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A DETAILED ANALYSIS OF ENTROPY PRODUCTION AND IMPROVEMENT OF THE THERMODYNAMIC CYCLE OF AN ADSORPTION REFRIGERATING PLANT

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A thermodynamic analysis of an adsorption refrigerating plant with closed loops for a working substance and auxiliary liquid heat carrier has been carried out in application to the adsorption pair "water–$CaCl_2$ impregnated into the pores of a silica gel." Using the obtained periodic solutions of the system of energy-balance equations for the heat carrier and the sorbent layer, the most thermodynamically effective modes of operation of the refrigerating plant have been determined as functions of governing parameters. The entropy production in various modules of the plant is calculated, and the main sources of entropy generation are revealed. This made it possible to suggest an improved scheme of an adsorption refrigerating cycle with regenerative heat exchangers connected at the inlet and outlet from the adsorbers. The possibility of a considerable increase in the coefficient of thermodynamic efficiency in such a system has been justified.

Recent decades have shown an increased interest in adsorption refrigerating cycles that use ecologically pure working substances instead of halogen-containing hydrocarbons (freons). These cycles are based on the periodic process of sorption–desorption of steam or alcohol on a selective porous adsorbent. Their advantage is the possibility of using a low-potential heat as an external energy source. However, the thermodynamic efficiency of the cycles developed is still much lower than that attainable theoretically [1–6].

In the present work, we carried out an analysis of the scheme of an adsorption refrigerating plant suggested in the literature. To elucidate the reasons for the insufficient efficiency of adsorption cycles it is necessary to investigate the production of entropy in various elements of the plant and reveal the main sources of its generation. This kind of investigation makes it possible to find technical solutions that lead to higher thermodynamic efficiency.

Principles of Operation of an Adsorption Refrigerating Plant. The general schematic diagram of an adsorption refrigerating plant with closed loops for both the working substance — steam — and an auxiliary liquid heat carrier is presented in Fig. 1. The basic elements of the diagram are: two adsorbers, an evaporator and condenser of steam, and systems of heating and external cooling of a heat carrier. Cyclic changes in an adsorbent and adsorbate occur in four stages: isobaric adsorption and regeneration of the adsorbent and isosteric heating and cooling (Fig. 2).

At the stage of moisture adsorption, a sorbent is connected with the evaporator, which has a temperature T_{ev}. Here, the heat spent on water evaporation is extracted from the cooling chamber. As a result of the process of adsorption, heat is released in the adsorber.

At the stage of regeneration, after the adsorbent has been saturated with moisture, the adsorber is connected to the condenser of temperature T_c and heats it. The moisture then gets desorbed from the sorbent and enters the condenser, which is connected to the evaporator. Thus, water circulates through a closed loop.

Before switching the adsorber from the stage of adsorption to regeneration, it is necessary to carry out isosteric heating in order to raise the steam pressure in the adsorber, which corresponds to the pressure in the evaporator, to that present in the condenser. This will exclude a back flow of steam possible at the moment of switching. Similarly, during switching from the stage of regeneration to adsorption, isosteric cooling is effectuated. Thus, on passing four stages, the cycle is completed, the sorbent returns to its initial state, and it is again suitable for being used in the next cycle.

