

SOLID SORPTION COOLERS FOR COOLING IN TRI-GENERATION

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Abstract

Solid sorption coolers have a good potential to be used in the air-conditioning, electronic thermal control and transport applications. Recently it is focused on the application in a small-scale combined cold, heat and power system, which utilises the motor waste heat for cold production (tri-generation system). The main feature of this cooler is the innovative adsorbent bed consisting on a heat pipe heat exchanger, in which the finned tubes (heat pipes) are coated with an active carbon fiber “Busofit” layer, saturated with different metal salts. In this way, the advantageous sorption properties of the complex compound (“Busofit” + metal salts) and the good heat transfer quality of the coated heat pipe are joined in an advanced sorption cooler, which can be heated by the low temperature heat source. This cooler ensures availability of two sources of cold. The first source of cold is generated inside the low temperature sorbent bed canister (“Busofit” saturated by BaCl_2) and the second source of cold is generated in the principal evaporator. The working fluid is ammonia.

The experimental results show a specific power of 500-550 W/kg of adsorbent (binder included). The most favorable situation for the cooler is the case, when two sources of cold are welcomed. From simple case – two reactors with two different salts to complicated system with three reactors, evaporator/condenser and two branch of coolers, acting out of phase to produce heat and cold simultaneously, this is the goal of this research program.

KEYWORDS

Tri-generation, solid sorption cooler/chiller, salts + active carbon fiber; adsorption; absorption; cold and heat generation

INTRODUCTION

Solid sorption coolers, or refrigerators are considered as an alternative to vapour compression systems in space cooling, industry and the building sector to satisfy the heating and cooling demand without increasing the electricity consumption [1-3]. In some recent years there is a problem to apply such coolers in combination with the engine for tri-generation (cold, heat and electricity). In design of non-electric coolers thermal consideration (heat and mass transfer in sorbent bed and evaporator) is the main aspect, that determine overall performance and reliability. A proper understanding of heat transfer and the temperature distribution, sorption capacity of components helps in determining the parts geometry and material selection. Solid sorption coolers ensure the cold and heat 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 to their compactness, complexity, cost, the range of working temperature [2, 4, 5]. The solid sorption technology advantages at first are related to the nature friendly refrigerants such as water, ammonia, CO_2 (no CFC, HCFC, HFC) and at second they are thermally driven and can be coupled with a low temperature waste heat, solar heat, burning fossil fuel, or biomass. The solid sorption coolers demonstrate its possibility to be served as a very effective thermal compressor. The optimisation of the sorption technologies is related with multi cascading cycles [2]. From previous publication [5, 6], it has been concluded, that solid sorption refrigerators based on reversible solid-gas sorption 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 243K-573K [6-13]. The results of first application of an active carbon fiber

“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 fiber was published in 1994 [5] and opens new opportunities in varying the sorbent properties. Now it became clear that the modification of common adsorbents by 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 fiber, or fabric „Busofit“) and chemical reactions of salts (NiCl₂, MnCl₂, BaCl₂), [5-6]. So the cycle performed in solid sorption cooler is a combination of monovariant (salts) and polivariant (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, thus increase the COP. Usually solid sorption machine performance can be characterised by the upgrading temperature, specific power production (cooling, or heating), coefficient of performance (COP), coefficient of amplification (COA) and exergetic efficiency. Coefficient of performance COP is defined as the efficiency in cold production (enthalpy of resorption and evaporation divided by heat flow supplied for regeneration), while the coefficient of amplification COA represents the ratio of heat production to the heat supplied for regeneration:

$$\text{COP} = (Q_{\text{res}} + Q_e)/Q_{\text{reg.}}; \quad (1)$$

$$\text{COA} = (Q_{\text{res}} + Q_{\text{abs}} + Q_c)/Q_{\text{reg.}} \quad (2)$$

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

$$\eta_{\text{ex}} = \text{COA} \left[\frac{1 - \frac{T_0}{T_h}}{1 - \frac{T_0}{T_s}} \right], \quad (3)$$

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 cooler performance: $\text{SCP} = Lm/t$, where L – latent heat of vaporisation, kJ/kg; m – mass of working fluid per kg of sorbent, kg; t – cycle time.

