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Evaluation of adsorbent materials for heat pump and thermal energy storage applications in open systems

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Abstract The evaluation of solid adsorbents in open sorption systems for heating, cooling and thermal energy storage (TES) applications is crucial for the ecological and economical performance of these systems. An appropriate adsorbent has to reach the temperature limit given by the heating/cooling system of the consumer. It has to provide high energy efficiency and a high energy density for storage applications. A method for an easy evaluation of different adsorbents for a specific application has been developed. The method is based on the adsorption equilibrium of the adsorbent and water vapor. The crucial property for the discussed field of applications is the differential heat of adsorption. Criteria for the evaluation of the adsorbent are the breakthrough curves (responsible for the dynamics of the process), the possible temperature lift (or the dehumidification) of the air, the thermal COP and the storage capacity.

Keywords Water vapor adsorption · Open sorption systems · Zeolite · Thermal energy storage · Desiccant cooling

Abbreviations

Q_{des}	desorption energy, kJ
Q_{cond}	condensation energy, kJ
Q_{ads}	adsorption energy, kJ
Q_{evap}	evaporation energy, kJ
ΔH_{d}	differential heat of adsorption, kJ/kg(adsorptive)
ΔH_{ads}	integral heat of adsorption, kJ/kg(adsorbent)
T_{in}	air temperature at inlet, °C
T_{out}	air temperature at outlet, °C
x_{in}	water content per mass of dry air, at inlet, g/kg
x_{out}	water content per mass of dry air, at outlet, g/kg
C_{ads}	water content of adsorbent, after adsorption, kg/kg
C_{des}	water content of adsorbent, after desorption, kg/kg
$c_{\mathrm{p,air}}$	specific heat capacity of air, kJ/(kg·K)
$c_{\mathrm{p,sorb}}$	specific heat capacity of dry adsorbent, kJ/(kg·K)
$c_{\mathrm{p,H2O}}$	specific heat capacity of air, kJ/(kg·K)
ΔF	change in free energy upon adsorption, kJ
ΔS	change in entropy upon adsorption, kJ/K
$L(T)$	heat of evaporation of water, kJ/kg
ρ_{Q}	energy storage density of adsorbent, MJ/m^3
m_{sorb}	adsorbent mass, kg
V_{sorb}	adsorbent volume, m^3
$\mathrm{COP}_{\mathrm{th}}$	coefficient of performance (theoretical), –
$\mathrm{COP}_{\mathrm{useable}}$	coefficient of performance (application conditions), –

1 Introduction

Adsorption systems are a promising alternative to conventional heating, cooling and storage devices of buildings or other thermal processes. Adsorption systems can be operated as “closed” or “open” systems. Closed systems are evacuated and only the adsorptive is evaporated/condensed and desorbed/adsorbed. There are some overviews in literature concerning this category of systems (Ahlefeld et al. 1981; Shelton 1992; Meunier 1999). Open sorption systems are operated in an open loop coupled to the ambient. Therefore water is used as the adsorptive. An air stream is trans-

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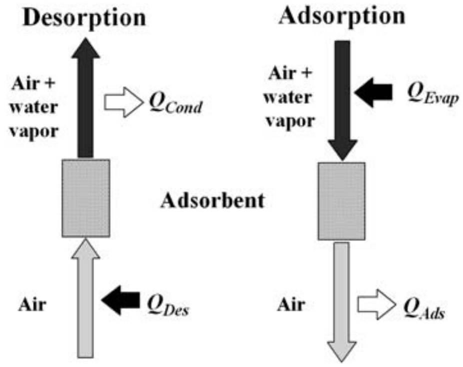


Fig. 1 Open sorption system (heat and mass fluxes)

porting water vapor and heat in and out of the packed bed of solid adsorbents (see Fig. 1).

These systems are the subject of this paper. They are able to reduce the primary energy consumption by providing high coefficients of performance (COP) for heating and cooling and a high energy density for storage applications. Actual systems can often combine their heating, cooling and storage ability, which makes them economically attractive. Concerning open sorption systems very few publications giving an overview of the existing activities can be found (Hauer 2007).

