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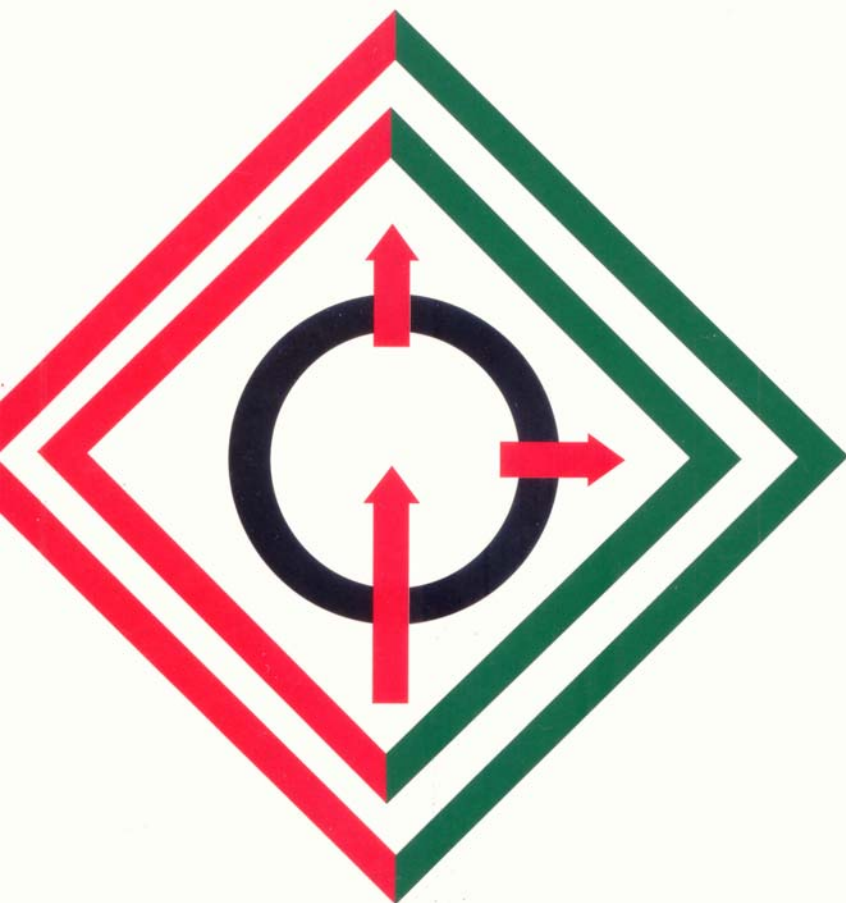
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THERMODYNAMICS  
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QUARTERLY

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ISSN 1231-0956



Vol. 28  
2007  
No. 3

Wydawnictwo IMP  
Gdańsk

## Solid sorption heat pumps for tri-generation

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**Abstract** Solid sorption heat pumps and coolers have a good potential to be used in the air-conditioning, electronic thermal control and transport applications. Recent application is focused on a small-scale combined cold, heat and power system, which utilizes the motor waste heat for cold production (tri-generation system). The main feature of this device is the innovative adsorbent bed consisting of a heat pipe heat exchanger, in which the finned tubes are coated with an active carbon fiber "Busofit", saturated with different metal salts (salt on the fiber). Owing to the advantageous sorption properties of the complex compound and the good heat transfer quality of the heat pipe, an advanced sorption heat pump can be heated efficiently by the low temperature heat source. The heat pump has two sources of cold, namely the low temperature sorbent bed canister and the principal evaporator. The working fluid is ammonia. The experimental results show a specific power of 500-550 W/kg of adsorbent. The most favorable situation is the case, when two sources of cold are welcomed. The goal of this research program is an improvement of the heat pump system from simple case of two reactors with two different salts to complicated system with three reactors, evaporator/condenser and two branches of coolers, acting out of phase to produce heat and cold simultaneously.

