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Method of determining the thermal conductivity of dispersed gas-saturated sediments under conditions of hydrate and ice formation

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ABSTRACT
This paper presents a new method of experimental investigation of thermal conductivity of fine-grained gas-saturated sediments during hydrate accumulation at temperatures above and below 0°C. The testing was conducted with a special gas hydrate experimental setup featuring an integrated measurement system for measuring thermal conductivity of the fine-grained sediments under high gas pressure. Measurements of soil thermal conductivity were carried out in steady-state thermal mode (the stationary thermal method). This method allows to quantify the impact of hydrate saturation and the extent of pore water to hydrate transition on the thermal conductivity of the fine-grained sediments.

RÉSUMÉ
Cet article présente une nouvelle méthode expérimentale d'investigation de la conductivité thermique des sédiments fins saturés en gaz lors de l'accumulation d'hydrates à des températures au-dessus et sous 0°C. Les essais ont été réalisés à partir d'un dispositif expérimental d'hydrate de gaz combiné à un système de mesure de conductivité thermique permettant l'étude des sédiments sous pression de gaz. La conductivité thermique des sédiments a été déterminée à partir de la méthode de flux de chaleur constant (régime thermique stationnaire). Cette méthode permet de quantifier l'impact de la saturation des hydrates et l'importance de l'eau interstitielle lors de la transition des hydrates sur la conductivité thermique des sédiments fins.

1. INTRODUCTION

In nature, gas hydrates (mainly methane hydrates) are often formed in the offshore sediments at depths below 300 meters, and in permafrost ground areas (Sloan, 1998; Max, 2000). In the permafrost areas, gas hydrates are primarily formed in soils of subpermafrost horizons.

Under long-term freezing conditions, the cooling effect in sediments is observed at great depths (hundreds of meters). This causes intersection of gas-bearing horizons and hydrate stability zone, which leads to formation of gas hydrate horizons ahead of the freezing front. It should be noted that increase in permafrost thickness, makes hydrate horizons undergo a process of freezing, which results in formation of naturally frozen hydrate-bearing soils.

Despite the fact that most hydrate formations are observed at great depths, some could be found in permafrost areas at shallow depths (up to 250 meters) under close to 0°C negative temperatures. Such formations are subject to high pressure, generated by the process of water crystallization in pores (the crystallization factor) and by external load (the baric factor) applied to concentrated gas accumulations (gas pockets) in frozen sediments (Yakushev & Chuvilin, 2000; Chuvilin et al., 1998). The baric factor is mainly caused by two reasons: transgression of the Arctic seas, and development of glaciation (Romanovsky, 1993). As a result, gas accumulations at relatively shallow depths of permafrost enter the zone of hydrate stability and transform into gas hydrates (Chuvilin et al., 1998; Chuvilin & Lupachik 2011). Thus, the processes of hydrate accumulation can occur in sub-permafrost horizons at low positive temperatures and at temperatures below 0°C in permafrost.

It is known that thermal conductivity of pore fluids water & ice are very different (0.6 and 2.23 W/(m•K), respectively), but for water & gas hydrate they are similar (0.6 and 0.55-0.65 W/(m•K), respectively) (Stoll & Bryan, 1979; Huang & Fan, 2004; Waite et al., 2007; Rosenbaum et al., 2007; Warzinski et al., 2008). Therefore, we can assume that thermal conductivity changes during hydrate formation will strongly depend on conditions of pore hydrates accumulation in sediments.

Today, thermal conductivity of hydrate-bearing soils is investigated poorly in comparison to the thermal conductivity of pure gas hydrates (Chuvilin & Bukhanov, 2014a,b). There are some individual data of thermal conductivity of artificially hydrate-bearing sediments, given by (Groysman, 1985), (Asher, 1987), (Fan et al., 2005), (Waite et al., 2007) and (Duchkov et al., 2006; Permyakov et al., 2011). Experimental estimation of thermal conductivity of soil containing natural gas hydrates was researched at Malik 5L-38 well (Mackenzie delta, Canada) (Wright et al., 2005). In general, it was found that thermal conductivity of frozen soils is significantly higher than that of hydrate-bearing frozen analogs. The thermal conductivity of hydrate-saturated sediments in frozen state is often higher than in non-frozen state.

