EXPERIMENTS ON SOLAR ADSORPTION REFRIGERATION USING ZEOLITE AND WATER

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Abstract - In developing countries there is a growing interest in refrigeration for food preservation. Especially in rural areas, simple solar refrigerators working independently, i.e. not being provided with electrical energy, would be very valuable. Mechanical refrigerators powered by solar cells are available, but are too expensive. In the last years, adsorption refrigerators using water as refrigerant and zeolite as adsorber have been successfully developed. The objective of our project is the use of solar thermal power to regenerate the adsorbent. First, a laboratory apparatus was constructed. The water vapor in the evaporator is adsorbed by zeolite and the water cools down to 0 °C. The zeolite is located in a vacuum tube solar collector which can be heated up to 180 °C by artificial sunlight. In doing so, the water is desorbed and condenses at ambient temperature. After the collector cools down the cooling process can start again. This process was investigated systematically and quantitatively with different kinds of zeolite and silica gel. Typical results are: At 150 °C heating temperature there is a cooling energy of 250 kJ per kg of zeolite. These experimental results constitute the basis for the simulation of a prototype. A storage volume of 125 l could be cooled down by the solar power gained from a collector area of 3 m². Such a refrigerator is simply made of glass and metal, and apart from that, only contains the "natural" materials water and zeolite. Therefore it could be built inexpensively in developing countries and produce cooling power without pollution.

1. INTRODUCTION

In southern developing countries up to 30 % of food is spoilt due to lack of refrigeration during transport and storage because conventional refrigeration systems are not affordable. Furthermore, electric power often is not available in the villages.

In areas with abundant sunshine, solar radiation is the most easily accessible energy source. Solar refrigerators can work independently of the electrical network. In Africa about 1800 solar refrigerators are used to store vaccines (WHO). Usually, cold is produced by a vapor compression cycle, which is driven by electric power gained by solar cells. However, the investment of about US $ 2000 is high and the population cannot afford such systems. In addition, the high-tech production of solar cells and the service of these refrigerators seems to be difficult in developing countries.

Therefore the solar refrigerator must be extremely simple and reliable; the local industries should be able to produce and repair it. In this respect adsorption refrigerators look promising. In the simplest case they consist of two vessels connected by a tube. They need no mechanical or electrical power, and are driven by low temperature thermal energy, which is easily gained by solar collectors. The technology of solar collectors is simpler than that of solar cells and collectors can be built "in a garage".

Especially simple is an adsorption cycle using the solid adsorbent zeolite and the refrigerant water. Both materials are cheap and neutral to the environment.

Early experiments on this were done in 1981 by Guilleminot. In the last years such adsorption refrigerators have been successfully developed by Maier-Laxhuber and Schwarz. These refrigerators are driven e. g. by the thermal waste energy of combustion engines.

The objective of our project is the use of solar thermal power to regenerate the adsorbent. In order to build this system simply, the adsorbent material shall be contained in the solar collector. This way additional heat exchangers, tubes, valves and so on are avoided.

An experimental rig was built to determine the desorption temperatures which can be reached with such a solar collector. Are these temperatures sufficient? How is the coefficient of performance influenced by the ambient temperature and the cooling temperature? Which cooling power can be achieved and which kinds of adsorbents are favorable? Could air in the system cause problems? All these experimental results should enable us to simulate and construct a prototype which is best suited for use in developing countries with great amounts of sunlight.
2. PRINCIPLES

2.1 Adsorbent
Zeolite is a mineral consisting of SiO₂-, AlO₂- groups and alkali-ions. It is capable of adsorbing water vapor and other gas molecules in the cavities of its complex crystal structure. A water content up to 25 % (kg water/kg zeolite) can be adsorbed and then the zeolite is heated up by the adsorption enthalpy. These processes are reversible. By heating up the zeolite to 150 - 250 °C the water can be desorbed. Zeolite is produced synthetically and the crystalline powder is pressed to pellets of about 0.5 mm diameter. Huge quantities of zeolite are produced by chemical industries and used as molecular sieves or for washing detergents.

