 2, \\ \frac{\partial}{\partial t}(\rho c T_{(j)}) + \rho_{g(j)} c_{g(j)} m S_{g(j)} v_{g(j)} \frac{\partial T_{(j)}}{\partial x} &= \\ &= \frac{\partial}{\partial x} \left( \lambda \frac{\partial T_{(j)}}{\partial x} \right), \quad (2) \\ m S_{g(j)} v_{g(j)} &= -\frac{k_{g(j)} \partial p_{(j)}}{\mu_{g(j)} \partial x}, \end{aligned}$$

where  $\rho_g$ ,  $v_g$ ,  $k_g$ ,  $c_g$ , and  $\mu_g$  are, respectively, the true density, velocity, permeability, specific heat, and dynamic viscosity of the gas phase;  $S_g$  is the gas saturation;  $p$  is the pressure;  $T$  is the temperature;  $\rho c$  is the volumetric specific heat of rocks;  $\lambda$  is the thermal conductivity of rocks. Hereafter the subscripts  $sk, g, i$ , and  $h$  refer to the parameters of rocks (skeleton), gas, ice, and hydrate, respectively; the subscripts 1 and 2 in braces refer to the respective parameters in domains 1 and 2 (Fig. 1).

Gas density is related with pressure and temperature by the Clapeyron–Mendeleev equation:

$$p_{(j)} = \rho_{g(j)} R_{g(j)} T_{(j)}, j = 1, 2,$$

where  $R_g$  is the gas constant.

The volumetric specific heat  $\rho c$  and the thermal conductivity  $\lambda$  of rocks are

$$\begin{aligned} \rho c &= (1-m) \rho_{sk} c_{sk} + m \sum_{j=g,i,h} S_j \rho_j c_j, \\ \lambda &= (1-m) \lambda_{sk} + m \sum_{j=g,i,h} S_j \lambda_j, \end{aligned}$$

where  $\rho_j$ ,  $c_j$ ,  $\lambda_j$ , and  $S_j$  ( $j = sk, g, i, h$ ) are, respectively, the true density, the specific heat, the thermal conductivity, and the saturation of the phases. The values  $\rho c$  and  $\lambda$  are assumed to be constant throughout the reservoir as the rock skeleton has the greatest contribution.

Proceeding from the Kozeny equation [Barenblatt *et al.*, 1982], gas permeability ( $k_g$ ) is related with gas saturation ( $S_g$ ) and absolute permeability ( $k_0$ ) as

$$k_g = k_0 S_g^3.$$

The conditions at the boundary between domains 1 and 2, with regard to heat and mass balance [Nigmatulin, 1987], are

$$\begin{aligned} m S_{g(1)} \rho_{g(1)} (v_{g(1)} - \dot{x}_{(s)}) &= m S_h \rho_h G \dot{x}_{(s)}, \\ m S_{g(2)} \rho_{g(2)} (v_{g(2)} - \dot{x}_{(s)}) &= 0, \\ m S_h \rho_h (1-G) \dot{x}_{(s)} &= m S_{i0} \rho_i \dot{x}_{(s)}, \quad (3) \\ \lambda \frac{\partial T_{(1)}}{\partial x} - \lambda \frac{\partial T_{(2)}}{\partial x} &= m S_h \rho_h L_h \dot{x}_{(s)}, \end{aligned}$$

where  $\rho_h$  and  $L_h$  are, respectively, the density of CO<sub>2</sub> hydrate and the heat of its formation;  $S_h$  is the hydrate

saturation;  $\rho_i$  is the ice density;  $\dot{x}_{(s)}$  is the speed of the moving phase transition front;  $G$  is the fraction of CO<sub>2</sub> in gas hydrate. The temperature and the pressure are assumed to be continuous along this boundary. Hereafter the subscript  $s$  refers to parameters at the boundary between domains 1 and 2.

