24. SORPTION THEORY FOR THERMAL ENERGY STORAGE

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Abstract. The theory of sorption processes and its relevance for thermal energy storage (TES) concepts shall be introduced. Starting from the thermodynamics of TES systems a motivation for sorption storage systems will be developed. The adsorption theory is based on the adsorption equilibrium. The equilibrium can be described by isotherms (curves of equal temperature), isobars (curves of equal water vapour pressure) and isosteres (curves of equal water concentration within the adsorbent). From the adsorption equilibrium the adsorption enthalpy or heat of adsorption can be calculated. The heat of adsorption describes the amount of energy involved in the process. The ratio of discharged to charged thermal energy and the possible storage capacity of different applications derived from the adsorption equilibrium and the heat of adsorption will be defined. A similar method—from the equilibrium to the storage capacity—will be shown for liquid sorbents.

Keywords: Adsorption, absorption, thermal energy storage, adsorption equilibrium, heat of adsorption

24.1. Introduction

Thermal Energy Storage can be realized by utilizing reversible chemical reactions. The number of possible reactions for this application from first principle is huge, however only very few are suitable concerning a usable reaction temperature. The process of adsorption on solid materials or absorption on liquids is the most investigated one. Figure 227 shows the process schematically.

 Adsorption means the binding of a gaseous or liquid phase of a component on the inner surface of a porous material. During the desorption step—the energetic charging step—heat is put into the sample. The adsorbed component, in this example water molecules, are removed from the inner surface. As soon as the reverse reaction—the adsorption—is started by adding water molecules to the sample, the molecules will be adsorbed and the heat, brought into the system during desorption will be released. The adsorption step represents the discharging process.
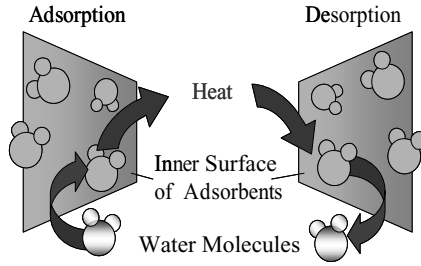
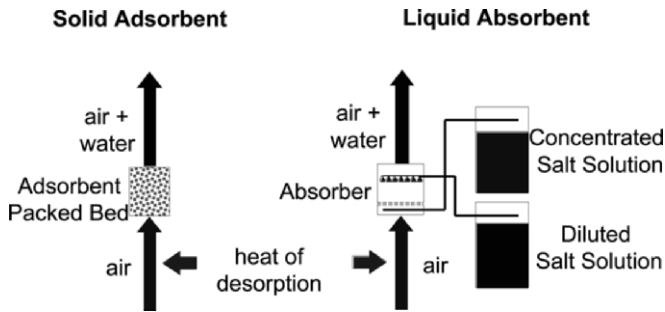*Figure 227.* Adsorption process of water vapor on solids

Figure 228. Examples of open sorption storage systems during desorption/charging

Figure 228 shows the examples of liquid and solid open sorption storage systems. In both cases the Desorption is activated by an hot air stream carrying the heat of desorption. For the solid a packed bed of adsorbent pellets and for the liquid solution a reactor are blown through, leaving the packed bed dry and the solution concentrated.

TES can be achieved by separating the desorption step (charging mode) from the adsorption step (discharging mode). After desorption the adsorbent and the absorbent can theoretically remain in the charged state without any thermal losses due to the storage period until the adsorption process is activated.

Figure 229 shows schematically the discharging of open sorption storages. Humid air blown through the storage becomes dry and can be used for
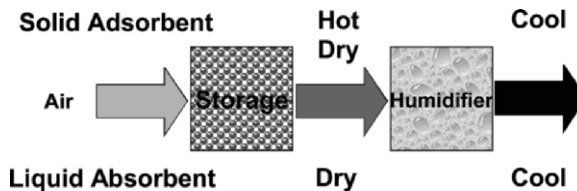

Figure 229. Examples of open sorption storage systems during adsorption/discharging

dehumidification or, by adding an humidification step, for cooling (desiccant cooling systems). If solid adsorbents are used the air might be very hot after the adsorption. This heat can be used for heating purposes.

