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MATHEMATICAL MODELING OF A CYLINDER WITH A SORBENT AND NATURAL GAS

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A cylinder for adsorption storage of natural gas is modeled. A system of differential equations describing the dynamics of nonequilibrium sorption is formulated. The process of withdrawal of gas from the cylinder is numerically analyzed.

As a result of the decrease in petroleum reserves, the harnessing of natural gas as motor fuel has increased in recent years. This has generated a need for the development and improvement of systems which are based on the use of sorbents for storage of natural gas on vehicles. Such systems have the main advantage that they make it possible to significantly decrease the re-fueling pressure, providing a volume storage density comparable with more traditional cylinders with a compressed gas.

Special features of the thermodynamic processes of filling an adsorption cylinder with natural gas and its discharge are described by the equation of equilibrium state $a_{\text{eq}} = a_{\text{eq}}(P, T)$ and the kinetic equation of sorption determining the rate of the sorption a tending to its equilibrium value $a_{\text{eq}}(P, T)$. When the gas is withdrawn from a cylinder filled with a sorbent, the endothermic process of desorption occurs in the cylinder. This process is due to the absorption of the heat of phase transition q_{st}, which causes the cylinder to cool. The cooling of the sorbent is undesirable, since it increases the unwithdrawn gas mass in the cylinder. When a vehicle moves and gas is withdrawn from the cylinder the initial pressure P_0 in it decreases to a certain final discharge pressure P_{e} (usually, at the level of several atmospheres). According to the equation of state, the lower the mean temperature of the sorbent $\overline{T}_{\text{e}}$, the larger the unwithdrawn gas mass $m_{\text{e}} \sim a(P_{\text{e}}, \overline{T}_{\text{e}})$. In a moving vehicle, there are many heated parts, the heat of which can be used to decrease the unwithdrawn gas mass by heating the cylinder, but this must not be in contradiction with the requirements of safety. In order to fulfill the requirements of economical efficiency and safety, the characteristics of the cylinder should be optimized. Because of this, in each specific case it is necessary to perform numerical calculations of the thermodynamic processes of filling and discharge of the cylinder. Of importance is allowance for the sorption kinetics, which can significantly change the estimates of the unwithdrawn gas mass. In the case where a local equilibrium model is used, all the intraparticle and film resistances to the heat and mass transfer are ignored. The sorption nonuniformity becomes more significant for fairly small sorbent particles and for rapid processes.

The process of withdrawal of the gas from a constant-volume cylinder occurs at variable pressure, temperature, and gas mass. The pressure regulator at the outlet from the cylinder provides the required gas flow rate, which depends on the velocity of the vehicle and other conditions of its motion.

The complete mathematical model of a cylinder for storage of a gas in the adsorbed form [1] is based on a simultaneous solution of the system of equations of conservation of energy, momentum, and mass and the equation of adsorption with regard for the deviation of the investigated system from the equilibrium state. According to [1], in the typical case of discharge of a cylinder, certain physical phenomena can be ignored. Thus, the pressure differences across the cylinder are small as compared with its level. Therefore, there is no need to consider the equation of balance of momentum in the sorbent layer. This conclusion is also supported by experimental data. In the experiments performed in [1, 2], the pressure differences across the cylinder with the adsorbed gas were no more than 2000 Pa, and the characteristic values were at a level of 700 Pa.

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In [3], the two-dimensional problem of hydrodynamics and heat transfer was solved as applied to a cylindrical vessel with a sorbent filled with natural gas. Instead of the Ergan equation, the nonstationary equation of momentum was used. The density of the compressed methane was determined with the use of the law of ideal gas, since the calculations were performed at pressures of 0-3.5 MPa and temperatures of 283–363 K, at which the mean value of the coefficient of methane compressibility is 0.97. In this work, the equilibrium dynamics of the packed sorbent layer was considered.

An analogous approach was used in [4-6] in the theoretical investigation of the system cylinder–adsorbed gas.

In [2], Barbosa Mota presents a simpler dynamic model of an adsorption cylinder, in which allowance is made for certain processes influencing the characteristics of a slow discharge. This model is based on the assumption that the pressure is uniform, the accumulation of the gas phase in the cylinder is absent, the gas flow is axial, and there is an equilibrium between the sorbent and methane. Calculation of a variant on a 486-33 personal computer took only 2 min, while calculation of the complete model [1] on a Vax 8650 computer took 45 min. An analysis of the calculated and experimental results provided support for the assumptions made and showed that the heat capacity of the cylinder walls and the external heat exchange significantly influence the behavior of the system vessel–sorbent–gas. The simplified model made it possible to perform optimization calculations.

Since adsorption represents an exothermic process, every final rate of adsorption or desorption is related to the temperature changes in the bulk of the sorbent. Theoretical and experimental investigations [2-4, 7-9] have shown that the heat of adsorption has a particularly significant effect at the stage of desorption, where the rate of withdrawal of gas is determined by the consumption of energy necessary for the movement of the vehicle. Under the actual conditions, the mass of the released gas is always smaller than under idealized isothermal operating conditions. For example, in [2] a decrease of 37 K in the sorbent temperature was observed when the cylinder was discharged, which caused a 25% decrease in the volume of the desorbed gas as compared with isothermal conditions.

