



Solar-Gas Solid Sorption Refrigerator

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Abstract. The general goal of this paper is to present the results of an investigation of a new environmentally friendly refrigerator. In this design a physical adsorption and chemical reactions are used simultaneously for a heat and cold generation. A solar refrigerator is made of a solar collector, adsorbed natural gas vessel (ANG), and compact, portable refrigeration system, which consists of two small adsorbers with heat pipe heat recovery system. An active carbon fiber “Busofit” saturated with different salts (CaCl_2 , BaCl_2 , NiCl_2) is used as a sorbent bed and ammonia is used as a working fluid. The main particularity of this refrigerator is consumption of solar energy with methane gas burner as a back-up. The system management consists only in actuating the special type valves to change the direction of the heating circuit and water valves to change the water cooling circuit. The goal of this work is the experimental determination of the main refrigerator parameters using solar/gas high temperature source of energy and air/water as a low temperature source of energy to cool and heat air/water.

Keywords: solar/gas refrigerator, adsorption, chemical reactions, heat recovery, heat pipes

Introduction

The concept of solar-powered refrigeration cycles is known and several refrigerators operating on this principle are commercially available. Solar powered refrigeration has been analyzed by Cohen and Cosar (1991). Solar sorption refrigeration with cycle day/night to produce the ice using solar energy was demonstrated by Guilleminot et al. (1988). Solar cooling processes using chemical reactions for the cycle day/night was realized by Speidel and Kleinemeier (1992). Bougard and Veronikis (1992) used ammonia/active carbon in solar refrigerator. A new hybrid system of solar powered water heater and adsorption ice maker was suggested by Wang (1999).

However, there has been a little research into the integration of short time cycles sorption machines of solar power with natural gas (Nguyen et al., 1996), or solar power with electrical immersion heater as a back-up

(Vasiliev et al., 1999). Use of methane as an alternative heating system would be more economical and application of solar power simultaneously would reduce the cost and size of solar collectors. Actually two different solid sorption refrigeration cycles are mostly used—adsorption and chemical reaction (Miles et al., 1992; Neveu et al., 1993; Meunier, 1998; Wang, 2000).

The combined action of physical adsorption and chemical reactions for the cold production in the same space and at the same time is attractive initiative to enhance the COP of a system (Vasiliev et al., 1994).

The use of heat pipes to improve the performance of carbon-ammonia adsorption refrigerator was mentioned by Vasiliev et al. (1996) and Critoph (2000). It was shown that heat transfer within an active carbon sorbent bed can be improved dramatically by the use of finned heat pipe. Solar guided sorption cycles can be also used in heat-driven refrigerators, or heat pumps in which the energy source is a burning fuel, or waste heat (Chua et al., 2001). The concept aim of such research program is to extract the most enthalpy

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from the low-grade heat before it is purged into the surrounding. It is easy to perform, if an autonomous low pressure ANG vessels are used together with gas burner (Vasiliev *et al.*, 2000) and the energy of the waste gas is used to heat the low temperature sorbent bed. A solar-gas refrigerator based on a reversible solid sorption phenomena is competitive, if the process allow to store the energy of a high density, and if the heating, or cooling power is enough for consumers.

Some theoretical research in this field was performed by Spinner *et al.* (2001). The application of the first and second law of thermodynamics in equivalent Carnot cycle concept applied to thermochemical solid/gas resorption system was demonstrated by Castaing-Lasvignottes and Neveu (1997).

Regarding the developing countries application there is a well documented need for food refrigeration, air-conditioning in areas that do not have access to grid electricity. Spoilage of many products, particularly fish, can be as high as 50%.

Our intention is to design a refrigerator, which would operate without grid electricity, consuming a chip energy (solar energy concentrator and autonomous, low pressure adsorbed natural gas storage system), that can be built and maintained in the country of use, be light and portable and that is low enough in cost. This can be achieved if we use a solar energy as a main source, a gas flame as a second (alternative, or additional) source of energy and a set of sorbent beds which are switched on and off alternatively. These sorbent beds are used

as a single storage systems with physical sorption (active carbon fiber "Busofit"), complex compound single stage systems with physical sorption and chemical reactions (active carbon fiber "Busofit" + CaCl_2), or a complex compound two stage systems ("Busofit" + BaCl_2 and "Busofit" + NiCl_2) with the internal and external heat recovery. The application of a constant source of energy ($\sim 1 \text{ kW}$) with special valves to heat and cool the sorbent beds alternatively increase a COP^R of the system, to compare with the application of periodically switched on and off sources of energy.

The Main Design of the Solid Sorption Refrigerator

Two sorbent bed adsorption refrigerator can be used as a single stage system, when each of two canisters is switched on and off alternatively, or as a two-stage system with heat recovery between sorbent beds (Figs. 1–3).

Solar concentrator (Figs. 1–3) is made from the aluminum plate as a tray (TV parabolic antenna) with diameter 1.8 m, the inner surface is covered by the metallic polymer film with high degree of reflection 0.68 (mirror). Aluminum nitride coating increase the absorption coefficient of a solar receiver up to 92%. This system needs to have a solar oriented mechanism to move solar concentrator.

Solar/gas refrigerator has a solar receiver 1 (Fig. 1) gas flame system to heat the water boiler 10, two sorbent bed canisters 2 and 6, connected by the heat

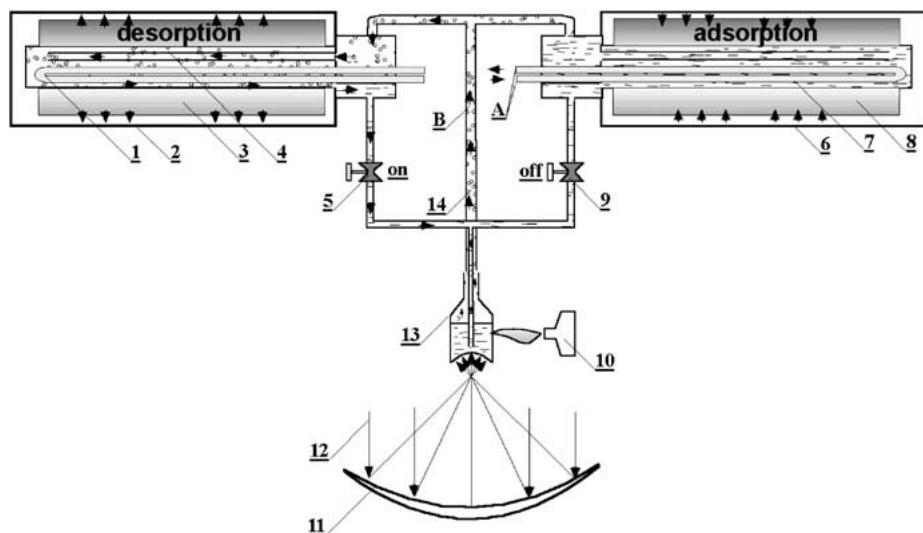


Figure 1. Solar solid sorption refrigerator, high temperature part.