At minimum, the price is US $ 0.5 per kg. Zeolite does not harm the environment. Obviously, the refrigerant (water) is neutral to the environment and is cheap.

2.2 Adsorption cycle
In principle, the refrigerator may be constructed out of two vessels, the evaporator and the adsorber, which are connected by a tube and a valve (Fig.1). The whole system is made devoid of air. In the evaporator only the vapor pressure of the water is present. When the valve is opened, the water vapor in the evaporator is adsorbed by the zeolite and thus the pressure is reduced. The water starts boiling and cools down to approximately 0 °C. Even undercooled water and ice can be produced. When the adsorbent is saturated, the refrigeration process stops. Now the adsorber vessel is heated up to 100-200 °C. The desorbed water vapor condenses in the connecting tube or in the evaporator at ambient temperature. After several hours the valve is closed and the adsorber cools down to ambient temperature. Then by opening the valve the refrigeration process can start again. In practice the zeolite can be regenerated during the day using solar energy and at night the refrigeration process can be started. The thermal insulation and the thermal capacity of the refrigeration chamber must be sufficient enough to avoid a big increase in temperature during the day. By means of two zeolite vessels a continuous refrigeration process may be realized: one is regenerated, the other is used as adsorber.

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### Table: Zeolite Properties

<table>
<thead>
<tr>
<th>Name of product:</th>
<th>Y-zeolite</th>
<th>Bayer-3A</th>
<th>Grace-4A</th>
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<td>zeolite</td>
<td>silica gel</td>
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<td>A</td>
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<td>K⁺</td>
<td>Na⁺</td>
<td>---</td>
</tr>
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<td>0.25</td>
</tr>
<tr>
<td>Producer:</td>
<td>Slovnaft Czech Republic</td>
<td>Bayer</td>
<td>Grace</td>
<td>Engelhard Germany</td>
</tr>
</tbody>
</table>

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*Fig. 1: Principle of adsorption cycle*
3. THEORY

In a closed vessel filled with zeolite the pressure of water vapor \( p_w \) at equilibrium is a function of the temperature \( T_z [K] \) and the water content \( c [\%] = \text{adsorbed mass of water [kg] / mass of adsorbent [kg]} \). If \( c \) is constant, then \( \ln (p_w, T_z) \) becomes a nearly linear function of the form \((-1/T_z)\). These functions have been measured for different water contents and different adsorbents by Henning and by Maier-Laxhuber and they constitute the basis of our calculation. When the desorption starts the zeolite is nearly saturated with water: "high" load \( c_h \). The desorbed water condenses in the evaporator or in a condenser. There the vapor pressure is equal to the saturation vapor pressure of water \( p_s \) at ambient temperature \( T_a \). The process stops when equilibrium is reached. Then the "low" load \( c_l \) of the zeolite causes a vapor pressure in the adsorber which is equal to the pressure in the condenser.

\[
p_w(c_l, T_z) = p_s(T_a) \tag{1}
\]

Both functions are known, \( T_z \) and \( T_a \) are measured, so the equation can be solved for \( c_l \). During refrigeration the water vapor is adsorbed by the zeolite while at ambient temperature \( T_a \). The adsorption stops when the zeolite is saturated containing the "high" water content \( c_h \). At equilibrium the pressure in the adsorber is equal to the saturation vapor pressure of the refrigerant at the temperature \( T_c \) ("cold").:

\[
p_p(T_c) = p_w(T_c, c_h) \tag{2}
\]

From this equation \( c_h \) can be calculated. In the adsorption cycle the mass of water \( m_w \) is adsorbed by the mass of zeolite \( m_z \):

\[
m_w = m_z (c_h - c_l) \tag{3}
\]

If \( m_w \) is evaporated, the refrigerant is cooled down by the cooling energy \( Q_c \):

\[
Q_c = r m_w \tag{4}
\]

\( r \): enthalpy of vaporization

Using these equations the specific cooling energy per mass of adsorbent \( q_c \) was calculated as a function of the heating temperature \( T_z \). In this calculation the cooling temperature and the ambient temperature were set constant: \( T_c = 30 \, ^\circ C \) and \( T_a = 0 \, ^\circ C \). Fig. 5 and fig. 6 show the results for two kinds of zeolite and silica gel. However, the resulting \( Q_c \) is not exactly equal to the maximum cooling power of the refrigerator, because the desorbed refrigerant and the evaporator vessel must also be cooled down by \( Q_c \).

