

## **SORPTION MATERIALS FOR APPLICATION IN SOLAR HEAT ENERGY STORAGE**

*P. Gantenbein, S. Brunold, F. Flückiger, U. Frei*

*Institute für Solartechnik SPF, University of Applied Sciences Rapperswil, Switzerland*

Phone: ++41(0)55 2224811, Fax: ++41(0)55 2106131, Internet: [www.solarenergy.ch](http://www.solarenergy.ch)

### **ABSTRACT**

Solar energy can be used in seasonal heating systems. The high amount of energy available in summer time is stored in water storage tanks for use in wintertime. In the case of well-insulated one family houses, with a yearly heat demand for domestic hot water and space heating of about 5000 kWh, water tanks with a volume in the range of 40 to 80m<sup>3</sup> have to be installed. To reduce the heat losses of the storage tank, an excellent thermal insulation is needed. So a heat loss free storage system with a high energy density is desirable. Using sorption materials for water vapour this task may be solved. Sorbent materials with a high uptake of water vapour and a high differential heat of adsorption should be selected. To integrate sorption energy storage systems in solar hot water plants sorbents with a low regeneration/drying temperature of maximum 200 °C should be used. During the charging mode in summer time water molecules are desorbed by heating (drying) the sorbent while in the discharging mode in cold seasons water vapour is adsorbed on the sorbent and the heat of evaporation and the binding energy is released. For sorbents with the necessary physical properties the known molecular sieves zeolite and silica gel are promising candidates. These two materials have theoretical energy densities of 220 kWh/m<sup>3</sup> (silica gel) and 188 kWh/m<sup>3</sup> (zeolite). But it has to be mentioned that in a sorption process the heat of evaporation of water has to be supplied by a heat source and the energy densities have to be seen in perspective. Two different system types – open and closed – are known. Sorption energy storage pilot plants are operating with either zeolite 13X (open) or with silica gel (closed).

In an open system in the ideal case the heat of evaporation for water can be supplied by ambient air of high humidity.

Open sorption storage systems for heating preferentially operate with zeolite 13X. In a wide range of air humidity zeolite 13X has the highest sorption capacity of water and a high differential heat of adsorption. So in our system we apply zeolite 13X to adsorb water vapour. The energy supply for the sorbent in the drying process and the drying time depend on the amount of adsorbed water and the desired charging level i.e. rest water content of the sorbent after drying. In the discharging mode a delay time for hot air coming out of the sorbent bed depends on the sorbent bed height. Zeolite 13 X has a short reaction zone length.

## INTRODUCTION

For long-term storage of solar thermal energy water tanks with volumes of more than  $50 \text{ m}^3$  are used [1, 2, 3]. To reduce energy loss due to the temperature difference of inside the tank and the surrounding outside of the tank thermal insulating materials have to be installed. Alternative ways to reduce the volume of seasonal heat energy storage tanks and to have a quasi loss free storage are the concepts of adsorption of water vapour on sorption materials like solid molecular sieves and silica gel. Heat energy densities in range of  $200 \text{ kWh/m}^3$  for zeolite [4] and  $230 \text{ kWh/m}^3$  in silica gel [5] are reported in the literature. Depending on the assumed temperature difference in a hot water storage tank these values are a factor of about 3.5 to 4 higher than for the conventional hot water tank. In the past few years sorption materials were applied for storage purpose in pilot plants [6, 7].

The two materials sorbent (molecular sieves, silica gel) and sorbate (water / water vapour) are kept in two different storage tanks. In the discharge mode the water vapour is adsorbed on the sorbent and the heat of evaporation and the binding energy is released. In the charging mode the sorbent has to be dried at elevated temperatures. The heat energy in the charging mode and the heat of evaporation in the discharging mode has to be supplied by an external heat source. This heat source can be a thermal solar collector as shown in Fig. 1. Sorption storage systems are thought to deliver the necessary heat at the time it is needed and as long as sorbent and sorbate are kept separate the energy storage is loss free. Such systems can be realised in an open or in a closed configuration. By supplying the open system with humid outdoor air the heat of evaporation comes from the environment. While in the evacuated closed system the heat of evaporation has to be supplied by a heat source like a thermal solar collector [5], Fig.1.

