

GAS HYDRATE FORMATION

THERMAL CONDUCTIVITY VARIATIONS OF GAS-SATURATED SEDIMENTS
DURING HYDRATE FORMATION AT DIFFERENT CONDITIONS.

Part 2. Results*

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In Part II of the publication, we report experimental results showing the behavior of thermal conductivity in gas-filled sediments during hydrate formation at different conditions: low positive and negative temperatures, freezing and thawing. Thermal conductivity increases or decreases as hydrate forms at positive or negative temperatures, respectively. The hydrate-saturated soil samples exposed to both freezing and thawing under gas pressures above the equilibrium have lower thermal conductivities than before the tests due to additional hydrate formation. The thermal conductivity behavior has been explained in two models of pore-space changes in gas-filled sediments associated with hydrate formation.

Thermal conductivity, hydrate-bearing sediments, gas hydrate, methane, hydrate

INTRODUCTION

Gas in frozen ground with gas-filled porosity can exist, either within permafrost or in chilled sub-permafrost sediments, in the form of hydrates, which are ice-like compounds of water and gas [*Istomin and Yakushev, 1992; Sloan, 1998*].

Although the first discoveries date back to the late 1960s, natural gas hydrates in permafrost remain poorly understood, because they are similar to ice in most of physical properties. However, the two differ in thermal conductivity, which in hydrate is four times lower than in ice being similar to that of water (0.55–0.65 against 2.23 W/(m·K) and 0.60 W/(m·K), respectively) [*Stoll and Bryan, 1979; Huang and Fan, 2004; Rosenbaum et al., 2007; Waite et al., 2007; Warzinski et al., 2008*]. Therefore, the thermal conductivity of fine-grained porous rocks saturated with hydrate may be expected to depend on the conditions of hydrate formation [*Chuvilin and Bukhanov, 2014*].

The thermal conductivity of hydrate-bearing rocks, especially permafrost, has been little investigated [*Chuvilin and Bukhanov, 2013, 2014*], with only few publications concerning its experimental measurements at different temperatures [*Groysman, 1985; Asher, 1987; Fan et al., 2005; Wright et al., 2005; Waite et al., 2007; Duchkov et al., 2009, 2012*]. The available data on thermal properties of hydrate-bearing sedi-

ments are rather qualitative, most often obtained without reference to the quantitative relations between the pore fluid phases (water, ice, gas, hydrate) and to the controls of hydrate formation in such rocks.

METHODS

The thermal conductivities of sediments were measured under gas pressure using an experimental system and methods specially designed by the authors. The measurements were applied to physical models and natural soil samples (Table 1) immediately in the pressure cell during formation of gas hydrate and ice at temperatures above and below 0 °C. The method details are reported in the sister publication [*Chuvilin and Bukhanov, 2014*].

The model samples were either pure fine sand (sand-1) or a sand-clay mixture (sand-1 plus 14 % kaolin clay). The natural samples were sandy silt (sand-2) from the Laptev Sea Arctic shelf permafrost and heavy-textured silt or loamy sand (silt) from permafrost near Vorkuta city. The sand fraction predominated in all samples and the variations of unfrozen water content were less than 0.1 % per 1 °C in the operation range of negative temperatures (below

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Table 1. Properties of soil samples

| Samples (soil type) | Grain size fractions, % | | | Mineralogy, % | | Salinity, % |
|------------------------|-------------------------|---------------|-----------|---------------------|-----|-------------|
| | 1–0.05 mm | 0.05–0.001 mm | <0.001 mm | | | |
| Sand-1 | 94.8 | 3.1 | 2.1 | Quartz | >90 | 0.01 |
| Sand-2 | 84.6 | 12.7 | 2.7 | Quartz | 54 | 0.40 |
| | | | | Microcline + Albite | 42 | |
| | | | | Illite | 4 | |
| Silt | 41.8 | 53.7 | 4.5 | Quartz | 38 | 0.08 |
| | | | | Microcline + Albite | 55 | |
| | | | | Illite | 9 | |
| Kaolin | 4.5 | 70.9 | 24.6 | Kaolin | 92 | 0.04 |

–3 °C, with regard to overheating). The total content of unfrozen water in the soil samples did not exceed 1–2 % at these conditions, or was even less, given the gas pressure effect on the equilibrium water content [Chuvilin and Istomin, 2012].

The pressure in the cell was maintained above the equilibrium to prevent hydrate dissociation during thermal conductivity measurements [Bukhanov, 2013].

The characteristic initial values of density (ρ) and porosity (n) of the soil samples were within 1.7–1.9 g/cm³ and 0.38–0.45, respectively, in all runs. Additionally, lower-density samples were prepared with the initial parameters $n \sim 0.6$ and $\rho = 1.3\text{--}1.4$ g/cm³.

