

Application of sorption heat pumps for increasing of new power sources efficiency

L.L. VASILIEV*
O.S. FILATOVA
A.P. TSITOVICH

Luikov Heat and Mass Transfer Institute, National Academy of Sciences of Belarus, P. Brovka 15, Minsk 220072, Belarus

Abstract In the 21st century the way to increase the efficiency of new sources of energy is directly related with extended exploration of renewable energy. This modern tendency ensures the fuel economy needs to be realized with nature protection. The increasing of new power sources efficiency (cogeneration, trigeneration systems, fuel cells, photovoltaic systems) can be performed by application of solid sorption heat pumps, refrigerators, heat and cold accumulators, heat transformers, natural gas and hydrogen storage systems and efficient heat exchangers.

Keywords: Sorbent materials; Heat pumps; Heat pipes; Heat exchangers; Fuel cells; Trigeneration

Nomenclature

C	–	thermal conductivity, J/kg
E	–	energy, J
F	–	fuel consumption, W
G	–	Gibbs energy, J
H	–	enthalpy, J
P	–	pressure, bar
Q	–	heat energy, W
S	–	entropy, J
T	–	temperature, K
W	–	electric power, J
η	–	efficiency

*E-mail address: Leonard_Vasiliev@rambler.ru

Subscripts

<i>h</i>	–	heat
<i>i</i>	–	ideal
<i>p</i>	–	practical
<i>t</i>	–	thermodynamic
<i>AS</i>	–	alternative source
<i>FC</i>	–	fuel cell
<i>HE</i>	–	exhausted heat
<i>SK</i>	–	sink
<i>SR</i>	–	source
<i>TR</i>	–	trigeneration

1 Introduction

The current century is expecting a development of a wide range of active and passive energy devices with application in energy management and power sources, electronic cooling, and bioengineering. Actually the energy situation is not sustainable since the most important fossil fuel reserves are diminishing and exhausting. They are not able to satisfy the demand of modern economic development. That is why the utilizing of nature friendly solar energy, wind, biomass fuels and solar hydrogen can be considered as an ultimate solution to the fast growing energy demand and greenhouse effect in atmosphere. Moreover it is very important to ensure the efficient consuming of the natural gas in low temperature technologies, converting it to hydrogen. One of the crucial low temperature technologies is the electrochemical power source, namely fuel cell that converts chemical energy of hydrogen in coupling with air into electricity and that generate hydrogen and oxygen when it is used reversibly as an electrolyzer. Unlike conventional power devices, i.e., steam turbines, gas turbines and internal combustion engines, which are based on certain thermal cycles, the maximum efficiency of fuel cells is not limited by the Carnot cycle [1], Fig. 1.

The other nature friendly energy generating technologies are based on applying of solar, wind energy and water resources. In general case low temperature power systems are significantly low-priced than high temperature ones while producing. This is a main concern for fuel cell technology in general since high cost is a major barrier for acceptance. For low-duty-cycle applications (such as owner-occupied dwellings and many portable devices) the direct system cost is an important factor while efficiency is less important. At the same time for high-duty-cycle applications (such as hospital power and some telecommunications devices) the cost of the unit is offset

by efficiency gains and reliability. Fuel cells are quite competitive in many applications owing to unmatched efficiency and potentially greater reliability than other energy systems (what is caused by significantly lower part counts, for example, and solid state construction in the case of SOFCs). On the other hand, since experience in manipulation with fuel cell systems is still small compared to many other energy systems, the risk cost is still considered to be high. In this respect, the low temperature systems enjoy an advantage over high temperature ones.

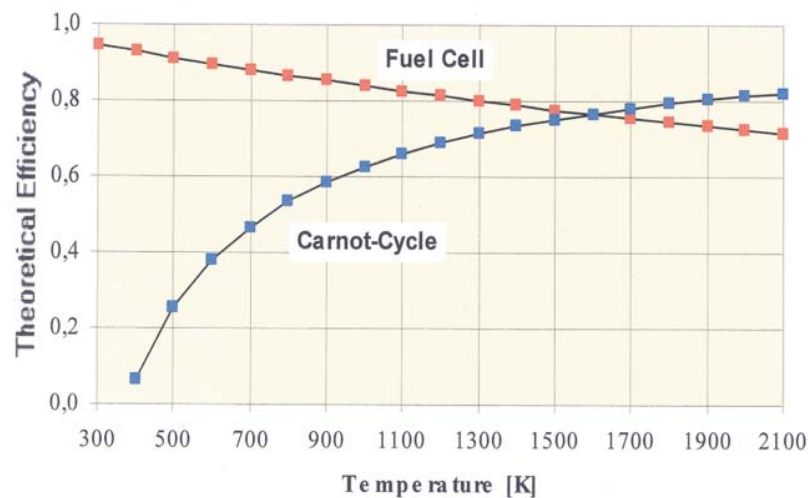


Figure 1. The efficiency of Carnot cycle and fuel cell cycle as a function of temperature.

One should expect the use of numerous technologies, often in a combination. Fuel cells are well suited to this requirement, and they can operate with batteries, turbines, and exchangers as partners. Car owners continually expect higher levels of comfort and ease of use. This led to increasing requirements for on-board electrical power. The use of electrical equipment such as electrical air conditioning during engine stand still is limited because of the batteries capacity. A fuel-based auxiliary power unit is one possible method of supplying this electrical power. But even fuel cells' efficiency can be improved since the heat dissipation inside reaches 50%. It can be realized by means of solid and liquid sorption machines [2]. Sorption machines (heat pumps, refrigerators, heat transformers, etc.) are a good way to combine exhausted gases of the fossil fuel resources, vapor and water,

alternative (solar, water, ground, air) and autonomous sources of energy to reduce the energy consumption down to 15–20%, Fig. 2 (coefficient of performance (COP) of the device is equal to 1.6).

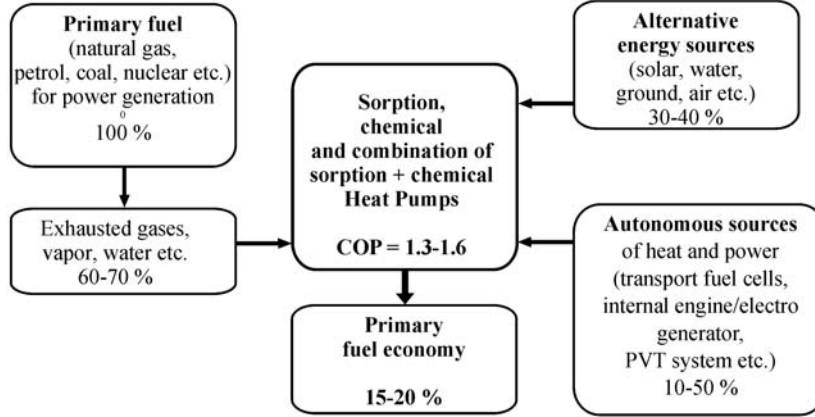


Figure 2. New possibilities to improve the efficiency of the fossil fuel due to alternative and autonomous energy sources application by sorption and chemical heat pumps.

