PHASE TRANSITIONS OF WATER IN GAS-SATURATED SEDIMENTS

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We have experimentally studied the peculiarities of water–gas-hydrate and water–ice phase transitions under gas pressure in dispersed methane-saturated sediments in the course of cyclic cooling-heating. Data on the conditions of hydrate and ice formation in the sediment pores have been obtained. It is shown that on cooling of dispersed rocks, only part of the pore water passes into hydrates; the rest (intimately bound with the particle surface) transforms into ice during further cooling. Hydrate formation in the studied sediments, compared with the system pure-water–gas, occurs at higher pressures and lower temperatures. It is demonstrated that the sediment dispersion and cooling-heating cycles affect the *PT*-conditions of formation and decomposition of gas hydrates. Petrography of frozen rocks artificially saturated in hydrates is studied.
Ice, gas hydrate, phase transitions, sediment system, experimental modeling

INTRODUCTION

Cooling of humid gas-saturated dispersed rocks can cause not only ice formation (at $T < 0$ °C) but also transition of part of the sediment water into gas hydrates if the sediment is suitable for the formation of hydrate within hydrate stability zone. The processes of ice and gas hydrate formation in dispersed systems have much in common (cementation of dispersed rocks and increase in their strength, redistribution of water and salt throughout the section, swelling, etc.), and zones of their occurrence are confined to zones of the Earth's crust cooling.

Today there are a number of models describing the synchronous hydrate and ice formation in rocks [1]. For example, when the front of sediment freezing moves downward, gas can concentrate at the boundary of frozen and melted deposits, and in transition of water into ice, the pressure of crystallization can reach the equilibrium pressure of gas hydrate formation. Thus, freezing of rocks can lead to the appearance of local hydrate stability zone and hydrate formation.

Study of the synchronous hydrate and ice formation in dispersed rocks is of paramount scientific interest, particularly estimation of the *PT*-conditions of the water–gas-hydrate and water–ice phase transitions in the rock pores. Today there are theoretical and experimental data on the effect of pressure on the temperature of ice and hydrate formation in the system pure-water–gas. Nevertheless, the kinetics of phase transitions of the sediment water is as yet imperfectly understood, and many quantitative characteristics of thermodynamic parameters are still debatable.

Some researchers have studied the kinetics of hydrate formation in pore space [2–4] and the effect of the sediment medium on the *PT*-conditions of formation and decomposition of gas hydrates [3, 5–7]. For example, in [3, 5, 6] it is shown that the hydrate formation in the pores of dispersed rocks occurs at lower temperatures and higher pressures as compared with the system pure-water–gas. At the same time, Cha et al. [7] demonstrated that the pressure of hydrate dissociation in clayey medium can be lower than that in the system pure-water–gas at equal temperatures.

The gas effect on the freezing temperatures of the sediment water has not been experimentally studied yet. Moreover, there are just a few data on the joint study of hydrate and ice formation (under gas pressure) in dispersed rocks. Note that the joint study of these processes is of great interest as they are similar in the physicochemical aspect and may synchronously occur on sediment freezing.

Table 1

Granulometric and Microaggregate Compositions of the Studied Sediments

Rock	Diameter of particles, mm								Name after classification by Okhotin [13], for sands — after classification by Sergeev [13]
	1–0.5	0.5–0.25	0.25–0.1	0.1–0.05	0.05–0.01	0.01–0.005	0.005–0.001	<0.001	
	Content of particles in each fraction, %								
Quartz sand	1	53	45	1	—	—	—	—	Fine- to medium-grained sand
Montmorillonite clay	0.0 (2.0)	0.0 (1.0)	0.2 (1.3)	0.1 (8.5)	18.8 (15.6)	7.3 (5.9)	20.1 (15.4)	53.5 (50.3)	Heavy clay
Kaolinite clay	0.7 (1.5)	0.5 (0.2)	0.4 (0.2)	2.9 (1.2)	19.5 (32.2)	11.2 (24.0)	40.2 (34.5)	24.6 (6.2)	Silty clay
Sand* admixed with clay particles (Ac) Ac = 2%	0.98	51.94	44.1	0.98	0.38	0.15	0.4	1.07	Fine sand
» Ac = 3%	0.97	51.41	43.66	1	0.56	0.22	0.6	1.61	
» Ac = 5%	0.95	50.35	42.76	0.96	0.94	0.37	1.01	2.68	
» Ac = 7%	0.93	49.29	41.86	0.94	1.32	0.51	1.41	3.76	Sandy loam
» Ac = 9 %	0.91	48.23	40.97	0.92	1.69	0.62	1.81	4.82	

