

## GAS HYDRATE FORMATION

DOI: 10.21782/EC2541-9994-2018-1(41-45)

**DISSOCIATION OF GAS HYDRATES IN FROZEN SANDS:  
EFFECT ON GAS PERMEABILITY****E.M. Chuvilin<sup>1,2</sup>, S.I. Grebenkin<sup>1</sup>**<sup>1</sup> *Lomonosov Moscow State University, Faculty of Geology, 1, Leninskie Gory, Moscow, 119991, Russia*<sup>2</sup> *Skolkovo Institute of Science and Technology, build. 3, Skolkovo Innovation Center, Moscow, 143026, Russia; chuviline@msn.com*

Special experiments have been carried out to assess gas permeability variations associated with dissociation of pore hydrate in frozen sand samples at negative temperatures. The experiments were run on an originally designed system using frozen samples artificially saturated with methane hydrate which either remained stable or dissociated upon pressure drop. The measurements under different pressures and temperatures showed that the sand samples became more permeable to gas as pore hydrate dissociated at a pressure below equilibrium (0.1 MPa) and temperatures of  $-5$  to  $-3$  °C. The magnitude of the gas permeability increase varied depending on initial hydrate and ice saturation of the samples.

*Gas permeability, frozen sand, gas hydrate, hydrate saturation, dissociation of gas hydrate, self-preservation*

**INTRODUCTION**

Gas hydrates are solid clathrate compounds of water and low molecular natural gases (e.g., methane) which originate and exist at low temperatures and high pressures in marine bottom sediments and in areas of permafrost [Istomin and Yakushev, 1992; Max, 2000]. The stability of permafrost gas hydrates has its upper and lower limits within and below permafrost, respectively. Therefore, hydrate-bearing rocks may exist under both negative and positive Celsius temperatures. Pore hydrates in permafrost dissociate in the case of disequilibrium as pressure decreases and temperature increases. The process develops in different ways at the top and base of the stability zone: it is rapid dissociation into water and gas in sub-permafrost hydrates at positive temperatures but slow within permafrost at the upper stability limit where it produces gas with ice or supercooled water rapidly converted to ice. The dissociation process decays with time due to self-preservation of gas hydrates which can persist for a long time as relicts outside the present zone of their thermodynamic stability [Ershov et al., 1991; Chuvilin et al., 1998; Chuvilin and Guryeva, 2008]. Thus, pore hydrates exist in permafrost at depths of 150–200 m within the present stability zone, as well as in the zone of metastability where the conditions were formerly favorable for their formation.

Slow dissociation of pore hydrates at the temperatures and pressures of shallow permafrost can change the properties of their frozen host sediments: thermal conductivity, mechanic strength, and gas permeability.

The thermal and mechanic properties of sediments containing pore hydrates prone to self-preservation were tested experimentally [Bukhanov et al., 2008; Chuvilin and Bukhanov, 2013]. Thermal conductivity was reported to increase from 0.6 to 2.09 W/(m·K) in 55 h at a temperature of  $-6$  °C as pore hydrate in frozen sand samples dissociated and the fraction of clathrate water reduced from 0.43 to 0.13.

Frozen rocks with self-preserving pore hydrates studied in the 1990s at  $-6$  °C and ambient pressure [Ershov et al., 1996] showed higher failure strength than their hydrate-free counterparts.

Recent triaxial testing of permafrost-associated ice- and methane hydrate-bearing clay samples [Li et al., 2016] demonstrated that both depressurization to below equilibrium and heating decreased the stability of the frozen samples; the strength decrease upon heating reached 2–2.5 times.

The experiments of Chuvilin et al. [2016] investigating the mechanical behavior of frozen samples with pore hydrates subject to self-preservation revealed stability loss upon dissociation of hydrates and related saturation decrease, though the total hydrate and ice saturation remained almost invariable. The hydrate saturation of a frozen sample reduced to 17 % while its strength became 1.3 times lower for the first 150 h after depressurization. However, the changes were minor in both saturation (15 %) and strength in the following 150 h when pore hydrates reached the stage of self-preservation.