2 Trigeneration systems based on sorption heat pumps

The cogeneration is simultaneous production of heat and power for consumption within a site. If we use a part of the heat or power to produce the cold (refrigeration), the system is termed as trigeneration. Sorption machines are well suited for this goal. Figure 3 shows a generalized diagram of a trigeneration system, based on the fuel cell application as a source of power in combination with low-grade heat and solid sorption (non-electric) heat pump. The another opportunity involves using of the amount of power generated by fuel cell, which exceeds the demand of the process and it is not economically feasible exporting power, refrigeration by compression (electric vapor compression) becomes a suitable option.

The overall first law efficiency for trigeneration system can be expressed by:

$$\eta_{TR} = (W + Q_{heat} + Q_{cold})/F, \quad (1)$$

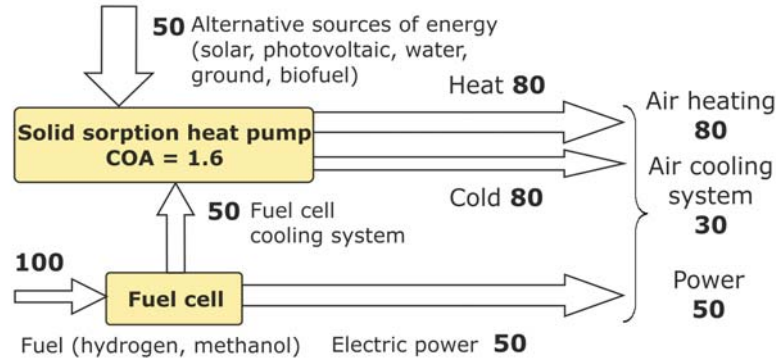


Figure 3. System of trigeneration based on fuel cell and solid sorption heat pump application.

where W_e is the power generated by fuel cell, Q_{heat} is the heat production ($Q_{heat} = Q_{HE} + Q_{AS}$), Q_{HE} is heat exhausted of the engine, Q_{AS} is heat of alternative sources, the Q_{cold} is the cold production, F is total fuel consumption.

The fuel cell efficiency is:

$$\eta_{FC} = \Delta G / \Delta H = 1 - T \Delta S / \Delta H, \quad (2)$$

where

$$\Delta G = \Delta H - T \Delta S = -nF \Delta E.$$

If we consider the heat engine (gas turbine/electro generator) instead of the fuel cell, the engine efficiency is:

$$\eta = W/Q = (Q_{SR} - Q_{SK})/Q_{SR} = 1 - Q_{SK}/Q_{SR}, \quad (3)$$

where Q_{SR} is heat available from source of heat engine, Q_{SK} is heat delivered to sink of heat engine.

The increasing efficiency of new power sources (cogeneration, trigeneration systems, fuel cells, photovoltaic systems) is considered to be performed with the help of solid sorption heat pumps, refrigerators, accumulators of the heat and cold, heat transformers, fuel gas (natural gas and hydrogen) storage systems and efficient heat exchangers [3,4]. Low temperature power systems are generally significantly less expensive for producing compared to high temperature ones.

2.1 The activated carbon fibre and salt particles on its surface for heat pumps

A new generation of solid sorption heat pumps and coolers [5–7] have a good compromise between chemical heat pumps [8–10] and adsorption heat pumps [11–17]. The sorbent bed of these heat pumps consists of adsorptive materials (for example, active carbon fibre) and micro/nano crystals (metal chlorides, metal hydrides etc.) attached to the surface of the carbon filament, Fig. 4 [18–20].

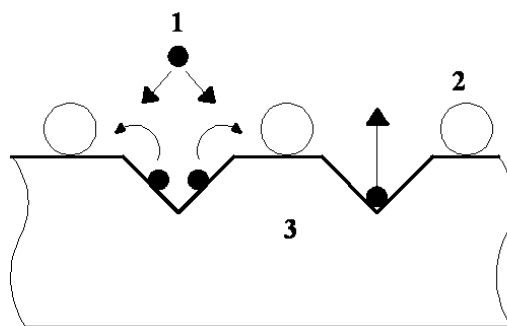


Figure 4. Composite sorbent material [16–18]: molecules of sorbate (ammonia) (1) absorbed by metal-chloride micro crystals (2) and adsorbed in micro pores of the activated carbon fiber "Busofit" (3).

Micro crystals of NiCl_2 , MnCl_2 and BaCl_2 on the surface of active carbon fibre ("Busofit") are suggested as a composite sorbent material due to its stability, low cost and suitable temperature range. This sorbent bed has the advantages of chemical heat pumps, e.g. high sorption capacity, and high speed of adsorption which is typical for adsorption heat pumps. Simultaneously there is a strong interaction (intensive heat and mass transfer) between adsorptive materials and chemical materials (active carbon/micro crystals) during the cycle of heating/cooling. If we have two adsorbers (reactors) filled with different complex compounds (salt crystals disposed on the filaments of active carbon), the cycle is separated into two main phases corresponding to different pressure levels. Due to the effect of adsorption/desorption of the carbon fibre this pressure difference is dynamically changing during the cycle (completely diverse comparing with chemical reactors). The carbon fibre as a fast sorbent material starts to react with ammonia at the early stage of heating/cooling time (up to 5 min)

and accomplishes its reaction after the chemical reaction of the salt is finished. The dynamic of the pressure change in the reactor is also fast and starts before the salts are beginning to react. During the regeneration stage carbon fibre as a host material helps to distribute salt microcrystals through the whole volume of a sorbent bed (ammonia capillary condensation, salts dissolution in the ammonia, salt rich liquid ammonia motion through the sorbent material due to capillary forces). Figure 5 shows ammonia sorption isotherms for the active carbon fibre “Busofit” and complex compound “Busofit”+CaCl₂.

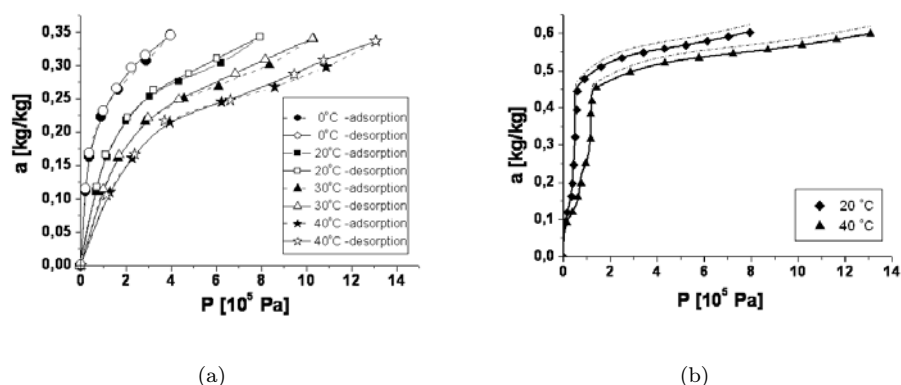


Figure 5. Dynamic ammonia sorption capacity at different temperatures vs. pressure: (a) for the active carbon fibre “Busofit” (adsorption/desorption); (b) for complex compound “Busofit”+CaCl₂ micro crystals (adsorption/synthesis, desorption/regeneration).