24.2. Thermodynamics

In this chapter the question "why are sorption systems interesting for thermal energy storage?" should be answered. The reason for ongoing research is the possibility of high storage capacity, or energy density of the storage medium by the utilization of chemical reactions.

It is useful to distinguish between *direct* and *indirect* thermal energy storage (TES) based on the thermodynamics of the process [1].

A direct TES is charged by a heat flux from a heat source to the storage (see Figure 230). In general a heat flux Q is coupled to a flux of entropy S. Both are in related by the equation $Q = TS$, where T is the temperature within the storage. Thus heat at high temperature is coupled to a smaller amount of entropy as heat at flow temperature. As a consequence it can be said, that the capacity of a thermal energy storage is at a given temperature of the heat source depending on the capacity of entropy uptake.

One known disadvantage of direct TES is the fact, that they have to be at a higher (or lower) temperature as the ambience. Due to this temperature difference (their exergy content) the are able to operate as heat (or cold) storage. A thermal insulation is necessary to avoid losses over the storage period.

The limitation of the storage capacity is, as mentioned before, caused by the limitation of entropy change ΔS within the storage (see Figure 4). For sensible and latent heat storage (so-called "direct" thermal energy storage) this is defined by the specific heat

$$c_P = T \left(\frac{\partial S}{\partial T} \right).$$
(1)

Within a temperature interval $\Delta T = T_2 - T_1$ the stored heat is

$$Q_{sens} = \int_{T_1}^{T_2} c_P \cdot \mathrm{d}T = \int_{T_1}^{T_2} T \left(\frac{\partial S}{\partial T} \right) \cdot \mathrm{d}T = \bar{T} \cdot \Delta S_{21}$$
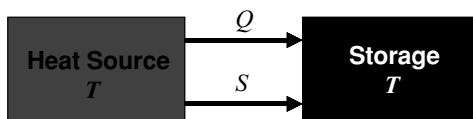(2)

Figure 230. Direct thermal energy storage (Q thermal energy, S entropy, T temperature)
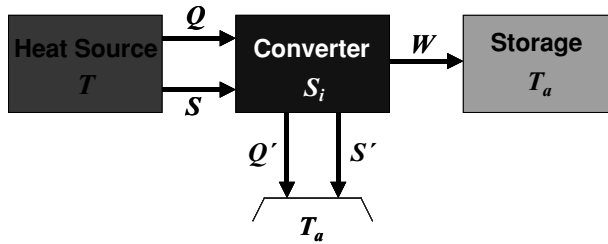
Figure 231. Indirect thermal energy storage by the conversion of thermal energy into work (S_i entropy production due to internal irreversibilities, Q' and S' waste heat and entropy of the converter, T_a ambient temperature, W work)

where Q_{sens} is the sensible heat,

$$Q_{lat} = \int_{T_1}^{T_2} c_P \cdot dT + \Delta H_{ls} = \bar{T} \cdot \Delta S_{21} + T_{ls} \cdot \Delta S_{ls} \qquad (3)$$

where Q_{lat} is the sensible and latent heat stored and ΔH_{ls} is the heat of fusion at the phase change temperature T_{ls}.

The reachable temperature difference ΔT is determined by the charging temperature T_C, which is given by the heat source.

One possibility to avoid this limitation is the conversion of heat into another kind of energy like mechanical or electrical energy. In this case (see Figure 231) the converter is producing entropy free work, which can be stored without theoretical limitations. Examples are pump storages, where water is pumped to a higher level, or flywheels, where kinetic energy can be stored.

In these systems the converter is producing waste heat, which has to be released to the ambient connected to an entropy flow caused by the irreversibilities within the converter. The discharging process will be a heat pump process, where the entropy has to be taken from the ambient. Therefore it is obvious that these systems have to be coupled to the ambient conditions. Such a storage is not self-sufficient. These systems are called "indirect" thermal energy storages.