Hydrate formation was with methane (99.98 %) stored in a bomb at a pressure $\sim 8\text{--}10$ MPa.

RESULTS AND DISCUSSION

Variations in thermal conductivity of rocks with water- and gas-filled porosity were analyzed at different conditions of hydrate formation:

(1) low positive temperatures ($t \approx +(2 \pm 1)$ °C), when hydrate formed from pore water;

(2) negative temperatures ($t \approx -(5 \pm 1)$ °C), when hydrate formed from pore ice;

(3) cooling from $+(2 \pm 1)$ to $-5\text{--}8$ °C, which froze up the surviving pore water (that eluded change to hydrate at positive temperatures) and induced additional hydrate formation in soil;

(4) warming from $-(5 \pm 1)$ to $+(2 \pm 1)$ °C, which melted the surviving pore ice (that eluded change to hydrate at negative temperatures) and induced additional hydrate formation in soil.

The influence of the hydrate formation conditions on the thermal properties of sand-silt soils was studied in samples undersaturated with water or ice.

Hydrate formation at $t > 0$ °C

To investigate hydrate formation at $t > 0$ °C in the pressure cell, undersaturated methane-bearing soil samples were cooled down from room to low positive ($t = +(2 \pm 1)$ °C) temperatures. The measured thermal conductivity values of different gas-filled soil samples remained almost invariable (within 2 %) as far as the fraction of water changed to hydrate (K_h , unit fraction) was below 0.40 (Fig. 1). However, they increased notably at $K_h > 0.40$ (Fig. 1): from 1.77 to 2.01 W/(m·K), or by 14 %, as K_h reached 0.46 in a silt sample with water content $W = 18$ % and from 1.85 to 1.96 W/(m·K) or by 9 % at $K_h = 0.50$ in sand-1 with $W = 16$ %.

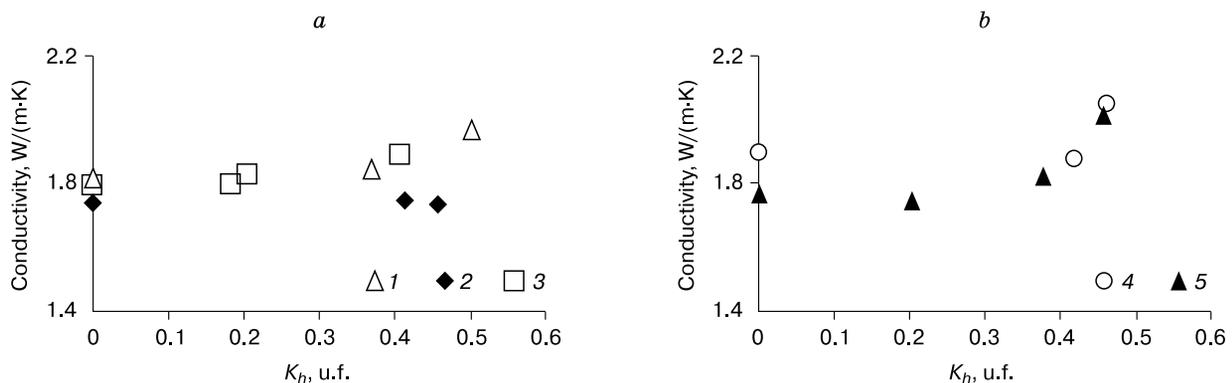


Fig. 1. Thermal conductivity of soils as a function of water fraction changed to hydrate (K_h) at $t = +(2 \pm 1)$ °C.

1 – sand-1, $W = 16$ %, $n = 0.43$; 2 – sand-1, $W = 10$ %, $n = 0.39$; 3 – sand-2, $W = 15$ %, $n = 0.40$; 4 – sand + 14 % kaolin, $W = 15$ %, $n = 0.38$; 5 – silt, $W = 18$ %, $n = 0.40$.

Measurements in the sample sand-1 at different initial water saturations can illustrate the dependence of thermal conductivity on the volume content of hydrate (H_v , Fig. 2). According to the experimental evidence, soil samples show correlation between their initial water saturation and thermal conductivity. Namely, thermal conductivity was 5 % higher in a $S_w = 56\%$ sand sample than in a $S_w = 41\%$ one. During hydrate formation, thermal conductivity increase was observed only in the wetter sand (but became notable only at $H_v > 13\%$), while the drier sample ($S_w = 41\%$) did not change much, though almost 50 % of pore water converted into hydrate ($K_h = 0.46$).