**Keywords:** Tri-generation; Heat pumps

### Nomenclature

$D$  - diameter, mm  
 $L$  - length, mm  
 $P$  - pressure, Pa

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$Q$	-	heat, W
$T$	-	temperature, °C, K
COA	-	coefficient of amplification
COP	-	coefficient of performance
SCP	-	specific cooling power

### Greek symbols

$\tau$	-	time, min
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### Subscripts

1,2,3,4	-	stages
in	-	inner
out	-	outward

## 1 Introduction

Solid sorption heat pumps or coolers are considered as an alternative to vapour compression systems in space cooling and heating, industry and the building sector to satisfy the heating and cooling demand without increasing the electricity consumption [1-3]. The intermittent solid sorption cooling cycle appears to be logical application for cooling in tri-generation and the activated carbon fibre with metal salts on its surface (salt on the fibre) and ammonia seems to be the suitable pair in terms of higher COP. In some recent years there is a problem to apply such heat pumps in combination with the gas engine and Stirling engine for tri-generation (cold, heat and electricity production). Actually no more than 1/3 of energy consumed in electrical vapour-compression heat pump is needed in solid sorption heat pump to achieve the same heating and cooling effect in tri-generation, Fig. 1. If we have an input of energy of the fuel in the gas engine equal to 100%, we can get 100% energy for air heating and 30% energy for air cooling + power output 25%, applying the solid sorption heat pump and low temperature natural sources of energy (solar, soil, water energy). Heat and mass transfer in the sorbent bed and in the evaporator is the main aspect, which determines overall performance and reliability of non-electric heat pumps and coolers. The role of heat and mass transfer intensification in solid sorption cycles is both to improve COP and maximise regenerative heating and to achieve faster cycle time and decrease the mass and the cost of the solid sorption machines. A proper understanding of heat transfer and the temperature distribution, sorption capacity of components helps to determine material selection and parts geometry. Solid sorption heat pumps ensure the cold and heat output (heating and cooling) simul-

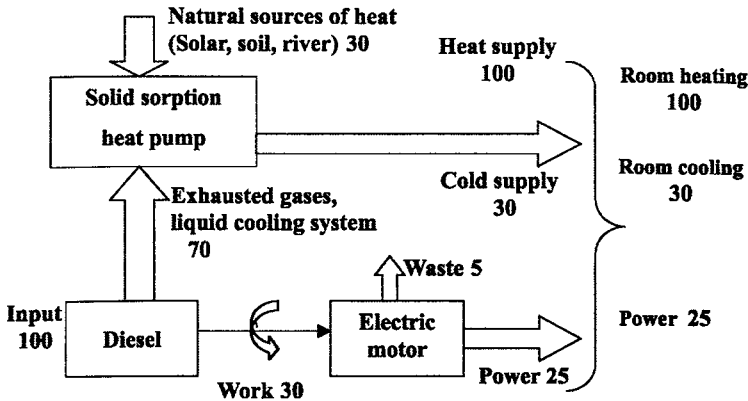


Figure 1. Gas engine and solid sorption heat pump for heating and cooling in tri-generation.

taneously. 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 to their compactness, complexity, cost, the range of working temperature [2, 4, 5]. The solid sorption technology advantages firstly are related to the nature friendly refrigerants such as water, ammonia, CO<sub>2</sub> (no CFC, HCFC, HFC) and secondly they are thermally driven and can be coupled with a low temperature waste heat, solar heat, burning fossil fuel, or biomass. The solid sorption machines demonstrate its possibility to be served as a very effective thermal compressor. The optimisation of the sorption technologies is related to multi-cascading cycles [2]. From previous publications [5, 6] it has been concluded, that solid sorption machines based on reversible solid-gas sorption cycles could have interesting application 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 of 243-573 K [6-13]. The results of first application of an active carbon fibre “Busofit” as sorbent material with acetone and ethanol as working fluids were published in 1992 [13]. An idea to combine the effect of chemical reactions of metal salts and physical adsorption of the active carbon fibre was published in 1994 [5] and new opportunities in

varying of the sorbent properties were opened. Now it became clear that the modification of common adsorbents by adding salts can be a tool for modifying sorption properties.