Another possibility to reach high storage capacities is the utilization of reversible chemical reactions. An ideal reaction scheme is a reversible dissociation of a solid or liquid compound AB to a solid or liquid component A and a gaseous component B.

$$AB \leftrightarrow A + B_g$$
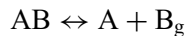
The component B should preferably be gaseous for various reasons:

- It is from the process engineering point of view much easier to separate a gaseous component from a condensed. This is necessary to prevent the reverse reaction and to provide a thermal energy storage without degradation.
- The evaporation of B is causing a significant increase in the reaction entropy. As we stated before is this necessary to reach a high energy density within the storage.
- A high reaction entropy increase influences the reaction temperature of the thermochemical dissociation equilibrium. Assuming that the reaction enthalpy and the reaction entropy have no significant temperature dependence, this simplified equation can be derived.

$$T_R = \frac{\Delta H}{\Delta S} \qquad (4)$$

where T_R is the reaction temperature, ΔH the reaction enthalpy and ΔS the reaction entropy. That means, a high entropy change is keeping the reaction temperature low.

The energy density of the storage is defined as $E_V = (V_A + V_B)$. If $V_A \ll V_B$ (because B is a gas) it can be simplified to $E_V = \Delta H/V_B$. The reaction enthalpy ΔH cannot be influenced, but the volume of B can be reduced by different processes:

- The gaseous component B can be condensed. Such a system is shown in Figure 232.
- The component B can be stored by a chemical condensation at a lower temperature. A storage medium like MgH_2 (at 400–500 °C is an example of such a system.
- The gas B is part of the atmosphere, like water vapor. In this case it can be stored in the ambience and its volume is not taken into account concerning the energy density. Such systems are called "open" systems (see Figure 233).
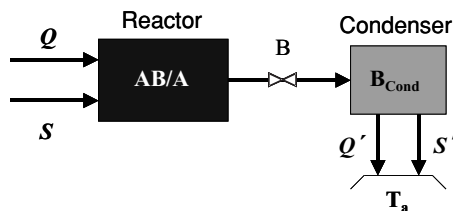

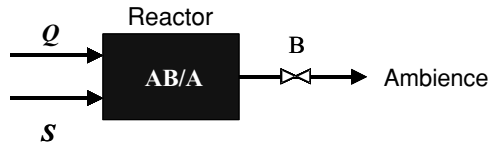*Figure 232.* Closed system with condensation of the gaseous component B

Figure 233. Open system releasing the gaseous component B into the ambience

A sorption process on the surface of a porous material, like Zeolite and other solid adsorbents, or within a concentrated salt solution, like LiCl and others, are examples for such chemical reactions for thermal energy storage.

24.3. Sorption Storage Systems for TES

24.3.1. CLOSED SORPTION STORAGE SYSTEMS

A closed sorption system is shown in Figure 8. It is based on the same physical effect as the open storage. However the engineering is quiet different from open sorption systems. Closed system could be more precisely described as evacuated or air-free systems. The operation pressure of the fluid to be sorbed can be adjusted in theses systems. In closed systems components, which are not existing in the atmosphere, can be used, because there is no connection to the ambience.

Figure 234 is showing a closed sorption system using water vapor as adsorptive. The heat has to be transferred to and from the adsorbent by an heat exchanger. This holds also for the condenser/evaporator. Heat has to be transported to the adsorber and at the same time the heat of condensation has to be distracted from the condenser in order to keep up the water vapor flow
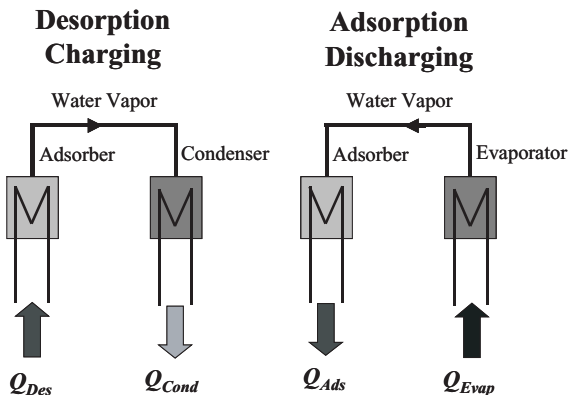

Figure 234. Closed sorption system

from the adsorber to the condenser during the desorption. During adsorption the heat of adsorption has to be taken from the adsorber and the heat of evaporation has to be delivered to the evaporator. Is this not possible, the sorption process will reach thermodynamic equilibrium and the flow of water vapor comes to a stop.