The active carbon filaments and micro/nano crystals enhance the COP of the system as compared with conventional chemical heat pumps. To minimize a void space and increase the adsorbent capacity of the active carbon fiber, “Busofit” has to be compressed together with a binder. The complex compound microstructure obtained in the Luikov Heat & Mass Transfer Institute has been studied by means of scanning electron microscopy on Carl Zeiss Supra 55. The SEM micrograph images of the activated fibre “Busofit” and the same fibre with CaCl₂ microcrystals on its surface are shown in Fig. 6.

The uniform distribution of micro/nano pores in the filament body allows to have a high porous volume inside for gases adsorption. The micro/nano crystals disposed on the filament surface increase the sorption capacity of the sorbent compound by 2–3 times. The results of the experi-

mental analysis of the sorption capacity of the active carbon fibre “Busofit” and “Busofit” + chemicals are presented in Tab. 1. The data are obtained for the room temperature except methane (253 K, $P = 6$ MPa).

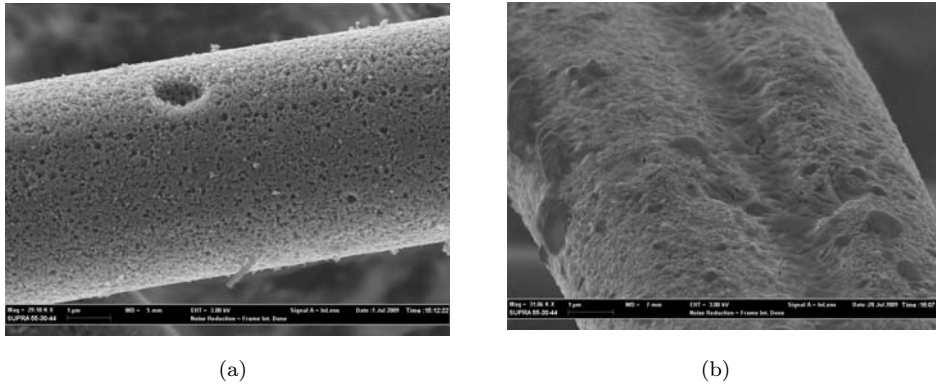


Figure 6. Activated carbon fibre "Busofit": (a) pure fibre; (b) saturated fibre with micro crystals CaCl_2 on its surface.

Table 1. Sorption capacity of new sorbent materials.

Full sorption capacity of the sorbent bed	Activated carbon fibre "Busofit"	"Busofit" + CaCl_2 , or "Busofit" + $\text{LaNi}_{4.5}\text{Al}_{0.29}\text{Mn}_{0.21}$
Methane, v/v	182	
Ammonia, g/g	0.35	0.62–1.03
Hydrogen, wt%	1.5	3.2
Methanol, g/g	0.55	

2.2 Two adsorbers heat pump

Adsorption refrigeration / heat pump technology based on the evaporation process has been widely discussed since the last decade. Some adsorption machines are already introduced at the market [21–27]. Due to extremely high thermal conductivity conventional heat pipes are convenient to use as thermal management devices for adsorption machines like heat pumps, coolers and heat transformers. Essential is a possibility to change the direction of a heat flow along the heat pipe during the cycle time and to use heat pipes

for cooling and heating of sorbent bed. Such heat pipes are made from copper envelope with copper sintered powder as a wick. To predict heat pipe parameters a special software was proposed, developed and used [28]. Heat pipe family qualified geometry is: round tube diameter 4–25 mm, length 0.1–0.8 m, wall thickness 0.2–1.0 mm. Pipe material is copper with 99.95% purity, wick is copper sintered powder with thickness 0.2–0.8 mm. Transport capacity is 10–500 W. Water, methanol and propane are mostly used as working fluids. The developed heat pipe mathematical model includes heat pipe parameters:

Input: heat pipe geometric parameters; capillary structure parameters, working fluid properties; material properties; heat flux.

Output: maximum heat flux Q_{max} along the heat pipe vs. working fluid temperature; capillary and boiling limits; heat pipe axial temperature profile; temperature drop between the evaporator and condenser.

The results of the numerical modelling verified by the experimental data have an accuracy of 10%.

Typical two-absorbers' heat pump with heat pipe thermal control is shown in Figs. 7–8. This thermal system enables heat pipe heat recovery between adsorbers by the liquid circulating loop and mechanical pump.

The parameters of the adsorption solar refrigerator (two adsorbers, condenser and evaporator) are shown in Tab. 2 [6,7]. Activated carbon fibre "Busofit" is used as the sorbent material, and ammonia as the working fluid. The copper/water heat pipes, ammonia loop heat pipes and carbon/steel ammonia vapor-dynamic thermosyphons are applied as the system of thermal control of the refrigerator.

2.3 Two reactors resorption heat pump

Nowadays the resorption technology is steadily improving. Its increase at sorption market is strongly related to the energy policy in different countries. Actual resorption technologies have advantages and drawbacks with regard of their compactness, complexity, cost, the range of working temperature [29]. Resorption heat pumps and coolers based on reversible solid-gas sorption cycles could have interesting application for space cooling, when a high temperature waste heat is available and/or the exigencies of the harsh external environment necessitates thermal control of an object [4,30].

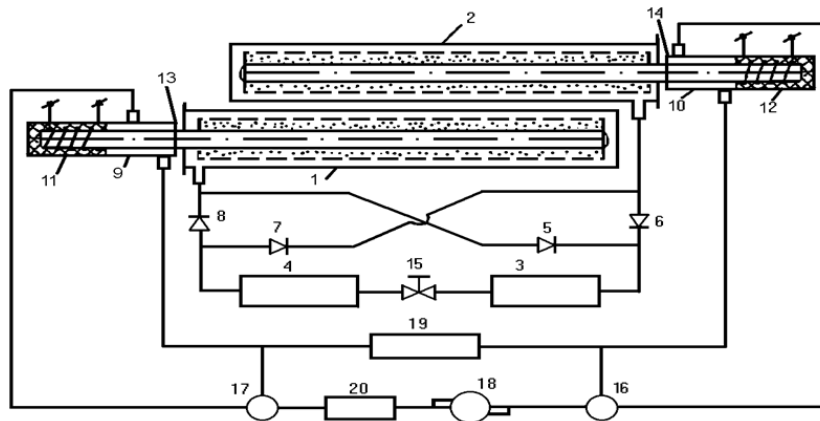


Figure 7. Scheme of two adsorbers heat pump with heat pipe thermal control: 1, 2 – adsorbers; 3 – condenser; 4 – evaporator; 5-8 – valves; 9, 10 – liquid heat exchangers; 11, 12 – heat pipe evaporators; 13, 14 – copper-water heat pipes; 15 – expansion valve; 16, 17 – reversing valve; 18 – liquid pump; 19 – liquid flow meter; 20 – thermostat.