The behavior of permeability during dissociation of pore hydrates in frozen saturated rocks is of special

interest due to implications for hydrocarbon migration in permafrost. Earlier we [Chuvilin and Grebenkin, 2015] found out that hydrate-saturated samples became times less permeable to gas when frozen due to freezing of residual water and additional hydrate formation. However, no relation was found between hydrate saturation and permeability of frozen rocks with dissociating pore hydrate.

In this work, special modeling experiments are applied to study variations in gas permeability of frozen sands upon pore hydrate dissociation at negative temperatures.

### METHODS

Gas permeability variations in frozen hydrate-bearing sand were investigated by means of gas flushing, using a method designed by the authors jointly with people from the Schlumberger Company [Chuvilin and Grebenkin, 2015]. The method allows creating and maintaining the required pressure and temperature for artificial freezing and hydrate saturation of soil samples. The procedure consists of several steps: (i) preconditioning of samples to provide user-specified water content and to saturate them with hydrate-forming gas in a special vessel; (ii) freezing of samples; (iii) testing the samples for gas permeability at different gas pressures and temperatures; (iv) processing the experimental data.

The system designed by the EkoGeosProm LLC (Fig. 1) can maintain sample temperatures and pressures from  $-15$  to  $+30$  °C and up to 100 bar, respectively.

The gas permeability of frozen hydrate-saturated samples was measured in the conditions of stable and dissociating pore methane hydrate. Samples with user-specified water contents were made by mixing air-dry soil aliquots with water which were then left for 30 min for uniform water saturation. The wet samples were placed in a rubber gasket 3 cm in diameter and

compacted layer by layer. The obtained 3 to 4 cm long cylinders were pressurized (to 60 bar), saturated with methane hydrate, and frozen. The temperature and pressure in the vessel was monitored during the experiment.

The gas permeability of samples saturated with methane hydrate was measured at a pressure above equilibrium ( $>25$  bar), as well as during dissociation of pore hydrates after gas pressure decreased to the ambient value (1 bar). The measurements during hydrate dissociation were taken periodically for 2 or 3 days at temperatures of  $-5$  °C or  $-3$  °C (sample Ts-4). After the end of the experiment, the final water and gas contents were determined in the soil samples removed from the pressure vessel.

The parameters of hydrate and ice saturation were estimated using the PVT method [Ershov, 2004; Chuvilin and Guryeva, 2009]. Main calculated parameters were hydrate coefficient, hydrate and ice saturations, and effective gas permeability.

*Hydrate coefficient* ( $K_H$  in unit fraction, u.f.) is the fraction of pore water converted to hydrate relative to the total amount of pore water in the sample:

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

where  $W_h$  is the percentage of water converted to hydrate relative to the dry weight (%);  $W$  is the water content, wt. %.

*Hydrate saturation* ( $S_h$ ):

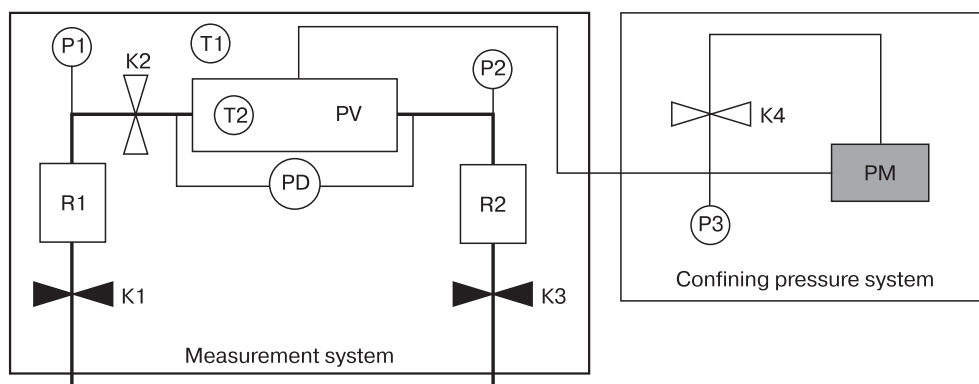
$$S_h = \frac{\rho m_h}{m \rho_h n} \cdot 100,$$

where  $\rho$  is the soil density, g/cm<sup>3</sup>;  $\rho_h$  is the hydrate density, g/cm<sup>3</sup>;  $m$  is the soil weight, g;  $m_h$  is the hydrate weight, g;  $p$  is porosity, u.f.