The main problem in the system design is the heat and vapor transport in and out of the adsorbent. Advanced heat exchanger technologies have to be implemented in order to keep up the high energy density in the storage, which would be reduced by the amount of "inactive" heat exchanger material.

Thermal energy storage can be realized by closing the valve between adsorber and condenser/evaporator after the desorption. The energy density expected is reduced compared to open sorption storages due to the fact, that the adsorptive (water vapor in this case) is part of the storage system and has to be stored as well. In the case of Zeolite or Silicagel as adsorbent this is about 30% to 40% of the weight of the storage material.

Closed systems are able to reach higher output temperatures for heating applications compared to open systems. Furthermore they can supply lower temperatures for cooling, e.g. it is possible to produce ice in the evaporator.

24.3.2. OPEN SORPTION STORAGE SYSTEMS

In an open sorption storage system air is transporting water vapor and heat in and out of the packed bed of solid adsorbents (see Figure 235) or a reactor where the air is in contact with a liquid desiccant. In desorption mode a hot air stream enters the packed bed or the reactor, desorbs the water from the adsorbent or the salt solution and exits the bed cooler and saturated. In adsorption mode the previously humidified, cool air enters the desorbed packed bed or the
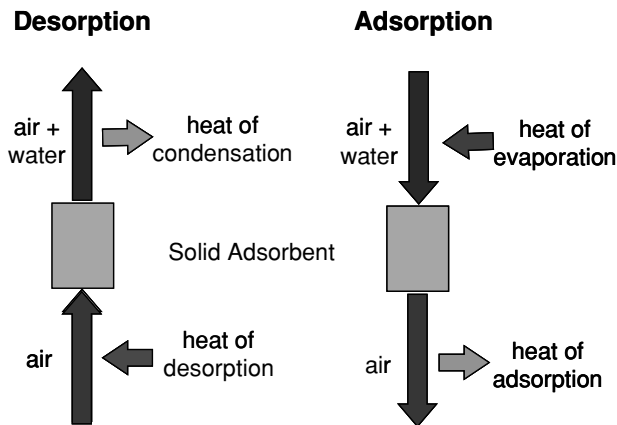

Figure 235. Open sorption storage system using a packed bed of solid adsorbent

concentrated solution. The adsorbent or the solution (or <u>ab</u>sorbent) adsorbs (or <u>ab</u>sorbs) the water vapor and releases the heat of sorption. The air exits warm and dry. In case of a solid adsorption it can be very hot. In case of a liquid absorption the dehumidification of the air is the main purpose.

The desorption energy Q_{Des} is the energy input to the thermochemical storage system, whereas the heat of adsorption energy Q_{Ads} can be used for heating. The heat of condensation Q_{Cond} can be additionally used, if it is available on a usable temperature level, which is depending on the inlet air conditions. The energy for evaporation Q_{Evap} has to be available at a low temperature level, which cannot be used otherwise (right scheme of Figure 235). The desiccant cooling process is based on the dehumidification of the air during the adsorption mode only.

Thermal energy storage is achieved by separating the desorption step (charging mode) from the adsorption step (discharging mode). After desorption the adsorbent can theoretically stay in this desorbed state, being referred to as charged in the following, without any thermal losses until the adsorption or absorptions process is activated.

24.4. Theory of Adsorption for TES

The theory of sorption storage systems will be explained for solid adsorbents. The basic results can be transferred to liquid absorbents.

To run adsorption storage systems efficiently the 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 adsorbents (zeolites and silica gels) was experimentally found [3,4]. 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 of the adsorbent. All these criteria can be calculated from the adsorption equilibrium as properties of the adsorbent.