EXPERIMENTAL APPARATUS

The sorbent bed for a solid sorption cooler

The main feature of the lab-scale cooler is the innovative sorbent bed with enhanced heat transfer properties. It consists on finned heat pipe heat exchanger with its external surface covered by the layer of an active carbon fiber “Busofit” saturated with salts. The complex compound is disposed between fins on the heat pipe outer surface. This sorbent bed is disposed inside the thin wall stainless steel canister. Such sorbent bed is considered as a new material, which has to possess thermodynamic properties that would provide a higher COP and specific energy per cycle, than the common materials. It has good dynamic properties with respect to heat and mass transfer for getting a high specific power of the unit operation. The most important particularity of the active carbon fiber “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. These general criteria have to be formulated for each particular adsorption technology, such as chilling, deep freezing, heat pumping, trigeneration, etc. Thus, they should have optimal properties in a particular range of temperature and adsorbate pressure.

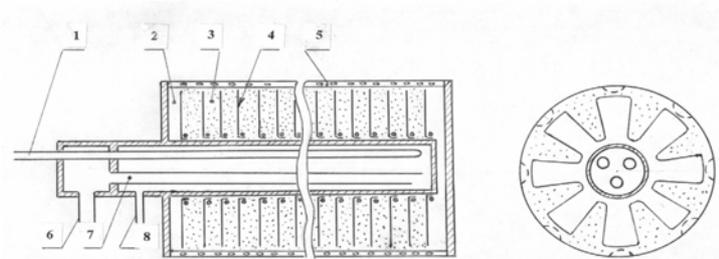


Fig. 1. Adsorber with complex compound ("Busofit" + metal salt) sorbent bed and heat pipe thermal control (longitudinal and cross section). 1 – water heat exchanger, 2 – vapor volume, 3 – sorbent bed, 4 – fin, 5 – stainless steel envelope, 6 – vapor entrance (to the therosyphon condenser), 7 – vapor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

In the experimental set-up (Fig.1) the adsorber is filled with a complex compound. To ensure the fast kinetics, efficient heat and mass transfer of the gas-solid reaction in the sorbent bed, it needs to have a good porosity and high thermal conductivity of porous media. The application of impregnated active carbon filaments and the salt as microcrystals on its surface ensures enhanced COP of the system close to 90% of theoretical limit, Fig.2.

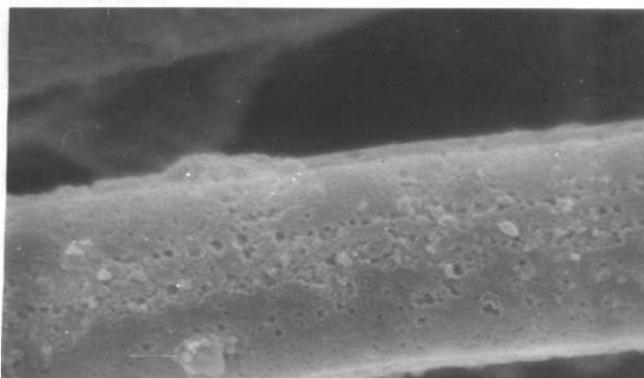


Fig.2. Complex compound filament ("Busofit" + CaCl_2), multiplied by 10000 times

„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 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). „Busofit“ has all advantages of the nano-tubes technology. This active carbon fiber is a universal adsorbent, which is efficient to adsorb different gases (H_2 , N_2 , O_2 , CH_4 , NH_3 , 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 $0.5\text{-}2 \text{ m}^2/\text{g}$;
- small number of mesopores with $50 \text{ m}^2/\text{g}$ specific surface.



