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REPOSITORY OF GAS HYDRATES

The article considers technology of production of gas hydrate with purpose it transportation and storage. The optimal parameters defined of storage of hydrates in terrestrial repositories at the nonequilibrium the conditions and melting of blocks with the internal source of energy preserved with ice crust. During research of kinetics of dissociation of samples of gas hydrate with the internal source of energy preservation with ice crust established that most of blocks to the moment of full dissociation long time was in the nonequilibrium conditions. In the process of dissociation of the samples was fixed effect self-preservation, melting of the surface of ice crust and freezing its basics. The dependence that describes the correlation-regressive relation between a surface area of hydrate block and the difference between fugacity of gas in the three-phase equilibrium and free gas was installed. The proposed gas hydrate technology makes it possible to solve the problem of diversification of sources of natural gas supplies, the development of a large number of small and medium sized remote gas deposits (including being in the form of gas hydrate), efficient use of resources associated gas, of shale gas and coal bed methane, and gas supply consumers in the absence of the pipeline.

Keywords: *storage of gas, hydrate technology, gas hydrate block, self-preservation, icy crust, dissociation, equilibrium conditions.*

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СХОВИЩА ГАЗОВИХ ГІДРАТІВ

Розглянуто технологію виробництва газогідрату з метою його транспортування і зберігання. Визначено оптимальні параметри зберігання в наземних гідратосховищах за нерівноважних умов і плавлення газогідратних блоків із внутрішнім джерелом енергії, законсервованих льодяною кіркою. У процесі дослідження кінетики дисоціації зразка газогідрату із внутрішнім джерелом енергії, законсервованого льодяною кіркою, встановлено, що переважна частина газогідрату до моменту повної дисоціації тривалий час знаходилась у нерівноважних умовах. У процесі дисоціації зразка зафіксовано прояв ефекту самоконсервації, плавлення поверхні льодяної кірки та наморозування її основи. Установлено залежність, що описує кореляційно-регресивний зв'язок між площею поверхні гідратного блока і різницею фугитивностей газу в трифазній рівновазі та вільного газу. З'ясовано, що запропонована газогідратна технологія дозволяє розв'язати проблему диверсифікації джерел постачання природного газу, розробки значної частини малих та середніх віддалених родовищ газу (в тому числі у формі газогідрату), ефективного використання ресурсів попутного нафтового газу, сланцевого газу та метану вугільних пластів, а також забезпечення споживачів газом за відсутності трубопроводу.

Ключові слова: *зберігання газу, газогідратна технологія, газогідратний блок, примусова консервація, льодяна кірка, дисоціація, рівноважні умови.*

Problem statement. Reserves of natural gas and other hydrocarbons rapidly are exhausted. 80% of the open gas fields are classified as small or average distant. Therefore, the problem of rational using of existing gas resources is relevant today. However the traditional technology of it using are often ineffective. For example, a large number of small and medium distant gas fields not developed because of the problem of accumulation and transportation.

Diversification of gas supply sources is important for many countries. Transportation of natural gas is carried out by pipelines or LNG-tankers at present. These technologies are effective the presence of significant reserves at the deposit and high level of investment [1]. In recent years, a technology based on the ability of molecules of gas and water to form gas hydrates, actively developed. Significant volumes of gas in the gas hydrate can keep a long time at atmospheric pressures and slight temperature below zero [2]. In 1 m³ of gas hydrate contains 160 m³ of methane [3, 4].

Recent research analysis and publications on the problem. However, the broad introduction technology in connection with the imperfections is not become yet. Some concepts of transporting of gas in hydrate form are considered today. However, transport of gas hydrates in equilibrium conditions at insignificant temperatures below zero and atmospheric pressure are the most attractive. The necessity of production of gas hydrate structures fit for transport and storage in these conditions lies at it basis. Granular gas hydrate is the main form of its transportation, but it has some flaws at present. Monolithic blocks of large size consider favorable variant. However, the technology their industrial production has not yet worked out [3]. To increase the efficiency of transportation and storage technologies of gas hydrates we suggest to produce it in the form of gas hydrate blocks with the internal source of energy and to preserve with ice crust. However, the parameters of storage and the dissociation of gas hydrate blocks, a key element of the proposed technology, are studied insufficiently [5, 6].