Therefore, hydrate formation at positive temperatures increases thermal conductivity only in wet samples ($S_w > 50\%$) while the changes remain insignificant at $S_w < 50\%$, even when hydrate consumes more than 40 % of pore water ($K_h > 0.40$).

Hydrate formation at $t < 0^\circ\text{C}$

Hydrate formation at $t < 0^\circ\text{C}$ was studied in frozen undersaturated ($S_i \approx 70\%$) methane-bearing soil samples in the same pressure cell, at temperatures $-(5 \pm 1)^\circ\text{C}$. Unlike the tests at low positive temperatures, the thermal conductivity of frozen samples decreased during hydrate formation, at K_h reaching 0.5 (Fig. 3). In the sample sand-1 ($W = 19\%$) it reduced from 2.32 to 1.80 W/(m·K), or by 22 %, as K_h increased from 0 to 0.5, but further changes at $K_h > 0.50$ were insignificant.

The thermal conductivity of frozen rocks with pore methane decreases during hydrate formation because the ice component, with its thermal conductivity as high as 2.23 W/(m·K), becomes smaller while the 0.6 W/(m·K) hydrate component (four times less conductive) increases.

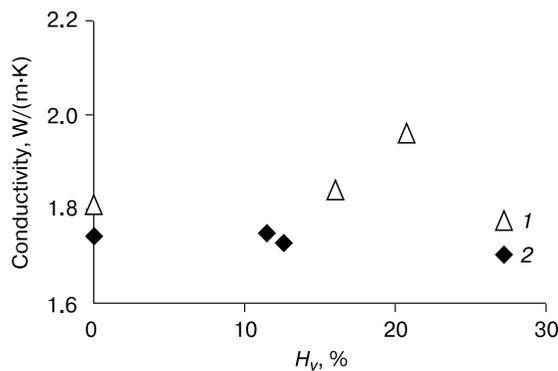


Fig. 2. Thermal conductivity of sand-1 as a function of hydrate volume content (H_v) at $t = +(2 \pm 1)^\circ\text{C}$ and different water saturations (S_w):

1 - $S_w = 56\%$; 2 - $S_w = 41\%$.

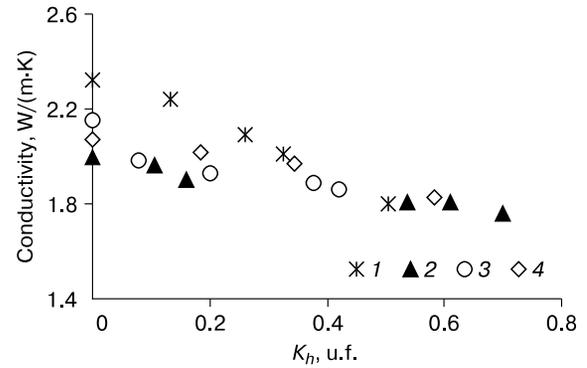


Fig. 3. Thermal conductivity of soils as a function of water fraction changed to hydrate K_h at $t = -(5 \pm 1)^\circ\text{C}$:

1 - sand-1, $W = 19\%$, $n = 0.40$; 2 - sand-1, $W = 22\%$, $n = 0.60$; 3 - sand-2, $W = 15\%$, $n = 0.38$; 4 - silt, $W = 24\%$, $n = 0.60$.

Effect of freezing

To study the effect of freezing on thermal conductivity variations, the samples saturated with hydrate at $t > 0^\circ\text{C}$ were cooled down from -5 to -8°C . Although hydrate had already consumed 44 to 50 % of pore water before freezing and hydrate formation had almost ceased, further cooling of the samples led to formation of additional hydrate in all runs (Table 2).

The change in the amount of water converted to hydrate, or relative dK_h , given by

$$dK_h = \frac{K'_h - K''_h}{K'_h} \cdot 100\%,$$

where K'_h and K''_h are the K_h values before and after freezing, respectively, was lower in sand than in silt (23–28 % against 39–52 %), i.e., more hydrate formed in silt on freezing. The same tendency was observed in the sand-clay samples: for instance, 5 % more of additional hydrate formed in sand with 14 % kaolin than in pure sand.