Figure 8. Two-adsorbers heat pump experimental set-up with evaporator for liquid cooling with $COP = 1.6$.

The resorption technology advantages at first are related to the nature friendly refrigerants such as water, ammonia, CO_2 (no CFC, HCFC, HFC) and at second they are thermally driven and can be coupled with waste

Table 2. Solar-gas refrigerator main parameters.

Solid-gas adsorber dimensions	$L = 1.2$ m $D = 0.05$ m
Carbon fiber “Busofit” mass in one adsorber	0.75 kg
Ammonia mass in one adsorber	0.35 kg
Water mass in one thermosyphon	1 kg
Ammonia mass inside one loop heat pipe	0.05 kg
Total mass of the refrigerator	22 kg
Temperature of the hot adsorber	120 °C
Condenser heat dissipating temperature	50 °C
Loop heat pipe temperature	0 °C
Finned evaporator temperature (without loop heat pipes)	-18 °C
Heating capacity (W/kg adsorbent)	350 °C

heat, solar heat, burning fossil fuel, or biomass. The third advantage of resorption systems relates with its ability to use a significant number of couples solid-gas [4]. Resorption systems have also a number of advantages in comparison with the conventional heat pumps or refrigeration machines. For example, in comparison with the existing liquid-gas absorption systems, solid-gas sorption systems have a wider range of working temperature and have few problems of corrosion and crystallization. Moreover, energy storage capacity is much higher than the liquid absorption heat pumps due to the larger reaction heat in the solid sorption systems. The heat/cold can be stored for long periods with low losses [31]. In conventional resorption systems the major entropy production is due to the superheating of the vapor during the cold production phase and de-superheating of the vapor during regeneration phase. Thermochemical resorption machines were demonstrated by different authors [32–34] where such pairs as $\text{MgCl}_2/\text{NH}_3$ - $\text{NiCl}_2/\text{NH}_3$ and $\text{BaCl}_2/\text{NH}_3$ - NiCl_2 were used.

A new stream in resorption heat pumps is related with complex compounds sorbent materials application (for example, as active carbon fibre and micro crystals of the salts on its surface) and heat pipe thermal management of reactors [35]. The heat pipe technique ensures the thermal control of the high-temperature reactors in the resorption refrigeration system.

Let us consider a simple resorption heat pump, Fig. 9. The quadrithermal thermodynamic cycle is used for heat and cold generation. “Busofit” action as a fast reacting material during the cycle decrease the pressure

drop between phases of cold production and regeneration thus increasing the COP. The salt impregnated in “Busofit” in the low temperature reactor is $\text{BaCl}_2 \cdot 8\text{NH}_3$ and its equilibrium curve is close to the NH_3 saturation curve. The high temperature reactor is filled with “Busofit” carbon fibre and NiCl_2 micro crystals. For both reactors their sizes are: length – 1000 mm, outer diameter – 50 mm, inner diameter – 49 mm. The total mass of the reactor is: fins – 480 g, reactor envelope – 615 g, reactor flanges – 120 g, heat pipe mass – 900 g. “Busofit”+ BaCl_2 mass is (340 + 270 g), “Busofit”+ NiCl_2 mass is (250 + 180 g).

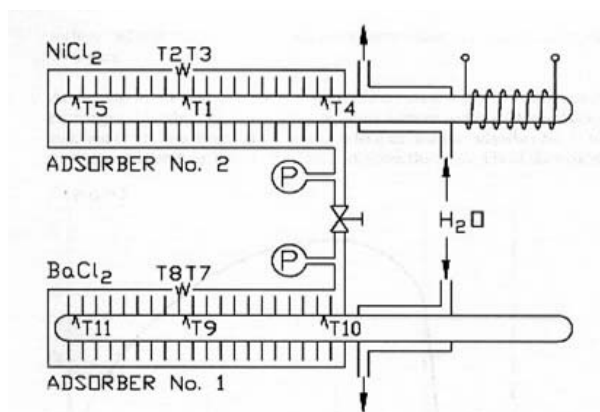


Figure 9. Sorption heat pump with two reactors ($(\text{“Busofit”} + \text{NiCl}_2)/\text{NH}_3$, $(\text{“Busofit”} + \text{BaCl}_2)/\text{NH}_3$) and two heat pipes for their thermal management: T1-T9 – thermocouples.

The basic cycle (Figs. 10, 11) is divided into two reaction phases (decomposition/desorption I at high temperature and synthesis/adsorption II at low temperature), separated by two transition stages of the reactors (cooling III and heating IV). During the cycle (near 60 min) the temperature of two reactors is changing between 50 and 220 °C. It can be noted that the time of cooling of the reactor is much faster than the time of its heating.

Temperature drop in the low temperature sorbent bed during the time of adsorption/synthesis is negligibly small compared with the temperature drop in high temperature bed during the time of desorption/regeneration. Pressure evolution between stages of heating/cooling is shown in Fig. 11. Internal heat recovery is enabled due to the mass transfer between the reactors. The external heat recovery is realized by heat pipe heat exchangers. The pump ensures water circulation between heat pipes.

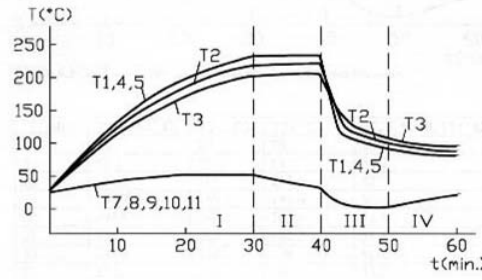


Figure 10. Temperature evolution in different part of the resorption heat pump during its heating/cooling: T1-T5 – thermocouples in different parts of the high temperature sorbent bed, T7-T11 – thermocouples in different parts of low temperature sorbent bed.

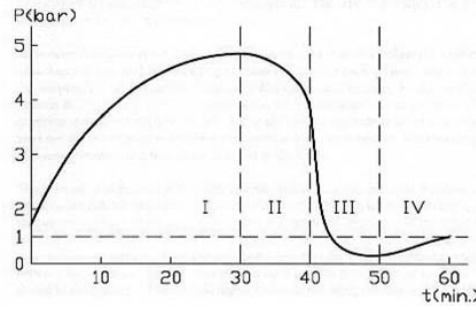


Figure 11. Cyclic pressure evolution in two reactors heat pump during its heating/cooling.