The objective of the present work is the mathematical modeling of the discharge of a heated adsorption cylinder with the radial direction of motion of the desorbed gas over a sorbent layer. The sorbent is heated with the help of a cylindrical heating element (HE) positioned on the axis of the cylinder. As an HE, a thermal tube, a thermosiphon, a single-phase heat exchanger, or an electric heating element can be used. The efficiency of the HE can be improved by using fins within the sorbent layer. In the subsequent discussion, we will assume that a thermal tube is used for the HE. The thermal tube represents a device with a high effective thermal conductivity equal to 10^3–10^4 W/(m·K), which makes it possible to transfer large heat fluxes to sorbent blocks at small temperature differences. A thermal tube can be easily mounted within the sorbent layer. The use of such a tube secures a small weight and small overall dimensions of the heat exchanger.

1. Mathematical Model of a System of Storage of Natural Gas in the Adsorbed State. The calculated element (Fig. 1) of the system of storage of natural gas in the adsorbed state (SSGAS) is bounded by the outer surface ($r = R$) of the metal body, the inner wall of the shell of the HE ($r = R_0$), and the planes of symmetry passing through the center of the fin ($z = 0$) and the center of the sorbent layer ($z = S$) between two neighboring fins. Along with the adsorbed gas there is a free gas in the cylinder. The free gas fills the macropores, while the adsorbed gas is predominantly confined by the forces of molecular interaction in the micropores.

The metal fin 1 in the form of a disk with a half-width δ is attached to the outer wall 3 of the HE. The annular sorbent layer 2 with radii r_0 and r_1 is adjacent to the fin of the HE. The thermal resistance of HE contact with the microporous sorbent is characterized by the coefficient of heat transfer α_s. Analogous contact resistances, but different in magnitude, can exist between the fin and the sorbent (α_{fs}) as well as between the fin and the outer wall of the HE (α_f).

On the outside the cylindrical sorbent layer is surrounded by a thin perforated aluminum tube for discharge of the gas released in the process of desorption. Since the thickness of the sorbent layer is much smaller than its length, the desorbed gas moves in the sorbent predominantly in the radial direction.

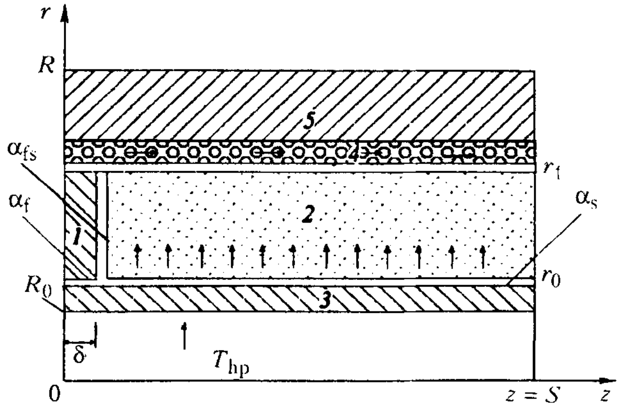


Fig. 1. Diagram of the calculated element of the SSGAS: 1) fin; 2) sorbent; 3) shell of the heating element; 4) channel for gas discharge formed by the perforated tube and the cylinder body; 5) cylinder body.

Between the perforated tube and the inner surface of the cylinder body there is the channel 4 through which the gas moves along the cylinder to the pressure regulator. The problem was set up with the assumption that at the cylinder outlet the gas flow rate is maintained constant with the help of the pressure regulator in the process of discharge. This factor, as well as the factor of heating/cooling the cylinder, determines the rate and character of a pressure change in the cylinder. The pressure in the cylinder increases when the cylinder is heated and, conversely, decreases when the gas is discharged from it. The resulting change in the pressure in the cylinder will depend on these two competing processes.

During the period of discharge the cylinder is cooled on the outside by contact with the environment with a temperature T_{env} and a coefficient of heat transfer α_{env} and is heated on the inside. Depending on the conditions of heating, a constant temperature T_{hp} or a constant density of the heat flux are mantained at the inner surface of the HE shell. The heat transferred from the HE to the center of the cylinder is distributed through the tube wall and the fin over the sorbent and is expended on heating all the structural materials and on maintaining the desorption reaction. A part of this heat is uselessly released to the environment. However, in the process of desorption the temperature in the sorbent layer can be decreased to such a degree that the sorbent will absorb heat from the environment.

In modeling we assumed that all the sorbent cells between the HE fins are under the same conditions. The resulting dependences for the entire cylinder can be obtained by simple summing over N identical cells.

The mathematical model of a cylinder filled with a sorbent and a gas is based on the following simplifying assumptions: 1) the pressure in the cylinder is uniform; 2) the resistance to the mass diffusion is small; 3) the temperature of the solid phase is equal to the temperature of the gas phase at each point, because of the high coefficient of volume heat transfer between them; 4) the free gas in the cylinder is ideal; 5) the heat energy expended on compressing or expanding the gas is not taken into account; 6) gas is flowing in the radial direction in the sorbent layer.

In accordance with the assumptions made, the model is described by the energy equation, the equation of mass balance, the approximate kinetic equation, and the equation of equilibrium state (equation of isothermic adsorption).