*Ice saturation* ( $S_i$ ):

$$S_i = \frac{(W - W_h) \rho_d \cdot 100 \%}{0.92n},$$

where  $\rho_d$  is the soil skeleton density.



**Fig. 1. Experimental layout for measuring gas permeability of soil samples.**

K1–K3 = membrane valves for gas supply; K4 = ball valve of hydraulic system; R1, R2 = gas supply receivers; P1–P3 = pressure sensors; PD = differential pressure sensor; PM = hydraulic pump with an oil container; PV = pressure vessel; T1, T2 = temperature sensors.

The  $K_H$  and  $S_h$  parameters were estimated for the methane hydrate formula  $\text{CH}_4 \cdot 5.9\text{H}_2\text{O}$ .

Effective gas permeability ( $K_g$ ) of frozen hydrate-bearing soil was calculated by solving the differential equation of mass transfer through the sample under the pressure gradient [Chuvilin and Grebenkin, 2015]:

$$K_g = \frac{2\eta L V_1 p_1 (p_{10} - p_{1k})}{S p_{10} (p_1^2 - p_2^2) t_1},$$

where  $\eta$  is the dynamic viscosity of gas, Pa·s;  $L$  is the length of sample, cm;  $S$  is the cross section area of sample,  $\text{cm}^2$ ;  $V_1$  is the gas receiver volume,  $\text{cm}^3$ ;  $p_1$  is the pressure at sensor 1 (Fig. 1) at the time  $t_1$ , bar;  $p_2$  is the pressure at sensor 2 at the time  $t_1$ , bar;  $p_{10}$  is the pressure at sensor 1 at the start time, bar;  $p_{1k}$  is the pressure at sensor 1 at the end time, bar;  $k$  is the gas permeability, mD.

### MATERIAL

We studied disturbed (non-monolithic) sand samples of marine permafrost ( $\text{mQ}_3$ ) from the South Tambei gas-condensate deposit in the Yamal Peninsula (sampling depth 36–46 m).

Fraction size, mm	1.0–0.5	0.5–0.25	0.25–0.1	0.1–0.05
Particle size distribution in fine sand, %	0.2	29.1	62.3	8.4

The particle size distribution was estimated by sieving and the constituent minerals were identified by X-ray diffraction (XRD). The samples consisted mostly of 0.25–0.10 mm particles (62.3 %) of quartz (93.7 %), with minor amounts of albite (5.1 %) and orthoclase (1.2 %). The density of the solid component was  $2.69 \text{ g/cm}^3$  and the salinity was 0.06 %; the specific surface area of sand was  $0.24 \text{ m}^2/\text{g}$ . The sand samples were 30 mm in diameter and 25–40 mm long (Table 1); their initial water content was specified in the range from 6 to 18 wt.%; the porosity was 0.40.