Hydrate saturation of domain 1 can be inferred from the third equation in system (3):

$$S_h = \frac{\rho_i S_{i0}}{\rho_h (1-G)}.$$

The initial and boundary conditions of the problem are

$$\begin{aligned} t = 0: \quad S_i &= S_{i0}, \quad T = T_0, \quad p = p_0 (x \geq 0); \\ x = 0: \quad T &= T_e, \quad p = p_e (t > 0). \end{aligned}$$

Based on system (2), the pressure conductivity and thermal diffusivity equations can be written as

$$\frac{\partial p_{(j)}^2}{\partial t} = \chi_{(j)}^{(p)} \frac{\partial}{\partial x} \left( \frac{\partial p_{(j)}^2}{\partial x} \right), j = 1, 2,$$

$$\frac{\partial T_{(j)}}{\partial t} = \chi^{(T)} \frac{\partial}{\partial x} \left( \frac{\partial T_{(j)}}{\partial x} \right) + \chi^{(T)} \frac{c_{g(j)} k_{g(j)} \rho_{g0}}{\lambda \mu_{g(j)}} \frac{\partial p_{(j)}}{\partial x} \frac{\partial T_{(j)}}{\partial x},$$

$$\text{where } \chi_{(j)}^{(p)} = \frac{k_{g(j)} p_{(j)}}{\mu_{g(j)} m S_{g(j)}}; \chi^{(T)} = \frac{\lambda}{\rho c}.$$

### Self-similar solution for temperature and pressure patterns

For analytical solutions, we introduce the self-similar variable  $\xi = x / \sqrt{\chi^{(T)} t}$  which allows writing the pressure conductivity and thermal diffusivity equations in the ordinary differential form:

$$-\xi \frac{dp_{(j)}^2}{d\xi} = 2\eta_{(j)} \frac{d}{d\xi} \left( \frac{dp_{(j)}^2}{d\xi} \right), j = 1, 2,$$

$$-\xi \frac{dT_{(j)}}{d\xi} = \frac{Pe_{(j)}}{p_0^2} \frac{dp_{(j)}^2}{d\xi} \frac{dT_{(j)}}{d\xi} + 2 \frac{d}{d\xi} \left( \frac{dT_{(j)}}{d\xi} \right),$$

$$\text{where } \eta_{(j)} = \frac{\chi_{(j)}^{(p)}}{\chi^{(T)}}; k_{g(j)} = k_0 S_{g(j)}^3; \text{ and}$$

$$Pe_{(j)} = \frac{\rho_{g0} c_{g(j)} k_{g(j)} p_0}{\lambda \mu_{g(j)}} \text{ is the Péclet number.}$$

The pressure conductivity equation is nonlinear as the coefficient before the second-order derivative includes the unknown function  $p_{(j)}$ . An approximate analytical solution can be obtained using Leibenson's linearization [Basniev *et al.*, 1993], i.e., the variable pressure  $p_{(j)}$  in the pressure conductivity  $\chi_{(j)}^{(p)}$  is assumed to be constant and equal to the initial reservoir pressure  $p_0$ .

Integrating the pressure conductivity and thermal diffusivity equations gives the pressure and temperature patterns within each domain:

$$\begin{cases} p_{(1)}^2 = p_{(s)}^2 + (p_e^2 - p_{(s)}^2) \int_{\xi}^{\xi_{(s)}} \exp\left(-\frac{\xi^2}{4\eta_{(1)}}\right) d\xi \left[ \int_0^{\xi_{(s)}} \exp\left(-\frac{\xi^2}{4\eta_{(1)}}\right) d\xi \right]^{-1}, \\ T_{(1)} = T_{(s)} + (T_e - T_{(s)}) \int_{\xi}^{\xi_{(s)}} \exp\left(-\frac{\xi^2}{4} - \frac{\text{Pe}_{(1)}}{2p_0^2} p_{(1)}^2\right) d\xi \left[ \int_0^{\xi_{(s)}} \exp\left(-\frac{\xi^2}{4} - \frac{\text{Pe}_{(1)}}{2p_0^2} p_{(1)}^2\right) d\xi \right]^{-1}, \end{cases} \quad 0 < \xi < \xi_{(s)}; \quad (4)$$

$$\begin{cases} p_{(2)}^2 = p_0^2 + (p_{(s)}^2 - p_0^2) \int_{\xi}^{\infty} \exp\left(-\frac{\xi^2}{4\eta_{(2)}}\right) d\xi \left[ \int_{\xi_{(s)}}^{\infty} \exp\left(-\frac{\xi^2}{4\eta_{(2)}}\right) d\xi \right]^{-1}, \\ T_{(2)} = T_0 + (T_{(s)} - T_0) \int_{\xi}^{\infty} \exp\left(-\frac{\xi^2}{4} - \frac{\text{Pe}_{(2)}}{2p_0^2} p_{(2)}^2\right) d\xi \left[ \int_{\xi_{(s)}}^{\infty} \exp\left(-\frac{\xi^2}{4} - \frac{\text{Pe}_{(2)}}{2p_0^2} p_{(2)}^2\right) d\xi \right]^{-1}, \end{cases} \quad \xi_{(s)} < \xi < \infty. \quad (5)$$