1.1. Equation of isothermal adsorption. The sorbent based on activated carbon is considered. The adsorption properties of activated carbons for gases are described with an accuracy sufficient for practical purposes by the potential theory of adsorption developed in [10, 11]. The Dubinin–Astakhov equation for the isothermal adsorption of methane within the temperature and pressure intervals that span the regions of supercritical states (T_{cr} = 190.77 K, P_{cr} = 4.626 MPa) is written in the form

$$a_{\mathrm{eq}} = \frac{W_0}{b} \exp\left(- B \frac{T^2}{\beta^2} \left[\ln \left(\left(\frac{T}{T_{\mathrm{cr}}} \right)^2 \frac{P_{\mathrm{cr}}}{P} \right) \right]^2 \right), \tag{1}$$

where W_0 is the limiting volume of the adsorption space representing the volume of activated carbon micropores, B is a constant dependent on the dimensions of micropores, b is a constant from the van der Waals equation, and β is the affinity coefficient.

The heat of the phase transition of sorption can be calculated with a Clausius–Clapeyron equation supplemented with corrections. In accordance with [12], the isosteric sorption heat of a gas mole is determined by the formula

$$q_{\mathrm{st}} = \left(1 - \frac{V_{\mathrm{a}}}{V_{\mathrm{g}}} \right) T R_{\mu}\, z_{\mathrm{g}} \left[\frac{\partial \ln P}{\partial \ln T} \right] \Bigg|_{a=\mathrm{const}} .$$

When the gas phase is ideal ($z_{\mathrm{g}} = 1$, $V_{\mathrm{a}} << V_{\mathrm{g}}$), the isosteric heat is calculated from the relation

$$q_{\mathrm{st}} = R_{\mu}\, T \left[\frac{\partial \ln P}{\partial \ln T} \right] \Bigg|_{a=\mathrm{const}} . \tag{2}$$

The limits of applicability of Eq. (2) are dependent on the degree to which the gas approximates the ideal gas, i.e., on the ratio between the partial molar volumes of the adsorbate and the gas phase and on the compressibility coefficient. In the case of a nonideal gas phase, the estimate obtained with (2) should be considered as being approximate. Because of this, many authors do not use Eq. (2) and address themselves to experimentally obtained values [4]. This strategy is used in the present work, where the calculations performed correspond to the experimentally obtained value $q_{\mathrm{st}} = 1150$ kJ/kg.

1.2. Approximate kinetic equation. Fairly high rates of desorption of molecules from microporous adsorbents are the necessary condition of efficient operation of the SSGAS on vehicles. Because of this, the SSGAS must be calculated with consideration for kinetic characteristics.

The process of desorption of molecules from bidispersed adsorbents such as activated carbons involves the following stages: escape of adsorbate molecules from the active centers on the adsorbent surface, diffusion of molecules in the initial porous structure, diffusion in secondary pores, evaporation from the outer surface of granules, and removal of the desorbate from the gas phase.

Estimation of the contribution of the rate of individual processes to the total rate of desorption, performed on the basis of the analysis of experimental data, has shown [11] that the velocity of molecular escape from the adsorbent surface is of crucial importance. The rate of mass transfer in adsorbent granules increases because of the migration of molecules over the surface of the pores. This transfer is given the name surface diffusion.

In practice, the dynamics of sorption is most frequently described by the Gluckauf equation [13], in which the motive force of the intradiffusion adsorption process is determined as the difference of the adsorbate concentrations in the solid phase:

$$\frac{da}{d\tau} = \beta_{\mathrm{k}} \left(a_{\mathrm{eq}} - a \right) , \tag{3}$$

where β_{k} is the kinetic coefficient.

Sakoda et al. [14-20] recommend assuming that the kinetic coefficient β_{k} in the approximate equation of the kinetics of sorption on activated carbons is equal to the total coefficient of mass transfer $\beta_{\mathrm{t}} = 15 D_{\mathrm{s}} / R_{\mathrm{p}}^2$.

The coefficient of surface diffusion D_{s} in a microporous sorbent is related to the temperature by the dependence $D_{\mathrm{s}} = D_{\mathrm{s}0} \exp\left[E / (R_{\mu} T) \right]$, where $D_{\mathrm{s}0}$ is a phenomenological constant.

For the sorption processes of filling an SSGAS with a gas and its discharge, we will use the kinetic equation in the form

$$\frac{da}{d\tau} = K_{s0} \exp\left(-\frac{E}{R_\mu T}\right)(a_{eq} - a) , \tag{4}$$

where $K_{s0} = 15D_{s0}/R_p^2$.

Thus, to describe the nonequilibrium desorption occurring in the process of discharge of a cylinder, it is necessary to use two equations. One of them (1) describes the dependence of the equilibrium value of the adsorption a_{eq} on the pressure and temperature, and the other (4) describes the time by which the nonequilibrium adsorption lags behind the equilibrium one a_{eq}. The relation of the magnitude of the adsorption a to the pressure manifests itself in Eq. (4) only as the dependence of a on $a_{eq}(P, T)$.

