

G E O P H Y S I C S

Experimental Modeling and Measurement of Thermal Conductivity of Sediments Containing Methane Hydrates

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Gas hydrates are clathrate compounds with gas molecules included into the cavities of a fine polyedric framework built by water molecules. A unit volume of methane hydrate can contain up to 170 volumes of gas [1]. Hydrates of hydrocarbon gases (mainly methane) are widespread in nature. Therefore, they attract interest as a promising energy source. The formation and existence of natural gas hydrates require adequate pressure (P), temperature (T), and availability of water and free gas (or sufficient concentration of gas dissolved in water). Such conditions exist in marine and oceanic sediments at depths greater than 300–500 m and in sedimentary rocks cooled by permafrost [1, 2]. Relatively recently, methane gas hydrates were found in the sediments of freshwater Lake Baikal near the bottom surface and at depths of 120–162 m ($P \sim 14$ –17 MPa and $T \sim 4$ –12°C) [3–5].

At present, the structure of even the most accessible subsea gas hydrate accumulations located in the upper layer of sediments around active gas sources is insufficiently studied. Geophysical methods for searching and outlining gas hydrate accumulations are absent. A solution for these problems is retarded primarily by insufficient studies of the hydrate-containing rocks.

The authors of the present paper worked out and produced a device that allows us to model the samples of methane hydrate-containing rocks and to measure their thermal conductivity. Thermophysical parameters can be assigned to the most interesting characteristics of hydrate-containing sediments, because they determine the dynamics of temperature field that controls

processes of the formation and decomposition of gas hydrates. In addition, there is good reason to believe that, based on measurements of thermal conductivity in situ, one can work out new geothermal methods for the discovery and evaluation of the gas hydrate content in the subsea sediments [6].

Figure 1 shows a scheme of the experimental setup. The device consists of a high-pressure (up to 40 MPa) camera and the ancillary equipment. The diameter and length of the working space of the camera are 40 and 155 mm, respectively. Constant temperature in the camera (deviations in temperature do not exceed 0.01°C) is maintained by a liquid-filled thermostat. The pressure is measured with a Burdon manometer with an accuracy of 0.015 MPa. A needle probe of constant power [7], inserted into the camera through its lower flange, is used to measure the medium thermal conductivity (λ) and temperature (T) at different stages of the experiment. The probe represents a tube (diameter 2 mm, length 120 mm) equipped with a heater (manganine wire with a resistance of ~44 Ohm) and a MMT-6 thermistor (rated resistance ~10 kOhm). Specific power of the heater is close to 1.3 W/m. The heater was put on for 3–5 min to measure the thermal conductivity. During this time, the device recorded the temperature change of the probe depending on time (thermogram). The slope of the linear interval of the thermogram depends on thermal conductivity of the medium, which can be calculated from the experimental data using the following formula [7]:

$$\lambda_i = \frac{Q}{4\pi} \frac{\ln \frac{t_i}{t_{i-1}}}{T_i - T_{i-1}}, \quad (1)$$

where λ is the coefficient of thermal conductivity, Q is the specific power of the heater, t is the heating time, and T is the probe temperature.

For the production of the hydrate-containing samples, 200 g of quartz sand was used as the mineral com-

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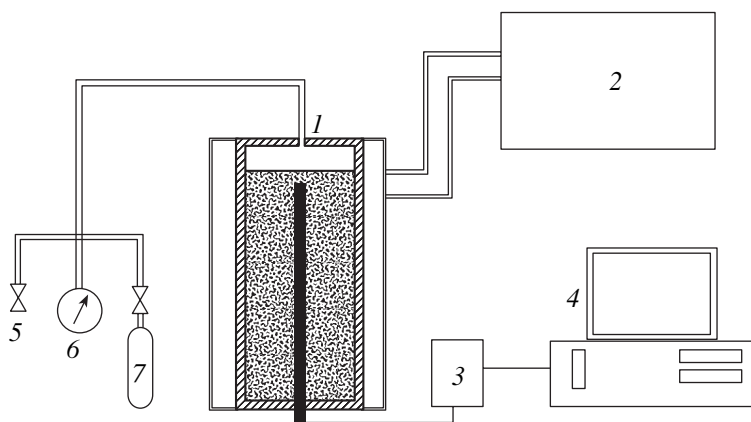


Fig. 1. Laboratory setup for modeling samples of hydrate-containing rocks. (1) High-pressure cylindrical camera (diameter 40 mm, height 155 mm); (2) thermostat; (3) device for the measurement of thermal conductivity and temperature in the camera (needle probe and recording system); (4) computer; (5) outlet valve; (6) manometer; (7) container with methane.

ponent. Its thermal conductivity in the dry state was close to $0.3\text{--}0.4\text{ W}/(\text{m} \cdot \text{K})$. The sand was mixed with grinded ice at a temperature of -5°C (the fraction of ice was $\sim 3\text{ wt } \%$) and loaded into the high-pressure camera. Porosity of the samples was close to 30% .