Study of thermal conductivity of frozen hydrate-saturated sediments under non-equilibrium conditions, i.e. during the self-preservation of methane hydrates was presented by Chuvilin et al., (2007) and Bukhanov et al., (2008). These papers present a method of definition of thermal conductivity, and also show differences in the values of thermal conductivity of frozen sediments with and without hydrates during self-preservation effect (anomalous preservation) of porous gas hydrates at temperatures below 0 ^{o}C and 0.1 MPa (Ershov et al., 1991; Stern et al., 2001; Chuvilin et al., 2011a). These differences are directly related to the hydrate content.

In recent years, some new experimental data was published on the influence of hydrate saturation and the proportion of pore water that transforms into hydrate, on the thermal conductivity of sediments at low positive (above 0^{o}C) and negative (below 0 ^{o}C) temperatures, (Chuvilin & Bukhanov, 2012). In addition, the authors evaluated the influence of freezing and melting processes on thermal conductivity of hydrate-saturated soils (Chuvilin & Bukhanov, 2014a). Based on the experimental results, the authors proposed models of structural and textural changes in gas-saturated sediments under different conditions of hydrate accumulations, including processes of freezing and melting (Chuvilin & Bukhanov, 2014b). New experimental setups and new experimental methodology have to be developed to estimate relation between conditions of gas-hydrate accumulation and thermal properties, in laboratory settings. This publication presents our method of experimental investigation of thermal conductivity in gas-saturated sediments during hydrate accumulation at low positive and at negative temperatures.

2. METHODS

Thermophysical studies of gas hydrates were conducted using a special experimental installation, which allows measuring thermal conductivity of gas- and water-saturated soil samples in a pressure cell under different temperatures and pressures. This setup consisted of a refrigerator to provide required temperature, a pressure cell with total volume 200 cm3, a gas tank (300 cm^{3} volume), a system of leading pipes, power supplies (12V for cooler & 20V for heater), and recording equipment (Fig. 1).

Thermal conductivity measurement system of dispersed media was built into the pressure chamber. This system was developed in collaboration with colleagues from Nature Management Institute in National Academy of Sciences of Belarus (Minsk).

The method of steady-state thermal regime is at the basis of determining thermal conductivity of dispersion media (Bertasi et. al., 1978). In the installation, this method was implemented by fixing temperature difference between opposite ends of investigated samples in steady state by a heater with constant power of 1 Watt (shown with red color in Fig. 1).

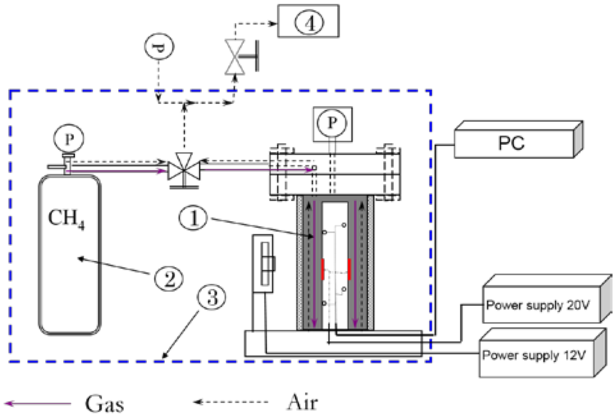

Fig.1. General layout of the installation to determine thermal conductivity of the soil samples under gas pressure.
1 –Pressure cell with a soil sample, 2 –Gas canister, 3 – Refrigerator, 4 –Vacuum pump.

It has been found experimentally that overheating of the sample during the transition time to steady-state thermal conditions ranged from 0.8 to 1.2 °. To prevent leakage of heat from main heater on the bottom of the inner cylinder, a protective heater and guard thermocouples were set up.

Accuracy of measurements of thermal conductivity of soil was found to fit the range of 5-7% with a confidence level of 0.95. In this case, the random error of measurement of thermal parameters does not exceed 4%. To control and maintain desired accuracy during calibration, we used reference materials with values of thermal conductivity in the range of 0.3 to 2.23 W/(m•K).

The subject of investigations were soil samples with disturbed structure (Tab. 1).

Table 1. Characteristics of tested soils.