Note. Numerals with and without parentheses show microaggregate and granulometric compositions, respectively.
* Quartz sand; ** montmorillonite clay.

INVESTIGATION TECHNIQUE

Study of hydrate and ice formation in pore space under pressure was carried out on the experimental setup which we designed together with the researchers of the Geological Survey of Canada in 1996 [2]. The setup is a metallic high-pressure chamber, into which a sediment sample container is immersed. It is equipped with an automatic system for recording temperature and pressure in the sample, which includes pressure and temperature transducers (measurement accuracies of 0.05 °C and 0.01 MPa, respectively); data from the latter are recorded, with a chosen time step, on a computer. During the experiments, the temperature transducers were maintained at three points of the sample, which provided control over the uniform variation of the temperature field.

The chamber was connected with a cylinder filled with methane (15 MPa, 99.98% CH_4) or nitrogen (15 MPa, 99.99% N_2). Cyclic temperature fluctuations in the chamber were initiated by a "Grunland" refrigeration unit.

We used clayey and sandy sediments and sand-clay mixtures as model samples. Their characteristics and compositions are listed in Table 1. The experiments were put on montmorillonite and kaolinite clays with initial water contents close to the plasticity limits of these clays: 20 to 190 wt.% and 40 to 50 wt.%, respectively. We also used fine- to medium-grained quartz sand. Sand-clay mixtures were prepared by adding montmorillonite clay particles (0–9% of the mixture) to sand. The initial water content of sand or sand-clay mixture was 17%.

For each experiment we prepared two identical samples through layer-by-layer compaction. One of them was placed into the hydrate formation setup, and the other served as a reference sample (without pressure).

The method of production of hydrate-saturated sediment samples corresponded to natural temperature
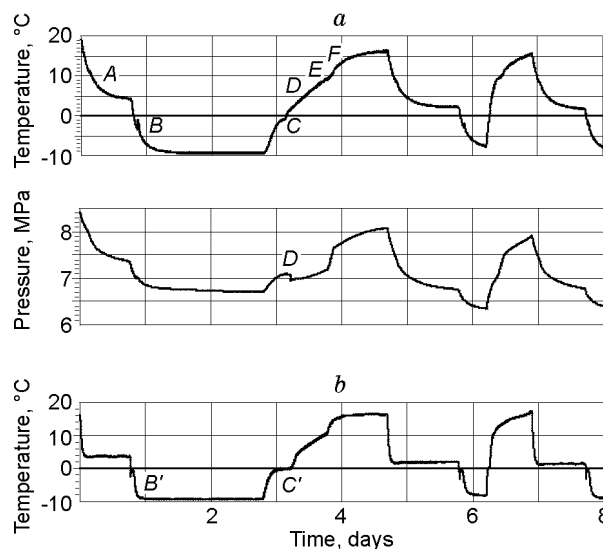
Fig. 1. Variation in *PT*-conditions on cyclic cooling-heating. Sand samples: *a* — methane-saturated, *b* — reference (W_0 = 17%, Ac (content of montmorillonite clay particles) = 7%).

