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Research paper

Termotechnical Characteristics Determination of Enclosing Structures for Hydrates Storage

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Abstract

In many countries around the world, gas hydrates use is seen as a promising alternative source of energy. The industrial infrastructure gas hydrates use requires the creation of reliable means for their storage and transportation.

In the paper the research installations schemes and the dissociated gas temperature regime hydrate experimental study results are given. The surface and propane hydrate deep layers temperature regime, which decomposes under atmospheric pressure, is analyzed. Convective and radiant heat transfer at the hydrate storage reservoir inner surface is considered and the temperature at the gas hydrates surface is determined. The method for determining the resistance to the tent heat transfer is developed and the dependence for the propane hydrate dissociation intensity is established. The research results can be used to reduce gas losses during gas hydrates storage and transportation under nonequilibrium conditions.

Keywords: *dissociation rate, gas hydrates, hydrate storage, resistance to heat transfer.*

1. Introduction

The industrial use of gas hydrates (GH) can become very significant in the energy supply of mankind. Gas hydrates are recognized as the most likely alternative fuel in many countries [1]. Their exploration and development are performed in France, Germany, the United States, Canada, Russia; but China and Japan are especially active. To obtain energy independence, Japan plans to start industrial extraction of methane from "combustible ice" near its islands, in 2023 [2]. China has begun experimental production of gas hydrates from the bottom of the South China Sea since 2017 [3]. Russia intends to extract gas hydrates in industrial quantities from 2020 [4]. However, effective technologies for the production, storage, and transportation of gas hydrates are still under development [5].

Overview of the latest sources of research and publications. It is proposed in [6] to synthesize and store the hydrate in sealed containers under excessive pressure. Considering the minimum pressure for methane hydrate formation is 35-40 bar, such tanks have too big steel intensity. The principal design of gas hydrates storage in the form of the hemisphere is given in [7]. The temperature regime of the storage depends on the thermal characteristics of dome and base and determines the hydrate storage period and its dissociation intensity. Methane hydrate dissociation at the negative temperature in the porous medium was considered in [8]. The transportation hydrodynamics of the dissociated hydrate mixture with liquid was investigated in [9]. Naturally occurring gas hydrates dissociation under water has been studied by a number of authors [10]. The hydrate dissociation effect on the soil elastic properties was considered in [11]. The analysis of literature sources indicates that there is insufficient information on the gas hydrates dissociation temperature regime under nonuniform conditions.

Selection of the unsolved parts of the general problem. This work was carried out to improve the methods of gas hydrates storage and transportation under nonuniform conditions. At atmospheric pressure and positive ambient temperature, they gradually dissociate into gas and water. Investigation of the gas hydrates dissociation process allows to determine the optimal conditions for their transportation and storage, to minimize gas losses.

