

GASES AND GAS HYDRATES IN THE EARTH'S CRYOSPHERE

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**ESTIMATION OF POTENTIAL GAS HYDRATE FORMATION
IN FINELY DISPERSED SOILS AT NEGATIVE TEMPERATURES:
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The article presents results of the experimental modeling of potential methane hydrate formation in the pore space of finely dispersed sediments at negative temperatures. As demonstrated by the experimental results, accumulation of pore methane hydrate in ice-bearing clays saturated with gas is possible in significant amounts even at sufficiently low temperatures (-6.5 °C). The experiments were conducted using a specially designed system, which allows studying the kinetics of gas hydrate accumulation in pore space of the frozen sediments. This research enables evaluation of the effect of clay component on the rate of pore methane hydrate accumulation in frozen sands, and provides valuable insights about pore gas hydrate accumulation in clayey soils depending on ice saturation. The hydrate accumulation kinetics and structure and textural features of frozen hydrate-saturated clayey silt samples with different initial size of ice inclusions were investigated.

Gas hydrates, frozen soils, hydrate formation, kinetics, clayey soils, hydrate saturation

INTRODUCTION

The area of permafrost distribution (cryolithozone) is interpreted as favorable environment for natural gas occurrence and preservation in the hydrate form. Potential accumulation of gas hydrate in permafrost is ensured by the presence of significant accumulations of natural gas (mainly methane) and appropriate pressure/temperature (P – T) and geochemical conditions for hydrate formation. Among numerous gas liberations from permafrost reported at early stages of oil and gas fields development in the northern West Siberia some may be associated with the processes of intrapermafrost gas hydrate formation and dissociation [Cherskiy *et al.*, 1983; Ginsburg, Soloviev, 1990; Are, 1998; Yakushev, 2009].

It is generally assumed that hydrate formation in permafrost regions are primarily associated with sandy beds with good reservoir properties where gas may accumulate during permanent freezing of soils, and with gas migration upward (through high permeability zones) from deep conventional gas reservoirs [Yakushev, 1989, 2009; Chuvilin *et al.*, 2000]. However, accumulation of natural gas in permafrost regions can also occur in finely dispersed soils, e.g. water-saturated sandy-clayey sediments of sublake talik zones. The sediments often contain substantial concentrations of organic carbon, which is used by microbes to produce methane and therefore serve as the source of formation of gases (mainly, methane and carbon dioxide) [Glotov, Glotova, 2015]. The freezing of such

gas-charged sediments in a closed system, may lead to pressure excess caused by gas compression created by the freezing front [Buldovicz *et al.*, 2018; Chuvilin, Davletshina, 2018; Istomin *et al.*, 2020]. In this case, the pressure may exceed the equilibrium pressure of hydrate formation, which will ultimately prime gas for conversion to gas hydrates [Istomin *et al.*, 2018].

The literature data analysis revealed that little has been investigated regarding to accumulation of gas hydrates at negative temperatures in the pore space of finely dispersed soils. The possibility of hydrate formation at negative temperatures in water-unsaturated permeable clayey soils containing ice inclusions is discussed in [Chuvilin *et al.*, 2002; Lei, Santamarina, 2018]. At this, some experimental results on the formation of pore gas hydrate in finely dispersed sediments at positive temperatures demonstrated that intensity of pore hydrate formation in such settings shows a declining trend, while the fraction of pore water converted into hydrate decreases with increasing soil dispersivity [Chuvilin *et al.*, 2003]. Thus, the experimental modeling of pore methane hydrate accumulation showed that upon adding 7 % of montmorillonite particles to sand sample with prespecified initial moisture content (10 %) the hydration coefficient decreases more than twice [Chuvilin *et al.*, 2005]. Besides, some research [Chuvilin *et al.*, 1999] addresses effects of clay particles in the sand matrix on the nature of hydrate accumula-

tion in the pore space. The implications that the authors demonstrated are that an increase in the clay content decelerates the water redistribution during hydrate formation and reduces the extent of pore water conversion to hydrate. In addition, hydrate saturation of sand samples containing clay particles at positive temperatures was experimentally studied, along with mechanical properties of hydrate-bearing sediments [Yang *et al.*, 2019].