24.4.1. ADSORBENTS

The most common classes of solid adsorbents are Zeolites and Silicagels. The main difference between the two is the way they are built. Zeolites have a crystalline structure and therefore a certain pore size. Silicagel have a pore
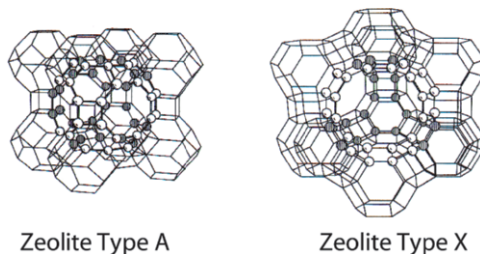
Zeolite Type A   Zeolite Type X

Figure 236. Crystalline structure of different Zeolite types

size distribution. Figure 236 shows two Zeolite types A and X and there crystalline structure. The pore size diameter of the A type is about 4 Å, while the diameter of the X type is about 10 Å. The chemical composition of the Zeolite types is given in Table 29. Some data describing Zeolites of type A and X are given in Table 30.

Figure 237 shows the pore size distribution of narrow pore (A) and wide pore Silicagel (B).

Silicagel is built of 99% SiO_2, while the rest are OH groups together with changing amounts of integrated water. The properties of Silicagel are shown in Table 31.

Concerning the application of these adsorbents as thermal energy storages the amount of water, which can be adsorbed is the most important property. Figure 238 shows the maximum water uptake of some commercially available adsorbents. Zeolite A can reach 25% and Zeolite 13X up to 32% of its dry weight. Narrow pore Silicagel can adsorb 38% water. Two special adsorbents Sizeo, which is a mixture of Zeolite and Silicagel, and SWS, which is a wide

TABLE 29. Chemical composition of Zeolite

Zeolite	Composition	Pore diameter	SiO_2/Al_2O_3
Type A	$Na_{12}[(AlO_2)_{12}(SiO2)_{12}] \cdot 27H_2O$	4.1Å	2.0–2.5
Type X	$Na_{86}[(AlO_2)_{86}(SiO_2)_{106}] \cdot 264H_2O$	7.4Å	2.0–3.0

TABLE 30. Properties of zeolites

Property	Type A	Type X
Inner surface (m^2/g)	800–1,000	800–1,000
Specific heat (kJ/kg K)	0.8–0.9	0.8–0.9
Heat conductivity (W/m K)	0.58	0.58
Packed bed density (kg/m^3)	750	700

TABLE 31. Properties of Silicagel

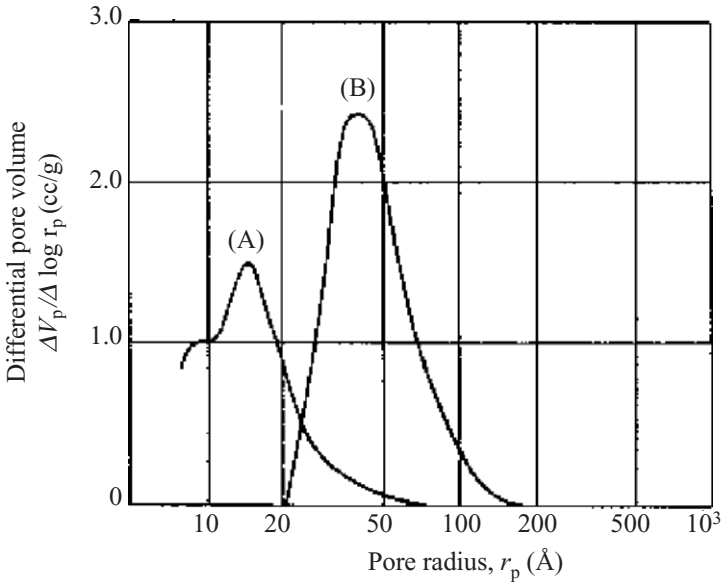| Property	Wide	Narrow
Inner surface (m^2/g)	300–500	600–800
Pore diameter (Å)	25–50	10–15
Specific heat (kJ/kg K)	0.92–1.0	0.92–1.0
Heat conductivity (W/m K)	0.14–0.2	0.14–0.2
Packed bed density (kg/m^3)	450	700