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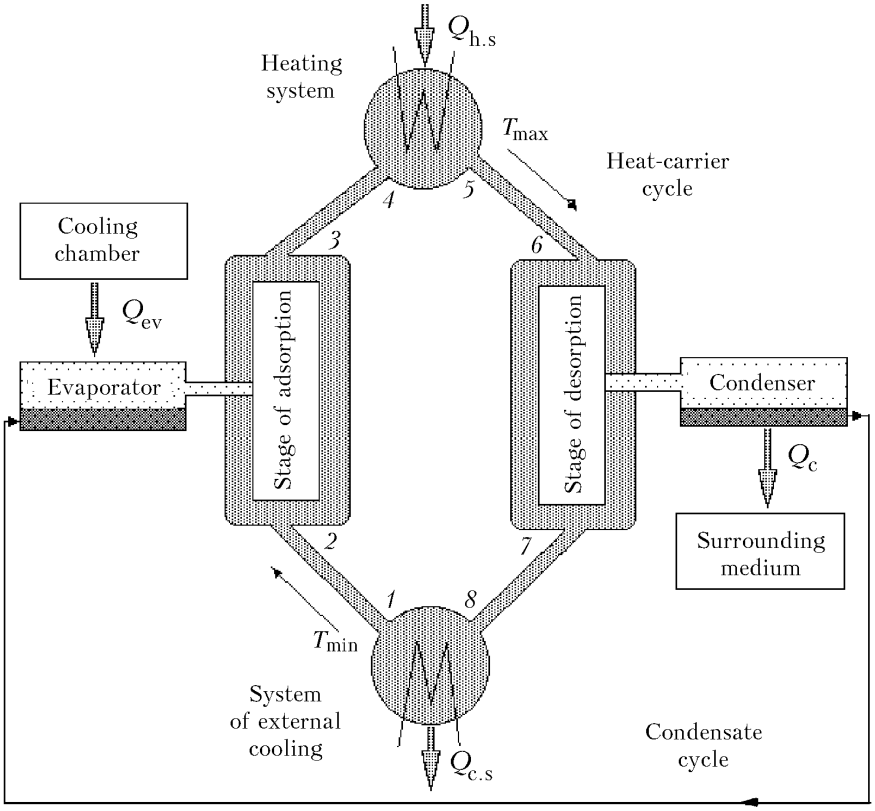

Fig. 1. Schematic diagram of a refrigerating plant with a closed heat-carrier loop.

The coefficient of the performance (COP) of the adsorption cycle is the ratio of the heat removed from the cooling chamber to the heat spent by an external source:

$$\mathrm{COP} = Q_{ev}/Q_{h.s}\,. \tag{1}$$

To increase the efficiency of the adsorbent-regenerating plant the heat which is released at the stage of adsorption is used [1, 2]. This is attained, for example, by using two adsorbers incorporated into the closed heat-carrier loop. Each of the adsorbers in such a plant operates in the same cycle conjugated with the evaporator and condenser but out of phase (Fig. 1): when adsorber 2–3 passes the stage of adsorption, adsorber 6–7 is at the stage of regeneration. Passing through adsorber 2–3, the heat carrier takes up the heat released here and then, passing through heating system 4–5, and due to the external heat source it is heated to a maximum temperature of the cycle and arrives at the stage of regeneration, where it gives up the heat to desorb the moisture and where it is cooled. Having passed through adsorber 6–7, the heat carrier enters cooling system 8–1, where its temperature is decreased to the temperature of the surrounding medium and can be used again at the stage of adsorption. The essence of the refrigerating plant operation is that heat is transferred from the cooling chamber into the surrounding medium with expenditure of the energy of the external source.

Mathematical Model of an Adsorption Refrigerating Plant. The same one-dimensional model of mass and energy transfer in the layer of an adsorbent and heat-carrier flux is adopted that was used earlier [3]. In each section of the adsorber a local adsorption equilibrium is assumed:

$$\varepsilon = \varepsilon\,(T_s, P)\,. \tag{2}$$

The interphase heat transfer is considered to be proportional to the difference in the temperatures of an external heat carrier and an adsorbent layer, which is equivalent to the condition α = const or to a constant Nusselt number. The equations of the energy balance for the heat carrier and sorbent layer, respectively, have the form

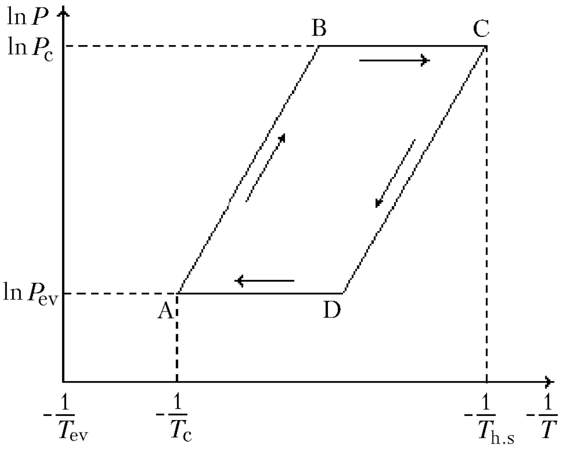

Fig. 2. Schematic representation of the adsorption cycle: A–B) isosteric heating; B–C) isobaric heating and desorption of steam; C–D) isosteric cooling; D–A) isobaric cooling and adsorption of steam.

