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CHEMICAL AND SORPTION HEAT ENGINES: STATE OF THE ART AND DEVELOPMENT PROSPECTS IN THE RUSSIAN FEDERATION AND THE REPUBLIC OF BELARUS

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The basic principles of operation of chemical and adsorption heat engines have been described. The advantages and new aspects of their application have been considered. A review of the state of the art in sorption technologies in different countries, as well as of the features of their application in Russia and Belarus is given.

Introduction. The efficiency of a heat device, whose limiting value for a heat engine delivering work was determined in 1824 by Carnot [1], has for a long time been considered as the main estimation criterion for its performance. Likewise, one can determine the limiting performance of a heat pump or a cooler (see below), which developers of these machines try to approach. The authors of [2] give, among other important criteria of performance of heat engines, the maximum efficiency at given capital investments, the minimum cost at a given efficiency, the best fit of the working fluid properties to the required output parameters, high reliability, low operational expenses, etc.

In the last few years, however, radically new criteria whose application dramatically changes the estimation of the performance of a heat device have appeared. The reason for using these criteria is the concern the world community shows in connection with the growing amount of "green-house" gases (GG) released into the atmosphere. This stimulated taking measures for the stabilization and moderation of such processes. The measures formulated in the Montreal and Kyoto protocols are basically reduced to the control of GG emissions, as well as to emission taxes and quotas. It is already clear that the measures being taken not only have ecological and economical consequences, but can also stimulate the development and application of a particular energy-saving technology. Thus, the serious restrictions applied for radical reduction of emissions of freons are the real motivation to stop using freons in cooling and heating systems. On the one hand, this spurs the development of compression heat engines (CHE) based on natural working substances. On the other hand, there appears a "niche" for chemical and sorption heat engines (ChHEs and SHEs) which can play an important role in the reduction of GG emissions. The application of these devices makes it possible to save much organic fuel due to the use of thermal wastes of power engineering, various industrial enterprises, housing and communal services, and natural sources of low-temperature heat.

The present work considers the technical, energy, and ecological aspects of using ChHEs and SHEs in the Russian Federation (RF) and the Republic of Belarus (RB). The basic principles and the state of the art in these technologies in the RF and the RB are discussed and compared to the world standard, and the features of application of ChHEs and SHEs in these countries determined by the climate and the available heat energy sources are considered. The directions of science and technology in which investigations in the RF and the RB are on the world level or determine it are analyzed in detail. Such analysis seems topical due to the fact that heat power engineering in these countries has to undergo considerable structural changes soon, which calls for significant investments [3]. One direction may be the development of chemical and sorption heat engines.

1. Chemical and Adsorption Heat Engines: Basic Principles, Performance, Working Pairs. Chemical and adsorption heat engines are considered now as a real alternative to compression devices. Their chief advantage is that they do not require electrical energy — heat suffices for their operation, including heat with a low-temperature poten-

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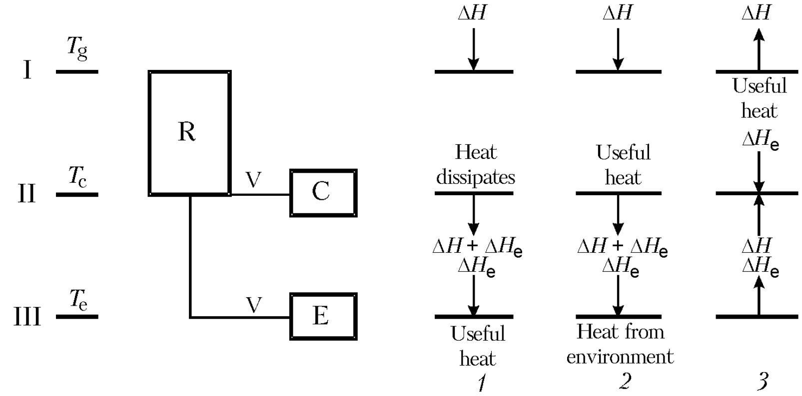


Fig. 1. Principle of operation of the chemical (sorption) heat engine.

TABLE 1. Values of Temperatures T_e, T_c, and T_g Providing Reversibility of the ChHE Cooling Cycle for Various Chemical Reactions and Limiting Performances of the Cycle

Reaction	T_e, °C	T_c, °C	T_g, °C	COP	$\Delta H_e/\Delta H$
$BaCl_2{\cdot}H_2O + H_2O \Leftrightarrow BaCl_2{\cdot}2H_2O$	5	28	50	0.82	0.80
$CaCl_2{\cdot}2H_2O + 2H_2O \Leftrightarrow CaCl_2{\cdot}4H_2O$	5	35	67	0.87	0.85
$MgCl_2 + H_2O = MgCl_2{\cdot}H_2O$	20	134.0	267.7	0.65	0.64
$MgCl_2{\cdot}H_2O + H_2O = MgCl_2{\cdot}2H_2O$	20	70.8	120.3	0.72	0.73
$SrBr_2{\cdot}H_2O + 5H_2O \Leftrightarrow SrBr_2{\cdot}6H_2O$	5	44.1	72.5	0.59	0.61
$SrBr_2{\cdot}H_2O + 5H_2O \Leftrightarrow SrBr_2{\cdot}6H_2O$	10	47.9	77.3	0.62	0.61
$MgO + H_2O = Mg(OH)_2$	20	186	367	0.51	0.50
$BaCl_2 + 8NH_3 \Leftrightarrow BaCl_2{\cdot}8NH_3$	–20	26.7	65.8	0.63	0.62
$BaCl_2 + 8NH_3 \Leftrightarrow BaCl_2{\cdot}8NH_3$	–5	39.9	76.4	0.62	0.62
$CaCl_2{\cdot}4NH_3 + 4NH_3 \Leftrightarrow CaCl_2{\cdot}8NH_3$	–20	45.6	100.9	0.57	0.57
$CaCl_2{\cdot}4NH_3 + 4NH_3 \Leftrightarrow CaCl_2{\cdot}8NH_3$	–5	58.8	111.3	0.56	0.56
$CaCl_2 + 2CH_3OH \Leftrightarrow CaCl_2{\cdot}2CH_3OH$	–40	21.0	90.6	0.73	0.72
$CaCl_2 + 2CH_3OH \Leftrightarrow CaCl_2{\cdot}2CH_3OH$	–20.5	43.1	116.1	0.74	0.72
$CaCl_2 + C_2H_5OH \Leftrightarrow CaCl_2{\cdot}C_2H_5OH$	21	57.6	94.6	0.81	0.83
$CaCl_2{\cdot}C_2H_5OH + C_2H_5OH \Leftrightarrow CaCl_2{\cdot}2C_2H_5OH$	21	45.5	70.1	0.79	0.81

tial, much of which is not being utilized now. The first chemical heat pump was made by Faraday on the basis of the NH_3–AgCl working pair in 1824 [4], i.e., much earlier than the first compression heat pump (1856/57, P. von Rittinger, Austria [5]). At the present time ChHEs and SHEs are increasingly being used (see, e.g., [6–8]).

The classical heat engine takes a quantity of heat Q_1 out of a thermostat with a high temperature T_1, gives up a quantity of heat Q_2 to a thermostat with a low temperature T_2, and delivers work $Q_1 - Q_2 = Q_1(1 - T_2/T_1)$. As opposed to it, the ChHE (SHE) utilizes and generates only heat energy and operates in the elementary case between three thermostats (I, II, and III) at a high (T_g), an intermediate (T_c), and a low (T_e) temperature (Fig. 1). These machines can convert heat energy operating in the following three modes (Fig. 1): cooling 1, heating 2, and increasing the temperature potential 3.

The elementary ChHE consists of a reactor R, an evaporator E, and a condenser C, which exchange the working fluid vapor V and are connected to thermostats I–III (Fig. 1). In the reactor, a chemical reaction proceeds between a nonvolatile S (sorbent) and a volatile V (sorbate) compounds

$$S + V \Leftrightarrow SV\,, \tag{1}$$

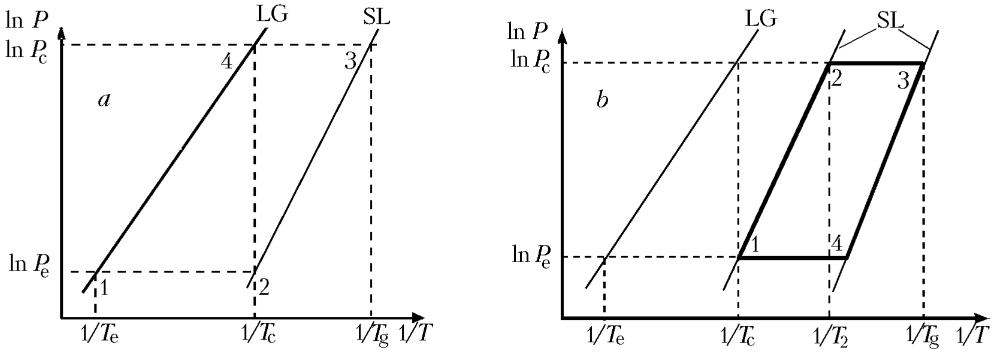


Fig. 2. Three-temperature cycle for the chemical (a) and adsorption (b) heat engines.

i.e., thermal-to-chemical energy conversion occurs. The evaporator is a source of a volatile substance V in the reaction of compound SV formation, and in the device C this substance condenses upon decomposition of the SV. Some examples of reaction (1) are given in Table 1 (as volatile compounds, water, methanol, ethanol, and ammonia are considered). Since the chemical compound (complex) SV and the condensate LV are pure phases, the pressure P of the component V in the reactor and condenser depends only on the temperature (monovariant equilibrium), and not on the degree of conversion (concentration of V in the bound state). These dependences, i.e., the SL (solid–liquid) and LG (liquid–gas) curves in Fig. 2a, are usually described by the equations [9]

$$\ln P = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}, \tag{2}$$

$$\ln P = -\frac{\Delta H_e}{RT} + \frac{\Delta S_e}{R}, \tag{3}$$

where ΔH^0 and ΔS^0 are the changes in the standard enthalpy and entropy upon SV formation, and ΔH_e and ΔS_e are the changes in the enthalpy and entropy upon evaporation of V. Equations (2) and (3) are integral forms of Van't Hoff and Clapeyron–Clausius equations.

As mentioned above, the ChHE can operate as a cooler (mode 1 in Fig. 1) and as a heater (mode 2). At the *regeneration stage*, which is common for these modes, a quantity of heat from the external source with temperature T_g is supplied to the reactor connected to the condenser with a temperature $T_c < T_g$. The equilibrium pressure of the compound V in the reactor is higher by an infinitely small value than in the condenser. Therefore, this compound resulting from the decomposition of the SV complex in the reactor is transferred to the condenser where it condenses at temperature T_c. In so doing, in the reactor heat ΔH is absorbed, and in the condenser a quantity of heat ΔH_e is released and is either used for heating (operation mode of a heater) or dissipates into the environment (operation mode of a cooler). Upon regeneration the ChHE begins to operate in one of the above-mentioned modes.

In the operation mode of a cooler, the environment is a thermostat with temperature T_c, and the temperature T_e is the required temperature of the cooler, i.e., the temperature at which the heat is taken out of the user device. The equilibrium pressure of the compound V in the evaporator at temperature T_e is higher by an infinitely small value than in the reactor at temperature T_c, and, therefore, the evaporated compound V is transferred to the reactor, where it forms a complex SV. Its formation heat ΔH dissipates into the environment, and in the evaporator a quantity of heat ΔH_e is absorbed and taken out of the user device to create the cooling effect. The performance (or the coefficient of performance of the refrigerating machine) is calculated as

$$\eta_{cool} = \Delta H_e / \Delta H. \tag{4}$$

The system thereby goes back to its initial (before regeneration) state.

In the operation mode of a heater (mode 2 in Fig. 1), the thermostat at temperature T_e is the environment, and the temperature T_c at which heat is moved to the user should correspond to the heating (usually $T_c \geq 40^oC$). The equilibrium pressure of the compound V in the evaporator at temperature T_e is higher by an infinitely small value than the pressure in the reactor at temperature T_c. Therefore, this compound formed by evaporation is transferred to the reactor, where it forms an SV complex (Fig. 2a). In so doing, in the evaporator a quantity of heat ΔH_e taken out of the environment is absorbed, and in the reactor a quantity of heat ΔH used for heating is released. The result of this stage is the transfer of the heat from the medium with a low temperature T_e, at which heat can be used free of charge, to the reactor with a higher temperature T_c, and the system goes back to its initial state. For heating, the heat evolved in the reactor and condenser is used, and the efficiency (amplification coefficient) is determined as

$$\eta_{\rm heat} = (\Delta H + \Delta H_e)/\Delta H = 1 + \eta_{\rm cool} > 1 \ . \tag{5}$$

In the third mode, the heat is equilibrium-absorbed at temperature T_c, and the useful heat ΔH is released in the course of the reaction of SV complex formation at a high temperature T_g with the efficiency

$$\eta_{\rm t.p} = \Delta H/(\Delta H_e + \Delta H) < 1 \ . \tag{6}$$

In calculating all efficiencies, the usual assumption was made that the heat expenditures for changing the heat capacity of the system are equal to zero, i.e., we either neglect the thermal mass of the system or assume an effective recuperation of the heat in it. Even if the recuperation is not complete or absent, expenditures in heating the system are usually small compared to the heat of chemical transformations; therefore, the approximation used is justified in this case as well.

The maximum theoretical performance of a heat engine operating between three thermostats with temperatures T_e, T_c, and T_g was obtained in [3, 10–12] for cooling

$$\eta_{\rm cool} = \left(\frac{1}{T_c} - \frac{1}{T_g}\right) \Bigg/ \left(\frac{1}{T_e} - \frac{1}{T_c}\right) \tag{7}$$

and heating

$$\eta_{\rm heat} = \left(\frac{1}{T_e} - \frac{1}{T_g}\right) \Bigg/ \left(\frac{1}{T_e} - \frac{1}{T_c}\right). \tag{8}$$

Using the methodology of these works, it is also easy to obtain the performance for the mode of increasing the temperature potential

$$\eta_{\rm t.p} = \left(\frac{1}{T_e} - \frac{1}{T_c}\right) \Bigg/ \left(\frac{1}{T_e} - \frac{1}{T_g}\right). \tag{9}$$

Thus, global thermodynamical analysis of the three-temperature (3T) thermal cycles leads to expressions (7)–(9), in which the performance is a function of the three temperatures of the cycle and is independent of the characteristics of the sorbent S–sorbate V working pair. Table 1 presents the values of temperatures T_e, T_c, and T_g providing reversibility of the cooling cycle of the ChHE, which were obtained directly from the experimental equilibrium curves for various chemical reactions, and the limiting performances calculated from Eqs. (7) and (4). Analysis of the performance of concrete cycles of the ChHE with account for the monovariant equilibria (2) and (3) leads to expressions (4)–(6), according to which the performance depends only on the enthalpy ratio between the evaporation and the chemical reaction, i.e., on the characteristics of the S–V working pair. It can be shown [13] that for a reversible SHE these definitions are equivalent, since the three temperatures of the ChHE cycle are not independent variables but are related by the Clapeyron–Clausius equation for the equilibrium of a pure liquid and the Van't Hoff equation for the chemical reaction. Other important consequences of this relation will be considered below. Comparison of the performances of the ChHE and SHE cycles without heat regeneration shows that for the ChHE the performance can reach the

Carnot performance, and for the SHE it is always lower because of the entropy regeneration upon heat transfer to the adsorber (from the adsorber) at a finite temperature difference [11].