After the mixture was loaded and the camera was blown out with the gaseous methane, its volume was filled with the gas under the pressure $1.2\text{--}2\text{ MPa}$ higher than the equilibrium one (i.e., 2.2 MPa at -5°C). The equilibrium pressure P is $\sim 2.2\text{ MPa}$. In the subsequent $4\text{--}5\text{ h}$, methane hydrate was formed in the camera and uniformly distributed over the sample volume. The process was tracked by pressure decrease in the system. After the completion of this process, the sample was heated up to 2°C in such a way that the system was constantly under conditions close to those near the equilibrium PT curve for the methane hydrate (by doing so, the additional formation of the hydrate was excluded). Then the pressure was increased again. The sample was exposed for $10\text{--}15\text{ h}$ at $T = 2^\circ\text{C}$. Pressure decrease in the system practically stopped, because the water remaining in the sample was probably blocked by the newly formed hydrate crust. Then, the pressure was adjusted in the camera, and the appropriate value was chosen for the beginning of measurements of the thermal conductivity. The used procedure provided the production of samples with a relatively high content (up to $2\text{--}3\text{ wt } \%$) of the hydrate uniformly distributed over the sediment volume. The pore space in the sample was partially filled with the methane and the remaining water. Magnitudes of thermal conductivity of the methane hydrate and water were of the same order of $\sim 0.5\text{ W}/(\text{m} \cdot \text{K})$ [8]. The magnitude of thermal conductivity of the gas was one order of magnitude lower.

We performed several series of experiments devoted to the formation of hydrate-containing sediments and the measurement of their thermal conductivity at different pressures of methane (the duration of experiment was $1.5\text{--}2\text{ days}$). As a result, we obtained numerous

thermograms, which were used to determine the λ value in the samples (with hydrates and without them) at different pressures and temperatures in the camera. Figure 2a shows two thermograms.

During the measurement of the thermal conductivity of the hydrate-containing samples situated in the stability region of the hydrate during the experiment, temperature rise was in line with the thermogram (Fig. 2a, 1). In the first 20 s after the heater was turned on, a quick nonlinear increase in temperature was observed. During $3\text{--}4\text{ min}$ after that, the uniform (linear) temperature increase was noted. At the end of the experiment, the temperature increase retarded sharply when the heat wave reached the steel camera wall. The thermal conductivity calculated using the linear part of the thermogram was $0.7\text{ W}/(\text{m} \cdot \text{K})$. The slight increase in λ value as compared to dry sand is caused by the partial substitution of the gas in the pores of the sample by the hydrate and water. A similar but more flat thermogram (Fig. 2a) was obtained when thermal conductivity of the sample was measured after the complete decomposition of hydrates and their complete substitution by water released during the decomposition. In this case, thermal conductivity was higher ($\lambda = 1.0\text{ W}/(\text{m} \cdot \text{K})$). Correspondingly, the influence of the camera wall was more rapid. Increase in thermal conductivity can be related both to the partial substitution of gas in pores by water and to the consequent better contact between mineral particles.

The most interesting results were obtained during measurements of λ in hydrate-containing samples under PT conditions close to equilibrium ones (Fig. 2a, 2 and 3). In these experiments, thermograms are significantly complicated. The curves are flatter. The signal about the attainment of camera wall by thermal wave is absent even 10 min after the beginning of the experiment. The thermograms actually testify to an apparently sudden increase in thermal conductivity of the medium in the camera. For example, at $P = 3.31\text{ MPa}$ (Fig. 2a, 2), the calculated thermal conductivity

