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NaX Zeolite, Carbon Fibre and $CaCl_2$ Ammonia Reactors for Heat Pumps and Refrigerators

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Abstract. The key elements of solid sorption machines are the chemical compressors-adsorbers. Two categories of the solid sorption system are analyzed: adsorbents NaX zeolite, carbon fibre "Busofit" with NH_3, and complex combinations that undergo chemical reaction and physical adsorption ($CaCl_2$ + carbon fibre "Busofit" with NH_3).

Two phase ammonia motion inside the adsorbent bed was checked. That accompanied $NH_3/CaCl_2$ solution redistribution between the cold and hot surfaces of the sorbent bed, resulting in a rich $CaCl_2$ concentration at the boundaries.

Solid sorption heat pump and refrigerator technology utilizing heat pipe heat recovery with a condensing/evaporating refrigerant holds considerable promise for bivariant (space and domestic) applications due to the variable temperature and variable load capabilities of such machines.

Keywords: heat pipe, heat pump, carbon fibre, ammonia

Introduction

The purpose of this paper is to describe the development work performed to design and fabricate a new cooler and heat pump. The system was based on heat pipe heat recovery and combined chemical reaction and physical adsorption phenomena in the same type of a sorbent bed. This work follows the first chemisorption refrigerator, which was fabricated in 1971 at the Phillips Research Laboratories (Prast et al., 1971).

Ammoniates or amino-derivatives actually are used in solid sorption machines over wide ranges of pressures (up to 50 bar) and temperatures (−50–300°C) (Spinner, 1993). These ammoniates are very stable and have no secondary reactions. It is possible to use such a system for low temperature refrigeration (down to −50°C by evaporation of NH_3), in multi-effect systems, in systems with a Joule-Thomson (J-T) valve with the net cooling effect due to expansion of the gas, and finally in thermotransformers able to bring the thermal potential of a source up to 250°C.

The heat and mass transfer inside these sorbent beds is decisive for the operational characteristics of such coolers and heat pumps. While pure powder sorbent beds have very low effective thermal conductances (0.05–1 $Wm^{-1}K^{-1}$), consolidated sorbent beds (e.g., anisotropic porous graphite binder with salts), have higher thermal conductance properties (Balat and Spinner, 1993; Valkov, 1992; Mauran et al., 1992; Groll, 1992) up to 40 W/mK. Metal chloride complex compounds, such as graphite intercalation compounds (GIC) (Rockenfeller et al., 1992; Touzain et al., 1992), have good intergranular contacts which ensure high effective thermal conductivity.

In order to develop an optimized sorbent bed (reactor) we need to consider some limiting effects in it. If we use complex compound "Busofit"-$CaCl_2$ there is a binding effect of the gaseous molecules to the films of $CaCl_2$ and heat and mass transfer between hot/cold heat pipe wall and complex compound. If we could realize two-phase heat and mass transfer on NH_3 inside of our reactor, the second limiting effect will be comparable to binding of NH_3 to $CaCl_2$ films in pores.

A new thermodynamic cycle based on the dual use of salts and carbon fiber reacting with NH_3 is proposed as a perspective alternative. Our principal interests have been centered around active carbon fibre "Busofit"/NH_3 and compound "Busofit"-$CaCl_2$/NH_3. "Busofit" saturated by $CaCl_2$ which give us the possibility to realize simultaneous adsorption of NH_3 at the carbon fibre surface and chemical reaction of $CaCl_2$ films between the carbon fibres with NH_3.

The NH_3 condensation inside the porous media during the heating mode of the reactor was analyzed and its capillary suction through the micropores to the hot surface of heat exchanger was determined, while NH_3 was evacuated through macropores towards the cold sorbent bed region (micro heat pipe open type action). A related study of the kinetics of acetone and ethanol sorption by "Busofit" was presented earlier by Vasiliev et al. (1992).