Thus, a large portion of water that survived from changing to hydrate at positive temperatures became consumed at $t < 0^\circ\text{C}$. Hydrate formation became more active as the surviving pore water froze up because cryotic deformation of the soil skeleton and release of dissolved gas produced new water-gas interfaces. The amount of hydrate additionally formed as a

Table 2. Formation of methane hydrate during freezing of residual pore water

| Samples (soil type) | W , % | dK_h , % | K'_h , u.f. | K''_h , u.f. |
|---------------------|---------|------------|---------------|----------------|
| Sand-1 | 16 | 23 | 0.50 | 0.61 |
| Sand + 14 % kaolin | 15 | 28 | 0.46 | 0.59 |
| Silt | 18 | 39 | 0.46 | 0.64 |
| Silt | 16 | 52 | 0.44 | 0.67 |

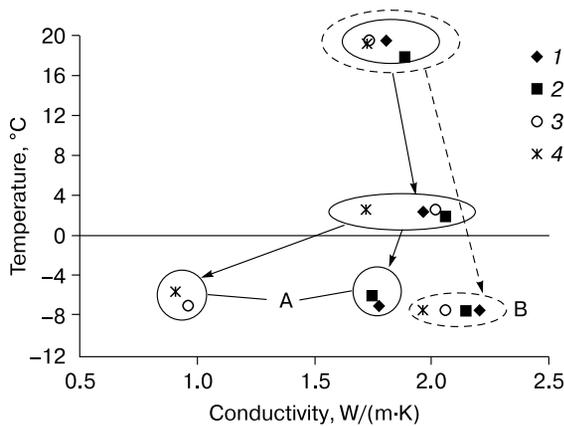


Fig. 4. Variations in thermal conductivity of gas-filled soils on cooling (to +2 °C) and freezing.

A: hydrate-bearing samples; B: hydrate-barren samples. Solid and dash lines correspond to samples saturated with gases that can and cannot form hydrates (methane and nitrogen, respectively).

1 – sand-1, $W = 16\%$; 2 – sand + 14 % kaolin, $W = 15\%$; 3 – silt, $W = 18\%$; 4 – silt, $W = 16\%$.

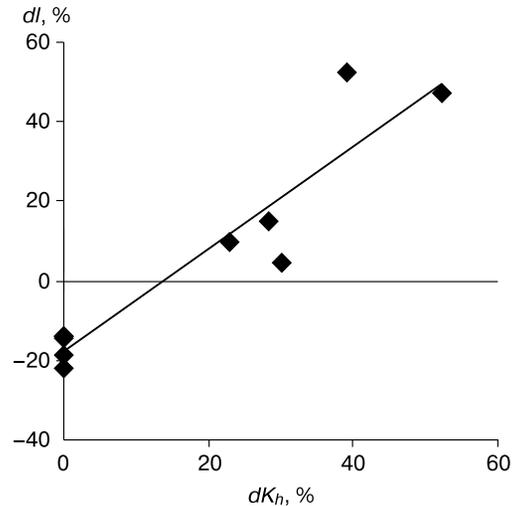


Fig. 5. Correlation of freezing-induced thermal conductivity reduction (dl) and additional hydrate formation (dK_h).

result of freezing depends mainly on soil mineralogy, clay content, and water saturation [Chuvilin and Kozlova, 2005; Chuvilin and Guryeva, 2009].

The experiments show that freezing of hydrate-saturated rocks affected their thermal conductivity (Fig. 4). The phase change from water to ice caused a dramatic decrease in thermal conductivity of hydrate-bearing samples (Fig. 4, A) unlike the hydrate-barren samples in which thermal conductivity regularly became 15–20 % higher (Fig. 4, B). The hydrate-bearing samples were of two groups: sand, including that mixed with finer-grained material (clay), and silt (Fig. 4, A). The freezing-induced thermal conductivity reduction was 10 % in sand but reached 50 % in silt: from 1.96 to 1.77 W/(m·K) in hydrate-bearing sand-1 ($W = 16\%$) and from 2.01 to 0.96 W/(m·K) in silt ($W = 16\%$).

The decrease was proportional to additional hydrate formation (Fig. 5): freezing led to 23 % increase of K_h in the sand-1 ($W = 16\%$) sample that showed 10 % thermal conductivity reduction but an almost 40 % K_h growth in the silt sample ($W = 18\%$) which became 50 % less conductive.

Thus, the thermal conductivity of hydrate-saturated rocks exposed to further freezing, which freezes up the surviving pore water, may decrease dramatically as a result of related additional hydrate formation. This behavior of thermal conductivity may be due to structure and texture changes in freezing gas- and hydrate-bearing soils. These are especially the

effects of heaving or cracking of hydrate-saturated soil, or formation of pore hydrate on grain boundaries, with its thermal conductivity as low as 0.35 W/(m·K) [Rosenbaum et al., 2007].

Effect of thawing

To study the effect of thawing on the behavior of thermal conductivity, the frozen sand samples that were saturated with hydrate at $t < 0$ °C were heated to $+(2 \pm 1)$ °C. The tests showed additional hydrate formation in sand, as in the case of freezing, but unlike the latter case it did not exceed 10 %. We likewise attributed more active hydrate generation on thawing to deformation of soil skeleton and formation of new water-gas interfaces [Chuvilin et al., 2011]. Additional hydrate formation on thawing of hydrate-saturated sand was more intense in the samples that initially contained more water. Namely, 10 % and 7 % of additional hydrate formed in the sand-1 and sand-2 samples with $W = 19\%$ and $W = 15\%$, respectively.

