

# THE WAY TO INCREASE THE EFFICIENCY OF NEW POWER SOURCES

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**ABSTRACT:** In the 21<sup>st</sup> 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 with the help of solid sorption heat pumps, refrigerators, accumulators of the heat and cold, heat transformers, natural and hydrogen storage systems and efficient heat exchangers.

## 1. INTRODUCTION

The 21<sup>st</sup> century will see the 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, as 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. At the same time it is very important to ensure the efficient consuming of the natural gas in low temperature technologies, converting it to hydrogen. One of the key low temperature technologies is the electrochemical power source, namely fuel cell that converts the 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 (Carno) 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 the photovoltaic system, solar, wind energy and water resources. Low temperature power systems are significantly inexpensive to build than high temperature ones in general case. Since a major barrier to acceptance, this is a main concern for fuel cell technology in general. For low-duty-cycle applications (such as owner-occupied dwellings and many portable devices) the direct system cost is an important factor and efficiency is less important. 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, with unmatched efficiency and potentially greater reliability than other energy systems (because of greatly lower part counts, for example, and solid state construction in the case of SOFTs) are quite competitive in many applications, even at present cost. On the other hand, since the experience and familiarity 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.

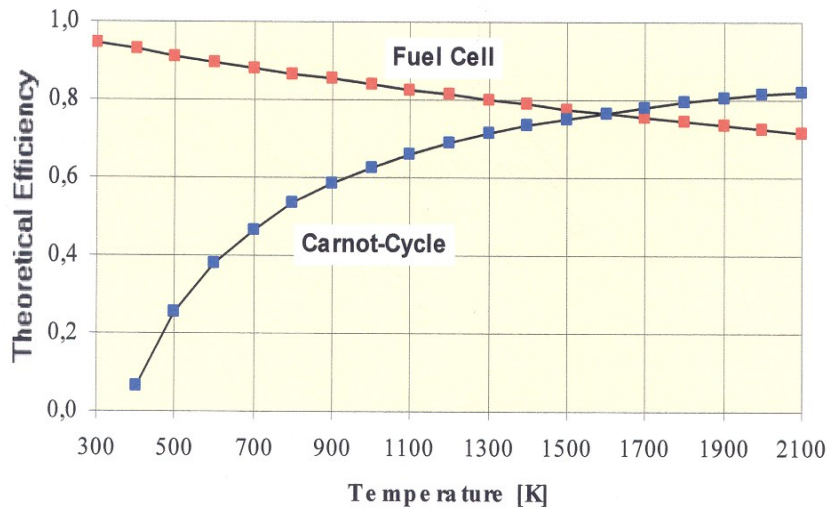


Fig. 1 The efficiency of Carnot Cycle and Fuel Cell Cycle as a function of temperature

We should expect to use many different technologies, often in combination. Fuel cells are well suited to this requirement, and operate with batteries, turbines, and exchangers as partners. Users of cars 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 due to the batteries capacity. A fuel-based auxiliary power unit is one possible method of supplying this electrical power. But even fuel cells need to improve their efficiency due to the heat dissipation inside on the level of 50%. It can be realized with the help of solid and liquid sorption machines [2]. Sorption machines (heat pumps, refrigerators, heat transformers, etc.) are a good way to combine the fossil fuel resources exhausted gases, vapor and water, alternative (solar, water, ground, air) and autonomous sources of energy to reduce the energy consumption down to 15–20%, Fig. 2.

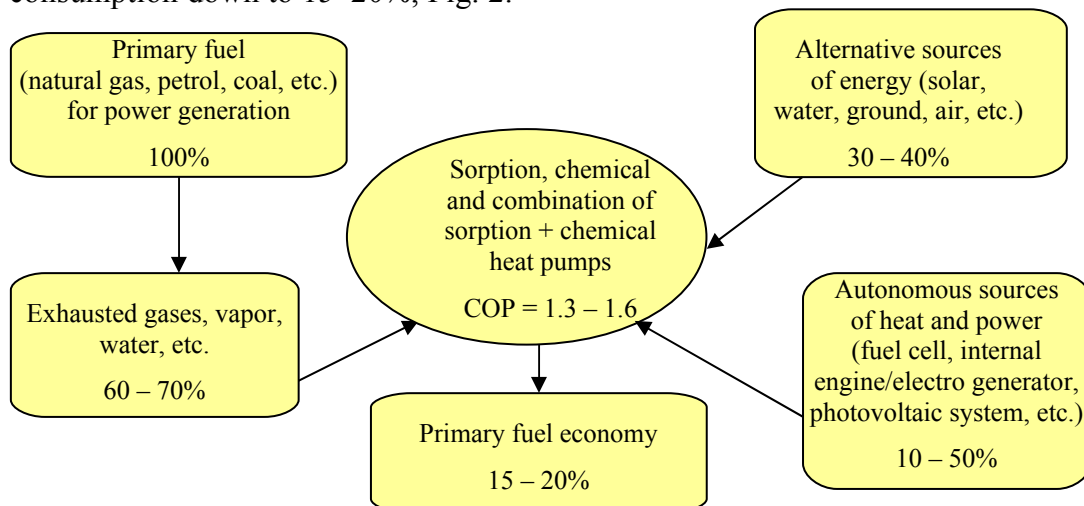


Fig. 2 New possibilities to improve the efficiency of the fossil fuel, alternative and autonomous energy sources application by sorption and chemical heat pumps

## 2. TRIGENERATION SYSTEMS BASED ON SORPTION HEAT PUMPS

The co-generation is simultaneous production of heat and power for consumption within a site. If we use the part of the heat or power to produce the cold (refrigeration), the system is termed as tri-generation. Sorption machines are well suited for this goal. Fig. 3 shows a generalize diagram of a tri-generation system, based of 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 is to use 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.