1.3. Continuity equation. The total density ρ' of the free and the adsorbed gases in the cylinder is expressed as $\rho' = \varepsilon c + \rho a$. In accordance with the assumptions made, the continuity equation for a cylindrical sorbent layer has the form

$$r\frac{\partial}{\partial\tau}(\varepsilon c + \rho a) + \frac{\partial}{\partial r} rcv = 0 . \tag{5}$$

In the process of heating and withdrawal of the gas the pressure in the cylinder changes. Its magnitude is determined with allowance for the fulfillment of the integral mass balance condition. The total mass of the gas in the calculated cell (Fig. 1) is determined by the integral $M_i = 2\pi\int_\delta^S\int_{r_0}^{r_1}(\varepsilon c + \rho a) r dr dz = M/N$, and the mass rate of the gas discharge out of the cell $g_i = g/N$ is given by the expression

$$\frac{dM_i}{d\tau} = -g_i . \tag{6}$$

The density of the free gas c is found from the equation of the ideal gas state:

$$c = \frac{P}{R_\mu T} . \tag{7}$$

Differentiating (7) with respect to time, we write

$$\frac{dc}{d\tau} = c\left(\frac{\partial \ln P}{\partial\tau} - \frac{\partial T}{T\partial\tau}\right) . \tag{8}$$

Substitution of the derivatives $dc/d\tau$ and $da/d\tau$ from (4) and (8) into (6) gives the equation

$$2\pi\int_\delta^S\int_{r_0}^{r_1}\left(\varepsilon c\left(\frac{d\ln P}{d\tau} - \frac{\partial T}{T\partial\tau}\right) + \rho K_{s0}\exp\left(-\frac{E}{R_\mu T}\right)(a_{eq} - a)\right) r dr dz = -g_i . \tag{9}$$

From this equation we can determine the rate of change in the pressure in the cylinder:

$$\frac{d\ln P}{d\tau} = (I_2 - I_3 - g_i)/I_1 , \tag{10}$$

where

$$I_1 = 2\pi \int_{\delta}^{S} \int_{r_0}^{r_1} \varepsilon c r dr dz\,; \quad I_2 = 2\pi \int_{\delta}^{S} \int_{r_0}^{r_1} \frac{\varepsilon c}{T} \frac{\partial T}{\partial \tau} r dr dz\,;$$

$$I_3 = 2\pi \int_{\delta}^{S} \int_{r_0}^{r_1} \rho K_{s0} \exp\left(-\frac{E}{R_\mu T}\right)(a_{eq} - a)\, r dr dz\,. \tag{11}$$

1.4. Equation of energy balance. The equation of heat energy balance for a sorbent in the cylindrical coordinate system can be written as follows:

$$r\,(\varepsilon c C_g + \rho C + \rho a C_a) \frac{\partial T}{\partial \tau} + r c v C_g \frac{\partial T}{\partial r} =$$

$$= \frac{\partial}{\partial r}\left(r \lambda_{eff} \frac{\partial T}{\partial r}\right) + \frac{\partial}{\partial z}\left(r \lambda_{eff} \frac{\partial T}{\partial z}\right) + r q_{st}\, \rho \frac{\partial a}{\partial \tau}\,. \tag{12}$$

Note that in the left-hand side of Eq.(12) the term corresponding to the axial convective motion of the gas in the porous sorbent is absent. Rearrangement of (12) with account for (1) and (4)-(9) gives the equation of heat balance

$$r\rho\,(C + aC_a) \frac{\partial T}{\partial \tau} = \frac{\partial}{\partial r}\left(r \lambda_{eff} \frac{\partial T}{\partial r} - \frac{g C_g T}{M} \int_{r_0}^{r_1} \rho' r dr\right) + \frac{\partial}{\partial z}\left(r \lambda_{eff} \frac{\partial T}{\partial z}\right) -$$

$$- r \varepsilon c T C_g \frac{d \ln P}{d\tau} + r q'_{st}\, \rho K_{s0} \exp\left(-\frac{E}{R_\mu T}\right)(a_{eq} - a)\,, \tag{13}$$

where $q'_{st} = q_{st} - TC_g$. In this equation, the effects of the nonequilibrium sorption and the existence of the free gas in the cylinder are taken into account. The influence of the sorption heat is modeled by the existence of an additional contribution to the heat capacity of the system and the existence of the source term in the right-hand side of the equation, related to the pressure change. Thus, the equation of equilibrium state (1), the kinetic equation (4), the equation of heat balance (13), and Eq. (10) describing the rate of change in the pressure in the cylinder in accordance with the integral law of conservation of mass form the system of functional equations for determining the variables T, P, and a.

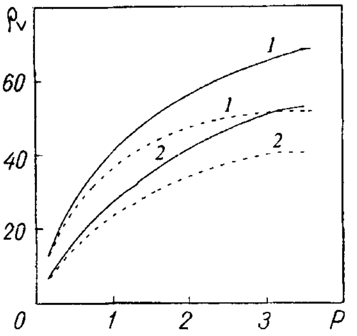
1.5. Initial and boundary conditions. In the calculations we assumed that at the initial stage of the process of desorption of methane and its withdrawal from the cylinder the initial pressure and temperature fields were as follows: $P|_{\tau=0} = P_0$ and $T(r, z)|_{\tau=0} = T_0(r, z) = T_{env}$. The pressure and the temperature determine the initial mass of the gas in the cylinder M_0 and, correspondingly, the initial mass in the calculated cell.

