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# Influence of Cycle Temperatures on the Thermochemical Heat Storage Densities in the Systems Water/Microporous and Water/Mesoporous Adsorbents

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**Abstract.** The adsorption equilibrium of water on microporous adsorbents (zeolites of NaA-, NaY- and NaX-type as well as their ion exchanged forms) and on mesoporous adsorbents (different silica gels and composite material i.e. silica gel + salt hydrate) has been studied experimentally and theoretically. Using the Dubinin theory of pore filling the characteristic curves of the adsorption systems and other relevant dependences such as isotherms, isobars, isosteres and the curve of the differential heat of adsorption were calculated. For all systems investigated the adsorption were calculated. $A_{\mathrm{ads}}$ and the desorption potential $A_{\mathrm{des}}$ of the closed heat storage system were estimated. These values define the working range of the adsorption/desorption cycle and allow to calculate the specific heat storage density $\Delta h_{\mathrm{sp}}$. On the basis of $\Delta h_{\mathrm{sp}}$ the different adsorbents were compared in order to select the optimal porous storage material for a given application.

The presented experimental and theoretical investigations show that the adsorption systems water-zeolite and water-composites are promising working pairs for thermochemical heat storage processes for hot tap water supply and space heating of single family dwellings. The advantage of the water-composite system is the low desorption temperature (solar energy) the main shortcoming the low temperature lift. The advantage of the water zeolite system is the high temperature lift, the shortcoming are the relative high desorption temperatures.

**Keywords:** thermochemical heat storage, water adsorption equilibrium, thermo-dynamical data, heat storage density, zeolites, composite adsorbents

## Introduction

Microporous and some mesoporous adsorbents are of increasing interest as storage materials mostly in combination with water as working fluid (Stach et al., 2001; Stach and Jänchen, 2000; Jänchen et al., 2004; Mugele, 2004) for application as heat transformers in adsorption heat pumps and thermochemical heat storage. These materials may be used in storages for the application of low temperature heat (e.g. solar energy) but as well of industrial waste heat. In most cases zeolites are the preferred microporous materials. They show a high energy density (if properly dehydrated) and as well a high temperature lift. Mesoporous adsorbents, in many cases they are represented by silica gels and aluminosilicates, posses a medium energy density and a limited temperature lift. Comparing both groups of adsorbents with analogous chemical composition but different pore systems it can be stated that the advantage of the mesoporous adsorbents are the low charging temperatures making it a preferred material for solar application.

In order to get a good performance of the heat transformation the adsorbents should be adapted to the special conditions of the transformation process. It is only possible if the crucial parameter of the porous materials for the given condition of the process are known. Crucial parameters are the temperature lifts and the energy density of the porous solids. These parameters are not known for the most adsorbents but have to be measured or calculated from data of the water adsorption equilibrium.

The main purpose of the presented paper is the experimental study of the physico-chemical properties of commercial and modified zeolites as representatives for microporous adsorbents and some special silica gels and by impregnation with salt hydrates modified silica gels (Levitzki et al., 1996; Aristov et al., 1996; Aristov et al., 1996) to evaluate for the studied systems the influence of cycle temperatures on storage density and temperature lift. It is intended to show how the nature of the porous character influence the properties of whole system.

## Experimental Section and Materials

Experimental investigations included measurements of the water adsorption/desorption equilibrium and of the storage energy density on synthesized and ion-exchanged zeolites, mesopores silicates and composite adsorbents. Composite adsorbents are two phase systems, consisting of a porous host matrix and a hygroscopic inorganic salt hydrates impregnated in the pore system. As porous matrix were used in our investigations different silicagels, zeolites, activated carbons and clay minerals. The porous matrix serve as a support for the finely dispersed salts and facilitates the heat and mass transfer.

In Table 1 some properties of the studied zeolites are compiled.

The water adsorption systems were investigated by thermogravimetry (TG) (SETARAM, 2000) differential scanning calorimetry (DSC) (SETARAM, 2000) microcalorimetry (MC) (SETARAM, 2000) and gravimetric measurements of the sorptions isotherms (Stach et al., 2001). The zeolites applied in this study were commercially available powders of the well known types NaA, NaY and NaX (Table 1). They were modified by standard procedures using exchange of $Na^+$ by $Li^+$, $Mg^{2+}$, $Ca^{2+}$, $Al^{3+}$, $Fe^{3+}$ and other cations (Stach et al., 2001).

Supports of the composite adsorbents were different silicagels and special alumino-silicates. They were impregnated mainly by concentrated solutions of $MgCl_2 \times 6H_2O$ and $CaCl_2 \times 6H_2O$ and afterwards dried.