Lithology	Particle size distribution, %			Mineral composition, %	Salinity, %
	1-0.05 mm	0.05-0.001 mm	<0.001 mm		
Sand	94.8	3.1	2.1	quartz > 90	0.01
Silty sand	41.8	53.7	4.5	quartz- 37 microcline + albite -55 illite - 8	0.08

The studied soils included quartz sand and poly-mineral silty sand. This silty sand was collected from permafrost horizons near town of Vorkuta. The initial values of porosity (n) and density (ρ) of sand samples were within 0.38-0.45 and 1.7-1.9 g / cm^3, respectively. In addition, we prepared samples with high initial porosity (n ≈ 0,6).

Pure methane (99.98%) was used for the experiments as hydrate-forming gas. Gas in the tank was under a pressure of about 8-10 MPa. Experimental investigation of thermal conductivity of sediments under methane pressure above the equilibrium were held at positive and negative temperatures.

Our methods of experiments under positive temperature focused on the following cases:

1) methane supply (up to 6 MPa) into the pressure cell with the sediment sample at room temperature (t≈ 21 ± 1 °C). Cooling it to a low positive temperature (+2 ± 1 °C)

2) hydrate saturation at +2 ± 1 ° C and under methane pressure above 4.2 MPa. The methane pressure is always above the equilibrium, ensuring that the process of hydrate accumulation occurs in all tested samples;

In the second case, thermal conductivity was studied at constant temperature -5 ± 1 °C and subsequent to thawing at a low positive temperature. The process of hydrate formation at low temperatures (-5 ± 1 ° C) started immediately after cooled methane (up to 6 MPa) saturated into the pressure cell with frozen sample. In this case, the hydrate was forming from pore ice.

At each stage, pressure, temperature and thermal conductivity of sediment sample were measured. For comparison, the same parameters were measured for a sample under atmospheric pressure and at excess pressure (3-4 MPa). This pressure was created by nitrogen (N_2), which under the experimental conditions did not form gas hydrates (Chuvilin & Bukhanov, 2012, 2014a).

PVT method and changes of thermobaric conditions were used to determine hydrate coefficient (K_h, u.f.) (Chuvilin & Kozlova, 2005). Hydrate coefficient describes the proportion of water, transformed into hydrate form. It is defined as following:

$K_h=W_h,/W$,

where W_h – the amount of water transferred into a hydrate (% by weight of dry sample),
W – total amount of water (initial moisture content,%).

Hydrate number 5.9 was used to calculate the parameters of hydrate content of sediments containing hydrate of CH_4.

3. EXPERIMENTAL DATA AND DISCUSSION

Thermal conductivity changes during hydrate accumulation in soil samples was studied under the following thermal conditions:

1) At low positive temperature (t > 0 °C)
2) At temperatures below 0°C (t< 0°C)

All experiments were performed on silty sand and fine sandy soil samples with incomplete degree of pore saturation with water or ice.

The common results of thermal conductivity changes in gas-saturated sediments under different conditions of hydrate accumulation, including processes of freezing and melting were presented by Chuvilin & Bukhanov, (2014a,b). In the current work, we focus on the experimental method.

3.1 Hydrate accumulation at temperature above 0°C

The process of hydrate accumulation at positive temperature was investigated during cooling the methane-saturated sediments in pressure cell from room temperature to a low positive temperatures (t=+2±1 °C). The typical gas hydrate accumulation pattern in the pore space during cooling are evident in changes of the hydrate coefficient with time (Fig. 2).

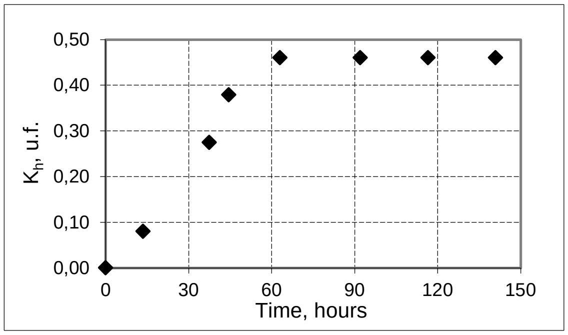

Fig. 2. Dynamics of hydrate accumulation in pore space of gas-saturated silty sand (W=18%; n=0,40), at t=+2±1 °C.

