ADSORPTION SPEED AND MASS TRANSFER ZONE ANALYSIS OF WATER VAPOUR ON THE SOLID SORBENT MATERIALS ZEOLITE AND SILICAGEL WITH THE FOCUS ON THE HEAT EXCHANGER DESIGN.

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1. INTRODUCTION

Thermal energy for domestic hot water and heating use is stored in water tanks. Depending on the time of charging and the consumption the size of the storage tank has to be adjusted. In solar thermal systems, tanks sizes are typically around 0.3 – 0.5 cubic meter for single family houses and in case of seasonal storage systems up to several hundreds of cubic meters in district heating systems. The costs for a storage system are depending on the materials used and the size. So, for reducing the costs, the total volume should be decreased and materials with a higher energy density than water are desirable. Based on a temperature difference of $\Delta T = 50 \, ^\circ C$ the energy density of water is approximately $58 \, \text{kWh/m}^3$.

The apparently promising concept of high energy density storage of water vapour adsorbed on granular solid sorption materials like zeolite and silicagel has been followed by different authors and groups [Duffie 1991, Hauer 2000, Mittlebach et al 2000]. In the adsorption process the heat of adsorption $\Delta h_A = \Delta h_v + \Delta h_B$ (heat of evaporation $\Delta h_v$; binding energy $\Delta h_B$) is released and the combined solid sorbent plus the adsorbed sorbate are heated up. Because the theoretical energy density of water vapour adsorbed on zeolite is in the region of $180 \, \text{kWh/m}^3$, the size of a water storage tank could be significantly reduced. While the measurements of the heat of adsorption $\Delta h_A$ of water vapour on Zeolite and Silicagel are nearly confirming these values [Hauer 2000], in the sorption storage system design, all the losses have to be considered. But a much more important point is that in case of discharging the storage tank the heat of evaporation $\Delta h_v$ has to be delivered to the system. So in principle, the storage system is a thermally driven heat pump. The environment or a solar thermal system can be used as the supplying energy source for the heat of evaporation $\Delta h_v$. In case of charging the sorption tank i.e. drying the sorbent material, thermal energy sources at temperatures of up to $200 \, ^\circ C$ for Zeolite and $120 \, ^\circ C$ for Silicagel are needed. Lower charging temperatures are leading to lower energy outputs of the storage system. As in case of delivering the required heat of evaporation to the system solar thermal vacuum tube collectors can be used to dry the sorbent material.

To supply the thermal energy into or out of the system heat exchangers have to be installed. While in a closed sorption system working under vacuum, i.e. in a system working at water vapour (sorbate) pressure, heat is manly transferred by conduction and radiation, in an open system, however, air can be used as the transport fluid for heat and water vapour, and so convection is the dominating heat transfer term over conduction and radiation heat transfer. In designing a closed system the low heat conductivity of zeolite and silicagel in the sorption unit has to be considered. So either short distances form the location where the adsorption process takes place to the heat removing apparatus are desirable or heat conduction increasing materials have to be built-in. A composite material of copper nano-powder / Silicagel was used by [CHUNG 2004] and [Mittelbach 2000] used metal wool reinforcing Silicagel fixed beds.

In the adsorption process, heat and mass transfer are directly coupled and can be described by the similar laws of Fourier (heat) and Fick (mass), respectively. Consequently a high power system requires large transfer areas. To store a high amount of energy either sorption materials with a high sorption capacity i.e. with a large inner surface
or large volumes are needed. Thus because of the low diffusion rate of water molecules in Zeolite and Silicagel the power output of a given volume of a fixed bed of solid sorption material is limited by the geometrical shape. If the cross sections for the heat transfer that face the vapour flow directly are small, the process will be diffusion limited and so will be the power of the system.

With the aim to design an efficient storage system, an experimental set-up to measure the speed of adsorption of water vapour on Zeolite and Silicagel and the temperature development in the fixed bed of solid sorbent material was built. The findings will help to understand how the process behaves and assist with the design of an efficient heat exchanger, which is one of the key components of the system. The current presentation deals with weight measurements under vacuum as a function of time and material and from it the power density in relation to the cross section of the fixed bed can be determined. The power $P$ will directly correlate with the uptake of water vapour as a function of time multiplied by the heat of adsorption $\Delta h_A$: $P \approx \frac{dm}{dt} \cdot \Delta h_A$.