For the heating application, the sorption system is operated as a thermally driven heat pump. Desorption energy Q_{des} is the driving energy, whereas condensation and adsorption energy Q_{cond} and Q_{ads} can be used for heating purposes. The energy for evaporation Q_{evap} has to be available at a low temperature level, which can not be used elsewhere. A gas fired adsorption heat pump in conjunction with solar collector for heating was developed (Hauer and Dallmayer 1996).

TES can be achieved by separating the desorption step (charging mode) from the adsorption step (discharging mode). After desorption the adsorbent can theoretically remain in the charged state without any thermal losses due to the storage period until the adsorption process is activated. A TES system containing 7000 kg of zeolite was installed and operated in a school building in Munich/Germany (Hauer and Dallmayer 1996; Hauer 2002b).

Cooling can be provided by humidifying the dry air leaving the packed bed of adsorbent during adsorption (desiccant cooling systems). The adsorption heat pump and the TES can be used for the cooling of buildings in summertime (Hauer and Dallmayer 1996; Hauer 2002b).

Because of the very high storage capacity of open storage systems, they can be used for the transportation of thermal energy. An interesting field of applications is the utilization of industrial waste heat. The collected waste heat can be integrated into various processes at another site. Especially interesting are drying processes, because hot and dry air can be delivered by these systems very efficiently. First studies of three actual industrial applications have shown that heat prices of oil and gas can be reached (Storch and Hauer 2006).

To run these systems efficiently, an appropriate adsorbent has to be used. The right choice is possible on the basis of the measured adsorption equilibrium. The adsorption equilibrium of water vapor and different technical adsorbents (zeolites and silica gels) was experimentally determined (Khelifa 1984; Hauer 1988). The differential heat of adsorption (ΔH_{d}) was calculated from the equilibrium data.

For the characterization of solid sorbents in thermal applications like heating, cooling and thermal energy storage the following criteria are defined: The possible temperature lift (and drop in humidity ratio), the breakthrough curves (responsible for the dynamics of the process), the thermal coefficient of performance and, for the thermal energy storage application, the energy density referring to the volume (or the mass) of the adsorbent. All these criteria can be derived from the adsorption equilibrium data as properties of the adsorbent.

2 Temperature lift

The temperature lift is defined as $\Delta T = T_{\mathrm{out}} - T_{\mathrm{in}}$. The possible ΔT is crucial for the design of sorption systems for heating applications. The temperature lift of each adsorbent can be very different under the same adsorption conditions. The temperature lift can be calculated as:

$$\Delta T = \Delta x \cdot \frac{\Delta H_{\mathrm{ads}}}{c_{\mathrm{p,air}} - \frac{\Delta x}{\Delta C} \cdot c_{\mathrm{sorb,eff}}} \tag{1}$$

where $\Delta x = x_{\mathrm{in}} - x_{\mathrm{out}}$ is the humidity ratio difference, ΔH_{ads} is the integrated differential heat of adsorption ΔH_{d} between C_{ads} and C_{des}, $c_{\mathrm{p,air}}$ is the heat capacity of the air, $\Delta C = C_{\mathrm{ads}} - C_{\mathrm{des}}$ is the difference in water concentration of the adsorbent and $c_{\mathrm{sorb,eff}} = c_{\mathrm{p,sorb}} + (C_{\mathrm{des}} \cdot c_{\mathrm{p,H2O}})$ is the effective heat capacity of the adsorbent.

Experiments showed an almost linear relation between T_{out} and x_{out} for the variation of desorption conditions at fixed adsorption conditions. Zeolite 13X and silica gel were used. Figures 2 and 3 show the experimental data. In the background the isosteres of each adsorbent are drawn. Starting from high x_{out} values (and low T_{out} values) going to high T_{out} values, each point represents a desorption with a higher temperature and a lower equilibrium water concentration of the adsorbent. The upper test sequence was found with adsorption using 20 °C saturated inlet air. The lower points were measured at a adsorption with $T_{\mathrm{in}} = 20\,^{\circ}\mathrm{C}$ and $x_{\mathrm{in}} = 7.72$ g/kg. Both curves are parallel and almost linear for each adsorbent.