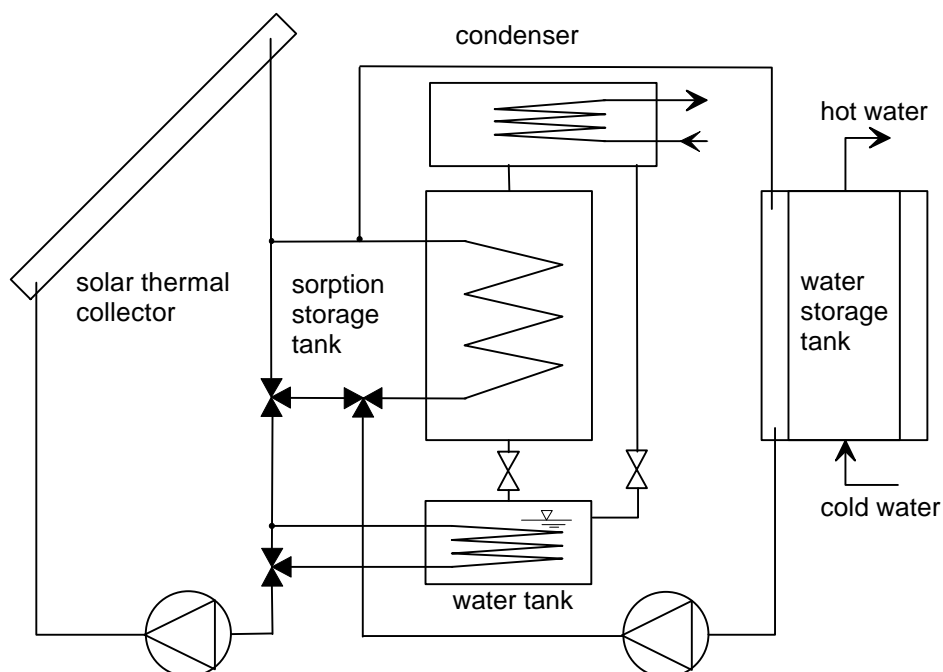


Fig. 1: Sketch of a closed solar sorption storage system with a puffer hot water storage tank.

Based on an assumed temperature difference of  $50 \text{ }^\circ\text{C}$  the calculation of the energy density of a hot water storage tank is shown. Then we show an estimation of the

theoretical heat energy density in sorption materials. After presenting a list of selection criteria's for sorption materials for solar heat energy storage the example of zeolite as a potential candidate is shown. Because of the high potential of sorption materials and the possibility to integrate sorption storage tanks in solar hot water systems we set up a "pseudo" open system. The first results are presented.

## **HOT WATER AND SPACE HEATING IN A ONE FAMILY HOUSE**

Combined systems for domestic hot water and space heating without an auxiliary heater, have to deliver all year round a temperature level in the range of 40 °C to 60°C, depending on the comfort needs of the inhabitants.

In an excellently insulated single family (4 persons) house in Central Europe, the energy need for hot water and space heating is about 5000 to 8000 kWh per year.

The solar system including the sorption storage tank has to be designed to meet this demand.

## **ENERGY STORAGE IN WATER STORAGE TANKS**

In case of storing heat energy in water the density of energy is calculated by:

$$Q_d = (c_p(T) \cdot \rho(T) \cdot \Delta T)_{\text{water}}, \quad (1)$$

Where  $c_p(T)$  is heat capacity of water,  $\rho(T)$  is the density of water (for data see [8]) and  $\Delta T = T_o - T_u$  is the temperature difference of the water at the storage level  $T_o$  (90 °C) and the "user temperature"  $T_u$  (40 °C). With this temperature levels the energy density  $Q_d$  in a water tank is 57 kWh/m<sup>3</sup>. So with the assumption of "seasonal" heat energy storage the average water volume for a storage tank is 50 m<sup>3</sup> (season: 180 days; 16 kWh per day; no additional heat source like solar collectors).

The loss of energy by heat conduction, convection and radiation depends on the temperatures inside the storage tank and the surrounding of the tank. To suppress the heat loss out of the tank a thermal insulation has to be installed. The thermal insulation leads to an increase of the total volume of the storage tank system.

