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## Resorption heat pump

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### Abstract

Resorption processes are based on at least two solid-sorption reactors application. The most favorable situation for the resorption heat pumps is the case, when the presence of a liquid phase is impossible. From simple case—two reactors with two salts to complicated system with two salts + active carbon fiber (fabric) and two branch of the heat pump acting out of phase to produce heat and cold simultaneously, this is the topic of this research program.

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*Keywords:* Resorption; Heat pump; Salts + active carbon fiber; Adsorption; Absorption; Cold and heat generation

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### 1. Introduction

Resorption systems are considered as an alternative to vapor compression systems in space cooling, industry and the building sector to satisfy the heating and cooling demand without increasing the electricity consumption [1–3]. Conventional (absorption) heat pumps cannot provide the temperature lifts 100–150 °C. A large variety of chemical heat pumps exist, but a few resorption chemical heat pumps are available in the literature. Resorption heat pumps provide high storage capacity and high heat of reaction as compared to sensible heat generated by absorption. They ensure the cold and hot output (heating and cooling) simultaneously. Nowadays the sorption technology is steadily improving and the increase at sorption market is strongly related to the energy policy in different countries. Actual sorption technologies (liquid and solid sorption cycles) have different advantages and drawbacks with regard of their compactness,

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complexity, cost, the range of working temperature [2,4,5]. 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 a low temperature waste heat, solar heat, burning fossil fuel, or biomass. The unique advantage of resorption systems related with its ability to use a significant number of couples solid–gas [5] without liquid phase and ensure the heat and cold production. The solid resorption machine demonstrates its possibility to be served as a very effective thermal compressor capable to reach the compression ratio more than 100 in one single cycle, which is impossible to have with a single stage vapor compression mechanical device. The optimization of the sorption technologies is related with multi-cascading cycles [2]. From previous publication [5,6], it has been concluded, that chemical heat pumps and refrigerators based on reversible solid–gas resorption cycles could have interesting applications for space cooling, when a high temperature waste heat source is available and/or the exigencies of the harsh external environment necessitates thermal control of an object. The vibration free operation and the large number of solid–gas alternatives make it possible to provide cooling and heating output in the temperature range 243–573 K [6–13]. Recently a micro technology in heat pumps systems is becoming available mostly for the electronic components cooling, fuel cells thermal control, heating/cooling vehicles, buildings and other applications. Mini sorbent bed canisters as compressors with some mini heat exchangers (miniature heat pipes) are considered as very interesting for such a case [7].

The goal of this work is an experimental verification of a basic possibility to advance two-effect sorption cycles using physical adsorption (active carbon fiber, or fabric “Busofit”) and chemical reactions of salts (NiCl<sub>2</sub>, MnCl<sub>2</sub>, BaCl<sub>2</sub>) in the same canister at the same time [5,6]. So the cycle performed in heat pump is a combination of monovariant (salts) and polyvariant (active carbon fiber) equilibrium with ammonia. We double the high heat of chemical reaction and sensible heat of physical adsorption to provide high storage capacity of a sorbent bed, increase the COP and ensure the temperature lift more 100 °C between cold and hot output. Resorption heat pump is simultaneously refrigerator and steam generator, based on the waste heat application (the low temperature energy source). Usually the heat pump performance can be characterized by the upgrading temperature, specific power production (cooling, or heating), coefficient of performance (COP), coefficient of amplification (COA) and exergetic efficiency. Actual temperature upgrade gives the temperature gain obtained from lower temperature (water) to the high level (steam), while the specific power production gives the amount of heat generated or extracted by the resorption heat pump to the amount of working substance used (“Busofit” + salts). Coefficient of performance COP is defined as the efficiency in cold production (enthalpy of resorption divided by heat supplied for regeneration), while coefficient of amplification COA represents the ratio of hot production to the heat supplied for regeneration:

$$\text{COP} = Q_{\text{res}}/Q_{\text{reg}},$$

$$\text{COA} = (Q_{\text{res}} + Q_{\text{abs}})/Q_{\text{reg}}.$$

Exergetic efficiency is defined as the ratio of output exergy and the input. These efficiencies could be represented as

$$\eta_{\text{ex}} = \text{COA} \left[ \frac{1 - \frac{T_0}{T_h}}{1 - \frac{T_0}{T_s}} \right],$$

where  $1 - (T_0/T_i)$  is the Carnot temperature;  $T_0$ —ambient temperature;  $T_h$ —high temperature;  $T_s$ —source temperature. The specific cooling power (SCP) is another important parameter of the resorption heat pump performance:  $\text{SCP} = Lm/t$ , where  $L$ —latent heat of vaporization, kJ/kg;  $m$ —mass of working fluid per kg of sorbent, kg;  $t$ —cycle time.

## 2. Experimental apparatus

### 2.1. The sorbent bed for a heat pump

The reactor (Fig. 1) of a heat pump is filled with a complex compound (active carbon fiber “Busofit” + salts). Salts ( $\text{CoCl}_2$ ) with carbon fibers were used in some experiments [11,12] as chemical heat pump sorbents. The first application of an active carbon fiber “Busofit” as sorbent material with acetone and ethanol as working fluids was done in 1992 [13]. To ensure a fast kinetics, efficient heat and mass transfer of the gas–solid reaction in sorbent bed, it needs to have a good porosity and high thermal conductivity of porous media. The application of impregnated active carbon filaments (Busofit) and the salt as microcrystals on its surface ensures enhanced COP of the system close to 90% of theoretical limit. “Busofit” as a fast sorbent material starts to react with ammonia in the early stage of heating/cooling time (up to 5 min) and accomplishes its action after the chemical reaction of the salt is finished. Therefore, the procedure of pressure change in the reactor is also fast and starts before the salts are beginning to react on ammonia flow. “Busofit” as a capillary-porous host material (binder) stimulates a distribution of salt microcrystals through the whole volume of a sorbent bed during the regeneration time (ammonia capillary condensation, liquid motion through the sorbent bed due to capillary forces action). “Busofit” is typical active carbon structure, which has all advantages of the nana-tubes technology. Due to its high permeability “Busofit” is convenient to apply as a sorbent bed for cycles with a forced convective heating/cooling, Fig. 2. This active carbon fiber is an universal adsorbent,

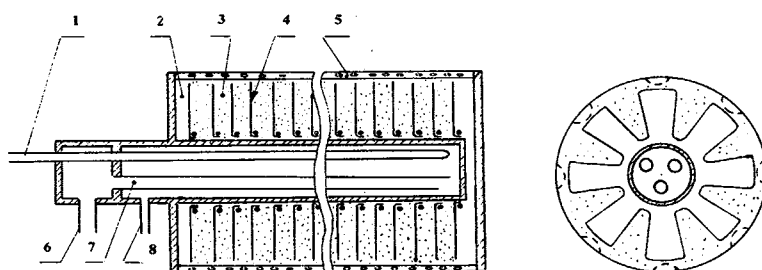


Fig. 1. Reactor with a sorbent bed (“Busofit” + salt) and a heat pipe thermal control (longitudinal and cross section): 1—water heat exchanger; 2—ammonia vapor distribution volume; 3—sorbent bed; 4—fin; 5—reactor envelope; 6—water vapor entrance (to the thermosyphon condenser); 7—heat pipe vapor channel; 8—heat pipe liquid exit.