The second important characteristic of ChHEs and SHEs is the specific power W_{sp}, i.e., the ratio of the power W absorbed in the evaporator (for cooling) or released in the condenser and adsorber (for heating) to the mass m (or volume V) of the sorbent:

$$W_{sp} = W/m \tag{10}$$

or

$$W_{sp} = W/V\,. \tag{11}$$

This quantity depends on both the thermodynamic characteristics of reaction (1) such as the amount of the sorbent exchanged in the cycle and on the dynamic parameters of the machine, primarily on the total time of the cycle. The latter in turn is determined by the intensity of the interrelated heat and mass transfer processes (which will be described in more detail below). The W_{sp} value may be of paramount importance for such applications of SHEs (ChHEs) as automotive [14, 15] and locomotive [16] air conditioning systems, ice makers on fishing boats [17], etc. In all these cases the low-temperature heat from the engine cooling system is in excess. Therefore, its performance (COP) in obtaining cold is of no decisive importance. The problem of obtaining a high specific power is put in the forefront, since the volume for placing the cooling device is limited [18]. In some works, such a characteristic of ChHEs and SHEs as exenergy efficiency was introduced [19], but it has not yet found wide application.

"*Sorbate–sorbent*" (*V–S*) *working pairs*. The choice of the working pair for ChHEs and SHEs strongly depends on the thermodynamic cycle of the device, which for SHEs is determined by the above-mentioned three temperatures (Fig. 2b). For ChHEs the temperature T_d at which decomposition of the SV complex occurs at a pressure of the volatile substance equal to its pressure in the condenser (P_c). For the reversible ChHE the temperatures T_e, T_c, and T_d cannot be chosen arbitrarily and are interrelated by the equilibrium equations (2) and (5) [4, 13] (Fig. 2a).

As sorbates, water, ammonia, and methanol are usually used. The chief advantages of water are a high evaporation heat and ecological cleanness, and its disadvantages are a low vapor pressure and a high freezing point. The first factor considerably retards the sorption/desorption dynamics, which sets limits on the specific power and dimensions of the device. Moreover, in this case more stringent requirements are placed on the system's air-tightness, and the influence of an even small amount of residual gases can be substantial. Freezing at 0^oC does not permit using this sorbate at low temperatures.

Ammonia has a low freezing temperature and a high pressure but a smaller evaporation heat as compared to water, and methanol is characterized by intermediate values of these characteristics. Works are known in which CO_2 [20], C_2H_5OH [21], CH_3NH_2 [22], HFC 134a [23], and other substances were used as a sorbate, but they are scarce. Water is usually used in air conditioners (T_e = 5–15^oC), methanol is used for air conditioning and making ice (T_e = –5–0^oC), and ammonia is also used for deep freezing.

Once the sorbate and the cycle have been determined, it is necessary to choose a sorbent optimal for a given cycle. The working pairs that seem to be promising for various applications are discussed in reviews [24–34]. At the present time the following working pairs are mainly used:

for absorption heat engines (AbHEs) ammonia–water and water–lithium bromide,

for adsorption heat engines (AdHEs) zeolite–water, silica gel–water, carbon–methanol, and carbon–ammonia,

for ChHEs metal chloride–ammonia and calcium chloride–methanol.

The substances used as solid sorbents are products of large-tonnage production (mainly for the needs of the chemical industry). Therefore, they are available, cheap, well-studied, and nontoxic. The synthetic (3A, 4A, 5A, 13Kh, etc.) and natural zeolites absorb a large amount of water (0.2–0.3 g/g) in a narrow interval at small values of the relative pressures P/P_0 (Fig. 3), which makes it possible to obtain a high value of the temperature difference ΔT in the evaporator and condenser but at the same time requires a high temperature for regeneration (150–200^oC). Silica gels, on the contrary, are easy to regenerate (60–100^oC) but give a small value of ΔT. Therefore, they are often used in cascade cycles [35]. In this connection, one has to look for new adsorbents for AdHEs, whose thermodynamic charac-

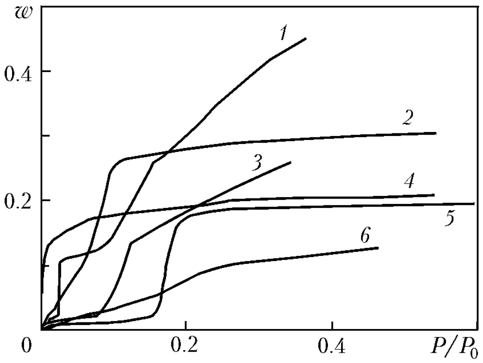


Fig. 3. Isotherms of water adsorption on SSV-1K (1), FAM-Z02 (2), SSV-5K (3), zeolite 13Kh (4), FAM-Z01 (5), and Fuji Davison RD silica gel (6). *w*, g/g.

teristics comply with the requirements for a particular cycle, especially one that operates from a low-potential heat source.

The usual approach to the search for a solid adsorbent is to compare commercially available materials (see, e.g., [36]). This selection is only a compromise since the thus found adsorbent is optimal for a given cycle only among those materials which are available in the catalogues. Analysis shows [14, 37, 38] that for different cycles the requirements for the optimal adsorbent may differ so widely that the known adsorbents cannot provide the requires properties. A more productive approach is that [37] based on the fact that for each particular cycle one can first formulate the requirements for the ideal adsorbent, optimal from the thermodynamical viewpoint for this cycle, and then synthesize a real adsorbent whose properties will be close to those of the optimal adsorbent. This approach will be discussed in more detail below.

2. New Aspects of Using ChHEs and SHEs in the Light of the Montreal and Kyoto Protocols. As mentioned above, the measures specified by the Montreal and Kyoto protocols can change the balance of energy technologies that has formed in the world (and in each country), in particular, stimulate the development and application of ChHEs and SHEs. In [39], a methodology was developed which makes it possible to perform, with account for these measures, a comparative analysis of the ecological and economical aspects of using ChHEs, SHEs, and the existing heating and cooling systems. This approach, in which such generalized parameters as total annual power consumption, mean value of the performance of a machine, average prices for energy, etc., was used in [40] with account for the specific conditions in Russia. Some of the results of such analysis will be discussed below.

Cooling systems. Under the climatic conditions in the RF and the RB, sorption heating systems may be in greater demand than sorption cooling systems. However, let us first consider the latter, since the analysis in this case will be more general. Indeed, for cooling devices there exist two sources of GG emission: direct emission due to freons and indirect emission due to the power consumption. To measure the total GG emission, the quantity

$$E = M\cdot\text{GWP}\cdot\tau + WA \tag{12}$$

is introduced [39]. Let us compare this characteristic for the SHE

$$E_\text{s} = \frac{Q_0}{\text{COP}_\text{s}\cdot\eta_\text{b}} A_\text{s} \tag{13}$$

and the conventional CHE

$$E_\text{c} = \frac{Q_0}{\text{COP}_\text{c}} A_\text{el} + M\cdot\text{GWP}\cdot\tau\,, \tag{14}$$

where the value of A_s depends on the kind of energy supplied: $A_s = A_{n.g}$, i.e., A_s is equal to the amount of CO_2 produced per 1 kW·h of heat obtained by burning natural gas, and $A_s = 0$ when heat wastes are used. The cooling load Q_0 and the working fluid mass M are proportional to the cooling power: W_{cool}: $Q_0 = H'W_{cool}$ and $M = mW_{cool}$.

Let us consider now two cases depending on the power source for regeneration:

1. Natural Gas SHE. Combining Eqs. (13) and (14), we can write the relative reduction in the GG emission due to the use of such a sorption heat engine:

$$\varepsilon = \frac{E_c - E_s}{E_s} = \beta\eta_b \frac{A_{el}}{A_{n.g}} - 1 + \frac{m}{H}\frac{\mathrm{GWP}\cdot\tau}{A_{n.g}} \cdot \mathrm{COP}_s \cdot \eta_b\,, \tag{15}$$

where $\beta = \mathrm{COP}_s/\mathrm{COP}_c$. The negative value of ε means that the natural-gas SHE is less environmentally friendly than the CHE. From (15) it is seen that ε depends not only on the characteristics of the machine (COP, GWP, τ, m), but also on its running time (H') and the method of electric energy generation (in terms of the values of A_{el} and $A_{n.g}$). In most cases, the direct emission of freons can be neglected and expression (15) is simplified:

$$\varepsilon \approx \beta\eta_b \frac{A_{el}}{A_{n.g}} - 1\,.$$

Consequently, $\varepsilon > 1$ if $A_{el}/A_{n.g} > \dfrac{2}{\beta\eta_b}$ or $\beta\eta_b > \dfrac{2}{A_{el}} A_{n.g}$.

Let us compare the SHE based on the LiBr–H_2O working pair with regeneration by burning natural gas ($A_{n.g} = 0.2$ kg CO_2/(kW·h), $\eta_b = 0.85$), which at present has the highest performance ($\mathrm{COP}_s = 1.2$), to the electric cooler. This analysis was carried out assuming $H' = 1000$ h/year and $A_{el} = 0.65$ kg CO_2/(kW·h) (which agrees with the data for the RF). It turned out that such an effective machine is environmentally more friendly only compared to the medium-performance CHE with $\mathrm{COP}_c \leq 3$, and only in the case where "foul" freon R-404a (GWP = 3800) is used. This means that in the majority of practical cases the application of the SHE aggravates the situation with GG emissions due to the indirect contribution of emissions (mainly of CO_2) because of the relatively low COP of the SHE. If electric power is generated at nuclear or water power stations ($A_{el} << 0.65$ kg CO_2/(kW·h), then the ecological advantage of the CHE increases to an even greater extent, as with the introduction of quotas for CO_2 emissions.

A similar approach can be used to analyze the total annual expenses of carbon for the production of cold (in the RF and the RB) by both technologies. Thus, for the natural gas-based SHE

$$C_s = \frac{Q_0}{\mathrm{COP}_s}\left(\frac{k_{n.g}}{\eta_b} + A_{n.g}q\right),$$

and for the electrical drive CHE

$$C_c = \frac{Q_0}{\mathrm{COP}_c}(k_{el} + A_{el}q)\,,$$

i.e., the annual saving will amount to

$$C = C_c - C_s = \frac{Q_0}{\mathrm{COP}_c}\left(k_{el} + A_{el}q - \frac{k_{n.g}}{\beta\eta_b} - A_{n.g}q\right). \tag{16}$$

Adsorption machines will be economically sounder than compression ones if $C > 0$ or

$$k_{el} + A_{el}q > \frac{k_{n.g}}{\beta\eta_b} + A_{n.g}q\,. \tag{17}$$

In the situation formed where the emission tax $q = 0$, to this end the condition

$$\frac{k_{el}}{k_{n.g}} > \frac{1}{\beta\eta_b} \tag{18}$$

should be fulfilled.

We assume $\eta_b = 0.85$ and $\beta = 0.3$, then the ratio $k_{el}/k_{n.g}$ should exceed 3.4. In accordance with the prices in the last few years this ratio in Russia exceeded 6, i.e., SHEs are economically sounder than compression heat engines despite the higher emissions of GGs [40]. Analogous conclusions were drawn in [41] in analyzing the efficiency of thermodynamical cycles at thermal power stations.

Upon the introduction of the emission tax the economical advantage of adsorption systems will remain al long as the relations

$$q \le \left(k_{el} - \frac{k_{n.g}}{\beta\eta_b}\right) \Big/ \left(\frac{A_{n.g}}{\beta} - A_{el}\right) \tag{19}$$

hold. The equality $A_{n.g}/\beta = A_{el}$ corresponds to the situation where the quantity of CO2 produced by SHEs and CHEs are equal. In this case, the economic efficiency is defined by relations (17).

2. *SHE with regeneration from heat wastes or solar energy.* Such a device is always environmentally friendly whatever the COP, since it does not produce GGs at all. Then the reduction in the CO_2 is equal to the emission for the case of CHEs, and the annual saving is defined by Eq. (18), in which $k_{n.g} = A_{n.g} = 0$. For a more detailed analysis, it is necessary to take into account the energy used to create the SHE proper and the CO_2 emission connected with it.

Thus, it may be concluded that the SHE, when "fed" by natural gas, can be more environmentally friendly than the CHE only in exceptional cases, whereas in using heat wastes or solar energy — always. This restricts the application of SHEs which nevertheless are of great interest in all cases where one can use for the regeneration the usually dissipating low-potential heat, in the first place, for automative air conditioning systems and especially in tri-generation systems (simultaneous generation of electric energy, heat, and cold).

Heating systems (*ChHPs and SHPs*). For the heating systems that are in greater demand under the climatic conditions in Russia, Ukraine, and Belarus, let us compare the emission of CO_2 for the sorption heat pump (SHP) and the conventional gas heater (GH) respectively:

$$E_s = \frac{Q_h}{\mathrm{COA}_s \cdot \eta_b} A_{n.g}\,, \tag{20}$$

$$E_b = \frac{Q_h}{\eta_b} A_{n.g}\,. \tag{21}$$

Assuming the same source of primary energy, we find the reduction in the emission ε:

$$\varepsilon = \frac{E_b - E_s}{E_b} = 1 - \frac{1}{\mathrm{COA}_s}\,. \tag{22}$$

As $\mathrm{COA}_s > 1$, we obtain a reduction in the emission. It can be substantial and amounts to 41% at $\mathrm{COA}_s = 1.7$ and 33% at $\mathrm{COA}_s = 1.5$. For the consumed energy cost, we get

$$C_s = \frac{Q_h}{\mathrm{COA}_s \cdot \eta_b} k_{n.g}\,, \tag{23}$$

$$C_b = \frac{Q_h}{\eta_b} k_{n.g}\,, \tag{24}$$

and for the saving share of this cost we get

$$\gamma = \frac{C_b - C_s}{C_b} = 1 - \frac{1}{\mathrm{COA_s}} = \varepsilon \, . \tag{25}$$

Thus, at $\mathrm{COA_s} > 1$ adsorption heat pumps are both more environmentally friendly and economically sounder than gas heaters. They proved even more advantageous upon the introduction of the saving GG emission quotas. In this connection, stipulated use of funds raised by selling quota to finance energy-saving projects, in particular, to organize and develop production of ChHEs and SHEs and create and expand a market for them, seems important. As such machines, one can use absorption systems based on the LiBr–H_2O pair with $\mathrm{COA_s}$ = 1.7 (41% of energy saving) or adsorption heat pumps based on the zeolite–water pair with two adsorbents, which gives $\mathrm{COA_s} \approx 1.5$ (33% of energy saving). Of great interest are adsorption heat pumps based on the selective water sorbent (SWS)–water pair with two adsorbers, which can lead theoretically to $\mathrm{COA_s} \approx 1.7$ at a regeneration temperature below 130°C [42, 43]. The latter fact makes it possible, on the one hand, to use for the regeneration low-potential heat (heat waste, solar energy, etc.), and, on the other hand, to use water instead of oil as a heat-transfer material. The use of heat wastes makes it possible to nullify the emission of CO_2 and even raise the funds by selling quota.

3. State of the Art in the Sorption Technologies in the World. It is known that a considerable part of the population of the Earth require heat pumps for heating and cooling [44, 45]. Electric vapor-compression heat pumps, in which instead of the ecologically harmful refrigerant R22 the safe refrigerants R410A and R407C are utilized [43], have found wide use. Ecologically safe working fluids for vapor-compression heat pumps are also propane, propylene, ammonia, and CO_2.

In western countries vapor-compression heat pumps have already been used for more than 30 years. For instance, in Sweden heat pumps provide 50% of the heating. On the whole, in the world, according to different data, from 90 to 150 million machines are operating now [44, 45]. The annual volume of their sales in the world is 125 billion US dollars, which is three times higher than the world volume of scales of arms. In Japan, every year about 3 million heat pumps are produced. The USA produces about 1 million geothermal heat pumps and mainly such pumps are used in newly-erected public buildings (this norm is enforced by the US Federal legislation). In about 75% of the heat pumps installed in Europe, free air serves as a source of low-temperature heat. The total volume of production of "water–air" class heat pumps designed only for heating instead of the heating gas-fired and liquid fuel boilers in Europe was 25,000 pieces in 2002 and 35,000 pieces in 2003. In South Europe (Italy, Spain, and Greece), "air–air" class systems prevail, and in North Europe mainly heat pumps that take heat out of the ground by means of a deepened coil heat exchanger are used. According to the forecast of the World Energy Committee, by 2020 the share of heat pumps in the heat supply will constitute 75% [46].