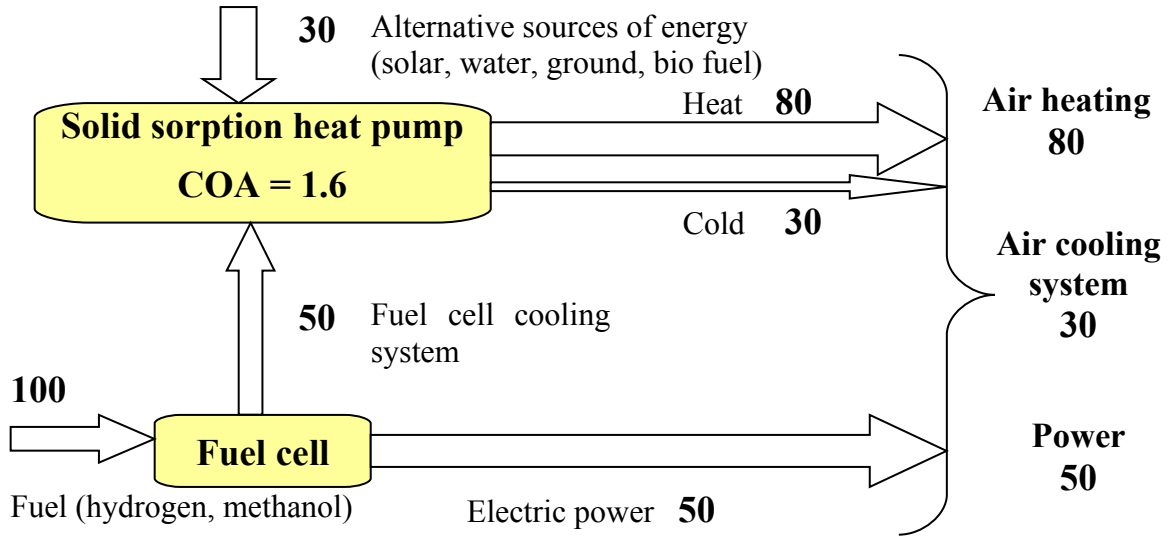


Fig. 3 System of tri-generation based on fuel cell and solid sorption heat pump application

The overall first law efficiency for tri-generation system can be expressed by:

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

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 (co-generation, tri-generation 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 [24-25]. Low temperature power systems are generally significantly less expensive to build than high temperature ones.

### 3. SOLID SORPTION HEAT PUMPS

Sorption Machines is collective indication of refrigeration machines and heat pumps in which the mechanically driven compressor is replaced by a *thermally* driven thermo-chemical or thermo-physical sorption loop. Sorption heat pumps and sorption refrigeration machines contrast with compression heat pumps by the following characteristics:

1. Sorption systems are heat driven (gas-driven, hot water driven, waste heat driven).
2. Sorption systems hardly have moving parts and therefore have a very low noise level, show minimal wear and tear, and have a very low need for maintenance.
3. Sorption systems conventionally work with natural refrigerants (mostly Ammonia (NH<sub>3</sub>) Hydrogen (H<sub>2</sub>), CO<sub>2</sub> and Water (H<sub>2</sub>O).
4. They can be built in an unlimited range of capacities, from a few tens of watts (refrigerator in minibar of hotel-room) to the Megawatt scale (industrial applications).
5. Systems can be designed for a broad range of operating temperatures.

#### 3.1 HEAT AND MASS TRANSFER IN THE SORBENT BED

The applied sorbent bed is activated carbon fibre (“Busofit”). The ideal sorbent bed in our case needs to have micropores volume near 50%, solid carbon near 40% and meso/macropores volume near 10%. The efficient system to perform a sorbent bed thermal control during the cycle of sorption/desorption is heat pipe heat exchanger. The sectional vessel with heat pipes for thermal management is shown on Fig.4. Each reactor of multireactor case is filled with briquette sorbent material. Due to its high permeability activated carbon fibre is welcomed for the cycles with a forced convection heating/cooling. It is the universal adsorbent, easily adsorbing different gases (H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub>, etc.) and has such advantages as:

- uniform surface pore distribution (0.6-1.6 nm);
- small number of macropores (100-200 nm), with its specific surface 0.5-2 m<sup>2</sup>/g;
- small number of mesopores with 50 m<sup>2</sup>/g specific surface.

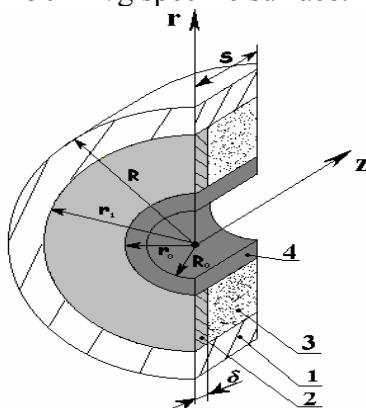


Figure 4: 1 - adsorber envelope; 2 – fin of heat pipe; 3- sorbent bed; 4 – heat pipe

Heat pipes are attractive to use in sorption heat machines due to its flexibility, high heat transfer efficiency, cost-effectiveness, reliability, long operating life, and simple manufacturing technology. Heat pipe metal fins serve for intensification of heat transfer in the sorbent bed, Fig.4, Fig.5. A flat rectangular or cylindrical form is convenient for compact solid sorption canister. Figure 6 illustrates a schematic of HP envelope with thermal contact of the heat pump sorption reactor and two calculation areas: S1 (the cylindrical reactor, the HP envelope and HP fins between the sorption material), and S2 (sorbent bed) with indication of boundaries between them. The calculation domain is bounded by external surface of the heat pump 2, the internal wall of HP (boundary 5), the symmetry planes at the middle of fins (boundaries 1 and 4) and at the middle of sorbent layer (boundary 3). The mathematical model of heat transfer and gas sorption processes in the reactor is based on the following assumptions: 1) the gas in the cylinder is ideal; 2) the temperature of the solid phase is equal to the temperature of the gas phase at each point, because of the high coefficient of the volumetric heat transfer between them; 3) heating and cooling of the sorbent material is carried out by heat pipe (HP) with inner heat transfer coefficient  $\alpha_{HP} = 10^3 - 10^4 \text{ W}/(\text{m}^2\text{K})$ . This coefficient is uniform along the surface and large in comparison with the thermal resistance of interface HP-sorbent bed.