The TG and DSC measurements were performed on a Setaram TG-DCS-111 equipment starting with 293 K up to temperature of 623 K with a heating rate of 10 K/min. in a nitrogen stream of 1 L/h. Before the gravimetric and calorimetric measurements the samples were saturated with water vapor of 10.5; 19.7 and in some cases 28.5 mbar at room temperature in a desiccator. The adsorption isotherms were measured gravimetrically at 293, 313 and 333 K with a common McBain quartz spring balance equipment with MKS Baratron pressure sensors. Adsorption and desorption branches of the isotherms were estimated.

The differential molar adsorption heats of water adsorption were studied at 313 K using a Calvet-type microcalotimeter (Setaram C80) which was connected to a standard volumetric adsorption apparatus, with MKS Baratron sensors. Before the measurements the samples (about 150 mg for isotherms and 500 mg for the heat measurements) were calcined in high vacuum

*Table 1.* Measured and extrapolated water adsorption capacity and integral heat of water desorption for some ion-exchanged zeolites (Stach et al., 2001).

| Zeolites | Si/Al | Elementary cell | $a$ [g/g] | $q_{in}$ [kJ/kg] | $q_{Na}/q_{Mg}$ [%] | $q_v$ [kJ/kg] | $q_v/q_{in}$ [%] |
|---|---|---|---|---|---|---|---|
| NaA | 1 | $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \times 27H_2O$[1] | 0.286 | 1080 | – | 698 | 65 |
| MgA | 1 | $Mg_6[(AlO_2)_{12}(SiO_2)_{12}] \times 27H_2O$[1] | 0.419 | 1948 | 180 | 1022 | 59 |
| NaY | 2.43 | $Na_{56}[(AlO_2)_{56}(SiO_2)_{56}] \times 268H_2O$ | 0.335 | 1217 | – | 817 | 67 |
| MgY | 2.43 | $Mg_{28}[(AlO_2)_{56}(SiO_2)_{56}] \times 268H_2O$ | 0.418 | 1638 | 135 | 1026 | 62 |
| NaX | 1.25 | $Na_{86}[(AlO_2)_{86}(SiO_2)_{86}] \times 264H_2O$ | 0.338 | 1289 | – | 824 | 64 |
| MgX | 1.25 | $Mg_{43}[(AlO_2)_{86}(SiO_2)_{86}] \times 264H_2O$ | 0.449 | 2682 | 208 | 1098 | 41 |

[1] pseudo elementary cell, $a$ = water adsorption capacity.

$q_{in}$ = integral heat of water desorption.

$q_v$ = heat of water vaporization.

$q_{Na}/q_{Mg}$ = percentage share of $q_{in}$ for Na-zeolites in $q_{in}$ for Mg-zeolites.

$q_v/q_{in}$ = percentage share of $q_v$ in $q_{in}$.

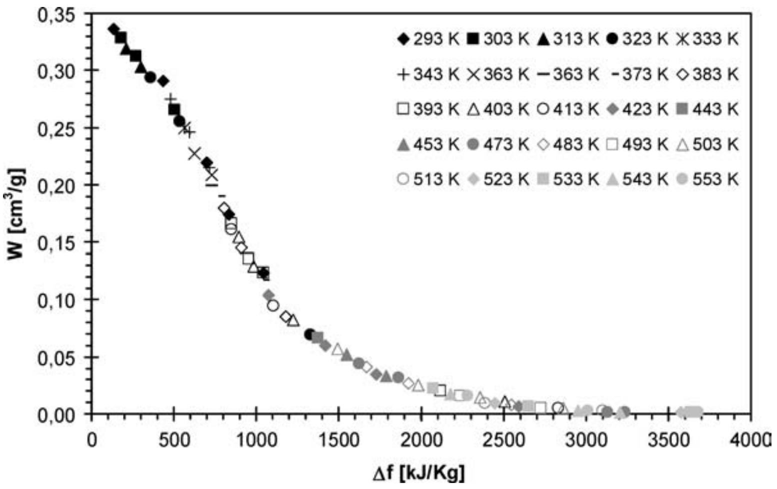

*Figure 1.* Characteristic curve of the system $H_2O$/NaX (Dubinin et al., 1967).

($<10^{-5}$ mbar) at 623 K (zeolites) and 523 K (composites) for 2 h, respectively.

*Theoretical Fundamentals*

For the description of the adsorption isotherms and the calculation of thermodynamic data Dubinins theory of pore filling (Dubinin, 1960, 1966, 1967) was used. These theory was primary developed for microporous activated carbons but it was found that it could as well be used for the adsorption processes in other microporous adsorbents as for example zeolites (Stach et al., 2002; Jänchen et al., 2004; Hauer, 2002, 2000; Nuñez, 1999, 2001) and also for silica gels et al.. In contrast to the potential theory of Polanyi (1932) the Dubinin approach considers not the inner surface of the micropores as crucial but the pore volume because the adsorbed molecules (comparable in size with the micropores) are influenced by overlapping adsorption potential thus generating large heats of adsorption. Dubinin defines the specific volume W of the adsorption space (cavities and pores of the microporous material) as:

$$W = a/\rho_{\mathrm{ads}} \tag{1}$$

(with $a$ = adsorbed amount $[g/g]$, depending on $T$ and $p$ and $\rho_{\mathrm{ads}}$ = density of the adsorbate [cm$^3$/g], depending on $T$) and the differential work of adsorption $A$ as:

$$A = -\Delta f = \mathrm{RT}(\ln p_{\mathrm{s}}/p) \tag{2}$$

(with $\Delta f$ = free energy and $p_{\mathrm{s}}$ = saturation pressure of the adsorptive in equilibrium with the liquid bulk phase at the studied temperature $(T)$).