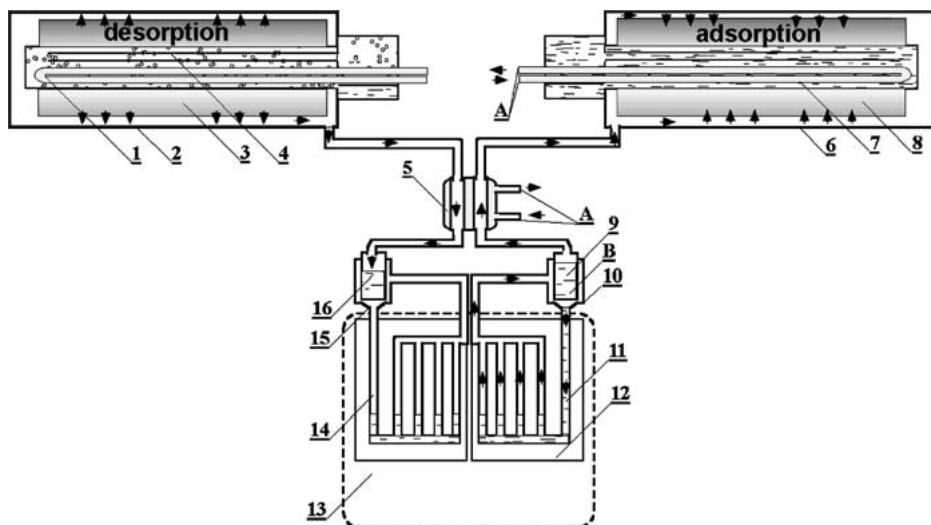


Figure 2. Solar solid sorption refrigerator, low temperature (ammonia) part.



Figure 3. General view of the solar solid sorption refrigerator.

recovery loop A, two phase heat transfer system B (vapor-dynamic thermosyphon), one condenser 5 (Fig. 2) with low temperature two evaporators 10, 16 and two cold panels 11, 14 (loop heat pipes) heated by the air. When there is a forced convection heating by the air from surrounding two low temperature finned evaporators can be used without loop heat pipes.

The two-phase heat transfer device B (Fig. 1) is designed to heat adsorbers and is made as a vapor-dynamic thermosyphon, which has a small boiler 13, two elongated cylindrical finned condensers 4 inside the sorbent bed canisters, vapor channel 14 and two flexible liquid pipes with special valves 5 and 9 to regulate the boilers water feeding. The basic particularity of this thermosyphon is the periodical switch on and off (by valves) the condensers with constant rate of the boiler heat load. The boiler 13 is disposed in the focus of a solar concentrator and simultaneously is heated by the gas flame of a gas burner 10, joint to the adsorbed natural gas vessel (ANG). The experimental data acquisition system includes the temperature sensors, vapor pressure gauge and computer. The gas flow rate is regulated as a function of the vapor temperature.

Two solid sorbent canisters 2 and 6 (Fig. 1) are filled with an active carbon fiber "Busofit" 3, 8 or are filled with "Busofit" saturated by chemicals and wrapped on the surface of condensers 4, 7 between fins. The length of the canister is 1.2 m, the outer diameter of the canister is 50 mm. When the composition "Busofit"-salt was used the full heat output was at least two times more (for the "Busofit"- CaCl_2 combination a full adsorption capacity is more than 0.85 kg of ammonia for 1 kg of a sorbent bed), but the time of reactions is increased from 12 min, up to 20–25 min. The full adsorption capacity of an active carbon fiber "Busofit" for different gases is presented on Table 1. The isotherms of ammonia adsorption/desorption on "Busofit" and "Busofit" + CaCl_2 are shown on Figs. 4–7.

Table 1. Full adsorption capacity of the sorbent bed.

Full adsorption capacity, kg/kg adsorbent	“Busofit” TM*	“Busofit” TM*- CaCl ₂
Acetone	0.61	
Ammonia	0.62	0.85
Ethanol	0.60	
Methanol	0.55	

The temperature evolution of the surface of the boiler 13 and canister No. 1 (2) and the canister No. 2 (6) are shown on Fig. 8. The main level of the boiler surface temperature is near 110°C, while the main tempera-

ture of the canisters during its maximum desorption after 5 cycles of the operation is 95°C. The temperature difference is near 15°C, it means that the thermal resistance between the source of the energy (boiler) and the sink of the energy (the surface of the canisters) is near $R = 0.015$ k/W.

The cooling power of the refrigeration may be defined as

$$P = Q_e/t, \quad (1)$$

where “ t ” represent the duration of a single cycle of the cooling/heating. The cooling power may also be expressed per mass of the adsorbent, or the adsorber.

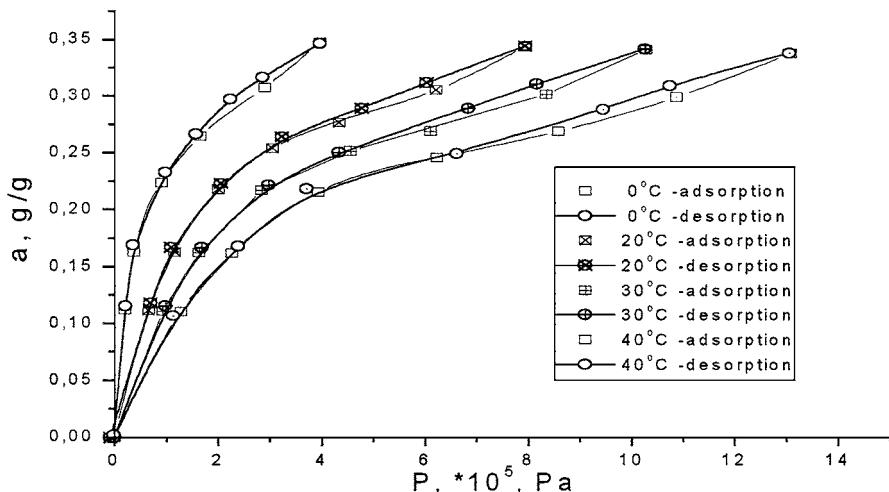
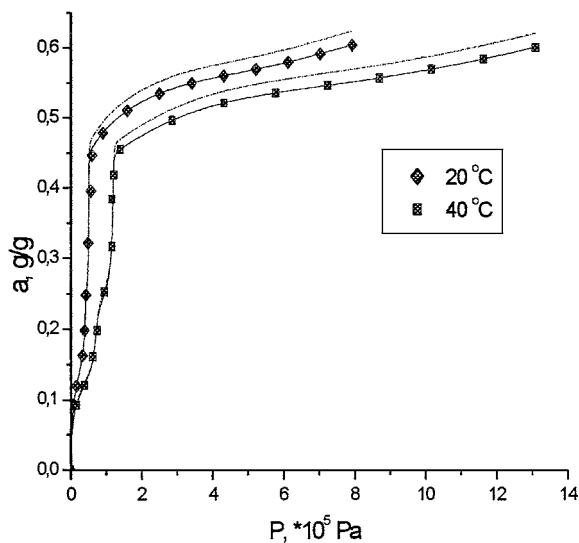


Figure 4. Adsorption/desorption isotherms of ammonia on the “Busofit”.