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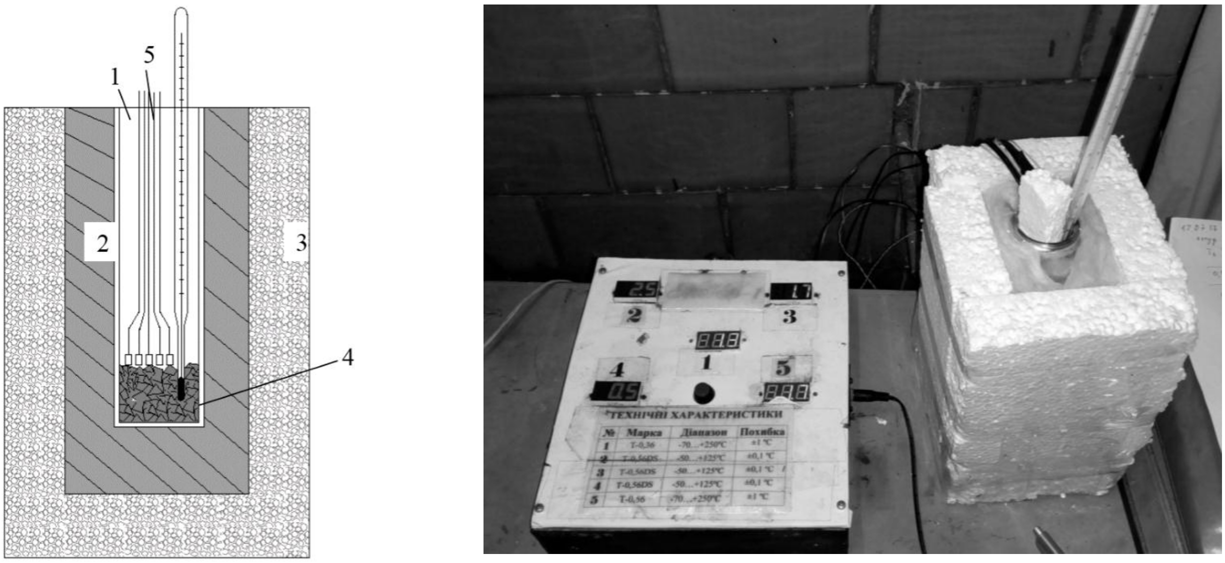
The purpose of work. The purpose of this work is to determine the thermal characteristics of the storage enclosing structures for the hydrates long-term storage at atmospheric pressure. The resistance to heat transfer of the storage enclosing structures should be determined considering the thermal processes occurring during the dissociation of GH under nonuniform conditions. To clarify the temperature regime on the surface and in the deep layers of the dissociating gas hydrate, it is necessary to apply experimental research methods. To carry out full-scale experiments, the propane gas hydrate is used. It has thermophysical characteristics similar to methane GH but does not require high pressures for production.

2. Main Body

The gas hydrate dissociation rate is determined by the heat flow to its surface. Therefore, the determination of the gas hydrate surface temperature is an important factor that needs to be clarified.

To carry out experimental studies to determine the dissociated gas hydrate surface temperature, the experimental equipment was designed. Its scheme and general view are shown in Fig. 1. To simulate a large array of GH, it was necessary to avoid heat significant losses into the environment in all directions except one. Therefore, the GH was inside the Dewar flask, placed in 2 layers of thermal insulation (2 cm of thick mineral wool, and 4 cm of thick polystyrene). For temperature measurement, electronic sensors ds18b20 were used. Their measurement accuracy was ± 0.1 ° C and the reference thermometer with graduating mark of 0.1 ° C.



№	Марка	Діапазон	Похибка
1	T-0,36	-70...+250°C	±1 °C
~~2~~	~~T-0,56DS~~	-50...+125°C	±0,1 °C
3	T-0,56DS	-50...+125°C	±0,1 °C
4	T-0,56DS	-50...+125°C	±0,1 °C
5	T-0,56	-70...+250°C	±1 °C

Fig. 1. Diagram and general view of the research plant

1 – Dewar flask; 2 – heat insulation layer of mineral cotton; 3 – heat-insulating layer of expanded polystyrene; 4 – gas hydrate; 5 – electronic temperature sensors

The Dewar flask was loaded with propane hydrate; electronic temperature sensors and a mercury thermometer. To reduce the outside air circulation effect, the Dewar flask was closed with styrofoam. Periodically, the position of the sensors relative to the hydrate was varied by turning along the vertical axis.

The experimental studies analysis indicates that hydrate structure temperature in different parts can differ substantially as a result of its heterogeneity. The conducted studies show that the surface temperature of the propane "dry" hydrate is in the range 0.3÷3.0 ° C. Its average value is + 1.1 ° C. After partial dissociation, ice crust appears on the hydrate surface and its melting temperature becomes 0 ° C.

To reduce the effect of the hydrate heterogeneity during measuring the mean temperatures on the hydrate surface and in its depth, during the following series of experiments sensors with the small surface area and high thermal conductivity were used, in particular, thermoelectric devices. Unlike electronic sensors, thermoelectric device are resistant to moisture penetration and after calibration has the accuracy of ± 0.05 ° C. To measure the thermoelectric devices EMF microvoltnanoammeter F136 was used.