As the frozen hydrate-bearing samples melted, their thermal conductivity decreased: e.g., from 1.86 to 1.72 W/(m·K), or by 8 %, in sand-2 ($W = 15\%$). Two main reasons of such decrease are (i) the thermal conductivity difference between the ice and water pore fluids and (ii) increase in the hydrate component.

Thus, both freezing and thawing cause thermal conductivity reduction in frozen soil saturated with methane hydrate at pressures above the equilibrium.

**STRUCTURE AND TEXTURE CHANGES
IN GAS-SATURATED SOILS ASSOCIATED
WITH HYDRATE FORMATION**

The reported data on variations in soil thermal conductivity associated with hydrate formation in the experimental conditions of low positive and negative temperatures, freezing and thawing prompt that this behavior is mostly controlled by phase transitions in pore fluids and by structure and texture changes in the main rock constituents.

Proceeding from the experiment results, the structure and texture changes during hydrate formation in soils with gas- and water-filled porosity can be described with two models of pore space changes: freezing of samples saturated with hydrate at $t > 0^\circ\text{C}$ (model 1) and thawing of samples saturated with hydrate at $t < 0^\circ\text{C}$ (model 2).

Model 1 includes several stages corresponding to different states of the samples (Fig. 6): the initial state before hydrate formation, cooling before hydrate formation, hydrate formation at $K_h > 0.40$, and the state after freezing.

Initially, before hydrate formation, the soil pores are partly filled with water which is in equilibrium with the hydrate-forming gas at pressures below equilibrium for the system “water-gas-hydrate” (Fig. 6, A).

Then, as the system cools down to the below-equilibrium temperature, active hydrate formation begins mainly along water-gas interfaces, while the pore space does not change much (Fig. 6, B). Thermal conductivity remains the same because its values for hydrate and pore water are similar. As hydrate consumes more than 40 % of pore water, local migration and redistribution of water in the pore space cause changes to the soil structure. Namely, water in films between soil particles moves inward the pores, closer to the water-gas interfaces where hydrate is forming [Aladko et al., 2006]. As a result of the local redistribution of pore water, soil particles may become more tightly packed and saturation will increase. This affects the thermal contacts in the hydrate-bearing soil (Fig. 6, C) shown up as an increase in thermal conductivity.

Freezing induces additional hydrate formation as the surviving pore water freezes up. The process can be accompanied by the formation of pore hydrate or ice, cracking, and hydrate formation on boundaries of grains or aggregates. The ensuing embrittlement of pore hydrate and ice and loosening of contacts between soil particles (Fig. 6, D) may account for the freezing-related thermal conductivity decrease observed in the experiments. Similar dramatic reduction of thermal conductivity in frozen hydrate-saturated