Ideal, thermodynamic and practical coefficients of performance of the resorption cycle (two different salts) are considered as follows:

$$COP_i = \frac{\Delta H_0}{\Delta H_1}, \quad (4)$$

$$COP_t = \frac{\Delta H_0 - C_p^{salt0}(T_0 - T_b)}{\Delta H_1 + C_p^{salt1}(T_h - T_0)}, \quad (5)$$

$$COP_p = \frac{\Delta H_0 - \sum C_p^{salt0+carbon+steel}(T_0 - T_b)}{\Delta H_1 + \sum C_p^{salt1+carbon+steel}(T_h - T_0)}. \quad (6)$$

For the combination of sorbent materials “Busofit”/BaCl₂ and “Busofit”/NiCl₂ the COP of the heat pump is close to 1.2 copper/water heat pipes ensure

the efficient heating/cooling and the heat recovery between the reactors 1 and 2.

2.4 Multi cascaded heat pumps

The optimization of the sorption technologies is sometimes related with multi-cascading heat pumps and coolers application [5, 6, 19, 20]. The Clapeyron-Clausius diagram of 3-reactors solid sorption cooler with two sources of cold is presented in Fig. 12 with four stages of the heating /cooling, Fig. 13. The results of experiments testify a possibility to have a resorption heat pump with simultaneous heat generation 1500 W (steam temperature about 120–130 °C and chilled water output about 3–5 °C) with COP up to 1.5. The most favorable situation for this device is the case, when two sources of cold are used to cool gas or liquid.

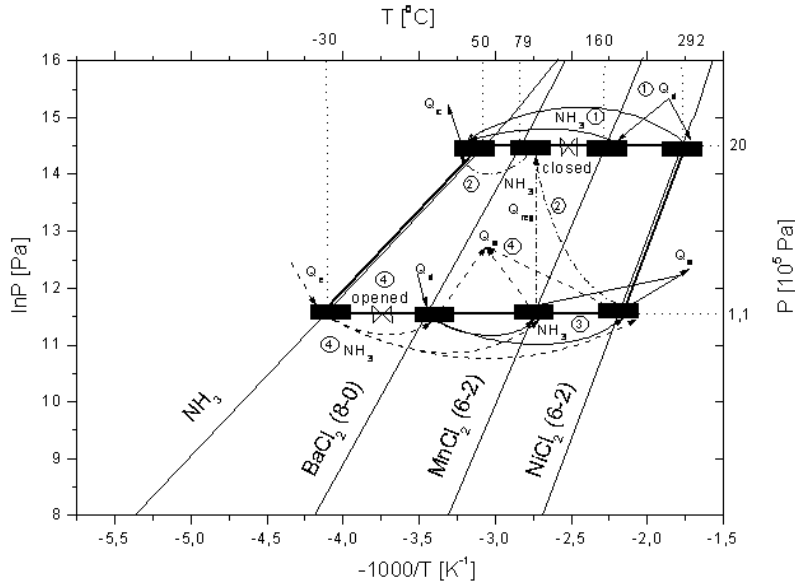


Figure 12. Clapeyron diagram of heat pump with two sources of cold.

An example of heat input/output in the evaporator/condenser (2) and the BaCl_2 reactor (3) via time of the cycle is presented in Fig. 14. The maximal charging power of MnCl_2 , NiCl_2 reactors is around 400 W each. Ammonia evaporation at 10 °C guarantees the cooling power of the evaporator near 200 W. The same cold generation is available in the low temperature reactor. The four stage heat and cold generation in heat pump with

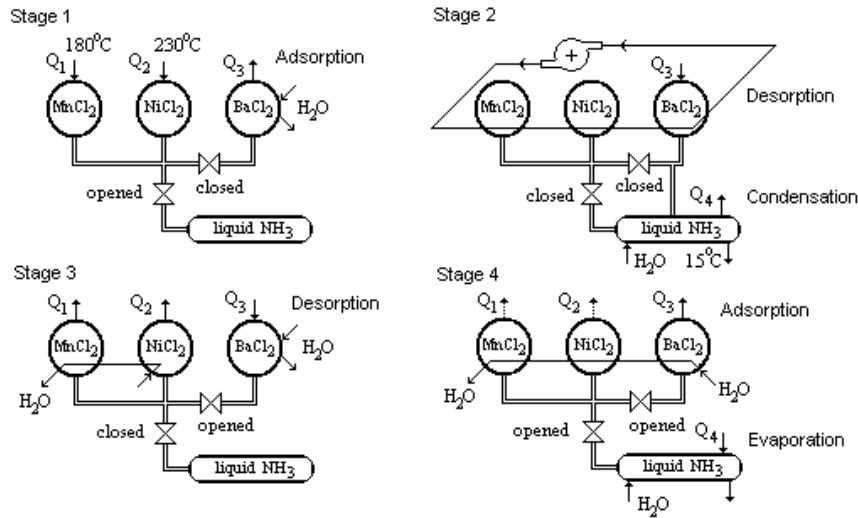


Figure 13. Advanced heat pump (“Busofit”+salts) with heat pipe heat recovery and two sources of cold, namely low temperature adsorber BaCl_2 and heat pump evaporator.

heat recovery and two sources of cold are shown in Fig. 14 as far as the temperature evolution on the heat pipe 1 (NiCl_2 /active carbon) and heat pipe 2 (MnCl_2 /active carbon) is shown in Fig. 15.

Now we consider the multistage ammonia complex compound heat pump capable to ensure the temperature lift more than 100°C . This re-sorption heat pump, Fig. 16, has six adsorbers (three and three adsorbers working out of phase) and three-stage working cycle. The heat pump is working with gaseous ammonia (no liquid). The sorbent is activated carbon fibre saturated by with BaCl_2 , MnCl_2 , NiCl_2 . Sorbent material is disposed between fins of the heat pipe. Thus the system ensures internal heat and mass recovery. The temperature lift between the steam flow (2) and fresh water output (3) is near 120°C . Water input temperature in the low temperature heat exchanger is 20°C . Internal heat recovery is realized by using of the adsorption/synthesis heat of high temperature solid/gas pair ($\text{NiCl}_2/\text{NH}_3$) to initiate the desorption/ regeneration of medium temperature solid/gas pair ($\text{MgCl}_2/\text{NH}_3$). The adsorption/synthesis heat of medium temperature solid/gas pair ($\text{MnCl}_2/\text{NH}_3$) is used to initiate the desorption/regeneration of low temperature solid/gas pair ($\text{BaCl}_2/\text{NH}_3$).