Fig. 3. Two blocks of high temperature (NiCl_2 + “Busofit”), mean temperature (MnCl_2 + “Busofit”), and low temperature (BaCl_2 + “Busofit”) adsorbers

The ideal sorbent bed needs to have micropores volume near 50%, solid carbon near 40% and meso/macropores volume near 10%. In conventional solid sorption refrigerators 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.

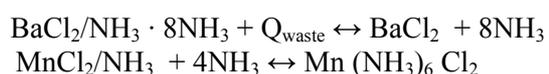
The used in experiments adsorber dimensions are $L = 1000$ mm, $D_{\text{out}} = 50$ mm, $D_{\text{in}} = 49$ mm. Vapor-dynamic stainless-steel thermosyphon is used as a heat pipe and a thermal control system. Its dimensions are $L = 1100$ mm, $D_{\text{out}} = 16$ mm, $D_{\text{in}} = 45$ mm, step between 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_2 mass is (340 g + 270 g), complex compound „Busofit“+ NiCl_2 mass is (250 g + 180 g), complex compound “Busofit” + MnCl_2 mass is (250 g + 230 g). The sorbent bed (salt with a monolithic fabric “Busofit”) has a form of cylinder, Fig.3.

Three adsorbers cooler

The basic operating schematic of the three adsorber’s cooler is shown on Fig.4. The solid sorbent cooler is consisted on two blocks of adsorbers (3+3) working out of phase. Total mass of the experimental set-up is 9 kg.

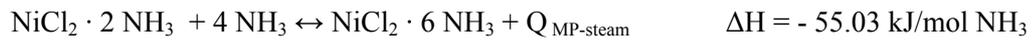
The ammonia vapour pressure is determined as a function of temperature for three different salts and active carbon fibre “Busofit”. In this analysis for simplicity we neglect the influence of active carbon fibres on the ammonia adsorption and desorption.

The selected salts are combinations of $\text{BaCl}_2/\text{NH}_3$ (LTS), MnCl_2 (MTS) and $\text{NiCl}_2/\text{NH}_3$ (HTS). The operation of the cooler is based on the following reactions:



$$\Delta H = +36.76 \text{ kJ/mol NH}_3$$

$$\Delta H = - 47.416 \text{ kJ/mol NH}_3$$



The heat input to the low temperature salt LTS initiates the ammonia vapour release and its flow to the low pressure vessels filled with MTS and HTS (medium and high temperature salts), where it is absorbing by MTS and HTS leading to the release of heat at T_M and T_H . Cooling the LTS with the help of the cooling fluid (water) 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].