2. EXPERIMENTAL

Figure 1 shows the experimental set-up with the two stainless steel vacuum tanks. In the upper tank the fixed bed is installed, while the lower tank contains the deionised water for sorbate which is evaporated with an immersed heat exchanger during the experiment. The water temperature in the water tank was controlled by an external thermostat. The fixed bed is formed by a 15 cm long and 10 cm wide cup shaped stainless steel tube with a coiled electrical heating on the outer side. The front side is covered by a metal fabric with a mesh width of 0.8 mm. Granular solid sorption material is filled in and the temperature dependant electrical resistance sensors Pt 100 are installed with a distance of 1 cm from each other; see position $z = 1$ to $5$ in Figure 1. The fixed bed is hanged from a double bending beam shaped arm of balance which delivers a weight dependant electrical voltage signal. The electrical cables are connected with electrical vacuum feed throughs.

![Figure 1: Schematic of the experimental set-up with two vacuum chambers to measure time dependent mass adsorption on granular zeolite and silicagel and the temperature development as a function of time and position $z$ (1 cm to 5 cm) in the fixed bed (ZM) of solid sorbent material. The lower chamber contains the sorbate water and the upper chamber the fixed sorbent bed container. In the upper left the fixed bed container is shown zoomed.](image)

A turbo-molecular pump connected to a mechanical vacuum pump was used. In the chamber containing the fixed bed a base pressure $p = 4 \times 10^{-7}$ mbar was reached. The water sorbate chamber was evacuated to the temperature...
dependent water vapour pressure, \( p(\text{H}_2\text{O}, T=20 \, ^\circ\text{C}) = 23.4 \, \text{mbar} \) [VDI-WÄRMEATLAS, 1997]. For pumping out the air solved in the deionised water in the lower tank, the procedure was performed three times.

Spherical zeolite 13 X particles with an average diameter of 1 mm and granular silicagel 490 with a particle size distribution of 3 – 5 mm were used as sorbent materials. The bulk densities are 650 kg/m\(^3\) for zeolite 13 X and 470 kg/m\(^3\) for silicagel 490. The BET surface of zeolite 13 X is in the range of 500 m\(^2\)/g and 800 m\(^2\)/g and for silicagel 490 it is 400 m\(^2\)/g [Yang R.T. 1997, Uetikon]. Zeolite 13 X and silicagel 490 have an average pore size of 1 nm and 9 nm, respectively. In humid air the water uptake \( c(p, T) \) of the two different sorbent materials is approximately 25 wt. % and 80 wt. % for zeolite 13 X and silicagel 490, respectively. The sorbent material fixed bed was dried at a temperature of \( T = 100 \, ^\circ\text{C} \) by the electrical heating and simultaneous pumping with the turbo-molecular and the mechanical vacuum pumps. The temperature \( T(t, z) \) and weight \( m(t) \) increase was measured in fixed beds of zeolite 13 X and silicagel 490 adsorbing water vapour of different vapour pressures \( p(T) \) and temperatures \( T \), respectively.

3. RESULTS AND DISCUSSION

For Silicagel the \( m(t) \) data points in Figure 2 show two different ranges separated at the measurement time \( t \) i.e. adsorption time \( t \) of about \( t = 300 \, \text{s} \) at a temperature \( T = 22 \, ^\circ\text{C} \) in the water tank. In both time ranges, from \( 0 \, \text{s} \) to \( t = 300 \, \text{s} \) and from \( t = 300 \, \text{s} \) to \( t = 3200 \, \text{s} \) the measured data are fitted with two linear functions. The slope of the first linear curve is \( \frac{dm}{dt} = 2 \times 10^{-2} \, \text{g/s} \) while the derivation of the second linear curve of \( \frac{dm}{dt} = 1.7 \times 10^{-3} \, \text{g/s} \) is more than an order of magnitude smaller. Zeolite 13 X shows similar behaviour but the two time ranges are separated at a time \( t \) of \( t = 400 \, \text{s} \) and in the first range the adsorbed water vapour per time \( t \) is with \( \frac{dm}{dt} = 3 \times 10^{-2} \, \text{g/s} \) 1.5 times higher than for Silicagel 490. In the second time range the mass adsorption speed is \( \frac{dm}{dt} = 5 \times 10^{-3} \, \text{g/s} \). In Figure 3 the mass \( m(t) \) data points as a function of time \( t \) are shown for Zeolite 13 X at a temperature \( T = 22 \, ^\circ\text{C} \) in the water tank.