The most important prerequisite to an active development of the heat pump engineering is the state financing backing. Many developed countries have state funds and programs stimulating energy saving at power-consuming enterprises. An example of such backing is the present Denmark practice of reducing taxes (mainly by reducing tax components in the rates for consumed power resources) for enterprises conducting regular power audits and continuous monitoring of power consumption and taking all energy-saving measures recommended by auditors with a payback time less than four years. Moreover, in this case enterprises can count on state subsidies of up to 30% of expenses for conducting power inspections. In Germany state organs promote acquisition, installation, and putting into operation of perfect heat pump systems for heating rooms and water for domestic purposes, which are produced in quantity and enter the commercial network [46].

Quantity production of absorption heat engines takes place so far mainly in Japan and the USA. Leaders on the market are the companies York, Trane, Carrier (USA), and Sanyo (Japan). In the last 5–7 years China (e.g., the companies Broad, Shuangliang, Zhejiang, etc.) has also been producing in quantity AbHEs for air-conditioning systems of industrial enterprises (absorption heat engines based on the lithium bromide–water pair). Interestingly, these companies, enjoying the support of the state, are able to introduce all the most advanced technologies. They are leading, in turnover, manufactures of absorption machines and have supplied to their own country alone over 20,000 units of equipment. The AbHEs manufactured in different countries have a power of 0.1–5 MW. Recently, lower-power absorp-

TABLE 2. Temperature Values of Various Low-Potential Heat Sources and Data on the Medium of the Intermediate Contour for Them

Source	Intermediate contour medium	Source temperature, ^oC
Ground water	Water	8—15
Ground	Antifeeze	2—10
Water inlet water	Water	6—10
River water	Antifeeze	1—10
Sewage	Water	10—17
Ambient air	Air	From –10 to +15
Exhaust air	Air	18—25

tion heat engines and coolers which can be used in individual houses and small settlements have entered the market. Their payback time is somewhat longer than for large machines.

At present adsorption technologies only begin to come into the market of energy saving technologies. Until recently, only adsorption water chillers that have been manufactured (since 1986) by the Japanese company Nishiyodo Kuchouki, Co. Ltd. on the basis of the Fuji RD silica gel–water working pair have been available commercially [8, 47, 48]. The properties of this working pair permit using for the regeneration heat with a temperature potential T_g = 50–90^{o}C (e.g., warm water from the cooling system of different engines). The minimum temperature of the adsorber is usually kept at 30^{o}C. At T_g = 90^{o}C and T_e = 15^{o}C the coefficient of performance of the refrigerating machine (COP) can reach 0.7. The manufacturer estimated the payback time of these machines as 2–3 years. Another company producing commercial adsorption chillers is Micon, Co Ltd. (Japan) [8]. In these machines, hot water at T_g = 75^{o}C is used and cold water at T_e = 9^{o}C is produced for air-conditioning applications, and the COP thereby is 0.6. Both kinds of adsorption heat engines (AdHE) are sold at the markets in the USA, Canada, and Europe. Their typical power is 0.1–0.5 MW.

For individual houses, of great interest are low-power adsorption heat pumps. Prototypes of such devices of power about 5–10 kW or more are subjected to tests in China, Germany, the Netherlands, Italy, Great Britain, Austria, Japan, Spain, and other countries [6, 7, 18, 30, 33, 49–56]. In the last few years, several European companies (SolarNext, Vaillant, SorTech AG, etc.) have been selling AdHEs of power 5–20 kW, in which for the adsorbent regeneration waste heat with a temperature of 60–100^{o}C, solar water or air heaters, or combustion heat of natural gas are used. Devices for reclaiming motor-car engine heat with the aim of using it for automative air conditioning are being actively developed [14, 15].

It should be noted that the use of sorption machines is especially expedient where a relatively cheap heat source is available for the sorbent regeneration (low- and high-pressure vapors or the liquid from the cooling systems of various engines, turbines or technological processes, exhaust gases, etc.). It is important that the development of sorption chillers will be strongly stimulated by the wide application in the future of energy cogeneration systems (sources of combined electricity and heat generation) and, accordingly, by the creation of tri-generation sources.

Another important factor of the operation of SHEs is the low-temperature heat source which has a marked effect on the design of the heat pump in terms of the economy and environment protection. Among the main sources are [46, 57]: 1) the ambient air; 2) the exhaust air (ventilation emission); 3) water of rivers ad lakes; 4) the ground and ground waters; 5) rocks.

Table 2 gives the temperature values of the sources taken from [46], as well as the medium of the intermediate contour for each of them.

4. Sorption Technologies in Russia and the Republic of Belarus: State of the Art and Specific Features of Application. The climate in the RF and the RB is cooler than in the countries of Western Europe, the USA, and Japan, so about 25% of the total amount of consumed energy is expended directly in heating [3]. This is mainly due to the burning of organic fuels with a corresponding emission of GGs into the atmosphere. In this connection, of great interest is the application of heat pumps for heating. In summer, there is also a certain niche for cooling systems (air conditioning, cooling of water, storage of foods). As mentioned above, cold production is also of great interest in automative air conditioning systems and especially in tri-generators which are simultaneously sources of electric energy, heat, and cold.

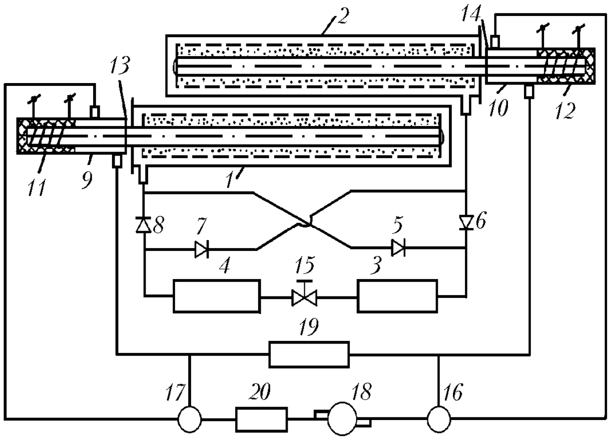


Fig. 4. Adsorption heat pump diagram: 1, 2) adsorbers filled with the sorbent; 3) condenser; 4) evaporator; 5–8) valves; 9, 10) liquid heat exchangers; 11, 12) heaters; 13, 14) heat pipes; 15) controlled restrictors; 16, 17) triple valves; 18) fluid-flow pump; 19) rotameter; 20) thermostat.

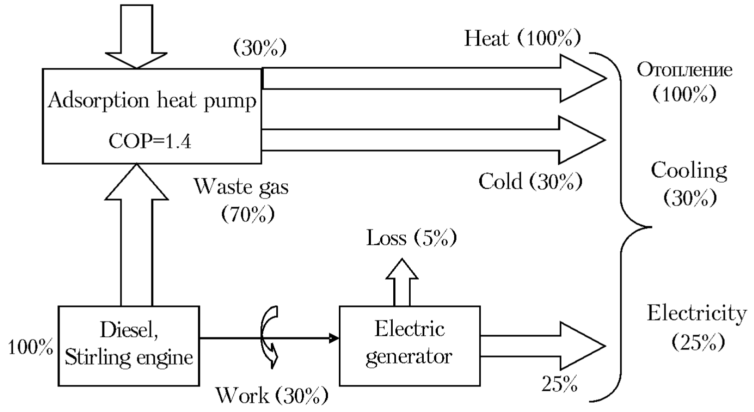


Fig. 5. Diagram of the sorption heat pump in a tri-generation system (electricity, heat, cold).

When a heat pump operates, the environment is used as a "free" source of low-temperature heat (T_e), and when a refrigerator operates, it is used to "sink" the average-temperature heat (T_c), i.e., some parameters of a cycle of the sorption heat pump (SHP) are directly determined by climatic conditions. This will be analyzed in more detail below. In this connection, let us consider in brief the specific features of using ChHEs and SHEs under the climatic conditions of the RF and the RB.

The Republic of Belarus is situated in a geographical zone where the average temperature in summer exceeds 20°C and in winter is close to 0°C. The adsorption reversible-cycle heat pumps developed at the Heat and Mass Transfer Institute, NAS of Belarus, permit obtaining from 20 to 30 kW/m^3 of thermal energy and up to 5 kW of cold. Such pumps save up to 15–20% of primary energy (fuel) for the production of electricity, heat, and cold (Fig. 4). Wide use of such power plants in Europe will provide an annual energy saving of up to $50 \cdot 10^2$ kJ, which is equivalent to $1.6 \cdot 10^9$ m^3 of natural gas (300 million euros). In this case, the amount of carbon dioxide released into the environment will be smaller by $3 \cdot 10^7$ tons.

Adsorption heat pumps are also of interest for transport applications. As part of the fifth frame program (EU F5 Energy program), in the European community the SOCOOL project aimed at creating energy tri-generation systems for domestic purposes has been completed recently. A 15–20% increase in the efficiency of such devices is due to the recovery of the heat of waste gases and spent water of diesel-generators or Stirling engines for producing cold with

Fig. 6. Sorption heat pump for air heating and water cooling with a power of 4 kW for heat and 1 kW for cold, developed at the Heat and Mass Transfer Institute, NAS of Belarus.

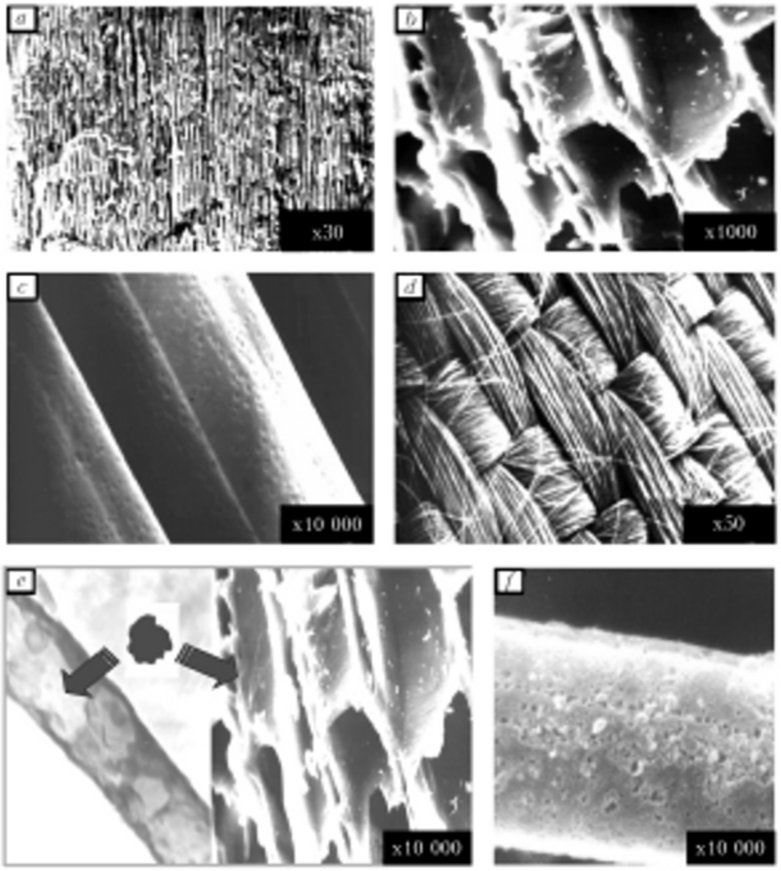


Fig. 7. Samples of the carbon sorbent [a, b) activated charcoal; c, d) activated carbon fiber] and of the sorbent-composite (e, f) for the heat pump.

the use of sorption technologies (Fig. 5). Sorption heat pumps and coolers of a new type should be cheap, reliable, durable and have a high thermodynamic efficiency. To reach this goal, it is necessary to intensify the process of heat and mass transfer in a porous sorbent and the heat exchange of the sorbent with the adsorber wall and the environment. Where diesel-generators are to be used, it is possible to recover the heat of both waste gases and the cooling

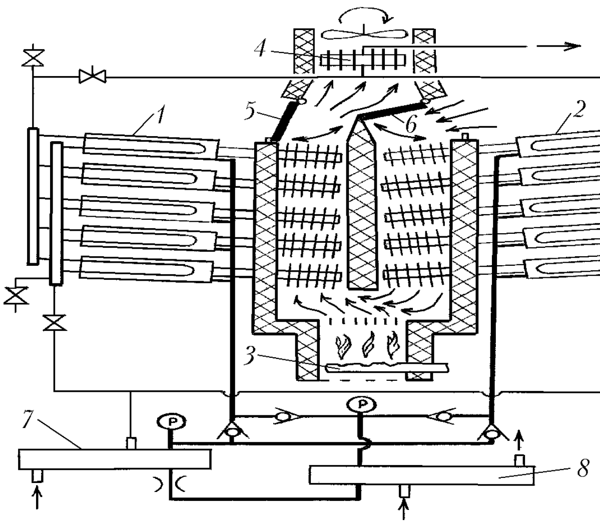


Fig. 8. Diagram of the sorption heat pump (Heat and Mass Transfer Institute, NAS of Belarus) for obtaining superheated vapor and hot and cold water (5–10°C): 1, 2) adsorbers; 3) gas burners; 4) boiler; 5, 6) cross-over gas bafflers; 7) evaporator; 8) condenser.

liquid. Good prospects for recovering released heat in modern fuel cells (especially high-temperature ones) inspire hope for wide application of these cells instead of steam turbines and electric generators at thermal power stations. To attain this goal, high-pressure sorption technologies (activated carbon/ammonia) are used, and where the coolant heat is to be recovered, low-pressure technologies (silica gel/water) are employed. The sorption technologies are noiseless because of the absence of a mechanical compressor. They do not use ecologically harmful refrigerants (CFC, HCFC, HFC). As mentioned above, solid sorption chillers with a cooling power of more than 100 kW have been developed and are produced in quantity.

At the Heat and Mass Transfer Institute, NAS of Belarus, new miniature refrigerators and heat pumps intended for use in rural areas have been developed. Analogous works are being carried out in the European community as part of the SOCOOL project. Figure 6 shows a sorption heat pump of power 4 kW designed for heating the air and cooling water. It consists of four adsorbers filled with a sorbent-composite ($CaCl_2$ microcrystals on the active carbon fiber surface). The evaporator of the heat pump is used for cooling water, and the condenser and the finned adsorbers are used for heating the air in a room.

The scientific and technological grounds of the heat pump design are based on innovative decisions: choice of an effective sorbent/sorbate pair, intensification of the heat and mass transfer processes inside the sorbent, as well as between the sorbent and the adsorber wall, increasing the specific capacity of the sorbent, etc. To provide a long service life of the heat pump, one has to solve many problems, including provision of compatibility of materials and heat-transfer agents, as well as a guarantee of the absence of noncondensable gases inside the refrigeration machine. To attain a high density of stored energy and a high thermodynamic efficiency of the heat pump, the sorbent should be cheap, nontoxic, noncombustible, environmentally friendly, and have a high sorption heat. The common sorbent are most often activated carbons, silica gels, zeolites, salts of metals, and composites of the above materials. Typical samples of carbon sorbents and composites (salt microcrystals on the fiber) are shown in Fig. 7.