Objectives. Therefore, installation of optimal parameters storage in the non-equilibrium conditions and dissociation of gas hydrate blocks with the internal source of energy preserved with ice crust is the purpose of the study. For conducting of experiments samples of gas hydrates ($d = 81$ mm, $h = 102$ mm,) are produced according to the technology (Fig. 1, a) that described in [5, 6]: 110 pellets were mixed with 375 cm³ hydrate a powdered of a porosity 0.51 (Fig. 1, c, 1, d); after the formation porosity of a homogeneous sample are 0.12 (Fig. 1, e, 1, f); cooled samples forcibly were preserved with a layer of ice (for this purpose, we applied at their surface in two steps certain amount of water (Fig. 2)).

A melting of the samples performed in the device illustrated in Pic. 3 at atmospheric pressure ($P_1 = 0.1$ MPa = const) and temperature $T_1 = 275.3$ K (initial temperature of the sample $T_0 = 263$ K). Volume of gas, which stand out, and changing of temperature at the surface, in the depth 7 – 10 mm and on the center of the sample recorded with the time.

Material research. The process took place in several stages: surface heating to the melting temperature of ice, melting of ice crust, slow dissociation of gas hydrate to the gas and water. Border of ice crust of hydrate cannot be installed on the surface of gas hydrates visually. Therefore the beginning of formation of microbubbles on the surface of the sample, which testified about the beginning of dissociation of gas hydrates, was considered the time of completion of melting crust. However, the structure of gas hydrates, its temperature and the temperature of the gas around of the sample match the settings manifestation of effect of self-preservation. So we considered that in the process of dissociation its surface always was covered with ice crust. This allowed mass of gas hydrate before moment of dissociation a long time is in nonequilibrium conditions. Rising of temperatures at the surface of the sample from 258 to 273 K and in the center of the sample on the some value was according to the formula [7].