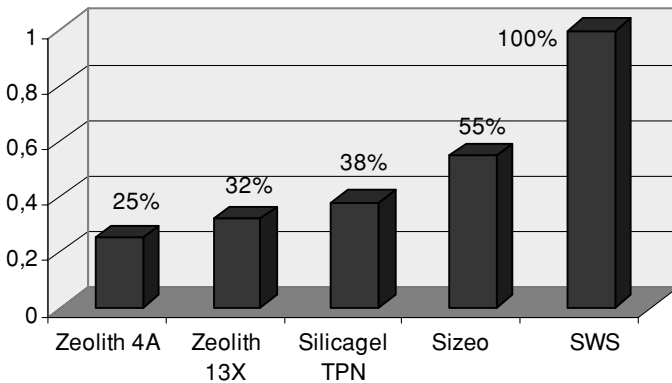Figure 237. Pore size distribution of Silicagels

Figure 238. Water uptake of different adsorbents

pore Silicagel filled with the liquid absorbent Lithium Chloride, can reach much higher values.

24.4.2. TEMPERATURE LIFT

The temperature lift is defined as $\Delta T = T_{air\ out} - T_{air\ in}$. 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

$$\Delta T = \Delta x \cdot \frac{\Delta H_{ads}}{c_{p\ air} - \frac{\Delta x}{\Delta C} \cdot c_{sorb\ eff}} \tag{5}$$

where $\Delta x = x_{in} - x_{out}$ is the humidity ratio difference, ΔH_{ads} is the integrated differential heat of adsorption ΔH_d between C_{ads} and C_{des}, $c_{p\ air}$ is the heat capacity of the air, $\Delta C = C_{ads} - C_{des}$ is the difference in water concentration of the adsorbent and $c_{sorb\ eff} = c_{sorb} + (C_{des} \cdot C_{H_2O})$ 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 239 and 240 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
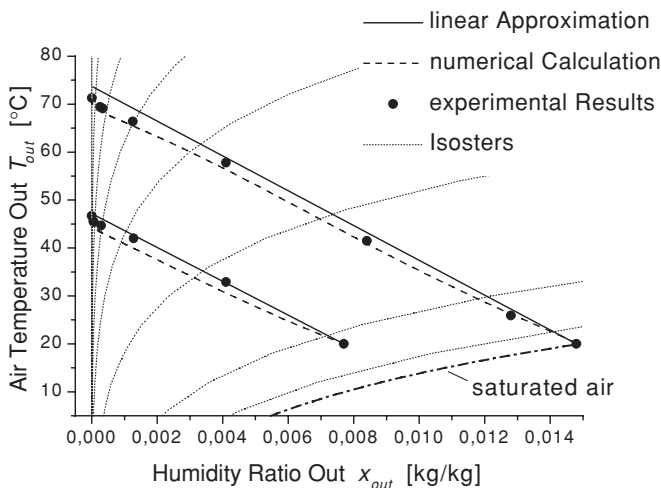

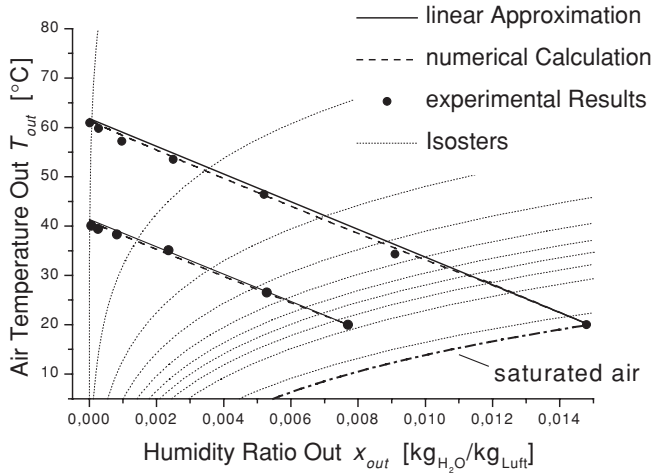*Figure 239.* T_{out}/x_{out}-Diagram for Zeolite 13X

Figure 240. T_{out}/x_{out}-Diagram for Silicagel

a adsorption with $T_{in} = 20\,°C$ and $x_{in} = 7.72$ g/kg. Both curves are parallel and almost linear for each adsorbent

The linear approximation in Figures 239 and 240 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 $T_{in} = 20\,°C$ and $x_{in} = 14.88$ g/kg, $x_{in} = 7.72$ g/kg respectively, in Figures 228 and 229.