As a thermal power source for the pump schematically represented in Fig. 8, a gas burner (or waste gases of the motor-generator) is used, and as a low-temperature power source, return water of the heat-supply system is used. When a gas burner is used, heating of the adsorbers and desorption of the sorbent occur. At the same time exhaust gases heat the water in the heat exchanger-recoverer from 6 to 50–60°C, and in this process 5 kW of thermal energy are generated. Gas transfer valves make it possible to organize a cooling–heating cycle of adsorbers by supplying periodically now cold air, now hot gases from the burner (internal combustion engine). Cold and hot gases are needed for the adsorption–desorption of the sorbent in adsorbers. Due to the operation of adsorbers, cooling of the water in

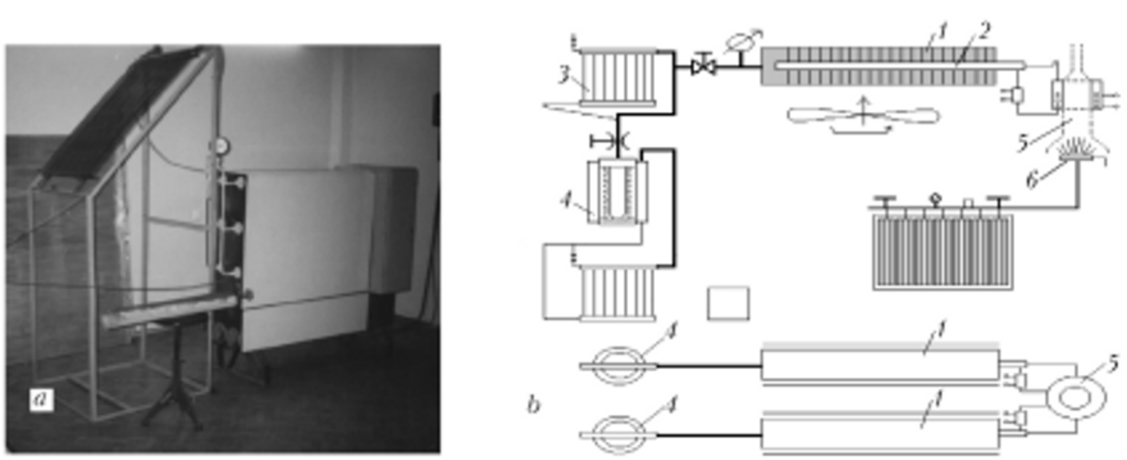


Fig. 9. External view (a) and diagram of the sorption two-stage heat pump: 1, 2) adsorbers; 3) condenser; 4) evaporator; 5) heat pipe; 6) gas burner.

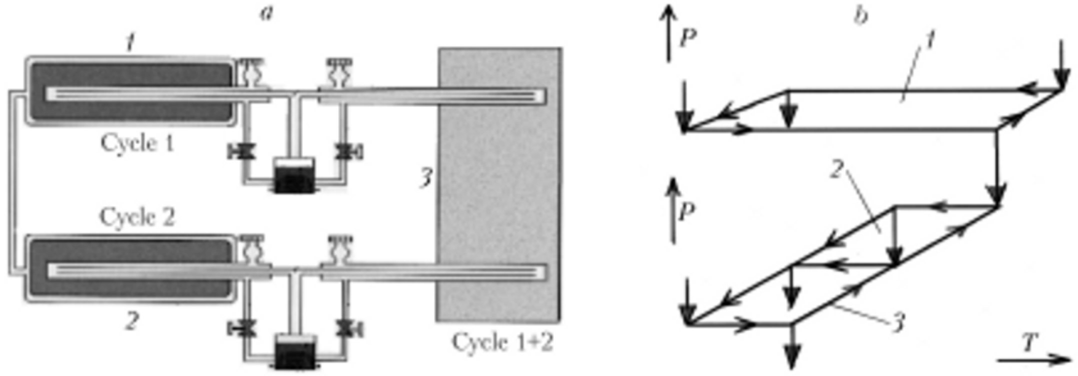


Fig. 10. Scheme (a) and Clapeyron–Clausius diagram (b) of the three-cascade sorption heat pump with internal regeneration: 1) high-temperature adsorber; 2) medium-temperature adsorber; 3) low-temperature adsorber (LiBr–water).

the liquid circulation loop to a temperature of 3–5^{o}C is attained and 1 kW of cold is generated. Such a facility is suitable for cooling milk on farms.

Figure 9 shows the external view and constructional arrangement of the heat pump containing six adsorbers with a total heat power of 3.6 kW with external and internal regeneration. Due to this the coefficient of performance (COP) of the pump reaches a value of 1.62, and the efficiency of cold production thereby is equal to 0.6.

For further increase in the performance of heat pumps based on solid and liquid sorbents and their adaptation to high-temperature heat engines, it is expedient to use the so-called two/three-cascade thermodynamic cycles. For example, it is convenient to recover waste heat of fuel cells with the help of adsorption heat pumps placed in series with low-temperature absorption heat pumps (LiBr–water). Waste gases of heat engines having a high temperature (600–800^{o}C) are directed through the heat exchanger to the adsorption heat pumps charged with high-temperature sorbents ($NaCl_2$) and desorption of the working substance of the pump is carried out. The waste gas temperature of the heat engine drops to 300–400^{o}C. The gas is conveyed to the medium-temperature adsorber ($MgCl_2$) and the process of working substance desorption is repeated. Finally, the cooled gas gets into the low-temperature absorber containing a LiBr–water pair, where water vapors are desorbed from the brine. Figure 10 gives a diagram of a three-cascade heat pump and a Clapeyron–Clausius diagram for it.

Sorption solar coolers. A solar cooler is a kind of a solid-sorbent heat pump in whose evaporator a temperature below the ambient temperature is maintained. The sorption technologies provide energy saving and environment protection due to the development of coolers using alternative sources of energy, primarily solar energy [52, 53].

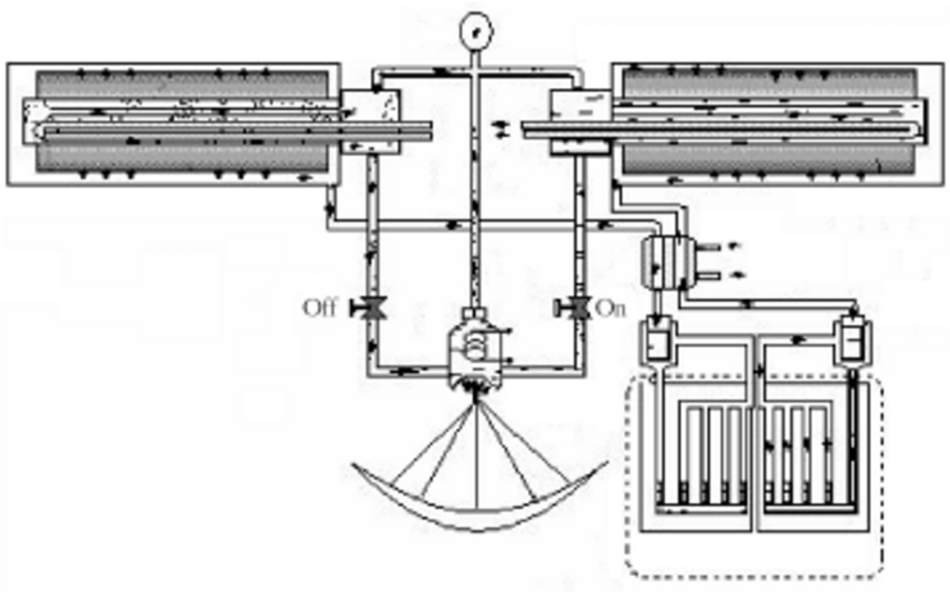


Fig. 11. Diagram of the sorption solar-radiation-concentrator cooler powered by solar and electric energy.

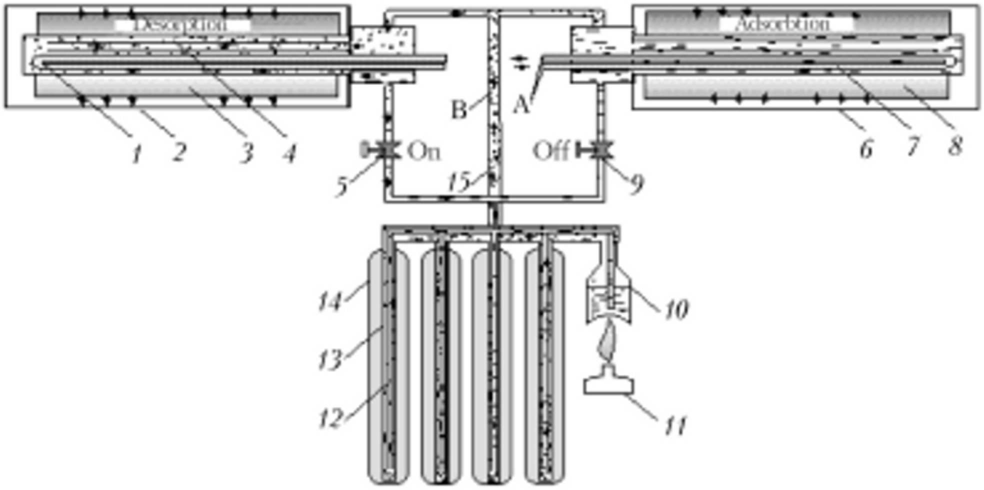


Fig. 12. Diagram of the two-adsorber solar cooler with vacuum diffuse solar radiation detectors-cylinders; 1, 7) heat changers; 2, 6) adsorbers; 3, 8) sorbent; 4) vapor channel inside the sorbent; 5, 9) liquid heat exchangers; 10, 13) evaporators of thermosyphons; 11) gas burner; 12) liquid duct of the thermosyphon; 14) vacuum glass cylinder; 15) vapor channel; A, inlet of the cooling liquid; B, vapor flow from the evaporator into the condenser.

Figure 11 schematically represents a solid-sorbent cooler using short cycles (20–30 min) developed at the Heat and Mass Transfer Institute, NAS of Belarus. In this device, solar energy is used for producing cold and heat. During daylight hours this process is realized with the help of solar energy, and in the night electric energy is used to produce cold. The solar cooler can heat water (1 kW of heat) and cool the air in the refrigerating chamber (200 W of cold). It consists of two adsorbers filled with the sorbent and a heat-pipe temperature control system. Solar energy heats the heat pipe evaporator, and the heated vapor is alternatily used for desorption of one of the adsorbers. In the heat pipes, water in the medium-temperature profile and ammonia in the low-temperature profile are used as a working fluid. The heat-pipe temperature control system makes it possible to dispense with mechanical pumps. The weight of the cooler does not exceed 20 kg.

Figure 12 shows a diagram of the second prototype of the solar cooler, in which a miniature gas burner is used as an energy source alternative to the sun. The main components of such a cooler are a solar collector (concentrator), sorbent-containing cylinders, an evaporator, and a condenser.

An important component of the solar cooler is also the two-phase temperature control system providing round-the-clock cold production. In this case, one does not have to wait for the night to come for the refrigerating chamber to cool down. As a result, the masses of the sorbent and the adsorber casing can be reduced considerably compared to the day/night coolers. Two modifications of the solar cooler have been developed. The first cooler has a solar concentrator, in whose focus the evaporator of the vapor-dynamic thermosyphon is always present. The second design is based on the use of commercial glass collectors-accumulators of solar radiation. Inside the collector a thermosyphon evaporator is situated. It takes energy out of the local solar concentrator situated in a cylinder. The structural arrangement of the solar cooler is convenient to use and permits using various numbers of vacuum cylinders depending on the heat load. A novel feature of the cooler lies in the design of the temperature control system (thermosyphon system with collectors/evaporators and collectors/condensers) and valves for switching the direction of liquid flow from the condensers to the evaporator. The temperature control system is used for periodical heating and cooling of the sorbent-containing cylinders.

In the European part of Russia, where most of the country's population reside, the climate is more continental. In the north and east of the RF the average temperature in winter may fall to $-30 - -50^{o}C$. Under cold winter conditions the air, as a rule, cannot be used as a low-temperature heat source, and the heat exchanger has to be placed deeper in the ground than in areas with a milder climate. Utilization of the heat of natural water reservoirs is promising. For instance, in West Siberia the evaporator temperature can be increased to $20–30^{o}C$ at the cost of geothermal waters.

Under cold climatic conditions, a liquid with a high vapor pressure, i.e., ammonia and methanol, should preferably be used. In summer, it is preferable to use water for cooling and air-conditioning systems.

As mentioned above, at the present time in Russia about 25% of energy is expended in heating domestic and industrial premises. Therefore, the application of SHEs in this sector of the economy can be the most advantageous from both the economical and ecological points of view. Excessive power resources are also spent in Russian industries where the power consumption of production exceeds by 1/3 that in Canada, is twice that in the USA, Sweden, and Finland, and 3–4 times higher than in the majority of other countries in Western Europe and in Japan.

At the present time in Russia only about 150 heat pumps with a total power of 77 MW are employed, whereas in the world the number of such devices is about one million times larger. At the same time we can speak of the availability of appreciable resources of low-potential heat which could be converted by heat pumps (HP). Let us consider the main heat sources for them:

1. It is first of all the waste heat arising in the heat supply system. According to L. A. Ogurechnikov's estimate, the annual amount of waste heat of the oil refineries and enterprises of the chemical industry and ferrous metallurgy is equivalent to 100–150 million tons of equivalent fuel [58]. With central heat production of 1470 million Gcal (data of 2001) its loss in the heat supply systems and consumers amounts to 40–50% (20% each in the heat supply system and in the consumers according to the Energy strategy data), which equals 590–735 million Gcal or 80–105 million tons of equivalent fuel. Half of the centrally produced heat is consumed in domestic applications with corresponding losses of 40–55 million tons of equivalent fuel. In all probability a considerable part of the above losses can be recovered by heat pumps at relatively high values of the power conversion factor.

2. Waste heat of heat power engineering objects. In the development scheme of the heat-supply system, there appears an economical niche for heat pumps for direct accumulation of heat from return heating water in a remote consumer at a price of waste heat. This becomes an alternative to the construction of expensive heat-supply systems in the center of heat loads of large cities. Thus, in the conditions of Omsk, as a result of utilizing waste heat from the thermoelectric plant with the use of the absorption heat pumps installed, saving of 0.22 tons of equivalent fuel on each 1 Gcal (final consumption) is possible [58]. Due to the recovery of waste gases by means of heat pumps it is possible to save per 1 Gcal in the final consumer 0.014 tons of equivalent fuel used on objects of the heat supply engineering.

The potential of natural high-temperature heat sources for heat pumps is very difficult to estimate, but it is obviously very high. For instance, the potential of Russia's geothermal sources alone amounts to 3450 PJ/g, or 118

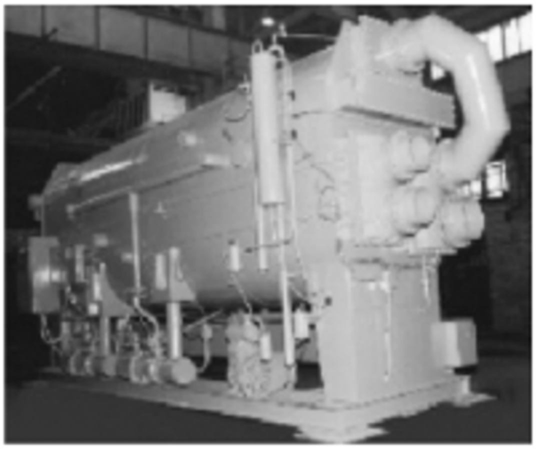


Fig. 13. Pilot-production vapor-compression heat pump for obtaining hot water in heating systems with simultaneous production of cold.

Fig. 14. Absorption heat engine created at the LLC "OKB Teplosibmash."

million tons of equivalent fuel [58]. At the same time it should be remembered that in the majority of cases (probably except for the use of geothermal heat sources) the power conversion factors for natural heat sources will be lower than for waste heat of the communal-domestic sector and production.

Estimates show that up to 20% of heat losses in the systems of centralized heat supply for housing and communal services can be used for conversion by heat pumps. For the estimation, heat pumps with powers that had already been attained in practice were taken: absorption lithium-bromide heat pumps made by the LLC "OKB Teplosibmash" [58], in which gas and vapor are used as a heating medium or fuel, and vapor-compression pumps made by the closed stock company "Energiya" [58], which operate on electronic power or gas. The advantages of absorption systems are first of all due to the fact that they operate in a steady-state regime and there is no need to alternately cool and heat the sorbent. Note that the vapor-based AbHP, being more environmentally friendly, can be economically sounder in the light of the existing system of GG emission charges.