variations in sediment in zones of natural hydrate occurrence. It included the following stages: immersion of the sample into the container, setting-up of the high-pressure chamber and saturation of the sediment with methane, elevation of pressure in the chamber to 7–8 MPa and its subsequent cooling to +2...+4 °C. After the completion of hydrate formation, the chamber was further cooled to –6...–7 °C, which ensured freezing of the hydrate-saturated sample. In the cyclic experiments, the chamber with sediment sample was subjected to cyclic cooling-heating in the temperature range +20 °C— +2...+4 °C— –6...–7 °C–+2...+4 °C—+20 °C—+2...+4 °C— –6...–7 °C (2–3 cycles). Then the atmospheric pressure was generated in the chamber, the latter was opened, and the frozen hydrate-bearing sediment sample was taken out and used in special laboratory studies [4].

In the experiments without hydrate formation (under nitrogen pressure), a similar procedure was used. In both runs, the control specimens were subjected, under atmospheric pressure, to the same temperature cycles.

RESULTS

Kinetics of phase transitions of water in methane-saturated dispersed systems. The obtained experimental data shed light upon the kinetics of phase transitions of water under gas pressure in the course of cyclic cooling-heating. In all experiments, cooling of methane-saturated samples led to hydrate formation and then, at negative temperatures, to ice formation. On heating, the samples underwent melting, secondary hydrate formation, and decomposition of methane hydrates. At atmospheric pressure, the reference samples exhibited just freezing and thawing of sediment water. Figure 1 shows typical experimental *P,T–t* curves for methane-saturated and reference sand samples containing 7% montmorillonite clay.

On cooling, when the conditions for hydrate formation are reached, the pore water partly transformed into hydrate, as evidenced from the typical drop in pressure in the system and relative stabilization of temperature (Figs. 1 and 2, *a*). The local maximum temperature after a slight overcooling of the system corresponds to the beginning of hydrate formation (point *A*). In our experiment, hydrate formation starts at *T* = 11.46 °C and *P* = 7.97 MPa. On subsequent cooling to negative temperatures, the remaining water (intimately bound with the particle surface) passes into ice. The points *B* (Fig. 1, *a* and 2, *b*) and *B'* (Fig. 2, *d*) correspond to the beginning of freezing of sediment water in the hydrate-saturated and reference samples, respectively. The temperature at which the freezing begins under methane pressure is –1.06 °C (at *P* = 7.03 MPa), and in the reference sample at atmospheric pressure, –0.27 °C.