According to the conditions (3), with regard to the solutions (4) and (5), the coordinate of the phase boundary  $\xi_{(s)}$  and the parameters  $p_{(s)}$  and  $T_{(s)}$  on this boundary are given by

$$(p_e^2 - p_{(s)}^2) \exp\left(-\frac{\xi_{(s)}^2}{4\eta_{(1)}}\right) \left[ \int_0^{\xi_{(s)}} \exp\left(-\frac{\xi^2}{4\eta_{(1)}}\right) d\xi \right]^{-1} = \frac{m\mu_{g(1)}\chi^{(T)} p_{(s)}}{k_{g(1)}} \left( \frac{\rho_h G S_h}{\rho_{g0}} + 1 - S_h \right) \xi_{(s)}; \quad (6)$$

$$(p_{(s)}^2 - p_0^2) \exp\left(-\frac{\xi_{(s)}^2}{4\eta_{(2)}}\right) \left[ \int_{\xi_{(s)}}^{\infty} \exp\left(-\frac{\xi^2}{4\eta_{(2)}}\right) d\xi \right]^{-1} = \frac{m\mu_{g(2)}\chi^{(T)} p_{(s)}}{k_{g(2)}} (1 - S_{i0}) \xi_{(s)}; \quad (7)$$

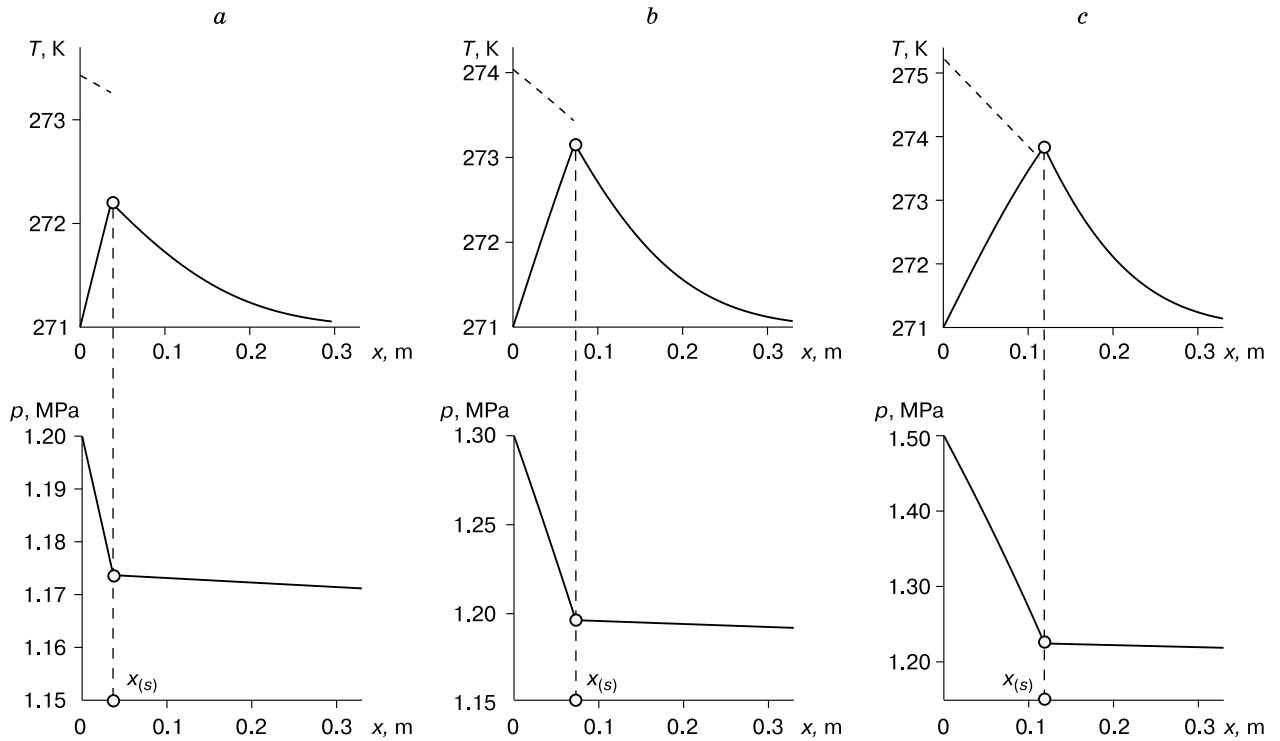
$$\begin{aligned} & (T_{(s)} - T_e) \exp\left(-\frac{\xi_{(s)}^2}{4} - \frac{\text{Pe}_{(1)}}{2p_0^2} p_{(s)}^2\right) \left[ \int_0^{\xi_{(s)}} \exp\left(-\frac{\xi^2}{4} - \frac{\text{Pe}_{(1)}}{2p_0^2} p_{(1)}^2\right) d\xi \right]^{-1} - \\ & - (T_0 - T_{(s)}) \exp\left(-\frac{\xi_{(s)}^2}{4} - \frac{\text{Pe}_{(2)}}{2p_0^2} p_{(s)}^2\right) \left[ \int_{\xi_{(s)}}^{\infty} \exp\left(-\frac{\xi^2}{4} - \frac{\text{Pe}_{(2)}}{2p_0^2} p_{(2)}^2\right) d\xi \right]^{-1} = \frac{m\rho_h L_h S_h}{\rho c} \xi_{(s)}. \end{aligned} \quad (8)$$