At the Institute of Thermal Physics, Siberian Branch of the RAS, pilot-production vapor-compression heat pumps of a new generation have been created for obtaining hot water in the heating and hot water (55–80^{o}C) supply systems with simultaneous generation of moderate cold (2–10^{o}C) for air-conditioning systems and for cooling various technological media (Fig. 13). If necessary, these machines can be employed as refrigerators. This work was awarded a Grand gold medal of the Siberian fair in the category "Energy and resource saving." Production of heat pumps of caloric power from 30 to 1000 kW has been started. Engineering design of heat pump stations, manufacture, delivery, installation, adjustment, putting in operation, and service are conducted by the LLC SKB IPI on a commercial basis to individual orders.

Commercial absorption lithium-bromide heat pumps and coolers of a new generation for heating and cooling water and other media have been developed (Fig. 14). These machines feature a smaller amount of metal, smaller sizes, and a longer service life (no less than 20 years). Commercial production of machines of various standard sizes has been started:

- coolers for cooling water from 6^{o}C or higher based on different kinds of heating sources (vapor, hot water, fuel) with a cooling power from 250 to 5000 kW;
- heat pumps for heating water to 55–80^{o}C with the use of waste low-potential heat (20–40^{o}C) and different kinds of heating sources with a heating power from 500 to 5000 kW.

Delivery of machines and engineering maintenance are realized by the company "Teplosibmash" on a commercial basis to individual orders.

Compression-type heat pumps, or thermotransformers, are environmentally friendly compact freon devices which permit obtaining heat for heating and for hot water supply due to the utilization of heat of a low-potential source. As such a source, industrial and purified domestic effluents, water of process cycles and natural reservoirs, heat

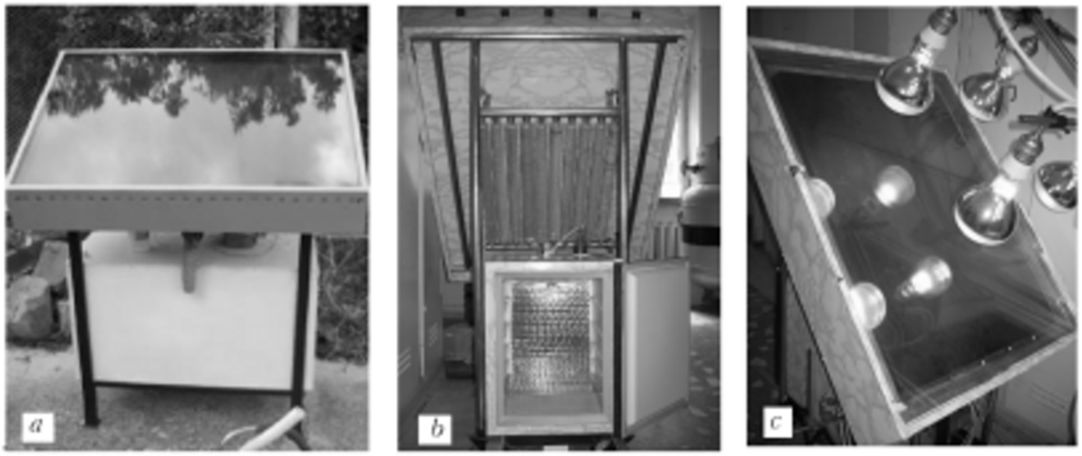


Fig. 15. Solar adsorption coolers according to [59] (a) and [60] [b) refrigerating chamber and condenser, c) heating by electric lamps].

of thermal waters, heat obtained in purifying flue gases, etc. can be used. The price of the heat generated by the heat pumps (depending on the performance) is 1.6–3.7 times lower than in the centralized heat supply.

As part of the INTAS international project 03-51-6260 "Solar assisted adsorption chiller using new adsorbent materials" (with the participation of teams from the Catalysis Institute, Siberian Branch of the RAS; the Joint Institute of High Temperatures of the RAS; the Moscow State University; the Institute of Engineering Thermal Physics of Ukraine; ITAE-CNR, and RWTH-Aachen), a solar assisted adsorption chiller was developed and made [59]; it passed a test for satisfaction in the Crimea in 2006 (Fig. 15a). This device uses water as a working fluid and the SSB-1K composite (calcium-chloride-modified silica gel), described in more detail below, as an absorbent. An analog made at the Catalysis Institute, Siberian Branch of the RAS, was subjected to tests in both sunlight and in heating by electric incandescent lamps (Fig. 15b). The latter regime permits creating controllable heating conditions and drawing, e.g., a comparison of various adsorbents [60]. The device has an area of the radiation absorption surface of 0.7 m^2, it contains about 20 kg of adsorbent, and is characterized by a solar coefficient of performance equal to 0.18–0.21 [59]. A solar adsorption refrigerator with an ammonia–calcium chloride working pair was created at the Astrakhan State University and is described in [61, 62].

The above analysis shows that the RF and the RB lag behind in the production and employment of heat pumps for heating and cooling. The state of the art in HPs in these countries is much worse than in the world, which calls for serious and urgent measures to eliminate this lag. This is crucial, since the RF and the RB have accumulated a large scientific and technological potential in the field of investigating ab- and adsorption-type heat engines. One result of this is the development and production in Russia of lithium-bromide absorption heat pumps and refrigerators of power 0.6–11 MW (see Table 3). For the conditions of the RB, heat supply systems for individual houses with the use of SHEs have been developed.

5. New Working Pairs for Adsorption Heat Engines. The adsorbent is one of the basic components of an AdHE and largely determines its output characteristics.

Influence of adsorbent properties on AdHE parameters. Criteria of choosing an adsorbent optimal for a particular cycle of the AdHE. An important point in developing an effective AdHE is the choice of an adsorbent providing optimal operating characteristics, among which are the coefficient of performance of the refrigerating machine COP and the specific cooling heat in one cycle Q_{cool}. As mentioned above, the COP value also directly determines the ecological cleanness of the AdHE. The question of choosing an adsorbent optimal for each particular cycle without heat regeneration was considered in [37, 38, 63, 64]. In these works, only thermodynamic analysis of the requirements for an optimal adsorbent was carried out, and some kinetic aspects are discussed in [60, 65].

Let us consider an ideal cycle of an adsorption cooler (AdC) using the Clapeyron–Clausius diagram (see Fig. 2b). As mentioned above, a cycle is fully determined by three temperatures: the coolant temperature in the condenser T_{c} and evaporator T_{e}, as well as the adsorbent dehydration temperature $T_3 = T_{\text{g}}$. In the case where all the three temperatures of the cycle are given, the efficiency of the AdC (COP) monotonically increases with increasing quantity of

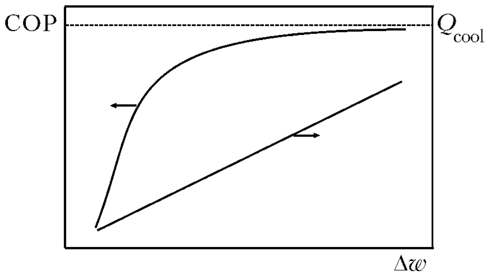


Fig. 16. COP and specific power of the adsorption cooler versus the specific quantity of water exchanged in a cycle (the dotted line corresponds to the asymptotic value of $\Delta H_{\text{ev}}/\Delta H_{\text{des}}$).

TABLE 3. Characteristics of Lithium-Bromide Absorption Heat Pumps

Parameters	Piston pump	Screw pump		
	NT-300	NT-500	NT-1000	NT-3000
Heat power, kW:				
for water of 8°C	300	500	1000	2500
for water of 25°C	400	800	1600	4000
Electric power consumption, kW·h				
for water of 8°C	90	150	300	630
Dimensions of the unit, m:				
compressor	4.5 × 1.8 × 1.7	2.8 × 2.2 × 1.1	4.0 × 1.5 × 2.3	5.2 × 2.0 × 3.0
condenser-evaporator		3.9 × 2.7 × 1.7	4.9 × 2.1 × 1.5	5.0 × 1.7 × 3.3
Weight, kg	4 300	9 700	15,000	22,000

the working fluid exchanged in the cycle Δw, asymptotically tending to $\Delta H_{\text{ev}}/\Delta H_{\text{des}}$, as schematically represented in Fig. 16 [63]. The specific cooling heat in the cycle $Q_{\text{cool}} = \Delta H_{\text{ev}}\Delta w$ grows even faster with increasing Δw. Thus, to increase the COP and Q_{cool}, it is necessary to use an adsorbent having a wider difference Δw between the extreme isosteres of the cycle 1–2 and 3–4 in Fig. 2. On the basis of this simple criterion a procedure was developed in [63, 64] which permits preliminary selection of materials that are promising for adsorption cooling proceeding from the sorption characteristics. It is based on the Polyanyi temperature invariance principle [65], according to which at different temperatures T' and T'' an equal degree of filling of the adsorption space with the adsorbate is attained at vapor pressures P' and P'' related by the relation

$$T'\ln\frac{P'}{P_s} = T''\ln\frac{P''}{P_s}. \tag{26}$$

From this principle follows a one-to-one correspondence between the adsorption value and the adsorption potential $\Delta F = -RT \ln \frac{P}{P_s}$ ln p, which was used later by M. M. Dubinin in the theory of volume filling of micropores [66, 67]. In this case, the volume of adsorbed working fluid is a function of only one variable (ΔF) rather than of the usual two variables (temperature and pressure), which considerably simplifies the analysis. It turned out that the Polyanyi temperature invariance principle is fairly universal and can be used for many adsorbents of both micro- and mesoporous nature [68].

If this principle is fulfilled, then to the extreme left isostere of the cycle 1–2, for which the adsorption is maximal ($w_{\max}$), there corresponds the adsorption potential $\Delta F_{\min}(T_e, T_c) = -RT \ln P(T_e)/P_s(T_c)$. Table 4 presents the values of both the adsorption potential $\Delta F_{\min}(T_e, T_c)$ and the quantity $\Delta F_{\max}(T_c, T_g)$ for the extreme right isostere with minimal adsorption at $T_e = 278$ K, $T_c = 303$ K, and $T_g = 353$ K. It is expedient to use the above-mentioned approach in looking for an optimal adsorbent among the already known materials satisfying the Polyanyi principle. In so doing, one can use the literature data on adsorption properties, including those obtained at temperatures and pressures other

TABLE 4. Adsorption Potential Values Corresponding to the Minimal and Maximal Adsorption

Working fluid	$\Delta F_{\min}(T_e, T_c)$, J/mole	$\Delta F_{\max}(T_e, T_g)$, J/mole
Water	3991.3	7072.5
Methane	3470.5	6225.4
Ammonia	2057.6	3717.8

TABLE 5. Experimental and Calculated Temperatures for the Methanol–Carbon TA90 Working Pair

T_e, ^oC	T_c, ^oC	$T_{2\exp}$, ^oC	$T_{2\text{calc}}$, ^oC	ΔT, ^oC
0	26.3	56.1	55.1	–1.0
0	30.6	63.0	64.6	1.6
0	36.1	77.2	77.0	–0.2
0	41.5	90.1	89.3	–0.8
0	50.1	110.5	109.4	–1.1
10	37.1	66.3	66.8	0.5
10	41.0	76.8	75.4	–1.4
10	46.5	87.2	87.7	0.5
10	51.7	102.3	101.2	–1.1

than the data realized in a real cycle of adsorption and absorption chemical heat engines (AChE). In particular, this analysis can be performed on the basis of only one adsorption isotherm or isobar. It is only essential that experimental data fall within the range of values of $\Delta F_{\min} \le \Delta F \le \Delta F_{\max}$. In [63, 64], this approach was used successfully in choosing water and methanol adsorbents for an adsorption cooler whose motive force is low-potential heat.

Consider now the case where for an AdHE cycle only the temperatures T_e and T_c are given and it is required to determine the minimum temperature $T_{\min} = T_d = T_2$ (Fig. 2) needed for isobaric desorption of the working fluid in the case where the pressure P_c is kept over the sorbent. Obviously, for adsorbents satisfying the Polyanyi principle this temperature can be calculated from the equality $\Delta F(T_e, T_c) = \Delta F(T_c, T_{\min})$. Another approach is to use the empirical Truton rule, according to which the sorption isosteres of the working fluid and the curve of its balance with vapor intersect at $T = \infty$ [2, 69, 70]. This statement differs from the formulation of the Truton rule accepted in chemistry, according to which the molar entropy of evaporation of any liquid is equal to about 89 J/(mole·K) [9]. The analysis performed by us has shown that the empirical rule performs well for the majority of the working pairs used in AdHEs: water Fuji Davison RD silica gel, water–zeolite 13X, water–composites "salt in a porous matrix," CO_2-carbon, methanol–carbon (AC-35, TA90), methanol–hydrophobic zeolite CBV 901 Y, and ammonia–carbon PX31, as well as for the main working pairs of AbHEs: ammonia–water, water–LiBr, and methanol–LiBr.

If this rule performs, then it is easy to obtain a universal relation between the three temperatures providing reversibility of a cycle:

$$T_c^2 = T_e T_g , \tag{27}$$

which is independent of the adsorbent and adsorbate nature. Note that in [12] this relation was obtained from the reversibility conditions of the cycle of an ideal absorption heat engine without considering the detailed form of the function $P(T)$. Table 5 gives the experimental ($T_{2\exp}$) and calculated from (27) ($T_{2\text{cal}}$) temperatures for the methanol–carbon TA90 working pair, as well as their difference ΔT. It is seen that the latter is equal to 1–2^{o}C, which is close to the exactness of finding $T_{2\exp}$.

From relation (13) several useful conclusions follow. For instance, the minimal desorption temperature for the cooling and heating cycles can be calculated as [12, 69, 70]

$$T_{\min} = \frac{T_c^2}{T_e} . \tag{28}$$

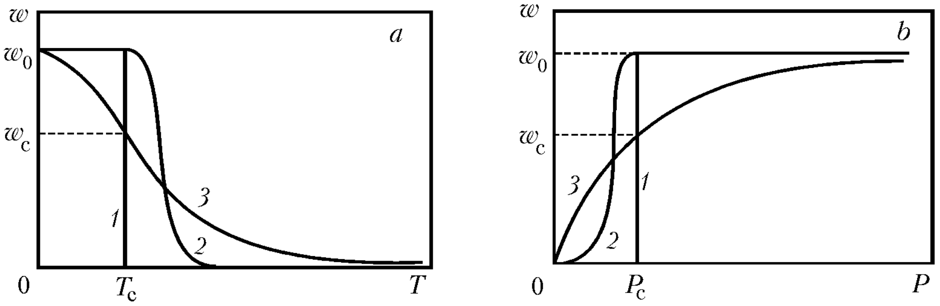


Fig. 17. Typical isobars $P = P_c$ = const (a) and isotherms $T = T_c$ = const (b) of adsorption in the case of mono- (1) and divariant (2, 3) equilibrium.

The external heat source used for desorption should apparently have a temperature $T_g \geq T_{min}$. If $T_g < T_{min}$, then the process cannot be realized because the pressure over the sorbent cannot reach the pressure in the condenser P_c. At $T_g = T_{min}$ the process will be reversible and the efficiency of the AdHE will be maximal:

$$\mathrm{COP}_{max} = \left(\frac{1}{T_c} - \frac{1}{T_g}\right) \Big/ \left(\frac{1}{T_e} - \frac{1}{T_c}\right).$$

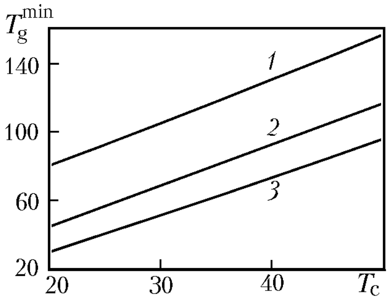
If $T_g > T_c$, then the efficiency decreases since the heat is transferred at a finite temperature difference between the adsorber and the external heat source. Consequently, the *optimal adsorbent* at pressure P_c should hold the maximal mass of the working fluid at $T < T_{min}$, and upon reaching the temperature T_{min} all of it should be removed. Thus, for such an adsorbent the desorption isobar at P_c should be stepped (Fig. 17, curves 1) as for systems with a monovariant type of equilibrium [37, 38]. For the real adsorbent the equilibrium is divariant, and therefore the maximum quantity of the working fluid should be exchanged in a narrow temperature range near T_{min} (Fig. 17, curves 2). It can easily be seen that this condition is satisfied by adsorbents SSV-1K, FAM-Z02, SSV-5K, and FAM-Z01, whose isotherms are given in Fig. 3.