$$\rho_f A_f c_f \frac{\partial T_f}{\partial t} = - \dot{m}_f c_f \frac{\partial T_f}{\partial z} - h\Pi \left(T_f - T_s\right) , \tag{3}$$

$$\rho_s A_s \left((c_s + \varepsilon c_a) \frac{\partial T_s}{\partial t} + \Delta H \frac{\partial \varepsilon}{\partial t} \right) = h\Pi \left(T_f - T_s\right) . \tag{4}$$

At the stages of adsorption and regeneration, these equations are supplemented with the boundary conditions

$$T_f (0, t) = T_{\min} \quad \text{or} \quad T_f (0, t) = T_{\max} . \tag{5}$$

At the stages of isosteric heating and cooling, the following additional condition is used:

$$\int_0^l \varepsilon (z, t) \, dz = \text{const} . \tag{6}$$

During the adsorption the pressure of the steam phase is considered constant along the layer and equal to the pressure of saturated steam at the evaporator temperature T_{ev}; correspondingly, in the case of desorption the steam phase pressure is considered to be equal to the saturation steam pressure at a condenser temperature T_c.

In an improved scheme of the adsorption refrigerating plant (Fig. 1), regenerative heat exchangers are installed between points 1 and 2, 3 and 4, 5 and 6, and 7 and 8. They are described by analogous energy balance equations (3) and (4), in which T_s is understood to be the temperature of the heat-accumulating material and there is no adsorption of water ($\varepsilon = 0$). We note that in the earlier thermodynamic analysis of regenerative heat transfer [7] the same equations were used.

Numerical calculations were carried out for the equilibrium function (2) that approximates experimental data for water adsorption on a promising composite adsorbent "$CaCl_2$ impregnated into the pores of the silica gel" [8] for the same temperature range that was considered in [3]:

$$T_{ev} = 276 \text{ K} , \quad T_{\min} = T_c = T_0 = 313 \text{ K} , \quad T_{\max} = 473 \text{ K} .$$

The result of numerical solution of the equations of the model is the acquisition of periodic solutions for the temperature profiles along the heat carrier and sorbent layer which makes it possible to calculate basic heat fluxes Q_{ev}, Q_c, $Q_{h.s}$, and $Q_{c.s}$.

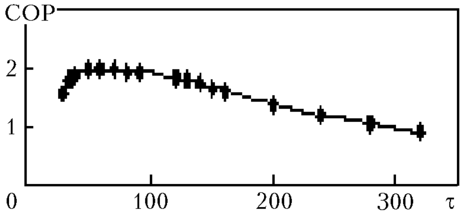

Fig. 3. Change in the coefficient of thermodynamic performance depending on the half-cycle duration ($N = 20$).

Investigation of the Optimal Duration of the Refrigerating Plant Cycle. Calculations show that the coefficient of performance (1) passes through a maximum with a change in the half-cycle duration. Figure 3 presents the corresponding dependence for the specific value of the number of transfer units in the adsorber ($N = 20$); in this case the maximum efficiency of the plant is attained at $\tau = 60$.

At small times, the low efficiency is attributed to the small amount of adsorbed moisture and correspondingly to the small value of Q_{ev}, since the heat carrier entering from the cooling system first cools the sorbent, which still remains hot after the stage of isosteric cooling. On increase in the duration of the half-cycle, the amount of adsorbed moisture and Q_{ev} increase, and correspondingly the efficiency increases. However, on excessive increase in the half-cycle duration, the quantity of heat $Q_{\text{h.s}}$ supplied by the heating system increases, whereas the quantity of the moisture adsorbed and Q_{ev} already attain their limiting value. As a result, the efficiency decreases.