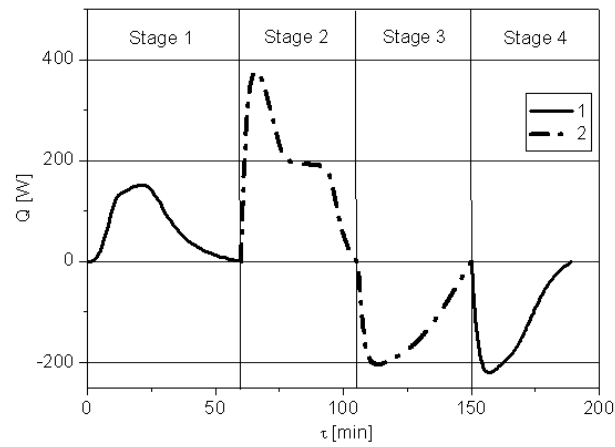


Figure 14. The heat input/output in the evaporator/condenser (1) and the low temperature carbon/BaCl₂ reactor (2) as a function of the cycle time.

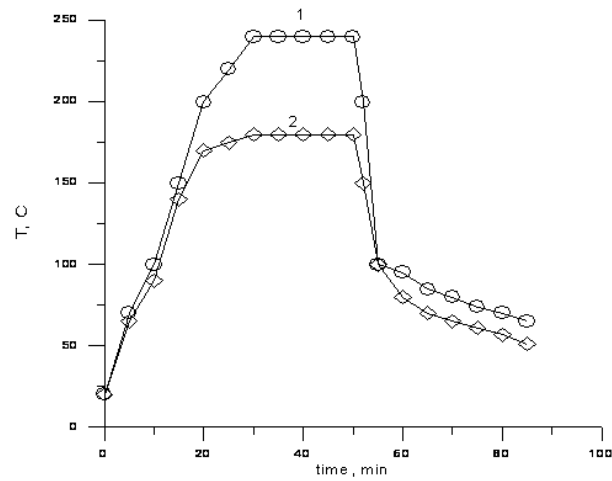


Figure 15. The temperature evolution on the heat pipe 1 and heat pipe 2 during the cycle heating/cooling.

The Clapeyron-Clausius diagram for such resorption heat pump is shown in Fig. 17 (dashed lines are temperature outputs). Such heat pumps are more efficient to compare with typical chemical heat pumps or typical solid

adsorption heat pumps due to combined action of physical adsorption and chemical reactions in the same volume and time of the cycle.

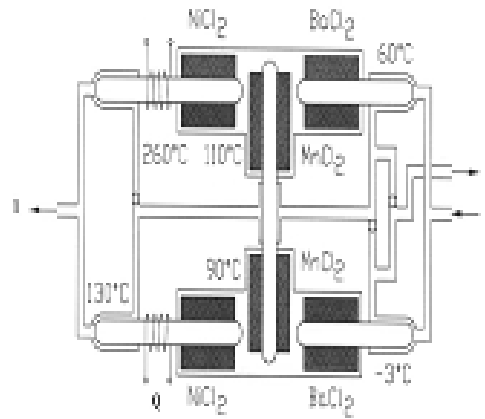


Figure 16. Six adsorbers' three-stage resorption heat pump with heat pipes thermal control. 1 – steam output, 2 – fresh water output, 3 – water input to heat exchanger (20 °C).

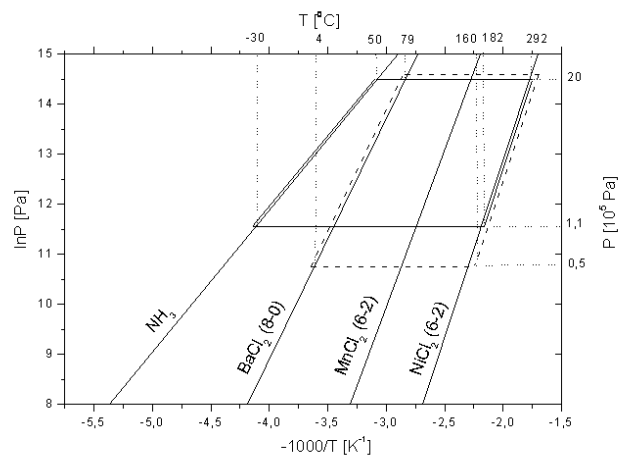


Figure 17. Clapeyron diagram for three-stage resorption heat pump (BaCl_2 , MnCl_2 , NiCl_2 + active carbon fibre “Busofit”) with a temperature lift near 100 °C.

The experimental data of the resorption heat pump are presented at Tab. 3. The sorbent bed in each adsorber is a complex compound involving active carbon fibre and micro crystals of salts on its surface and in macro/meso pores. For the term of simplification the adsorbers are indicated as NiCl_2 , MnCl_2 and BaCl_2 adsorbers. The above mentioned experimental data testify the possibility to apply the high temperature energy of the fuel cell (SOFC) and gas or diesel engine to generate power, heat and cold, what can be used for the air-conditioning and water cooling systems combining with such resorption heat pump.

Table 3. Evolution of the temperature and pressure field inside the three salts sorption heat pump as the function of the cycle time.

Time [min]	T_2 [°C]	T_3 [°C]	T_4 [°C]	T_5 [°C]	T_6 [°C]	T_7 [°C]	T_8 [°C]	Q_h [W]	Q_w^{Ba} [W]	Q_w^{MnNi} [W]	P [bar]
0	60	18	50	80	4	130	150	1000	0	0	0.9
5	100	32	90	100	20	170	200	1000	176	0	3
10	80	32	100	120	40	175	220	1000	176	0	5
15	75	32	105	140	40	180	240	800	176	0	11
20	70	32	110	155	38	180	240	700	147	0	12
25	65	30	110	160	35	180	240	600	117	0	12
30	60	28	110	160	30	180	240	400	117	0	10
35	60	28	110	160	28	180	240	300	118	0	8,5
38.9	99	24.2	106	151	25	151	202	0	60	0	
39	100	24	105	150	25	150	200	0	59	8000	7
40	100	20	80	120	18	148	180	0	0	8000	2
40,1	100	20	80	120	19	148	179	0	-3	882	
45	80	15	70	100	10	146	170	0	-74	882	0.8
50	75	12	65	90	5	142	163	0	-118	808	0.6
55	70	10	62	88	5	140	160	0	-147	735	0.4
60	65	8	58	85	3	138	158	0	-176	661	0.4
65	60	8	52	82	3	135	153	0	-176	580	0.6
70	60	9	48	78	3.5	130	150	0	-162	580	0.6

The symbols adopted in the table stand for: $T_1 = 20$ °C – water temperature at the heat pump entrance, T_2 – water temperature at the heat pump exit (MnCl_2 and NiCl_2 adsorbers), T_3 – water temperature at the BaCl_2 adsorber exit, T_4 – temperature at the MnCl_2 adsorber surface (without thermal insulation), T_5 – temperature at the NiCl_2 adsorber surface (without thermal insulation), T_6 – temperature at the BaCl_2 adsorber surface (without thermal insulation), T_7 – temperature at the heat pipe thermal

control system surface (MnCl_2 adsorber), T_8 – temperature at the heat pipe thermal control system surface (NiCl_2 adsorber), Q_h – total heat input to adsorbers (NiCl_2 and MnCl_2), Q^{Ba} – heat output to heat a cooling water (BaCl_2 adsorber), Q^{MnNi} – heat output from NiCl_2 and MnCl_2 adsorbers to cooling water, P – pressure in adsorbers.