Figure 18 shows the dependences $T_{min}(T_c)$ calculated from (28) for three different modes of cooling: air conditioning (T_e = 10°C), ice making (T_e = –5°C), and deep freezing (T_e = –30°C). Let us consider in more detail some examples.

Air conditioning. One of the most high-demand applications of adsorption and absorption heat engines is automative air conditioning [14, 15]. In this case, the necessary temperature in the evaporator T_e = 7–12°C and the condenser temperature T_c = 35–45°C. Relation (28) permits estimating the minimal temperature needed to regenerate the adsorbent. For the most drastic conditions (T_e = 7°C, T_c = 45°C)·T_{min} = 88°C, and for mild conditions (T_e = 12°C, T_c = 35°C)·T_{min} = 60°C. In the second case, heat from the engine cooling system can be used for adsorbent regeneration since its temperature potential T_g is usually above 80°C [14, 15]. The first of the above modes can also be realized, though with much difficulty, by means of this heat, since its temperature potential is below 95°C, and the difference of 7°C may be insufficient to provide the required air-conditioning power.

Air conditioning in a room is easier to realize: even in a hot climate (T_c = 45–50°C), to obtain T_e = 10°C, a minimal regeneration temperature of 84–95°C is required and can be attained with the help of fairly simple and cheap solar energy (SE) [59, 71] — using equipment or cooling heat of different engines [8, 14, 15] which usually dissipates.

Ice production. In a hot climate (T_c = 45–50°C), to obtain ice (T_e = 0°C), a heat source with a minimal temperature of 100–110°C is required, which is more difficult to realize in simple SE-using equipment. For this purpose it is necessary to use selective coatings or vacuum insulation [71], which considerably raises the price of the equipment. In a moderate climate (T_c = 30°C)·$T_g \geq$ 63°C, which is easy to attain under the conditions of solar radiation typical in summer, e.g., of the middle part of Russia. Note that in solar adsorption coolers regeneration is carried out in the daytime, and cold is produced by night, at a lower temperature of the adsorber equal to the ambient temperature. This permits obtaining a lower temperature in the evaporator as well. Such a case of heat accumulation in the daytime is described in more detail below. Twenty-four-hour production of cold is possible by using the solar coolers



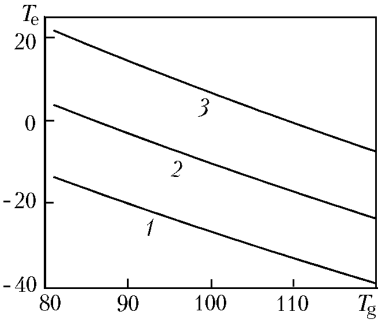


Fig. 18. Minimal temperature of the external heat source $T_g^{\min}$ as a function of the condenser temperature for three variants of adsorption cooling: deep freezing (1), ice production (2), and air conditioning (3). $T_g^{\min}$, T_c, $^{\circ}$C.

Fig. 19. Evaporator temperature versus the external source temperature at various condenser temperatures: 1) T_c = 30; 2) 40; 3) 50°C. T_e, T_g, $^{\circ}$C.

developed at the Heat and Mass Transfer Institute of the National Academy of Sciences of Belarus [84–86]. The original heat control system permits refrigerant recirculation in a short cycle time (20–30 min).

Deep freezing. To cool the evaporator down to the temperature $T_c = -18^{\circ}$C as recommended for deep freezing provided that the condenser is at $T_c = 2^{\circ}$C, it is necessary to carry out regeneration of the adsorbent at a temperature exceeding 64°C. Even at $T_e = -50^{\circ}$C the minimal regeneration temperature is still easy to attain: $T_g \geq 112^{\circ}$C. This shows that adsorption devices can be effective for obtaining relatively low temperatures needed, e.g., for storing vaccines or drying thermolabile substances [34]. The AdHE (ChHE) potential for these purposes has not yet been practically realized.

In this connection it is tempting to estimate the minimal temperature $T_e^{\min}$ which can be obtained in the evaporator if a heat source with temperature T_g is available and the condenser temperature is equal to T_c. From the universal equation (27)

$$T_e^{\min} = \frac{T_c^2}{T_g} \tag{29}$$

follows. Thus, having a heat source with $T_g = 80^{\circ}$C, in a cool climate ($T_c = 20^{\circ}$C) it is possible to obtain $T_e = -30^{\circ}$C, and in a hot climate ($T_c = 45^{\circ}$C) only $T_c = +13^{\circ}$C can be obtained, i.e., the influence of the condenser (adsorber) temperature is strong. Figure 19 shows the function $T_e(T_g)$ at three rather high values of T_c calculated by Eq. (29). It is seen, for example, that the temperature of -18°C recommended for freezing is attainable even at an ambient temperature $T_c = 30^{\circ}$C while adsorbent regeneration occurs at only 87°C. In particular, if for the solar adsorption cooler in the daytime (at the regeneration stage) it was possible to heat the adsorbent to temperature T_g, then by night at a temperature of the adsorber T_c equal to the ambient temperature (which is lower than in the day-time) it will also be possible to attain a much lower temperature in the evaporator $T_e^{\min}$ (night) than in realizing the cooling stage in the daytime: $T_e^{\min}(\text{day}) = T_c^2(\text{day})/T_g > T_e^{\min}(\text{night}) = T_c^2(\text{night})/T_g$. Since at $T_g = 67^{\circ}$C $T_c(\text{day}) = 30^{\circ}$C and $T_c(\text{night}) = 16^{\circ}$C, we obtain $T_e^{\min}(\text{night}) = -29^{\circ}\text{C} \ll -3^{\circ}\text{C} = T_e^{\min}(\text{day})$. Figure 20a shows the function $T_e(T_c)$ calculated by Eq. (29). It is seen that even at a low regeneration temperature in the evaporator, in principle, a temperature below -20°C can be attained if the adsorber and condenser are kept at a temperature not higher than $+20^{\circ}$C.

The universal relation (27) also permits estimation of the maximum temperature $T_c^{\max}$ which is attainable in the condenser (at the stage of desorption) and in the adsorber (at the stage of adsorption) if the temperatures of the external heat source T_g and evaporator T_c are given:

$$T_c = \sqrt{T_g T_e}\ . \tag{30}$$

Such estimation is of interest for analyzing environmentally friendly and energetically effective adsorption heaters. For instance, using, as an evaporator, a reservoir with a temperature of 5°C and expending for the sorbent regeneration

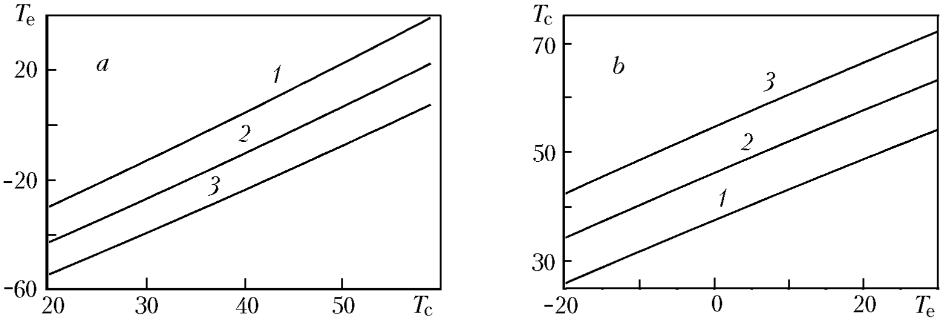


Fig. 20. Evaporator temperature versus the condenser temperature (a) and condenser temperature versus the evaporator temperature (b) at various temperatures of the external source: 1) T_g = 120; 2) 100; 3) 80°C. T_c, T_e, °C.

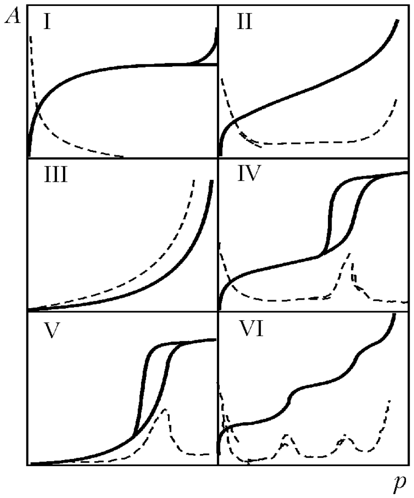


Fig. 21. Adsorption isotherms (solid lines) and their derivatives (dashed lines): I–IV) various types of isotherms according to [73, 74].

heat Q at a temperature of 70–80°C in the condenser and adsorber one can obtain a heat (1.5–1.8)·Q at a temperature of 35–40°C, which suffices for heating, e.g., the floor in domestic or office premises. If ground waters with a temperature of 20–25°C (reserves of this natural heat source are enormous in many parts of Russia) are used for evaporation, then a heat with a temperature potential of 45–50°C can be obtained. The functions $T_c(T_e)$ calculated by (30) at various values of T_g are presented in Fig. 20b.

If the adsorbent regeneration stage is carried out in summer using solar energy and thus accumulating it, then at the adsorption stage in winter this accumulated energy can be obtained in the adsorber at a temperature $T_c \leq T_c^{max}$. In this case, the heat pump operates as a thermal energy accumulator completing a cycle in a year. For countries where the price difference between "day" and "night" electricity (e.g., in Japan [71]) is great, a ChHE (AHE) can be used to accumulate supplies of "cheap" electricity by night with the aim of using the accumulated heat in the daytime. In this case, a high value of T_c^{max} can be obtained, since the electric heater permits attaining high values of the regeneration temperature T_g. For instance, at T_g = 300°C and T_c = 5°C T_c^{max} = 126°C. In such a process, it is necessary to use reactions proceeding at high temperatures, e.g., $MgO + H_2O = Mg(OH)_2$, or adsorbents with a high regeneration temperature, e.g., zeolites.

Thus, the universal relation (27) makes it possible to formulate requirements for the adsorbent optimal for a particular cycle of the AdHE (without heat regeneration) in a given climatic zone. For instance, Figure 18 shows that to make ice, e.g., in a hot climate (T_c = 45°C), a heat source with $T_g \geq 105$°C is needed, whereas in a cool climate (T_c = 20°C) a source with $T_g \geq 47$°C suffices. In the first case, an adsorbent which holds the working fluid at a tem-

TABLE 6. Values of Temperature T_d Corresponding to the Transitions between Various Hydrates of Salts in the Mass and Disperse (pores of size 15 nm) States at a Pressure of Water Vapors of 56.3 mbars

Salt	Transition	T_d, °C	
		Mass state	Disperse state
Na_2SO_4	$1 \Rightarrow 7$	39	46
	$7 \Rightarrow 10$	37	—
Na_2HPO_4	$0 \Rightarrow 2$	53—55	—
	$2 \Rightarrow 7$	45—49	—
$Ca(NO_3)_2$	$0 \Rightarrow 2$	65—67	70—72
$MgSO_4$	$0 \Rightarrow 1$	114	210—270
	$1 \Rightarrow 2$	99—101	155—210
	$2 \Rightarrow 4$	71—75	—
	$4 \Rightarrow 6$	59—63	—
$CaCl_2$	$0 \Rightarrow 1/3$	> 155	—
	$1/3 \Rightarrow 2$	104—108	110—115
	$2 \Rightarrow 4$	71—73	76—80
LiBr	$0 \Rightarrow 1$	155	155
	$1 \Rightarrow 2$	104—108	115—135
LiCl	$0 \Rightarrow 1$	80—87	76—80
	$1 \Rightarrow 2$	100—105	87—98

perature of up to 105°C and then releases heat in a narrow temperature range at $T \geq 105°C$ is needed. In the second case, the process proceeds at a much lower temperature.

In this connection, it is interesting to analyze the applicability of the known types of adsorbents in AdHEs. To this end, let us use the classification proposed first in [73], according to which most adsorption isotherms may be classified under five types (I–V). Moreover, we have considered the relatively rare stepped isotherms which in [74] are classified under type VI. All of the above isotherms are given in Fig. 21. It turned out that those materials can be promising for use in adsorption cooling systems, which are able to reversibly sorb/desorb a large amount of the working fluid w in a relatively narrow range of variation of the adsorption potential ΔF (or relative pressure $p = P/P_0$). Thus, the derivative $dw/d(\Delta F)$ or dw/dp for these adsorbents should be large in the required range of ΔF or p values. Adsorbents with isotherms of types I, IV, V, and VI satisfy this criterion.

Theoretically ideal isotherms seem to be stepped isotherms of type VI, which for conventional one-component adsorbents can be obtained only in exotic cases. To realize such isotherms, it was suggested to modify the conventional sorbents by inorganic salts [37, 38]. In so doing, a change in the sorption value occurs due to the proceeding of a chemical reaction between the working fluid and the salt with the formation of salt crystal solvates whose equilibrium is monovariant. Exactly such adsorbents will be considered below in more detail.

Development of methods of purposeful synthesis of composite adsorbents of water for adsorption heat pumps. Since the largest possible amount of the working fluid should be exchanged in a narrow temperature range near T_{min}, it is best of all to use, as sorbents, solid substances whose equilibrium with the working fluid is monovariant as, e.g., in reaction (1) of the gas-solid type. Indeed, it is the ChHPs that permit, in principle, attaining the maximum performance in a simple cycle without heat regeneration [13]. Therefore, inorganic salts may be more promising than conventional adsorbents with a divariant type of equilibrium. The decomposition temperatures of complexes of some salts with water at a pressure of 56.3 mbars (which corresponds to $T_c = 35°C$) are given in Table 6. It is seen that for the considered hydrates the decomposition temperature varies between 37 and 155°C, so that for any temperature potential of the external source it is possible to select an adequate hydrate. A similar situation is observed for ammonicates [75]. For reactions of a salt with lower alcohols the thermodynamical data are very limited [76, 77], which makes impossible thermodynamic selection of a salt and one has to employ an exhaustion method [64].

Despite the above advantages of ChHPs with massive salts, their practical application is hindered by several serious factors:

a) considerable increase in the volume of the solid phase in the course of complexing (for complexes with ammonia it may reach 3–4 times) [17, 22, 78];

b) hysteresis in reaction (1), as a result of which decomposition of a complex may occur at a much higher temperature than its formation [79–81];

c) low rate of reaction (1) due to the nondeveloped reaction surface and/or the formation on the surface of the salt of a new phase, gas diffusion through which is hindered [81, 82];

d) corrosion activity of salts and complexes when in contact with metal parts of the ChHP.

To overcome these difficulties and intensify the heat transfer, new two-component sorbents of ammonia [83–93], water [37, 38, 41, 79, 94–106], and methanol [64, 107] were proposed. In these sorbents, microcrystallites of the active salt were placed on the outer or inner surface of a less active component — a matrix acting as a dispersive agent and promoting the intensification of the heat and mass transfer in a sorbent layer. Placing micro- and nanoparticles of metal salts on the surface of active carbon fibers "salt on the fiber surface" stimulates the process of heat and mass transfer, increases the permeability of the system, accelerates the process of gas filtration through the sorbent, and improves the sorption capacity of the composite [109]. The cycles of sorption/desorption of the working fluid in a heat engine are expedited. Sorption of the working fluid by such materials is mainly due to the reaction with the salt as in ChHEs, but the implementation is as in AdHEs. Two-component adsorbents of the type "salt in a porous matrix" and "salt on the fiber surface" offer much more possibilities for varying their properties than single-component ones. Indeed, for the latter only the chemical nature of the adsorbent (silica gel, aluminum oxide, zeolites, etc.) and its porous structure can be varied. For composites, one can additionally vary the chemical nature and the technique of introducing a second component, as well as the component ratio.