Calculation of Entropy Production in Various Modules of the Refrigerating Plant. In [3], no comparison was made between the contributions of individual modules to the overall production of entropy in the refrigerating plant. Below, we present expressions for calculating entropy production in various modules which are similar to those given in [3]:

$$\Delta S_{\text{irr}}^{\text{h.s}} = \dot{m} c_{\text{f}} \int_0^t \left(\ln \frac{T_{\max}}{T_3(l, t)} + \frac{T_3(l, t)}{T_{\max}} - 1 \right) dt \,, \tag{7}$$

$$\Delta S_{\text{irr}}^{\text{c.s}} = \dot{m} c_{\text{f}} \int_0^t \left(\ln \frac{T_{\min}}{T_7(l, t)} + \frac{T_7(l, t)}{T_{\min}} - 1 \right) dt \,, \tag{8}$$

$$\Delta S_{\text{irr}}^{\text{c}} = - c_{\text{v}} A_{\text{s}} \rho_{\text{s}} \int_0^{t_{\text{c}}} \int_0^l \left[\ln \frac{T_{\text{c}}}{T_{\text{s}}} + \frac{T_{\text{s}}}{T_{\text{c}}} - 1 \right] \frac{\partial \varepsilon}{\partial t} dtdz \,, \tag{9}$$

$$\Delta S_{\text{irr}}^{\text{ev}} = c_{\text{liq}} A_{\text{s}} \rho_{\text{s}} \int_0^{t_{\text{ev}}} \int_0^l \left[\ln \frac{T_{\text{ev}}}{T_{\text{c}}} + \frac{T_{\text{c}}}{T_{\text{ev}}} - 1 \right] \frac{\partial \varepsilon}{\partial t} dtdz \,, \tag{10}$$

$$\Delta S_{\text{irr}}^{\text{ads23}} = \int_0^t \int_0^l h \Pi \frac{(T_{\text{f}} - T_{\text{s}})^2}{T_{\text{f}} T_{\text{s}}} dzdt + c_{\text{v}} \int_0^{t_{\text{ev}}} \int_0^l \rho_{\text{s}} A_{\text{s}} \left(\ln \frac{T_{\text{s}}}{T_{\text{ev}}} + \frac{T_{\text{ev}}}{T_{\text{s}}} - 1 \right) \frac{\partial \varepsilon}{\partial t} dzdt \,, \tag{11}$$

$$\Delta S_{\text{irr}}^{\text{ads67}} = \int_0^t \int_0^l h \Pi \frac{(T_{\text{f}} - T_{\text{s}})^2}{T_{\text{f}} T_{\text{s}}} dzdt \,, \tag{12}$$

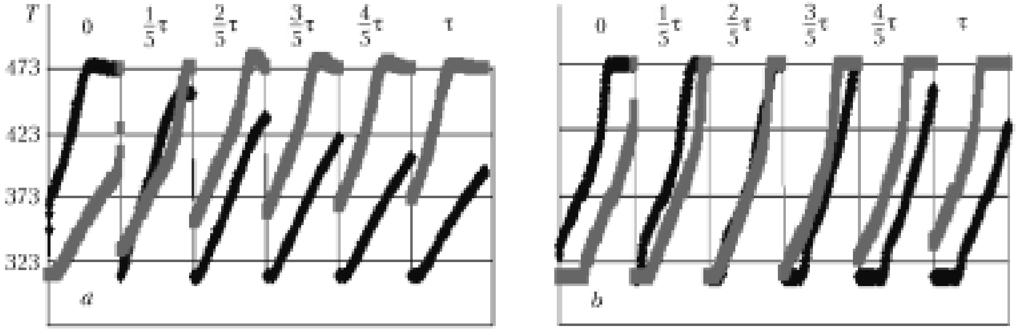

Fig. 4. Distribution of the heat-carrier temperature over the height of adsorbers for different time instants without regenerative heat exchangers (a) and with them (b). Black color, at the stage of cooling; gray color, at the stage of heating.

$$\Delta S_{\rm irr}^{\rm reg} = \int_0^t \int_0^l (1 - \delta) A\alpha \frac{(T_{\rm f} - T_{\rm s})^2}{T_{\rm f} T_{\rm s}} dz dt \, . \tag{13}$$

It should be noted that expressions (11) and (12) for adsorbers were obtained in a more compact form convenient for analysis as compared to those given in [3] due to the joint use of energy balance equations (3) and (4).