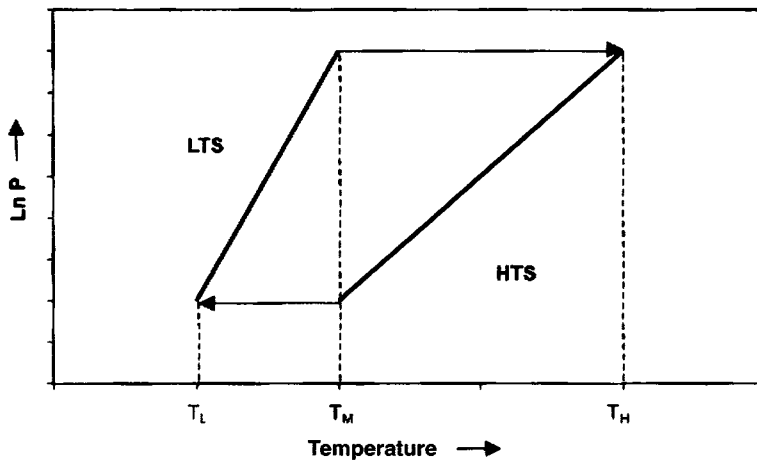


Fig. 2. Vapor pressure as a function of temperature for the adsorber No. 1 (LTS) and adsorber No. 2 (HTS).

which is efficient to adsorb different gases ( $H_2$ ,  $N_2$ ,  $O_2$ ,  $CH_4$ ,  $NH_3$ , etc.). The monolithic disc made from “Busofit” has such features as:

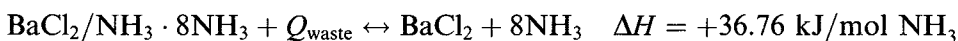
- high rate of adsorption and desorption;
- uniform surface pore distribution (0.6–1.6 nm);
- small number of macropores (100–200 nm), with its specific surface 0.5–2  $m^2/g$ ;
- small number of mesopores with 50  $m^2/g$  specific surface.

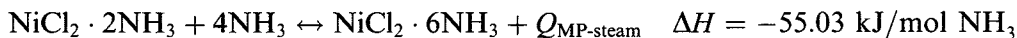
The ideal active carbon sorbent bed needs to have micropores volume near 50%, solid carbon near 40% and meso/macropores volume near 10%. In conventional heat pumps the major entropy production in resorption systems is due to the superheating of the vapor during the cold production phase and de-superheating of the vapor during regeneration phase, the main part of reaction is used for pressurization and de-pressurization of the gas in reactors. “Busofit” action as a fast reacting material decrease the pressure drop between the phase of cold production and regeneration, thus increasing the COP.  $NiCl_2$ ,  $MnCl_2$  and  $BaCl_2$  are the most convenient salts with “Busofit” as a binder due to its stability, low cost and suitable temperature range.

### 3. Two reactors heat pump

The basic operating principle of two reactors chemical heat pump is shown in Fig. 2. The ammonia vapor pressure is determined as a function of temperature for two different salts. In this analysis for simplicity of analysis we neglect the influence of active carbon fibers on the ammonia adsorption and desorption.

The pair of salts that was selected for this experiments is the couple  $BaCl_2/NH_3$  (LTS) and  $NiCl_2/NH_3$  (HTS). The operation of the heat pump is based on the following reactions:





The heat input to the low temperature salt LTS initiate the ammonia vapor release at high pressure at the temperature  $T_M$ . The ammonia flow from the high pressure vessel to the low pressure vessel filled with high temperature salt (HTS), where it is absorbing by HTS leading to the release of heat at  $T_H$ . Cooling the LTS with the help of cooling fluid at  $T_L$  and heating the HTS with heat supplied at  $T_M$  regenerates the system. The cycle can start all over again. Resorption heat pump is less complicated than conventional sorption heat pump (no evaporator, no condenser) and easily integrates in the system with the process steam and chilled water production [4]. The system includes a high temperature sorbent bed (HTS) and low temperature sorbent bed (LTS). Medium pressure steam (MP) and cooling water is available with the help of heat exchangers.