Hydrate accumulation in the sample naturally decreases over time, due to changes in the hydrate accumulation mechanism (Chuvilin & Guryeva, 2008). The initial stage has the most active hydrate formation. Therefore, the main hydrate accumulation in the sample occurs within the first 45-50 hours. During this time, K_h grows almost to 0.45. Then, there is a sharp drop in the rate of hydrate formation, while K_h practically remains unchanged at 0.46. Active hydrate accumulation at the initial stage is the result of well- developed gas-water contacts. Over the time, the formation of gas hydrate film at the interface of pore water-gas hampers gas access to the pore water; this causes decrease in the rate of hydrate accumulation. The speed of gas hydrate accumulation is limited by permeability of gas hydrate film, which dramatically decreases as film thickness increases. Upon reaching certain film thickness, the process of hydrate accumulation practically stops, despite the fact that the residual water content of the pore exceeds the equilibrium water content at a given temperature and pressure conditions (Chuvilin & Guryeva, 2008).

Thermal conductivity of gas-saturated silty sand (W = 18%) during hydrate accumulation at positive temperatures is presented in Fig. 3.

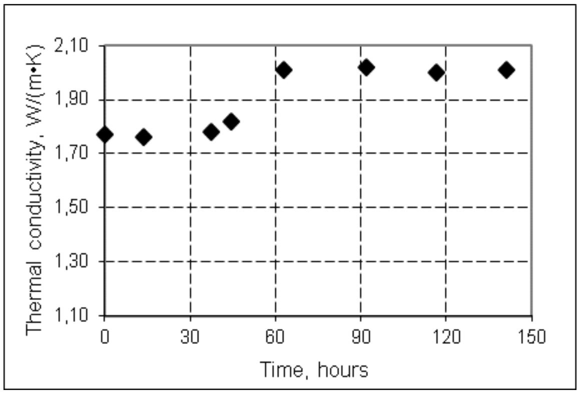

Fig. 3. Thermal conductivity of gas-saturated silty sand (W=18%, n=0.40) during hydrate accumulation at t=+2±1 °C.

It can be seen that the change of thermal conductivity in time is irregular. Three characteristic regions can be distinguished. The first portion is characterized by a small change in the thermal parameter (1.77 to 1.78 W/(m•K)), over the first 40 hours. Variation of thermal conductivity in this area is not more than 3%, and does not exceed the measurement accuracy. The second section shows more intensive growth of the thermal conductivity from 1.78 to 2.01 W/(m•K) and lasts for the next 20 hours. Increase of thermal parameter in the second section is 13%.The third section, which begins 60 hours after the experiment start, is characterized by almost constant value of the thermal conductivity of 2.01 W/(m•K). Variation of values in this sector did not exceed 3-4%, which is ranged with accuracy of determinations.

Comparison of thermal conductivity changing in time and hydrate accumulation of silty sand (W=18%), show that during the first 40 hours with increasing of K_h up to 0.27 the thermal conductivity is practically constant. In the next 20 hours, there is an increasing of K_h and thermal conductivity of hydrate-saturated sediments, and these parameters reach maximum values in the same time. Further, both parameters do not change within the next 100 hours.

From these data, we conclude that at low amount of pore water passing into the gas hydrate, the thermal conductivity of the tested soils varies slightly (less than 2%). This can be explained by the fact that the values of thermal conductivity of gas hydrate and water are very similar. Noticeable changes in thermal conductivity of gas-saturated sediment samples are observed for large values of the hydrate coefficient (K_h more than 0.30-0.40). In this case (when more that 30-40% of pore water transfer into hydrate state), there is a local migration and redistribution of water in the pore space that cause structure changes in investigated soils. Namely, water in films between soil particles moves inward the pores, closer to the water-gas interfaces where hydrate is forming (Chuvilin & Bukhanov, 2014b). As the result of local redistribution of pore water, soil particles may become more tightly packed and saturation will increase. This effects on thermal contacts in the hydrate-bearing soil and shown up in increasing of thermal conductivity.

3.2 Hydrate accumulation at negative temperature

The process of hydrate accumulation at temperatures below 0 ° C is investigated on frozen sediment samples with methane at temperature of -5 ± 1 ° C. The dynamics of methane hydrate accumulation in pore space of frozen sample is shown in Fig. 4.