On heating, thawing of the samples is detected by the specific behavior of temperature (Fig. 1). The difference in the thawing temperatures of the sample under pressure (*C* = –0.95 °C) and reference sample (*C'* = –0.15 °C) is approximately the same as that between their freezing temperatures (*B* and *B'*) (Fig. 2, *c*, *d*). This indicates a significant effect of the pore pressure on the temperature of phase transitions.
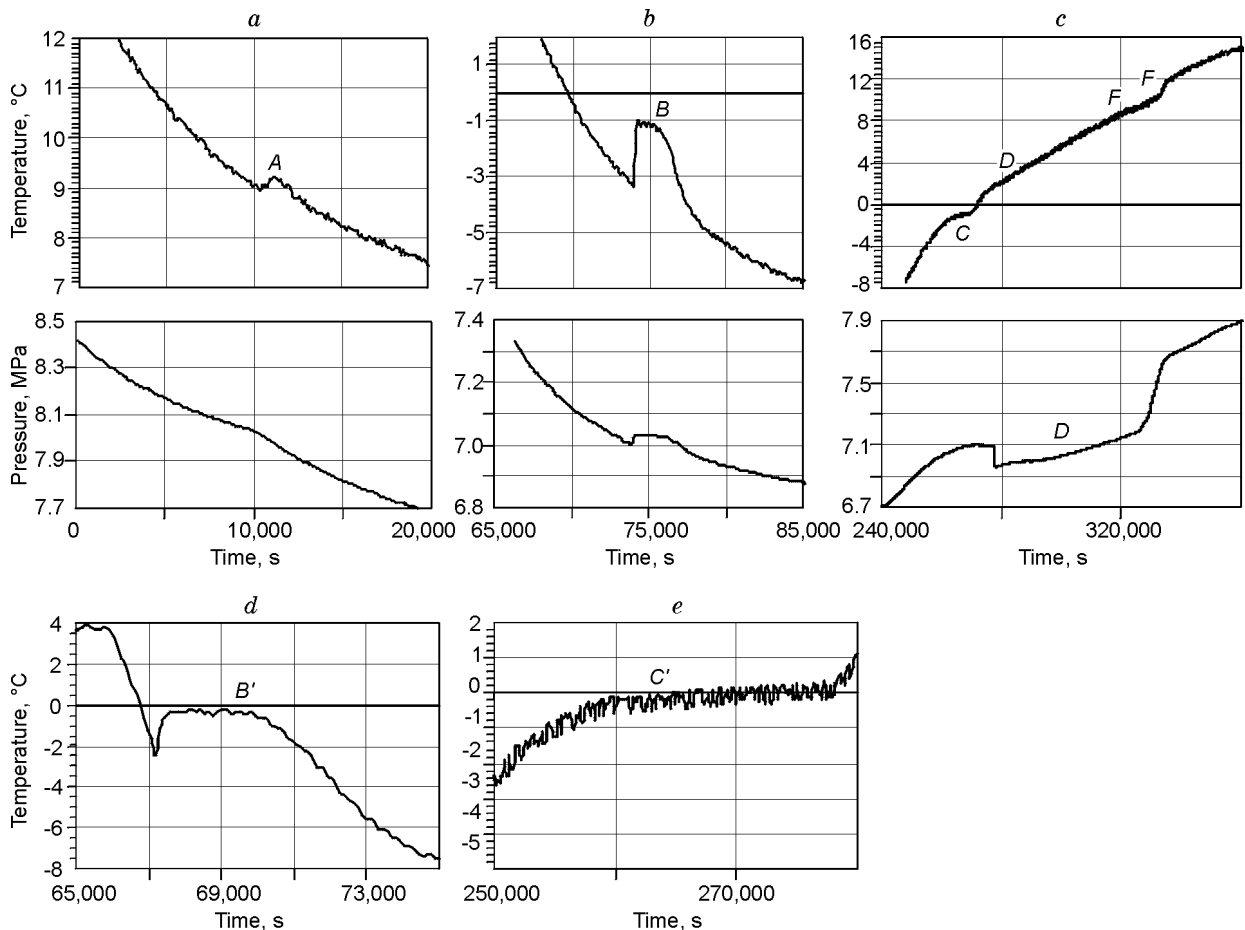
Fig. 2. Variation in *PT*-conditions on phase transitions in sand samples ($W_0 = 17\%$, Ac = 7%) in the first cycle of cooling-heating. *a* — Hydrate formation in the methane-saturated sample; *b* — freezing of the hydrate-containing sample; *c* — thawing of the methane-saturated sample—secondary hydrate formation—decomposition of hydrates; *d* — freezing of the reference sample; *e* — thawing of the reference sample.

After the release of sediment water on ice thawing, at pressure above its equilibrium value, the methane-saturated sample exhibits "secondary hydrate formation" (point *D*). At this stage, the sediment water partly transforms into hydrate, which is evidenced from a drastic drop in pressure in the system (Figs. 1, *a* and 2, *c*). A specific feature of the site *C-D* is that ice thawing and hydrate formation here can proceed synchronously.

On subsequent heating to temperatures above the equilibrium one, hydrates decompose (segment *E-F* in Figs. 1, *a* and 2, *c*). The point *E* marks the beginning of hydrate decomposition, $E = 9.2$ °C at $P = 7.17$ MPa. The point *F* (12.0 °C) at $P = 7.67$ MPa) corresponds to the complete decomposition of hydrates in the sample pores.