4. EXPERIMENT

4.1 Experimental apparatus

The experimental setup is shown schematically in fig. 2 and as a photo in fig. 3. The sun simulator consists of three lamps with 1200 W electric power ( bulb type Osram HGI-T400/DH). The spectrum is similar to the solar spectrum and the incident irradiation in the plane of aperture is 300 W/m². This radiation is focused onto a vacuum tube collector by a parabolic mirror.

4.2 Starting procedure

500 g of dry adsorbent pellets are soaked by a known mass of water and placed into the solar absorber. Then the vacuum pump is started and the zeolite is heated up by the solar simulator. The desorbed water condenses in the condenser which is held at 10 °C and the water drops fall into the evaporator. One part of the water vapor is pumped out and this water condenses in a cooling trap and can be measured. After six hours the valves are closed and the "sun" is switched off.
In the following course of the experiment the vacuum pump is not used again. When the collector has cooled down to ambient temperature, the valve between collector (adsorber) and evaporator is opened and the first refrigeration process is started. By this procedure the desired status of the experiment has been reached: The air is pumped out and the water mass in the apparatus is known.

4.3 Experimental cycle
The experimental cycle corresponds to the proposed adsorption cycle of the solar refrigerator working without a vacuum pump. As an example, the measured temperatures of one experiment are shown as a function of time in fig. 4. In the beginning, the zeolite was saturated with water ($c_h = 20\%$). The solar collector was heated up by the solar simulator and after six hours the temperature of the zeolite reached $175\,^\circ C$. The water vapor pressure was 50 mbar. The condenser was not cooled and the water vapor condensed at approximately $30\,^\circ C$. During this process the water content decreased to $c_l = 8\%$. At $t = 6\,h$ the valve was closed and the "sun" was switched off.

At $t = 8\,h$ the collector had cooled down and by opening the valve the refrigeration process was started. Due to the adsorption enthalpy the temperature of the zeolite increased up to $70\,^\circ C$, at which point the rate of adsorption decreased and the adsorber temperature slowly tended to ambient temperature. The refrigerant was quickly cooled down to $-3\,^\circ C$ (undercooled water). Over time the cooling power decreased and due to the heat flow from the surroundings the temperature of the refrigerant slowly increased to $10\,^\circ C$ after 12 hours.

This experimental procedure was repeated for different desorption temperatures and different kinds of zeolite as well as one kind of silica gel.

5. RESULTS
During experiments, some temperatures were nearly constant. The cool temperature $T_c$ of the refrigerant depends on the rate of evaporation and the heat flow from the surroundings. $T_c$ varied between 0-10 $^\circ C$. According to our calculations, its influence on the cooling energy is negligible. These values of $T_c$ are sufficient for the cooling of food.

The condenser is cooled by the surrounding air and the condenser temperature was always approximately $T_a = 30\,^\circ C$, slightly higher than room temperature ($25\,^\circ C$).

The temperature of the zeolite increases in the beginning of the adsorption process, but later on it tends to $T_a = 30\,^\circ C$.

The maximum water content $c_h$ depends on $T_c$ and $T_a$, both of which were nearly constant in all experiments. The measured $c_h$ lies between 16-20 $\%$ for all kinds of zeolite. The maximum water content of silica gel was lower: $c_h = 16\%$.

The low water content $c_l$ depends on the heating temperature $T_z$ and the constant condenser temperature. For all kinds of examined adsorbents $T_z$ was varied between 90 and 180 $^\circ C$.
There is nearly no desorption from zeolite at $T_z = 90\,^\circ C$. At $T_z = 170\,^\circ C$ cl descends to 6-8%. Silica gel can be regenerated at lower temperatures: $c_r = 7\%$ at $T_z = 90\,^\circ C$ and $c_r = 2.6\%$ at $T_z = 170\,^\circ C$. The most important result is the cooling energy $Q_c$, which is equal to the evaporation enthalpy of the adsorbed mass of water. In fig. 5 and fig.6 the experimental results for $q_c$ (cooling energy/mass) are shown as a function of heating temperature.