The experimental data on effects of the clay component on the kinetics of pore methane hydrate formation in sands are provided in [Zhang *et al.*, 2017]. Their research results show that an increase in montmorillonite content up to 30 % in the sandy-clayey mixture entails almost 5-fold decrease in the rate of methane hydrate formation. Another research results [Uchida *et al.*, 2004] showed that a decrease in water content in clayey soils essentially affect the gas hydrate equilibrium conditions making them shift to a region of higher pressures and lower temperatures. Thus, the experimentally lowered moisture content has caused a 1.5 °C temperature shift in kaolinite clay and 6–10 °C shift in montmorillonite clay. Results of other study of the conditions for gas hydrate existence in clayey soils are provided in [Cha *et al.*, 1988; Yakushev, 2019].

Analysis of the literature data revealed a paucity of experimental studies of the process of hydrate formation in finely dispersed soils. Accumulation of pore hydrate therein is considered mostly at temperatures above 0 °C. Given that naturally occurring gas hydrates tend to form in freezing and permanently frozen finely dispersed sediments, an experimental modeling of the processes of gas hydrate formation in the pore space of dispersed soils under temperatures below zero is increasingly becoming particularly topical. These research results will enable quantification of gas hydrates accumulated in dispersed water-unsaturated sediments, along with analysis of the clay

component effects on hydrate formation in gas-charged sands.

EXPERIMENTAL METHODS

The experimental modeling aimed to determine and calculate the parameters characterizing P – T conditions and the kinetics of gas hydrate accumulation in dispersed soils at negative temperatures. The soil samples were saturated with hydrate at temperatures of –3.0...–6.5 °C, specifically, with pressurized pure methane (CH₄ content was 99.98 vol.%) cooled to the experimental temperature.

A special experimental setup designed to reproduce and study the hydrate accumulation processes in frozen sandy-clayey soils (Fig. 1) provides for simulating the P – T conditions in the soil samples over a wide range of temperatures and pressures. The system consists of a metal pressure cell whose lid can be tightly sealed which accommodates a container with the prepared soil placed inside. The pressure cell is equipped with special holes for gas input sleeve and two holes (0.5 cm deep) for pressure and temperature sensors (accurate up to 0.05 °C and 0.005 MPa) providing for changes in P – T conditions in the sample to be automatically recorded onto a PC with integrated ADC [Chuvilin *et al.*, 2019].

After the container with soil was placed in the pressure cell, the sample was slowly vacuumed with a low-power pump connected to the gas input sleeve and vacuum system. Upon vacuuming the soil sample, the pressure cell was filled with a hydrate-forming gas, where the temperature was maintained (accuracy: 0.1 °C) by circulation of liquid from the HAAKE Phoenix C40P refrigerated bath along the “thermal coat” around the pressure cell.

Naturally deformed soils were chosen to be the object of study involving modeling of the pore gas hydrate accumulation conditions for finely dispersed soil and artificial saturation of samples with hydrate (Table 1). To study the effect of the amount of clay

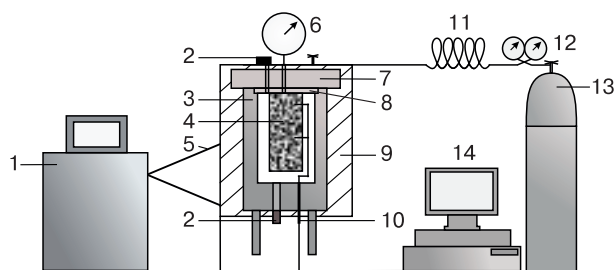


Fig. 1. Sketch of experimental setup for studying the kinetics of the formation and dissociation of pore gas hydrates.

1 – cryothermostat; 2 – pressure sensors with gas intake and vacuum inlets; 3 – pressure cell; 4 – container with soil samples; 5 – hose for circulating liquid; 6 – digital pressure gage; 7 – metal lid; 8 – tephlon gaskets; 9 – “thermal coat”; 10 – thermistor input sleeve; 11 – gas tube; 12 – pressure regulator; 13 – gas bomb; 14 – PC with ADC.