The summation of expressions (7)–(13) yields overall production of entropy for the half-cycle $\Delta S_{\rm irr}$. The accuracy of calculations by Eqs. (7)–(13) was controlled with the aid of independent determination of $\Delta S_{\rm irr}$ from the equation of total entropy balance in the refrigerating plant for the half-cycle:

$$\Delta S = Q_{\rm h.s}/T_{\max} + Q_{\rm ev}/T_{\rm ev} - Q_{\rm c.s}/T_{\min} - Q_{\rm c}/T_{\rm c} + \Delta S_{\rm irr} = 0 \, . \tag{14}$$

The discrepancy between the results of calculations of $\Delta S_{\rm irr}$ by two methods did not exceed 1%.

We will give the results of calculation of the relative contribution of each of the modules of the refrigerating plant to the overall entropy production (for the scheme without regenerative heat exchangers) for a set of the system parameters corresponding to $N = 20$ and the optimal cycle duration $\Delta S_{\rm irr}^{\rm ads1}/\Delta S_{\rm irr} = 0.229$; $\Delta S_{\rm irr}^{\rm ads2}/\Delta S_{\rm irr} = 0.170$; $\Delta S_{\rm irr}^{\rm h.s}/\Delta S_{\rm irr} = 0.231$; $\Delta S_{\rm irr}^{\rm c.s}/\Delta S_{\rm irr} = 0.287$; $\Delta S_{\rm irr}^{\rm ev}/\Delta S_{\rm irr} = 0.024$; and $\Delta S_{\rm irr}^{\rm c}/\Delta S_{\rm irr} = 0.057$. It is seen that the greatest contribution to the entropy production is made by the systems of heating of the circulating heat carrier by the external source and its cooling by atmospheric air.

It follows from Eqs. (7) and (8) that the greater the difference between $T_3(l, t)$ and $T_{\max}$, the larger the entropy production in the heating system. Similarly, the greater the difference between $T_7(l, t)$ and $T_{\min}$, the larger the entropy production in the cooling system.

Improved Scheme of a Refrigerating Plant with Regenerative Heat Exchangers Included. A comparative analysis of entropy generation in the modules of the plant shows that to increase its thermodynamic efficiency it is first of all necessary to decrease the entropy production in the systems of heating and cooling by decreasing temperature drops between $T_{\max}$ $T_3(l, t)$ and $T_7(l, t)$ $T_{\min}$. This can be attained by involving regenerative heat exchangers at the inlet and outlet between points 1 and 2, 3 and 4, 5 and 6, and 7 and 8.

The effect from the use of such heat exchangers is the smoothing of the temperature profiles in the system, as demonstrated in Fig. 4. Figure 4a shows a change in the temperature profile in the adsorber in time for a system without thermal regulation. The figure consists of six fragments relating to successive time moments reckoned from the beginning of a half-cycle with a $(1/5)\tau$ step. In each fragment, the heat-carrier temperature is laid over the ordinate axis, and the coordinate along the apparatus height is laid on the abscissa axis. The distributions of temperature at the stage of cooling and adsorption of steam from the evaporator is given in black; those at the stage of adsorber heating (including isosteric heating and regeneration of the adsorbent) are given in gray. The left-hand edge of the fragment corresponds to the entry of heat carrier at the stage of cooling; the right-hand side — at the stage of heating. It is seen from the graphs that at the stage of cooling there is a gradual increase in the difference between the temperature of the external source $T_{\max} = 200^{\circ}$C and the temperature of the heat carrier leaving the adsorber (the right-hand side