Figure 5. Experimental and calculated ammonia isotherms of “Busofit + CaCl₂”. Dashed lines indicate calculated data.

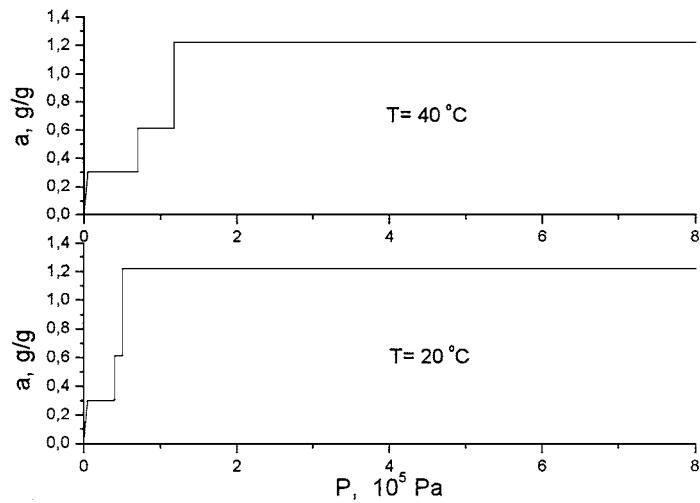


Figure 6. Thermodynamic equilibrium of a composition $\text{NH}_3\text{-CaCl}_2$ [US patent No. 4319626].

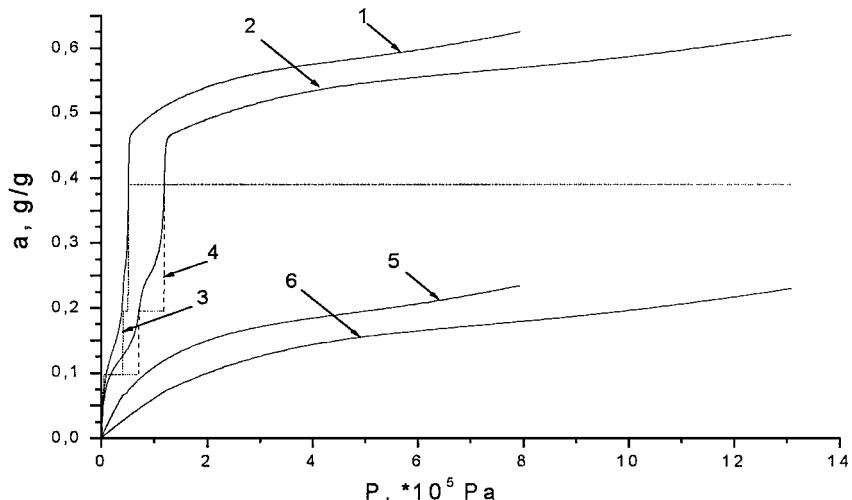


Figure 7. Adsorption isotherms of "Busofit + CaCl_2 ": (1) 20°C; (2) 40°C; (3) $\text{CaCl}_2 \cdot \chi_1$ (20°C); (4) $\text{CaCl}_2 \cdot \chi_1$ (40°C); (5) "Busofit" $\cdot \chi_2$ (20°C); (6) "Busofit" $\cdot \chi_2$ (40°C).

The mass of the adsorber is equal to the sum of masses of the adsorbent, metal wall of canisters and heat pipe heat transfer system:

$$Q_e = \Delta W \text{mL} - C_{\text{pw}}m \Delta W(T_c - T_e) \quad (2)$$

$$\text{COP}^R = Q_e / (Q_{\text{se}} + Q_{\text{ad}}) \quad (3)$$

The total heat of adsorption is equal:

$$Q_{\text{ad}} = \Delta H_{\text{ad}} \Delta W m_b \quad (4)$$

$$Q_{\text{se}} = m C_p (T_3 - T_1) + m_b C_{\text{pb}} (T_3 - T_1)$$

$$+ m_b W_i C_p (T_2 - T_1) = m_b W_{\text{av}} C_{\text{pb}} (T_3 - T_2) \quad (5)$$

where

ΔH_{ad} : the heat of adsorption,

W_i : amount of ammonia vapor present in the "Busofit" during the isosteric phase of heating,

W_{av} : the average value of the amount of ammonia vapor in "Busofit" during the adsorption phase,

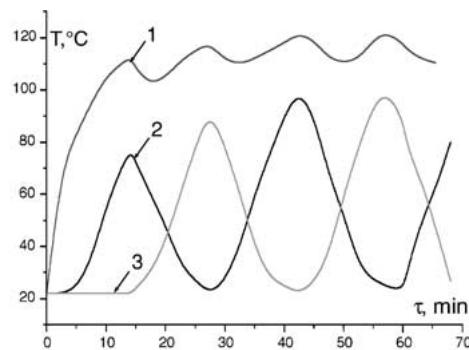


Figure 8. (1) Temperature evolution of the evaporator surface; (2) canister No. 1 surface; (3) canister No. 2 surface.

M_S : total mass of stainless steel tubes of canisters,
 C_{ps} , C_{pb} : specific heat capacities of stainless steel and “Busofit”,
 T_1 , T_3 : denote the minimum and maximum temperatures of the system, while
 T_2 : represent the temperature at the beginning of the desorption time.

Description of the Refrigerator Operation

Single Stage System with “Busofit”

The rate of the adsorption/desorption of ammonia on the surface of “Busofit” can be evaluated by the isotherms analysis at different temperatures of the sorbent bed (Fig. 4).

In order to study the sorption capacity of the adsorbent it is necessary to know the quantity of gas adsorbed on each point of the cycle. There is a general need to have a good fit of experimental isotherms and temperature and to extrapolate some isotherms beside the experimental field (Figs. 4–7). For the carbon fiber “Busofit” the approach of Dubinin is well adapted and allows to link quite simply the physical properties of “Busofit” to the capacity of adsorption of the carbon fiber.