Table 1. Mineralogy and salinity of the analyzed soils

Soil	Mineralogy, %	Salinity, %	
Sand	Quartz	>90	0.01
Montmorillonite clay	Montmorillonite	93.4	1.99
	Andesine	2.9	
	Biotite	2.9	
	Calcite	0.8	
Clayey silt	Quartz	46.4	0.70
	Albite	25.3	
	Chlorite	10.4	
	Muscovite	7.4	
	Potassium feldspar	6.5	
	Kaolinite	4.2	

Note. The mineralogy is represented by elements whose content exceeds 1 %.

Table 2. Particle size distribution

Soil	Particle size distribution, %			Lithology
	1–0.05 mm	0.05–0.001 mm	<0.001 mm	
Sand	94.8	3.1	2.1	Fine sand
Montmorillonite clay	0.3	46.2	53.5	Heavy clay
Clayey silt	21.1	55.8	23.1	Heavy silty clayey silt

Note. Lithology is given according to classifications of E. Sergeev (sand) and V. Okhotin (clays).

fraction on intensity of gas hydrate accumulation in frozen methane-charged sand samples, we used sandy-clayey mixtures prepared from quartz sand admixed with montmorillonite clay in different percentages. The constituent minerals were identified by X-ray diffractometry; the particle size distribution (Table 2) was determined according to the State Standard document GOST 12536-2014 [2014], the physical properties of the studied soil samples were analyzed following procedures prescribed by GOST 5180-2015 [2015] and Building Code and Regulations SNiP 2.02.04-88 [1990]. While the initial weight moisture content of the samples varied from 15 to 24 %, the porosity of the samples averaged 0.4–0.6.

The method of soil samples preparation for the experiments involved the steps described below. The cooled air-dry soil was mixed with chipped ice in the amount required for obtaining the specified moisture content. After that the sample was left for half an hour at $-6...-7$ °C. Thus prepared and cooled wet soil was compacted layer-by-layer in a metal cylindrical container (10 cm high and 4.6 cm in diameter) and placed in the pressure cell, which was sealed and vacuumed and then filled with hydrate-forming gas pressurized at 4–6 MPa.

After the decay of hydrate formation processes (i.e. deceleration of the rate of pressure decline), the kinetics of pore hydrate accumulation was evaluated at each moment of time and hydrate storage capacity parameters were determined using the pressure-volume-temperature (PVT) method. This technique enables quantification of the absorption of methane during hydrate formation, which can be inferred from pressure and temperature variations in the test cell. A detailed calculation scheme is provided in [Chuvilin et al., 2019].

Table 3. Methane hydrate accumulation conditions

Soil*	Moisture content, %	Pore occupancy, u.f.	Temperature, °C	p_0 , MPa	Time, h	Hydrate saturation, %	Hydration coefficient
Sand	15	0.57	-4.0	5.7	100	37	0.45
Sand with m/m clay (10 %)	17	0.81	-3.0	4.4	56	18	0.17
Sand with m/m clay (20 %)	17	0.67	-5.0	4.5	100	14	0.15
Clayey silt ($S_i = 28$ %)	18	0.28	-6.5	5.1	150	7	0.17
Clayey silt ($S_i = 41$ %)	24	0.41	-6.5	6.1	140	11	0.20

* m/m =montmorillonite; S_i = ice saturation.

The volume content of hydrate (H_v , %) was determined using the formula

$$H_v = \frac{M_h \rho}{M_s \rho_h} \cdot 100 \%,$$

where M_h is the weight of pore gas hydrate (g); M_s is the weight of soil sample (g); ρ is the initial (prior to hydrate saturation) sample density (g/cm^3); ρ_h is the skeleton density of empty square lattice of methane hydrate (without gas molecules, as in pure ice) (ρ_h for CH_4 is assumed to be $0.794 \text{ g}/\text{cm}^3$) [Chuvilin, Bukhanov, 2017].