A simple one-stage experimental set-up (Fig. 3) is composed of two reactors (adsorber Nos. 1 and 2). The experimental set-up ensures mass recovery between the adsorber No. 1 (LTS) and adsorber No. 2 (HTS) through the valve and the heat recovery by heat pipe heat exchanger. During experiments with two reactors (Figs. 4 and 5) the valve was opened. One reactor is filled with  $\text{BaCl}_2 + \text{“Busofit”}$ , the second is filled with  $\text{NiCl}_2 + \text{“Busofit”}$ . The reacting gas is ammonia. The reactor dimensions are  $L = 1000 \text{ mm}$ ,  $D_{\text{out}} = 50 \text{ mm}$ ,  $D_{\text{in}} = 49 \text{ mm}$ . Vapor-dynamic stainless-steel thermosyphon is used as a heat pipe and a thermal control system. Its dimensions are  $L = 1100 \text{ mm}$ ,  $D_{\text{out}} = 16 \text{ mm}$ ,  $D_{\text{fin}} = 45 \text{ mm}$ , step between fins— $5 \text{ mm}$ , fin thickness— $0.25 \text{ mm}$ . The mass of reactor is summarized with: fins— $480 \text{ g}$ , reactor envelope— $615 \text{ g}$ , reactor flanges— $120 \text{ g}$ , thermosyphon— $900 \text{ g}$ . Complex compound “Busofit” +  $\text{BaCl}_2$  mass is ( $340 \text{ g} + 270 \text{ g}$ ), complex compound “Busofit” +  $\text{NiCl}_2$  mass is ( $250 \text{ g} + 180 \text{ g}$ ). The sorbent bed (salt with a monolithic fabric “Busofit”) has a form of cylinder. The heat and mass transfer is a dominating factor during the reactions with all its limitations. Two heat pipes provide heat transfer enhancement between two reactors. Steel/propane heat pipe is used for low temperature reactor and steel/water heat pipe is applied for high temperature reactor. Metal fins are fixed on the heat pipe surface to increase the heat transfer between sorbent bed and heat pipe envelope. An electric cartridge heater and water heat exchanger have a good thermal contact with the heat pipe evaporator.

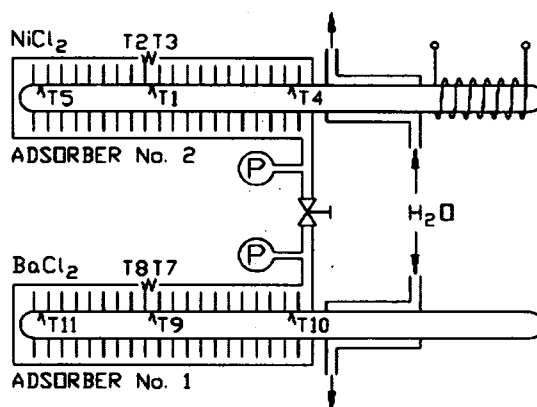


Fig. 3. Resorption two reactors heat pump with a heat pipe thermal control, T1–T11-thermocouples.

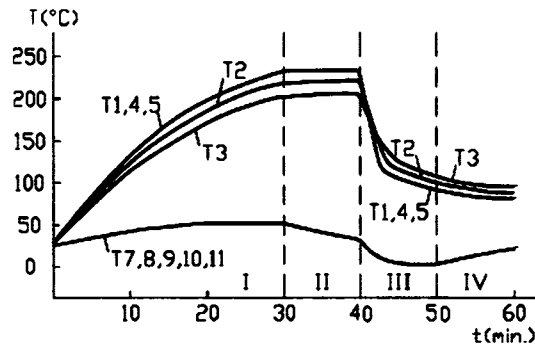


Fig. 4. Temperature evolution in different part of the resorption heat pump during its heating/cooling. T1–T5-thermocouples disposed in the high temperature sorbent bed, T7–T11-thermocouples disposed in the low temperature sorbent bed.