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

$$\Delta T_{max} = x_{in} \frac{\Delta H_{ads}(C_{max})}{c_{p\,air} - \frac{x_{in}}{C_{max}} \cdot c_{Adsorbent}}. \tag{6}$$

This point can be easily calculated from the adsorption equilibrium of each adsorbent. As shown in Figures 2 and 3 the linear approximation gives a sufficient accurate estimates ($\pm 5\%$ 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 [4].

24.4.3. 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.
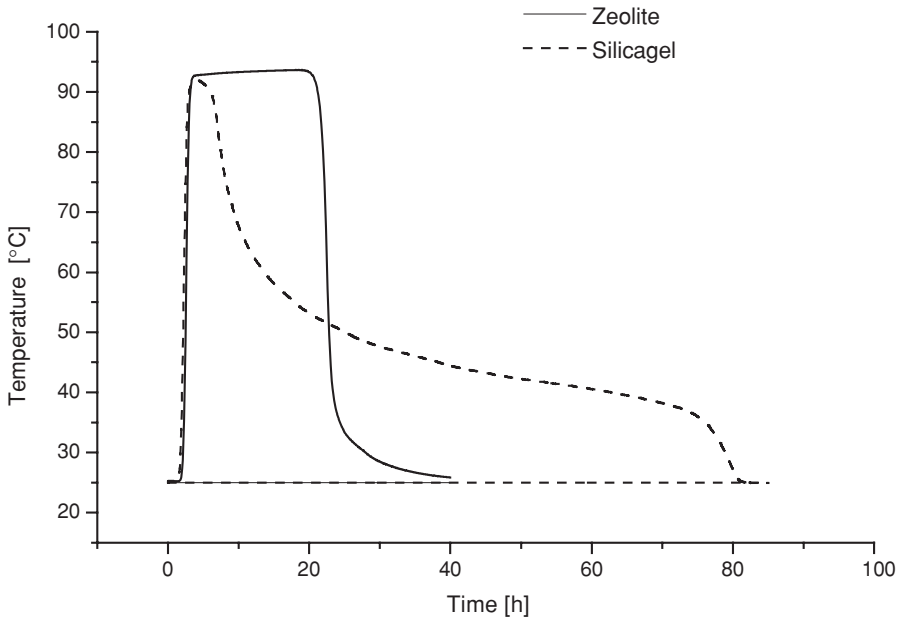
Figure 241. Thermal breakthrough curves (adsorption) for Zeolite and Silicagel

Figure 241 shows the shape of two thermal breakthrough curves for Zeolite and Silicagel 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. Silicagel has a falling outlet temperature just after reaching the maximum. The adsorption using zeolite is about half long as the silicagel adsorption.

The shape of the breakthrough curve is depending on the behavior of the so called mass transfer zone (MTZ). Figure 242 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 Silicagel 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 (Silicagel curve in Figure 242).