Pore occupancy, or percentage of pore space filled with hydrate (S_h , %) is found as

$$S_h = \frac{H_v}{n}.$$

The hydration coefficient (K_h), or fraction of water converted to hydrate, is given by

$$K_h = \frac{W_h}{W},$$

where W_h is the percentage of water converted to hydrate (% of dry sample weight) and W is the total amount of moisture (initial water content, %). W_h is found from the weight of pore hydrate (based on its chemical formula) M_h .

Parameters of hydrate storage capacity for soils containing CH_4 hydrate were derived from the chemical formula of methane hydrate and using hydrate number 5.9.

RESULTS AND DISCUSSION

In all the experiments conducted, the formation of methane hydrate occurred in frozen ground samples. The experimental (preset) initial P – T parameters in frozen methane-saturated ground samples are

listed in Table 3. The variations in initial pressure (p_0) varied from 4.4 to 6.1 MPa (Table 3), while parameters of hydrate accumulation in frozen methane-charged ground samples were inferred from the analysis of pressure and temperature conditions during the experiments.

Depending on the type of soil, initial moisture content and conditions of hydrate formation, the hydrate saturation (S_h) of frozen samples at above the equilibrium pressure varied from 7 to 37 %, and the hydration coefficient (K_h) – from 0.15 to 0.45. The percentage of pore space filled with ice for the samples ranged from 28 to 81 %.

The experiment results reported intense hydrate accumulation ($S_h < 11$ %) in methane-charged frozen clayey silt samples containing 23 % clay particles ($d < 0.001$ mm), at ice saturation $S_i = 28$ and 41 %. At this, the fraction of pore water converted to hydrate was 17 and 20 % at initial ice saturations $S_i = 28$ % and $S_i = 41$ %, respectively.

In the case of hydrate formation in frozen clayey soil, significant accumulation of methane hydrate in the pore space is basically possible even at essentially low temperatures (-6.5 °C), which is however almost 2.5 times lower than for pure sand (Table 3). Such a decrease in the hydration coefficient associated with sands passing into clayey silts can be explained by higher contents of bound water owing to the variations in soil's parameters: enhanced soil dispersivity and salinity, and lowered soil permeability. In this context, an increase in the bound water content will reduce the intensity of phase change to hydrate by shifting the phase equilibria to the region of lower temperatures and higher pressures, thereby reducing the driving force of hydrate formation (Δp). A slowdown in hydrate accumulation with appearing clay particles was observed in the frozen samples of sandy-clayey mixtures (Table 3). Thus, when adding montmorillonite particles to sand (up to 20 %), the hydration coefficient decreased from 45 % (in pure sand) to 15 % during hydrate formation.

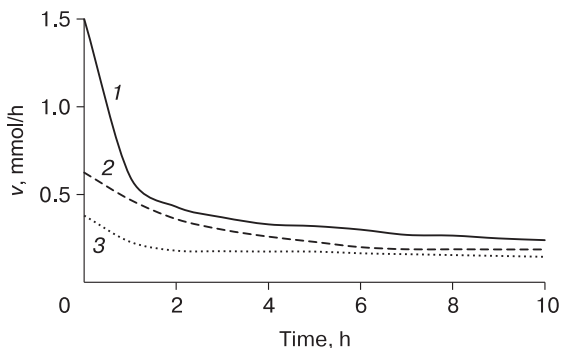


Fig. 2. Methane absorption rate (v) during pore hydrate formation in the frozen soil samples:

1 – sand, $W = 15$ %; 2 – sand with 10 % fraction of montmorillonite clay, $W = 17$ %; 3 – sand with 20 % fraction of montmorillonite clay, $W = 17$ %.

Effect of the clay component

The experiments allow to trace the influence exerted by the clay component contents on the kinetics of pore methane hydrate accumulation in sands. The experiments were conducted on frozen samples of sandy-clayey mixtures with 10 and 20 % content of montmorillonite clay at hydrate formation temperature $T = -3...-5$ °C.

The intensity of methane hydrate accumulation in the pore space of the frozen sandy-clayey samples can be inferred from the methane absorption rate during hydrate formation within the first 10 hours after the experiment start (Fig. 2).