## **ENERGY STORAGE IN SORPTION SYSTEMS**

In the sorbent - sorbate system the heat of evaporation  $\Delta h_v$  and the binding energy  $\Delta h_B$  are released by bringing together the two materials in time heat energy is needed. Ideally this gives the possibility of a loss free energy storage because in the tank no high temperature level has to be kept for long time. But in real sorption system the thermal loss will depend on the design i.e. the specific heat of the apparatus and the operating temperature level.

The heat of adsorption ( $\Delta h_A = \Delta h_v + \Delta h_B$ ) of water vapour on silica gel and on alumina reaches approximately 11 kcal (45 kJ) per mole water while zeolite reaches a value of approximately 15 kcal (62 kJ) per mole water [9]. So with a mass density in the range of  $\rho(\text{sorbent}) = 400 - 780 \text{ kg/m}^3$  in a silica gel sorbent bed with spherical pellets and a water uptake of  $c(T, p) = 40 \text{ wt.}\%$  the heat energy density;

$$Q_d = \Delta h_A \cdot \rho(\text{sorbent}) \cdot c(T, p) \cdot (1000/M_{\text{water}}) \cdot (1/3600), \quad (2)$$

reaches values from approximately 110 kWh/m<sup>3</sup> to 220 kWh/m<sup>3</sup>. For a zeolite 13 X pellet bed with an average mass density  $\rho$  (sorberent)= 650 kg/m<sup>3</sup> and a maximum water uptake of  $c(T, p) = 30$  wt.% the heat energy density is approximately 188 kWh/m<sup>3</sup>. These values are 2 to 4 times higher than for a water storage tank. But it has to be mentioned that in a sorption process the heat of evaporation of water has to be supplied by a heat source and the energy densities are put in perspective. In real sorption materials  $c(T, p)$  and  $\rho$  (sorberent) strongly depend on the morphology and it is obvious that the numbers for the heat energy densities are theoretical values.

In sorption storage systems the conditions of the sorption material like the regenerating temperature and operating temperature  $T(z)$  and load  $c(T, p)$  at this two temperature levels have to be considered. As well as one has to keep in mind that besides water molecules in an open system the adsorption of other molecules (O<sub>2</sub>, N<sub>2</sub>, CO<sub>2</sub>, ...) will occur.

The lower heat of adsorption for silica gel leads to a lower regeneration temperature of about 150 °C in charging mode. For zeolite, to achieve a water content  $c(T, p)$  lower than 2 wt.%, the regeneration temperature is in the range of 200 °C or even higher.

The heat of adsorption (adsorption enthalpy) released in the discharging mode from load  $c(1)$  to the load  $c(2)$  is calculated as follows:

$$\Delta h_A(T, p) = \int_{c(1)}^{c(2)} \Delta h_d(T, p) dc, \quad (3).$$

Where  $\Delta h_d(T, p)$  is the differential heat of adsorption i.e.  $\Delta h_d = d\Delta h_v + d\Delta h_B$ . The differential heat of adsorption  $\Delta h_d$  has a hyperbolic like dependence on the load  $c(T, p)$  of the sorberent [6] and reaches the value of  $\Delta h_v$  of water because at high coverage no more binding sites for water molecules on the sorberent are free and the adsorption resembles the liquefaction of water vapour. This is an important hint for an optimum operation temperature of the sorption system, because the heat of evaporation of water strongly depends on the temperature -  $\Delta h_v$  (40 °C) = 2406 kJ/kg and  $\Delta h_v$  (100 °C) = 2257 kJ/kg [8].

While depending on the time between the charging mode and the discharging mode the sensible heat of the sorberent  $Q_S = (c_p(T)_{real} * \rho(T) * \Delta T)_{sorberent}$  is lost because the sorberent bed and the storage tank is cooling out. The dry sorberent zeolite 13 X has for  $c_p(T)$  approximately 1.07 kJ/kgK and for  $\rho(T)$  approximately 650 kg/m<sup>3</sup>.

## SELECTION OF THE SORPTION MATERIAL

The layout and the design of a sorption system depend on the task it has to fulfil. The selection of the sorption material has to be done considering following aspects. As mentioned above a high heat of adsorption is desirable. But high values of this physical property are leading to high drying temperatures in the charging mode. The temperatures have to be achieved in our case by thermal solar collectors. A high surface area and a high porosity of the sorberent are leading to a high uptake of water vapour. In Table 1 a list of selection criteria is shown.