The boundary conditions were set for four surfaces (Fig. 1):

$$\left.\frac{\partial T}{\partial z}\right|_{z=0} = 0\,, \quad \left.\frac{\partial T}{\partial z}\right|_{z=S} = 0\,; \tag{14}$$

$$-\lambda \left.\frac{\partial T}{\partial r}\right|_{r=R} = \alpha_{env}(T - T_{env})\,, \tag{15}$$

$$-\lambda \left.\frac{\partial T}{\partial r}\right|_{r=R_0} = \frac{Q_{hp}}{2\pi R_0 S N} \quad \text{or} \quad T|_{r=R_0} = T_{hp}\,. \tag{16}$$



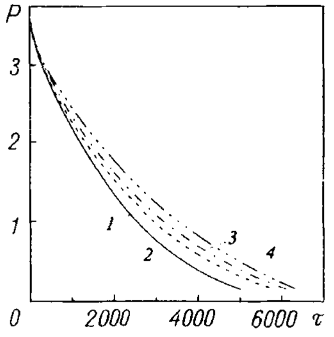


Fig. 2. Volume storage density of methane vs. pressure for different ambient temperatures: T_{env} = 223 (1) and 313 K (2); the continuous curve denotes the adsorbed and compressed gases; the dashed curve denotes the adsorbed phase. ρ_v, nm^3/m^3; P, MPa.

Fig. 3. The dynamics of change in the pressure in the process of discharge of the gas from the SSGAS for T_{env} = 273 K and different temperatures of the heated surface: 1) heat pipe is shut down; 2) T_{hp} = 283, 3) 303, and 4) 323 K. τ, sec.

The first condition (16) corresponds to the situation where the power Q_{hp} is known, and the second condition corresponds to the situation where the heating power is not limited and the temperature T_{hp} is set. This temperature is maintained at the inner surface of the heat pipe due to the contact of its evaporation zone with a large heated body, such as an engine.

1.6. The method of finite-difference solution. For the solution of the formulated mathematical problem with the initial and boundary conditions, we used the method of finite elements [21, 22] on a fixed grid. The number of triangular elements in the calculated region was from 200 to 300. The iteration algorithm of sequential solution of the equations of the system with mutual refinement was used.

2. Results of the Numerical Investigation. In the process of discharge of the adsorption cylinder the pressure changed within the prescribed interval from P_0 = 3.5 MPa to P_e = 0.15 MPa. Most of the numerical experiments were performed at a temperature T_{hp} on the heated surface with $r = R_0$. This temperature can change in the process of actuation of the heat pipe within several seconds, and then becomes practically constant (with time) after the establishment of the stationary regime. The conditions of actuation of the heat pipe were modeled by linearly changing its temperature for 120 sec from the initial value T_0 to the stationary value T_{hp}.

A set of calculations was performed in the interval of the ambient temperatures from 233 to 313 K. In this case, the properties of the sorbent corresponded to the properties of "Busofit-AUTM-2" microporous carbon fiber [23]. The empirical coefficients in the equations of nonequilibrium isothermal adsorption (1) and (4) were as follows: $W_0/b = 0.128$, $B/\beta^2 = 0.96 \cdot 10^{-5}$, E/R_μ = 940 K, and $K_{s0} = 7.5 \cdot 10^{-2}$ sec^{-1}.

The body of the cylinder of black steel had the following geometrical characteristics: length, 1.52 m; outside radius, 0.1095 m; thickness of the walls, 0.0065 m. The height of the finning disks was in line with the external boundary of the cylindrical sorbent layer. The radius of the heat pipe R_0 was equal to 0.02 m, and the radius of the outer sorbent layer was 0.086 m.

In the calculations, the parameters of the problem were varied in the following ranges: temperature of the surface of the heat pipe, 0–200°C; rate of gas withdrawal, 0.2–0.7 g/sec; thickness of the aluminum fin, 0.5–3 mm; step of finning, 0.02–0.3 m. It was assumed that the initial temperature is equal to the ambient temperature. The data of the basic calculation corresponded to T_{env} = 273 K, T_{hp} = 303 K, g = 0.3 g/sec, α_{env} = 3 W/(m^2·K), $\alpha_s = \alpha_{fs}$ = 500 W/(m^2·K), and α_f = 1000 W/(m^2·K). Since the coefficients of heat transfer were relatively high, their influence was negligibly small, which corresponds to the existence of a nearly ideal heat contact between the porous sorbent and the metal. However, it does not always happen that such an opti-

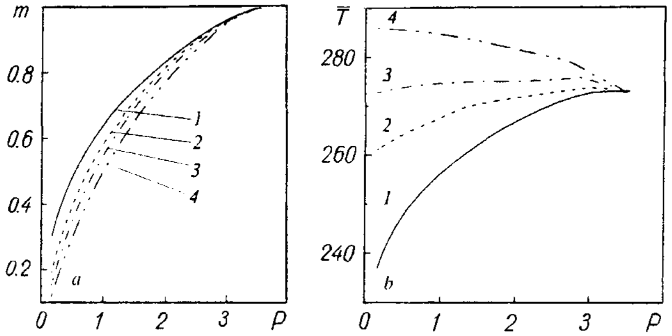


Fig. 4. Dynamic coefficient of filling the cylinder (a) and mean temperature of the sorbent (b) vs. pressure in the SSGAS for $T_{\rm env}$ = 273 K and different temperatures of the heated surface: 1) heat pipe is shut down; 2) $T_{\rm hp}$ = 283; 3) 303, and 4) 323 K. $\bar{T}$, K.

mistic situation occurs. The thermal resistance of contact depends on the technological fastening of the fins and can be very high. We performed a special series of calculations with the aim of determining the values of these resistances. The calculated data were compared with the experimental results.