Table 1. Properties of fine sand samples

Sample	Length, mm	Diameter, mm	Water content, %	Density (bulk soil)	Density (skeleton)	Porosity $n$ , u.f.
				g/cm <sup>3</sup>		
Ts-1	29	30	17.8	1.88	1.62	0.40
Ts-2	35	30	10.3	1.72	1.62	0.40
Ts-3	31	30	6.7	1.66	1.62	0.40
Ts-4	40	30	13.0	1.87	1.62	0.40

Table 2. Properties of frozen hydrate-saturated sand samples and their gas permeability at  $-5^\circ\text{C}$  and above-equilibrium pressure

Sample	Initial water content, wt. %	Saturation, %		Effective gas permeability $K$ , mD
		ice	hydrate	
Ts-1	17.8	29.1	65.4	<0.01
Ts-2	10.3	4.9	63.8	0.03
Ts-3	6.7	2.3	32.9	1.0
Ts-4	13.0	34.7	41.8	0.02

### GAS PERMEABILITY OF FROZEN SAND SAMPLES AT STABLE AND DISSOCIATING PORE HYDRATES

The effect of pore hydrate dissociation on gas permeability of frozen sediments was studied using specially prepared samples of sand with different contents of methane hydrate and ice. At above-equilibrium pressure ( $>25$  bar), hydrate saturation of the samples varied from 32.9 to 65.4 % (Table 2) depending on initial water content and hydrate formation conditions, while residual water not converted to hydrate froze to ice. Ice saturation was from 2.3 % in the sample with an initial water content of 6.7 wt.% to 34.7 % in the case of 13 wt.%  $\text{H}_2\text{O}$ . The total saturation with ice and hydrate was from 35.2 % in a relatively dry sample (Ts-3) to 94.5 % in a sample initially containing 17.8 wt.%  $\text{H}_2\text{O}$ . Gas permeability of frozen samples was low when the pore hydrate was stable (1.0 mD in sample Ts-3 with low water content) and decreased further with increasing hydrate and ice saturation to below the resolution limit for the measurement system (0.01 mD) in sample Ts-1 (Table 2).

The gas permeability of frozen sediments with dissociating pore hydrate measured at equal time intervals after depressurization at a constant negative temperature, mostly  $-5^\circ\text{C}$  (Table 3) increased with time. Samples with initial water contents of 6.7, 10.3 and 13 wt.% became more permeable already in 1 h after pressure drop. Gas permeability was growing for first 48 h of observations and then remained almost invariable, about the initial value prior to hydrate saturation. The stabilization was faster at a warmer temperature: 4 h at  $-3^\circ\text{C}$  against 6 h at  $-5^\circ\text{C}$  (Fig. 2).

Gas permeability of sample Ts-1 with a high water content (17.8 wt.%) was not measured for the first 6 h while the total hydrate and ice saturation was 94.5 %; in 24 h, it was 0.03 mD but did not exceed 0.06 mD in 48 hr and did not change any longer. The

Table 3. Time-dependent gas permeability changes upon pore pressure drop to ambient value at  $-5^{\circ}\text{C}$

Time, h	Gas permeability, mD			
	Ts-1	Ts-2	Ts-3	Ts-4**
0*	<0.01	0.03	1.00	0.02
1	<0.01	0.10	1.04	0.3
4	<0.01	0.10	1.08	0.5
6	<0.01	0.50	1.14	0.5
24	0.03	1.00	1.30	0.6
48	0.06	1.10	1.40	0.7
60	0.06	1.10	1.40	0.7

\* Gas permeability of frozen hydrate-saturated samples at pressure above equilibrium. \*\* For sample Ts-4 at  $-3^{\circ}\text{C}$ .

gas permeability change in frozen hydrate-bearing samples at pressures below equilibrium is related with pore hydrate dissociation. As shown by our previous studies [Chuvilin and Guryeva, 2008; Chuvilin et al., 2011], pore hydrates in frozen sediments dissociate rapidly for the first few hours after depressurization, but then the process decays and stops. Gas permeability stabilizes because the dissociation decays as a result of hydrate self-preservation at negative temperatures. For instance, hydrate contents in sample Ts-4 became almost twice lower (14 % against 25 %) for the first 2 h of dissociation at  $-3^{\circ}\text{C}$ . Then the process decayed, and the hydrate contents reduced further to 2.4 % in the following 9 h and reached 1.9 % in the end of the run. Figure 3 shows especially rapid permeabil-