The purpose of the second series of studies was to clarify the temperatures distribution in the inner layers and on the surface of the propane hydrate large mass. To achieve it, all the temperature sensors (thermocouples) were located inside the GH and only one was on its surface. For the studies, a "dry" GH with the gas capacity of 40 ml of gas/ml of water was used. Scheme and design of the research facility are shown in Fig. 2.

Progress of the research. Thermocouples at different heights were placed into the Dewar flask, Fig. 2.

Then, the propane hydrate was poured and tamped. The measured temperatures were recorded in the table. The results of temperature measurements are shown in Fig. 3

Analysis of the obtained data indicates that the propane hydrate upper layer of the "dry" crust, uncovered with ice-crust, is in the above-zero temperature range of 0.5 ÷ 0.8 ° C. The deepest layer is in conditions close to thermodynamic stability at the temperature of -0, 8 ° C. There is a transition region of about 50 mm thick, where a significant temperature gradient is observed, Fig. 4. The temperature distribution in the near-surface layer of propane hydrate is well approximated by the dependence

$$t_x = t_\infty + (t_0 - t_\infty)\ell^{-kx}, \tag{1}$$

where $t_\infty -$ the temperature of the hydrate thermodynamically stable layer is ° C; $t_0 -$ temperature on the hydrate surface. ° C; k – approximation coefficient, m^{-1}; x is the distance from the surface, m. For propane hydrate, the approximating coefficient is $k = 50$.

The mathematical model of the hydrate dissociation thermal regime is based on the nonlinear Fourier heat-transfer equation with heat sinks. Considering the conditions for carrying out the experimental studies, it can be assumed that the temperature field changes only along one coordinate axis. The one-dimensional Fourier heat-transfer equation with heat sinks [12] has the form

$$\frac{\partial t}{\partial \tau} = \frac{\lambda}{c\rho}\frac{\partial^2 t}{\partial x^2} + \frac{q_{V(x)}}{c\rho}, \tag{2}$$

where t is the temperature, ° C; λ is the hydrate thermal conduction, W / (m · ° C); c – its heat capacity, J / (kg · ° C); ρ – density, kg / m^3; q_V – heat sinks, W / m^3.

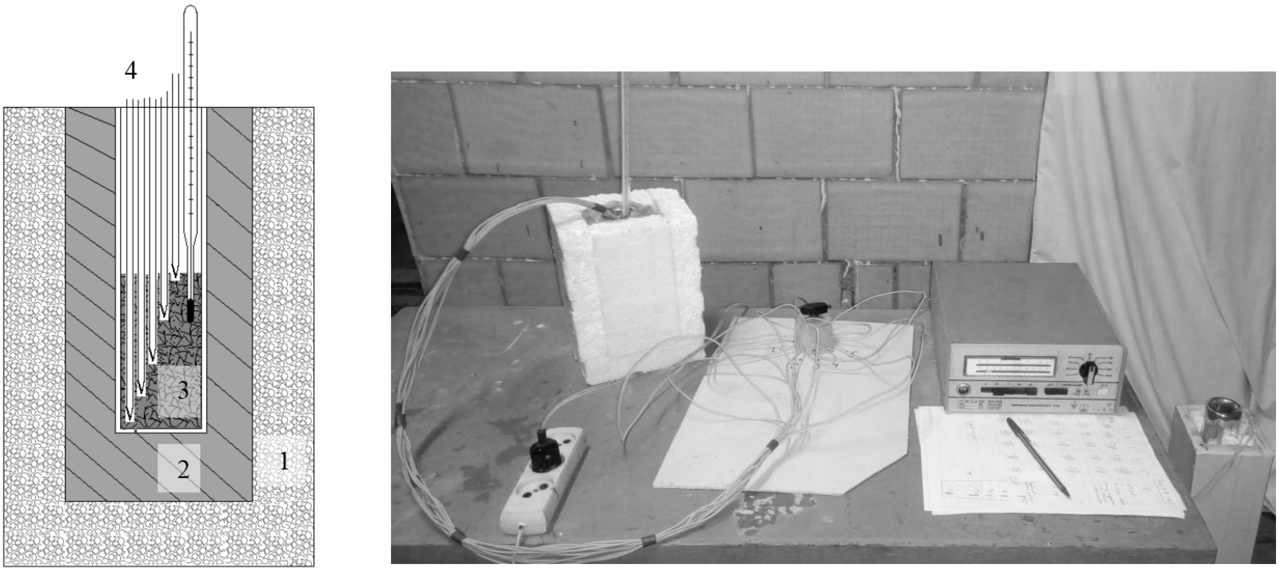


Fig. 2. Scheme and general design of the testing machine

1 – expanded polystyrene layer; 2 – a layer of mineral wool; 3 – gas hydrate inside the Dewar flask; 4 – thermocouples