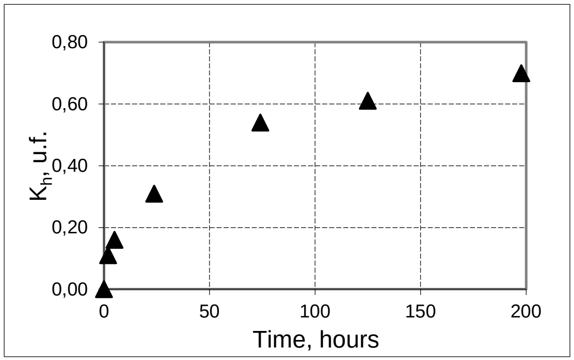

Fig. 4. The dynamics of methane hydrate accumulation in frozen sand (W = 22%, n = 0.60) at t=-5 ± 1 °C.

Unlike hydrate accumulation at positive temperature, the intensity of methane hydrate accumulation in frozen soil is significantly lower, but the hydrate formation at negative temperatures proceeds smoothly. This leads to the fact that values of hydrate accumulation in frozen samples during prolonged time can be compared with values of hydrate accumulation at positive temperatures (Chuvilin et al., 2011b). This rate of hydrate accumulation is associated with a feature of the processes of hydrate formation at negative temperatures. Special investigations on interaction of ice particles with gases CO_2 and CH_4 show that gas hydrates at negative temperatures are formed directly on the surface of ice particles (Kuhs et al., 2000; Wang et al., 2002; Staykova et al., 2003).It was found that at negative temperature there forms loose hydrate which has high gas permeability, and it does not lead to a drastic attenuation of the transformation of the ice particles to hydrate. A similar mechanism is, obviously, characterized for transition of pore ice into hydrate, which is confirmed by dynamics of gas hydrate accumulation in frozen sediments.

In contrast to hydrate accumulation at positive temperatures in frozen sediments its thermal conductivity decreased (Fig. 5). Thus, during the first 50 hours during hydrate growth thermal conductivity decreases by 8% (up to 1.81 W/(m•K)). Subsequently, the decreasing intensity of thermal conductivity is decayed, in the next 125 hours the values of thermal conductivity do not exceed 3%.Most likely this trend of decreasing thermal conductivity of frozen sediments during hydrate accumulation is associated with the decrease in the proportion of ice component, which has a high thermal conductivity (2.23 W/(m•K)), and with the increasing in the proportion of hydrate component, whose thermal conductivity is four time less (0.6 W/(m•K)).

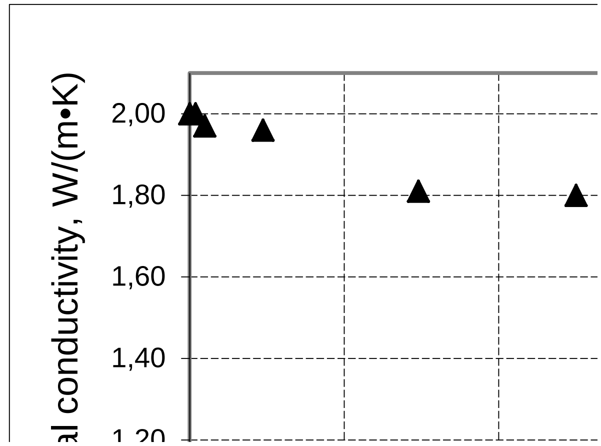

Fig. 5. Changes in thermal conductivity of gas-saturated sand (W = 22%, n=0,60) during hydrate accumulation at t= -5±1 °C.

4. CONCLUSIONS

New experimental research technique to study thermal conductivity of gas-saturated sediments under different temperature and pressure conditions was developed. This technique allows to investigate thermal conductivity of gas-, water-, hydrate- and ice-bearing sediments under gas pressure up to 7 MPa. It is possible to quantify the impact of hydrate saturation and the degree of transition of the pore water into hydrate form on the thermal conductivity of sediments and trace the influence of hydrate formation conditions on their thermal conductivity.

The accuracy of determining thermal conductivity is estimated at 5-7% with the confidence level of 0.95. In this case, the random error of measurement of thermal parameter does not exceed 3-4%.

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