![Figure 2: Increase of mass as a function of time in the fixed bed of Silicagel 490 by adsorption of water vapour at a pressure of \( p(\text{H}_2\text{O}, T=22 \, ^\circ\text{C}) = 24.8 \, \text{mbar} \). In the first \( t = 300 \, \text{s} \) the data points can be fitted by a liner function (1) with a slope of \( \frac{dm}{dt} = 2 \times 10^{-2} \, \text{g/s} \), while the measured data at a time \( t > 300 \, \text{s} \) can be approximated by a liner function (2) with a slope of \( \frac{dm}{dt} = 1.7 \times 10^{-3} \, \text{g/s} \).](image-url)
Figure 3: Increase of mass as a function of time in the fixed bed of Zeolite 13 X by adsorption of water vapour at a pressure of $p(H_2O, T=22\, ^\circ C) = 24.8\, m\, bar$. In the first $t = 400\, s$ the data points can be fitted by a linear function (1) with a slope of $\frac{dm}{dt} = 3 \times 10^{-2}\, g/s$, while the measured data at a time $t > 400\, s$ can be approximated by a linear function (2) with a slope of $\frac{dm}{dt} = 5 \times 10^{-3}\, g/s$.

Figure 4 shows the temperature $T(z, t)$ as a function of position $z$ and time $t$ in the fixed bed. Up to a reaction time of $t = 220\, s$, the silicagel 490 $T(z, t)$ curves are convex. For a time $t > 220\, s$ the $T(z, t)$ concave shaped curves are making a transition to a stretched s-curve. The $T(z, t)$ curves in the zeolite 13 X fixed bed show a different behaviour. They already are concave at a reaction time $t$ of $t = 40\, s$ and this form is even intensified for a longer reaction time $t$.

The time lag in the temperature increase at the deeper positions $z$ in the fixed bed is correlated with the delayed adsorption of water vapour on the sorbent material particles. An adsorption mass transfer zone (MTZ) can be determined through the temperature measurement in the fixed bed. From the data in Figure 4 (left) a MTZ length of $L = 5\, cm$ to $6\, cm$ is derived for silicagel 490 and for zeolite 13 X $L = 1 – 2\, cm$, Figure 4 (right).

Figure 4: Temperature $T(z, t)$ increase in the fixed bed by adsorption of water vapour on Silicagel 490 (left) and on zeolite 13 X (right) as a function of position $z$ and time $t$. The position $z$ of the temperature sensors $z = 1$ to $5$ is shown in Fig. 1.
The dynamic behaviour of zeolite 13 X and silicagel 490 under adsorption of water vapour is different. Zeolite 13 X shows a higher water vapour uptake rate than silicagel 490. Two adsorption speed ranges were identified for silicagel 490 and zeolite 13 X. At the beginning of the adsorption process the measured curves \( m(t) \) can be approximated by linear functions. The transition from the higher gradient to the lower gradient takes place at an adsorption process time of approximately \( t = 300 \) s for silicagel 490 and \( t = 400 \) s for zeolite 13 X. SAHA 1995, BOELMAN 1995 and BOELMAN 1997 are reporting about operational conditions and coefficient of performance COP of an adsorption refrigeration machine working with silicagel. The optimum cooling power output is in a cycle time of \( t = 250 \) s to \( t = 300 \) s while the COP of the machine increases up to a cycle time of \( t = 1800 \) s. For a measurement time \( t > 1 \) h the weight \( m(t) \) increases as a function of time \( t \) for the two sorbent materials Silicagel and Zeolite is again reduced compared to the previous two time ranges. These data are not shown here but are important in the scaling up of a laboratory system and will be discussed and presented in the future.