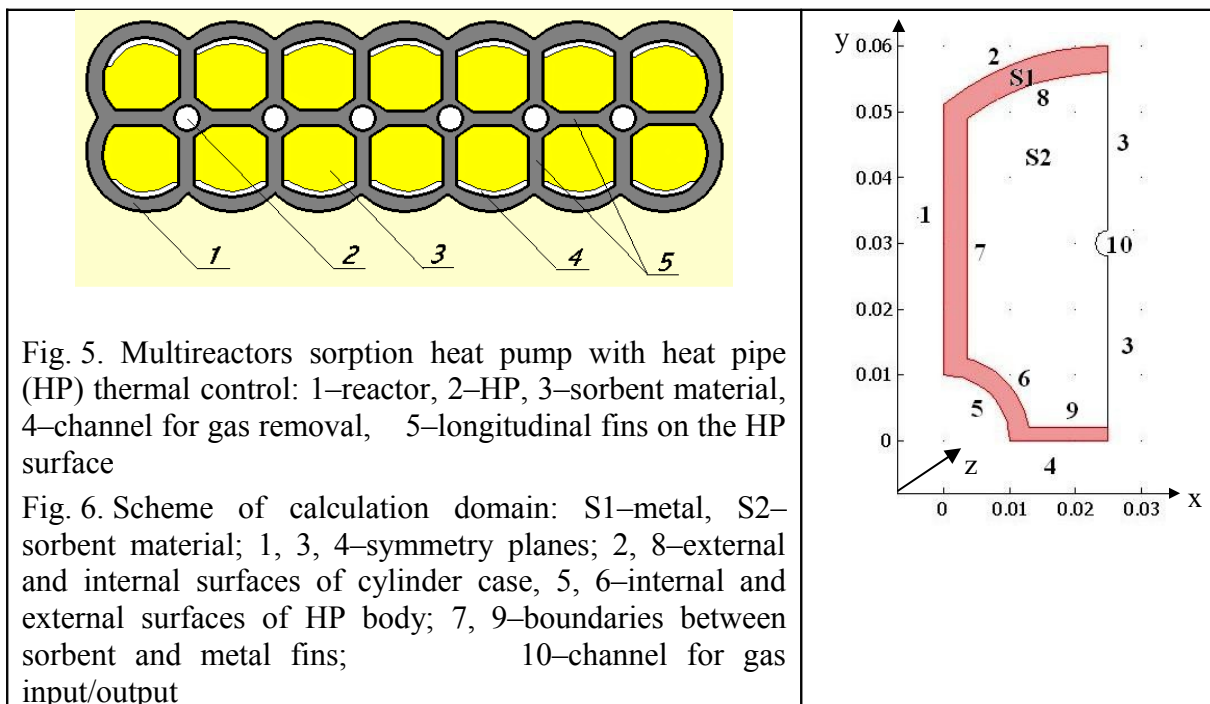


Fig. 5. Multireactors sorption heat pump with heat pipe (HP) thermal control: 1–reactor, 2–HP, 3–sorbent material, 4–channel for gas removal, 5–longitudinal fins on the HP surface

Fig. 6. Scheme of calculation domain: S1–metal, S2–sorbent material; 1, 3, 4–symmetry planes; 2, 8–external and internal surfaces of cylinder case, 5, 6–internal and external surfaces of HP body; 7, 9–boundaries between sorbent and metal fins; 10–channel for gas input/output

The dynamic model of the sorbent bed has the components [3 – 5]:

1) Dubinin – Radushkevich equation of the state of gas

$$a_{eq} = \frac{W_0}{v_a} \exp \left\{ - \left[ \frac{R_\mu T \ln(P_{sat} / P)}{E} \right]^2 \right\}, \quad (1)$$

where

$$P_{sat} = P_{cr} (T / T_{cr})^2 ; \quad (2)$$

2) the equation of sorption kinetic

$$\frac{\partial a}{\partial \tau} = K_{s0} \exp\left(-\frac{E}{R_{\mu} T}\right) (a_{eq} - a), \quad (3)$$

where  $K_{s0} = 15D_{s0} / R_p^2$ ,  $D_{s0}$  - phenomenological constant,  $R_p$  – the average radius of particle;

3) energy conservation equation

$$(\varepsilon \rho_g C_g + \rho C + \rho a C_a) \frac{\partial T}{\partial \tau} + \nabla \cdot (-\lambda \nabla T + \rho_g C_g T \mathbf{u}) = q_{st} \rho \frac{\partial a}{\partial \tau} - \beta_g T \varepsilon \frac{\partial P}{\partial \tau} \quad (4)$$

4) mass balance

$$\frac{\partial (\varepsilon \rho_g)}{\partial \tau} + \nabla (\rho_g \mathbf{u}) + \nabla (-D \nabla a) = -\frac{\partial}{\partial \tau} (\rho a); \quad (5)$$

5) momentum balance

$$\rho_g \frac{\partial \mathbf{u}}{\partial \tau} + \frac{\eta}{K} \mathbf{u} = \nabla \left[ -P \mathbf{I} + \eta (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) \right]. \quad (6)$$

For the ideal gas ( $z_g = 1$ ,  $V_a \ll V_g$ ), the isosteric heat is calculated from the relation

$$q_{st} = R_{\mu} T \left[ \frac{\partial \ln P}{\partial \ln T} \right] \Big|_{a=const} \quad (7)$$

In the case of a nonideal gas, the estimation obtained with (7) should be considered as being approximate. Equations system (1)–(7) defines four variables  $T$ ,  $P$ ,  $a$ ,  $\mathbf{u}$ , dependent from space coordinates and time.

Initial conditions for them are:

$$T(\tau_0) = T_0, \quad P(\tau_0) = P_0, \quad T(\tau_0) = T_0, \quad P(\tau_0) = P_0, \quad \mathbf{u}(\tau_0) = 0, \quad a(\tau_0) = a_{eq}(T_0, P_0) \quad (8)$$

Basic boundary conditions are :

At the external side of the reactor envelope (boundary 2) the conditions of convective heat transfer with environment with external heat transfer coefficient:

$$\mathbf{n} \cdot \mathbf{q} = \alpha_{env} (T - T_{env}), \quad \mathbf{q} = -\lambda \nabla T, \quad (9)$$

where  $\mathbf{n}$  is the unit vector of exterior surface normal.

Depending on the conditions at the internal surface of the HP body (boundary 5) the temperature  $T_{HP}$  or heat flux from fins to sorbent material is:

$$\mathbf{n} \cdot \mathbf{q} = q_{HP}, \quad \mathbf{q} = -\lambda \nabla T, \quad q_{HP} = \alpha_{HP} (T_{HP} - T), \quad (10)$$

where  $\alpha_{HP}$  is the heat transfer coefficient from HP working fluid (saturated vapor in HP) to the internal surface of HP body.

The heat flux is equal to zero at symmetry planes. For boundary condition 10 where the cylindrical aperture for gas supply is located, the heat flux depends on temperature  $T_i$

$$-nq = q_0, \quad q = \lambda \nabla T - \rho_g C_p u, \quad q_0 = -\rho_g C_p T_i (u \cdot n) \quad (11)$$

To solve the set of equations (1)–(7) the method of finite elements for fixed mesh was used [6]. Convergence precision was equal to  $10^{-6}$ . The system of equations with a sorption source is stiff and allows integration only with a small time step. For achievement of required accuracy and numerical stability the integration step did not exceed 2 s.

### 3.2 The activated carbon fibre and salt particles of its surface

A new generation of solid sorption heat pumps and coolers have [19-21] a good compromise between chemical heat pumps [10-12] and adsorption heat pumps [3-9]. 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.7.