The experimental estimates of the methane absorption rate (v) during hydrate formation show that, depending on the clay fraction in the sandy soil at the initial moment, it changes by more than 3 times (Fig. 2). Thus, the beginning of the experiment demonstrated implications of the montmorillonite clay content (%) in sands for the variations of v as follows: up to 1.5 mmol/h (zero, pure sand), as low as 0.63 mmol/h (10 %); $v \leq 0.38$ mmol/h (20 %). The difference between methane absorption rates in frozen sand samples with different montmorillonite clay contents levels off with time. Thus, after 10 hours after the start of the experiment, the value for methane absorption in the sand samples with higher content of clay particles (up to 20 %) decreased less than twice (Fig. 2).

The kinetics of methane hydrate accumulation in sand samples with different contents of montmorillonite clay, calculated from the methane absorption parameters during hydrate formation, is shown in Fig. 3.

Analysis of the kinetics of methane hydrate accumulation shows that an increasingly higher clayey fraction of sandy soil will accordingly depress the intensity of pore hydrate formation with time. This can

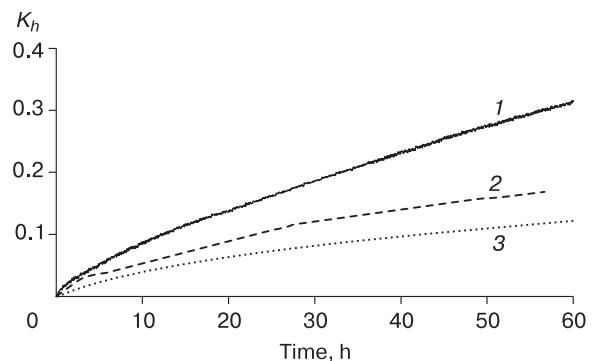


Fig. 3. Kinetics of methane hydrate accumulation in the pore spaces of the samples of different composition ($T = -3...-5$ °C):

1 – sand, $W = 15$ %; 2 – sand with 10 % fraction of montmorillonite clay, $W = 17$ %; 3 – sand with 20 % fraction of montmorillonite clay, $W = 17$ %.

be deduced from variations of the hydration coefficients for the studied soils, inasmuch as the difference between them tends to be more accentuated with time (Fig. 3). As a result, in 60 hours time from the experiment start, the fraction of water converted to hydrate was 31 % in sand, while the hydration coefficient K_h decreased to 17 % in sandy soil admixed with 10 % clay, and $K_h \leq 12$ % with 20 % clay.

Implications of ice saturation for hydrate accumulation in clayey soils

The kinetics of methane hydrate accumulation in frozen ice-bearing clayey soils is largely dictated by the percentage of pore space filled with ice. The influence of ice contents on the intensity of hydrate accumulation in the pore space of frozen thinly dispersed soils is best traced in clayey silt samples with varying degrees of pore space filled with ice ($S_i = 28$ and 41 %). The experiments were run at a temperature -6.5 °C, the hydrate saturation time totaled to 150 h (Fig. 4).

The experiment results indicate more intense hydrate accumulation at the initial time in the higher ice-saturated sample (41 %). Thus, almost 14 % of the pore water thus converted into hydrate during 6 hours after the onset of the run in the sample with $S_i = 41$ %, while the conversion did not exceed 8 % in the sample with $S_i = 28$ %. Notably, hydrate saturation in the sample with higher ice content at that time was 8 %, and less than 3 % in the frozen clayey silt with $S_i = 28$ %. However, the intensity of hydrate accumulation continued to slow down with its decay interpreted to be much faster in the more ice-saturated sample against the less ice-saturated one, which in large part is explained by significantly reducing permeability during pore hydrate formation. Consequently, the hydration coefficients at the end of each run were found to be close in value: $K_h = 19.5$ % (sample with $S_i = 41$ %) and $K_h = 17$ % (sample with $S_i = 28$ %). The fact that the intensity of hydrate accumulation differed remarkably at early stage of the experiment in samples with different ice saturation can primarily account for large gas-ice contact in the sample of frozen clayey silt with higher ice content. Alter-