A review of composite adsorbents of ammonia and water has been done recently in [108]. The principal conclusions can be summarized as follows:

a) placing the salt in the matrix pores or on the surface of an active carbon fiber makes it possible to solve the above problems: matrices from busophite, vermiculite, and ACF make it possible to "soften" the great change in the salt volume in the chemical reaction [92, 109], the "synthesis–decomposition" hysteresis can be eliminated or reduced appreciably [79], the hydration rate of the dispersed salt is determined by the mass transfer rather than by the chemical reaction [109–112], and capsulization of the salt in the pores prevents it from contacting the wall and avoids corrosion;

b) adsorption of water by the composite is not a linear superposition of adsorption by the salt and matrix, i.e., synergism of properties is observed [79]. In particular, the pressure (and consequently the temperature) of reaction (1) can be shifted by placing the salt in the matrix pores. For instance, the temperature of the formation of hydrates and methanolates increases with decreasing size of the pores [37, 39] (Table 6) and decreases for the formation of ammonia complexes [92]. This effect permits "precise adjustment" of the transition (reaction (1)) temperature to the temperature required for a particular cycle;

c) the salt in the pores forms two phases — a bulk crystalline phase and a surface X-ray-amorphous phase, which differ qualitatively in the character of water absorption. The sorption equilibrium of composite sorbents with water vapors depends on the ratio between the crystalline and amorphous phases, which can be varied in the process of synthesis by changing the content of the salt, pH of the impregnating solution, and the calcination temperature of the composite [110–103].

Recently a new direction connected with systems of tri-generation of energy (electricity, heat, cold) has appeared in the practical realization of solid-sorbent heat engines [112, 113]. Using sorption heat engines jointly with internal or external combustion engines (diesel, Stirling machine) or with fuel cells for stationary applications makes it possible to considerably upgrade the efficiency of using fuel and provide environment protection.

CONCLUSIONS

1. The employment of ChHEs and SHEs in the RF and the RB provides strong possibilities for energy saving in the power engineering, industry, and housing and communal services. The main heat sources for these heat engines

are heat of natural gas burning, waste heat of enterprises and heat supplying systems, as well as geothermal and ground waters. As a low-temperature heat source, heat of the ambient and exhaust air, the ground, natural reservoirs, ground waters, effluents, etc. is used in the evaporator.

2. The state of the art in developing HPs in these countries is much worse than in the world: for instance, in the RF about 150 HPs operate against 150 million heat pumps operating in the world. Drastic and urgent measures are required to eliminate this lag.

3. ChHEs and SHEs are preferable to CHEs since they don't use electric energy. Their advantages may grow due to the signing by Russia of the Kyoto protocol. In this connection, it seems important to use the proceeds obtained from selling quotas for the emission of green-house gases to finance energy-saving projects, in particular, to develop production of CHEs and SHEs and their market.

4. Under the climatic conditions of the Russian Federation and the Republic of Belarus of particular interest is the use of HPs for heating. Sorption cooling systems may find application in summer, including use of solar energy as a high-potential heat source.

5. The RF and the RB have built up a serious scientific and technological potential in the field of the investigation of sorption-type HPs, as well as the intensification of the heat and mass transfer by means of heat pipes. A new family of composite adsorbents of water, ammonia, and methanol for air-conditioning systems has been developed.

6. On the basis of the acquired knowledge and experience, prototypes of adsorption systems for air conditioning and ice making have been developed and tested. Production of new composite adsorbents for SHEs has been set up. For the RB conditions, networks of heat supply for individual houses with the use of SHEs have been developed.

7. Since in the heat power engineering of the RF and the RB a considerable structural reorganization is to take place soon, which calls for significant investments, it would be rational to allocate part of the funds to the introduction of the available heat pump technologies (including vapor-compression ones) and the development of new heat engines of the chemical and sorption type.

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NOTATION

A, amount of CO_2 produced per 1 kw·h of energy consumed by the device; $A_{\rm s}$, $A_{\rm el}$, $A_{\rm n.g}$, amount of CO_2 for SHEs, in producing electric energy, and in using natural gas; $C_{\rm s}$, $C_{\rm c}$, $C_{\rm b}$, total annual costs of consumed power for SHEs, CHEs, and gas-fired boilers; $\mathrm{COA_s}$, amplification coefficient for STPs; COP, coefficient of performance of a refrigerating machine; $\mathrm{COP_s}$ and $\mathrm{COP_c}$, coefficient of performance of a refrigerating machine for SHEs and CHEs; E, volume of "green-house" gas GG released into the atmosphere; ΔF, adsorption potential; GWP, global warming potential; H', running time of the device; H, enthalpy; ΔH, SV formation heat; ΔH^0 and ΔS^0, changes in standard enthalpy and entropy upon SV formation; $\Delta H_{\rm e}$ and $\Delta S_{\rm e}$, changes in enthalpy and entropy caused by evaporation; $\Delta H_{\rm ev}$ and $\Delta H_{\rm des}$, heat of evaporation and desorption; $k_{\rm el}$ and $k_{\rm n.g}$, cost of 1 kW·h of electric energy and heat resulting from natural gas burning; M, working fluid mass; m, sorbent mass; P, pressure; P_0, fixed pressure; $P_{\rm s}$, pressure of saturated adsorbate vapors; $P_{\rm c}$, equilibrium pressure in the condenser; $p = P/P_0$; Q, heat; $Q_{\rm h}$, annual heat release; Q_0, annual average cooling load; $Q_{\rm cool}$, specific heat of cooling in a cycle; q, tax on the release of 1 kg of CO_2 into the atmosphere; R, universal gas constant; S, entropy; T, temperature; T_1, T_2, T_3, temperatures corresponding to positions 1, 2, 3 in Fig. 2; $T_{\rm g}$, $T_{\rm c}$, and $T_{\rm e}$, temperatures of the external source, condenser, and evaporator; $T_{\rm d}$, desorption temperature; V, sorbent volume; W, power; $W_{\rm sp}$, specific power; W', annual energy consumption; $W_{\rm cool}$, cooling power; w, ratio of the adsorbed gas mass to the sorbent mass; Δw, quantity of the working fluid exchanged in a cycle; ε, relative decrease in the GG emission; γ, share of economy of costs of energy consumption; η, performance of a heat engine; $\eta_{\rm cool}$, coefficient of performance of a refrigerating machine; $\eta_{\rm heat}$, gain coefficient; $\eta_{\rm t.p}$, coefficient of change in the temperature potential; $\eta_{\rm b}$, efficiency of heat generation in the combustion chamber; τ, annual loss of the working fluid. Subscripts: b, boiler; c, condenser; cal, calculated; d, desorption; e, evaporator; el, electric energy; exp, experimental; g, external source (gas); h, heat release; max, maximum; min, minimum; n.g, natural gas; s, sorption; des, desorption; ev, evaporation; heat, heating; cool, cooling; t.p, temperature potential; sp, specific.

REFERENCES

1. S. Carnot, *Réflexions sur la puissance motrice du feu et sur les maschines propres à développer cette puissance*, Paris (1824).
2. G. Alefeld and R. Radermacher, *Heat Conversion Systems*, CRC Press, Boca Raton (1994).
3. Proceedings of the Annual Meeting of the Russian Academy of Sciences, *Vestn. Ross. Akad. Nauk*, **76**, No. 5, 3–46 (2006).
4. W. M. Raldow and W. E. Wentworth, Chemical heat pumps — a basic thermodynamic analysis, *Solar Energy*, **23**, 75–79 (1979).
5. P. Rittinger, *Theoretisch-praktische Abhandlung ueber ein fur alle Gattungen von Fluessigkeiten anwendbares neues Verdampfungsverfahren mittelst einer und derselben Waermemenge, welche zu diesem Behufe durch Wasserkraft in ununterbrochenen Kreislauf versetzt wird. Mit spezieller Ruecksicht auf den Salzsiedeproze dargestellt*, Verlag von Friedrich Manz, Wien (1855).
6. L. L. Vasil'ev, Environment friendly coolants and cooling cycles for the Republic of Belarus, *Énergoeffektivnost'*, No. 8, 21–23 (2005).
7. L. L. Vasil'ev and L. E. Kanonchik, Sorption engines — an efficient energy saving technology, *Énergoeffektivnost'*, No. 7, 14–16 (2002).
8. L. L. Vasil'ev, O. S. Filatova, and A. A. Antukh, New technologies of efficient use of natural gas in the Republic of Belarus, *Énergoeffektivnost'*, No. 1, 8–11 (2007).
9. M. F. Karapetyants, *Chemical Thermodynamics* [in Russian], Khimiya, Moscow (1978).
10. M. Felli, Absorption refrigeration thermodynamics, *ASHRAE Trans.*, Pt. 1A, No. 2748, 234–241 (1983).
11. F. Meunier, Second-law analysis of a solid adsorption heat pump operating on reversible cascade cycles: application to the zeolite–water pair, *Heat Recovery Systems*, **5**, 133–141 (1985).
12. R. M. Tozer and I. W. James, Fundamental thermodynamics of ideal absorption cycles, *Int. J. Refrig.*, **20**, No. 2, 120–135 (1997).
13. V. E. Sharonov and Yu. I. Aristov, Chemical and adsorption heat pumps: comments on the second law efficiency, *Chem. Eng. J.*, **7**, No. 8 (2007).
14. D. Tchernev, A waste heat driver automotive air conditioning system, in: *Proc. Int. Sorption Heat Pump Conf.*, 24–26 March 1999, Munich (1999), pp. 65–70.
15. B. J. Jones and M. A. Lambert, Adsorbent–refrigerant selection for automotive adsorption heat pump, *AIAA*, 9286–9297 (2004).
16. Y. Z. Lu, R. Z. Wang, M. Zhang, and S. Jiangzhou, Adsorption cold storage system with zeolite–water working pair used for locomotive air conditioning, *Energy Conversion Management*, **44**, 1733–1743 (2003).
17. L. W. Wang, R. Z. Wang, J. Y. Wu, and K. Wang, Compound adsorbent for adsorption ice maker on fishing boats, *Int. J. Refrig.*, **27**, 401–408 (2004).
18. M. A. Lambert and B. J. Jones, Review of regenerative adsorption heat pumps, *J. Thermophys. Heat Transfer*, **19**, No. 4, 471–493 (2005).
19. B. N. Okunev and M. S. Safonov, A detailed analysis of entropy production and refinement of the thermodynamic cycle of an adsorption cooler, *Inzh.-Fiz. Zh.*, **79**, No. 4, 146–152 (2006).
20. V. Goetz and A. Guillot, An open activated carbon/CO_2 sorption cooling system, *Ind. Eng. Chem. Res.*, **40**, 2904–2913 (2001).
21. I. I. El-Sharkawy, K. Kuwahara, B. B. Saha, et al., Experimental investigation of adsorption of ethanol onto activated carbon fibers for possible application in adsorption cooling systems, *Appl. Thermal Eng.*, **26**, No. 8–9, 859–865 (2006).
22. K. Fujioka, T. Sekiguchi, and Yu. Kato, Numerical investigation of reaction and thermal characteristics of reactor beds for gas-solid chemical heat pumps, in: *Proc. HPC-06*, 12–14 September 2006, New Castle (2006), pp. 41–42.
23. N. D. Banker, K. Srinivasan, and M. Prasad, Performance analysis of activated carbon + HFC 134a adsorption coolers, *Carbon*, **42**, 113–123 (2004).
24. B. Spinner, Ammonia-based thermochemical transformers, *Heat Recovery Systems*, **13**, No. 4, 301–307 (1993).

25. N. C. Srivastava and I. W. Eames, A review of adsorbents and adsorbates in solid–vapor adsorption heat pump systems, *Appl. Thermal. Eng.*, **18**, 707–714 (1998).
26. F. Meunier, Solid sorption heat powered cycles for cooling and heat pumping applications, *Appl. Thermal Eng.*, **18**, 715–729 (1998).
27. M. Pons, F. Meunier, G. Cacciola, R. E. Critoph, M. Groll, L. Puiganer, B. Spinner, G. Restuccia, and F. Ziegler, Thermodynamics- based comparison of sorption system for cooling and heat pumping, *Int. J. Refrig.*, **22**, 5–17 (1999).
28. G. Cacciola and G. Restuccia, Adsorption heat pumps: a new way for energy saving and CFCs replacement, in: A. Dabrowski (Ed.), *Adsorption and Its Application in Industry and Environmental Protection Studies in Surface Science and Catalysis*, Vol. II, Elsevier, Amsterdam (1999), pp. 949–978.
29. F. Meunier and V. Goetz, Energy storage comparison of sorption systems for cooling and refrigeration, *Solar Energy*, **71**, No. 1, 47–55 (2001).
30. A. O. Dieng and R. Z. Wang, Literature review on solar adsorption technologies for ice-making and air conditioning purposes and recent developments in solar technology, *Renewable Sustainable Energy Rev.*, **5**, 313–342 (2001).
31. F. Ziegler, State of the art in sorption heat pumping and cooling technologies, *Int. J. Refrig.*, **25**, 450–459 (2002).
32. R. Critoph and Y. Yang, Review of trends in solid sorption refrigeration and heat pumping technology, in: *Proc. Inst. Mech. Eng.*, Part E, *J. Mech. Proc. Eng.*, **219**, 1–16 (2005).
33. R. Z. Wang and R. G. Oliveira, Adsorption refrigeration — an efficient way to make good use of waste heat and solar energy, *Progr. Energy Combust. Sci.*, **32**, 424–458 (2006).
34. B. Dawoud, A hybrid solar-assisted adsorption cooling unit for vaccine storage, *Renewable Energy*, **32**, 947–964 (2007).
35. M. Z. I. Khan, B. B. Saha, K. C. A. Alam, A. Akisawa, and T. Kashiwagi, Study on solar/waste heat driven multi-bed adsorption chiller with mass recovery, *Renewable Energy*, **32**, No. 3, 365–381 (2007).
36. T. Nunez, H.-M. Henning, and W. Mittelbach, Adsorption cycle modelling: characterization and comparison of materials, in: *Proc. Int. Sorption Heat Pump Conf.*, 24–26 March 1999, Munich (1999), pp. 209–217.
37. Yu. I. Aristov, An optimal sorbent for adsorption heat pumps: thermodynamic requirements and molecular design, in: *Proc. VI Int. Seminar "Heat Pipes, Heat Pumps, Refrigerators,"* 12–15 September 2005, Minsk, Belarus (2005), pp. 342–353.
38. Yu. I. Aristov, New composite adsorbents for conversion and storage of low temperature heat: activity in the Boreskov Institute of Catalysis, *J. Heat Transfer Soc. Japan*, **45**, No. 192, 12–19 (2006).
39. F. Meunier, Sorption contribution to climate change mitigation, in: *Proc. Int. Conf. Sorption Heat Pumps*, 24–27 September 2002, Shanghai (2002), pp. 1–9.
40. Yu. I. Aristov, Some ecological and economical aspects of the use of adsorption heat devices in Russia, *Chemistry of Stable Development*, **12**, 751–755 (2004).
41. L. L. Vasil'ev, L. E. Kanonchik, and A. A. Antukh, Contemporary thermodynamic cycles in power engineering — a means for reducing carbon dioxide emissions into the atmosphere and increasing the performance of power stations, *Energoeffektivnost'*, No. 11, 16–18 (2002).
42. Yu. I. Aristov, G. Restuccia, G. Cacciola, and V. N. Parmon, A family of new working materials for solid sorption air conditioning systems, *Appl. Thermal Eng.*, **22**, No. 2, 191–204 (2002).
43. G. Restuccia, Yu. I. Aristov, G. Maggio, G. Cacciola, and M. M. Tokarev, Performance of sorption systems using new selective water sorbents, in: *Proc. Int. Sorption Heat Pump Conf.*, 24–26 March 1999, Munich (1999), pp. 219–223.
44. H. J. Laue, Regional European report "Heat pumps — status and trends," *Int. J. Refrig.*, **25**, 414–420 (2002).
45. R. Lazarin, Heat pump technology: state-of-the-art, in: *Proc. 5th Int. Conf. on Sustainable Energy Technologies*, 30 August–1 September 2006, Vicenza, Italy (2006), pp. 105–110.
46. http://energyoutlet.com/
47. M. Matsushita et al. Adsorption chiller using low-temperature heat sources, *Energy Conservation*, **39**, No. 10, 96 (1987).