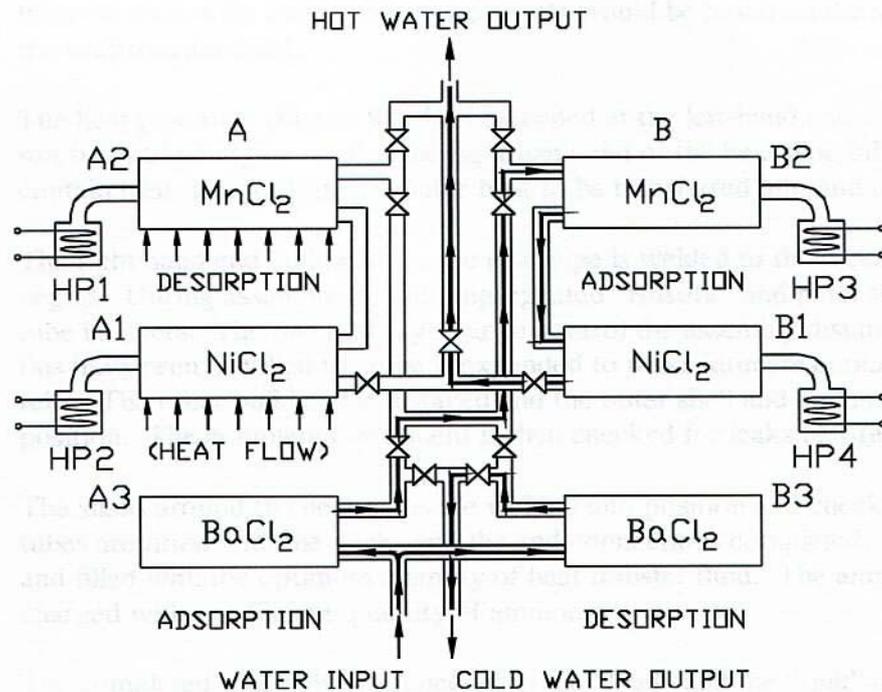


Fig. 4. Six adsorbers cooler (“Busofit” + salts) with internal heat recovery

The system includes a high temperature sorbent bed (HTS) and low temperature sorbent bed (LTS). Medium pressure steam (MP), hot water and cooling water on the cooler output is available in such a device. Continuous operation of the cooler is possible when two batch units are foreseen operating in an alternating way, Fig. 4. During the phase of high-pressure adsorbers A, B are absorbing the heat from the electric heaters (or gas flame) with desorption/decomposition of ammonia, while the low temperature adsorbers A1, B1 are cooling by the water heat exchanger, and absorbing ammonia (absorption/regeneration). The low temperature adsorbers A1, B1 have thermal contacts with a thermal sink, typically the ambience. Low temperature sources (water) coupled to the device upgrade heat to a higher temperature. It means that the ambient temperature of the liquid (water) – the low temperature source of energy, is upgrade to a temperature of the superheated vapour, or hot water at the exit. Internal heat recovery is enable due to the mass transfer between adsorbers and the external heat recovery is realized due to the water heat exchangers. The COP of such device with heat and mass resovery is near 1.44.

Cooler with three adsorbers + condenser/evaporator, tri-generation approach

Three adsorbers cooler can be modified, if we add to the above mentioned device the condenser/evaporator, Fig. 5. This cooler enables the constant rate of the heating/cooling procedure, two branches of the system are working out of phase and two sources of cold are available (BaCl_2 adsorber and evaporator). This modified cooler development is focused on the small-scale combined cold, heat and power (tri-generation) system application, which utilises the engine waste heat for cold production.

The condenser/evaporator is performed as a stainless steel container $L = 370 \text{ mm}$ and $D = 50 \text{ mm}$. The inner walls of container are covered with the capillary-porous layer to enhance heat transfer with evaporation.

The modified experimental set-up (Fig. 5) is very flexible for its application to analyze the parameters: 1) of a resorption cooler (gas cooling system) and 2) of a solid sorption cooler (liquid cooling system with the evaporator). The resorption cooler application was published in [14]. In this paper we consider working parameters of the ammonia solid sorption cooler with the evaporator/condenser. The experimental set-up consists on three sorbent bed ($\text{BaCl}_2/\text{NH}_3$ (LTS), MnCl_2 (MTS) and $\text{NiCl}_2/\text{NH}_3$ (HTS)) contacting with the evaporator/condenser through the valve.

There are two possibilities to apply the waste heat of the engine for the cold production:

1. The waste heat of engine (motor/electric generator) as the gas exhaust and liquid engine cooling system is used to heat three adsorbers simultaneously. The cycle of the cold production is divided on two stages.

1. At the first stage (time τ_1) adsorbers with sorbent bed NiCl_2 , MnCl_2 , and BaCl_2 initially are at the room temperature and start to be heated up to the temperature 230°C , 180°C and 90°C by the exhaust gas and the cooling water system of the engine. This stage devoted to desorb ammonia inside the sorbent bed and condense the ammonia vapor in the evaporator/condenser. The evaporator/condenser is cooling with the cold water flow (heat exchanger).
2. At the second stage (time τ_2) BaCl_2 , NiCl_2 and MnCl_2 adsorbers are cooled down the room temperature. Simultaneously the ammonia evaporating/boiling in the evaporator ensure the cold generation due to adsorption of the ammonia vapor in three adsorbers, Fig.6.