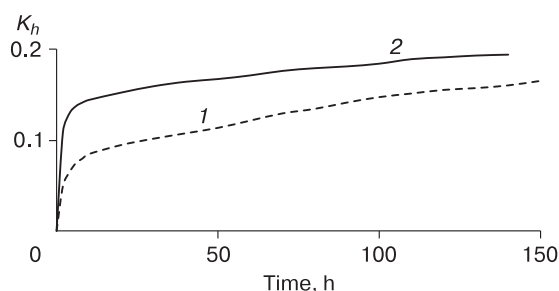


Fig. 4. Effect of ice saturation on the kinetics of pore methane hydrate accumulation in the frozen clayey silt samples ($T = -6.5$ °C).

1 – $S_i = 28$ %; 2 – $S_i = 41$ %.

natively, a slight difference in the values of K_h at the end of the experiments is explained by reduced hydrate formation process because of a dense hydrate film developed on the surface of ice inclusions, thereby gradually arresting the process of hydrate accumulation.

Effect of the size of ice inclusions

The influence of the size of ice inclusions on the kinetics of methane hydrate accumulation in clayey soils was modeled using the samples of ice-soil mixture (clayey silt admixed with ice particles of different sizes). While the prepared clayey silt samples were equated in initial moisture content $W = 20$ %, the admixed ice inclusions differed in size (0.5–1.0 and 2–4 mm). The soil skeleton density in the prepared samples was 1.2 g/cm³ for clayey silt with smaller ice inclusions and 1.1 g/cm³ for clayey silt with coarser ice inclusions. The experimental data on the kinetics of hydrate accumulation in clayey silt samples containing variously sized ice inclusions are shown in Fig. 5.

Results of these studies indicate that accumulation of methane hydrate tends to be more intensive in the sample with smaller ice inclusions, which is distinctly expressed at the initial stage of hydrate formation. Thus, after 10 hours of the experiment, K_h for clayey silt with admixed ice inclusions reached 13 % in the case their size was 0.5–1.0 mm, while it did not exceed 3 % at their size 2–4 mm. As such, an essential difference in the hydration coefficients caused by the changing size of ice inclusions is primarily attributed to enlargement of the gas-ice contact surface because of the reducing size of ice inclusions. In 100 hours after the start of the experiment their difference between the runs has remarkably diminished, i.e. in the initial period K_h in the sample with small ice inclusions was 4 times higher as compared to the sample of clayey silt with large ice inclusions, while its value was higher not more than twice at the end of the experiment (in 100 hours time).

Upon cessation of hydrate accumulation at negative temperatures, the samples of clayey silt with dif-

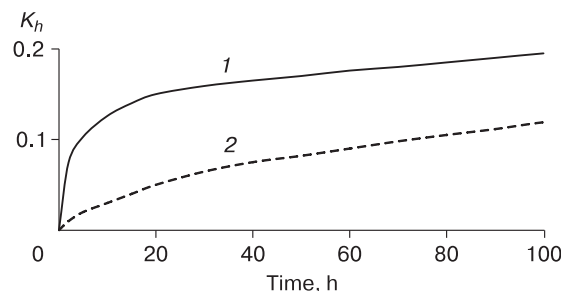


Fig. 5. Effect of the size of ice inclusions on the kinetics of hydrate accumulation in the frozen clayey silt samples ($T = -6...-7$ °C).

Size of ice inclusions: 1 – 0.5–1.0 mm; 2 – 2–4 mm.