24.4.4. THERMAL COEFFICIENT OF PERFORMANCE AND ENERGY DENSITY

The thermal COP can be defined according to Figure 235 (neglecting Q_{evap}) as $COP_{th} = (Q_{cond} + Q_{ads})/Q_{des}$. The energies are defined per mass of ad-
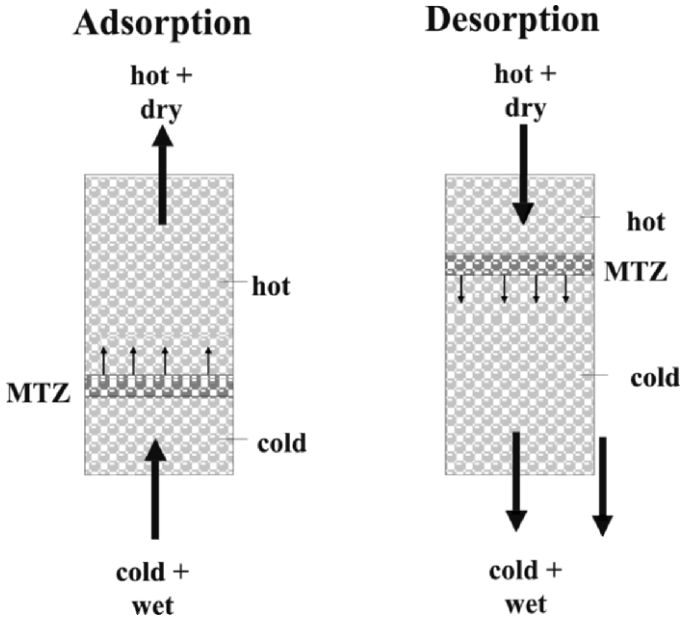
Figure 242. Mass transfer zone for ad- and desorption

sorbent. 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:

$$Q_{des} = Q_{cond} + Q_{bind} + Q_{sens} \tag{7}$$

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 $Q_{sens} = \Delta T_{sorb} c_{sorb\ eff}$. The condensation energy Q_{cond} and the binding energy (caused by the adsorption forces) Q_{bind} is defined according to Figure 243. 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:

$$\begin{aligned} Q_{cond} &= (C_{ads} - C_{des}) \cdot L(T) \\ Q_{bind} &= \int_{C_{des}}^{C_{ads}} (\Delta F + T\Delta S) \cdot dC \end{aligned} \tag{8}$$

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 [5], which can be determined from the adsorption equilibrium.
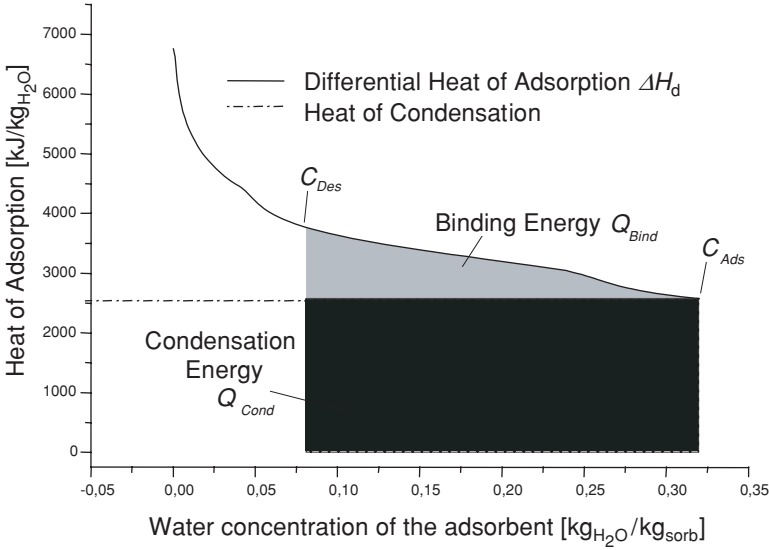
Figure 243. Definition of Q_{cond} and Q_{bind} for Zeolite as an example

Q_{ads} depends on the actual application. For the heat pump is $Q_{ads} = Q_{des}$. For long-term TES, Q_{sens} cannot 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 Figure 235) due to the dynamic profile of the outlet temperature $T_{out}(t)$ 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 can lead to drastic reductions in COP_{th} especially for adsorbents with low energy of binding Q_{bind} like silicagel [4].

The energy density ρ_Q is defined as

$$\rho_Q = \frac{(Q_{cond} + Q_{bind}) \cdot m_{sorb}}{V_{sorb}} = (Q_{cond} + Q_{bind}) \cdot \rho_{sorb} \qquad (9)$$

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}.

24.4.5. CONCLUSIONS

Using the methods presented in this chapter, 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 [4].

The methods described in this chapter can be transferred to liquid sorption processes with slight modifications. The example of concentrated salt solutions and water absorption is described by Kessling [6].

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