Solid Sorption Experimental Device

The experimental setup shown in Fig. 1 consists of an NH_3 bottle, calibrated gas volume, vacuum pump,

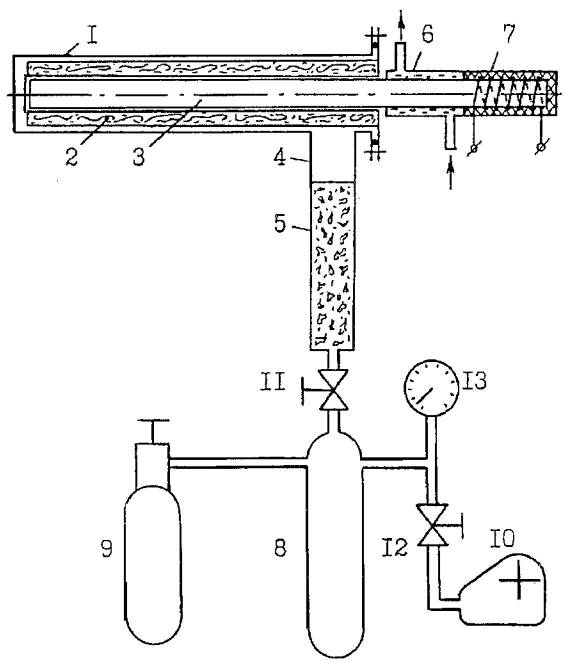

Figure 1. Schematic diagram of a test apparatus. 1—adsorber shell; 2—sorbent bed; 3—heat pipe; 4—evaporator/condenser; 5—nickel screen; 6—HP liquid heat exchanger; 7—electric heater; 8—calibrated vessel; 9—ammonia bottle; 10—vacuum pump; 11,12—flow valves; 13—pressure gauge.

pressure gauge and a fixed volume vessel in which the sorbent beds of different kinds could be tested.

The procedure of solid sorbent (2) heating and cooling is performed by the copper-water heat pipe with a mild steel envelope inside of the reactor (1). The heat pipe (3) has a water cooling jacket (heat exchanger 6) and an electric cartridge heater (7). The NH_3/solid sorbent experimental device includes an ammonia bottle (9), calibrated gas volume (8), vacuum pump (10), pressure gauge (13) and flow control valves (11–12). The solid sorbent cooler (1–7) and calibrated bottle were inserted into the hot chamber with thermal control, where pressures up to 20 bar were reached.

In our research program the test solid sorbents are (NaX) zeolite, activated carbon fibre "Busofit" and the complex compound "Busofit"-$CaCl_2$. "Busofit" cloth has a thickness of 0.7 mm and a specific surface up to 2400 m^2/g.

The sorbent bed was an annular solid of length $L = 300$ mm, outer diameter $d_{out} = 36$ mm, and inner diameter $d_{in} = 22$ mm. "Busofit" thermal conductivity is $\lambda_{eff} = 0.2$ Wm^{-1} K^{-1}. Naturally in future we are planning to improve this thermal conductivity using consolidated carbon fibre because this parameter limits heat transfer.

The outer wall of the sorbent bed cylinder is made from a stainless steel screen and is permeable for gas diffusion. The inner wall of the sorbent bed cylinder is made from a mild steel tube (heat pipe envelope) and is non-permeable. The adsorber shell, evaporator/condenser and all the pipes of the experimental device are made from mild steel. The adsorber shell (1) is a cylinder with an outer diameter of $d_{out} = 47$ mm, an inner diameter of $d_{in} = 40$ mm, and a length of $L = 360$ mm. The condenser/evaporator (4) is a cylinder of length $L = 200$ mm, outer diameter $d_{out} = 37$ mm, and inner diameter $d_{in} = 30$ mm.

The condenser/evaporator (4) is filled with metallic nickel foam (Ni foam) wick (5) to improve the heat transfer between the wall of the condenser/evaporator and the wick which is saturated by NH_3. The wick porosity is 95%.