The theory of micro porous volume filling, worked out by M.M. Dubinin, is widely used for quantitative characteristic of adsorptive properties and basic varieties of porous structure. The basic equation of this theory is Dubinin-Astakhov’s equation, which describes the equilibrium gas adsorption on the adsorbents with micro porous homogeneous structure that has the fol-

lowing form:

$$a = (W_o/v) \exp(-[A/E_o\beta]^n) \quad (6)$$

Dubinin-Radushkevich’s equation is a special case of Dubinin-Astakhov’s equation, ($n = 2$):

$$a = (W_o/v) \exp(-BT^2[\lg(P_s/P)]^2) \quad (7)$$

The empirical coefficient in the Eq. (7) for the ammonia adsorption ACF “Busofit AYTM-055” case: $W_o = 0,491$ and $B = 8,56 \times 10^{-6}$.

The affined coefficient, β is an independent argument and is defined as a ratio of two gas substances adsorptive potentials at invariable adsorbent in the Eq. (7). The ammonia calculated affined coefficients to benzene (this substance is usually taken as a standard one) differ from each other in different references. The β ammonia coefficient to benzene for ACF like “Busofit”, $\beta_{Busofit} = 0,309$ was obtained on the experimental material.

Another important sorbent characteristic is a peculiar porous size. It can be defined according to the empiric expression for slit-like porous model, proposed by M.M. Dubinin: $x = k/E_o$, where x is the half-width of the micro pore, nm; E_o is the characteristic energy of benzene, 20.5 kJ/mole; k is the constant of proportionality, equal 12.0. The porous peculiar size of the ACF “Busofit AYTM -055” is 11,7 Å. In these relationships: a is the sorption capacity, g/g, mmole/g; $A = RT \ln(P_s/P)$ is the characteristic sorption energy, kJ/mole; B is the structural constant, which characterizes the size and distribution of micro pores, K^{-2} ; E_o is the characteristic energy of standard gas (usually benzene) kJ/mole; P is the pressure, Pa , kPa , MPa ; T is the temperature, $^{\circ}\text{C}$, K; R is the universal gas constant, $\text{kJ}/(\text{mole K})$; V is the volume, m^3 ; W_o is the micro porous volume limit cm^3/g ; z is the compressibility factor; β is the affined coefficient, v is the adsorptive substance molar volume cm^3/mmole .

It is very important to estimate the COP of the process. The thermodynamic cycle is defined by three levels of temperatures- T_{evap} , T_{amb} , T_{ad} and the two levels of pressure P_{evap} , P_{cond} .

The refrigerator works on a four-phases cycle:

- isosteric heating,
- desorption/condensation,
- isosteric cooling,
- adsorption/evaporation.

$$\text{COP}^R = \text{cold output}/\text{high-grade heat input}$$

The density of the adsorbed vapor is given by the Dubinin relation:

$$\text{with } \rho(T) = \rho_b - (\rho_b - \rho_0)$$

The saturating vapor pressure is obtained from Clapeyron equation:

$$\ln(P_0) = -\Delta H/RT + \Delta S/R \quad (\text{for } T < T_c)$$

and by extrapolation of this equation for the temperature T greater than T_c .

The energy required to start the refrigerator functioning comes mainly from the heat supplied to the solar collector and the gas flame burner. The air is considered as a second low temperature source of energy. During the cloudy days, or when solar energy is insufficient gas flame-heating system is switched on automatically in parallel with the solar heater to maintain the heating load 1 kW. However, a small amount of work is required by the valve system to switch on and off vapor-dynamic thermosyphon 15 (Fig. 1) to heat or to cool one sorbent bed after another (two step heat machine). This is in contrast to conventional vapor-compression systems, which require shaft work for the compression process. The main parameters of the refrigerator are included in the Table 2. Two special valves 5 and 9 (Fig. 1) give a possibility to switch on and off one, or another adsorber (2, 6).

Table 2. Solar-gas refrigerator main parameters.

Solid-gas adsorber dimensions	$L = 1.2 \text{ m}$ $D = 0.05 \text{ m}$
Carbon fiber "Busofit" mass in one adsorber	0.75 kg
Ammonia mass in one adsorber	0.35 kg
Water mass in one thermosyphon	1 kg
Ammonia mass inside one loop heat pipe	0.05 kg
Total mass of refrigerator	22 kg
Temperature of a hot adsorber	120°C
Condenser heat rejection temperature	50°C
Loop heat pipe temperature	0°C
Finned evaporator temperature (without loop heat pipes)	-18°C
Heating capacity (W/kg adsorbent)	350

The temperature of the carbon fiber 3 and 8 inside the adsorber 2 and 6 is increasing up to 110–120°C and there is a high-pressure ammonia generation in pores, the process being endothermic.

The superheated ammonia is entering to the condenser 5 (Fig. 2) and is cooling and condensing on the cold surface of the water (A) heat exchanger (Fig. 2). The liquid ammonia (B) enters the porous evaporator 6, or 7 and is stored in the liquid reservoir, disposed inside the evaporator. The first half of a cycle is over. During the second half of a cycle the active water cooling of adsorber 2, or 6 (Fig. 1), (water heat exchanger A) is starting, the sorbent bed temperature is falling down to 20–30°C, and the ammonia pressure is falling down to 0.5 bar or less.

When the pressure in the adsorber becomes lower than the ammonia pressure in the evaporator, the process of the liquid ammonia evaporation inside the porous structure is beginning with intense evaporator wall cooling down to -30°C.

The evaporators 16, 9 (Fig. 2) are thermally connected with the surrounding through the loop heat pipes 11 and 14. Coaxial heat pipe condensers are disposed on the outer surface of the evaporators. Multi-bent heat pipe evaporating part is heating by the air. These two heat pipes are used as a second ammonia circuit thermally connected with the first ammonia circuit (evaporators 16, 9). When the temperature of the evaporator 16, 9 is decreasing and becomes lower than the air temperature, the ammonia evaporation in the heat pipe 11, 14 is starting with further its condensation on the outer surface of the evaporator 16, 9. Heat transfer between the air and cold heat pipe panels is realized by the natural convection, the temperature of heat pipe being lower (-3°C).

Periodical switching on and off the loop heat pipe is realized automatically following the adsorption/desorption cycles of the sorbent bed.

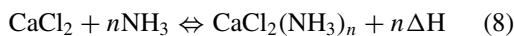
The second alternative is to use finned evaporators and fan to heat these evaporators by the air. Such a device is more compact, but needs to use an electric energy for the fan action.

The total reaction of the cycle (Fig. 8) is practically achieved in 12 min. The temperature evolution of the boiler is synchronized with the temperature evolutions of adsorbers. The boiler has his mean temperature near 110°C during all the cycles. We don't need to switch on and off the heat supply system of the refrigerator, but we need only to cool and heat the sorbent bed periodically, changing the sorbent bed temperature with the help of

the heat pipe condensers and a liquid cooling circuit A (Fig. 2).