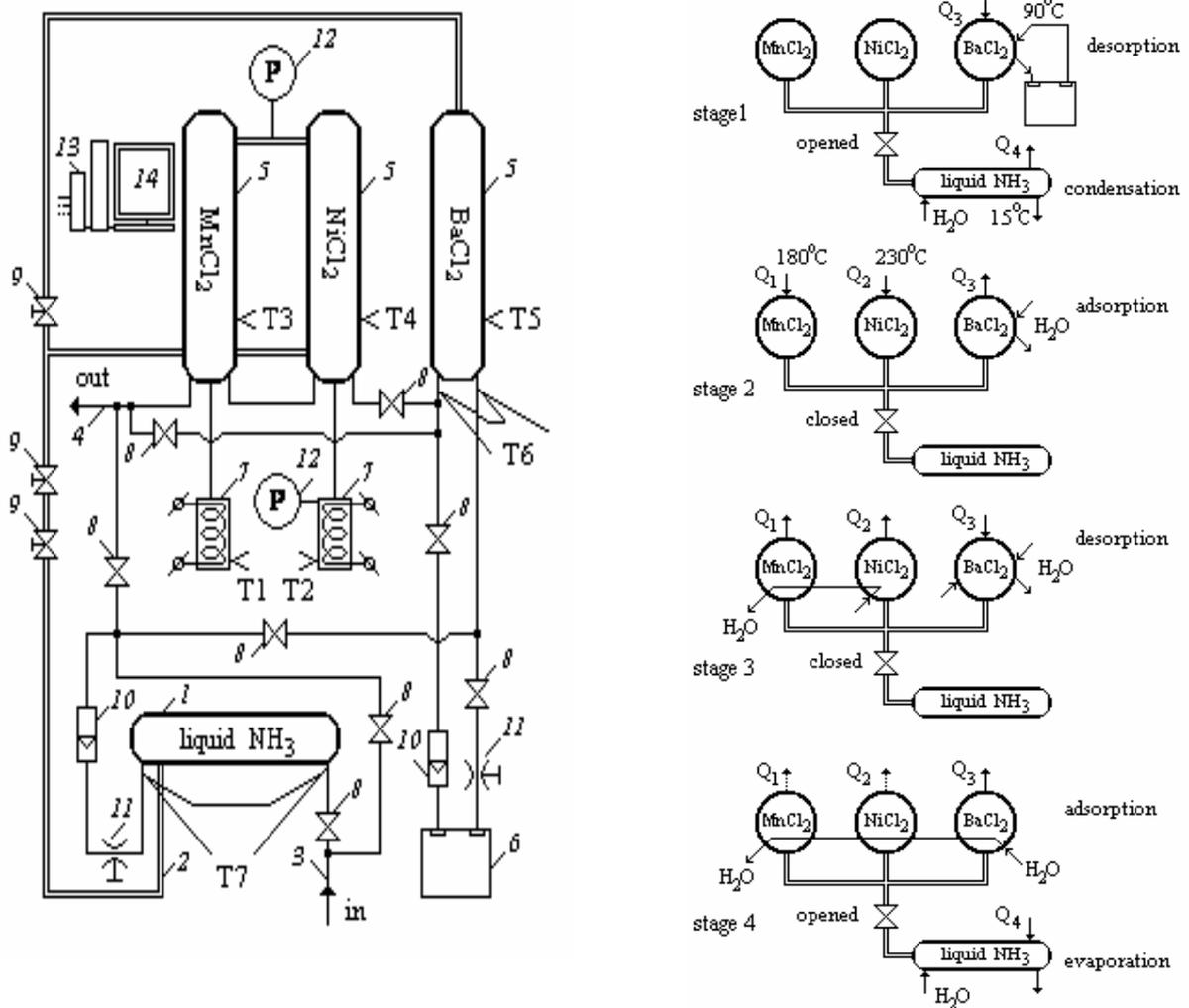


Fig.5. Three adsorbers cooler with condenser/evaporator for tri-generation system development