To solve the resulting system of equations, the pressure  $p_{(s)}$  is expressed from (6) and substituted into (7), which leads to the transcendent equation with respect to a single unknown  $\xi_{(s)}$  (solved by the bisection method in this study); then the pressure  $p_{(s)}$  and the temperature  $T_{(s)}$  at the boundary  $\xi_{(s)}$  are found by equations (6) and (8).

### Regimes of gas hydrate formation

Gas hydrates form with the release of latent heat of phase change, which interferes with the temperature pattern of the porous reservoir we model. The obtained solutions have been checked for thermodynamic consistency requiring the local temperature in domain 1 to be lower than the temperature of CO<sub>2</sub> hydrate decomposition found from the pressure distribution according to our solution (i) and the local temperature in domain 2 to be below 273 K or the ice melting point (ii).

Temperature and pressure variations along the coordinate  $x$  were plotted for different pressures  $p_e$  of injected CO<sub>2</sub> at the time  $t = 3.5$  hr (Fig. 3), for a system with the parameters  $m = 0.2$ ;  $p_0 = 1.15$  MPa;  $T_0 = 271$  K;  $S_{i0} = 0.6$ ;  $T_e = 271$  K;  $k_0 = 2 \cdot 10^{-15}$  m<sup>2</sup>;  $\rho_{sk} = 2400$  kg/m<sup>3</sup>;  $\rho_i = 900$  kg/m<sup>3</sup>;  $\rho_h = 1100$  kg/m<sup>3</sup>;  $G = 0.28$ ;  $R_{g(1)} = 189$  J/(K·kg);  $R_{g(2)} = 520$  J/(K·kg);  $\mu_{g(1)} = 1.3 \cdot 10^{-5}$  Pa·s;  $\mu_{g(2)} = 10^{-5}$  Pa·s;  $c_{g(1)} = 800$  J/(K·kg);  $c_{sk} = 1200$  J/(K·kg);  $c_{g(2)} = 1560$  J/(K·kg);  $c_i = 2100$  J/(K·kg);  $\rho c = 2.5 \cdot 10^6$  J/(K·m<sup>3</sup>);  $\lambda = 2$  W/(m·K);  $p_{s0} = 1.02$  MPa;  $T_{*glh} = 7.6$  K;  $T_{*gih} = 19$  K.



**Fig. 3.** Variations of reservoir temperature  $T$  and pressure  $p$  along the coordinate  $x$  at different pressures of injected  $\text{CO}_2$ ;  $p_e = 1.2$  MPa (a),  $p_e = 1.3$  MPa (b), and  $p_e = 1.5$  MPa (c).

Dash lines are equilibrium temperatures of  $\text{CO}_2$  hydrate formation corresponding to calculated pressures.

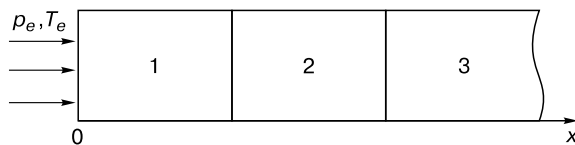
The specific heat of the ice- $\text{CO}_2$  hydrate transition per hydrate unit mass is assumed to be  $L_h = 1.6 \cdot 10^5$  J/kg [Anderson, 2003]. Dash lines show equilibrium temperatures of  $\text{CO}_2$  hydrate formation corresponding to the calculated pressures. At relatively small gas injection pressures (with respect to the other values used in calculations), the reservoir temperature is below the equilibrium temperature of  $\text{CO}_2$  hydrate decomposition in domain 1 and below the ice melting point in domain 2 (Fig. 3, a). Thus, the solution with a single phase transition front (phase boundary) faithfully describes the hydrate formation process.