Single Stage System (Complex Compound "Busofit" + CaCl_2)

Let us consider the single stage refrigerator, in which the canister is filled with an active carbon fiber "Busofit" + CaCl_2 . Ammonia is a working fluid. The chemical reaction of ammonia with the main sorbent material CaCl_2 is performed as:



The canister during its first half cycle—cooling, is connecting to a heat exchanger (condenser + evaporator). The working fluid accumulated in the evaporator starts to boil, and we have the reaction $L_{(\text{liq})} \rightarrow L_{(\text{gas})}$, $\Delta H_{\text{vap}} > 0$. This reaction is endothermic with cold production in the evaporator. The canister during its first half cycle is operating as absorber, in which the chemical reaction of the gaseous ammonia with CaCl_2 takes place:



The composition of "Busofit" with CaCl_2 as a complex compound sorption media is very convenient, because "Busofit" has 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 specific volume of micropores is 0.48 cm^3/g , with total packing porosity 0.43–0.48. The change of the volume and mass (expansion factor) for CaCl_2 microcrystals disposed on the "Busofit" surface during absorption/regeneration occurs inside the volume of macropores and mesopores of "Busofit" and don't affect the "Busofit" structure. The coupled action of "Busofit" and CaCl_2 increase the thermal conductivity of a system, increase the gas permeability into the interfiber space, increase its sorption capacity to NH_3 , maintain a high porosity of a sorbent bed during the solid-gas reaction and finally increase the performances of a solid sorption refrigerator.

On the photo (Fig. 9) the uniform disposition of the microcrystals on the "Busofit" carbon fiber surface is demonstrated. The experimental isotherms of the complex compound "Busofit"- CaCl_2 are shown on Fig. 5. A strong influence of CaCl_2 on the slope of the isotherms is evident. The experimental set-up to determine "Busofit" + ammonia isotherms was filled with 128 g of CaCl_2 and 248 g of "Busofit". The ammonia sorption capacity of this complex compound at the temperature $T = 20^\circ\text{C}$ and $P = 800 \text{ kPa}$ was 0.604 g/g, the total mass of the ammonia was 227.1 g. "Busofit" had ammonia adsorption capacity 85 g, CaCl_2 had ammonia adsorption capacity 142.1 g. Small part of CaCl_2 (12.5 g) didn't react with ammonia.

The typical curves of the thermodynamic equilibrium of the system $\text{NH}_3-\text{CaCl}_2$ are presented on Fig. 6, the isotherms of the chemical reaction of CaCl_2 and NH_3 are analyzed at $T = 20^\circ\text{C}$ and $T = 40^\circ\text{C}$. On Fig. 9 the isotherms of the complex compound

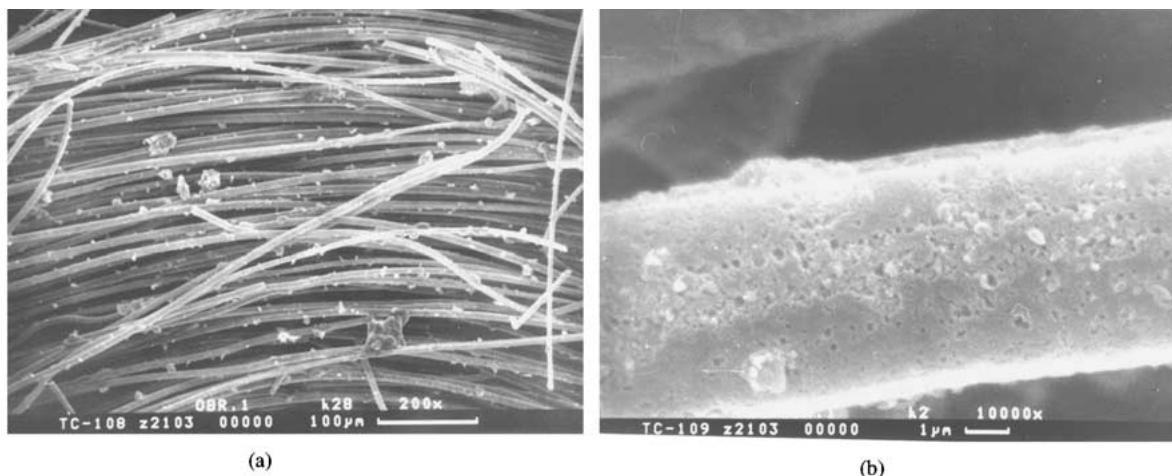


Figure 9. (a) Photo "Busofit + CaCl_2 " multiplied by 200 times; (b) Photo "Busofit + CaCl_2 " multiplied by 10000 times.

“Busofit” + CaCl_2 are shown multiplied on the mass ratio coefficients $\chi_1 = 0.32$ for “Busofit”, and $\chi_2 = 0.68$ for CaCl_2 . The sum of these two isotherms for “Busofit” and CaCl_2 for the temperature $T = 20^\circ\text{C}$ and $T = 40^\circ\text{C}$ can be considered as an integral isotherm, typical for this complex compound. These experimental data testify the independent action of “Busofit” and CaCl_2 during the ammonia sorption, when a physical adsorption and a chemical reaction with ammonia take place.

A calculation based on a 70 min of working of the solid sorption refrigerator leads to a power of about 350 W/kg of the reactive mass. The considered reactive mass is the sum of all the reactants masses: metal chloride + ammonia + active carbon fiber. Note that the utilization of high thermal conductivity carbon fibers can lead to highest power, the use of pitch-based carbon fibers ($\lambda = 100$ to 500 W/m · K) permits to obtain a total reaction in less than 12 min and can give more than 1100 W/kg of the total mass of reactants.

This combination “Busofit” + CaCl_2 in one reactor with the condenser/evaporator is very useful for the designing of the portable and light autonomous cooler for space and hazardous conditions (a self-regulating cooling system to remove metabolic heat from the coolant loop in a life support system used in space activity, or hazardous conditions, like fire, etc.). There is a possibility to perform the temperature and humidity control of the space suit very efficiently (Fig. 10, Table 3).