Table 1: Criteria for the selection of the sorption material.

- High uptake of water (operating temperature level)
- High adsorption energy (chemisorptions)

- High energy density (thermal energy density at the operating temperature)
- Regeneration by heat (solar thermal)
- Low regeneration temperature (physisorption)
- Low regeneration time
- Length of the active bed (sorption characteristic)
- Ageing behaviour (high number of cycles)
- Transport form (granular, bulk, layers – problem of heat and mass transfer)
- Easy to handle
- Low costs

The criteria listed above are partly contradictory and an optimum has to be found.

The surface area per weight of three different sorbents is:

Silica gel 750 – 850 m<sup>2</sup>/g; zeolite 500 – 800 m<sup>2</sup>/g; alumina 250 m<sup>2</sup>/g [9].

### OPEN VERSUS CLOSED SYSTEM

Heat energy storage sorption systems can be designed in two different configurations:

- Open – sorbent, sorbate (water) and air for heat and mass transport [4, 6]
- Closed – sorbent and sorbate (water) in an evacuated system [5, 7]

Each of these system types has its advantages and its disadvantages and the selection of appropriate sorbent is very important. In the open system air is the heat and water vapour transporting fluid. But in the closed evacuated system no fluid is

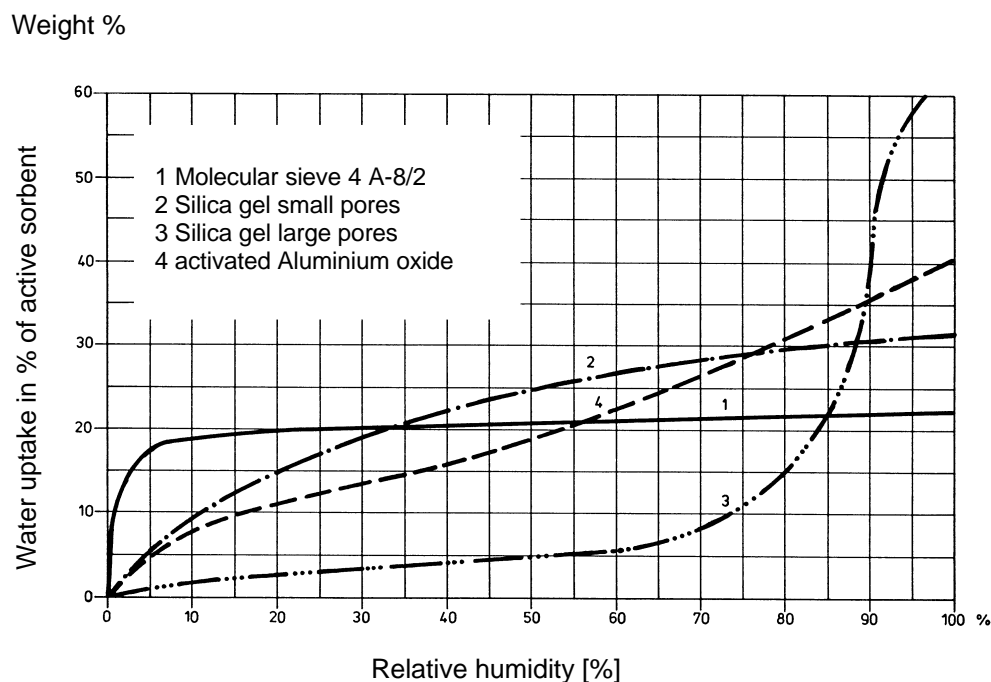


Fig 2: Water uptake  $c(T, p)$  of different sorbents depending on the relative air humidity at  $T = 25 \text{ }^\circ\text{C}$  and  $p_{\text{max}} = 2340 \text{ Pa}$ . Data form CU Chemie Uetikon AG.

supporting the heat transfer and either special heat exchanger have to be installed [5, 7] or the heat exchangers have to be coated by sorption material.