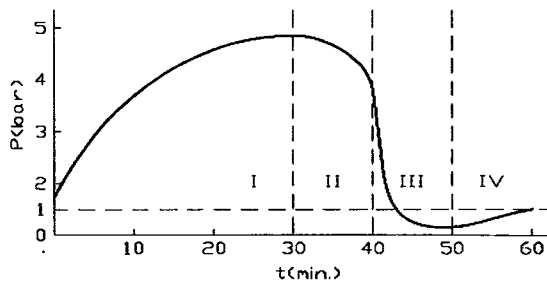


Fig. 5. Pressure evolution in two reactors heat pump during its heating/cooling.

The system consists of two different complex compounds with different chemical potentials, which are able to absorb/desorb ammonia vapor. The salt impregnated in “Busofit” in the low temperature reactor (adsorber No. 1) is  $\text{BaCl}_2 \cdot 8/\text{O NH}_3$  and its equilibrium curve is close to the  $\text{NH}_3$  saturation curve to avoid the low pressure in the reactor. The salt impregnated in “Busofit” in the high temperature reactor (adsorber No. 2) is  $\text{NiCl}_2 + 6/\text{O NH}_3$ . The basic cycle is divided into two main reactions phases (decomposition/desorption at high temperature and synthesis/adsorption at low temperature), separated by two intermediate steps (heating and cooling of the reactor), allowing the reactor to reach the reaction phase conditions. The reaction of desorption is considered as an endothermic. The heat supplied at low temperature to adsorber No. 1 leads to the release of ammonia vapor at high pressure. When this ammonia vapor flows to the high temperature adsorber No. 2, it is absorbing/adsorbing by the complex compound ( $\text{NiCl}_2 + \text{“Busofit”}$ ), leading to the release of heat at high temperature. The temperature of reactors is changing between 50 °C and 220 °C, depending on the reaction phase. It can be noted (Figs. 4 and 5), that the rate of cooling of the low temperature reactor is much faster than the rate of its heating due to micro heat pipe effect inside the sorbent bed. There is a vapor condensation on the cold surface of reactor with a latent heat release, capillary suction of the liquid in micropores with adsorption/absorption of ammonia.

The COP of the resorption cycle (two different salts) is:

$$\text{Ideal COP}^i = \Delta H_1 / \Delta H_2$$

$$\text{Thermodynamic COP} = (\Delta H_1 - C_p^{\text{loaded (salt1)}}(T_1 - T_b)) / (\Delta H_2 + C_p^{\text{loaded (salt2)}}(T_h - T_1))$$

$$\text{Practical COP} = \left( \Delta H_1 - \left( \sum C_p(\text{salt1} + \text{carbon} + \text{steel}) \right) (T_1 - T_b) \right) / \left( \Delta H_2 + \left( \sum C_p(\text{salt2} + \text{carbon} + \text{steel}) \right) (T_h - T_1) \right)$$

For the combination  $\text{BaCl}_2\text{-NiCl}_2$  the  $\text{COP} = 1.2$  was experimentally obtained with open valve. In order to evaluate the heat pump parameters, reliable thermodynamic and experimental data are required. Internal heat recovery is enabled due to the mass transfer between the reactors and the external heat recovery is realized due to the water heat exchangers action between the reactors. The temperature (Fig. 4) and pressure (Fig. 5) evolution inside the experimental set-up testify the efficient functioning of such a heat pump. The time of a cycle, consist on four time intervals (I–VI), Figs. 4 and 5. The time interval I is related with the sorbent bed heating procedure (by heat pipe) in the reactor No. 2. An ammonia vapor is generating in the sorbent bed. The pressure increasing in the reactor No. 2 and reactor No. 1 initiate the procedure of the ammonia absorption/adsorption in the sorbent bed of the adsorber No. 1 with heat release and the temperature lift from the ambient up to 50 °C. Due to the vapor condensation and micro heat pipe mechanism of heat and mass transfer inside the porous structure there is no noticeable temperature gradients inside the sorbent bed. On the contrary, during the ammonia generation in the reactor No. 2 (the time interval I) temperature gradients inside the sorbent bed are noticeable due to the low effective thermal conductivity of the porous structure. At the time interval II the electric heater ceased to heat the reactor No. 2. A pressure and temperature inside the reactor is nearly constant due to its heat capacity and the sensible heat of the system. At the time interval, III the cooling of the sorbent bed (reactor No. 2) started up due to the heat pipe cooling and a sharp decrease of pressure. This pressure decrease and cooling of the sorbent bed related with the ammonia generation (and cold production) in the low temperature reactor No. 1 and ammonia absorption/adsorption by the sorbent bed in the high temperature reactor No. 2. Due to the same effect of ammonia capillary condensation in the pores of the sorbent bed and micro heat pipe mechanism of heat and mass transfer inside the porous structure the temperature gradients in the high temperature sorbent bed (reactor No. 2) were negligibly small. At the time interval VI the reactor No. 2 has an energy supply, it means the beginning of a new cycle of the heat pump action.