Experimental Procedure

The sorbent bed is heated in advance up to 450 K during 2 h using the heat pipe (3) and electric heater (7). The vacuum pump is constantly switched on. Then sorbent bed is cooled by allowing cool (290 K) water to flow through the HP heat exchanger (6) till steady state is reached. The pressure relief valve on the bottle (9) is opened and ammonia flows into the calibrated volume (8), then the valves (11–12) are closed.

The NH_3/solid sorbent sample is subjected to a pressure step of NH_3, allowing the ammonia enter from the calibrated volume (8), and the valve (11) is opened. The decrease in the pressure of volume (8) corresponds to the ammonia adsorption in solid sorbent sample. The rate of NH_3 adsorption is controlled by the pressure fall (pressure gauge 13) in the calibrated volume (8) to the equilibrium state. The calibrated volume (8) is 1000 cm^3. Knowing the NH_3 pressure and density, we can calculate the mass of adsorbed ammonia.

The measurements are global, but they provide very useful information on the differences between a granular bed of NaX zeolite and an activated carbon fibre "Busofit", or a combination of $CaCl_2$ with "Busofit". Repeating the procedure of the NH_3 diffusion from the bottle (8) to the sorbent bed (2) at different pressures and temperatures, controlled by the heat pipe, we found the adsorption isotherms for NH_3 on the solid sorbent as a function of pressure. The ammonia/"Busofit" system provides by far the largest cooling capacity for the system, which has approximately 200 W average capacity over the entire heating and cooling cycle of 30 min.

Experimental Results

Test data results are shown in Figs. 2 to 4 and in Table 1. The experimental data are presented on the isothermal diagrams and are easily represented by a Clausius-Claperyron chart. The temperature of saturation for the evaporating/condensing cycle is determined using the saturation curve for ammonia. Experimental data and an example of a typical sorption heat pump cycle is shown in Fig. 2 for a sample of (NaX) zeolite/ammonia. The data presented in this paper are closely related to data published by Shelton and Miles (1989).

The sorption isotherms for activated carbon fibre "Busofit"/NH_3 are shown in Fig. 3, and for the compound $CaCl_2$-"Busofit"/NH_3 are shown in Fig. 4. During the first portion of the cycle (2-3), the sorbent bed is heated from 303 K to about 350 K to pressurize NH_3 from 5 MPa to about 15 MPa. When the sorbent is further heated to 555 K the ammonia is vented at high pressure. Cooling to 454 K results in depressurization and further cooling to 303 K results in readsorption at low pressure, thus completing the cycle.

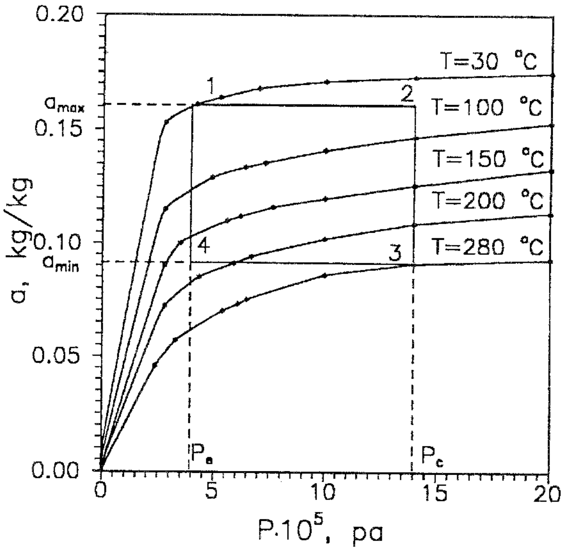

Figure 2. Adsorption isotherms for ammonia on (NaX) zeolite.