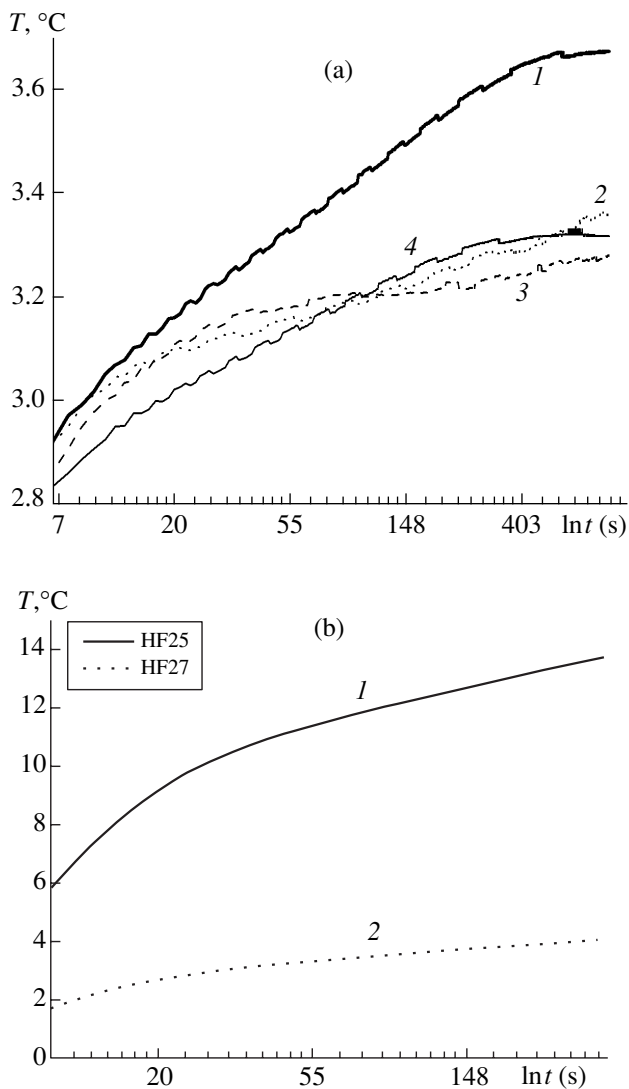


Fig. 2. (a) Thermograms (graphs of temperature measurement in the sample after turning on the heater of permanent power) based on the determination of thermal conductivity of model samples of hydrate-containing rocks. The initial composition of the sample is a mixture of quartz sand and grinded ice. Mean density of water-sand mixture (without the consideration of gas mass) is 1.56 g/cm^3 . The initial temperature in all experiments was 2.2°C . The rest of the data (methane pressure P , maximum temperature of the experiment T_m , equilibrium temperature of methane hydrate decomposition at pressure P , and calculated thermal conductivity λ_p) are indicated for individual graphs: (1) $P = 4.59 \text{ MPa}$, $T_m = 3.7^\circ\text{C}$, $T_p = 5.8^\circ\text{C}$, composition (wt %): sand 96.2, water 1.6, hydrate 2.2; $\lambda_p = 0.7 \text{ W/(m K)}$; (2) $P = 3.31 \text{ MPa}$, $T_m = 3.4^\circ\text{C}$, $T_p = 2.4^\circ\text{C}$, composition (same as in graph 1); $\lambda_p = 1.33 \text{ W/(m K)}$; (3) $P = 3.25 \text{ MPa}$, $T_m = 3.3^\circ\text{C}$, $T_p = 2.2^\circ\text{C}$, composition (wt %): sand 96.2, water 2.2, hydrate 1.6; $\lambda_p = 5.7\text{--}4 \text{ W/(m K)}$; (4) $P = 2.98 \text{ MPa}$, $T_m = 3.3^\circ\text{C}$, $T_p = 1.3^\circ\text{C}$, composition (wt %): sand 96.1, water 3.9, hydrate 0; $\lambda_p = 1.0 \text{ W/(m K)}$. (b) Thermograms recorded during in situ variations in thermal conductivity of sediments in the Dvurechenskii mud volcano area of the Black Sea [9, 10]. (1) Station 25, $\lambda_p = 1.0 \text{ W/(m K)}$; (2) Station 27, $\lambda_p = 3.2 \text{ W/(m K)}$.

increases to 1.3 W/(m K) . At $P = 3.25 \text{ MPa}$ (Fig. 2a, 3) when equilibrium temperature is lower, λ reaches 4–5 W/(m K) .