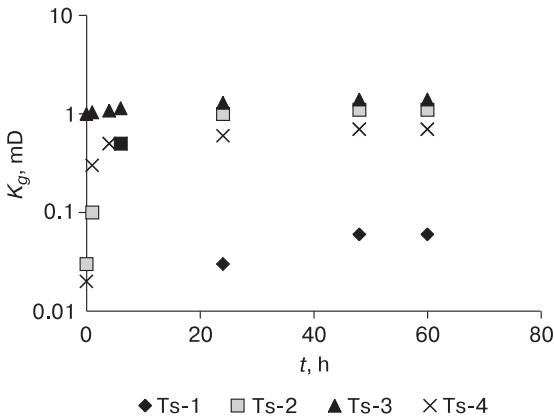


Fig. 2. Variations of gas permeability ( $K_g$ ) in frozen samples (Ts-1, Ts-2, Ts-3, Ts-4) during dissociation of pore hydrates.

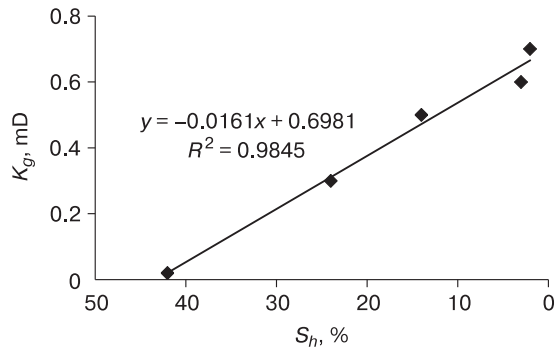


Fig. 3. Variations of gas permeability ( $K_g$ ) as a function of hydrate saturation ( $S_h$ ) in a frozen sand sample (Ts-4) during dissociation of pore hydrate ( $t = -3^{\circ}\text{C}$ ,  $p = 0.1\text{ MPa}$ ).

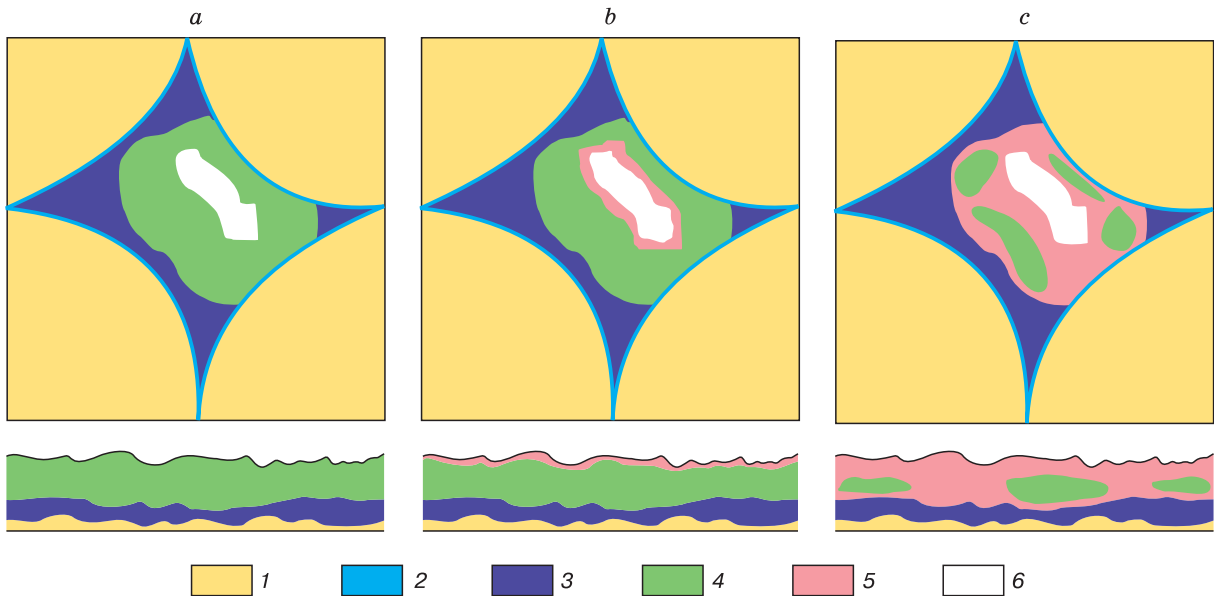


Fig. 4. Model of pore filling in frozen hydrate-bearing soil at negative temperatures ( $-3^{\circ}\text{C}$  to  $-5^{\circ}\text{C}$ ) and below equilibrium pressure.