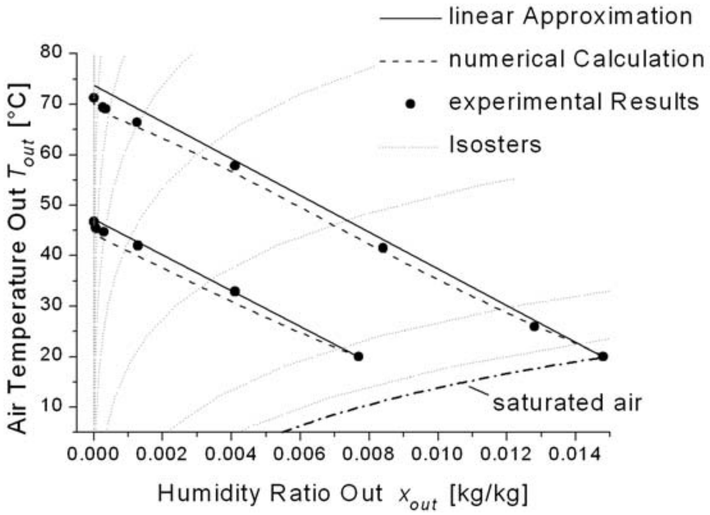


Fig. 2 $T_{\text{out}}/x_{\text{out}}$-Diagram for zeolite 13X

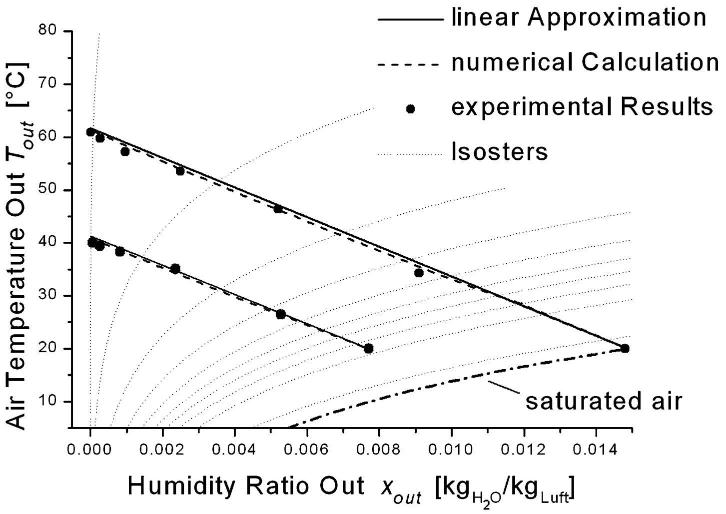


Fig. 3 $T_{\text{out}}/x_{\text{out}}$-Diagram for silica gel

The linear approximation in Figs. 2 and 3 was found by assuming, that no change in the incoming air conditions T_{in} and x_{in} will occur, if the adsorbent has reached its equilibrium at T_{in} and x_{in}. This case is represented by the dot at $T_{\text{in}} = 20\,°\text{C}$ and $x_{\text{in}} = 14.88$ g/kg, $x_{\text{in}} = 7.72$ g/kg respectively, in Figs. 2 and 3.

For the second point of the linear approximation the maximum ΔT has to be found. Assuming that the highest temperature $T_{\text{out,max}}$ can be reached after a complete desorption and that all of the water vapor within the air stream will be adsorbed ($\Delta x = x_{\text{in}}$), $\Delta T_{\max}$ can be written as:

$$\Delta T_{\max} = x_{in}\frac{\Delta H_{\text{ads}}(C_{\max})}{c_{\text{p,air}} - \frac{x_{\text{in}}}{C_{\max}} \cdot c_{\text{p,sorb}}} \qquad (2)$$

This point can be easily calculated from the adsorption equilibrium of each adsorbent. As shown in Figs. 2 and 3 the linear approximation gives a sufficient accurate estimates (±5% of the experimental values) within a range of realistic conditions to predict T_{out} and x_{out} under given de- and adsorption conditions for each adsorbent.