The mass adsorption speed \( \frac{dm}{dt} \) in the fixed bed is controlled by the type of material (chemical composition, polarity, porosity etc.) with water vapour uptake capacity \( c(p, T) \), the temperature \( T \) of the material and the water vapour pressure in the system, the particle size and shape (relation of surface \( S \) to volume \( V \)), which determines the void fraction, and the relation of the cross-section \( A \) to the length \( L \) of the fixed bed.

By multiplying \( \frac{dm}{dt} \) with the heat of evaporation \( \Delta h_v(T = 22 \, ^\circ C) = 2450 \, \text{kJ/kg} \) [VDI-WAERMEATLAS 1997] of water and dividing the product by the cross-section \( A \), a lower boundary of the heating power density and an upper limit of the cooling power density of \( 6.4 \, \text{kW/m}^2 \) for silicagel 490 and \( 9.5 \, \text{kW/m}^2 \) for zeolite 13 X can be calculated at the start of the adsorption process. The power density is directly dependent on the water vapour pressure i.e. from the mass of water vapour supplied to the sorbent fixed bed.

Table 1 summarizes the power density values in the water vapour pressure range of \( p(H_2O, T=10 \, ^\circ C) = 12.1 \, \text{mbar} \) to \( p(H_2O, T=32 \, ^\circ C) = 47.9 \, \text{mbar} \).

<table>
<thead>
<tr>
<th>Temperature ( T ) [(^\circ C)]</th>
<th>Water vapour pressure [mbar]</th>
<th>Power density zeolite [kW/m(^2)]</th>
<th>Power density silicagel [kW/m(^2)]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>12.1</td>
<td>6.3</td>
<td>2.9</td>
</tr>
<tr>
<td>22</td>
<td>24.8</td>
<td>9.5</td>
<td>6.4</td>
</tr>
<tr>
<td>29</td>
<td>37.7</td>
<td>35.4</td>
<td>-</td>
</tr>
<tr>
<td>32</td>
<td>47.9</td>
<td>-</td>
<td>10.6</td>
</tr>
</tbody>
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The coupling of the heat and mass transfer and the aim for high energy density and a high power density requires a compromise in order to be optimised. The power density of an adsorption heat storage system is directly correlated to the speed of adsorption of sorbate onto the sorbent material. While the adsorption process takes place the heat of adsorption \( \Delta h_A(c, T) \) is released and the temperature of the combined sorbent material and the adsorbed sorbate components is increased. The weight of the sorbent is increased by the temperature and time dependant mass flow of sorbate onto the sorbent multiplied by the process time \( t \).

A solution of the mass balance equation in the bulk of the fixed bed and in a particle is shown in Figure 5 right. The qualitative curves are calculated with a parabolic concentration profile \( c(r/R_p) \sim (r/R_p)^2 \), which is according to YANG, 1998 and DO, 1997 a reasonable assumption. Judging Figure 2, 3 and 5, right and considering the total mass in the experimental fixed bed it can be seen that the maximum concentration \( c(p, T) \) of water adsorbed on zeolite and silicagel are far from the theoretical in the measured time range. So the 6 g of water on silicagel 490 and the 12 g of water on zeolite 13 X in the first 300 s and 400 s are mainly adsorbed on the surface of the sorption materials. Because of the vapour pressure curve \( p(T, c) \) of silicagel and zeolite, the higher system temperature limits the water uptake \( c(T, p) \) at a given pressure [CHUA 1999, CHANG 2000, CIACCOLA 1995]. DUNNE 2001 and TATLIER 2004 are therefore reporting and arguing to apply solid sorption material layers for adsorption cooling.
These results have been considered in the design of the heat exchangers immersed in the granular water vapour adsorbing materials. The heat exchangers are the key components of a thermo-chemical energy storage system. Because of the low heat conductivity of Zeolite and Silicagel and the low heat transfer rates in the fixed-bed configuration, a distance of the adsorbing material to the heat conduction surfaces should not be exceeded. This led VAILLANT, 2002 to the construction of a fin tube heat exchanger with a fin distance of one particle diameter. But the high mass relation of the heat exchanger to the sorption material is still resulting in massive thermodynamic penalties.