a: stable gas hydrate (pressure above equilibrium); b: soon after pressure drop to below equilibrium; c: pressure below equilibrium, metastable gas hydrate. Top panel: pore sketch; lower panel: water phase on particle surface. 1 – soil particles; 2 – bound (unfrozen water); 3 – ice 1; 4 – hydrate; 5 – ice 2; 6 – gas.

ity increase within a hydrate saturation range from 40 to 25 %. Sample Ts-4 demonstrated linear hydrate saturation dependence of gas permeability (Fig. 3).

Therefore, pore hydrates influence strongly the gas permeability of soils, though the total saturation changes insignificantly while hydrate converts to ice. The reason may be in different formation mechanisms of pore hydrate and ice, as well as in the microstructure changes the frozen soils undergo during pore hydrate dissociation. Initially, at pressures above equilibrium, pore hydrate in a frozen sample contacts with gas and with ice (ice 1) phases (Fig. 4). Right after depressurization, surface gas hydrate dissociates into gas and water; the water freezes up and forms an ice film (ice 2) around hydrate, whereby the dissociation rate declines and residual hydrate becomes metastable. Frozen soil becomes more permeable (Fig. 5) as hydrate and ice change in specific volume while pore hydrate converts to ice via the liquid water phase and the sample microstructure changes.

Calculations show that pore hydrate dissociation leads to increase (8.9 %) of free gas-filled pore space in the sample, which is related linearly with gas permeability (Fig. 5). According to previous studies [Chuvilin and Grebenkin, 2015; Chuvilin et al., 2016], even minor reduction of pore space in samples may cause abrupt permeability loss at certain hydrate and ice saturation values. On the other hand, gas permeability increases upon hydrate dissociation and related pore space expansion, and almost impermeable frozen hydrate-bearing rocks may become permeable.

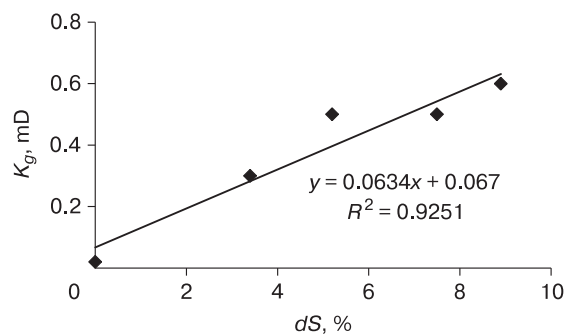
## CONCLUSIONS

The experimentally observed gas permeability in frozen hydrate-bearing sediments increases upon dissociation of pore hydrate after depressurization. The gas permeability increase at below-equilibrium conditions ( $t = -5, -3\text{ }^{\circ}\text{C}$ ,  $p = 0.1\text{ MPa}$ ) depends on initial contents of hydrate and ice. Namely, a sand sample with moderate total hydrate and ice saturation (35 %) became only  $>1.5$  times more permeable but the difference exceeded ten times when the saturation reached  $\sim 69\%$ . Dissociation of pore hydrate in an almost impermeable ( $<0.01\text{ mD}$ ) sample with hydrate and ice saturation as high as  $\sim 95\%$  increased its permeability to  $0.06\text{ mD}$  in. Therefore, permafrost soils become more permeable to gas as their pore hydrates dissociate.