Weight %

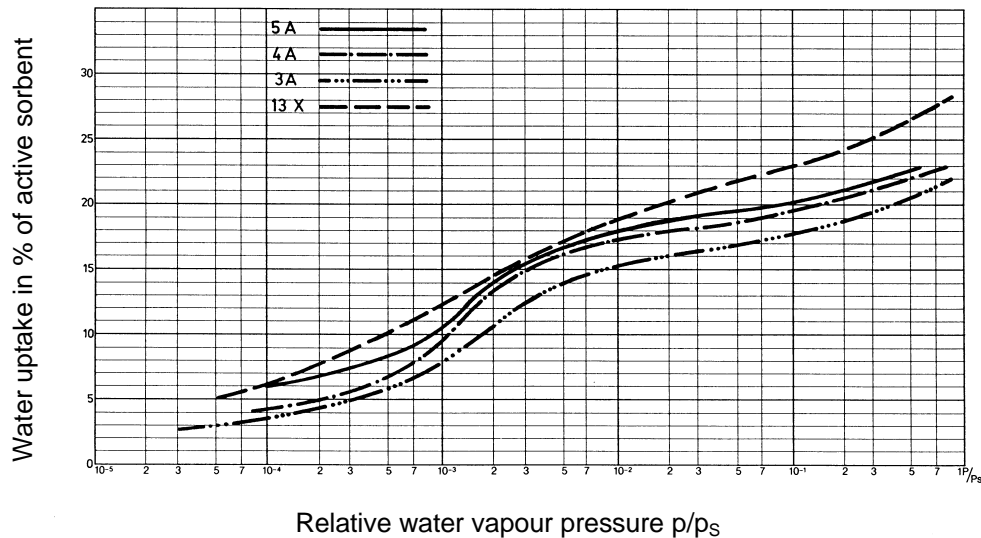


Fig 3: Water uptake  $c(T, p)$  of different zeolites depending of the relative air humidity at a temperature of 25 °C. 13 X has the highest sorption capacity. Data from CU Chemie Uetikon AG.

In relation to the selection of the sorbent for these system types in Fig. 2 the uptake of water vapour depending on the air humidity of different sorbents are shown. And while we favour one sorption material the water uptake strongly depends on their preparation i.e. surface area and porosity, Fig. 3.

In an open system with zeolite as sorbent the water uptake is highest for air humidity lower than approximately 35 % r.h. while in the range of air humidity higher than 35 % r.h. the uptake is higher with silica gel.

Water vapour is the only gas in the closed and evacuated system, so the total pressure is equal to the partial pressure of water vapour. And in this case the uptake of water vapour by silica gel is higher than the uptake of water vapour by zeolite. But what also can be seen in the Fig. 2 (curve 2 and 3) the pore size of the material is very important.

## RESULTS OF OUR PSEUDO OPEN SYSTEM

For starting our work on sorption storage systems we set up an experimental “pseudo” open system to measure temperature profiles, flow of air, and flow of water and relative air humidity. The idea is to find out the behaviour of the system under defined initial conditions. And based on these results we are able to formulate the necessary operation parameters to reach the desired output temperature of the hot water. The airflow was set to 50 m<sup>3</sup>/h. This results in air speed of 0.2 m/s in the empty tube and thus to a Reynolds number of 23.3 for the used particles with a diameter of 2.5 mm.

In the discharging mode the first part of the sorption bed is heated by adsorption of water vapour and the hot air is transporting this energy to the rest of the sorption bed. Which means that the sensible heat first has to be supplied to the sorption storage material. So after a delay time of about 12 minutes hot air is transporting energy to the

heat exchanger, Fig. 5. This means that the sorption front and the temperature front are moving through the sorption bed with a certain speed depending on the air mass flow and humidity of the air. In our system the high temperature front moves with a speed of 3 to 4 cm/min. The total heating time is in the range of 92 Min. But while the temperature  $T_{13}$  of the outlet air is higher than  $80\text{ }^{\circ}\text{C}$  the first zones of the sorption bed ( $T_9$ ) are cooling down to the temperature  $T_4$  of the inlet air.