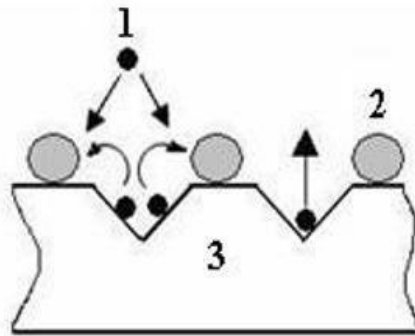


Figure 7: Composite sorbent material [16-18]: a) molecules of sorbate (ammonia) (1) absorbed by metal-chloride micro crystals (2) and adsorbed in micropores of the activated carbon fiber “Busofit”(3)

Microcrystals of  $\text{NiCl}_2$ ,  $\text{MnCl}_2$  and  $\text{BaCl}_2$  on the active carbon fibre “Busofit” surface are suggested as a composite sorbent material due to their stability, low cost and suitable temperature range. This sorbent bed has the advantages of chemical heat pumps (high sorption capacity) and high speed of adsorption, typical for adsorption heat pumps. Simultaneously there is a strong interaction (intensive heat and mass transfer) between adsorptive materials and chemical materials (active carbon/microcrystals) during the cycle of heating/cooling. If we have two adsorbers (reactors) filled with different complex compounds (salts disposed on the active carbon filaments), the cycle is separated in two main phases corresponding to two pressure levels, Fig.8-Fig.10. Due to the effect of adsorption/desorption of the carbon fibre this pressure difference is dynamically changing in the cycle (completely different comparing with chemical reactors). The carbon fibre as a fast sorbent material starts to react with ammonia in

the early stage of heating/cooling time (up to 5 min, Fig.4b) and accomplish 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 reach ammonia motion through the sorbent material due to capillary forces). The active carbon filaments and microcrystals enhanced the COP of the system to compare with conventional chemical heat pumps. To minimize a void space and increase the adsorbent capacity of the active carbon fiber we need to compress “Busofit” together with a binder. The complex compound microstructure obtained in the Luikov Heat & Mass Transfer Institute has been studied using Scanning Electro Microscope (SEM). The characterization should reveal a porous structure with a uniform micro and nano pores distribution on the filament surface. There is also a uniform distribution of microcrystals on the filament surface without formation of agglomerates. Fig. 10 shows also that for maximal concentration of chemicals on the filament surface the structure of the salt around the fiber is porous which is favorable for heat and mass transfer. The results of the experimental analysis of the sorption capacity of the active carbon fiber “Busofit” and fiber “Busofit” + chemicals are presented in the Table 4; the data are obtained for the room temperature, except methane (253 K). Figure 5 shows ammonia sorption isotherms for the active carbon fiber “Busofit” and complex compound “Busofit+CaCl<sub>2</sub>”. Combination “Busofit” + metal hydrides have some particularities to compare with the combination “Busofit” + metal chlorides. As an example the parameters of solar/gas cooler with complex compound application are presented on the Table 1, [20-21].

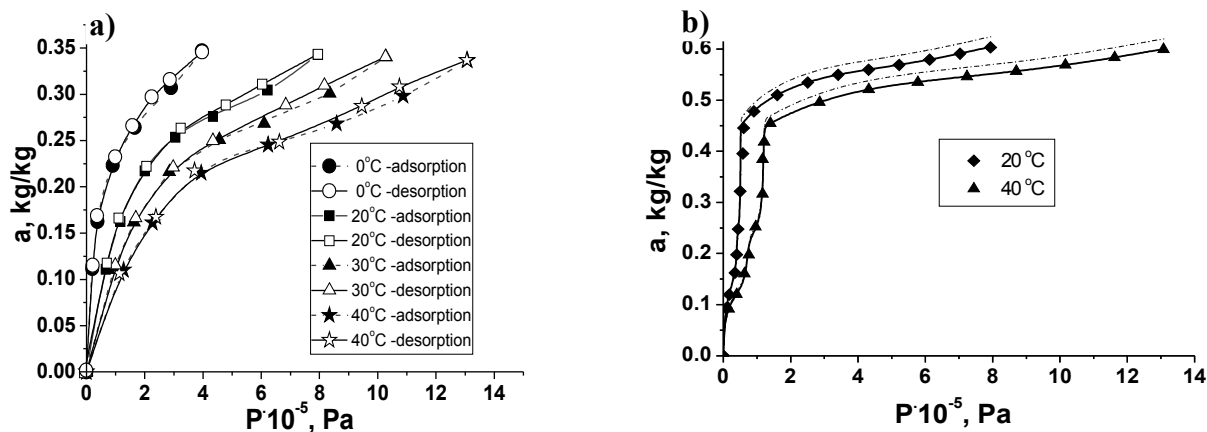


Figure 8a: Dynamic ammonia sorption capacity (adsorption/desorption) for the active carbon fibre “Busofit” at different temperatures versus pressure;

Figure 8b: Dynamic ammonia sorption capacity (adsorption/cyntesis, desorption/regeneration) for complex compound (“Busofit” + CaCl<sub>2</sub> microcrystals) at 20 °C and 40 °C versus pressure.

The photo of the activated fibre “Busofit” and the same fibra with CaCl<sub>2</sub> microcrystals on its surface are shown on Fig. 9-10. The uniform distribution of micro/nano pores (Fig.9) in the filament body allow to have a high porous volume inside to adsorb gases. The micro/nano crystals deposit on the filament surface increase the sorption capacity of the sorbend compound 2-3 times, Table 1.



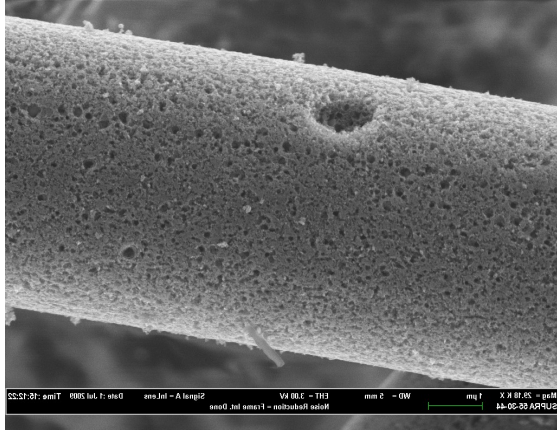


Figure 9 Activated carbon fibre “Busofit”

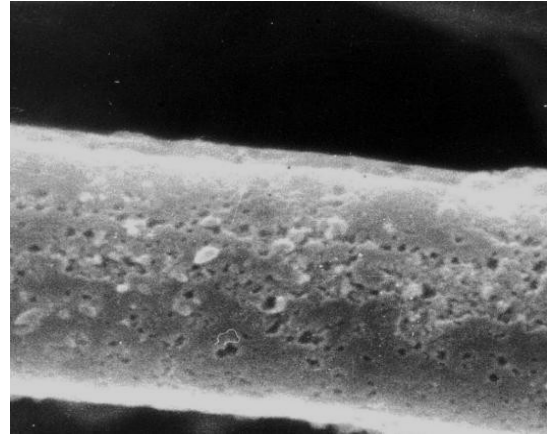


Fig.10 Activated carbon fibre “Busofit” with microcrystals  $\text{CaCl}_2$  on its surface