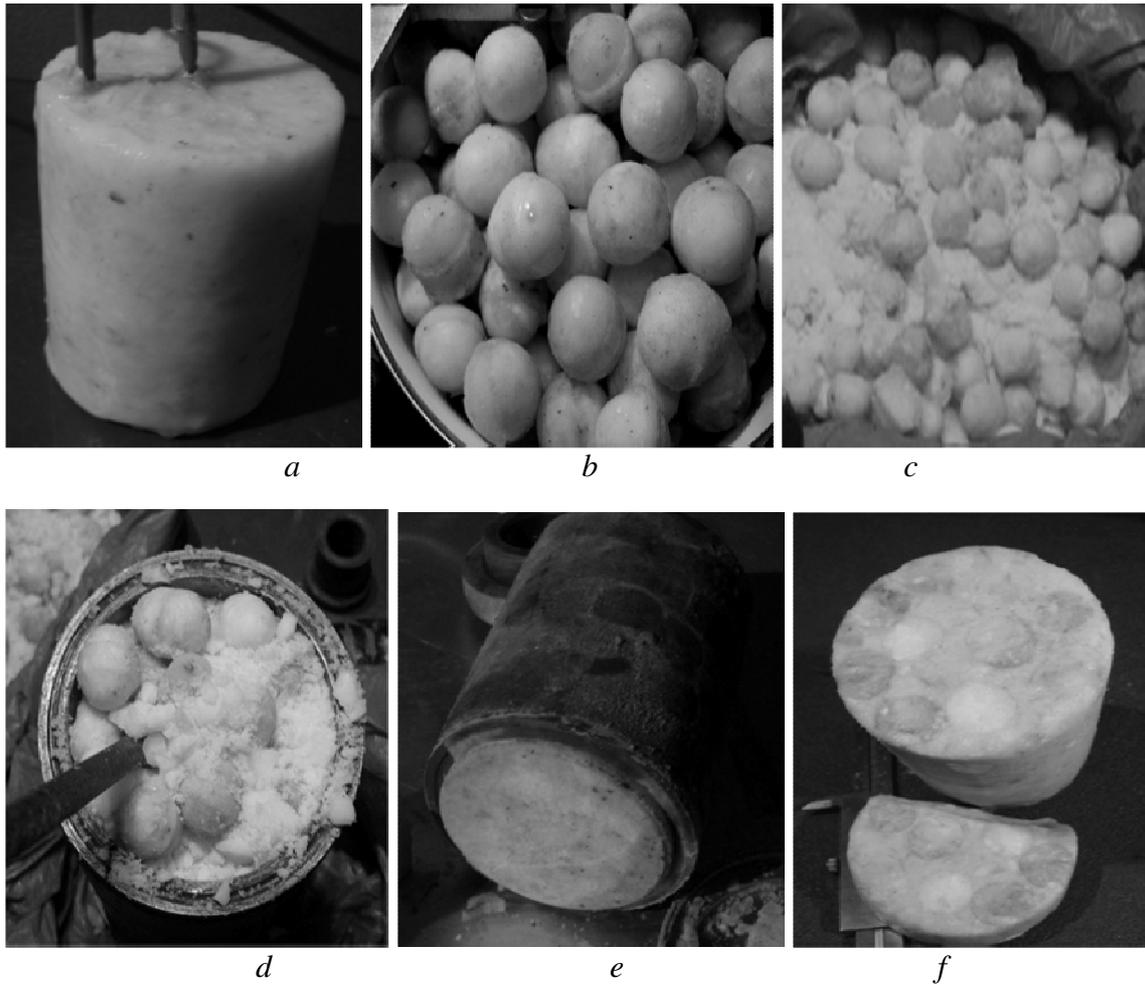


Figure 1 – Stages of formation of gas hydrate blocks:
a – hydrate unit with the built with temperature sensing devices
b – granular hydrates; c – mixing of granulated and powdered of gas hydrates;
d – load the mixture into the form; e – sample after formation of gas hydrates;
f – cross-sectional of the sample hydrate

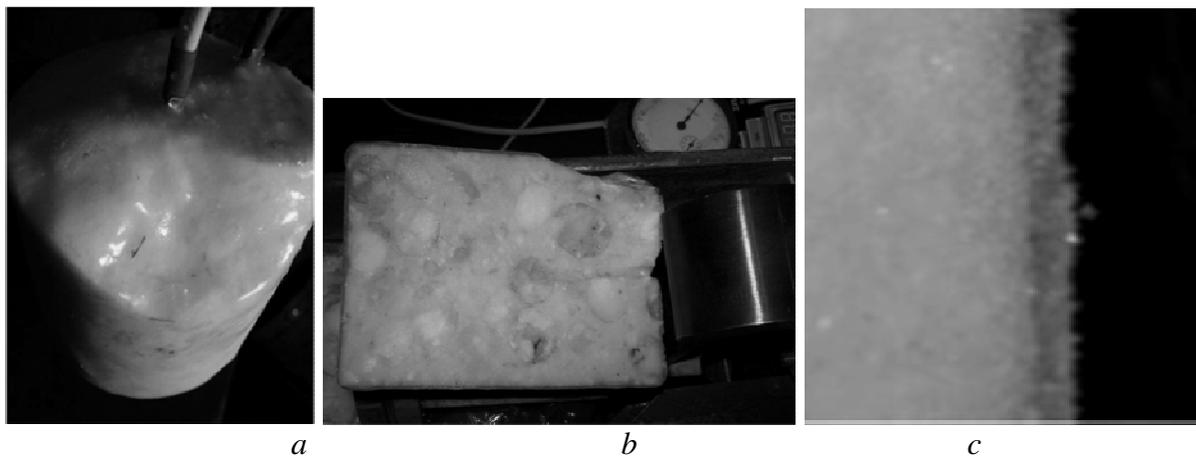


Figure 2 – Force preservation of hydrate block with ice crust:
a – typical shine of layer of ice at the sample;
b, c – ice crust cross section of the sample



Figure 3 – A device for studying the melting of process of gas hydrates

$$\theta/\theta' = f(Fo, Bi), \quad (1)$$

where θ and θ' – the dimensionless values of temperature.

Surface of the sample contacted with the gas which released because it was placed under the glass case during experiment (Fig. 3) Complex process of convective heat exchange in this case we considered as a elementary thermal conductivity, taking into account the equivalent coefficient of thermal conductivity λ_{ek} and the coefficient of convection ε_k ($\varepsilon_k = \lambda_{ek} / \lambda_p$, where λ_p – the thermal conductivity of the gas phase).