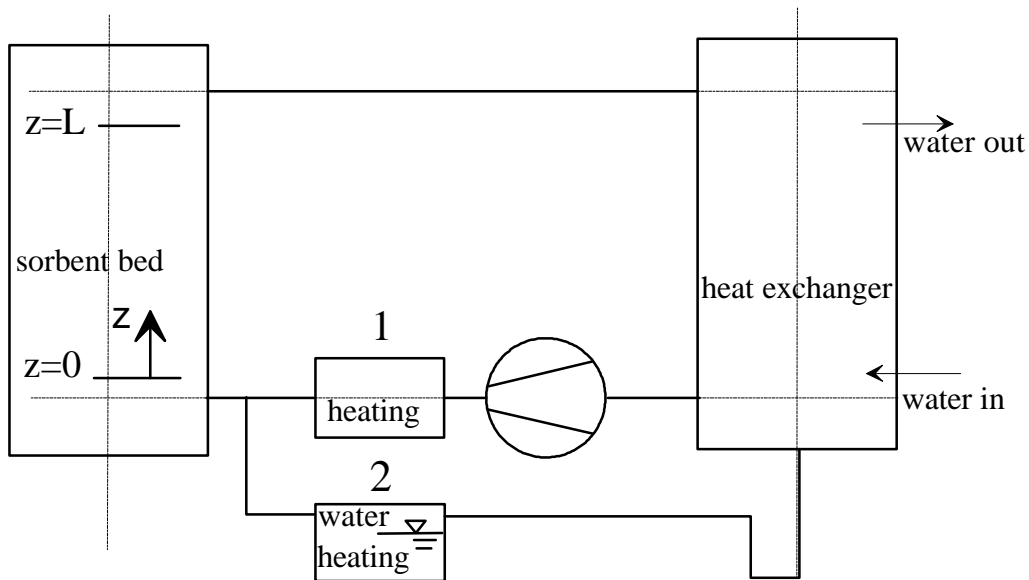


Fig 4: Sketch of the “pseudo” open sorption storage system with air for transporting heat and water vapour. Heating 1 is for the charging mode and heating 2 for the discharging mode. They will be replaced by a solar thermal heating.

Fig. 6 shows the charging mode at an inlet air temperature of  $100\text{ }^{\circ}\text{C}$ . The temperature  $T_{13}$  of the outlet air has two characteristic time regions. For the first 75 Min a stationary state at a temperature of slightly lower than  $50\text{ }^{\circ}\text{C}$  is reached after a delay time of approximately 12 to 16 Min. In this time the sorbent bed is heated and lifted the temperature level at which the total mass transfer from the zeolite bed to the air is constant. In the second region of the temperature  $T_{13}$  curve an increase of the temperature can be observed. At these conditions the sorbent bed is drying out and the drying speed is decreasing. The outlet air temperature increases up to  $92\text{ }^{\circ}\text{C}$  and the drying time is approximately 7 hours.

Looking at the steep ascent in the temperature profile  $T_{13}$  (Fig. 5) a steep descent of the load front  $c(T, p, z)$  (where  $z$  is the geometrical coordinate in the sorption bed with  $z=0$  at the entrance and  $z=L$  at the exit, Fig. 4) in the zeolite 13 X sorbent bed can be concluded. This means that zeolite 13 X has a short mass transfer zone (active bed).