Recently a micro technology in solid sorption coolers 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 mini heat exchangers (miniature heat pipes) are considered to be interesting options for such a case [7].

The goal of this work is an experimental verification of a basic possibility to advance sorption cycles using physical adsorption (active carbon fibre, or fabric "Busofit") and chemical reactions of salts ( $\text{NiCl}_2$ ,  $\text{MnCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{BaCl}_2$ ) [5, 6]. So the cycle performed in solid sorption cooler is a combination of monovariant (salts) and polivariant (active carbon fibre) 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, thus increase the coefficient of performance (COP) and specific cooling power (SCP).

## 2 Experimental set-up

### 2.1 The sorbent bed for a solid sorption heat pump

The main feature of the lab-scale cooler is the innovative adsorber with the sorbent bed inside, Fig. 2. Sorbent bed is the most important part of the cooler and hence the performance of adsorber depends highly on the characteristics of the sorbent bed. It consists of finned heat pipe heat exchanger with its external surface covered by the thin layer of an active carbon fibre "Busofit" saturated with salts. This sorbent bed is located inside the thin wall stainless steel tubular canister.  $\text{NiCl}_2$ ,  $\text{MnCl}_2$  and  $\text{BaCl}_2$  are the most convenient salts for "Busofit" as a binder due to its stability, low cost and suitable temperature range. Such compound is considered as a new material, which has to possess thermodynamic properties that would provide a higher COP and SCP per cycle, than the common materials. The most important particularity of the active carbon fibre "Busofit" is its ability to be used as a fast and efficient heat and mass exchanger with the forced convection (filtration) of the reacting gas through the bed. Adsorber dimensions are  $L = 1000$  mm,  $D_{out} = 50$  mm,  $D_{in} = 49$  mm. Vapor-dynamic stainless-steel/water thermosyphon (heat pipe heat exchanger) is used as a thermal control system. Its dimensions are  $L = 1100$  mm,

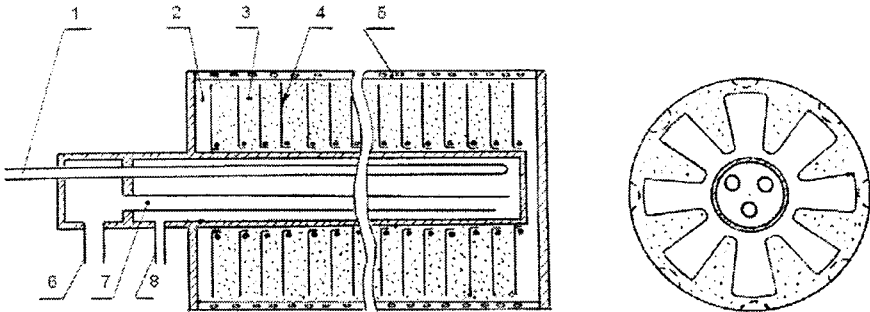


Figure 2. Adsorber with complex compound (“Busofit” + metal salt) sorbent bed and heat pipe for thermal control (longitudinal and cross section): 1 – water heat exchanger, 2 – vapor volume, 3 – sorbent bed, 4 – fin, 5 – stainless steel envelope, 6 – vapor entrance (to the thermosyphon condenser), 7 – vapor channel, 8 – condensed water exit.

$D_{out} = 16 \text{ mm}$ ,  $D_{fin} = 45 \text{ mm}$ , step between fins – 5 mm, fin thickness – 0.25 mm. The mass of reactor is summarised with: fins – 480 g, reactor envelope – 615 g, reactor flanges – 120 g, thermosyphon – 900 g. Complex compound “Busofit”+BaCl<sub>2</sub> mass is (340+270 g), complex compound “Busofit”+NiCl<sub>2</sub> mass is (250+180 g), complex compound “Busofit” + MnCl<sub>2</sub> mass is (250+230 g). The sorbent bed (salt with a monolithic fabric “Busofit”) has a form of cylinder, Fig. 2.