Table1. Sorption capacity of new sorbent materials

Full sorption capacity of the sorbent bed	Activated carbon fibre “Busofit”	“Busofit” + $\text{CaCl}_2$ or “Busofit” + $\text{LaNi}_{4.5}\text{Al}_{0.29}\text{Mn}_{0.21}$
Methane, $T = 253 \text{ K}$ , $P = 6 \text{ Mpa}$ , v/v	182	
Ammonia, g/g	0.35	0.62 – 1.03
Hydrogen, wt%	1.5	3.2
Methanol, g/g	0.55	

### 3.3 Two adsorbers heat pump

Adsorption refrigeration / heat pump technology based on the evaporation process has been widely discussed since the last decade and some adsorption machines are already in the market [4-10]. Conventional heat pipes due to their superthermal conductivity 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 in time and to use heat pipes for cooling and heating sorbent bed. Such heat pipes are made as a copper envelope with copper sintered powder as a wick. The software was proposed, developed and used for prediction of heat pipe parameters [ ]. Heat pipe family qualified geometry: round tube diameter 4-25 mm, length 0.1 m – 0.8 m, wall thickness 0.2 -1.0 mm. Pipe material – Copper 99.95% purity, wick - copper sintered powder with thickness 0.2-0.8 mm. Transport capacity 10 -500 W. Water, methanol and propane are mostly used as working fluids. The heat pipe mathematical model developed include heat pipe parameters:

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

**Output:** maximum heat flow  $Q_{\max}$  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 adsorbers heat pump, with heat pipe thermal control in shown on Fig.11 - 12. The experimental set-up has: 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. This thermal system enables heat pipe heat recovery between adsorbers by the liquid circulating loop and mechanical pump.

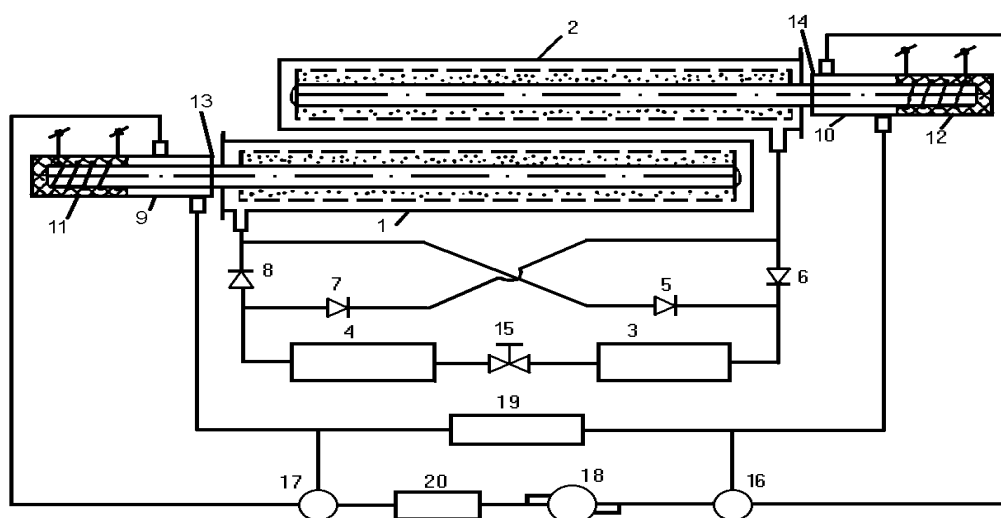


Figure 11. Two adsorbers heat pump with heat pipe thermal control

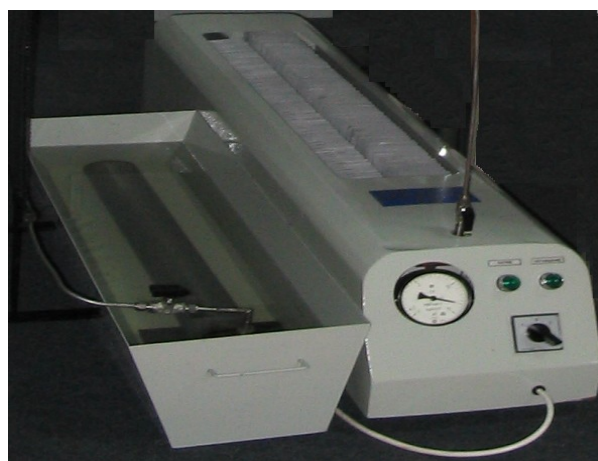


Figure 12. Two-adsorbers heat pump experimental set-up with evaporator for liquid cooling with COP =1.6

The parameters of the adsorption solar refrigerator (two adsorbers, condenser and evaporator) are shown in the Table 2. 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 vapordynamic thermosyphons are applied as the system of thermal control of the refrigerator [ ].

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

### 3.4 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 different advantages and drawbacks with regard of their compactness, complexity, cost, the range of working temperature [22]. 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 [25-26]. The resorption technology advantages at first are related to the nature friendly refrigerants such as water, ammonia, CO<sub>2</sub> (no CFC, HCFC, HFC) and at second they are thermally driven and can be coupled with waste heat, solar heat,

burning fossil fuel, or biomass. The third advantage of resorption systems relate with its ability to use a significant number of couples solid-gas [25]. 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 longer time periods with low losses [1]. 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 [11-13] in which such pairs as  $MgCl_2 / NH_3$  -  $NiCl_2 / NH_3$  and  $BaCl_2 / NH_3$ -  $NiCl_2$  were used.

A new stream in resorption heat pumps is related with complex compounds sorbent materials application (for example, as active carbon fibre and microcrystals of the salts on its surface) [16]. The above mentioned sorbent bed has the advantages of chemical heat pumps (high sorption capacity) and high speed of adsorption, typical for adsorption heat pumps. Simultaneously there is a strong interaction (intensive heat and mass transfer) between adsorptive materials and chemical materials (active carbon/microcrystals) during the cycle of heating/cooling. The heat pipe technique ensures the thermal control of the high-temperature reactors in the resorption refrigeration system.