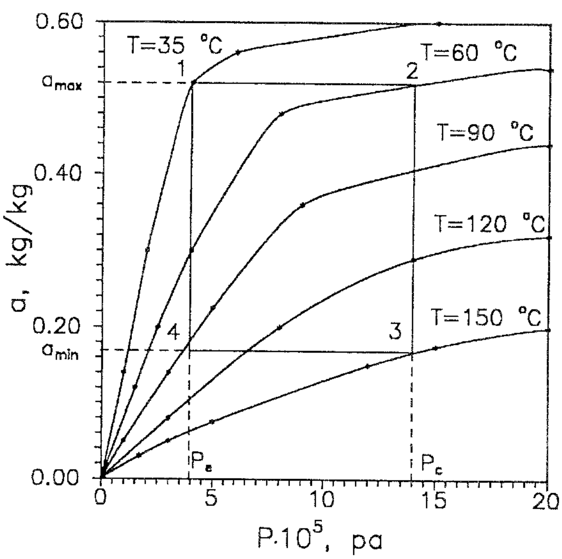

Figure 3. Adsorption isotherms for ammonia on "Busofit" activated carbon.

The rectangle 1, 2, 3, 4 in Figs. 2 to 4 is composed from two isosteric lines 1-2; 3-4 and two isobars 4-1; 2-3. The isobar 4-1 corresponds to the pressure level inside the evaporator during the adsorption, the isobar 2-3 corresponds to the pressure level in condenser during desorption.

The isosteric line 1-2 at point 1 gives the sorbent temperature at the end of adsorption, while the isosteric line 1-2 at point 2 gives the sorbent temperature at the

Table 1. Experimental data on adsorption/desorption of ammonia in (NaX) zeolite, "Busofit" and compound $CaCl_2$-"Busofit".

Sorbent	T_{des} °C	T_e/T_c °C	Δa_m kg/kg	ρ kg/m^3	$\Delta a\rho$ kg/m^3	τ_{ads} min	τ_{des} min	Q^* kW/m^3	q^* W/kg
NaX	280	0/35	0.07	700	49	12	10	46.9	67
"Busofit"	150	0/35	0.35	250	87.5	17	15	49.8	199
"Busofit"-95% $CaCl_2$	150	0/35	0.43	520	223.6	40	35	62.76	120

T_{des}—the temperature of desorption; T_e/T_c—the ratio of the temperatures in evaporator-condenser; Δa_m—the dynamic value of adsorption NH_3 amount; τ_{ad}—the time of adsorption; τ_{de}—the time of desorption, Q^*—the average capacity per kW m^{-3}of sorbent over the entire heating cooling cycle; q^*—the average capacity W kg^{-1} of heat pump over the entire heating and cooling cycle.

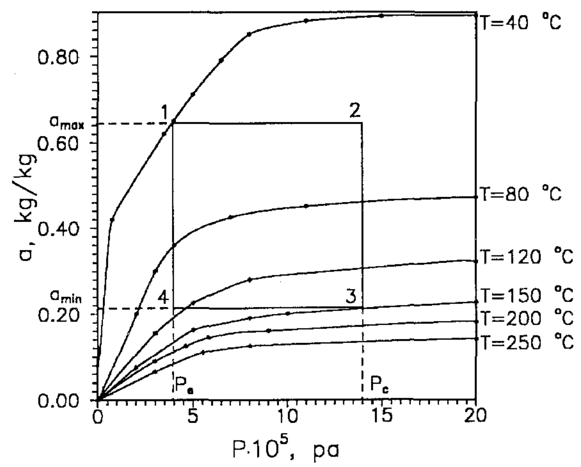

Figure 4. Adsorption isotherms for ammonia on $CaCl_2$-"Busofit" activated carbon.

beginning of desorption. The isosteric line 3-4 at point 3 represents the temperature of the sorbent bed at the end of desorption, and the isosteric line 3-4 at point 4 represents the temperature of the sorbent bed at the beginning of adsorption. Moving the rectangle 1, 2, 3, 4 on Figs. 2–4 we can calculate the dynamic value of NH_3 as Δa_m in the cycle: $\Delta a_m = a_{max} - a_{min}$.