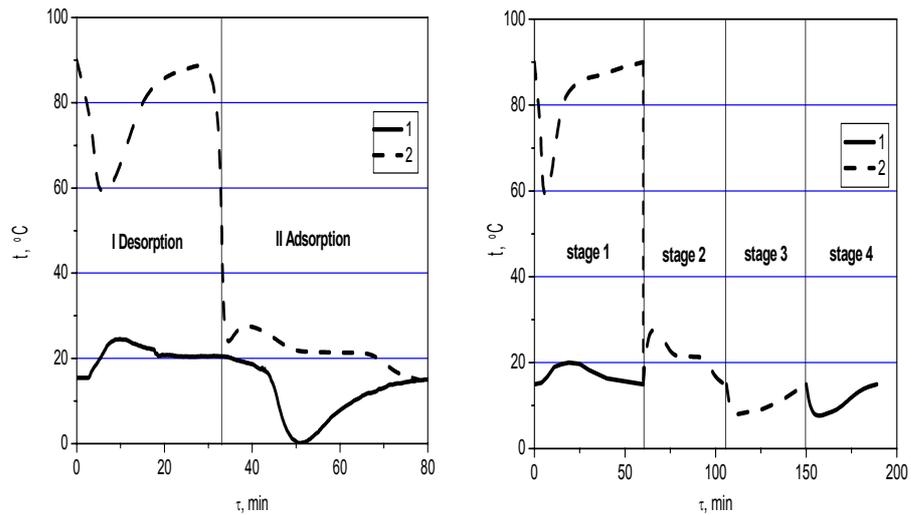


Fig.6. Temperature evolution of water flow as a function of cycle time on the output of the evaporator/condenser (1) – the first cooler prototype, and on the output of the BaCl₂ adsorber (2) – the second cooler prototype

So for this cooler prototype we use two different waste heat – the high temperature heat of the gas on the engine output and the low temperature waste heat of the engine liquid cooling system.

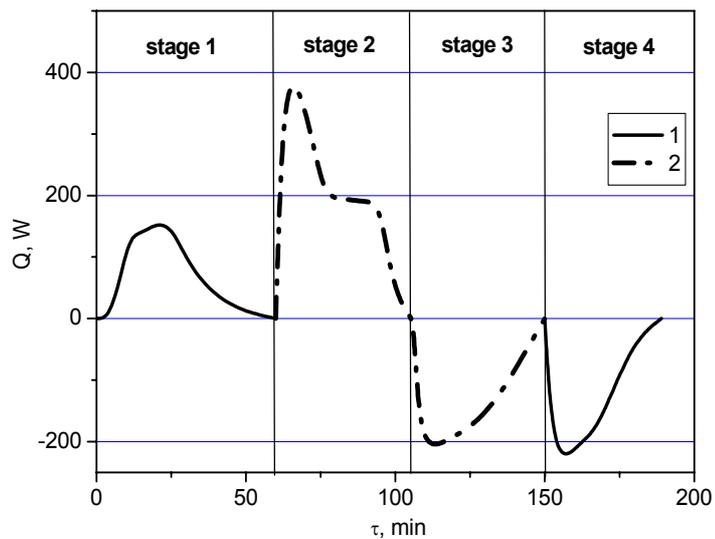


Fig.7 Heat input/output in the evaporator/condenser (1) and the low temperature BaCl₂ adsorber (2) as a function of cycle during the time of adsorption and desorption of the sorbent bed.

The second prototype is oriented only on the high temperature waste heat of the engine.