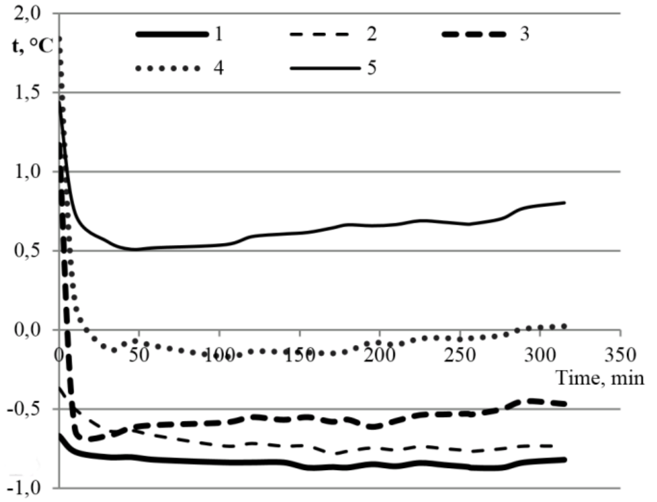


Fig. 3. Distribution of temperatures on the surface (line 5) and in the depth (lines 1 ÷ 4) of the propane hydrate massif

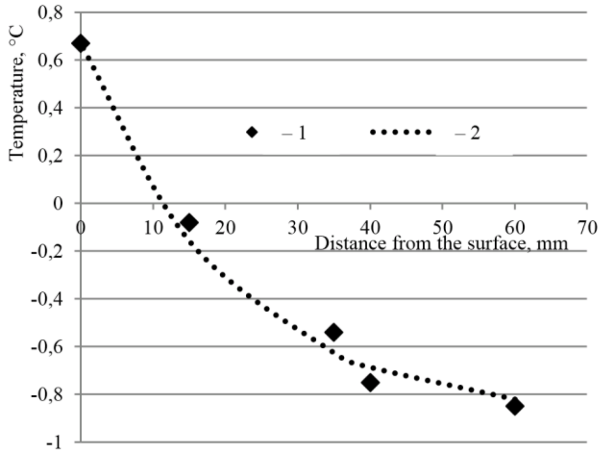


Fig. 4. Distribution of temperatures at the hydrate surface (dataset 1 – average temperature, obtained from experimental data, dataset 2 – approximation curve)

Since the problem is stationary, the temperature variation rate is zero, and the partial derivative of the temperature with respect to the spatial coordinate can be replaced by the total derivative. Thus, the power of volumetric heat sinks can be defined as a coordinate function, W / m^3

$$q_{V(x)} = -\lambda \frac{d^2 t}{dx^2}\,. \tag{3}$$

After substituting the second derivative from Eq. (1) in (3), the distribution of heat volume flows into hydrate is obtained, W / m^3

$$q_{V(x)} = -\lambda k^2 (t_0 - t_\infty)\ell^{-kx}\,. \tag{4}$$

The propane hydrate thermal conduction is λ = 0.5 (W / (m ° C)), the surface temperature of the hydrate is t_0 = 0.7 ° C, the temperature of the hydrate thermodynamically stable state hydrate is t_∞ = 0.9 ° C. So, after substituting (4), the value of the volumetric heat sinks is obtained, W / m^3

$$q_{V(x)} = 2000\ell^{-50x}\,. \tag{5}$$

Equation (5) shows that on the surface of a dissociative GH, there are heat sinks of 2000 W / m^3. In the deep layers, their power drops rapidly and at a depth of 50 mm is only 164 W / m^3.