Table 3. Solar-gas refrigerator (single stage-complex compound) main parameters

Solid-gas adsorber dimensions	$L = 1.2 \text{ m}$
	$D = 0.05 \text{ m}$
Carbon fiber “Busofit” mass in one adsorber	0.75 kg
CaCl_2 mass in one adsorber	0.32 kg
Ammonia mass in one adsorber	0.92 kg
Water mass in one thermosyphon	1 kg
Ammonia mass inside one loop heat pipe	0.05 kg
Total mass of refrigerator	22 kg
Temperature of a hot adsorber	120°C
Condenser heat rejection temperature	50°C
Loop heat pipe temperature	0°C
Finned evaporator temperature (without loop heat pipes)	-18°C
Heating capacity (W/kg adsorbent)	850

Two-Stage System (Complex Compound “Busofit” + NiCl_2 and “Busofit” + BaCl_2)

For this two-stage system there is an internal heat and mass recovery between two sorbent bed (two canisters), filled with different types of a complex compound. The first canister is filled with “Busofit” + BaCl_2 , the second canister is filled with “Busofit” + NiCl_2 . The experimental set up to analyze the two-stage system of

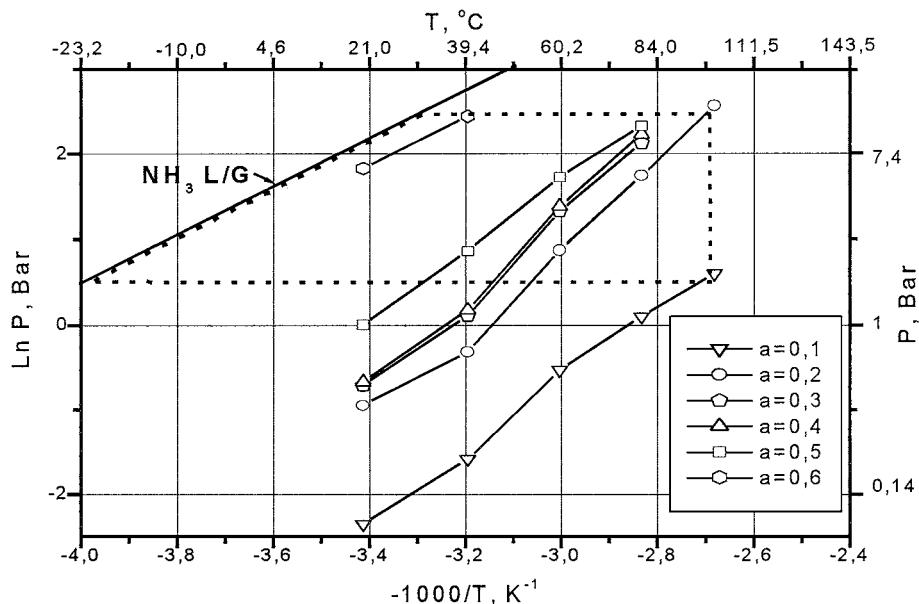


Figure 10. Clapeyron diagram for the complex compound “Busofit” + CaCl_2 and ammonia in the refrigeration cycle.

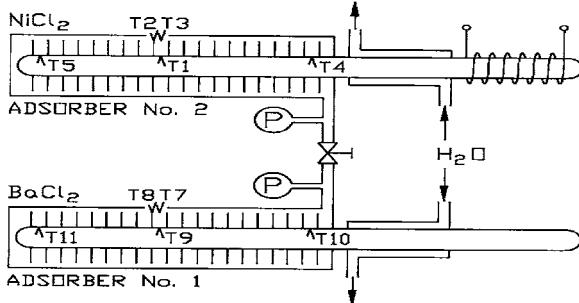


Figure 11. Two-stage solid sorption experimental set-up.

cold generation as resorption refrigerator is shown on Fig. 11.

Following Castaing-Lasvignottes and Neveu (1997) for two salts resorption systems, application of the first and second law of thermodynamic gives:

$$\begin{cases} Q_{\text{reg}}^1 + Q_{\text{abs}}^1 + Q_{\text{reg}}^2 + Q_{\text{abs}}^2 = 0 \\ \frac{Q_{\text{reg}}^1}{T_{\text{reg}}^1} + \frac{Q_{\text{abs}}^1}{T_{\text{abs}}^1} + \frac{Q_{\text{reg}}^2}{T_{\text{reg}}^2} + \frac{Q_{\text{abs}}^2}{T_{\text{abs}}^2} + \Delta_i S = 0 \end{cases} \quad (10)$$

Neglecting internal irreversibility's, for external irreversibility's we have:

$$\Delta_i S^{\text{ext}} = \sum \left(\int \frac{\delta q_i}{T} - \frac{1}{T_i} \int \delta q_i \right);$$

and introducing the entropic temperature term as:

$$\tilde{T} \equiv \frac{\int \delta q_i}{\int \frac{\delta q_i}{T}}$$

We obtain the following system:

$$\begin{cases} Q_{\text{reg}}^1 + Q_{\text{abs}}^1 + Q_{\text{reg}}^2 + Q_{\text{abs}}^2 = 0 \\ \frac{Q_{\text{reg}}^1}{\tilde{T}_{\text{reg}}^1} + \frac{Q_{\text{abs}}^1}{\tilde{T}_{\text{abs}}^1} + \frac{Q_{\text{reg}}^2}{\tilde{T}_{\text{reg}}^2} + \frac{Q_{\text{abs}}^2}{\tilde{T}_{\text{abs}}^2} = 0 \end{cases} \quad (11)$$

$$\begin{aligned} R_1 & \left\{ \begin{aligned} Q_{\text{reg}}^1 + Q_{\text{abs}}^1 &= \Delta Q \\ \frac{Q_{\text{reg}}^1}{\tilde{T}_{\text{reg}}^1} + \frac{Q_{\text{abs}}^1}{\tilde{T}_{\text{abs}}^1} &= \Delta S \end{aligned} \right. ; \\ R_2 & \left\{ \begin{aligned} Q_{\text{reg}}^2 + Q_{\text{abs}}^2 &= \Delta Q \\ \frac{Q_{\text{reg}}^2}{\tilde{T}_{\text{reg}}^2} + \frac{Q_{\text{abs}}^2}{\tilde{T}_{\text{abs}}^2} &= -\Delta S \end{aligned} \right. \end{aligned} \quad (12)$$

With internal heat recovery, the Coefficient of Performance (COP) is:

$$\text{COP} = \frac{(1/\tilde{T}_{\text{abs}}^2) - (1/\tilde{T}_{\text{reg}}^2)}{(1/\tilde{T}_{\text{reg}}^1) - (1/\tilde{T}_{\text{abs}}^1)} \times \left[1 + \frac{\Delta Q}{Q_{\text{reg}}^2} \left(\frac{(1/\tilde{T}_{\text{abs}}^2) - (1/\tilde{T}_{\text{abs}}^1)}{(1/\tilde{T}_{\text{abs}}^2) - (1/\tilde{T}_{\text{reg}}^2)} \right) \right] \quad (13)$$

$$\begin{aligned} \text{COP} &= \frac{1 - (\tilde{T}_{\text{abs}}^2/\tilde{T}_{\text{reg}}^2)}{(\tilde{T}_{\text{abs}}^1/\tilde{T}_{\text{reg}}^1) - 1} + \frac{\Delta S}{Q_{\text{reg}}^2} \frac{\tilde{T}_{\text{abs}}^1 - \tilde{T}_{\text{abs}}^2}{(\tilde{T}_{\text{abs}}^1/\tilde{T}_{\text{reg}}^2) - 1} \\ &= \text{COP} c^{4\tilde{T}} + \frac{\Delta S}{Q_{\text{reg}}^2} \frac{\tilde{T}_{\text{abs}}^1 - \tilde{T}_{\text{abs}}^2}{(\tilde{T}_{\text{abs}}^1/\tilde{T}_{\text{reg}}^1) - 1} \end{aligned}$$

The internal mass and heat recovery in the multi-salt reactor and the external heat recovery by the heat pipe heat exchanger can be realized from high temperature chemical salt pairs in the regeneration phase to a low temperature pairs in the absorption phase. The COP of such a system will be higher than for a simple system without heat recovery.