Let us consider a new resorption heat pump, Fig.13. 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  $BaCl_2 \cdot 8/0 NH_3$  and its equilibrium curve is close to the  $NH_3$  saturation curve. The high temperature reactor is filled with „Busofit“ carbon fibre and  $NiCl_2$  microcrystals. For both reactors their size is :  $L = 1000$  mm,  $D_{out} = 50$  mm,  $D_{in} = 49$  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 g + 270 g), „Busofit“+  $NiCl_2$  mass is (250 g + 180 g). The basic cycle, Fig.14-15, 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 the temperature of two reactors is changing between 50 °C and 220 °C, Fig.15. It can be noted that the time of cooling of the reactor is much faster than the time of its heating. COP of the Resorption Cycle (two different salts) is considered as:

$$\text{Ideal COP}^i = \Delta H_0 / \Delta H_1;$$

$$\text{Thermodynamic COP} =$$

$$(\Delta H_0 - C_p^{(salt0)} (T_0 - T_b)) / (\Delta H_1 + C_p^{(salt1)} (T_h - T_0))$$

$$\text{Practical COP} =$$

$$(\Delta H_0 - (\Sigma C_p (\text{salt0} + \text{carbon} + \text{steel}) (T_0 - T_b)) / (\Delta H_1 + (\Sigma C_p (\text{salt1} + \text{carbon} + \text{steel})) (T_h - T_0))$$

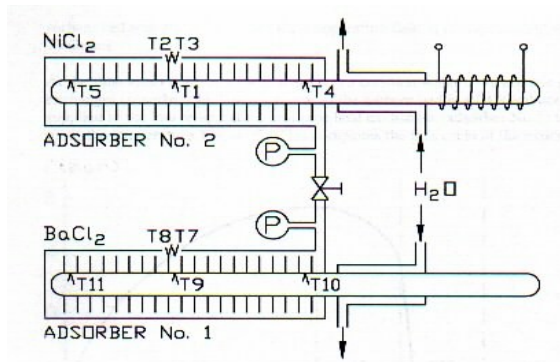


Figure 13: Sorption heat pump with two reactors (“Busofit”-NiCl<sub>2</sub>) /NH<sub>3</sub> ; “Busofit”-BaCl<sub>2</sub>) /NH<sub>3</sub>). Two heat pipes are used for thermal management of the reactors.

For the combination of sorbent materials “Busofit”/BaCl<sub>2</sub> and “Busofit”/NiCl<sub>2</sub> the heat pump COP = 1.2 is close to reality. Copper/water heat pipes with sintered powder wick ensure the efficient heating/cooling and the heat recovery between the reactors 1 and 2. The 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, Fig.14. The time of the total cycle is near 60 min.

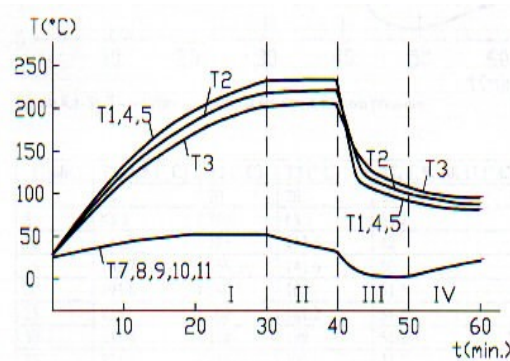


Figure 14: Temperature evolution in different part of the resorption heat pump during its heating/cooling. T1-T5 – thermocouples in different parts of the high temperature sorbent bed, T7 – T11 – thermocouples in different parts of low temperature sorbent bed.

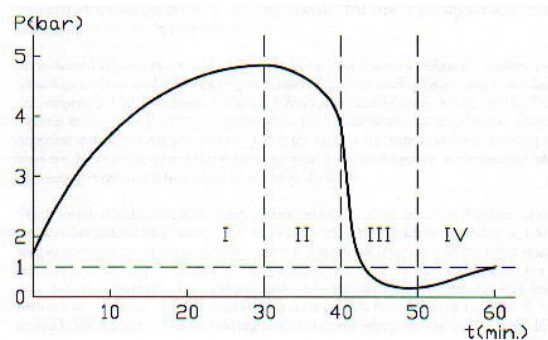


Figure 15: Cyclic pressure evolution in two reactors heat pump during its heating/cooling.

The pressure evolution between stages of heating/cooling is shown of Fig.15. Internal heat recovery is enable due to the mass transfer between the reactors. The external heat recovery is realized by heat pipe heat exchangers and pump with water sirculation between heat pipes.

### 3.5 Multi cascaded heat pumps.

The optimization of the sorption technologies is sometimes related with multi-cascading heat pumps and coolers application [17-20]. The Clapeyron diagram of 3 reactors solid sorption cooler with two sources of cold is presented on Fig.16 with four stage of the heating /cooling.

Since the operating modes of heat pumps are different it is necessary to reduce the non-productive period of the topping cycle. The thermal coupling can be realized by heat pipe heat exchanger between reactors to ensure the internal and the external heat and mass recovery, Fig8. The results of experiments testify a possibility to have a resorption heat pump with simultaneous heat generation 1500 W (steam  $T = 120\text{ }^{\circ}\text{C} - 130\text{ }^{\circ}\text{C}$ ) and chilled water output ( $T = 3\text{ }^{\circ}\text{C} - 5\text{ }^{\circ}\text{C}$ ) with COP up to 1.5.

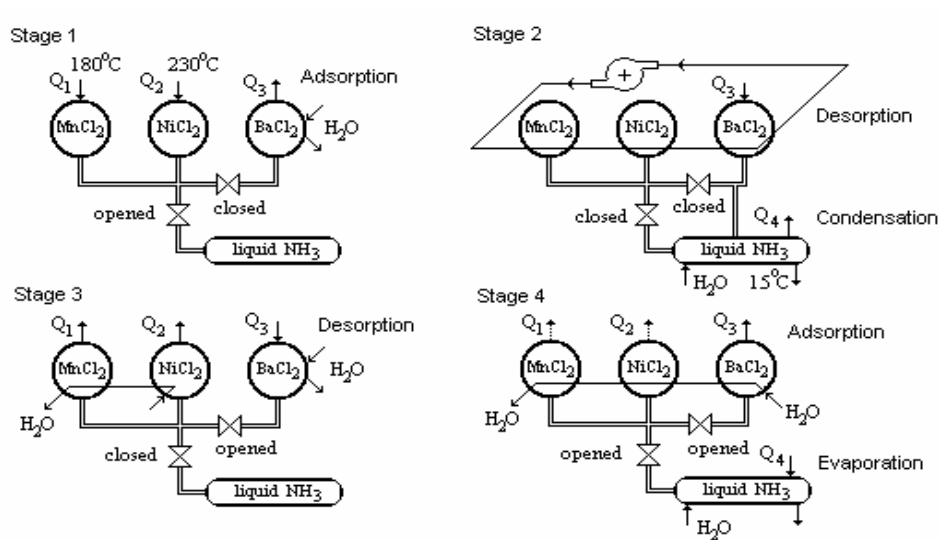


Figure 16: Advanced heat pump (“Busofit” + salts) with heat pipe heat recovery and two sources of cold – low temperature adsorber  $\text{BaCl}_2$  and heat pump evaporator

The next option of solid sorption cooler (Fig. 16) has two sources of cold - the low temperature resorption reactor and the principal evaporator (similar to heat pipe evaporator with enhanced heat transfer surface inside). The working fluid is ammonia. The Clapeyron diagram for such dual cooler is shown of Fig.17. The most favorable situation for this cooler is the case, when two sources of cold are used to cool gas, or liquid.