### 3.1. Four reactors heat pump

Continuous operation of a heat pump is possible when two batch units are foreseen operating in an alternating way, Fig. 6. During the phase of high-pressure reactors A, B are absorbing the heat from the electric heaters with desorption/decomposition of ammonia, while the low temperature reactors A1, B1 are cooling by the water heat exchanger, and absorbing ammonia (absorption/regeneration). The low temperature reactors A1, B1 have thermal contacts with a thermal sink, typically the ambiance. Low temperature sources (water) coupled to a resorption



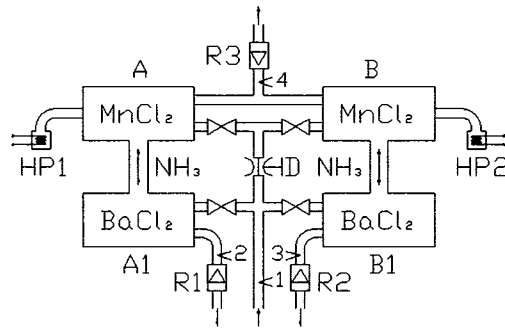


Fig. 6. Four reactors (two branches A and B) resorption heat pump with  $\text{MnCl}_2$  and  $\text{BaCl}_2$  salts + “Busofit”: 1–4—thermocouples; R1–R4—water flow meters; HP1–HP2—heat pipes with electric heaters in the evaporators.

heat pump upgrade heat to a higher temperature. It means that the ambient temperature of the liquid (water)—the low temperature source of energy, is upgraded to a temperature of the superheated vapor at the heat pump exit. Four reactors resorption heat pump enables the constant rate of the heating/cooling procedure, two branches of the heat pump are working out of phase. The monovariance of the equilibria used in the solid–gas chemical reaction system (salts) implies that the mass of working fluid is independent of the constraints  $T_H$ ,  $T_M$ ,  $T_L$ . The polyvariance of the equilibria used in the solid–gas adsorption/desorption (active carbon fibers) implies that the mass of working fluid depends of the constraints  $T_H$ ,  $T_M$ ,  $T_L$ . It is interesting experimentally to determine the role of such combination as complex compound salts + “Busofit”.

Low temperature reactors A1 and B1, filled with complex compound ( $\text{BaCl}_2$  + “Busofit”) are heated/cooled by water heat exchangers. The high temperature complex compound ( $\text{MnCl}_2$  + “Busofit”) is disposed in high temperature reactors A and B. These high temperature reactors are heated by heat pipes HP1 and HP2 and cooled by the water heat exchanger with heat recovery. The cycle of the heat pump functioning is divided on two main phases corresponding to two levels of pressure, which is typical for two different sorbent bed, Fig. 5. In Fig. 7 the pressure evolution in two different branches of four reactors heat pump is demonstrated. Heat and mass recovery between these two different couples of reactors can be organized by the valves and heat pipe thermal control. The time of the heat pump cycle is near 7000–7500 s. The low thermal conductivity of salt (about 0.1 W/m K) and a high expansion factor of reaction with the gas are