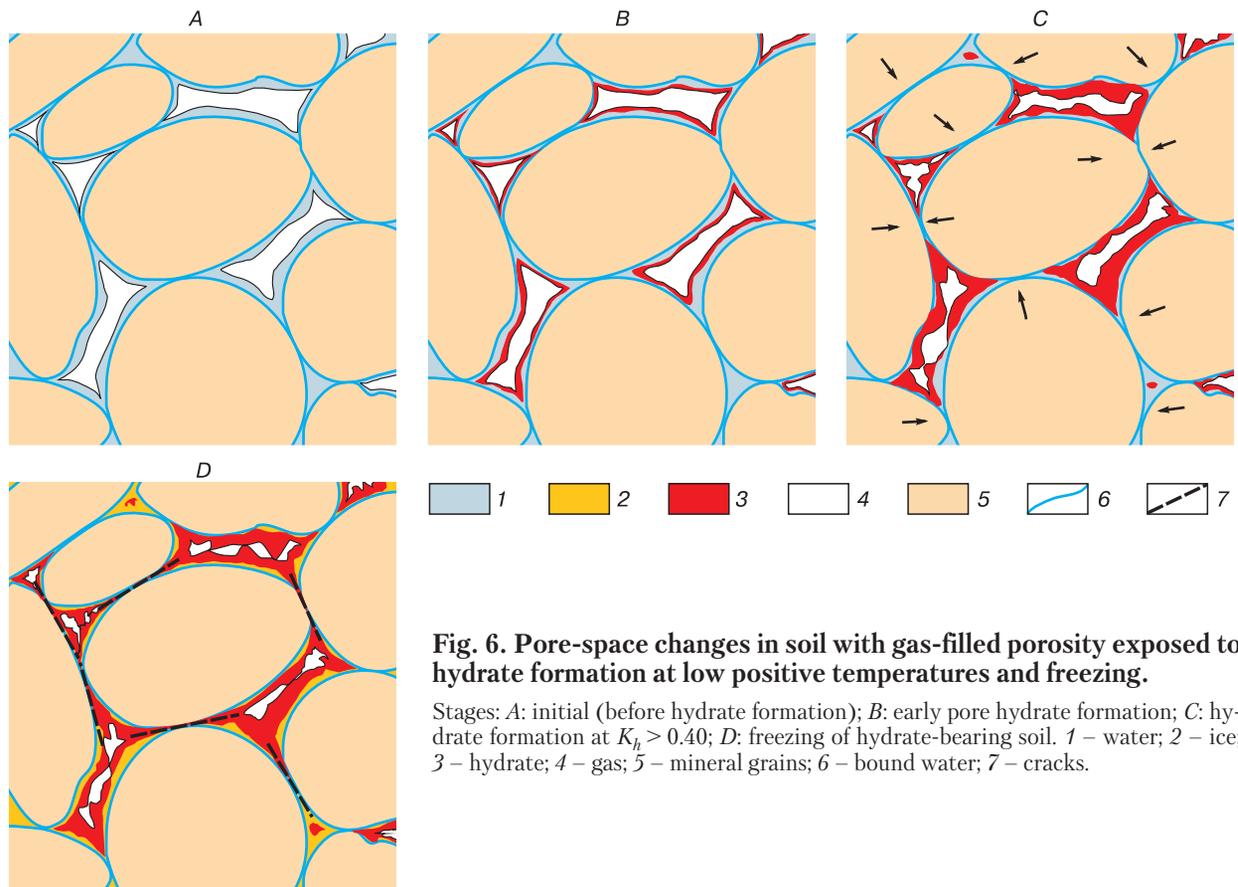


Fig. 6. Pore-space changes in soil with gas-filled porosity exposed to hydrate formation at low positive temperatures and freezing.

Stages: A: initial (before hydrate formation); B: early pore hydrate formation; C: hydrate formation at $K_h > 0.40$; D: freezing of hydrate-bearing soil. 1 – water; 2 – ice; 3 – hydrate; 4 – gas; 5 – mineral grains; 6 – bound water; 7 – cracks.