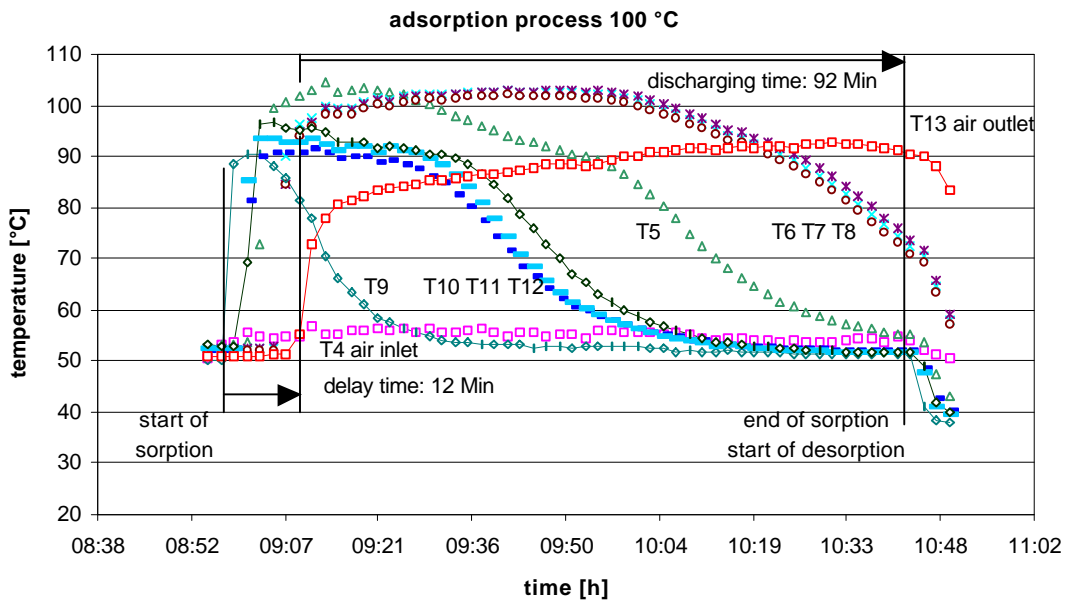


Fig. 5: Adsorption / discharging process in the zeolite 13X sorbent bed with spherical pellets. Temperature profiles in the sorbent and in the heat and water vapour transporting air. For the position of the temperature sensor T4 to T13 see Fig. 6.

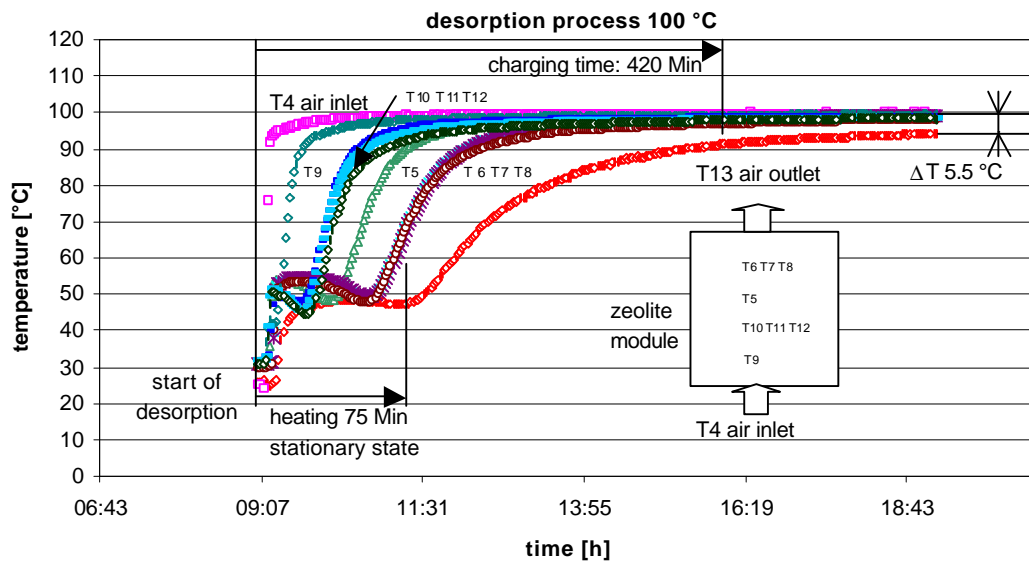


Fig. 6: Desorption / charging process at 100 °C inlet air temperature in the zeolite 13X sorbent bed with spherical pellets. Temperature profiles in the sorbent and in the heat and water vapour transporting air.



## CONCLUSIONS

In solar energy storage systems sorption materials like zeolite and silica gel can be applied. A choice of the appropriate sorbent has to be taken. In our zeolite 13X – water vapour sorption system charging and discharging modes can be simulated under specific experimental initial conditions. The time of discharging the sorption bed is shorter than the time of charging. Zeolite 13 X has a short reaction zone moving with a speed of 3 to 4 cm/min through the sorbent bed. At the chosen air flow and air humidity the heat and mass transfer are considerable.

Further measurements on the system will be done to determine the dependence of the charging time on the charging temperature level. And then an estimation of the heat and mass transfer coefficients depending on the Reynolds number based on the real pellet size distribution can be done.