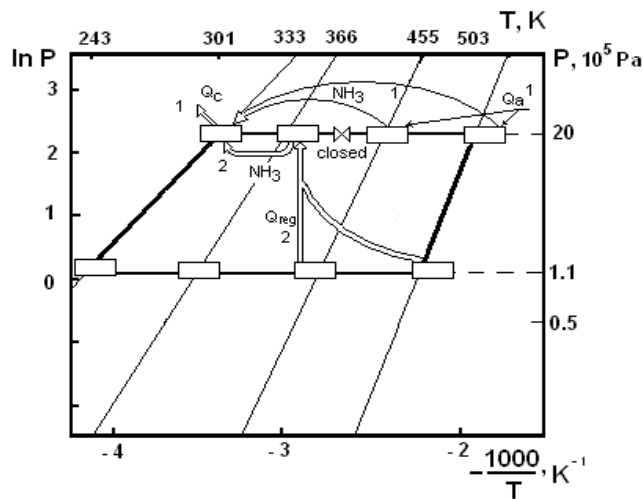


Figure 17: Clapeyron diagram of solid sorption cooler with two sources of cold

An example of heat input/output in the evaporator/condenser (1) and the  $\text{BaCl}_2$  reactor (2) via time of the cycle is presented on Fig.16, Fig.17. The max charging power of  $\text{MnCl}_2$ ,  $\text{NiCl}_2$  reactors is around 400 W each. Ammonia evaporation at 10 °C guarantee 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 the solid sorption cooler (“Busofit” + salts) with heat recovery and two sources of cold ( low temperature reactor carbon/ $\text{BaCl}_2$  and evaporator) are shown on Fig.18 with the temperature evolution on the heat pipe 1 ( $\text{NiCl}_2$ /active carbon) and heat pipe 2 ( $\text{MnCl}_2$ /active carbon).

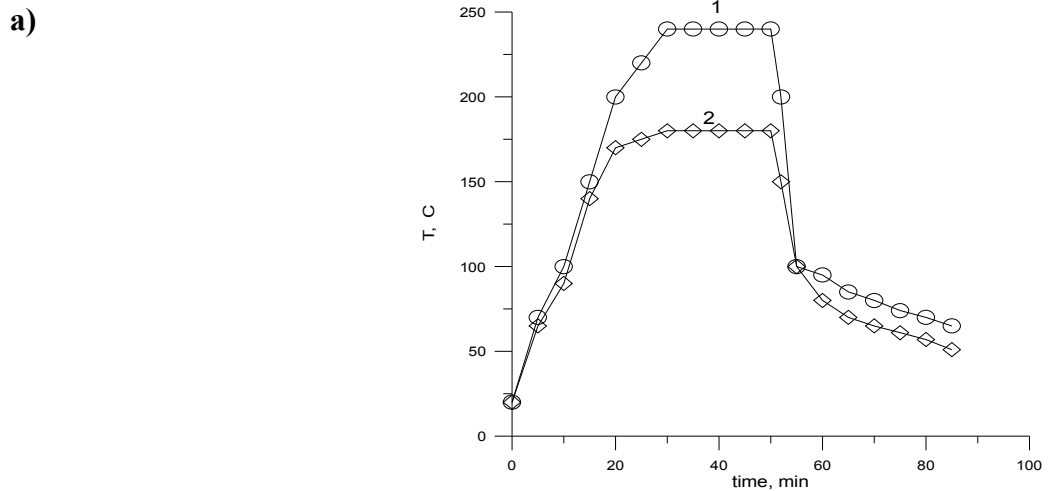


Figure 18: a) The heat input/output in the evaporator/condenser (1) and the low temperature carbon/BaCl<sub>2</sub> reactor (2) as a function of the cycle; b) the temperature evolution on the heat pipe 1 and heat pipe 2 during the cycle heating/cooling

Now we consider the multistage ammonia complex compound heat pump capable to ensure the temperature lift more than 100°C. This resorption heat pump, Fig. 19 has three stage and six adsorbers (three and three adsorbers working out of phase). The heat pump is working with gaseous ammonia (no liquid). The heat pump has activated carbon fibre with BaCl<sub>2</sub>, MnCl<sub>2</sub>, NiCl<sub>2</sub> microcrystals on its surface. 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 (1) and fresh water output (2) is near 120 °C. The temperature of the water input in the low temperature heat exchanger is 20 °C. Internal heat recovery consists of using the adsorption/synthesis heat of high temperature solid/gas pair (NiCl<sub>2</sub>/NH<sub>3</sub>) to initiate the desorption/ regeneration of medium temperature solid/gas pair (MgCl<sub>2</sub>/NH<sub>3</sub>). The adsorption/synthesis heat of medium temperature solid/gas pair (MnCl<sub>2</sub>/NH<sub>3</sub>) is used to initiate the desorption/regeneration of low temperature solid/gas pair (BaCl<sub>2</sub>/NH<sub>3</sub>).

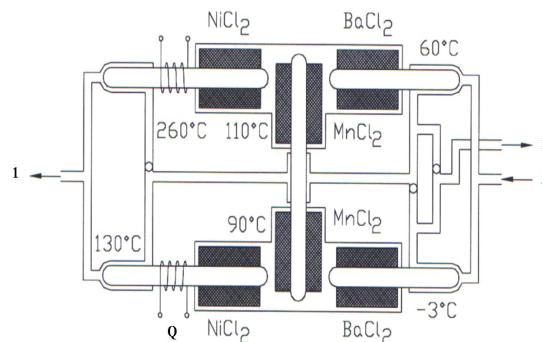


Figure 19: Six adsorber three-stage resorption heat pump with heat pipes thermal control. 1 – steam output, 2 – fresh water output, 3 – water input to heat exchanger (20°C)



Figure 20: Three stage resorption cooler Clapeyron diagram ( $\text{BaCl}_2$ ,  $\text{MnCl}_2$ ,  $\text{NiCl}_2$  + active carbon fibre “Busofit”) with a temperature lift near  $100^\circ\text{C}$