In the following cycles of cooling-heating of the samples under methane pressure, their structures and textures change, and the pore water, after its phase transitions, acquires a definite structural memory. In passing from the first to subsequent cycles, the phase points shift to the region of higher *T* and lower *P* values (closer to the theoretical curve for the system water–free-gas). In this case the content of gas hydrates in the pores increases as a result of loosening of the sediment and formation of its new structure, more suitable for hydrate accumulation. This tendency was observed in all cyclic experiments.

Note that on cyclic cooling-heating, water in clayey sediments exhibits the same phase transitions as in sandy sediments but of somewhat specific character related to the energetic heterogeneity and greater structuring of sediment water in clays. For example, in contrast to sandy sediments, clays show no overcooling of the samples in phase transitions of sediment water both into hydrate and into ice. Moreover, these phase transitions proceed in a range of temperatures rather than at their particular values.
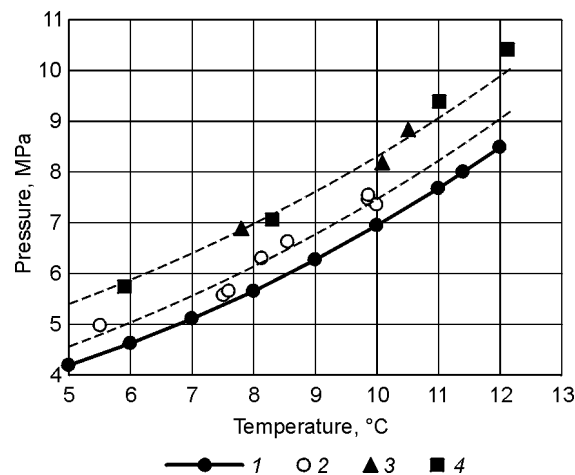
Fig. 3. *PT*-**diagram of methane hydrate decomposition in dispersed sediments.** *1* — PT_{theor}, *2* — **sand** ($W_0 = 17\%$), *3* — **montmorillonite clay** ($W_0 = 70\text{–}170\%$), *4* — **kaolinite clay** ($W_0 = 40\text{–}50\%$).

Formation and decomposition of methane hydrates in dispersed systems. As mentioned above, when the temperature of methane-saturated sediment decreases, the first phase transition of sediment water at positive temperatures is formation of gas hydrates. As in the case of ice formation, this process in dispersed systems is related to the origin of centers of crystallization, the intensity of which depends on the degree of overcooling of the system and on its structure. Analysis of the obtained experimental data shows that formation of methane hydrates in the studied sandy and clayey sediments occurs at higher pressures and lower temperatures as compared with the system pure-water–gas [5].

An increase in content of montmorillonite clay particles shifts hydrate formation into the region of still higher pressures and lower temperatures. This seems to be due to an increase in content of intimately bound water as the sediment dispersity grows. For example, for pure sands the differences between their temperature and pressure of hydrate formation and those in the system pure-water–gas are no more than 0.4 °C and 0.3 MPa, respectively, and for sands with 9% clay particles they reach 2.4 °C and 1.5 MPa.

When heating sediments to higher-than-equilibrium temperatures, gas hydrates begin to decompose. We have established that this process also occurs at higher pressures and lower temperatures as compared with the system pure-water–gas (Fig. 3).

Figure 3 shows the *PT* curves for decomposition of methane hydrates in sandy and clayey sediments. The conditions were chosen so that the initial water content of clays of different mineral compositions corresponded to their plasticity limits. The diagram is constructed for clayey sediments with initial water content close to the upper limit of plasticity; hence, the sediments have nearly the same energy of binding of their pore water with the particle surface. Exponential approximation of the obtained values shows that the *T* and *P* values of methane hydrate decomposition in the studied clayey sediments differ from those in the system pure-water–gas by 2 °C and 1.3 MPa, respectively. In the studied sandy sediments these differences are slightly smaller — 0.8 °C and 0.5 MPa, respectively. This seems to be due to the difference in contents of free (weakly bound with the mineral surface) water between the two types of sediments.