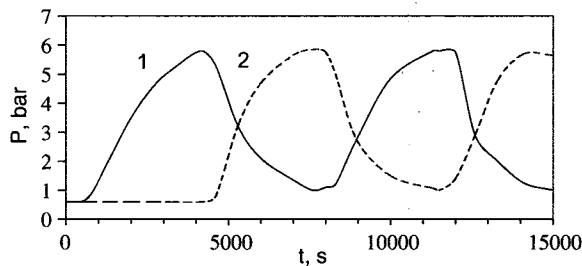


Fig. 7. Four reactors resorption heat pump with the complex compound sorbent bed (salts + “Busofit”). Pressure evolution in two branches of reactors A–A1 and B–B1 is a function of time.

two important reasons to reduce the heat pump performance. During the high-pressure phase, the ammonia pressure was equal 5–6 bars. We observe a very high rate of ammonia absorption by the high temperature reactors A and B, which stimulate a high power generation in the sorbent bed during the first minutes of the exothermal reaction and release the heat flow to the ambient, while the low temperature reactors A1, B1 are functioning, desorbing/regenerating ammonia and absorbing the heat flow from the water heat exchanger (cold generation). When two reactions are complete, the system has to be regenerated (i.e. prepared to a new heat and cold production phase). The electric heaters, which are switched on and off, ensure the energy supply to a sorbent bed alternatively, the total energy consumption of heat pump is constant. An example of the power evolution in this heat pump is shown in Fig. 8. A calculation based on a 30 min of the heat pump action leads to a power release of about 350 W/kg of the reactive mass. The considered reactive mass is the sum of all reactants masses—metal chloride + ammonia + carbon. Waste heat (water) at 20–30 °C is considered as a low temperature heat source. During the heat pump action the high temperature heat (steam) becomes available at 120 °C. In some experiments the heat flow was supplied to the high temperature reactors A and B with periodical change of power level each 25 min from 440 to 220 W and back, Fig. 10. The experiments with a periodical changing of the energy supply from 800 to 440 W were not successful, due to the low heat transfer in the low temperature reactors A1, B1. It means that the reactor filled with a low thermal conductivity complex compound ( $\text{BaCl}_2$  + “Busofit”) limited the cold generation. As a conclusion periodical medium pressure steam production is typical for such device (Fig. 8 and Fig. 10). At the same time a chilled water is available as a low temperature output of the resorption heat pump. The four-reactor resorption heat pump provides scope for heat and mass recovery in addition to delivering continuous cooling and heat generation. Recovery of the internal heat of reaction is an efficient method, which has resulted in improving the system performance. It is known, that the heating and cooling capacity can be significantly increased with mass recovery. Sensible heat recovery with the sensible heating of the sorbent bed from intermediate temperature to heat source temperature is an additional system requirement while the sensible cooling of the bed from intermediate temperature to refrigeration temperature reduces the cooling output. The results of the experiments with water flow cooling show, that the mode of the heat and mass transfer in low temperature reactors A1 and B1 (Figs. 8–10) is not efficient due to the low effective thermal conductivity of the sorbent bed and the low heat transfer coefficient on the wall of tubular water

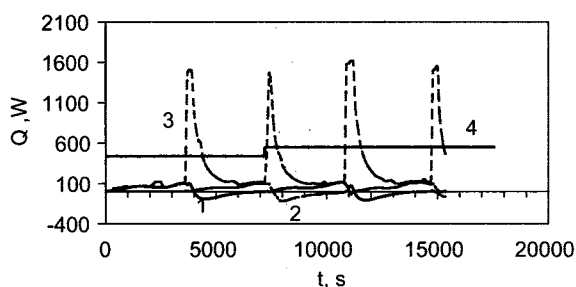


Fig. 8. Energy balance of four reactors resorption heat pump with a complex compound (salts + “Busofit”): 1—cold generation in the reactor A1; 2—heat generation in the reactor B1; 3—water vapor heat output in the reactor B; 4—heat input to the reactor A (heat pipe heating mode).