The set of experiments was performed with these adsorbents on the experimental setup shown in Fig. 1 and described in Table 1. In each experiment, the end of desorption was the time at which the condenser (4) temperature decreased to 305 K. The end of adsorption was when the temperature of the evaporator rose to 276 K.

Following the experimental data analyses the conclusion is that the "Busofit"-$CaCl_2/NH_3$ complex compound is superior to NaX/NH_3 and to "Busofit"/NH_3 combinations with a point of view of volume limitations and low temperature of desorption.

NaX/NH_3 and "Busofit"/NH_3 reactors have different temperatures of desorption (280°C and 150°C, respectively). They could be recommended for 2 reactor combinations with heat recovery by heat pipe heat exchangers in order to increase the COP of the system. The combination of NaX/NH_3 in one reactor, with the temperature of desorption being 280°C and "Busofit"/NH_3, or "Busofit"-$CaCl_2/NH_3$ in the second reactor, with the temperature of desorption being 150°C, using two evaporators and two condensers would allow the thermodynamic COP to approach 1.

The following experimental data were obtained with two small models. Characteristics of the units are presented in Table 2. In this case the thickness of the sorbent beds is 7 mm and 0.4 mm aluminum fins are used with a spacing of 7 mm to improve the effective thermal conductivity of sorbent bed. The "Busofit"/NH_3 reactor No. 1 has a flexible link to the cylindrical condenser/evaporator. The stainless steel reactor is heated by a heat pipe heat exchanger equipped with an electric

Table 2. Characteristics and performance data of tested coolers.

Cooling unit	No. 1 (sorbent "Busofit")	No. 2 (sorbent "Busofit"-$CaCl_2$)
Reactor volume	0.15 10^{-2} m^3	0.2 10^{-2} m^3
Sorbent mass	50 g	120 g
NH_3 mass	27 g	100 g
Copper/water heat pipe mass	500 g	500 g
Total cooler mass	1700 g	2000 g
Desorption/adsorption cycle	30 min	40 min
Mean heat flux Q in the evaporator (T_e = 20°C)	25 W	40 W
Cold output Q_e	300 W/kg	330 W/kg

cartridge heater. The condenser is cooled during desorption by 20°C water flow, while the evaporator is heated by air at 20°C. The "Busofit"-$CaCl_2/NH_3$ reactor No. 2 has a flexible link to the cylindrical condenser/evaporator. The reactor is heated by a heat pipe heat exchanger equipped with an electric cartridge heater. The condenser is cooled during desorption by 20°C water flow, while the evaporator is heated by air at 20°C. The "Busofit"-$CaCl_2$ mass ratio is 1:1. The experimental data on these coolers are shown Figs. 5–7.

The optimum cycle time could be determined using Figs. 3–4, and 5–8 to reach a desired temperature. For example, the beginning of desorption (Fig. 5) for the "Busofit"/NH_3 combination corresponds to the temperature 60°C (point 2 on the diagram 3), and a time interval of 2 min.

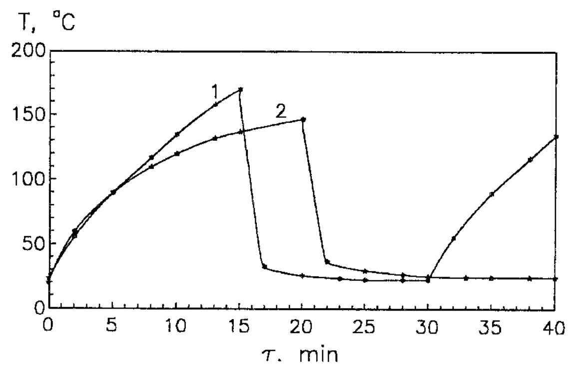

Figure 5. Transient heat pipe temperature evolution as a function of desorption/adsorption cycle: 1—"Busofit"/NH_3; 2—"Busofit"-$CaCl_2/NH_3$.