On the other hand, this source of cold is a consequence of the gas hydrate dissociation. The integral over the heat sinks divided into the heat of the phase transition allows determining the hydrate melting rate depending on f the temperature at its surface, m / s

$$\frac{dx}{d\tau} = \frac{\lambda k^2}{r_V}(t_\infty - t_0)\int_0^\infty \ell^{-kx}dx = \frac{\lambda \cdot k(t_\infty - t_0)}{r_V}\,. \tag{6}$$

The specific fusion heat of propane hydrate dissociation is r_m = 6.64 · 10^3 kJ / kg, and its density is ρ = 0.899 kg / m^3 [13]. The volumetric heat of propane hydrate dissociation, J / m^3, is

$$r_V = r_m \cdot \rho = 6.64 \cdot 10^6 \cdot 0.899 = 5.97 \cdot 10^6\,. \tag{7}$$

To solve equation (6), it is necessary to set the temperature on the gas hydrate surface. Since all heat supplied to the GH is used for its dissociation, the heat balance equation for the surface layer is

$$\frac{dx}{d\tau}=\frac{1}{r_V}\left[\alpha_K\left(t_\Gamma-t_0\right)+\alpha_\Pi\left(t_\Pi-t_0\right)\right], \tag{8}$$

where α_K is the convective heat flow coefficient on the surface, W / (m^2 · ° C); α_Π – coefficient of radiant heat exchange, W / (m^2 · ° C); t_Γ is the gas temperature in the layer, ° C; t_Π is the temperature of the dome inner surface, ° C. Considering the approximate equality of the convective heat flow conditions at the dome inner surface and on the hydrate surface, expression (8) is

$$\begin{aligned}\frac{dx}{d\tau}&\approx\frac{1}{r_V}\left[0{,}5\alpha_K\left(t_\Pi-t_0\right)+\alpha_\Pi\left(t_\Pi-t_0\right)\right]=\\&=\frac{0{,}5\alpha_K+\alpha_\Pi}{r_V}\left(t_\Pi-t_0\right)\end{aligned}\quad . \tag{9}$$

The system of equations 6 and 9 makes it possible to obtain temperature values on the hydrate surface, ° C

$$t_0=\frac{\lambda k t_\infty+\left(0{,}5\alpha_K+\alpha_\Pi\right)t_\Pi}{\lambda k+0{,}5\alpha_K+\alpha_\Pi}\,. \tag{10}$$

To solve equation 10, heat transfer coefficients α_K and α_Π must be determined.

Suppose that laminar gas circulation is observed in the interlayer between the hydrate and the dome, for which the criteria derivative critical value (Gr · Pr) KR = 2 · 10^7 [14]. Pr number for propane at 0 ° C is Pr = 0.79. Considering the coefficient of thermal expansion β = 1/273, the free-falling acceleration g = 9.81 m / s^2 and the coefficient of propane kinematic viscosity at 0 ° C ν = 3.7 · 10^{-6} m^2 / s, the distance where the laminar regime ends can be determined by the formula, m

$$l_{KR}=\sqrt[3]{\frac{\left(Gr\cdot\mathrm{Pr}\right)_{KR}\cdot\nu^2}{\beta g\left(t_\Gamma-t_0\right)}}=\frac{0{,}213}{\sqrt[3]{t_\Gamma-t_0}}\,. \tag{11}$$

Analysis of equation (11) shows that the laminar regime is relatively small, about 10÷15 cm. Therefore, the turbulent regime is observed in the dome gas layer of the large storage.

For the turbulent regime of gas circulation in the vertical interlayer between the hydrate and the dome, the criterion equation of free convection near the vertical layer can be applied [14]

$$Nu_x=0{,}135\left(Gr_x\cdot\mathrm{Pr}\right)^{1/3}. \tag{12}$$

Substitution of the propane thermophysical characteristics at normal conditions considering its thermal conductivity 0.0158 W / (m ° C) in equation (12) makes it possible to determine the average coefficient of convective heat flow by formula

$$\overline{\alpha}_K=2{,}72\sqrt[3]{t_\Gamma-t_0}\,. \tag{13}$$

The coefficient of radial heat exchange between the dome inner surface and the HG is calculated by the formula [14]

$$\alpha_\Pi=C_0\varepsilon_{1-2}\varphi_{1-2}b_{1-2}, \tag{14}$$

where C_0 is the radiation of Planck radiator, W / (m² • K4); ε_{1-2} – reduced radiation factor; φ_{1-2} is the irradiation coefficient; b_{1-2} – temperature coefficient. For parallel areas φ_{1-2} = 1, the average temperature coefficient in the temperature range 0÷5 ° C is b_{1-2} = 0.84.