The set up will be modified to an open system. In this configuration the environment will supply the heat of evaporation for water – the system will act as an heat pump. The heat of evaporation is the dominating part of the energy gain in open systems.

## ACKNOWLEDGEMENT

We gratefully acknowledge the support by the Swiss „Bundesamt für Energie“.

## LIST OF VARIABLES

Temperature	$T_o$	[K]
Temperature	$T_u$	[K]
Temperature difference	$\Delta T$	[K]
Temperature (sorption bed)	$T(z)$	[K]
Pressure	$p$	[Pa]
Specific heat	$c_p(T)$	[kJ/kgK]
Real specific heat (sorbent)	$c_p(T)_{real}$	$c_p(T)_{dry} + c(T, p) \cdot c_p(T)_{water}$ [kJ/kgK]
Density	$\rho(T)$	[kg/m <sup>3</sup> ]
Density	$\rho$ (sorbent)	[kg/m <sup>3</sup> ]
Load / water uptake	$c(T, p)$	[kg <sub>Water</sub> /kg <sub>Sorbent</sub> ], [weight %]
Load / water uptake (sorption bed)	$c(T, p, z)$	[kg <sub>Water</sub> /kg <sub>Sorbent</sub> ], [weight %]
Energy density (water)	$Q_d(T)$	[kJ/m <sup>3</sup> ]
Sensible energy (sorbent)	$Q_s(T)$	[kJ/m <sup>3</sup> ]
Heat of evaporation	$\Delta h_v(T, p)$	[kJ/kg]
Binding enthalpy	$\Delta h_B(T, p)$	[kJ/kg]
Differential heat of adsorption	$\Delta h_d(T, p)$	[kJ/kg]
Adsorption enthalpy	$\Delta h_A(T, p)$	[kJ/kg]
Molecular weight of H <sub>2</sub> O	$M_{water}$	18.015 [g]

## REFERENCES

[1] Jenni J., Sonnenenergieanlagen mit hohem Deckungsgrad für Warmwasser und Heizung, Jenni Energietechnik AG, CH-3414 Oberburg, 1993.

[2] Seiwald H, Hahne E., *Underground seasonal heat storage for a solar heating system in Neckarsulm / Germany*  
Proceedings of the 8<sup>th</sup> International Conference on Thermal Energy Storage Vol. 1 p. 213 - 219, TERRASTOCK 2000, Stuttgart, Germany.

- [3] Lichtenfels A., Reineck K.-H., *The design and construction of the concrete hot water tank in Friedrichshafen for the seasonal storage of solar energy*  
Proceedings of the 8<sup>th</sup> International Conference on Thermal Energy Storage Vol. 1 p. 257 - 262, TERRASTOCK 2000, Stuttgart, Germany.
- [4] Schölkopf W., Hauer A., Fischer S., *Wärmespeicherung für Raumheizung im Verbund mit einem Fernwärmenetz*  
VDI BERICHTE NR 168, 1994.
- [5] Mittelbach W., Hardt C., Henning H.-M., *Experimentelle Untersuchung eines thermochemischen Wärmespeichers im Technikumsmassstab*  
Achstes Symposium Thermische Solarenergie 13. – 15. Mai 1998, OTTI Technologie Kolleg Kloster Banz, Deutschland.
- [6] Hauer A., *Thermochemical energy Storage in Open Sorption Systems – Temperature Lift Coefficient of Performance and Energy Density*  
Proceedings of the 8<sup>th</sup> International Conference on Thermal Energy Storage Vol. 1 p. 391 - 396, TERRASTOCK 2000, Stuttgart, Germany.
- [7] Mittelbach W., Nuñez T., Luginsland F., Henning H. M., *Solid sorption thermal energy storage for solar heating systems*  
Proceedings of the 8<sup>th</sup> International Conference on Thermal Energy Storage, Vol. 1 p. 415 - 420, TERRASTOCK 2000, Stuttgart, Germany.
- [8] VDI-WÄRMEATLAS Recherchieren – Berechnen –Konstruieren  
Herausgeber: Verein Deutscher Ingenieure, Springer Verlag Berlin Heidelberg 1997.
- [9] Yang R. T., *Gas separation by adsorption processes*  
Series on Chemical Engineering, Vol. I, Imperial College Press 1997.