As the $10^3 < Gr_p \cdot Pr_p < 10^6$, coefficient of convection was determined according to the formula

$$\varepsilon_k = 0.105 \cdot (Gr_p \cdot Pr_p)^{0.3}, \quad (2)$$

where Gr_p , Pr_p – criteria of Grashof and Prandtl.

Hence, λ_{ek} amounts to 0.057 W/(m·K) and $\alpha = \lambda_{ek}/x = 1.66$ W/(m²·K).

Criterion Bio can be written as

$$Bi = \frac{\alpha R}{\lambda_{zz}} = \frac{\lambda_{ek} R}{x \lambda_{zz}}, \quad (3)$$

where λ_{zz} – the thermal conductivity of gas hydrates, W/(m·K); R – radius of the sample of cylindrical shape, m; $Fo = a \tau R^2$.

Considering the calculated values of criteria Bi and Fo and influence of length of a cylinder for heating, and used the graphs of dependencies $\theta_c/\theta' = f_c(Fo, Bi)$ and $\theta_o/\theta' = f_o(Fo, Bi)$ for the cylinder of infinite length, we defined time during which surface of hydrate block was warmed to the temperature $t_c = 273.15$ K. The process lasted during 5100 s.

Thus the temperature at the center of the sample rose to $t_o = 271.4$ K.

This interval determines the balance of heat flow, which goes to the crust of ice and the surface of the sample, namely, the difference between temperature melting of ice and air, melting of ice and hydrate, equilibrium temperature of gas hydrate and the temperature of the sample, intensity of heat exchange between air and surface of the sample and the thermal conductivity of hydrates.

Then we observed the following: process of heating the inside of the sample continued, and the temperature its surface remained the same ($T_{melt} = 273$ K = const); there was a gradual melting formed on the surface of ice crust and draining of water; dissociation of hydrate layer adjacent to crust (because endothermic the process of the system seeks to equilibrium what at atmospheric pressure is at temperatures below 273 K) observed and

supercooled water appeared at the same time; evolution of gas during of dissociation of the gas hydrate from the surface of the sample observed as individual of bubbles. When the initial temperature is slightly higher than the equilibrium, they broke integrity of the ice layer and came out through the surface periodically for some time. However the crust of ice at the site of the destruction rapidly recovered as a result of crystallization of layer of supercooled water; crystallization of supercooled water with the formation of ice on the border of crust and hydrate of a new layer ice; the gradual decrease in the size of the sample and moving of contact surface of phase («gas – water», «water – ice», «ice – supercooled water», «supercooled water – hydrates») to the center of the sample.

Under similar conditions, the process ($P_3 = R_{pie}$) in case of isobaric of process of dissociation of gas hydrates ($V = \text{const}$) when a equilibrium pressure in the volume of a gas stops. This process describe a mechanism of cessation of dissociation of gas hydrates, which occurs under by crust of ice to formed on the surface of hydrate blocks too. At the same time heating of preservation hydrate in ice leads to the establishment of equilibrium pressure in its pores for hydrate of this composition. That is preservation of gas hydrate structures with the ice crust allows to create and sustain thermobaric conditions of stability of gas hydrate masses at the time when the sample is stored in nonequilibrium conditions.

The simplified process of heating of surface of hydrate the blocks can be considered as nonstationary thermal a process with the boundary conditions of third kind. The differential equation of thermal conductivity for an infinite length of cylinder of radius R will be followed

$$\frac{\partial \vartheta}{\partial \tau} = a \left(\frac{\partial^2 \vartheta}{\partial r^2} + \frac{1}{r} \cdot \frac{\partial \vartheta}{\partial r} \right). \quad (4)$$

The initial conditions for $\tau = 0$ $\theta = \theta'$, where $\theta' = t_{noe} - t'$; t_{noe} – air temperature, K; t' – initial temperature of the hydrate block, K.

Boundary conditions for

$$\lambda_{ze} \frac{\partial \theta}{\partial r} = \alpha \theta. \quad (5)$$

Solution a relatively of dimensionless values θ_n/θ' , θ_0/θ' , where θ_n – surface temperature, θ_0 – temperature in the center of the block is a function of two criteria: $Bi = \alpha R/\lambda_{ze}$ and $Fo = \alpha \tau/R^2$. Dependencies $\theta_n/\theta' = f(Bi, Fo)$ are presented graphically in the work [7]. Time, surface temperature and in the center of hydrate block are defined here. The process of melting of the ice crust is schematically shown in Fig. 4.