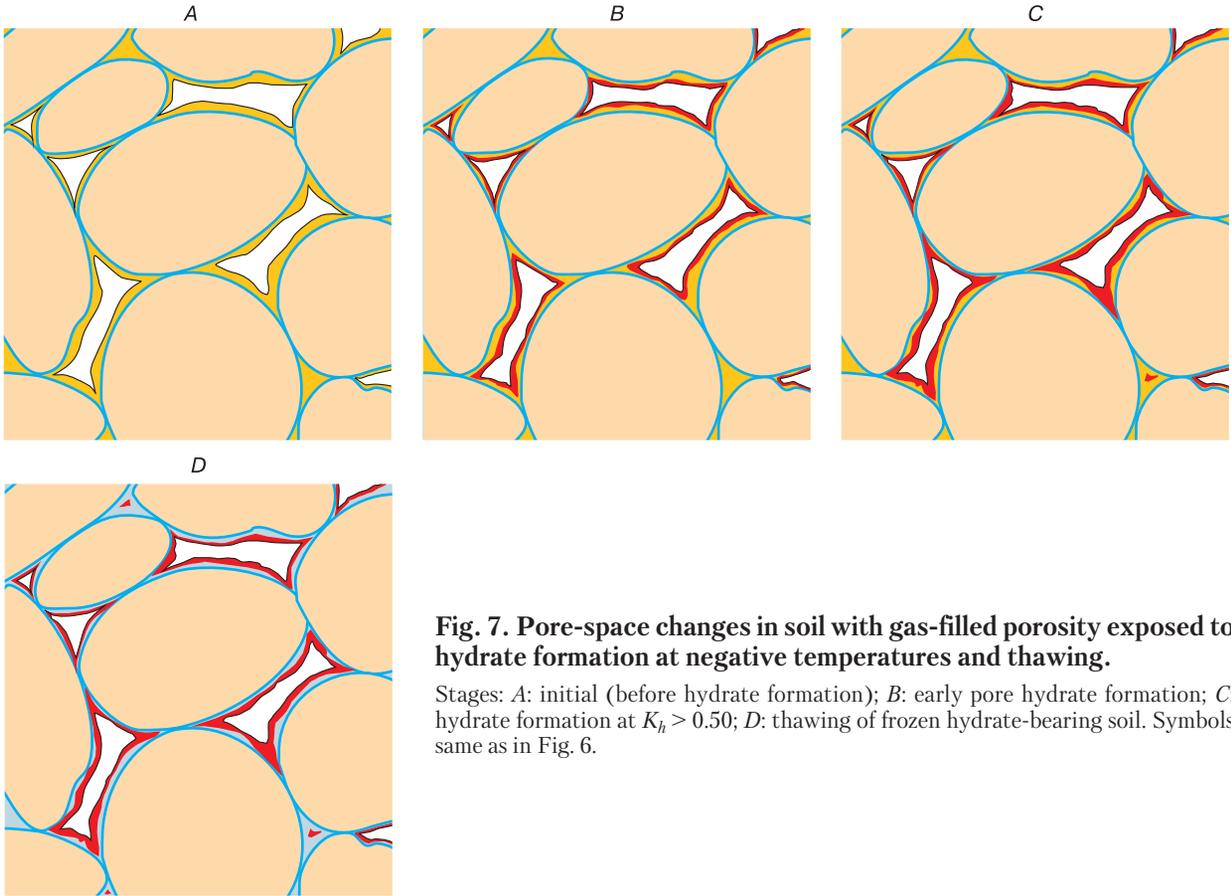


Fig. 7. Pore-space changes in soil with gas-filled porosity exposed to hydrate formation at negative temperatures and thawing.

Stages: *A*: initial (before hydrate formation); *B*: early pore hydrate formation; *C*: hydrate formation at $K_h > 0.50$; *D*: thawing of frozen hydrate-bearing soil. Symbols same as in Fig. 6.

soils at non-equilibrium conditions was reported in [Bukhanov *et al.*, 2008; Chuvilin and Bukhanov, 2013]. The low thermal conductivity was explained in the cited papers by growth of cracks and voids in porous hydrate-bearing soil that resulted from freezing and partial dissociation of pore hydrate at self-preservation.

Model 2, for hydrate saturation at $t < 0^\circ\text{C}$ and subsequent thawing of soil samples, likewise includes several stages (Fig. 7): before, in the beginning, and during hydrate formation ($K_h > 0.50$), and during thawing. Before hydrate formation, the soil has gas- and ice-filled porosity at a gas pressure below the equilibrium (Fig. 7, *A*). Hydrate formation begins as the gas pressure exceeds the equilibrium, and pore ice converts to hydrate (Fig. 7, *B*). Gas hydrate expands from the surface inward the pore ice along cracks and structure defects. Then, as ever more ice changes to hydrate, the hydrate formation process decays, at $K_h > 0.50$ (Fig. 7, *C*). The changes in the pore ice/hydrate ratio during hydrate formation at $t < 0^\circ\text{C}$ decrease thermal conductivity of frozen soil because the more conductive ice component with $2.23\text{ W}/(\text{m}\cdot\text{K})$ decreases while the four times less conductive ($0.6\text{ W}/(\text{m}\cdot\text{K})$) hydrate component increases. Further on, as the conversion of pore ice into hydrate

slows down at $K_h > 0.50$, thermal conductivity decreases only slightly. Thawing of hydrate-bearing soil under a pressure below the equilibrium causes melting of the surviving pore ice giving rise to new water-gas interfaces and thus induces additional hydrate formation (Fig. 7, *D*).

Thawing of frozen hydrate-bearing soil reasonably decreases its thermal conductivity because the low conductive component appears in the pore space.

CONCLUSIONS

The reported experimental results have demonstrated the behavior of thermal conductivity in soils with water- and gas-filled porosity which experience hydrate formation in the conditions of low positive and negative temperatures, freezing and thawing.

During hydrate formation at $t > 0^\circ\text{C}$, thermal conductivity changed insignificantly (within 2–3 %) when small amounts of water converted to ($K_h < 0.40$) but increased notably when hydrate consumed more than 40 % of pore water ($K_h > 0.40$). The increase reached 14 % in silt with $W = 18\%$ at $K_h = 0.46$.

Hydrate formation at $t < 0^\circ\text{C}$ led to regular decrease in thermal conductivity, to 22 % in the $W = 19\%$ sand sample at $K_h = 0.50$.

Both freezing and thawing of soil samples saturated with hydrate at low positive and negative temperatures, respectively, led to thermal conductivity reduction: about 10 % for sand and 50 % for silt in the former case and 8 % in the latter case.

The observed thermal conductivity behavior results from pore space changes associated with additional hydrate formation, as it was explained in two models.