There is an intensive mass transfer between “Busofit” and micro crystals of salt during the heating/cooling cycle. “Busofit” stimulates the thermal treatment of the salt to prepare its activity. It has a good porosity and high permeability to ensure the fast kinetics, efficient heat and mass transfer of the gas-solid reaction in the sorbent bed. “Busofit” 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 pressure change in the reactor is also fast and starts before the salts are beginning to react with ammonia. “Busofit” as a capillary-porous host material (binder) stimulates the distribution of micro crystals through the whole volume of a sorbent bed during the time of regeneration (ammonia capillary condensation, liquid motion through the sorbent bed due to capillary forces action). This active carbon fibre is a universal adsorbent, which is efficient to adsorb different gases (H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub>, etc.). The monolithic sorbent disc 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<sup>2</sup>/g;
- small number of mesopores with 50 m<sup>2</sup>/g specific surface.

The ideal sorbent bed needs to have micropores volume near 50% and meso/macropores volume near 10%. In conventional solid sorption refrigerators 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, the main part of reaction is used for pressurization and de-pressurization of the gas in reactors. “Busofit” action as a fast reacting material decreases the pressure drop between the phase of cold production and regeneration, thus increasing the COP. The main advantage of the “Busofit” is its regular micro pore distribution on the surface of the filament. These pores are active even the surface of the filament is partly covered with the salt microcrystals, Fig. 3. During adsorption/desorption the ammonia vapor forms the vapor channels through the micro crystals conglomerates. The calculated COP of the sorbent bed (BaCl<sub>2</sub>/NH<sub>3</sub>) is 0.57. The experimentally determined COP of BaCl<sub>2</sub>/NH<sub>3</sub> adsorber including the enthalpy of metal tube is 0.44. The application of impregnated active carbon filaments and microcrystals on its surface ensures enhanced COP of the system close to 90% of theoretical limit. These general criteria have to be formulated for each particular sorption technology, such as chilling, deep freezing, heat pumping, tri-generation, etc. Thus, they should have optimal properties in a particular range of ammonia temperature and pressure.

## 2.2 Cooler with three adsorbers + condenser/evaporator. Tri-generation approach

We consider working parameters of the ammonia solid sorption cooler with the evaporator/condenser. This cooler development is focused on the small-scale combined cold, heat and power production (tri-generation), which utilizes the engine waste heat for heat and cold generation. The device is consisted of two blocks of adsorbers (3+3) working out of phase. The selected salts are combinations of BaCl<sub>2</sub>/NH<sub>3</sub> – low temperature sample

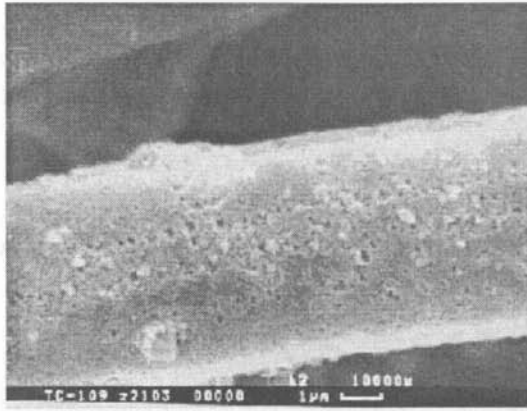
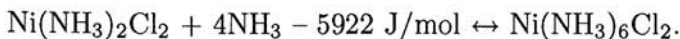
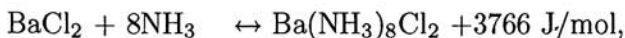


Figure 3. Active carbon filament covered with a thin layer of salt micro crystals (“Busofit” +  $\text{CaCl}_2$ ), multiplied by 10 000 times.

(LTS),  $\text{MnCl}_2/\text{NH}_3$ - medium temperature sample (MTS) and  $\text{NiCl}_2/\text{NH}_3$ - high temperature sample (HTS). Total mass of the experimental set-up is 9 kg.

During the experiments the ammonia vapour pressure is recorded as a function of temperature for three different salts and active carbon fibre “Busofit”. In this analysis for simplicity we neglect the influence of active carbon fibres on the ammonia adsorption and desorption.