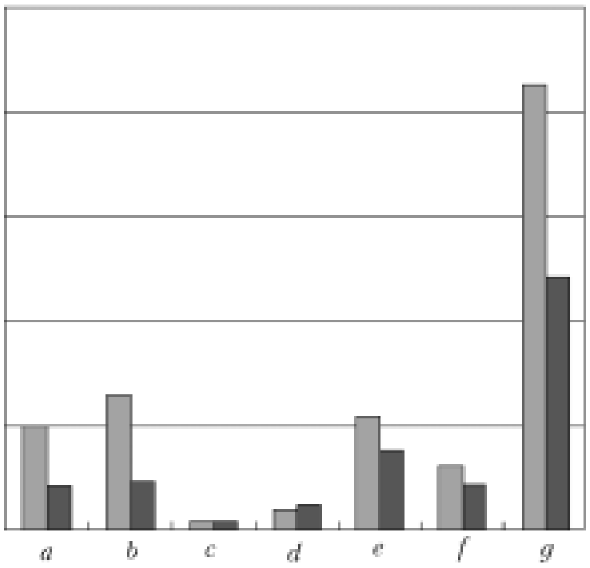

Fig. 5. Comparison between entropy productions (rel. units) for two different schemes of an adsorption plant: gray color, an adsorption cycle without regenerative heat exchangers; black color, an adsorption cycle with regenerative heat exchangers; a) heating system; b) cooling system; c) evaporator; d) condenser; e) adsorber at the stage of adsorption; f) regenerator at the stage of desorption; g) overall production of entropy.

of the fragments). Correspondingly, at the stage of heating the temperature at the outlet of the heat carrier from the adsorber more and more deviates from the temperature of the surrounding temperature $T_0 = 40^{\circ}\text{C}$ (the left-hand side of the fragments).

Figure 4b contains similar curves for a system with thermogenerators. In this case, the distribution of temperature in the composite system that includes an adsorber and two adjacent regenerators is shown. For the curves shown in black, the left-hand side of each fragment corresponds to the entry of a heat carrier from the cooling system into the regenerator connected to this system, whereas the right-hand side corresponds to the outlet of the heat carrier from the regenerator connected to the system of heating. At the same time, at the stage of heating (curves given in gray) the right-hand side of the fragment corresponds to the entry of the heat carrier from the system of heating into the regenerator and the left-hand side — to the outlet of the heat carrier from the regenerator to the cooling system. It is seen that the jumps of temperature on the entry of the heat carriers into the systems of heating and cooling sharply decrease in this case.

On the whole, the production of entropy in the second system decreases almost twofold (see Fig. 5), which corresponds to a considerable increase in the performance coefficient of the cycle — at the given temperature levels $T_{\min}$, $T_{\max}$, T_0 from 1.7 to 2.15. In this case, the exergic efficiency of the system defined as

$$\eta = \frac{Q_{\text{ev}}\left(\dfrac{T_0}{T_{\text{ev}}} - 1\right)}{Q_{\text{h.s}}\left(1 - \dfrac{T_0}{T_{\max}}\right)},$$

increases from 0.7 to 0.85.

It is interesting to compare the efficiency of the considered system of heat transfer conjugated with the process of steam adsorption–desorption with the results of the thermodynamic analysis [7] of a simpler heat-transfer system with a chemically inert heat-accumulating material. At the same number of transfer units $N = 20$ in the considered system of comparison, a value of the exergic efficiency is attained which is equal to 0.88. The closeness of the resulting value $\eta = 0.85$ to the indicated one is, on the one hand, due to the adopted approximation of quasi-equilibrium adsorption (2), i.e., to the allowance for only the temperature nonequilibrium state of the process. On the other hand, this points to the fact that further perfection of the system structure will no longer yield an additional thermodynamic gain.

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NOTATION

A, cross-sectional area, m^2; c_a, c_f, c_s, and c_v, heat capacity of the adsorptive, heat carrier, sorbent, and steam, J/(K·kg); h, heat-transfer coefficient, J/(sec·m^2·K); ΔH, heat of adsorption, J/mole; l, length of adsorber, m; m_f, heat-carrier flux, kg/sec; N, number of transfer units; P, pressure; Q, heat, J; S, entropy, J/K; T, temperature, K; T_0, temperature of the surrounding medium, K; t, time, sec; z, coordinate along the height of the adsorbent layer, m; α, volumetric coefficient of heat transfer in a regenerative heat exchanger, J/(sec·m^3·K); δ, fraction of a free volume filled with a heat carrier in the regenerative heat exchanger; ε, moisture content; η, exergic efficiency of the system; ρ, density, kg/m^3; Π, perimeter of the heat-transfer surface, m; τ, duration of a half-cycle. Subscripts: a, adsorptive; ads23(67), adsorber 23(67); c, condenser; c.s, cooling system; ev, vaporator; f, fluid (heat carrier); h.s., heating system; irr, irreversible; liq, liquid; reg, regenerative heat exchanger; s, sorbent; v, vapor; min, minimum; max, maximum.

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