The main measure of the efficiency of an SSGAS is the volume storage density ρ_v that represents the ratio of the volume occupied by the gas contained in the cylinder under normal conditions to the actual volume of the cylinder. Along with this quantity, the dynamic coefficient of filling the cylinder m is used in analyzing the process. At the initial moment this quantity is equal to unity, and at the discharge pressure the coefficient of filling shows the fraction of unwithdrawn gas mass $m_e \sim a(P_e, \bar{T}_e)$. Other characteristics of the process are the time of discharge, the mean-volume temperature of the sorbent layer $\bar{T}$, and the pressure in the cylinder P.

Figure 2 shows the dependence of the volume storage density of methane in the cylinder with allowance for a free gas and without allowance for it for different ambient temperatures. It is evident that at pressures of 2–4 MPa it is necessary to take into account the presence of the compressed gas in the SSGAS, the fraction of which can account for 30%. As follows from Fig. 2, the cylinder filled with "Busofit-AUTM-2" carbon fiber can provide a volume storage density of methane of 50–60 nm^3/m^3 at a re-fueling pressure of 3.5 MPa and temperatures of 233–313 K. This value is almost twice as high as that in traditional systems of storage of natural gas in the compressed state at the same pressure.

Figures 3 and 4 show the curves of change in the pressure, the dynamic coefficient of filling, and the mean temperature of the sorbent in the process of discharge of the cylinder for four variants of the heating conditions. In one variant, the influence of the pressure was excluded, which was achieved in the numerical experiment by positioning the nonconducting interlayers ($\alpha_s = \alpha_f = \alpha_{fs} = 0$) between the heat-pipe body, the sorbent, and the fin (Fig. 1). Thus, in the variant where the heat pipe was shut down the sorbent layer thermally interacted only with the environment, and at all the remaining boundaries the heat flux was absent.

The heating of the cylinder, characterized by the temperature $T_{\rm hp}$, significantly influences the pressure in it (Fig. 3). As this temperature increases, the pressure in the cylinder decreases more slowly at the same gas flow rate. As a result, at $T_{\rm hp}$ = 323 K, at the final stage of the discharge process the unwithdrawn gas mass decreases by a factor of three, from 30 to 10%, as compared with the variant where the heat pipe is shut down (Fig. 4a). When the heating is absent, the sorbent layer is cooled by 35 K as a consequence of the endothermic reaction of desorption (Fig. 4b), which decreases the time for which the cylinder can be used. An increase in the heating power makes it possible to withdraw the gas from the cylinder more completely, with the result that the run of the vehicle increases by approximately one-third. When the temperature of the heated surface $T_{\rm hp}$ was equal to 303 K, the absorbed heat of desorption was compensated and the process of discharge of the cylinder was performed under conditions approximating the isothermal conditions (Fig. 4a).

Figure 5 shows the results of the calculations aimed at optimizing the conditions of heating the cylinder. A very high temperature of the heat pipe can cause an overheating of the sorbent and an inadmissible increase in pressure. A very low temperature can make impossible a proper compensation for the spontaneous

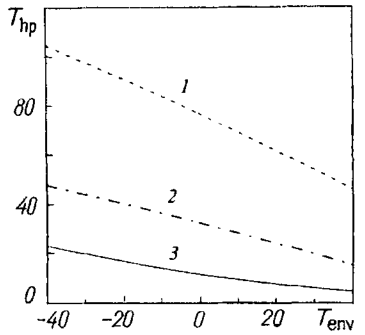


Fig. 5. Temperature of the heat-pipe surface, at which the unwithdrawn gas mass in the SSGAS accounts for 15% (at a pressure of 0.15 MPa), vs. ambient temperature for different gas flow rates: 1) $g = 0.5$, 2) 0.3, and 3) 0.2 g/sec. T_{hp}, T_{env}, °C.

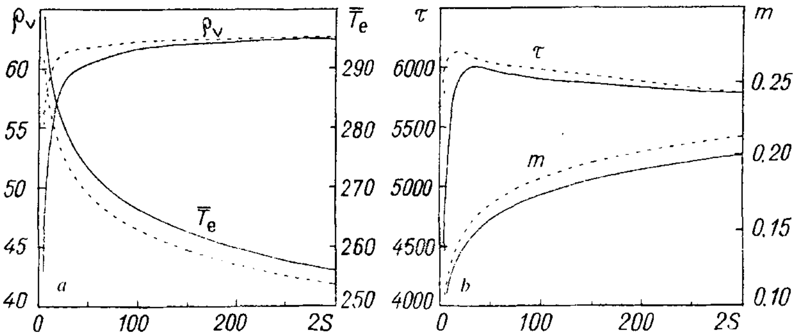


Fig. 6. Influence of the width of the step and the thickness of the finning of the heat pipe on the volume storage density and the mean temperature of the sorbent (a) and on the discharge time and dynamic coefficient of filling (b) at the final stage of the process of withdrawal of the gas from the SSGAS: $2\delta = 3$ mm (continuous curve); 1 mm (dashed curve). ρ_v, nm^3/m^3; $\bar{T}_e$, K; $2S$, mm.

cooling of the sorbent layer as a result of desorption. In this case, as in many other cases, the heat pipe serves as an element of the thermal control system. In Fig. 5, the temperature of the heat pipe required to ensure that at the final stage of the discharge process the unwithdrawn gas mass in the cylinder is 15% of the initial gas mass is plotted on the axis of ordinates, and the ambient temperature is plotted on the abscissa. At an average gas flow rate g of 0.3 g/sec and an average ambient temperature T_{env} of 273 K, this temperature was equal to 100°C, which corresponds to a power of the additional heating of about 300 W. When the ambient temperature decreases in winter, it is necessary to increase the temperature of the heat pipe. The rate of gas withdrawal can also be increased by increasing the heat-pipe temperature.