The operation of the cooler is based on the following reactions:



This device enables near constant rate of the heating/cooling procedure, two branches of the system are working out of phase and two sources of cold are active ( $\text{BaCl}_2$  adsorber and evaporator). The condenser/evaporator has dimensions  $L = 370 \text{ mm}$  and  $D = 50 \text{ mm}$ . The inner walls of container are covered with the capillary-porous layer to enhance heat transfer with evaporation [14].

Two prototypes of the experimental set-up are available:

1. resorption cooler (gas cooling system) [15];
2. solid sorption cooler with evaporator/condenser.



The Clausius-Clapeyron diagram ( $\ln P$  as a function of  $1/T$ ) for the resorption cooler (dashed lines) and solid sorption cooler is shown on Fig. 4. There are two possibilities to apply the waste heat of the engine for the cold

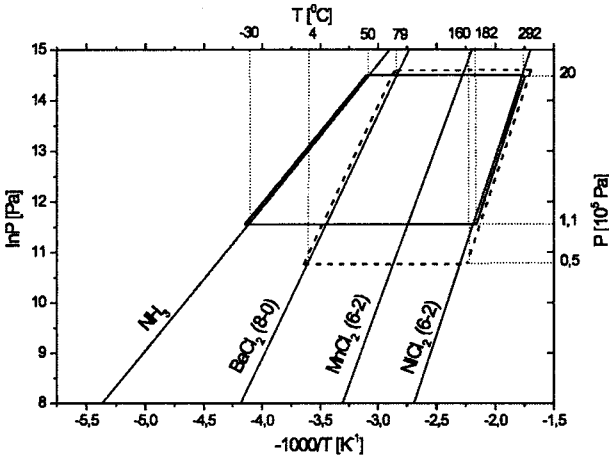


Figure 4. Clapeyron diagram of the heat pump with high temperature ( $\text{NiCl}_2 + \text{“Busofit”}$ ), mean temperature ( $\text{MnCl}_2 + \text{“Busofit”}$ ), and low temperature ( $\text{BaCl}_2 + \text{“Busofit”}$ ) adsorbents. Dashed lines – resorption heat pump with cold generation in the low temperature adsorbent  $\text{BaCl}_2$ .

generation using solid sorption cooler with evaporator/condenser:

A. This is a first prototype of the solid sorption cooler. The exhaust gas and liquid engine cooling system are used to heat three adsorbents simultaneously. The cycle of the cold production is divided into two stages, Fig. 5.

1. At the first stage (time  $\tau_1$ ) adsorbents with sorbent bed ( $\text{NiCl}_2$ , and  $\text{MnCl}_2$ ), initially are at the room temperature and start to be heated up to the temperature  $230^\circ\text{C}$  and  $180^\circ\text{C}$  by the exhaust gas. Low temperature adsorbent ( $\text{BaCl}_2$ ) is heated by the cooling liquid system of the engine up to  $90^\circ\text{C}$ . This stage is encompassed ammonia desorption inside the sorbent bed. The ammonia vapor is condensing in the evaporator/condenser. The temperature evolution of the liquid flow at the exit of the evaporator heat exchanger (1) and  $\text{BaCl}_2$  heat exchanger (2) as a function of cycle time is shown on Fig. 5. The hot

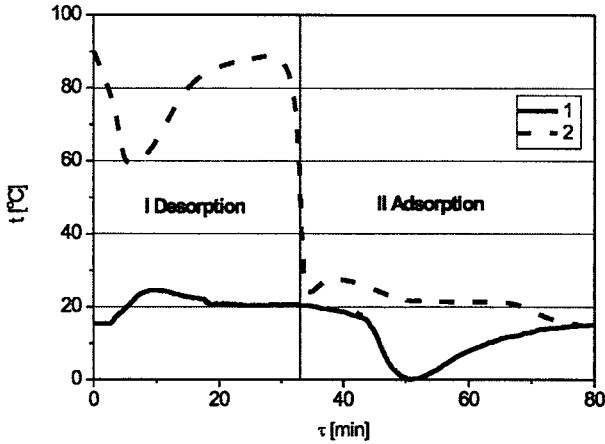


Figure 5. First prototype of the sorption cooler. Temperature evolution of water flow on the output of the heat exchanger of the evaporator/condenser (1), and on the output of the water flow heat exchanger of the  $\text{BaCl}_2$  adsorber (2), heated by the gas engine liquid cooling system.