For these reasons, a rib heat exchanger with nine heat conduction fluid carrying pipes in parallel was built, considering the pressure $p$ and temperature $T$ depending heat transfer coefficients in the bulk of the fixed bed [VDI-WAERMEATLAS 1997, SCHLUENDER 1984]. The distance from one rib to a other was set to $d(1) = 7$ mm in the $x$ direction and the distance of the pipes was either $L = 45$ mm in the $z$ direction and $L = 60$ mm in the $y$ direction. In Figure 5 a schematic of a part of the rib heat exchanger is shown. First results show a temperature increase of up to $T = 80 \, ^\circ C$ in the external fluid carrying cycle in the experimental sorption storage system at a water vapour pressure of $p(H_2O, T=20 \, ^\circ C) = 23.4$ mbar in the water tank.

![Figure 5: Schematic of a heat exchanger section with marked parameters (left). The heat exchanger can be either cylindrical or rectangular. On the right hand, a qualitative concentration profile $c(r/R_p)$ in a spherical solid sorption particle depending on the diffusion resistance $k$ during adsorption is shown (right). The particle with a diameter $2R_p$ as shown is not to scale compared to the concentration profile $c(r/R_p)$.](image)

By exploiting the heat pump effect in the adsorption process of water vapour on Zeolite or Silicagel in a closed sorption system, energy sources in the temperature range of approx. $T_{low} > 10$ $^\circ C$ can be used to reach water temperatures of $T_w > 50$ to $55$ $^\circ C$ in a heating system. To avoid the growth of legionella in the hot water for domestic purpose, a water temperature of $55$ $^\circ C$ has to be exceeded. But it will be a challenge to achieve a combination of high energy density and a high power density, as well as low costs of such a system because of the unrivalled low water price.

4. FUTURE WORK

The experiments were done without cooling the fixed bed and so the sorption materials reached a steady state at an equilibrium temperature $T_{eq}$ that is higher than in case of cooling the sorbent material. By cooling the fixed bed to a temperature level lower than the equilibrium temperature $T_1 < T_{eq}$ in the adsorption process, the load $c(T, p)$ with water vapour will be higher, $c(T_1, p) > c(T_{eq}, p)$ for $T_{eq} > T_1$, and so the power will be increased. Keeping the focus on a closed heat storage system, the long term dynamical behaviour of a fixed bed adsorption unit has to be known. Various questions remain to be answered. For instance: Is the mass transfer zone travelling with a constant speed through the fixed bed independent of the depth $z$? Or, is there a limit in the length $L$ because of the water vapour pressure drop while it is flowing through the granular material? What is the optimum particle size distribution to a constant flow i.e. a constant power density? The future work will be dealing with identifying
system designs to achieve optimum power density and energy density. In addition further work will be needed to scale up the laboratory system to a single family house prototype sorption heat pump / storage system.

5. CONCLUSIONS

The sorption materials silicagel 490 and zeolite 13 X have a high water vapour adsorption rate at the beginning of the adsorption process for a time of \( t = 300 \) s and \( t = 400 \) s, respectively. Correlating with the water vapour pressure \( p \), the power densities are at \( p(H_2O, T=22 \, ^\circ C) = 24.8 \, \text{mbar} \times 6.4 \, \text{kW}/\text{m}^2 \) for silicagel 490 and 9.5 \( \text{kW}/\text{m}^2 \) for zeolite 13 X. Cooling of the fixed bed will increase the concentration \( c(T, p) \) of water on the sorption material. But the cooling has to be done effectively and because of the low heat conductivity and the diffusion controlled adsorption on sorption materials layers on the heat transporting surfaces, the choice of heat exchangers would be appropriate for this application. Because of the low total capacity for water vapour the layers would have to be regenerated (dried) after a reaction time \( t \) of \( t = 300 \) s to \( t = 400 \) s. For a long-term thermal energy storage a compromise between power density and energy density will have its consequences in the design and scale up of a system. Increasing the cross-section of the fixed bed will increase the heating or cooling power of the system.

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