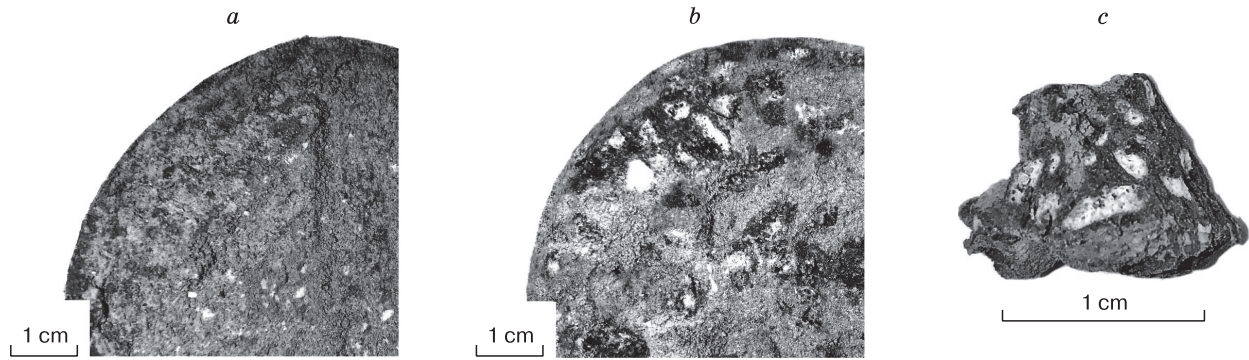


Fig. 6. Structure of the frozen hydrate-containing clayey silt samples with different initial sizes of ice inclusions after hydrate saturation at negative temperatures and completion of freeze-thaw cycle.

a – 0.5–1.0 mm; *b, c* – 2–4 mm.

ferent sizes of ice inclusions were exposed to warming until they reached low positive temperatures (1–2 °C) under above the equilibrium P – T conditions, thereby allowing the residual pore ice to convert to hydrate. Later, the samples were cooled to a lower temperature (–6 °C), which resulted in the freezing of residual pore water that had not converted to hydrate. After that, the frozen samples were withdrawn for the structural and textural analysis. The photographs in Fig. 6 display transverse chips of the studied frozen hydrate-containing clayey silt samples.

The morphological studies have shown that a sample with initial ice inclusions 0.5–1.0 mm in size is characterized by the formation of scattered ice-hydrate inclusions (up to 1–2 mm), whereas a clayey silt sample with initially large ice inclusions (2–4 mm) demonstrates the presence of variously shaped ice-hydrate porphyry from 1 to 5 mm in size (Fig. 6).

The conducted experimental simulation has revealed specific features of gas hydrate formation at negative temperatures in finely dispersed soils, which allowed to evaluate the effects of the clay component on intensity of pore methane hydrate accumulation in frozen sands, to identify the patterns of pore gas hydrate accumulation in clayey soils depending on ice saturation, as well as to compare the kinetics of accumulation and to evaluate the structural-textural characteristics of frozen hydrate-containing clayey silt samples enriched with ice inclusions of different initial sizes.

CONCLUSIONS

The experimental studies of gas hydrate formation in finely dispersed soils confirm the possibility of methane hydrate accumulation at negative temperatures in the pore space of finely dispersed sediments.

The research results indicate that enhanced dispersivity of soil is capable to reduce the fraction of

pore ice converted into hydrate. Thus, an increase in the content of montmorillonite clay particles in sands (up to 20 %) during hydrate formation has lead to a 3-fold decrease in the fraction of pore ice converted to hydrate (from 45 to 15 % in pure sand).

The experiments provide insights into the kinetics of methane hydrate accumulating in frozen finely dispersed soils unsaturated with ice which is found to be affected by the percentage of pore space filled with ice. The simulation results showed that in the higher ice-saturated clayey silt sample, the intensity of hydrate accumulation was remarkably higher at the beginning of the experiment, however the difference in the hydration coefficients depending on the ice saturation was tending to decline with time, along with decaying hydrate formation process and decreasing permeability. Thus, the hydration coefficients for the two analyzed samples of clayey silt (ice saturation: 28 and 41 %) differed by more than 6 % at the beginning and by 2.5 % at the end of the experiments.

The role played by ice inclusion sizes in the formation of methane hydrate was experimentally shown on the samples of ice-soil mixture of clayey silt with ice particles of different sizes. The research result indicate more intensive methane hydrate accumulation in the sample with smaller sizes of ice inclusions because of the increased gas-ice contact surface. Thus, over 10 hours of the experiment, the hydration coefficient reached 13 % in a mixture of clayey silt with ice inclusions 0.5–1.0 mm in size, while in the clayey silt sample containing 2–4 mm ice inclusions it did not exceed 3 %. Finally, the structural and textural features of ice hydrate formations formed in silts were analyzed during the experiments.

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