It is easier to produce the cold from a high temperature source such as heat of the exhaust gas (450 °C– 500 °C) rather than a low temperature source such as engine cooling liquid (90 °C). Instead of the engine cooling liquid system we use the cooling system of the high temperature adsorbers MnCl₂, NiCl₂ to heat the low temperature adsorber BaCl₂ and desorb the ammonia inside the sorbent bed.

In the experiments the total energy supply for two high temperature adsorbers MnCl₂, NiCl₂ was imitated by the electric heaters through the heat pipes and was equal near 1400 kJ for the cycle. The energy supply to the BaCl₂ adsorber was ensured by the hot (90 °C) water flow (at the output of the MnCl₂, NiCl₂) during the time of its cooling (waisted heat). So there is a heat recovery procedure

available to apply the wasted heat from MnCl_2 , NiCl_2 output to heat the low temperature adsorber BaCl_2 during the time of ammonia desorption.

For this case the cycle of the cooler functioning is composed from four stages of the cycle:

1. At the first stage (time τ_1) adsorbers with sorbent bed MnCl_2 and NiCl_2 are heated by the gas flame (electric heater) with further desorption of NH_3 . During procedure of ammonia desorption the superheated vapor is condensing in the condenser/evaporator and is partly adsorbing by the low temperature sorbent bed of BaCl_2 .
2. At the second stage (time τ_2) adsorbers with MnCl_2 and NiCl_2 are disconnected from the evaporator/condenser (the valve is closed) and the procedure of adsorbers cooling by the water circuit is starting. The cooling water cools adsorbers, its temperature is increasing up to $90^\circ\text{C} - 95^\circ\text{C}$. The water flow with temperature $90^\circ\text{C} - 95^\circ\text{C}$ on the output of adsorbers enters the low temperature BaCl_2 adsorber and heats it and desorb NH_3 inside the sorbent bed. Generating ammonia vapor is condensing in the evaporator/condenser.
3. At the third stage (time τ_3) the procedure of all three adsorbers (MnCl_2 , NiCl_2 and BaCl_2) cooling is finished. Now adsorbers MnCl_2 , NiCl_2 are connecting with the low temperature adsorber BaCl_2 through the opened valve. The valve, connecting adsorber BaCl_2 with the condenser/evaporator now is closed. More strong adsorbers MnCl_2 , NiCl_2 suck the ammonia from the adsorber BaCl_2 . The desorption of the ammonia vapor inside BaCl_2 adsorber is the reason of cold generation.
4. The final fourth stage (time τ_4) is responsible for the main cold generation in the evaporator. All three adsorbers now are connecting by the valve with the condenser/evaporator.

An example of a typical charge-discharge power profile of the cooler is presented on Fig.7. The max charging power of MnCl_2 , NiCl_2 adsorbers is around 400 W each. Evaporation in the range of 10°C results in cooling power of 200 W.