There is an interesting possibility of combining different sorption heat pumps for increasing of its total efficiency. For example it is possible to develop cascaded cycles with the topping resorption/adsorption cycle and bottoming absorption (LiBr/water) cycle, Fig. 18. Since the operating modes of both heat pumps are different, for reducing of the non-productive period of the topping cycle, the thermal coupling can be realized with heat pipe heat exchangers for the internal and the external heat and mass recovery. The LiBr/water absorption chiller cycle is designed for maximum chilling capacity, thermally coupled with adsorption ammonia/complex compound (carbon fibre/ NiCl_2) sorbent bed with the heat pipe heat exchangers. This heat pump is capable to ensure the heat recovery of high temperature fuel cells. So, the solid sorption heat pumping and refrigeration is promising technology for the combining of the low temperature thermal sources of energy with the high temperature cycles, thus increasing the efficiency of total energy consumption and ensuring the nature protection against the CO_2 dangerous concentration in the atmosphere [36,37].

The hydrogen fuel cells with solid sorption heat pumps as a trigeneration technology, powered by reformed diesel fuel as the means of providing electrical power, is a real possibility to improve modern energy delivery and consumption. Another possibility for thermal integration of trigeneration systems is considered as a special case of the application of cogeneration systems where a fraction of the shaft work or residual heat is used for running a refrigeration system [18]. The gas turbine is used as a prime mover for power production and cooling is accomplished by a typical compression-refrigeration system.

3 Conclusions

New power sources efficiency (fuel cells, photovoltaic systems, cogeneration, trigeneration systems) have a good perspective to be increased by combining with the renewable energy resources through solid sorption heat pumps, refrigerators, accumulators of the heat and cold, heat transformers, natural gas and hydrogen storage systems.

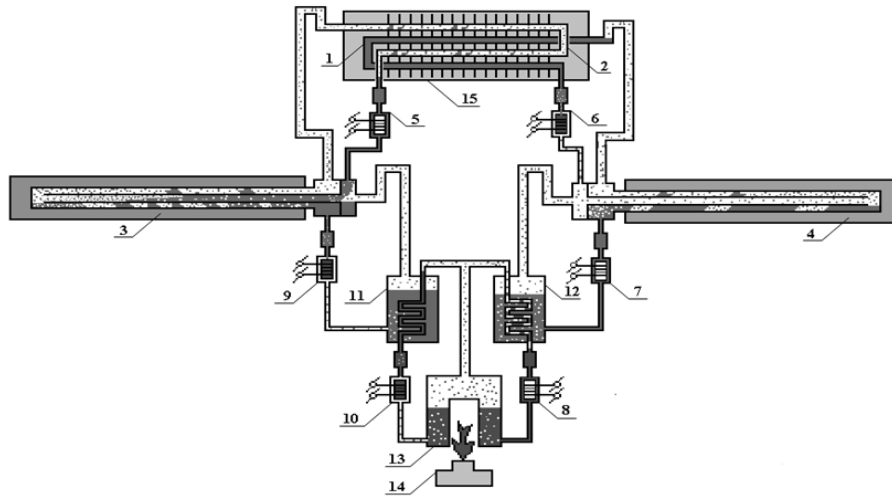


Figure 18. Two-stage solid sorption heat pump with complex compound sorbent bed inside (combination with solid sorption stage (adsorption) and liquid sorption stage (absorption)): 1, 2 – low temperature heat exchangers; 3, 4 – high temperature adsorbers filled with “Busofit” + NiCl_2 micro crystals, fluid is ammonia; 5-10 – valves; 11, 12 – heat pipe based heat exchangers; 13 – mini-boiler; 14 – gas flame; 15 – LiBr/water low temperature absorber with heat recovery by heat pipes.

The developed and tested experimental set-up offers the possibility of saving 15–20% of primary energy for cooling, heating and power demands. The additional experiments with set-up based on the coupling salts NiCl_2 , MnCl_2 , BaCl_2 with an active carbon fibre “Busofit” have demonstrated a possibility to have a cooler with two different independent sources of cold (low temperature BaCl_2 adsorber and evaporator) with simultaneous heat generation and chilled water production with $\text{COP}_{cooling}$ equal to 0.6 and the heat pump COP near 1.6.

There is also an interesting possibility of combining different sorption heat pumps for increasing of its total efficiency. Moreover, for heat pumps with groups of adsorbers working out of phase, for reducing of the non-productive period of the topping cycle, the thermal coupling can be realized with heat pipe heat exchangers for the internal and the external heat and mass recovery.