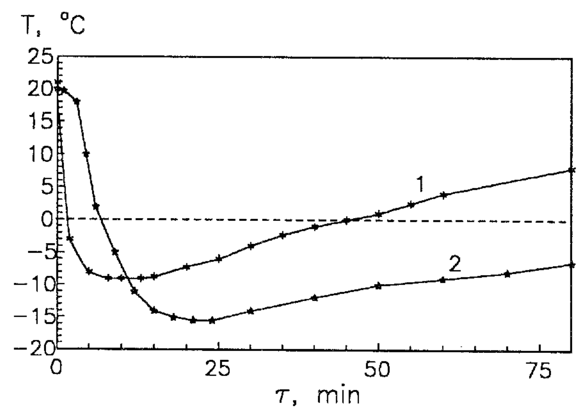

Figure 6. Transient evaporator temperature T_e evolution for pair (natural convection heating): 1—"Busofit"/NH_3; 2—"Busofit"-$CaCl_2/NH_3$.

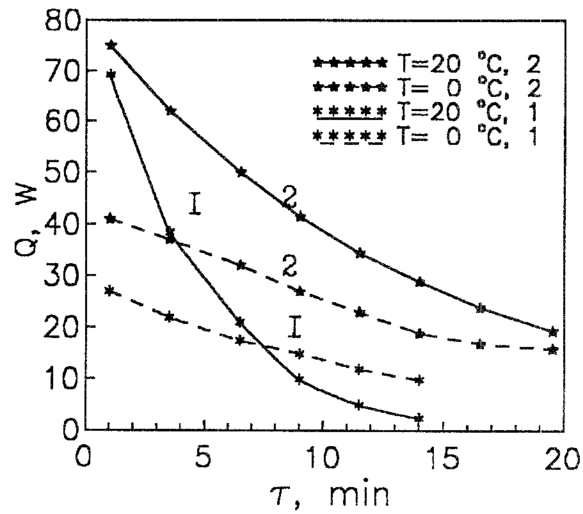

Figure 7. Transient evaporator cold output for "Busofit"/NH_3 pair: 1—"Busofit"/NH_3; 2—"Busofit"-$CaCl_2/NH_3$.

Heat pipe heat exchangers with finned outer surfaces for this case are very useful with a point of view of uniform sorbent bed cooling and heating.

Conclusions

A new developed technology of the carbon fibre production gives some extra possibilities to develop the advanced thermodynamic cycles using solid-gas reactions, particularly solid adsorption. The necessary equilibrium thermodynamic data for 3 types of sorbents—NaX, carbon fibre "Busofit" and "Busofit"-95% $CaCl_2$ were determined. A specific power output of 47 kW m^{-3} for NaX, 50 kW m^{-3} for carbon fibre "Busofit", and 62.7 kW m^{-3} for compound "Busofit"-95% $CaCl_2$ was obtained.

Ammoniated $CaCl_2$ solutions in the carbon fibre cloth circulated by capillary forces seems to be economically attractive for large volume storage and transportation, if efficient two-phase flow heat transfer in the sorbent bed could be realized.

Two new small coolers based on "Busofit"/NH_3 and "Busofit"-$CaCl_2/NH_3$ pairs with a flexible link between the reactor and evaporator were tested and 300 W/kg and 330 W/kg cold output was observed. At two adsorber cycle with a combination of NaX/NH_3 in one reactor (with a desorption temperature of 280°C) and "Busofit"/NH_3 or "Busofit"-$CaCl_2/NH_3$ in the second reactor (with a desorption temperature of 150°C) using two evaporators and two condensers allows us to obtain a cooling COP close to 1, if these reactors would be optimized.

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