liquid ( $95^\circ\text{C}$ ) enters from the gas engine to the  $\text{BaCl}_2$  adsorber heat exchanger and is cooled during the second stage of the cycle.

- At the second stage (time  $\tau_2$ )  $\text{BaCl}_2$ ,  $\text{NiCl}_2$  and  $\text{MnCl}_2$  adsorbers are cooled down to the room temperature and adsorb the ammonia from the evaporator. The liquid ammonia evaporating/boiling in the evaporator ensures the cold generation. In this cooler we use two different waste heat namely the exhaust gas and the heat of the liquid cooling system.

**B.** The second prototype of cooler is oriented on the application of high temperature waste heat of the engine-exhaust gas, Fig. 6. This mode of cold generation is more efficient, because the heat and mass recovery of the high temperature adsorbers is used to preheat the low temperature adsorber. The Clapeyron ( $\ln P - 1/T$ ) diagram, Fig. 7, for such a case is more complicated because an interaction between evaporator/condenser, active carbon fibre and three different salts is performed during the cycle with heat recovery. The Clapeyron diagram analysis of the cooler shows the possibility to have two cold generators (the low temperature adsorber and

the evaporator/condenser) and apply the cold and heat production in the air-conditioning systems. The volume for liquid ammonia in the evaporator exceeds the volume of ammonia adsorbed by three sorbent bed in adsorbers. It is convenient to get the cold from a high temperature source of energy such as the exhaust gas (450–500°C). We use the cooling system of the high temperature adsorbers  $MnCl_2$ ,  $NiCl_2$  to heat the low temperature adsorber  $BaCl_2$  and desorb the ammonia inside the sorbent bed, Fig. 7.

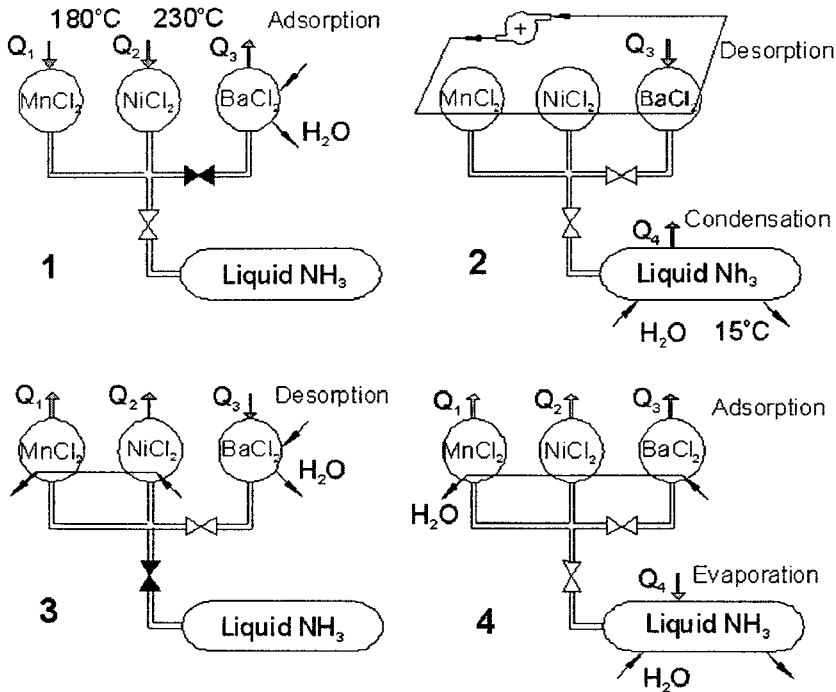


Figure 6. Solid sorption heat pump (“Busofit” + salts) with heat recovery and two sources of cold namely low temperature adsorber  $BaCl_2$  and evaporator.