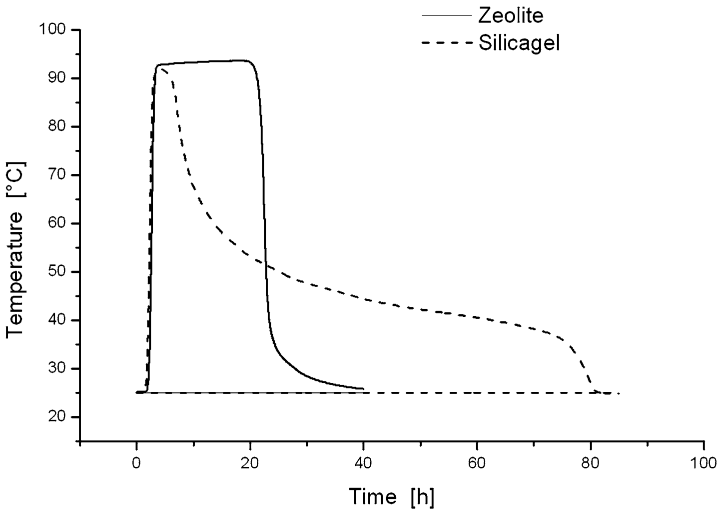
3 Breakthrough curve

The time dependent changes in the properties of the outlet air of an adsorber is called the breakthrough curve. In most applications, like gas drying, it is referring only to the changes in the water content. For thermal applications also the temperature change is important.

Figure 4 shows the shape of two thermal breakthrough curves for zeolite 13 X and silica gel in adsorption. The adsorption is following a desorption using 130 °C and the inlet air is saturated with water vapor at 25 °C.

Zeolite is reaching its maximum outlet temperature and is keeping that almost constant until the adsorption is over. Silica gel has a falling outlet temperature just after reaching the maximum. The adsorption using zeolite is about half long as the silica gel adsorption.

Fig. 4 Thermal breakthrough curves (adsorption) for zeolite and silica gel



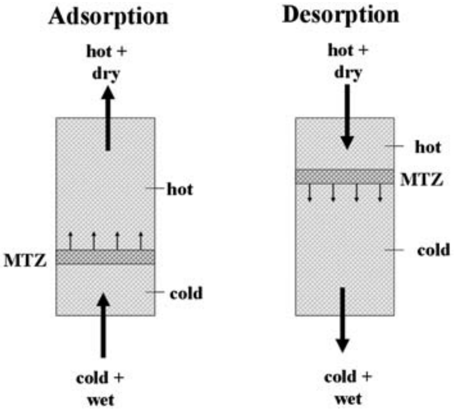


Fig. 5 Mass transfer zone for ad- and desorption

The shape of the breakthrough curve is depending on the behavior of the so called mass transfer zone (MTZ). Figure 5 shows schematically the MTZ within a packed bed of adsorbent. Within the MTZ the properties of the incoming air are changed to the outlet air properties.

The dimension of the MTZ within the packed bed can be constant, expanding or shrinking. The zeolite curve is caused by a constant or slightly shrinking MTZ, whereas the silica gel curve is caused by e expanding MTZ. With the expanding MTZ cooler and more humid air is reaching the end of the bed. This leads to the falling outlet temperature and a rising water content, which can be observed (silica gel curve in Fig. 4).

4 Thermal coefficient of performance and energy density

The thermal COP can be defined according to Fig. 1 (neglecting Q_{evap}) as $\text{COP}_{\text{th}} = (Q_{\text{cond}} + Q_{\text{ads}})/Q_{\text{des}}$. The energies are defined per mass of adsorbent. They can be calculated from the adsorption equilibrium in order to find the theoretical COP_{th} of the system. The energy for desorption Q_{des} can be divided into three different parts:

$$Q_{\text{des}} = Q_{\text{cond}} + Q_{\text{bind}} + Q_{\text{sens}} \tag{3}$$

The sensible heat Q_{sens} has to be brought into the system to heat up the packed bed of adsorbent pellets to T_{in}. Q_{sens} is defined as $Q_{\text{sens}} = \Delta T_{\text{sorb}} c_{\text{sorbeff}}$. The condensation energy Q_{cond} and the binding energy (caused by the adsorption forces) Q_{bind} is defined according to Fig. 6. Q_{cond} and Q_{bind} only depend on the differential heat of adsorption and the water concentration C of the adsorbent at the end of the de- and adsorption process:

$$Q_{\text{cond}} = (C_{\text{ads}} - C_{\text{des}}) \cdot L(T) \tag{4}$$

$$Q_{\text{bind}} = \int_{C_{\text{des}}}^{C_{\text{ads}}} (\Delta F + T\Delta S) \cdot dC \tag{5}$$

where $L(T)$ is the heat of evaporation for water vapor, $(\Delta F + T\Delta S)$ is the heat of binding taken from Dubinins theory of volume filling for vapor adsorption (Bering et al. 1966), which can be determined from the adsorption equilibrium.

Q_{ads} depends on the actual application. For the heat pump is $Q_{\text{ads}} = Q_{\text{des}}$. For long term TES, Q_{sens} can not be used due to thermal losses. For a desiccant cooling system only Q_{cond} can be used during adsorption.

The thermal COP_{th} can be calculated directly from the adsorbents equilibrium data, the differential heat of adsorption respectively. Losses in the usable energies Q_{cond} (during desorption) and Q_{ads} (during adsorption, see Fig. 1) due to the dynamic profile of the outlet temperature $T_{\text{out}}(t)$ have to be taken into account for a final characterization of the investigated adsorbents. Only energy above (or below) a temperature limit, given by the heating (or cooling) system of the building, can be utilized. This fact

Fig. 6 Definition of Q_{cond} and Q_{bind} for zeolite as an example

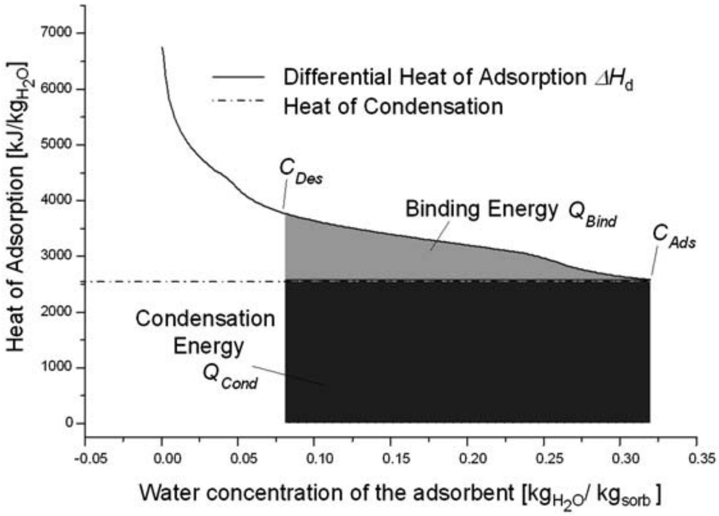
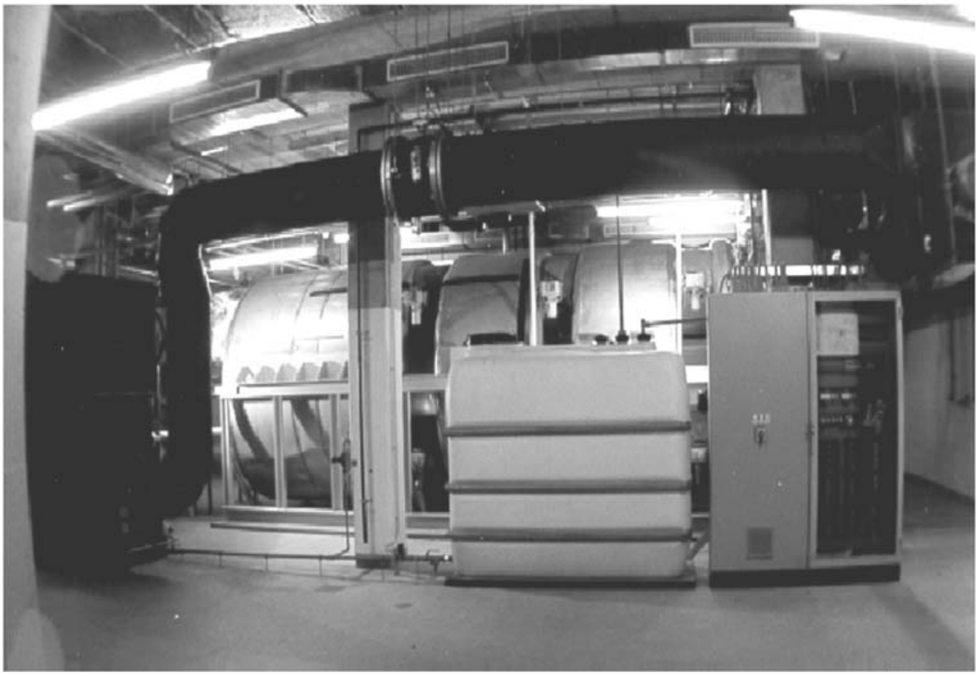