The following set of curves reflects the results of investigating the dependence of the volume storage density of the gas in the SSGAS on the geometrical characteristics of the finning of the heat pipe. The existence of the finning makes it possible to perform a more uniform heating of the sorbent layer. However, in this case the system becomes more expensive and the effective space of the cylinder decreases, which decreases the volume storage density. Because of this, it is of importance to determine reasonable parameters of the finning. The influence of the finning parameters on the characteristics of the cylinder is illustrated in Fig. 6. On the one hand, a decrease in the step of finning contributes to a better heating of the sorbent and decreases the dynamic coefficient of filling the cylinder m at the final stage of the discharge process. On the other hand, more closely spaced fins of the heat pipe decrease the effective volume, the mass of the sorbent, the mass of the accumulated gas, and the time of discharge of the cylinder, and this effect manifests itself more strongly in the case

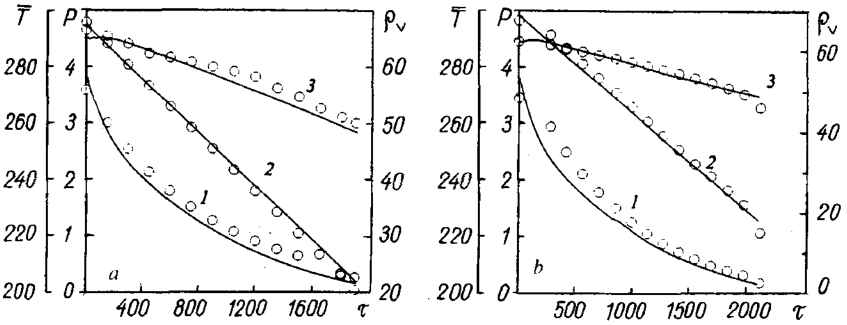


Fig. 7. Experimental points and calculated curves of the values of the mean temperature of the sorbent (3), the pressure (1), and the volume storage density of methane (2) as functions of time in the process of discharge of the SSGAS: a) $Q_{\text{hp}} = 0$; b) 80 W.

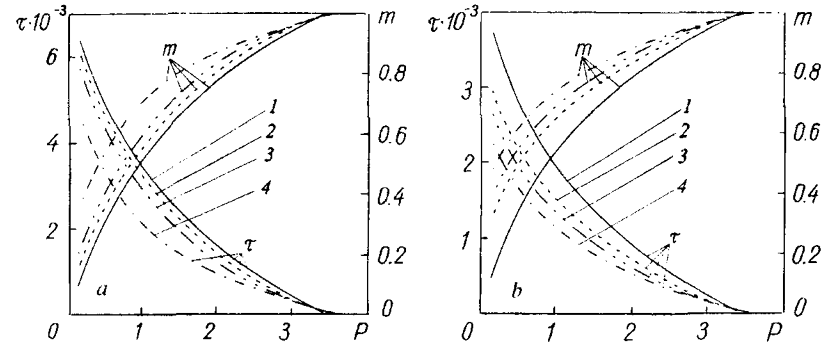


Fig. 8. Influence of allowance for the kinetics on the characteristics of the SSGAS discharge: a) $g = 0.3$ g/sec; $T_{\text{hp}} = 273$ K; 1) equilibrium model; 2) K_{s0}; 3) $0.5K_{s0}$; 4) $0.2K_{s0}$; b) $g = 0.5$ g/sec; heat pipe is shut down; 1) equilibrium model; 2) $2K_{s0}$; 3) K_{s0}; 4) $0.5K_{s0}$.

of thick fins. Moreover, very thin fins with a thickness of less than one millimeter are not technological. An increase in the thickness of an aluminum fin from 1 to 3 mm only negatively influences the volume storage density. Fins with a thickness of 1–1.5 mm are quite sufficient to achieve the effect of heating.

As is seen from Fig. 6b, the maximum on the curve of the dependence of the time of discharge of the cylinder on the width of the finning step corresponds to the step $2S = 30$ mm for a fin thickness of 1 mm and to the step $2S = 40$ mm for a fin thickness of 3 mm. The use of a finning step larger than 70–80 mm does not improve the efficiency of the cylinder and causes a marked decrease in the volume storage density. The number of fins corresponding to the maximum on the curve $\tau(S)$ provides a sufficiently small unwithdrawn gas mass that does not exceed 15%.

To verify the reliability of the mathematical modeling we compared the results of the calculations with the experimental data on the withdrawal of methane [24] obtained at the Laboratory of Porous Media of the Academic Scientific Complex "Heat and Mass Transfer Institute," National Academy of Sciences of Belarus.