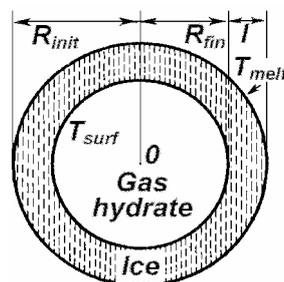


Figure 4 – Scheme of the melting process of ice crust

For simplification of calculations initial temperature of gas hydrates in the volume of the block assume uniform and equal to the temperature melting point of ice $T_{sunt} = 273.15 \text{ K} = \text{const}$. The temperature on the side surface immediately rises to the temperature $T_{melt} > T_{surf}$, and is supported throughout the process of melting of ice cover. At the same time a liquid layer with thickness $R_{init} - R_{fin} = l$ forms on surface of the cylinder. The problem is formulated as follows:

$$\frac{\partial T(r, \tau)}{\partial \tau} = a \left(\frac{\partial^2 T(r, \tau)}{\partial r^2} + \frac{1}{r} \frac{\partial T(r, \tau)}{\partial r} \right), \quad \tau > 0, R_{fin} < r < R_{init}. \quad (6)$$

The initial conditions for: $T(R_{init}, 0) = T_{melt}$.

Boundary conditions: $T(R_{init}, \tau) = T_{melt} = const$, $T(R_{fin}, \tau) = T_{surf} = const$.

Heat flux q occurs according with the law thermal conductivity Fourier, hence receive ratio

$$q = \lambda_{pi0} \frac{\partial T_{pi0}(r, \tau)}{\partial r} = -\alpha_{pi0} (T_{melt} - T_{surf}) = \rho_{\pi} L \frac{dR_{fin}}{d\tau}, \quad (7)$$

where $\alpha_{pi0} = \lambda_{pi0}/l$; λ_{pi0} – thermal conductivity of the liquid.

Suppose the distribution of temperature in the layer of water occurs according with the law of distribution for hollow cylinder in the steady state [8]

$$T(r, \tau) = - \frac{(T_{surf} - T_{melt}) \ln r + T_{melt} \ln R_{fin} - T_{surf} \ln R_{init}}{\ln \left(\frac{R_{init}}{R_{fin}} \right)}. \quad (8)$$

The solution (8) satisfies boundary conditions and the differential equation (7). Substituting (8) into (7), we obtain

$$\lambda_{pi0} \frac{T_{surf} - T_{melt}}{R_{fin} \ln \frac{R_{init}}{R_{fin}}} = \rho_{\pi} L \frac{dR_{fin}}{d\tau} \quad (9)$$

Equations (9) also is differentiated obtain the formula for the description of dependency of layer thickness l of water on the time τ .

$$\frac{R_{fin}^2}{2} \ln \frac{R_{init}}{R_{fin}} - \frac{1}{4} (R_{init}^2 - R_{fin}^2) = \frac{\lambda_{pi0} (T_{surf} - T_{melt})}{\rho L} \tau. \quad (10)$$

For approximate calculate the time of melting of ice crust we assume the temperature of hydrate blocks at each point equal to the temperature of melting of ice $T_{surf} = 273.15$ K. And the temperature on the side surface immediately increases to temperature $T_{melt} = 275.3$ K and is supported throughout the process. When the thickness of ice crust 3 mm. time of its melting according to (10) was 1020 s and approximately corresponds to the experimental data. For the description of the process of dissociation of gas hydrates, we used the equation in which the driving force of the process is expressed through the difference of fugacity of gas for three-phase equilibrium and of the free gas [9]

$$-\frac{dn_H}{d\tau} = kA(f_{eq} - f), \quad (11)$$

where n_H – number of moles of gas hydrates, mol; τ – time, s; k – coefficient; A – the surface area of gas hydrates which dissociates (melts) m^2 ; f_{eq} and f – fugacity of gas for three-phase equilibrium and of the free gas, respectively, Pa.