*The study was supported by grants 16-17-00051 from the Russian Foundation for Basic Research and 17-05-00995 from the Russian Science Foundation.*

## References

Bukhanov, B.A., Chuvilin, E.M., Guryeva, O.M., Kotov, P.I., 2008. Experimental study of the thermal conductivity of the frozen sediments containing gas hydrate. Proc. 9<sup>th</sup> Intern. Conf. on Permafrost (Fairbanks, USA, 29 June–3 July 2008). Fairbanks, University of Alaska, Volume 1, pp. 205–209.



**Fig. 5. Gas permeability ( $K_g$ ) of frozen hydrate-bearing sand (Ts-4) as a function of free pore space expansion ( $dS$ ) during hydrate-to-ice conversion.**

- Chuvilin, E.M., Bukhanov, B.A., 2013. Experimental study of the thermal conductivity of frozen hydrate-saturated sediments at atmospheric pressure. *Kriosfera Zemli* XVII (1), 69–79.
- Chuvilin, E.M., Bukhanov, B.A., Guryeva, O.M., Istomin, V.A., Takeya, S., Hachikubo, A., 2011. Experimental study of self-preservation mechanisms during gas hydrate decomposition in frozen sediments. Proc. 7<sup>th</sup> Intern. Conf. on Gas Hydrates. Edinburgh, United Kingdom, pp. 1–9.
- Chuvilin, E.M., Bukhanov, B.A., Grebenkin, S.I., Doroshin, V.V., Iospa, A.V., 2016. Strength of frozen soils containing pore hydrates subject to self-preservation: An experimental study, in: Proc. 5<sup>th</sup> Conf. of Russian Geocryologists (Moscow, 14–17 June 2016), Book 3, Univ. Kniga, Moscow, pp. 180–186.
- Chuvilin, E.M., Grebenkin, S.I., 2015. Gas permeability variations in gas-filled soils upon hydrate formation and freezing: an experimental study. *Earth's Cryosphere* XIX (2), 59–64.
- Chuvilin, E.M., Guryeva, O.M., 2008. Experimental study of self-preservation effect of gas hydrates in frozen sediments. Proc. 9<sup>th</sup> Intern. Conf. on Permafrost. Fairbanks, Univ. of Alaska, Volume 1, pp. 263–267.
- Chuvilin, E.M., Guryeva, O.M., 2009. Experimental investigation of  $\text{CO}_2$  gas hydrate formation in porous media of frozen and freezing sediments. *Kriosfera Zemli* XIII (3), 70–79.
- Chuvilin, E.M., Yakushev, V.S., Perlova, E.V., 1998. Gas and gas hydrates in the permafrost of Bovanenkovo gas field, Yamal Peninsula, West Siberia. *Polarforschung (Erschienen 2000)* 68, 215–219.
- Ershov, E.D. (Ed.), 2004. *Methods for Geocryological Studies*. Moscow University Press, Moscow, 507 pp. (in Russian)
- Ershov, E.D., Lebedenko, Yu.P., Chuvilin, E.M., Istomin, V.A., Yakushev, V.S., 1991. Features of gas hydrates in permafrost. *Doklady AN USSR* 321 (4), 788–791.
- Ershov, E.D., Yakushev, V.S., Chuvilin, E.M., 1996. Laboratory studies of frozen natural and artificial hydrate-containing rock samples. Proc. 2<sup>nd</sup> Intern. Conf. on Natural Gas Hydrates, Toulouse, France, pp. 609–615.
- Istomin, V.A., Yakushev, V.S., 1992. *Naturally Occurring Gas Hydrates (in Russian)*. Nedra, Moscow, 235 pp.
- Li, Y., Liu, W., Zhu, Y., Chen, Y., Song, Y., Li, Q., 2016. Mechanical behaviors of permafrost-associated methane hydrate-bearing sediments under different mining methods. *Appl. Energy* 162, 1627–1632.
- Max, M.D. (Ed.), 2000. *Natural Gas Hydrate in Oceanic and Permafrost Environments*. Kluwer Acad. Publ., London, 414 pp.

Received May 15, 2017