A cylinder of volume 12.5 liters was tested at an ambient temperature T_{env} of 290 K at a constant heating power Q_{hp}. In this case, the gas flow rate was 0.2 g/sec. Figure 7 shows the dynamics of change in the mean-volume temperature of the sorbent, the pressure, and the volume storage density in the case where the heating element is shut down and the heating power $Q_{\text{hp}} = 80$ W. As follows from Fig. 7, all the basic parameters of the discharge agree satisfactorily with the experimental data. At the final stage of the process of withdrawal of the gas from the cylinder, the mean temperature of the sorbent increased as a result of heating by 7 and 8 deg in the calculation and in the experiment, respectively, and the time of discharge increased by 300 and 320 sec.

One of the objectives of the present work was to allow for the influence of the kinetics of sorption on the characteristics of a cylindrical vessel with a sorbent and methane. In actual adsorption systems for storage of a gas, the deviation from the equilibrium state can be very large. The developed nonequilibrium model makes it possible to analyze the process of withdrawal of the gas from such systems. Below we present the results of the calculations performed for different values of the preexponential factor K_{s0} in the kinetic equation (4). The change to the exponential model corresponds to an infinitely large K_{s0}. Figure 8a shows the dependences of the dynamic coefficient of filling and the current time of the process on the pressure in the cylinder. It is seen that at the value of K_{s0} determined experimentally under the conditions of discharge of a 12.5-liter cylinder, the infinitely rapid reaction differs insignificantly from the ideal reaction. However, under other conditions, such an important characteristic of the cylinder as the unwithdrawn gas mass can be significantly worse when the kinetics is taken into account. For comparison, a variant of calculation of the discharge of an SSGAS with no heating is presented in Fig. 8b. The deviation from the thermodynamic equilibrium becomes more marked at a low thermal conductivity of the sorbent and high contact resistances to the heat transfer.

CONCLUSIONS

1. A mathematical model of a cylindrical vessel filled with a sorbent and natural gas has been developed. This model is based on a two-dimensional nonstationary equation of heat balance, accounting for the deviation of sorption from the equilibrium state.
2. A numerical investigation of the SSGAS in the temperature range from −40 to +40°C and the pressure range from 0 to 3.5 MPa showed that this system of storage of natural gas in the adsorbed state is highly efficient.
3. When an adsorption transporting cylinder is used under extreme conditions of a high gas flow rate and negative ambient temperatures, the unwithdrawn gas mass in it can account for 30–50% of the initial gas mass. The unwithdrawn gas mass can be decreased by heating the sorbent with the use of a heat exchanger based on heat pipes. The use of a heat pipe in an SSGAS makes it possible to decrease the fraction of the unutilized gas to 10–15%. In this way, the run factor can be increased by 20%.
4. The dependence of the required temperature of the heated surface of the heat pipe on the ambient temperature and the gas flow rate was calculated. The calculations performed allow one to analyze the influence of individual factors on the operating characteristics of the SSGAS.

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NOTATION

a, current, or nonequilibrium, adsorption, kg/kg; c, density of free gas, kg/m^3; C, specific mass heat of the sorbent skeleton, J/(kg·K); C_g, specific mass heat of the free gas, J/(kg·K); C_a, heat capacity of the adsorbed methane, J/(kg·K); E, activation energy, J/kg; g, mass flow rate of the gas flowing out of the cylinder, kg/sec, g/sec; g_i, mass flow rate of the gas flowing out of the calculated cell of the cylinder, kg/sec; K_{s0}, preexponential factor in the approximate kinetic equation; m, dynamic coefficient of filling the cylinder; m_e, unwithdrawn gas mass; M, mass of the gas in the cylinder, kg; M_i, mass of the gas in the calculated cell, kg; N, number of calculated cells in the cylinder; P, pressure, Pa; q_{st}, heat of phase transition, or isosteric sorption heat, J/kg; Q_{hp}, power of heating of the entire cylinder, W; r and z cylindrical coordinates, m; R, outside radius of the cylinder shell, m; R_0, inside radius of the heating-element shell, m; r_0 and r_1, inside and outside radii of the annular layer of the sorbent, m; R_μ, gas constant, J/(kg·K); R_p, mean radius of the particles, mm; T_{hp}, temperature at the inner surface of the heating-element shell, K, °C; $2S$, finning step, m, mm; T, temperature, K, °C; $\overline{T}$, mean temperature of the sorbent layer, K; v, component of the velocity vector, m/sec; V_a, partial molar adsorption volume; V_g, molar gas-phase volume; z_g, coefficient of gas compressibility; α, coefficient of heat transfer, W/(m^2·K); ε, porosity determined as a part of the volume occupied by the free gas (not bound by adsorption); 2δ, fin thickness, m, mm; λ_{eff}, effective thermal conductivity of the sorbent layer, W/(m·K); ρ, density of the sorbent skeleton, kg/m^3; ρ', total density of the free and adsorbed gases in the cylinder, kg/m^3; ρ_v, volume density of storage, nm^3/m^3; τ, time, sec. Subscripts: eq, equilibrium conditions; a, adsorbate; cr, critical state; e, finite value; env, environment; hp, heat pipe; 0, initial value; s, sorbent; f, fin; t, transfer.

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