This dependence is used for processing of experimental results:

$$-\frac{dn_H}{d\tau} = kA^\alpha (f_{eq} - f)^\beta, \quad (12)$$

where α, β – empirical coefficients.

Equation (12) logarithm problem, enter the a replacement $\tilde{Y} = \ln Y$, $a_0 = \ln K$, $\tilde{X}_1 = \ln A$, $\tilde{X}_2 = \ln(f_{eq} - f)$, proceed to the linear equation. The calculation is performed by least squares. The next equity received:

$$\tilde{Y} = 1.43\tilde{X}_1 - 1.75\tilde{X}_2 - 1.82. \quad (13)$$

The empirical coefficients are determined and adequacy of mathematical model to experimental data is checked.

Thus, the equation that describes the connection between the surface area of hydrate block and difference of fugacity of gas in three-phase equilibrium and the free gas is as follows:

$$-\frac{dn}{d\tau} = 0,1622 \cdot A^{1.426} \cdot (f_{eq} - f)^{-1.75} . \quad (14)$$

Graph of dependence of rate of dissociation of hydrate block from the time is shown in Fig. 5.

Mass fraction of gas residue in the samples in the process of dissociation with the time is determined according to the formula

where V_{fin} – volume of gas as contained in sample at present, m^3 ; V_{init} – initial gas content in the sample, m^3 .

Dependence of the mass fraction of gas remaining in the sample from time to time (Fig. 6), is established and empirical coefficients are determined

$$n_r = V_{fin} / V_{init}, \quad (15)$$

$$y = 1.056 \exp(-0.59\tau). \quad (16)$$

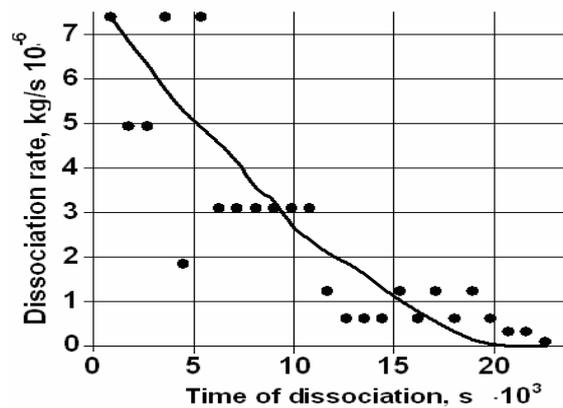


Figure 5 – The dependence of dissociation rate of the sample of gas hydrates on the time

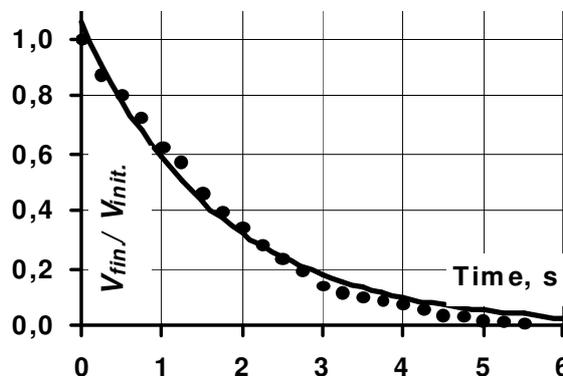


Figure 6 – The dependence of the mass fraction of gas remaining in the sample, with initial it of dissociation

Thus, the heating of surface of hydrate block with an internal source of energy preservation with ice crust to the melting point of ice is not accompanied by the active dissociation of gas hydrates and is controlled by heat balance of the crust.

Conclusions. During research of kinetics of dissociation of samples of gas hydrate with the internal source of energy preservation with ice crust established that most of blocks to the moment of full dissociation long time was in the nonequilibrium conditions. In the process of dissociation of the samples was fixed effect self-preservation, melting of the surface of ice crust and freezing its basics (as a result of crystallization of supercooled water formed after of dissociation of the surface of layer of hydrates). The dependence that describes the correlation-regressive relation between a surface area of hydrate block and the difference between fugacity of gas in the three-phase equilibrium and free gas was installed. Dissociation of the samples of gas hydrate produced according to the proposed technology, occurred not damaging them integrity at the heating for a long time. Thermobaric the equilibrium conditions were established for a given hydrate at the heating of preservation with the ice crust of the sample of gas hydrates in its pores.

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