To reduce the radiant component of the heat flow, the inner layer of the coating is covered with aluminium foil, which has ε_1 = 0.05. For the hydrate, the value of the radiation coefficient analogous to snow ε_2 = 0.95 is assumed. Considering these values

$$\varepsilon_{1-2}=\frac{1}{\frac{1}{\varepsilon_1}+\frac{1}{\varepsilon_2}-1}=\frac{1}{\frac{1}{0{,}05}+\frac{1}{0{,}95}-1}\approx 0{,}05\,. \tag{15}$$

After substituting all the quantities into equation (14), it is obtained

$$\alpha_\Pi=5{,}67\cdot 0{,}05\cdot 1\cdot 0{,}84=0{,}24\,. \tag{16}$$

Substituting the heat flow coefficients into equation (10), an expression for determining the temperature on the propane hydrate surface is obtained

$$t_0=\frac{0{,}5\cdot 50t_\infty+\left(1{,}36\sqrt[3]{t_\Gamma-t_0}+0{,}24\right)t_\Pi}{0{,}5\cdot 50+1{,}36\sqrt[3]{t_\Gamma-t_0}+0{,}24}\,. \tag{17}$$

Since the convective heat flow coefficients on both sides of the gas layers are approximately equal, it is obtained

$$t_\Gamma-t_0\approx\frac{t_\Pi-t_0}{2}\,. \tag{18}$$

Considering expression 18, formula 17 becomes

$$t_0=\frac{25t_\infty+\left(1{,}08\sqrt[3]{t_\Pi-t_0}+0{,}24\right)t_\Pi}{25+1{,}08\sqrt[3]{t_\Pi-t_0}+0{,}24}\,. \tag{19}$$

The results of temperature calculating on the hydrate surface and the dissociation rate for different temperatures of the dome inner surface are shown in Fig. 5.

The heat-insulating properties of the hydrate storage dome are provided not only with the gas layer but also with the resistance to heat flow of all dome structural elements. The total resistance to heat flow of the entire enclosing structure is determined by the formula

$$R_\Sigma=\frac{1}{\alpha_3}+R_i+R_\Gamma+R_{\Gamma\Gamma}, \tag{20}$$

where α_3 – coefficient of heat exchange at the dome outer surface, W / (m^2 · ° C); R_i – resistance to heat flow of the heat-insulating layer (m^2 · ° C) / W; R_Γ – resistance to heat flow of the gas layer, (m^2 · ° C) / W; $R_{\Gamma\Gamma}$ is the resistance to heat flow of the near-surface layer HG, (m^2 · ° C) / W.

According to [14, 15], the heat flow coefficient on the dome outer surface can be taken as 23 W / ($m^2 \cdot °$ C). Resistance to the heat flow of the gas layer considering approximation, for which Pearson correlation coefficient is 0.9984, ($m^2 \cdot °$ C) / W

$$R_{\Gamma} = \frac{t_{\Pi} - t_0}{\lambda k (t_0 - t_{\infty})} \approx \frac{18{,}75}{\lambda k} (t_{\Pi} - t_0)^{-0{,}28}. \tag{21}$$