The Clausius-Clapeyron diagram ( $\ln P$  as a function of  $1/T$ ) for such resorption heat pump (dashed lines are temperature outputs) is shown on Fig. 20. 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. The experimental data of the resorption heat pump are presented on Table 2. The sorbent bed in each of adsorbers is a complex compound – active carbon fibre + microcrystals of salts on its surface and in macro/meso pores. For the term of simplification the adsorbers are indicated as  $\text{NiCl}_2$ ,  $\text{MnCl}_2$  and  $\text{BaCl}_2$  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 for the air-condition systems and water cooling combining with such resorption heat pump. There is an interesting possibility to combine different sorption heat pumps to increase its total efficiency. For example it is possible to develop cascaded cycles with the topping resorption/adsorption cycle and bottoming absorption ( $\text{LiBr}/\text{water}$ ) cycle, Fig. 21. Since the operating modes of both heat pumps are different and to reduce 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 water/lithiumbromide absorption chiller cycle is designed for maximum chilling capacity, thermally coupled with adsorption ammonia/complex compound ( $\text{NiCl}_2/\text{carbon fibre}$ ) sorbent bed with the heat pipe heat exchangers. This heat pump ensures the heat recovery of high temperature fuel cells. So, the solid sorption heat pumping and refrigeration is promising technology to combine the low temperature thermal sources of energy with the high temperature cycles, thus increasing the efficiency of total energy consumption and ensure the nature protection against the  $\text{CO}_2$  dangerous concentration in the atmosphere [14–15].

Table 2. Evolution of the temperature and pressure field inside the three salts sorption heat pump as the function of the cycle.

Time (min.)	T <sub>2</sub> (°C)	T <sub>3</sub> (°C)	T <sub>4</sub> (°C)	T <sub>5</sub> (°C)	T <sub>6</sub> (°C)	T <sub>7</sub> (°C)	T <sub>8</sub> (°C)	Q <sub>h</sub> (W)	Q <sub>w</sub> <sup>Ba</sup> (W)	Q <sub>w</sub> <sup>MnNi</sup> (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	800	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

$T_1$  – water temperature at the heat pump entrance ( $T_1 = 20^\circ\text{C}$ ),  $T_2$  – water temperature at the heat pump exit (MnCl<sub>2</sub> and NiCl<sub>2</sub> adsorbers),  $T_3$  – water temperature at the BaCl<sub>2</sub> adsorber exit,  $T_4$  – temperature at the MnCl<sub>2</sub> adsorber surface (without thermal insulation),  $T_5$  – temperature at the NiCl<sub>2</sub> adsorber surface (without thermal insulation),  $T_6$  – temperature at the BaCl<sub>2</sub> adsorber surface (without thermal insulation),  $T_7$  – temperature at the heat pipe thermal control system surface (MnCl<sub>2</sub> adsorber),  $T_8$  – temperature at the heat pipe thermal control system surface (NiCl<sub>2</sub> adsorber),  $Q_h$  – total heat input to adsorbers (NiCl<sub>2</sub> and MnCl<sub>2</sub>),  $Q_w^{Ba}$  – heat output to heat a cooling water (BaCl<sub>2</sub> adsorber),  $Q_w^{MnNi}$  – heat output from NiCl<sub>2</sub> and MnCl<sub>2</sub> adsorbers to cooling water,  $P$  – pressure in adsorbers.

The hydrogen fuel cells with solid sorption heat pumps as a tri-generation 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 to thermal integration of tri-generation systems is considered as a special case of the application of co-generation systems where a fraction of the shaft work or residual heat is used for running a refrigeration system [16]. The gas turbine is used as a prime mover for power production and cooling is generated by a typical compression-refrigeration system.

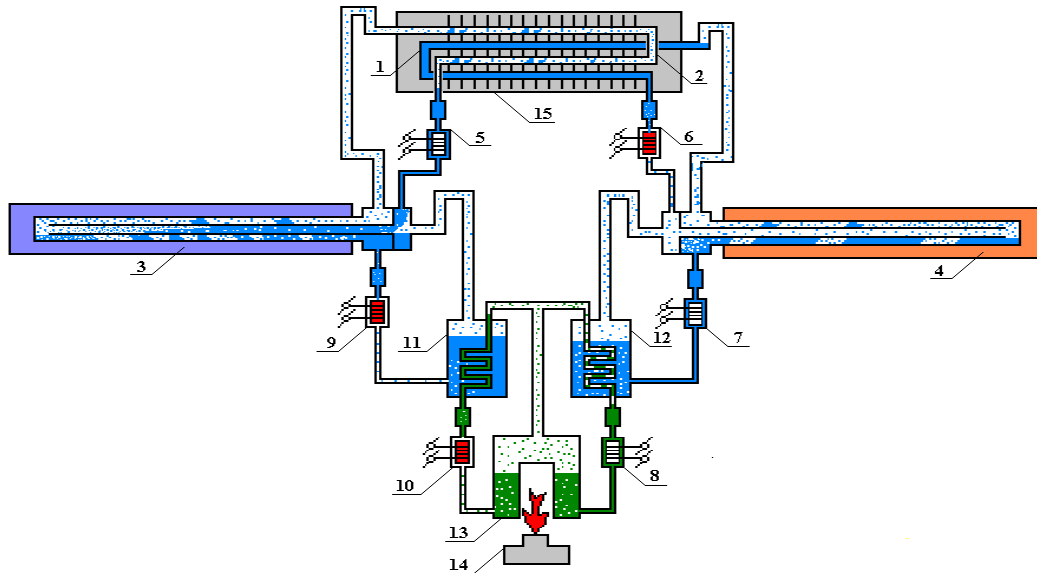


Figure 22: Two stage solid sorption heat pump with complex compound sorbent bed inside (combination with solid sorption stage (adsorption) and liquid sorption stage (absorption)): 1, 2 – low temperature heat exchangers; 3, 4 – high temperature adsorbers filled with “Busofit”+NiCl<sub>2</sub> micro crystals, 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

## CONCLUSIONS

New power sources efficiency (co-generation, tri-generation systems, fuel cells, photovoltaic systems) have a good perspective to be increased combined with the renewable energy resources through solid sorption heat pumps, refrigerators, accumulators of the heat and cold, heat transformers, natural and hydrogen storage systems.

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<sub>2</sub>, MnCl<sub>2</sub>, BaCl<sub>2</sub> with an active carbon fibre “Busofit” have demonstrated a possibility to have a cooler with two different independent sources of cold (low temperature BaCl<sub>2</sub> adsorber and evaporator) with simultaneous heat generation and chilled water production with COP<sub>cooling</sub> equal 0.6 and the heat pump COP near 1.6.

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