An active carbon fiber "Busofit" with high permeability, porosity and capillary potential is used as a fast sorbent bed and as a host material for different salts. This carbon fiber insures the uniform distribution of thin (2–3 μm) films of microcrystals on the porous host material surface.

Carbon fiber "Busofit" as a fast sorbent material is reacting with ammonia in the early stage of heating/cooling time (up to 5 min), increasing the pressure in the reactor then salts begin to react as a very effective sorbent bed. "Busofit" as a capillary-porous host material stimulate the salt thin film distribution through the whole volume of a sorbent bed during the regeneration time (ammonia capillary condensation, liquid motion through the sorbent bed due to action of capillary forces). Due to its high permeability the use of "Busofit" is also suitable for sorption cycles coupled with forced convection heating/cooling.

In the conventional thermo-chemical cycles the major entropy production in resorption systems is due to the superheating of vapor during the cold production phase and de-superheating of vapor during regeneration phase, the main part of reaction is used for pressurization and de-pressurization of reactors. In our case "Busofit" acts as a fast reacting material, which decreases the pressure drop between the cold production and regeneration phases thereby increasing the COP

of the system. During the regenerating and cold production phases there is a strong interaction between "Busofit" and the salts, the ammonia migrating from "Busofit" to salts and back. This phenomenon is not yet fully understood and needs further investigation.

Some tests with two small reactors configured as resorption refrigerator and cross over valves were performed, using a simple experimental set-up (Fig. 11). This is made up of two reactors (active carbon fiber, salts and ammonia) with an interconnecting valve between them. The low temperature reactor No. 1 was filled with active carbon fiber "BUSOFIT" (masse 60 g) saturated with BaCl_2 (mass 60 g). The high temperature reactor No. 2 was filled with and active carbon fiber "Busofit" (masse 65 g) saturated with NiCl_2 (masse 70 g).

The low temperature reactor No. 1 was heated/ cooled with a heat transfer device—heat pipe (propane as working fluid). Similarly the high temperature reactor No. 2 was heated/cooling with heat pipe (water as working fluid).

The pressure (Fig. 12) inside two reactors was measured and recorded as a function of time during its heating/cooling. The optimal mass of ammonia inside the system was 56 g, it means that at the room temperature most of the ammonia mass was concentrated in the high temperature reactor No. 2, saturated with NiCl_2 , the equilibrium pressure in the system was equal 1.4 bar. At the time interval $\Delta\tau_1 = 30$ min the heat flow was supplied to the reactor No. 2 through the 100 W heat pipe.

There are four time intervals (Fig. 13) of the system heating/cooling. The first time interval (0–30 min) is related with the high temperature (reactor No. 2) sorbent bed heating and the temperature rise of the heat pipe surface $T_{1,4,5}$, the temperature of the heat pipe fin

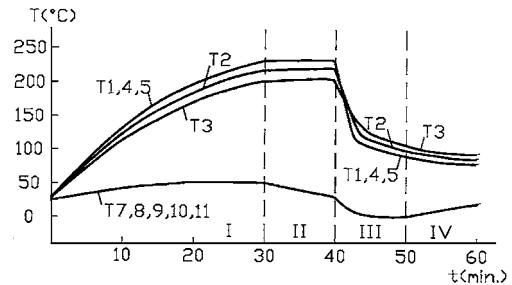


Figure 13. Temperature field evolution inside two-stage reactors during the cycle of the heating/cooling.

end T_2 and the temperature of the reactor surface T_3 . This heating period of time is stimulated by the heat pipe and is a reason of the ammonia desorption from "Busofit" and ammonia regeneration from NiCl_2 .

Simultaneously there is a temperature rise in the second low temperature reactor No. 1 ("Busofit" + BaCl_2) due to the internal heat and mass recovery. The temperature of the heat pipe surface $T_{9,10,11}$, heat pipe fin end T_8 , and reactor No. 1 surface T_7 is increasing up to 50°C and there is a very intense heat transfer during ammonia absorption on BaCl_2 and adsorption on "Busofit" surface. The heat load of the heat pipe is 100 W, the pressure inside the refrigerator is increasing up to 8 bar.

The temperature evolution inside the low temperature sorbent bed (reactor No. 1) is shown on Fig. 4 (for thermocouples positioned on the heat pipe surface, the end of the heat pipe fin and at the reactor surface (7–11)). The temperature drop inside this sorbent bed was less than 1°C due to the very efficient two-phase heat transfer of ammonia. The temperature T_{\max} of the sorbent bed in reactor No. 2 ("BUSOFIT" + NiCl_2) was 240°C. The temperature T_{\max} of the sorbent bed in the reactor No. 1 ("BUSOFIT" + BaCl_2) was 50°C. After 30 min of the reactor No. 2 heating by the heat pipe the source of high temperature energy was switched off and during the second time interval Δt_2 , (Fig. 4) the process of ammonia regeneration (reactor No. 2) and absorption (reactor No. 1) was accomplished in the adiabatic conditions. At the time interval $\Delta t_2 = 10$ min the temperature of the heat pipe (reactor No. 2) was maintained constant 240°C and a cooling water ($T = 18^\circ\text{C}$) was supplied to the heat exchanger of the heat pipe (reactor No. 1) and the sorbent bed temperature was decreased down to 28°C.

At the beginning of the third period of time $\Delta t_3 = 10$ min, (Fig. 13) the water cooling was functioning ($T = 28^\circ\text{C}$) to cool the reactor No. 2 by the heat pipe.