48. Y. Yonezawa et al. Adsorption refrigeration system, US Patent No. 4881376 (1989).
49. Y. L. Liu, R. Z. Wang, and Z. Z. Xia, Experimental performance of a silica gel–water adsorption chiller, *Appl. Thermal Eng.*, **25**, 359–375 (2005).
50. A. Freni, F. Russo, S. Vasta, M. M. Tokarev, Yu. I. Aristov, and G. Restuccia, An advanced solid sorption chiller using SWS-1L, *Appl. Thermal Eng.*, **27**, No. 13, 2200–2204 (2007).
51. T. Nunez, W. Mittelbach, and H.-M. Henning, Development of an adsorption chiller and heat pump for domestic heating and air-conditioning applications, *Appl. Thermal Eng.*, **27**, No. 13, 2205–2212 (2007).
52. L. L. Vasiliev, D. A. Mishkinis, A. A. Antuh, and L. L. Vasiliev, Jr., Solar-gas solid sorption refrigerator, *Adsorption*, **7**, 149–161 (2001).
53. L. L. Vasiliev, N. V. Gulko, and V. M. Khaustov, Solid adsorption refrigerators with active carbon–acetone and carbon–ethanole pairs, *Solid Sorption Symp.*, Paris (1992), pp. 92–99.
54. Ch. Schweigler, Design and operation of a solar heating and cooling system with absorption chiller and latent heat storage, in: *Proc. 2nd Int. Conf. on Solar Air Conditioning*, 17–18 October 2007, Tarragona, Spain (2007), pp. 50–55.
55. L. L. Vasiliev, D. A. Mishkinis, and L. L. Vasiliev, Jr., Complex compound/ammonia coolers, *SAE Technical Papers Series 961462*, *26th Int. Conf. on Environmental Systems*, Monterey (1996).
56. Th. Berntsson, Heat sources — technology, economy and environment. International system in a green building, *Int. J. Refrig.*, **25**, 428–438 (2002).
57. V. E. Nakoryakov, V. I. Suslov, and Yu. I. Aristov, Report on the integration project No. 166 of the Siberian Branch of the Russian Academy of Sciences for the years of 2004–2006, Novosibirsk (2006).
58. Yu. I. Aristov, D. M. Chalaev, B. Dawoud, L. I. Heifets, O. S. Popel, and G. Restuccia, Solar driven adsorptive chiller: at the interfaces between chemical and thermal engineering, *Chem. Eng. J.*, **128**, No. 5, 845–853 (2007).
59. Yu. I. Aristov, Thermodynamic and dynamic optimization of a solar assisted adsorption air-conditioning unit, in: *Proc. 2nd Int. Conf. on Solar Air Conditioning*, 17–18 October 2007, Tarragona, Spain (2007), pp. 238–240.
60. M. F. Rudenko, Solar driven coolers, *Kholod. Tekh.*, No. 2, 6 (1999).
61. M. F. Rudenko and A. K. Ilyin, Investigation of the operation of a solar dry adsorption refrigeration unit, *Thermal Eng.*, **50**, No. 10, 126 (2003).
62. D. M. Chalaev and Yu. I. Aristov, Evaluation of the operation of a low-temperature adsorption cooler: influence of the properties of the water adsorbent, *Teploénergetika*, No. 3, 73–77 (2006).
63. L. Gordeeva, A. Freni, G. Restuccia, and Yu. Aristov, Methanol sorbents "salt inside mesoporous silica": the screening of salts for adsorptive air conditioning driven by low temperature heat, *Ind. Eng. Chem. Res.*, **46**, 2747–2752 (2007).
64. B. N. Okunev, L. I. Heifets, and Yu. I. Aristov, A new methodology of studying the dynamics of water sorption/desorption under real operating conditions of adsorption heat pumps: Modeling of coupled heat and mass transfer, *Int. J. Heat Mass Transfer*, (2007) (in press).
65. M. Polanyi, Theories of the adsorption of gas, *Trans. Faraday Soc.*, **28**, 316 (1932).
66. M. M. Dubinin, *Progress in Surface and Membrane Science*, Academic Press, New York (1975).
67. M. Jaroniec, Fifty years of the theory of volume filling of micropores, *Carbon*, **27**, No. 1, 77–83 (1989).
68. L. E. Haseler, Absorption cycle heat pumps for domestic heating, Report AERE-G 104R, AERE Harwell (1978).
69. R. E. Critoph, Performance limitation of adsorption cycles for solar cooling, *Solar Energy*, **41**, No. 1, 21–31 (1988).
70. J. A. Duffie and W. E. Beckman, *Solar Engineering of Thermal Processes*, Wiley, New York (1991).
71. Yu. Kato, K. Ando, and Y. Yoshizawa, Study on a regenerative fuel reformer for a zero-emission vehicle system, *J. Chem. Eng. Japan*, **36**, 860–866 (2003).
72. S. Brunauer, L. S. Deming, W. S. Deming, and E. Teller, Types of adsorption isotherms, *JACS*, **62**, 1723 (1940).
73. S. J. Gregg and K. S. W. Sing, *Adsorption*, *Specific Surface*, *and Porosity* [Russian translation], Mir, Moscow (1984).

74. Ph. Touzan, Thermodynamic values of ammonia-salts reactions for chemical sorption heat pumps, in: *Proc. Int. Sorption Heat Pump Conf.*, 24–26 March 1999, Munich (1999), pp. 225–238.
75. P. O'D. Offenhartz, F. C. Brown, R. W. Mar, and R. W. Carling, Engineering prototype studies on the calcium chloride-methanol chemical heat pump for solar air conditioning, heating, and storage, *J. Sol. Energy Engn, Trans. ASME*, **102**, 59–65 (1980).
76. R. W. Mar and R. W. Carling, The calcium chloride–ethanol system, *Thermochim. Acta*, **45**, 213–217 (1981).
77. K. Fujoka, K. Oido, and Yu. Hirata, Investigation on the structure of calcium chloride reactor beds for chemical heat pumps, in: *Proc. 3rd Int. Conf. on Heat Powered Cycles*, October 2004, Cyprus (2004), Paper No. 2217.
78. I. A. Simonova and Yu. I. Aristov, Sorption properties of calcium nitrate dispersed in silica gel: influence of the pore size, *Zh. Fiz. Khim.*, **79**, No. 8, 1477–1481 (2005).
79. J. Trudel, S. Hosatte, and M. Ternan, Solid–gas equilibrium in chemical heat pumps: the NH_3–$CoCl_3$ system, *Appl. Thermal Eng.*, **19**, 495–511 (1999).
80. N. Z. Lyakhov and V. V. Boldirev, Dehydration of crystalline hydrates, *Rus. Adv. Chem.*, **41**, 1960–1996 (1972).
81. B. Delmon, *Introduction a la Cinetique Heterogene*, Ed. Technip, Paris (1969).
82. B. Spinner, Ammonia-based thermochemical transformers, *Heat Recovery Systems and CHP*, **13**, No. 4, 301–307 (1993).
83. S. Mauran, M. Lebrun, P. Prades, M. Moreau, B. Spinner, and C. Drapier, Active component and its use as reaction media, US Patent 5, 283, 219, February 1 (1994).
84. L. L. Vasiliev, L. E. Kanonchik, F. F. Molodkin, and M. I. Rabetsky, Adsorption heat pump using carbon fiber/NH_3 and heat pipes, in: *Proc. 5th IEA Heat Pump Conf.*, 22–26 September 1996, Toronto, Canada (1996), pp. 35–43.
85. L. L. Vasiliev, D. A. Mishkinis, A. A. Antuh, and L. L. Vasiliev, Jr., A solar and electrical solid sorption refrigerator, *Int. J. Thermal Sci.*, **38**, 220–227 (1999).
86. L. L. Vasiliev, D. A. Mishkinis, A. A. Antukh, A. G. Kulakov, and L. L. Vasiliev, Jr., Resorption heat pumps, *Appl. Thermal Eng.*, **24**, 1893–1903 (2004).
87. Z. Aidom and M. Ternan, Salt impregnated carbon fibers as the reactive medium in a chemical heat pump: the NH_3/$CoCl_2$ system, *Appl. Thermal Eng.*, **22**, 1163–1173 (2002).
88. K. Fujioka, K. Hatanaka, and Yu. Hirata, Composite reactants of calcium chloride combined with functional carbon materials for chemical heat pumps, in: *Proc. VI Int. Seminar "Heat Pipes, Heat Pumps*, *Refrigerators*,*"* 12–15 September 2005, Minsk, Belarus (2005), pp. 306–315.
89. K. Wang, J. Y. Wu, R. Z. Wang, and L. W. Wang, Composite adsorbent of $CaCl_2$ and expended graphite for adsorption ice makers on fishing boats, *Int. J. Refrig.*, **29**, 199–210 (2006).
90. V. E. Sharonov, J. V. Veselovskaya, and Yu. I. Aristov, Ammonia sorption on composites "$CaCl_2$ in inorganic host matrix": isosteric chart and its performance, *Int. J. Low Carbon Techn.*, **1**, No. 3, 191–200 (2006).
91. Y. Zhong, R. E. Critoph, R. N. Thorpe, Z. Tamainot-Telto, and Yu. I. Aristov, Isothermal sorption characteristics of the $BaCl_2$–NH_3 pair in a vermiculite host matrix, *Appl. Thermal Eng.*, **27**, No. 14–15, 2455–2462 (2007).
92. E. A. Levitskii, Yu. I. Aristov, M. M. Tokarev, and V. N. Parmon, "Chemical heat accumulators" – a new approach to accumulating low potential heat, *Sol. Energy Mater. Sol. Cells*, **44**, No. 3, 219–235 (1996).
93. Yu. I. Aristov, M. M. Tokarev, V. N. Parmon, G. Restuccia, H.-D., Burger, W. Mittelbach, and H.-M. Henning, New working materials for sorption cooling/heating driven by low temperature heat: properties, in: *Proc. Int. Sorption Heat Pump Conf.*, 24–26 March 1999, Munich (1999), pp. 247–254.
94. Yu. I. Aristov, *Thermochemical Storage of Energy: New Methods and Materials*, Author's Abstract of Doctoral Dissertation (in Chemistry), Novosibirsk (2003).
95. M. M. Tokarev, *"Calcium Chloride in a Porous Matrix" Composite Sorbents*, Author's Abstract of Candidate Dissertation (in Chemistry), Novosibirsk (2003).
96. L. G. Gordeeva, *New Materials for Thermochemical Storage of Energy*, Author's Abstract of Candidate Dissertation (in Chemistry), Novosibirsk (2000).

97. Yu. I. Aristov, New family of materials for adsorption cooling: material science approach, *J. Eng. Thermophys.*, **16**, No. 2, 63–72 (2007).
98. L. G. Gordeeva, I. S. Glaznev, V. V. Malakhov, and Yu. I. Aristov, Influence of the interaction of calcium chloride with the silica gel surface on the phase composition and sorption properties of a dispersed salt, *Zh. Fiz. Khim.*, **77**, No. 11, 2019–2023 (2003).
99. L. G. Gordeeva, I. S. Glaznev, and Yu. I. Aristov, Sorption of water by sodium, copper, and magnesium sulfates dispersed in silica gel and aluminum oxide mesopores, *Zh. Fiz. Khim.*, **77**, No. 10, 1930–1935 (2003).
100. L. G. Gordeeva, A. V. Gubar', L. M. Plyasova, V. V. Malakhov, and Yu. I. Aristov, "Salt in silica gel pores" composite sorbents of water: influence of the salt-surface interaction on the chemical and phase composition and sorption properties, *Kinet. Katal.,* **46**, No. 5, 780–786 (2005).
101. L. G. Gordeeva, E. V. Savchenko, I. S. Glaznev, V. V. Malakhov, and Yu. I. Aristov, Impact of phase composition on water adsorption on inorganic hybrides "salt/silica," *J. Colloid Interface Sci.*, **301**, 685–691 (2006).
102. G. Restuccia, A. Freni, S. Vasta, and Yu. I. Aristov, Selective water sorbents for solid sorption chiller: experimental results and modelling, *Int. J. Refrig.*, **27**, No. 3, 284–293 (2004).
103. G. Restuccia, A. Freni, S. Vasta, M. M. Tokarev, and Yu. I. Aristov, Environmentally friendly adsorption cooler based on the "$CaCl_2$ in silica gel" composite: a laboratory prototype, *Chemistry of Stable Development*, **12**, 211–216 (2004).
104. G. Restuccia, A. Freni, S. Vasta, M. M. Tokarev, and Yu. I. Aristov, Adsorption cooling machine based on the "calcium chloride in silica gel–water" working pair, *Kholod. Tekh.*, No. 1, 2–6 (2005).
105. L. Gordeeva, A. Freni, G. Restuccia, and Yu. Aristov, A new family of methanol sorbents for adsorptive air conditioning driven by low temperature heat, in: *Proc. Int. Conf. on Heat Powered Cycles*, 11–14 September 2006, Newcastle (2006), pp. 21–22.
106. Yu. I. Aristov and L. L. Vasil'ev, New composite sorbents of water and ammonium for chemical and adsorption heat pumps (a Review), *Inzh.-Fiz. Zh.*, **79**, No. 3, 160–175 (2006).
107. Yu. I. Aristov, I. S. Glaznev, A. Freni, and G. Restuccia, Kinetics of water sorption on SWS-1L (calcium chloride confined to mesoporous silica gel): Influence of grain size and temperature, *Chem. Eng. Sci.*, **61**, No. 5, 1453–1458 (2006).
108. Yu. I. Aristov, I. S. Glaznev, L. G. Gordeeva, I. V. Koptyug, L. Yu. Ilyina, J. Kärger, C. Krause, and B. Dawoud, Dynamics of water sorption on composites "$CaCl_2$ in silica": single grain, granulated bed, consolidated layer, in: C. Conner, J. Fraissard (Eds.), *Fluid Transport in Nanoporous Materials*, *Series II: Mathematics, Physics and Chemistry*, Springer, Amsterdam (2006), pp. 553–565.
109. L. L. Vasiliev, L. E. Kanonchik, A. G. Kulakov, D. A. Mishkinis, A. M. Safonova, and N. K. Luneva, Activated carbon fiber composites for ammonia, methane and hydrogen adsorption, *Int. J. Low Carbon Technol.*, **1**, No. 2, 95–111 (2006).
110. Yu. I. Aristov, I. S. Glaznev, A. Freni, and G. Restuccia, Kinetics of the water sorption by the composite sorbent "$CaCl_2$ in CSC pores": influence of the pore size and temperature, *Kinet. Katal.*, **47**, No. 5, 793–798 (2006).
111. Yu. I. Aristov, I. V. Koptyug, L. G. Gordeeva, L. Yu. Ilyina, and I. S. Glaznev, Dynamics of the sorption of water vapors in a bed of the "$CaCl_2$ in silica gel" sorbent: influence of the porous structure of the bed, *Kinet. Katal.,* **47**, No. 5, 799–804 (2006).
112. A. A. Antukh, L. L. Vasil'ev, and O. S. Filatova, Heat pump for the systems of energy tri-generation (electricity, heat and cold), *Énergoeffektivn.*, No. 1, 16–18 (2006).
113. L. L. Vasil'ev, Sorption heat pumps for the Republic of Belarus, *Énergoeffektivn.*, No. 5, 17–18 (2004).