The total pressure $p$ in the apparatus was registered by the datalogger. Generally when the adsorber is heated, $p$ is approximately 70 mbar, while the saturation pressure in the condenser is 40 mbar at 30 $^\circ C$. During adsorption $p$ is lower than 2 mbar while the saturation pressure in the evaporator is i.e. 10 mbar at 7 $^\circ C$.

The total pressure may increase due to leaks or desorption of air from inner surfaces. The air molecules are then adsorbed by the zeolite and the adsorption of water molecules is reduced. Furthermore, the boiling temperature of the refrigerant increases and the rate of evaporation decreases. In order to test this influence air was let in the apparatus by means of a valve. A partial pressure of air $p_L = 10$ mbar reduces the cooling power significantly and at $p_L = 20$ mbar the cooling power is nearly zero.

In addition, the efficiency of the whole system depends on the efficiency of the solar collector. The thermal capacity of the collector was calculated according to the masses of metal, zeolite and glass. When the solar simulator was switched off, the solar collector cooled down and the temperature was measured as a function of time.

With the known incident radiation as well as all the previous results, the parameters of our solar collector could be calculated. The optical efficiency is $\eta_0 = 0.85$ and the heat loss coefficient for the cylindrical surface of the collector is $k = 2.6$ W/(m²K).

**Fig. 4: Typical results of experimental cycle**

![Graph showing temperature vs. time for Zeolite and Water](image-url)
6. DISCUSSION

The cooling energy per mass, which has been calculated theoretically, is shown in fig. 5 and fig. 6 as a function of heating temperature. In the same figures the experimental results are also shown. In experiment and in the theoretical calculation the cool temperature $T_c$ is approximately 0-5 °C.

The condensation temperature and the temperature of the zeolite during adsorption are $T_a = 30$ °C.

The theoretical cooling energy of the Y-zeolite is based on the experiments of Maier-Laxhuber. The experimental results with the Y-zeolite should fit to these results.

We did other experiments with Bayer 3A and Grace 4A. These kinds of zeolite have a width of the pores of 3 nm and 4 nm respectively. Our theoretical result for Na-5A zeolite is based on experiments of Henning. This kind of zeolite has a width of the pores of 5 nm and therefore the results should be comparable to our experiments with Bayer 3A and Grace 4A.

In all experiments the cooling energy only amounts to approximately 70 % of the theoretical value. The theoretical calculations are based on the equilibrium water vapor pressure of zeolite which is reached after an "infinite" time. However, the adsorption and desorption processes in this experiment were stopped after several hours. Therefore the adsorbed mass of water and the resulting cooling energy are lower than predicted by theory. Taking this into account, experiment and theory correspond satisfyingly. The dependence of cooling energy on heating temperature is similar in theory and in experiment.

These results may be summarized as follows. If zeolite is used as adsorber, a heating temperature of 100 °C is too low to desorb water, whereas temperatures higher than 200 °C do not increase the cooling power any more. Hence desorption temperatures of 120-180 °C are necessary. The comparison of the results of the different kinds of zeolite shows that the examined zeolite with Y-structure gives higher cooling power than the A-zeolite. That may be caused by the different size of the pores in the crystal structure.

In fig. 6 the theoretical and experimental results for silica gel are shown. The theoretical calculation is based on the experiments of Henning. Our experiment was done with a different kind of silica gel and therefore the comparison between theory and experiment can only be approximate. Here, temperatures of 90 - 110 °C are sufficient for desorption and the maximum of cooling power is reached at 150 °C desorption temperature. Thus, silica gel is to preferred as adsorber if the temperatures are in the range of 100-150 °C. However, in our experiments the adsorption rate of water vapor by silica gel was significantly lower than the adsorption by zeolite. The resulting cooling power was lower and the temperature of the refrigerant only went down to 10 °C in contrast to 0 °C and below in the case of zeolite.