Fig. 7 The open sorption system with zeolite tanks in the background



can lead to drastic reductions in COP_{th} especially for adsorbents with low energy of binding Q_{bind} like silica gel.

The energy density ρ_Q is defined as

$$\rho_Q = \frac{(Q_{\text{cond}} + Q_{\text{bind}}) \cdot m_{\text{sorb}}}{V_{\text{sorb}}} = (Q_{\text{cond}} + Q_{\text{bind}}) \cdot \rho_{\text{sorb}} \tag{6}$$

where m_{sorb} is the mass, V_{sorb} is the volume and ρ_{sorb} is the density of the adsorbent. ρ_Q can be determined according to the COP_{th} for an experimentally found density of the adsorbent ρ_{sorb}.

5 Example: sorption storage system for district heating

An open sorption storage system using zeolite 13X has been installed in a school building in Munich/Germany and connected to the local district heating network (Hauer 2002b). Figure 7 shows the zeolite containers in the background. A better power balance of the network can be achieved by off-peak charging of the zeolite storage. The system can be disconnected from the network during heat demand peaks and can deliver heat to the buildings heating system. To match the heat load of the building, the storage has to contain 7000 kg of zeolite 13X beads. The zeolite system is under operation since the heating period 1997/98.

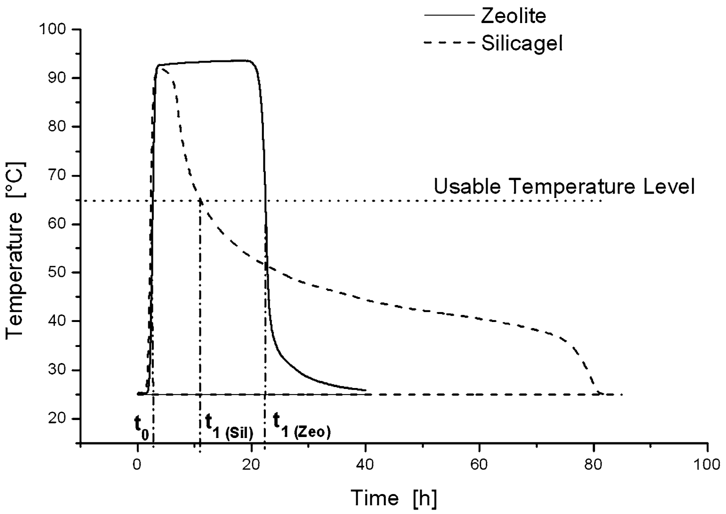


Fig. 8 Thermal breakthrough curves with usable temperature limit

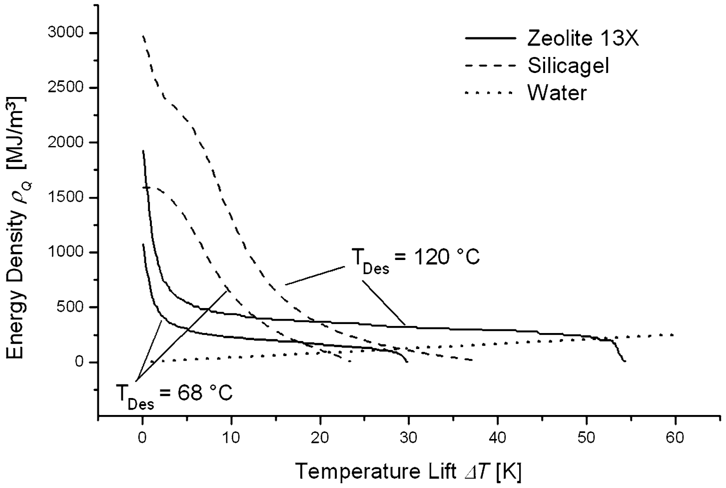


Fig. 9 Energy density of sorption storage system depending on the possible temperature lift

Up to 6000 m^3/h air can be blown through the zeolite. Charging temperature supplied by the district heating system is 130 °C. For the adsorption the inlet air can be humidified to a dewpoint of 25 °C.

The possible temperature lift can be seen in Fig. 4. Silica gel and zeolite can reach almost the same maximum temperature of about 90 °C. The reason for this is the desorption temperature of 130 °C. At this temperature, the silica gel is almost completely desorbed, whereas the zeolite still has a water content of 9%.

Comparing the two adsorbents with respect to the thermal COP, it is interesting to start without temperature restrictions. If any outlet temperature above T_{in} is usable, COP_{th} takes its maximum value with a certain advantage for silica gel. However, if a temperature limit is introduced as shown in Fig. 8, the period with usable outlet conditions is significantly reduced in the case of silica gel. This leads to a lower $COP_{useable}$.

Table 1 shows the different COPs for silica gel and zeolite. The experiments were carried out with zeolite 13X. The measured COP in the experiment was 86% of the theoretical value.