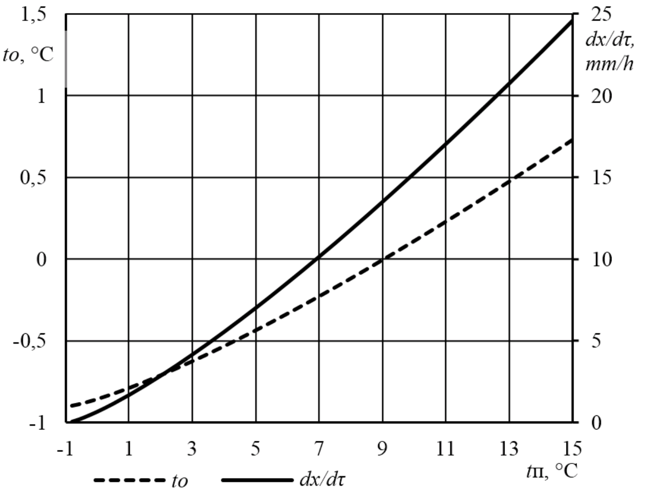


Fig. 5. surface temperature of the hydrate (t_O) and dissociation rate (dx / $d\tau$)

Resistance to heat flow near the surface layer HG, ($m^2 \cdot °$ C) / W

$$R_{\Gamma\Gamma} = \frac{t_0 - t_{\infty}}{\lambda k (t_0 - t_{\infty})} = \frac{1}{\lambda k}. \tag{22}$$

Considering all the components

$$R_{\Sigma} = \frac{1}{23} + R_i + 0{,}75 (t_{\Pi} - t_0)^{-0.28} + \frac{1}{25}. \tag{23}$$

To analyse the obtained dependencies, calculations of the hydrate dissociation depending on the heat transfer resistance for several cities were performed, Table 1. The results of the calculations (Fig. 6) indicate a nonlinear relationship among the hydrate dissociation rate and the enclosing structure thermal resistance of the hydrate storage.

Table 1: Climate data for some cities

Temperature range, ° C	Period duration for cities, h		
	Poltava	Kiev	Lviv
-4,9÷0	1224	1225	1039
0,1÷5	1128	1480	1678
5÷8	803	654	1133

The depth of hydrate dissociation during the heating season can be determined by integrating the melting rate in time, m

$$X = \int_0^{\tau = n} \left(\frac{dx}{d\tau} \right) d\tau \approx \frac{\lambda \cdot k}{r_V} \sum_0^n (t_0 - t_{\infty}) \Delta n, \tag{24}$$

where n is the duration of the heating period, s; Δn - the environmental temperature period within the preset temperature range, sec. The calculating results X for certain cities are shown in Fig. 6.

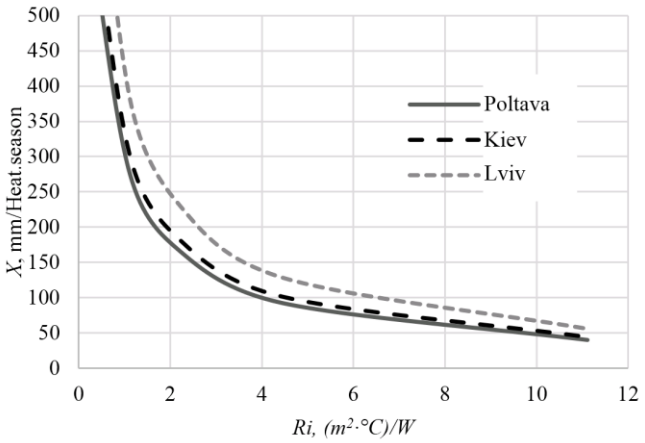


Fig. 6. Dependence of the propane hydrate dissociation rate (X) on the thermal resistance of the insulating layer (Ri) for different climatic conditions

Similar graphs for other regions can be constructed; based on the given costs calculation, the thermal insulation optimal thickness of the hydrate storage dome can be determined.

3. Conclusion

The scientific novelty of the work is to consider the hydrate temperature regime in calculating the heat flow resistance of hydrate storage heat-insulating coating. The results of dissociated propane hydrate temperature regime experimental studies are given. A mathematical model for calculating the gas hydrates decomposition in nonequilibrium conditions is developed. The practical significance of the study results is to determine the numerical relationship between the hydrate dissociation rate, climatic data and the coating thermal protection properties. Prospects for further scientific developments in this direction are the optimization of constructive solutions for the hydrate storage enclosing structures.

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