In the experiments the total energy supply for two high temperature adsorbers  $MnCl_2$ ,  $NiCl_2$  was simulated by the electric heaters (instead of the exhaust gas) through the heat pipes and was equal near 1400 kJ per cycle. The energy supply to the  $BaCl_2$  adsorber was ensured by the hot (90°C) water flow (at the output of the  $MnCl_2$  and  $NiCl_2$  heat pipe heat exchangers) during the time of its cooling (wasted heat).

The cycle is divided into four stages:

1. At the first stage (time  $\tau_1$ )  $MnCl_2$  and  $NiCl_2$  adsorbers are heated

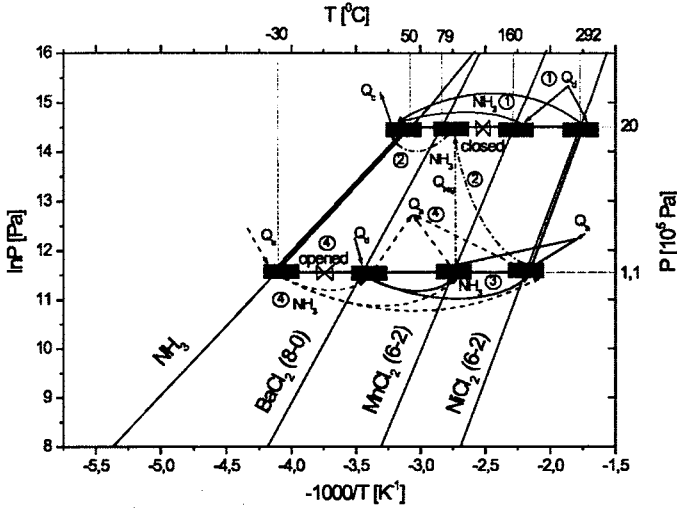


Figure 7. Clapeyron diagram of the solid sorption cooler with heat recovery for two cold generation sources ( $\text{BaCl}_2$ ,  $\text{MnCl}_2$ ,  $\text{NiCl}_2$ + “Busfit”) and the condenser/evaporator.

by the exhaust gas (electric heater) with further desorption of  $\text{NH}_3$ . The superheated vapor is condensing in the condenser/evaporator and is partly adsorbing by the low temperature sorbent bed of  $\text{BaCl}_2$  adsorber.

2. At the second stage (time  $\tau_2$ )  $\text{MnCl}_2$  and  $\text{NiCl}_2$  adsorbers are disconnected from the evaporator/condenser (the valve is closed) and cooled by the water circuit. The water flow on the output of adsorbers with temperature of  $90 - 95^{\circ}\text{C}$  enters the low temperature  $\text{BaCl}_2$  adsorber and heats the sorbent bed with heat pipe heat exchanger. This procedure is accompanying the ammonia desorption. Ammonia vapor is condensing in the evaporator/condenser.
3. At the third stage (time  $\tau_3$ ) all three adsorbers ( $\text{MnCl}_2$ ,  $\text{NiCl}_2$  and  $\text{BaCl}_2$ ) are cooled down to the ambient temperature. Now adsorbers  $\text{MnCl}_2$  and  $\text{NiCl}_2$  are connecting to the low temperature adsorber  $\text{BaCl}_2$  through the opened valve. The pass from the  $\text{BaCl}_2$  adsorber to the condenser/evaporator is closed. More strong adsorbers  $\text{MnCl}_2$ ,  $\text{NiCl}_2$  suck the remaining part of ammonia from the adsorber  $\text{BaCl}_2$ .

The desorption of the ammonia inside  $\text{BaCl}_2$  adsorber stimulates the cold generation (resorption phenomena).

- All three adsorbers now are connecting with the condenser/evaporator by the valve. The final stage (time  $\tau_4$ ) is responsible for the main cold generation in the evaporator. The temperature evolution of the liquid flow on the exit of heat exchanger of the evaporator (solid line 1) and  $\text{BaCl}_2$  adsorber (dashed line 2) is shown on Fig. 8.