At higher pressures of injected gas (Fig. 3, b), the reservoir temperature beyond the phase boundary (domain 2) rises above 273 K in local zones where ice

should melt. Thus, there arise another phase boundary and another domain saturated with methane and water (Fig. 4).

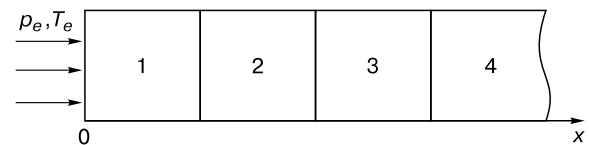
Further increase in the injected gas pressure (Fig. 3, c) leads to reservoir temperature rise above the equilibrium temperature of  $\text{CO}_2$  hydrate decomposition within some part of domain 1, where the mixture of gaseous and hydrate carbon dioxide thus becomes overheated. It means the existence of one more phase boundary and, correspondingly, another domain, saturated with carbon dioxide and water, between the  $\text{CO}_2$  + gas hydrate and  $\text{CH}_4$  + water domains (Fig. 5).

Gas hydrate formation with two phase boundaries and three domains occurs at  $T_{(s)} > 273$  K on the boundary  $\xi_{(s)}$ , where  $T_{(s)}$  is the temperature at the



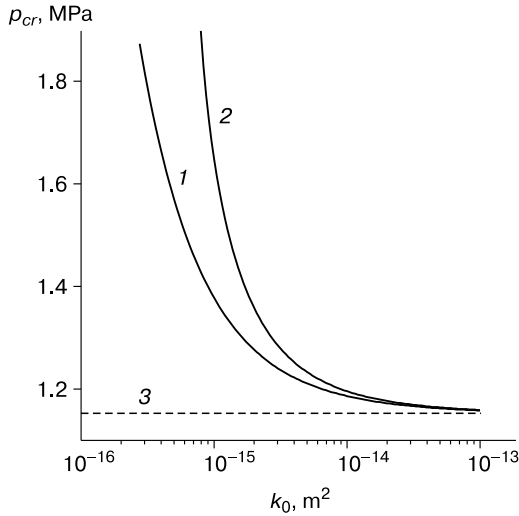
**Fig. 4.** Gas hydrate formation with two phase boundaries.

1 – saturation with  $\text{CO}_2$  hydrate and free carbon dioxide; 2 – saturation with water and methane; 3 – saturation with ice and methane.



**Fig. 5.** Gas hydrate formation with three phase boundaries.

1 – saturation with  $\text{CO}_2$  hydrate and free carbon dioxide; 2 – saturation with water and carbon dioxide; 3 – saturation with water and methane; 4 – saturation with ice and methane.



**Fig. 6. Critical pressure of injected CO<sub>2</sub> ( $p_{cr}$ ) as a function of reservoir permeability  $k_0$ .**

1 – two phase boundaries; 2 – three phase boundaries; 3 – initial reservoir pressure.

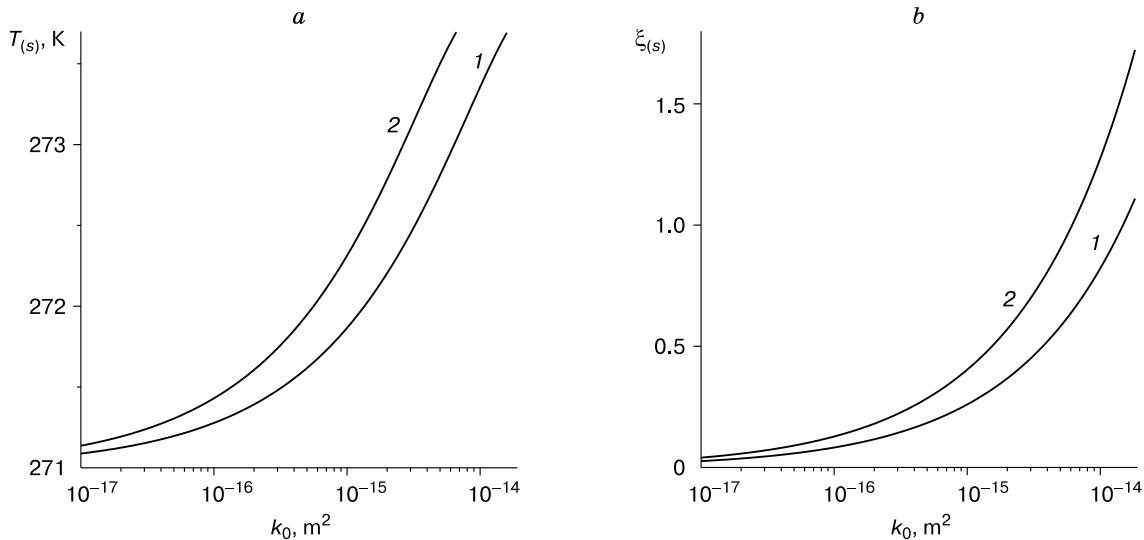
phase boundary found by (8). Three phase boundaries and four domains arise at  $T_{(s)} > T_{(1)s}$  on the boundary  $\xi_{(s)}$ , where  $T_{(1)s}$  is the temperature of gas hydrate decomposition found by (1) corresponding to the pressure  $p_{(s)}$ .