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References

- Aladko, E.Ya., Dyadin, Yu.A., Zhurko, F.V., et al., 2006. Equilibrium conditions for dissociation of pore gas hydrates. *Gazovaya Promyshlennost. Special Issue. Gas Hydrates*, 18–27.
- Asher, G.B., 1987. Development of computerized thermal conductivity measurement system utilizing the transient needle probe technique: Dissertation T3335. Golden, Colorado, USA, Colorado School of Mines, 109 pp.
- Bukhanov, B.A., 2013. Variations in Thermal Conductivity of Gas- and Hydrate-Bearing Rocks at Different Pressures and Temperatures (in Russian). Author's Abstract, Dissertation (Candidate in Geology and Mineralogy). Moscow, 24 pp.
- 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, in: Proc. 9th International Conference on Permafrost, Fairbanks, Alaska, pp. 205–209.
- Chuvilin, E.M., Bukhanov, B.A., 2013. Thermal conductivity of frozen hydrate-bearing soil at atmospheric pressure: An experimental study. *Kriosfera Zemli*, XVII (1), 69–79.
- Chuvilin, E.M., Bukhanov, B.A., 2014. Variation in the thermal conductivity of gas-saturated sediments during hydrate formation and freezing–melting. Part 1. Method of researches. *Kriosfera Zemli*, XVIII (1), 70–76.
- Chuvilin, E.M., Guryeva, O.M., 2009. Formation of pore SO₂ hydrate in freezing and frozen rocks: An experimental study. *Kriosfera Zemli*, XIII (3), 70–79.
- Chuvilin, E.M., Istomin, V.A., 2012. Temperature effects on equilibrium water content in hydrate-bearing rocks, in: Proc. Xth International Conference on Permafrost, Salekhard, vol. 3, pp. 571–574.
- Chuvilin, E.M., Kozlova, E.V., 2005. Formation of frozen hydrate-bearing rocks. *Kriosfera Zemli*, IX (1), 73–80.
- Chuvilin, E.M., Lupachik, M.V., Guryeva, O.M., 2011. Kinetics research of ice transition into gas hydrate in porous media, in: Furukawa, Y., Sazaki, G., Uchida, T., Watanabe, N. (Eds.), *Physics and Chemistry of Ice*, Hokkaido Univ. Press, Sapporo, Japan, pp. 127–132.
- Duchkov, A.D., Istomin, V.E., Sokolova, L.C., 2012. A geothermal method for detecting gas hydrates in the bottom sediments of water basins. *Russian Geology and Geophysics*, 53 (7), 704–711.
- Duchkov, A.D., Manakov, A.Yu., Kazantsev, C.A., et al., 2009. Thermal conductivity measurements in synthetic samples of bottom sediments saturated with methane hydrate. *Izv. RAN, Fizika Zemli*, No. 8, 42–50.
- Fan, S., Huang, D., Liang, D., et al., 2005. Thermal conductivity of combination gas hydrate and hydrates and mixtures, in: Proc. 5th International Conference on Gas Hydrates, Trondheim, Norway, vol. 2, pp. 668–676.
- Groysman, A.G., 1985. Thermal Properties of Gas Hydrates (in Russian). Nauka, Novosibirsk, 94 pp.
- Huang, D., Fan, S., 2004. Measuring and modeling thermal conductivity of gas hydrate-bearing sand. *J. Chem. and Eng. Data*, 49, 1479–1482.
- Istomin, V.A., Yakushev, V.S., 1992. Naturally Occurring Gas Hydrates (in Russian). Nedra, Moscow, 235 pp.
- Rosenbaum, E.J., English, N.J., Johnson, J.K., et al., 2007. Thermal conductivity of methane hydrate from experiment and molecular simulation. *J. Phys. Chem. B*, 111, 13194–13205.
- Sloan, E.D., 1998. Clathrate hydrates of natural gases. 2nd Edition, Marcel Dekker, New York, 705 pp.
- Stoll, R.D., Bryan, G.M., 1979. Physical properties of sediments containing gas hydrates. *J. Geophys. Res.*, 84, 1629–1634.
- Waite, W.F., Stern, L.A., Kirby, S.H., et al., 2007. Simultaneous determination of thermal conductivity, thermal diffusivity and specific heat in structure I methane hydrate. *Geophys. J. Intern.*, 169, 767–774.
- Warzinski, R.P., Gamwo, I.K., Rosenbaum, E.J., et al., 2008. Thermal properties of methane hydrate by experiment and modeling and impacts upon technology. Proc. 6th International Conference on Gas Hydrates, Vancouver, Canada, pp. 803–812.
- Wright, J.F., Nixon, F.M., Dallimore, S.R., et al., 2005. Thermal conductivity of sediments within the gas–hydrate–bearing interval at the JAPEX/JNOC/GSC et al. Mallik 5L38 gas hydrate production research well. *Geol. Surv. Canada Bull.*, 585, 10.

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