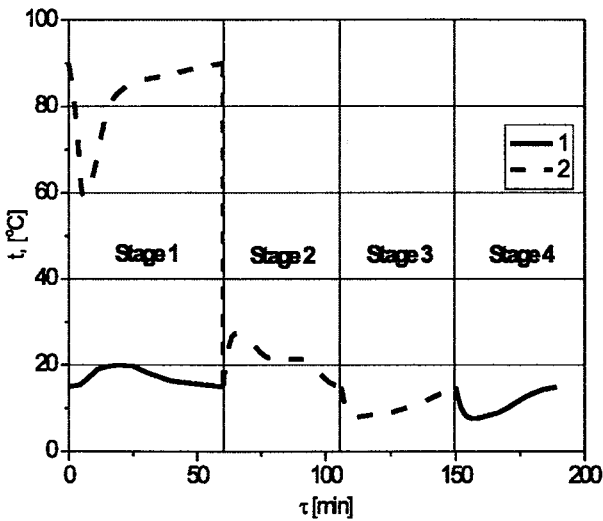


Figure 8. Second prototype of the sorption cooler. Temperature evolution of the water flow on the exit of water heat exchanger of the evaporator (solid line 1) and  $\text{BaCl}_2$  adsorber (dashed line 2).

An example of a typical charge-discharge power profile and heat input/output in the evaporator/condenser (1) and the  $\text{BaCl}_2$  adsorber (2) via time of the cycle is presented on Fig. 9. The maximal charging power of  $\text{MnCl}_2$ ,  $\text{NiCl}_2$  adsorbers is around 400 W each. Evaporation in the range of  $10^\circ\text{C}$  results in cooling power of 200 W. In this experimental set-up the pressure and temperature sensors allow to check the dynamic of the pressure and temperature evolution of the sorbent bed, ambient temperature, the temperature of the vapor output and the temperature of the chilling water. The mass flow meters were used for the calculation of the degree of advance of chem-

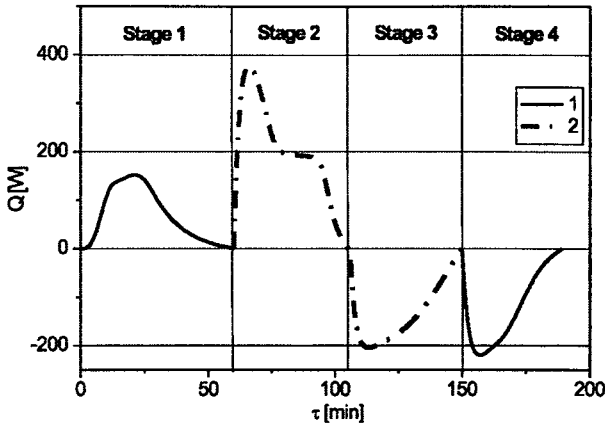


Figure 9. Second prototype of the sorption cooler. Heat input/output in the evaporator/condenser (1) and the low temperature  $\text{BaCl}_2$  adsorber (2) as a function of cycle during the time of adsorption and desorption.

ical reactions and physical adsorption. The value for  $\text{COP}_{cooling}$  is 0.44 for one cooler (three adsorbers + evaporator/condenser). For two sets of equipment the value for  $\text{COP}_{cooling}$  is 0.6.

### 3 Summary

1. The developed and tested experimental set-up offers the possibility of saving 15-20% of primary energy for cooling, heating and power demands.
2. Experiments with two different set-ups based on the coupling salts  $\text{NiCl}_2$ ,  $\text{MnCl}_2$ ,  $\text{BaCl}_2$  with an active carbon fibre "Busofit" have demonstrated a possibility to have a heat pump with two different independent sources of cold (low temperature  $\text{BaCl}_2$  adsorber and evaporator) with simultaneous heat generation and chilled water production with  $\text{COP}_{cooling}$  equal 0.6.

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