In contrast, higher cooling power is achieved with zeolite if temperatures greater than 150°C can be reached.
In the course of our work a lot of experimental data was obtained which could only be described partially in this publication. This experiment has shown us what pitfalls to avoid. The data together with our experience constitute the basis for the following approximate simulation of a prototype. The cooling chamber is a cube of volume 0.125 m³. It is thermally insulated by a layer of polystyrol which is 20 cm thick. The temperature in the cooling chamber is assumed to be 0 °C, the ambient temperature 30 °C. By heat conduction 0.3 kWh thermal energy flow through the walls per day. In addition, 20 kg of meat, having ambient temperature, are put into the refrigerator constituting a cooling load of 0.7 kWh. In total, the cooling load is 1 kWh per day.

The adsorption refrigerator is characterized by the following parameters: The solar collector consists of four vacuum tubes of 20 cm diameter, each 2 m long. The tubes together contain 16 kg of zeolite. The area of aperture is 3 m² and parabolic reflectors behind the tubes focus the whole incident radiation onto the tubes. These parabolic trough collectors need not be adjusted during the day. The solar collector used in our experiment has an efficiency of 30 % at 150 °C. If we assume a mediocre solar irradiance of 4 kWh/(m²d), we gain 4 kWh thermal energy per day. 2 kWh of which are used to heat the collectors and the contained zeolite mass up to 150 °C. The desorption energy is higher than the evaporation enthalpy and the remaining thermal energy of 2 kWh is able to desorb 1.5 kg of water. The vapor streams through a tube and an open valve into the condenser, which is cooled by the surrounding air of approximately 30 °C. Due to the condensation enthalpy, the temperature in the interior of the condenser is somewhat higher, i.e. 35 °C. The heat exchanging surfaces must be large enough to minimize this difference, because the condensation temperature has a great influence on the efficiency of the adsorption cycle.

The desorbed water is accumulated in the condenser. In the late afternoon the valve between condenser and solar collector is closed and the collector cools down to ambient temperature.

At night, a second valve at the bottom of the condenser is opened and by force of gravitation the water flows through a tube into the cold evaporator. Then the valve between condenser and solar collector is opened as well. The water vapor streams from the evaporator to the solar collector and is adsorbed in the zeolite.

In the course of the night, the former desorbed water mass of 1.5 kg is now re-adsorbed and thus the needed cooling energy of 1 kWh is produced.

The evaporator has to be constructed in such a way that the surface of the refrigerant is approximately 40cm x 40 cm. By cooling down to 0 °C, the water is frozen and a thickness of ice of 4 cm may easily be achieved. Thus, approximately 5 kg of ice have been produced. The next day, the solar collector is heated up again and during the day no cooling power by adsorption is available. By means of the stored mass of ice a cooling energy of about 0.5 kWh is provided and a temperature increase of the cooling chamber is avoided.

By means of thermostatic valves the operation of the whole adsorption cycle may be done automatically.

In case of vacuum problems the refrigerator could be equipped with a manually operated vacuum pump to restore the vacuum every few days.

8. CONCLUSIONS

It has been proven, that cold can be produced by a very simple...
adsorption cycle using zeolite as adsorbent and water as refrigerant. The adsorbent material is contained in a solar tube collector developed by the authors. A solar irradiation of 300 W/m² is sufficient to reach desorption temperatures of 170 °C. The resulting cooling energy density is 350 kJ/kg zeolite and the COP is 8 % (cooling energy/ solar energy). However, a partial air pressure of about 10 mbar may cause problems. Silica gel can be regenerated at lower temperatures but the cooling power is lower. The experimental results and the theoretically calculated cooling power correspond satisfactorily. On this basis a prototype was simulated: In a sunny region a solar collector area of 3 m² is sufficient to power a small household refrigerator. Our next step will be the actual construction of the prototype we have simulated.

REFERENCES

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Report:

Thesis:

Thesis:

Private Communication:

ACKNOWLEDGEMENTS:
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Wolf M. (1999)

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