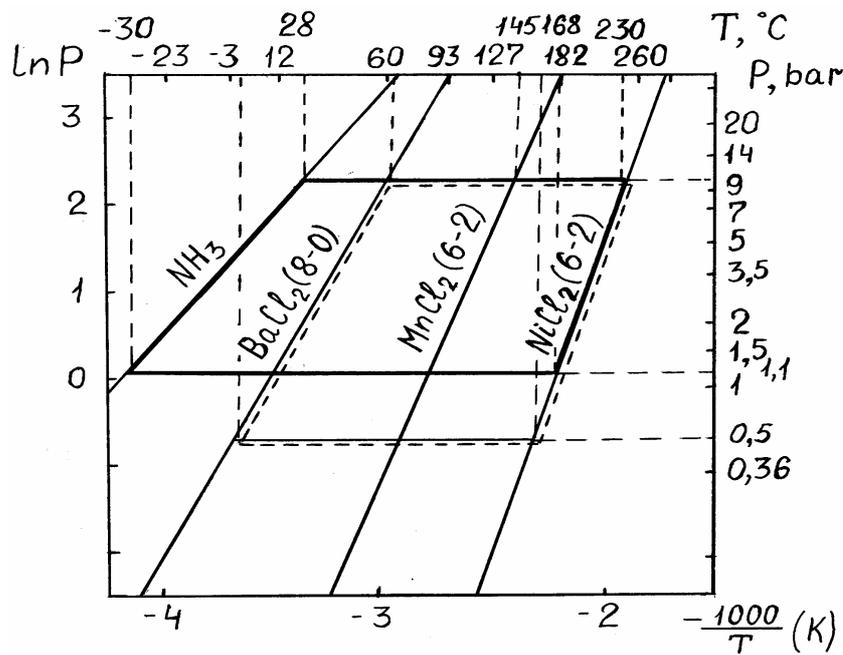


Fig.8. Clapeyron diagram for two cold generation sources in the solid sorption cooler (BaCl_2 , MnCl_2 , NiCl_2 + “Busofit”) with the condenser/evaporator

In this experimental set-up the pressure and temperature sensors allow to check the dynamic evolution of the pressure and temperature 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 chemical reactions and physical adsorption.

The Clapeyron diagram analysis of the cooler show the possibility to have two cold generators (the low temperature adsorber and the evaporator/condenser) and apply the cold and heat in the air-

conditioning systems. The value for $COP_{cooling}$ is 0.41 for one cooler (three adsorbers + evaporator/condenser). For two sets of equipment (Figs. 4-5) the value for $COP_{cooling}$ is 0.6.

The first prototype of the system with tri-generation is shown on Fig. 9.

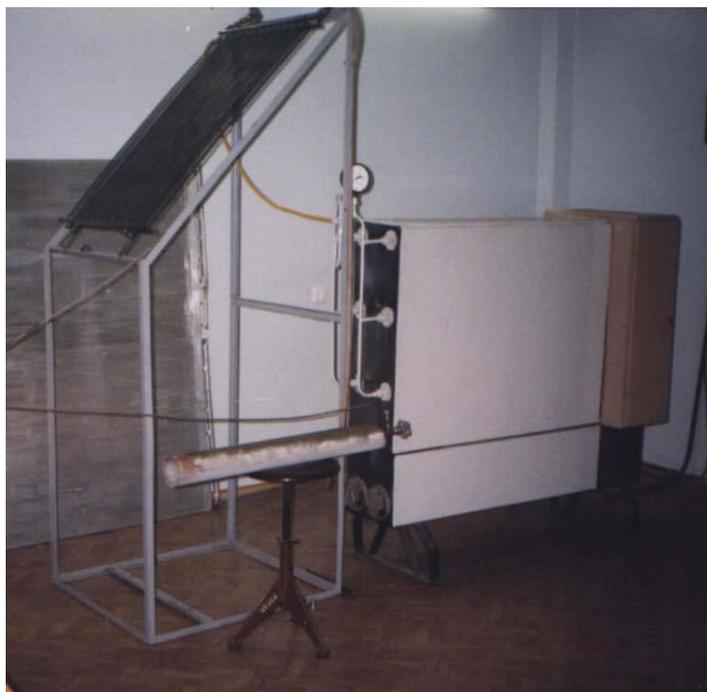


Fig. 9. Three adsorbers cooler with the evaporator/condenser for the tri-generation system

CONCLUSIONS

The developed and tested experimental set-up offers the possibility of saving 15 – 20% primary energy for cooling, heating and power demands.

Experiments with 2 different set-up based on the coupling salts $NiCl_2$, $MnCl_2$, $BaCl_2$ with an active carbon fiber „Busofit“ demonstrate a possibility to have a cooler with two different independent sources of cold (low temperature $BaCl_2$ adsorber and evaporator) with simultaneous heat generation and chilled water production with $COP_{cooling}$ equal 0,6.

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