These inequalities were used in numerical experiments with large ranges of parameters in order to find such critical injected gas pressure  $p_{cr}$  above which two or three phase boundaries arise in the gas

hydrate formation process. The calculations showed that the  $p_{cr}$  value depends mainly on the permeability and initial pressure of the reservoir.

The permeability dependences of gas injection pressure that control the gas hydrate formation regimes have been plotted for the same initial temperature of the injected gas and the reservoir (Fig. 6). Other parameters in the plots of Fig. 6 are as in Fig. 3. Dash line 3 parallel to the x axis (the horizontal asymptote of the solid curves) shows the initial reservoir pressure. The critical pressure  $p_{cr}$  decreases with permeability (Fig. 6), and gas injection into poorly permeable porous rocks at low  $p_e$  produces two domains of CO<sub>2</sub> + gas hydrate and CH<sub>4</sub> + ice. Progressive increase in injected gas pressure or reservoir permeability gives rise, successively, to the third and fourth domains saturated with methane + water (domain 3) and carbon dioxide + water (domain 4).

As shown by plots in Fig. 7 for two different CO<sub>2</sub> injection pressures, the temperature at the phase boundary and its self-similar coordinate increase proportionally to permeability, and the rate of this increase is faster at higher gas pressures. Therefore, the results presented in Figs. 3 and 6 can be explained by release of latent hydrate formation heat. Inasmuch as the rate of phase transition is controlled by mass transfer in the reservoir, gas injection pressure or permeability increase leads to faster gas hydrate formation and, hence, to greater heat release. The heat released at very fast hydrate formation exceeds the heat loss and causes ice melting creating domains saturated with gas (CO<sub>2</sub> or CH<sub>4</sub>) and water.



**Fig. 7. Temperature  $T_{(s)}$  at phase boundary (a) and self-similar coordinate  $\xi_{(s)}$  of phase boundary (b) as a function of reservoir permeability  $k_0$  at different pressures of injected gas:  $p_e = 1.2$  MPa (1) and  $p_e = 1.25$  MPa (2).**

## CONCLUSIONS

We have modeled the formation of CO<sub>2</sub> hydrate by injection of gaseous carbon dioxide into an ice-rich methane reservoir and obtained self-similar solutions in a plane-parallel approximation for reservoir pressure and temperature. The solutions show gas hydrate formation with one, two, or three phase boundaries, depending on the pressure of injected CO<sub>2</sub> and the reservoir permeability. Correspondingly, injection at a low pressure into a poorly permeable methane reservoir produces two domains with gaseous CO<sub>2</sub> + hydrate CO<sub>2</sub> and ice + methane. As the gas injection pressure and the reservoir permeability progressively increase, ice melting caused by heat excess gives rise to additional domains of methane + water (domain 3) and then CO<sub>2</sub> + H<sub>2</sub>O (domain 4).

Therefore, it is possible to avoid CO<sub>2</sub> hydrate decomposition and risks posed by ice melting to mechanic strength of rocks by maintaining relatively low pressure of CO<sub>2</sub> injection, especially in the case of high reservoir permeability. These results have implications for the choice of strategies that secure subsurface CO<sub>2</sub> sequestration and its safe disposal as gas hydrate in porous reservoirs, as well as for the conditions of CO<sub>2</sub> hydrate stability.

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