Received 4 November 2008

References

- [1] SIMANDER G.R.: *Fuel cell technology for natural gas*. E.V.A. – The Austrian Energy.
- [2] ARISTOV Y.I., VASILIEV L.L., NAKORYAKOV V.E.: *Chemical and sorption heat engines: state of the art development prospects in the Russian Federation and the Republic of Belarus*. J. Eng. Physics & Thermophysics **81**(2008)1, 17–47.
- [3] VASILIEV L., NIKANPOUR D., ANTUKH A., SNELSON K., VASILIEV L., JR., LEBRU A.: *Multisalt-carbon chemical cooler for space applications*. J. Eng. Physics & Thermophysics **72**(1999), 595–600.
- [4] LEPINASSE E., MARION M., GOETZ V.: *Cooling storage with resorption process. Application to a box temperature control*. Appl. Therm. Eng. **21**(2001), 1251–1263.
- [5] VASILIEV L.L., GULKO N.V., KHAUSTOV V.M.: *Solid adsorption refrigerators with active carbon-acetone and carbon-ethanol pairs*. Solid Sorption Refrigeration Symposium, Paris 1992.
- [6] VASILIEV L.L., MISHKINIS D.A., ANTUKH A.A., VASILIEV L.L., JR.: *A solar and electrical solid sorption refrigerator*. Int. L. Thermal Sci. **38**(1999), 220–227.
- [7] VASILIEV L.L., MISHKINIS D.A., ANTUKH A.A., VASILIEV L.L., JR.: *A solar-gas solid sorption refrigerator*. J. Adsorption **7**(2001), 149–161.
- [8] Raldow W.M., Wentworth W.E.: *Chemical heat pumps — a basic thermodynamic analysis*. Solar Energy, **23**(1979), 75–79.
- [9] WONGGSUWAN W., KUMAR S., NEVEU P., MEUNIER F.: *Review of chemical heat pump technology and applications*. Appl. Therm. Eng. **21**(2001), 1489–1519.
- [10] POELSTRA S., HAIJE W.G., DIJKSTRA J.W.: *Techno-economic feasibility of high-temperature high-lift chemical heat pumps for upgrading industrial waste heat*. Appl. Therm. Eng. **22**(2002), 1619–1630.
- [11] MEUNIER F.: *Second law analysis of a solid adsorption heat pump operating on reversible cascade cycles: application to the zeolite-water pair*. Heat Recovery Systems **5**(1985), 133–141.
- [12] TOZER R.M., JAMES I.W.: *Fundamental thermodynamics of ideal absorption cycles*. Int. J. Refrig. **20**(1997)2, 120–135.
- [13] EL-SHARKAWY I.I., KUWAHARA K., SAHA B.B., KOYAMA S., NG K.C.: *Experimental investigation on adsorption of ethanol onto activated carbon fibers for possible application in adsorption cooling system*. Appl. Therm. Eng. **26**(2006), 859–865.
- [14] SHARKAWY I.I., SAHA B.B., KOYAMA S. HE L., NG K.C., YAP C.: *Experimental investigation on activated carbon-ethanol pair for solar powered adsorption cooling applications*. Int. J. Refrig. **31**(2008), 1407–1413.
- [15] LU Y.Z., WANG R.Z., ZHANG M., JIANGZHOU S.: *Adsorption cold storage system with zeolite–water working pair used for locomotive air conditioning*. Energy Conversion & Management **44**(2003), 1733–1743.
- [16] WANG L.W., WANG R.Z., WU J.Y., WANG K.: *Compound adsorbent for adsorption ice maker on fishing boats*. Int. J. Refrig. **27**(2004), 401–408.
- [17] LAMBERT M.A., JONES B.J.: *Review of Regenerative Adsorption Heat Pumps*. J. Thermophysics & Heat Transfer **19**(2005)4, 471–493.

- [18] VASILIEV L., KANONCHIK L., ANTUKH A., KULAKOV A., ROSIN I.: *Waste Heat Driven Solid Sorption Coolers*. SAE Technical Paper 941580, 1994.
- [19] VASILIEV L.L., MISHKINIS D.A., VASILIEV L.L., JR.: *Complex compound/ammonia coolers*. SAE Technical Paper Series 961462, 26th Int. Conf. on Environmental Systems, Monterey 1996.
- [20] VASILIEV L.L., KANONCHIK L.E., ANTUKH A.A., KULAKOV A.G.: *NAX zeolite, carbon fiber and CaCl₂ ammonia reactors for heat pumps and refrigerators*. J. Adsorption **2**(1996), 311–316.
- [21] NEVEU P., CASTAING J.: *Solid-gas chemical heat pumps: field of application and performance of the internal heat of reaction recovery process*. Heat Recov. Syst. CHP **13**(1993), 233–251.
- [22] CRITOPH R.E.: *Performance limitations of adsorption cycles for solar cooling*. Solar Energy **41**(1988), 21–31.
- [23] WANG R.Z.: *Adsorption refrigeration research in Shanghai Jiao Tong University*. Renew Sust Energy Rev. **5**(2001), 1–37.
- [24] SAHA B.B., KOYAMA S., KASHIWAGI T., AKISAWA A., NG K.C., CHUA H.T.: *Waste heat driven dual-mode, multi-stage, multi-bed regenerative adsorption system*. Int. J. Refrig. **26**(2003), 749–757.
- [25] ARISTOV YU.I., GLAZNEV I.S., FRENI A., RESTUCCIA G.: *Kinetics of water sorption on SWS-1L (calcium chloride confined to mesoporous silica gel): Influence of grain size and temperature*, Chem. Eng. Sci. **61**(2006), 1453–1458.
- [26] MAURAN S., LAHMIDI H., GOETZ V.: *Solar heating and cooling by a thermochemical process*. First experiments of a prototype storing 60 kWh by a solid/gas reaction. Solar Energy **82**(2008), 623–636.
- [27] LI T.X., WANG R.Z., WANG L.W., LU Z.S., CHEN C.J.: *Performance study of a highefficient multifunction heat pipe type adsorption ice making system with novel mass and heat recovery processes*. Int. J. Therm. Sci. **46**(2007), 1267–1274.
- [28] VASILIEV L.L., ANTUKH A.A., MAZIUK V.V., KULAKOV A.G., RABETSKY M.I., VASILIEV L.L., JR., OH SE MIN: *Miniature heat pipes, experimental analysis and software*. Proc. of the 12th Int. Heat Pipe Conf., Moscow - Kostroma, May 19–24, 2002.
- [29] SPINNER B., STITOU D., GRINI P.G.: *Cascading Sorption Machines: New Concepts for the Power Control of Solid-Gas Thermochemical Systems*. Towards Sustainable Technologies, Proc. of the 1996 Absorption Heat Pump Conf., Montreal, Sept. 17–20, 1996, Vol. 2, 531–538.
- [30] VASILIEV L.L., MISHKINIS D.A., ANTUKH A.A., KULAKOV A.G., VASILIEV L.L., JR.: *Multisalt-carbon portable chemical heat pump*. Proc. of the Int. Sorption Heat Pump Conf., Changhai, China, Sept. 24–27, 2002, 463–468.
- [31] MEUNIER F.: *Solid sorption heat powered cycles for cooling and heat pumping applications*. Appl. Therm. Eng. **18**(1998), 715–729.
- [32] LEPINASSE E., GOETZ V., CROZAT G.: *Modelling and experimental investigation of anew type of thermochemical transformer based on the coupling of two solid-gas reactions*. Chem. Eng. Proc. **33**(1994), 125–134.

-
- [33] CHOI H.K., NEVEU P., SPINNER B.: *System modeling and parameter effects on design and performance of ammonia based thermochemical transformer*. Proc. Int. Absorption Heat Pump Conf., Montreal 1996.
- [34] GOETZ V., SPINNER B., LEPINASSE E.: *A solid-gas thermochemical cooling system using BaCl₂ and NiCl₂*. Energy, **22**(1997), 49–58.
- [35] VASILIEV L.L., MISHKINIS D.A., ANTUKH A.A., KULAKOV A.G.: *Resorption heat pump*. Appl. Therm. Eng. **24**(2004), 1893–1903.
- [36] AIDOUN Z., TERNAN M.: *Salt impregnated carbon fibres as the reactive medium in a chemical heat pump: the NH₃-CoCl₂ system*. Appl. Therm. Eng. **22**(2002), 1163–1173.
- [37] AIDOUN Z., TERNAN M.: *The synthesis reaction in a chemical heat pump reactor filled with chloride salt impregnated carbon fibers: the NH₃-CoCl₂ system*. Appl. Therm. Eng. **22**(2002), 1943–1954.