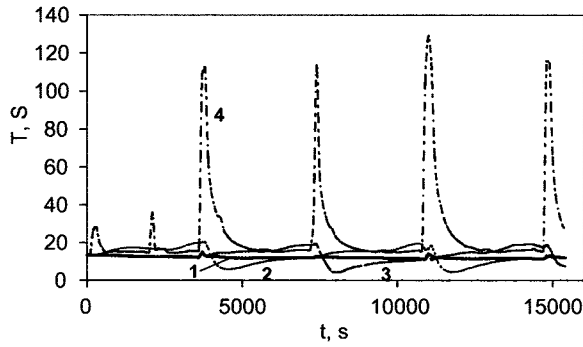


Fig. 9. Temperature field evolution inside four reactors heat pump: 1—water entrance to A1; 2—water cooling in A1; 3—water heating in B1; 4—water (vapor) heating in A.

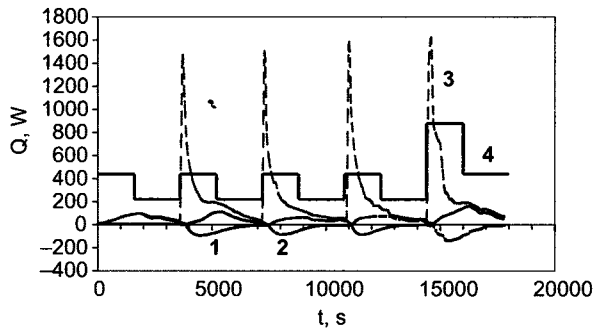


Fig. 10. Energy supply, heat and cold generation in four reactors heat pump with different heating mode of high temperature reactors A and B.

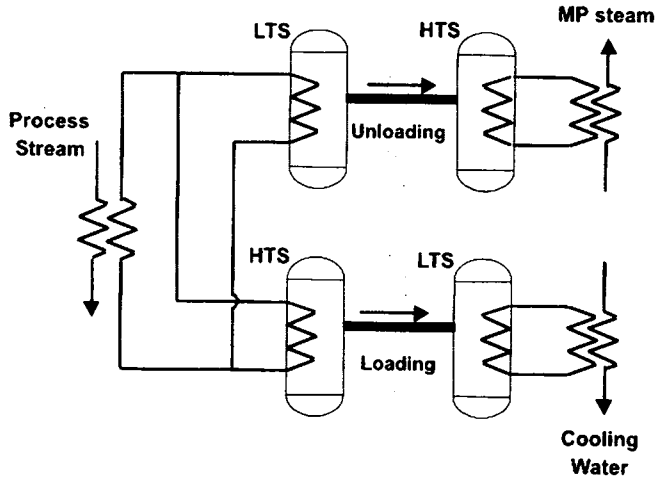


Fig. 11. Process flow diagram for a salt/vapor chemical heat pump [4].

heat exchanger. The configuration of process streams (heat treatment of different substances) during the function of such heat pumps, Fig. 11, is changing periodically following the cycle change.

#### 4. Conclusions

Experiments with two different set-up based on the coupling salts  $\text{NiCl}_2$ ,  $\text{MnCl}_2$ ,  $\text{BaCl}_2$  with an active carbon fiber “Busofit” demonstrated a possibility to have a resorption heat pump with simultaneous heat generation (steam at  $T = 120\text{--}130\text{ }^\circ\text{C}$ ) and chilled water production ( $T = 3\text{--}5\text{ }^\circ\text{C}$ ) with COP near 1.2. Heat recovery by the heat pipe thermal regulation and internal mass regeneration between the reactors out of phase could increase this COP up to 1.4–1.5. The resorption heat pump with heat output 1400–1500 W is an autonomous, portable device, allowing the user to apply this system in space or on the ground (underwater, underground), to supply, or postpone the heating and cooling production, and to control the heat and cold output. The device has no moving parts, is noiseless and light. The pressure control regulation of the heat pump functioning is reliable and simple.

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