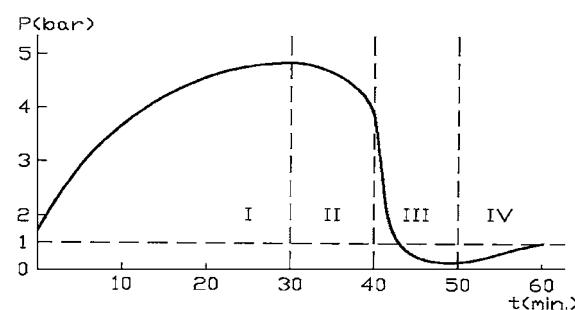


Figure 12. Pressure evolution in the two-stage solid sorption refrigerator during its heating-cooling cycle.

The temperature of the reactor No. 2 surface T_3 , the temperature of the heat pipe surface $T_{1,4,5}$ and the temperature of the heat pipe fin T_2 were quickly decreased down to 100°C (micro heat pipe phenomena is functioning inside the sorbent bed). Simultaneously there was a sharp pressure drop in the system from 5 bars to 0.3 bar followed with the regeneration of ammonia from the chemical and desorption of ammonia from “Busofit” in the reactor No. 1. Very high two-phase heat transfer inside the reactor No. 1 (the same micro heat pipe phenomena) was performed with a small the temperature drop between the sorbent bed and finned heat pipe (T_{7-11}). The temperature of the sorbent bed (“BUSOFIT” + BaCl₂) was decreasing (Fig. 4) from $T = 28^\circ\text{C}$ down to $T = 0^\circ\text{C}$ during 3 min and then was constant during 7 min (the time period $\Delta t_3 = 10$ min).

At the time interval $\Delta t_4 = 10$ min the cooling water circulation through the heat pipe heat exchanger (reactor No. 1) was cut and the water source was supplied to the high temperature heat pipe heat exchanger (reactor No. 2). Within 3 min there was a sharp temperature decrease inside the sorbent bed from $T = 240^\circ\text{C}$ down to 130°C with the water vapor generation (with a temperature drop inside sorbent bed of 40°C), subsequently the temperature field in the sorbent bed remained nearly constant for 7 min.

At the time interval $\Delta t_4 = 10$ min there was a constant water circulation in the heat pipe heat exchanger (reactor No. 2, temperature of the sorbent bed is 80°C) and there was an intense cooling of this reactor. The water was supplied to the low temperature heat pipe heat exchanger (reactor No. 1) to heat a sorbent bed up to the temperature $T = 18^\circ\text{C}$. With this the first cycle of the functional experimental set-up was completed. The all necessary experimental data are presented on Table 4. The refrigeration COP^R of the system during the experiment was 0.44, while the heat pump COP^{HP} was near 1.44. The external heat recovery between the high temperature reactor No. 2 and low temperature reactor No. 1 was realized by the water heat transfer circuit with a small pump (Fig. 12). Water was pumped through the heat exchanger on the heat pipes surface.

ANG vessels (Fig. 14) application as a gas-fired source of energy for solid sorption refrigerators is very attractive (Vasiliev *et al.*, 2000). Autonomous source of energy as ANG vessel with its convenient non-cylindrical shape is unique system for a gas fired solid sorption machines, especially for vehicles. There is a direct similarity between the ANG vessel and solid sorption adsorber of such machine. Both need to be heated during des-

Table 4. Temperature and pressure evolution in the two-stage solid sorption refrigerator (“Busofit” + BaCl₂ and “Busofit” + NiCl₂) as a function of time during the cycle of its heating/cooling.

t (min)	$T_{1,4,5}$ (°C)	T_2 (°C)	T_3 (°C)	$T_{7,8,9,10,11}$ (°C)	P (bar)
0	20	20	20	20	1.4
5	83.3	76.6	68.3	34.2	3.8
10	133.3	125	112.5	42	5.3
15	168.7	158.3	141.6	50	6.4
20	193.8	180.5	160	51.5	7.7
25	215	202	181.2	51.5	7.5
30	231.3	218	198	51.2	7.7
35	231.3	218	198	41.7	7.4
40	231.3	218	198	29.2	6
45	102	110	124.6	1.2	0.5
50	89.6	98	107	0	0.3
55	81.3	90.8	100	7.8	0.6
60	80.1	89	98.5	18	1

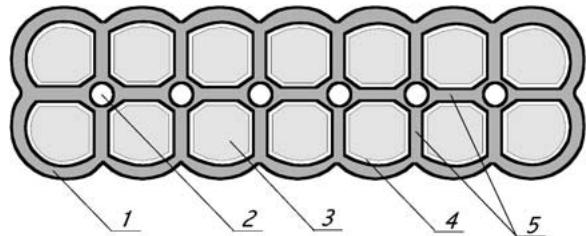


Figure 14. 14 cylinder ANG vessel for methane storage, cross section (1) vessel envelope; (2) heating elements (heat pipes); (3) sorbent bed; (4) gas channels; (5) metal fins to heat/cool a sorbent bed.

orption cycle and cooled during adsorption cycle. The difference is in the time of this cycle. For ANG vessels this time is long (some hours) and for the solid sorption machines this cycle is short (some minutes). The ANG vessel during its discharge could be considered as a heat sink for the solid sorption machine (something like its condenser surface) to increase its COP. Good thermal contact between the ANG vessel and solid sorption machine is essential and can be ensured by heat pipe heat exchangers.

Conclusions

A solar and gas solid sorption refrigerator with 1.8 m² collection surface was designed and studied. The ratio between solar energy and gas flame energy supply is automatically maintained on the total level of 1 kW.

Three modifications of sorbent bed in the reactor of the refrigerator were tested. The first modification was made as a single stage system with pure adsorption ("Busofit"). The dynamic sorption capacity of this refrigerator is 0.35 kg/kg. The second modification was performed as a single stage system with complex compound sorbent bed ("Busofit" + CaCl₂) to combine the physical adsorption and chemical reactions in the same volume in the same time. The dynamic sorption capacity of the second modification is 0.6 kg/kg. The third modification was realized as a two-stage system ("Busofit" + BaCl₂ and "Busofit" + NiCl₂) to increase the COP^R due to the internal and external heat recovery. This cooling system don't need to be used with the evaporator/condenser, due to its functioning in gaseous phase, which is important for the space applications. The first prototype of the refrigerator is an adsorption machine with very short (12 min) non intermittent cycles that uses the active carbon fiber "Busofit" as a sorbent bed and ammonia as a working fluid. The second one is a complex compound sorbent bed ("Busofit" + CaCl₂) machine with the time of a cycle 25–30 min. The COP^R is near 0.43. The third type of the refrigerator is performed as a two-stage system with COP^R more than 0.44. There is considerable scope for the application of such a hybrid gas/solar sorption systems where intermittent, or low solar insolations currently restricts their use. Such a working fluid as ammonia and energy sources like solar/gas are attractive on the environmental ground. Calculations for a combined refrigeration and power-generation system operating on gas/solar energy with heat recovery shows that a COP^R of 0.75 is achievable.

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