We have analyzed the parameters of gas hydrate decomposition in sands with various contents of montmorillonite clay particles and in the system pure-water–gas. We have established that the temperature difference (d*T*) depends little on the clay content and averages about 1 °C, whereas the pressure difference (d*P*) slightly increases with clay content.

Study of ice formation in dispersed sediments under gas pressure. We studied freezing of sediment water under gas pressure in two experiments: (1) under nitrogen pressure, when no hydrate formation in pores is possible, and (2) on cooling of hydrate-bearing sandy rocks under methane pressure, when the sediment water remaining after hydrate formation turns into ice. We compared the obtained data with the freezing and thawing temperatures of the reference samples at atmospheric pressure.

In the reference sand samples without clay admixtures, sediment water froze and thawed at temperatures
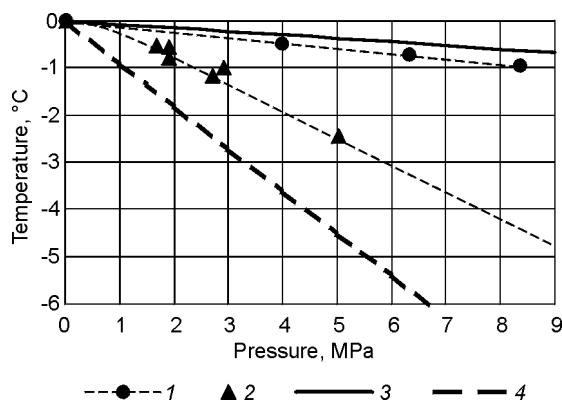
Fig. 4. Freezing temperature vs. gas pressure. Gas: *1* **— nonhydrate-
forming nitrogen,** *2* **— hydrate-forming methane in sand samples;
calculated data for open (***3***) and closed (***4***) systems.**

close to 0 °C. With increasing content of clay particles, the freezing temperatures regularly decreased from –0.04 °C in pure sands to –0.33 °C in sands containing 7% clay (Fig. 4).

In the sample under nitrogen pressure, the coefficient of reduction in the freezing temperature of sediment water with growing pressure is about 0.1 °C/MPa. Figure 4 shows that this coefficient is close to the experimental value for closed systems [8] and to the coefficient calculated by the Clapeyron-Clausius equation.

Ice formation in hydrate-bearing sediments is related to the residual, not passed into hydrate, sediment water, the amount of which depends on the conditions and number of cycles of hydrate formation. Clay particles, in turn, also affect the freezing temperature of sand-clay mixtures. This calls for special investigations. Therefore, it is more correct to consider the experimental freezing temperatures of the samples under methane pressure only for sands without clay admixture. A linear approximation of the obtained data shows that the coefficient of reduction in the freezing temperature of sediment water with growing gas pressure in the hydrate-bearing sample shifts toward the curve for an open system (when the pressure in water remains constant and the pressure upon ice grows). That is, compared with the hydrate-free sediment, the hydrate-bearing sediment has the above-mentioned coefficient closer to that in an open system [9] — 0.55 °C/MPa. This seems to be due to a smaller amount of liquid phase in the hydrate-bearing sample and, hence, to a more intimate binding of sediment water with the surfaces of hydrate and mineral particles.

Petrographic study of frozen hydrate-bearing rocks. At negative temperatures and drop in pressure in the chamber to the atmospheric one, the hydrate-saturated sediments remained stable owing to self-conservation of gas hydrates. We observed just a partial surface decomposition of hydrates, which terminated in a few minutes because of the formation of a protecting ice film at the surface of gas hydrate inclusions [10]. This permitted us to study the hydrate-bearing samples (composition, structure, and properties) in a refrigerating chamber at atmospheric pressure, using some petrographic methods applied in geocryology [11].