We believe that anomalous changes in thermograms and calculated thermal conductivity are caused by the partial dissociation (not more than 5%) of hydrates near the needle probe under the influence of heat released by the heater. During the decomposition of hydrates, heat is absorbed around the heater (54.19 kJ/mol of methane hydrate [1]), and gas with anomalously low thermal conductivity is released. These processes have an opposite influence on the rate of probe temperature growth when the heater is permanently switched on. The first process attenuates the growth rate, while the second process accelerates the rate. Judging from the experimental data (Fig. 2a), precisely the first process leads to the complication of thermograms and the increase in calculated values of thermal conductivity. We can state that these trends undoubtedly indicate the presence of a significant amount of hydrates in the sediments. We discussed the possibility of prospecting implication of local anomalies in thermograms in [6, 9]. Our new data widen significantly the prospecting scope. In addition, the geothermic method can be used in the prospecting for subsurface gas hydrate pools. At the same time, the needle probe of constant power method is obviously unsuitable (both in laboratory and in situ) for the measurement of thermal conductivity in hydrate-containing sediments when they are located under PT conditions close to the phase boundary.

Of course, samples used in our experiments do not represent the exact model of real marine or lacustrine sediments. The sediments contain more free gas, and their formation mechanism differs from the natural one. Nevertheless, we suppose that even our imperfect laboratory model of real sediments yields a correct qualitative pattern. This statement is confirmed, in particular, by the results of field experiments. In situ measurements of bottom sediments in the Dvurechenskii mud volcano area of the Black Sea (Sorokin flexure located south of the Crimea Peninsula) yielded not only normal thermograms (Fig. 2b, 1), but also anomalous ones (Fig. 2b, 2) [9, 10]. Thermal conductivity values, calculated from these thermograms recorded at the adjacent points, differ significantly. At the first station, we obtained $\lambda = 1.0 \text{ W/(m K)}$, which is usual for Black Sea sediments. At the second station, the value was three times greater ($\lambda = 3.2 \text{ W/(m K)}$). These results are explained from the standpoint of our experiments. Anomalous thermograms testify to the presence of gas hydrate inclusions in the sediments at the point of measurements. The presence of methane gas hydrates in the sediments of this area was also confirmed by core samples [9, 10]. On the other hand, these field data confirm our conclusions about the possibility of using anomalous thermograms as an indicator of the presence of gas hydrates in the sediments.

The laboratory setup created as a result of the research allows us to model the samples of hydrate-containing bottom sediments. Based on this setup, we already managed to perform a series of experiments that explain the anomalies of thermal conductivity measured in situ and to suggest a geothermic method of the prospecting for hydrate-containing sediments. Continuation of the research in this field would hopefully allow us to develop the geothermic technology for the discovery and survey of subsurface gas hydrate pools above the bottom.

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REFERENCES

1. V. A. Istomin and V. S. Yakushev, *Gas Hydrates under Natural Conditions* (Nedra, Moscow, 1992) [in Russian].
2. G. D. Ginsburg and V. A. Solov'ev, *Submarine Gas Hydrates* (VNIIOkeanologiya, St. Petersburg, 1994) [in Russian].
3. M. I. Kuz'min, G. V. Kalmychkov, V. F. Geletii, et al., Dokl. Akad. Nauk **362**, 541 (1998) [Dokl. Earth Sci. **362**, 1029 (1998)].
4. J. Klerx, T. I. Zemskaya, T. V. Matveeva, et al., Dokl. Akad. Nauk **393**, 822 (2003) [Dokl. Earth Sci. **393**, 1342 (2003)].
5. A. D. Duchkov, Ros. Khim. Zh. **47** (3), 91 (2003).
6. V. A. Golubev, Dokl. Akad. Nauk **358**, 384 (1998) [Dokl. Earth Sci. **358**, 118 (1998)].
7. R. Von Herzen and A. E. Maxwell, J. Geophys. Res. **64** (10), 1557 (1959).
8. W. F. Waite, J. Pinkston, and S. H. Kirby, in *Proceedings of the Fourth International Conference on Gas Hydrates, Yokohama, Japan, 2002* (Yokohama, 2002) p. 728–733.
9. R. Kutas, J. Poort, J. Klerx, et al., Geofiz. Zh. **27**, 128 (2005).
10. R. I. Kutas, O. P. Kravchuk, and M.I. Bevzyuk, Geofiz. Zh. **27**, 238 (2005).