Table 1 Values of COP_{th} for zeolite and silica gel

	Zeolite 13X	Silica gel
Max. COP_{th}	1.64	1.80
COP_{usable}	1.07	0.91
Exp. COP_{th}	0.92	–

The energy storage density, like the thermal COP, depends on the required temperature level. Figure 9 shows this dependence. Using a desorption temperature of 120 °C the energy density for zeolite is higher, if a temperature lift above 21 K is required. If a lower temperature lift is acceptable, silica gel shows much higher values.

In Fig. 9 the energy density of a hot water storage is added. The water system can achieve higher densities, if it is working close to the highest temperature lift the sorption storages are able to reach. In the lower regions the sorption storages show much higher values.

Comparing the desorption temperature of 120 °C to 68 °C, it can be seen that in the latter case there is only a small range of temperature lift with zeolite showing a higher energy density than the silica gel and both sorption storages being better than the water system.

In the actual storage application in Munich a temperature lift of 40 °C was required. In this case, using a desorption temperature of 130 °C, an energy density of 491 $\mathrm{MJ/m^3}$ is possible. If the sensible heat of the desorption can be utilized as well, 552 $\mathrm{MJ/m^3}$ can be reached. In the experiments 446.4 $\mathrm{MJ/m^3}$ was measured, which is 81% of the theoretical value.

6 Conclusions and outlook

Using the methods presented in this paper, adsorbents for energy applications can be evaluated on the basis of the adsorption equilibrium. The possible temperature lift and the dehumidification of the air, the dynamic behavior of the air properties, the thermal COP and the energy density of a TES can be calculated in advance. Boundary conditions of the actual application, e.g. temperature of the heat source or usable temperature level of the buildings heating system can be directly included in the calculation and influence the choice of the appropriate adsorbent.

Future research activities will have to focus on the question of adsorbent stability. New applications will ask for stable materials under all conditions. Especially high temperatures and high humidities at the same time (during Desorption) are able to destroy the inner structure of some zeolites. For applications like the transportation of thermal energy by sorption storages mechanical stability of the pelletized material is also crucial. The problem of stability has to be solved in order to bring energy applications closer to their commercialization.

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