Structure of frozen hydrate-bearing sediments. We have visually established that hydrate formation proceeds both at free frontal surfaces of the samples, producing a growing gas hydrate layer ("gas hydrate caps"), and in the sediment pores, forming hydrate cement with inclusions similar to frozen rocks. Formation of both gas hydrate and ice inclusions and structures is related to redistribution of pore water and structural transformations of the sediment [12]. As cooling of hydrate-bearing sediments to negative temperatures leads to freezing of pore water that has not passed into hydrates, we suggest that the studied samples are cryohydrates.

The cryohydrate structure of the studied frozen hydrate-bearing rocks depends on their dispersity and has specific features.

1. Sands with a massive cryohydrate structure and thick, up to 1.5 cm, "gas hydrate caps". The hydrate is milky-white, dense, often with globular segregations up to 3 mm across. This structure is the result of active frontal migration of pore water to the flange surfaces of the samples.

2. The studied kaolinite and montmorillonite clay samples have no hydrates at their frontal surfaces, but there are abundant hydrate inclusions inside them, which form a porphyritic texture. This texture is most distinct in montmorillonite. Grayish hydrate porphyries up to 0.5 cm across have a specific greasy luster. This cryohydrate structure seems to be related to local migration of pore water to the centers of crystallization of gas hydrates inside the sample.

3. The sand-clay mixtures have a cryohydrate structure typical of both sands and clays. An increase in the content of clay particles is accompanied by reduction in the thickness of "gas hydrate caps" and increase in hydrate content inside the samples, resulting in lenticular structure or porphyritic texture. This is related to changes in the ratio of frontal (toward the frontal surfaces) to local (toward the centers of crystallization) migration of pore water. For example, the maximum thickness of a "hydrate cap" is no more than 5 mm even at minor content of clay particles; the hydrate is snow-like, loose. The sand samples with 5, 7, and 9% montmorillonite contain only thin hydrate needles. With increasing content of clay particles, the massive cryohydrate structures of the samples become more diverse; the samples acquire a porphyritic texture, with hydrate inclusions reaching 6 mm across. Moreover, the sand samples with >7% clay contain not only hydrate porphyries but also lenticular hydrate inclusions up to 1.5 mm thick and up to 5–6 mm long.

Some properties of frozen hydrate-bearing sediments. When studying the frozen hydrate-bearing rocks, we determined some of their physical properties (water content, density, porosity, gas and hydrate content, and degree of filling of pores with gas hydrate, ice, and free gas). We compared the obtained results with those for the reference (hydrate-free) samples that had undergone the same cyclic fluctuations of temperature at atmospheric pressure.

Analysis of the sediment samples before and after the experiments has shown that sands undergo the most considerable redistribution of water in phase transitions (Table 2). In the core of the hydrate-bearing sandy samples, water content decreased by 5–10% as a result of migration of pore water to the frontal surfaces, where "gas hydrate caps" formed. Note that the reference sand samples, in which only ice formed, show no redistribution of water. On addition of montmorillonite clay to sand, the redistribution of water is suppressed and virtually disappears when the clay content reaches 5%. In both kaolinite and montmorillonite clays, the water content of the frozen hydrate-bearing and reference samples is close to the initial one, and the redistribution of water throughout the sample is insignificant (Table 2).

We have established that the gas and hydrate contents of the studied samples are intimately related to the type of cryohydrate structure and water content, which, as mentioned above, depend strongly on dispersity. In pure sands gas content does not exceed 0.5 cm^3/g. An increase in content of montmorillonite clay leads to a 10-fold increase in gas content of sand samples and reaches 3–4 cm^3/g at Ac = 5%. On subsequent growth in the amount of clay at constant water content (W_0 = 17%), the amount of gas decreases. Thus, there exists an optimal content of clay admixture ensuring the maximum gas formation at a given water content (Table 2) [4].

Table 2

Some Physical Properties of Frozen Hydrate-Saturated Samples

Depth range of sampling, cm	Sand	Sand-clay mixtures					Clays					
		W_0* = 17%					Montmorillonite				Kaolinite	
		Ac**, %					W_0, %					
	0	2	3	5	7	9	90	105	110	190	40	50
Water content, %												
0–2	24	11	13	16	15	16	91	97	113	200	39	42
2–4	3	15	16	15	15	16	87	105	110	181	37	43
4–6	13	16	16	16	15	16	89	105	100	180	42	56
6–8	17	17	16	16	17	17	91	104	100	187	43	45
Gas content, cm^3/g												
0–2	0.17	0.18	0.15	2.75	4.75	1.48	0.91	3.09	4.37	2.80	2.04	0.74
2–4	0.03	0.34	0.46	2.61	3.77	1.21	1.01	2.18	4.38	1.81	0.58	0.95
4–6	0.27	0.30	0.31	2.61	2.84	0.98	0.71	0.93	1.70	1.48	0.91	0.92
6–8	0.68	0.17	0.12	4.48	0.72	1.75	1.24	0.73	1.70	2.22	0.85	4.85

* W_0 — initial water content (before hydrate formation), %.
** Ac — content of montmorillonite clay, %.

The experimental data on clay sediments show that their gas amount depends on their initial water content. For example, gas content in montmorillonite clay increases at water content close to the upper limit of the rock plasticity and reaches 5 cm³/g. At lower and higher initial water contents, the amount of gas averages ca. 2 cm³/g, which is, however, much higher than that in the clay-free sands. In kaolinite clay, the maximum gas content, 4.85 cm³/g, is also revealed in the sample with initial water content close to the upper limit of the rock plasticity (W_0 = 47%).

The density of frozen hydrate-bearing sediment is intimately related to hydrate content. The hydrate-saturated samples are less dense than those with low gas content and the reference samples. This might be related to deconsolidation of the sediment as a result of swelling on hydrate formation. For example, the hydrate-saturated sand-clay mixture (Ac = 5%) has a density of 1.5 g/cm³, whereas the hydrate-free reference sample, 1.7 g/cm³.

CONCLUSIONS

The performed experiments on hydrate and ice formation in rocks of different grain sizes suggest the conclusions below.

1. Cyclic fluctuations of temperature in dispersed methane-saturated sediments under gas pressure are accompanied by phase transitions of sediment water into gas hydrates and ice. When cooling, as the equilibrium *PT*-conditions of methane hydrate formation are reached, sediment water partly transforms into hydrates. On subsequent cooling to negative temperatures, the remaining water passes into ice. On heating, part of the thawing water passes into hydrate ("secondary hydrate formation"). On further heating, as the equilibrium *PT*-conditions of methane hydrate formation are reached, hydrates in the sample pores decompose. "Secondary hydrate formation" is related to both the transition of released water into hydrate and facilitation of gas migration to the residual water owing to the structure-textural transformations in the sediment caused by the primary hydrate formation and freezing.

2. Formation of methane hydrates in the studied sediments occurs at higher pressures and lower temperatures as compared with the system pure-water–gas. This difference grows with decreasing of sediment grain size. In passing from studied sands to clays, the temperature varies from 0.8 to 2 °C, and the pressure, from 0.5 to 1.3 MPa.

3. Under gas pressure, water–ice phase transition in hydrate-bearing rocks occurs at lower temperatures as compared with hydrate-free sediments. The reduction coefficient in the freezing temperature of sediment water in the hydrate-bearing sands is ca. 0.55 °C/MPa, and that in the sands under pressure of gas not forming hydrates, ca. 0.1 °C/MPa.

4. The experimental study of the structure and some properties of frozen rocks artificially saturated with hydrates has shown the influence of the sediment composition and cyclic fluctuations of temperature on mass transfer and structure formation in phase transitions of sediment water into hydrates and ice. An increase in rock dispersity suppresses mass transfer and increases hydrate content inside the samples, which reaches a maximum at optimal water content, specified for each type of sediment. An increase in the number of cycles of water–hydrate and water–ice phase transitions leads to loosening of the sediment and increase in hydrate content in the pores of dispersed rocks.

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