Plotting $W$ in dependence on A it was found for many adsorption systems with activated carbon that almost all experimental prints are described by one single curve (Dubinin, 1960). The relation $W = f(A)$ is called "characteristic curve" showing for many adsorption systems an invariance of temperatures (Dubinin et al., 1966). In Fig. 1 the characteristic curve of the system $H_2O$/NaX is plotted including equilibrium data (expressed by symbols in the temperature range $T$ = 293 K to 523 K (Dubinin et al., 1966).

The presented adsorption system shows a pronounced temperature invariance, i.e. all measured points of adsorption isotherms are described by one single curve. Knowing the characteristic curve of an adsorption system, the vapor pressure curve of the adsorptive ($p_{\mathrm{s}} = f(T)$) and the temperature dependence of the adsorptive density ($\rho_{\mathrm{ads}} = f(T)$) all thermodynamic relations can be calculated.

In principle the characteristic curve may be constructed using only one measured isotherm. No other adsorption model allows the extrapolation of one measured isotherm to other with different temperatures. This is why the Dubinin theory is often used to parametrize the thermodynamic characteristics (Nuñez et al., 1999).

The differential enthalpy of adsorption q is found as

$$q = \mathrm{h}_e + A - T\Delta \mathrm{s} \tag{3}$$

($\mathrm{h}_e$—evaporazation enthalpy, $\Delta s$—differential adsorption enthalpy)

The differential adsorption entropy follows from the characteristic curve as

$$\Delta s = \alpha(\delta A/\delta \ln W) \qquad (4)$$

($\alpha$ - volume expansion coefficient of the adsorptive bulk phase).

In the following the Dubinin theory will be used to analyze the thermochemical heat storage process. This storage process (Nuñez et al., 1999) proceeds in two steps:

- desorption of the water (as working fluid) by heating of the adsorber to a temperature $T_{des}$
- adsorption of water vapor on the adsorbents in the adsorber at temperature $T_{ads}$

During the desorption phase of a thermochemical cycle the desorbed water is condensed at a temperature $T_{co}$ and in the adsorption phase the water is evaporated at a temperature $T_{ev}$. The four defined temperatures ($T_{ads}$, $T_{des}$, $T_{co}$ and $T_{ev}$), derived from the conditions of the concrete heat storage process, determine the adsorption work A in the adsorption/desorption cycles.

The maximum value of the adsorption work $A_{max}$ determinated by the desorption and condensation temperature is given in the following equation

$$A_{max} = \mathrm{RT}_{des} \ln[\mathrm{p}_s(T_{des})/p(T_{co})] \qquad (5)$$

the minimum account of adsorption work $A_{min}$ depends on the adsorption and evaporation temperature follows from

$$A_{min} = \mathrm{RT}_{ads} \ln[\mathrm{p}_s(\mathrm{T}_{ads})/\mathrm{p}(\mathrm{T}_{ev})]. \qquad (6)$$

In the Fig. 2 both limiting values of the adsorption work are shown in the characteristic curve of one NaX zeolite.

The chosen temperatures for the heat storage process (in Fig. 2) are derived from practical reasons. Groundwater with $T \approx 283$ K is often used as heat source and heat sink for evaporation ($T_{ev}$) and condensation ($T_{co}$) of water. Therefore all calculations were performed with $T_{ev} = T_{co} = 283$ K. As adsorption temperature $T_{ads} = 333$ K was selected and as desorption temperature $T_{des} = 423$ K. Using this temperatures values of $A_{min} = 429$ [kJ/kg] and $A_{max} = 1164$ [kJ/kg] were found and plotted in Fig. 2 as perpendicular lines.

It should be emphasized:

- that under the given temperatures only the part of the characteristic curve between $A_{min}$ and $A_{max}$ delivers adsorption equilibrium data and
- that the limiting values of the adsorption work do not depend on the adsorption equilibrium but on the liquid/vapour equilibrium of water.

From Fig. 2 follows the difference of the sorption volumes for the zeolite:

$$\Delta W = W_{ads}(333\,\mathrm{K}) - W_{des}(423\,\mathrm{K}) \qquad (7)$$

and with $\rho_{ads} \sim 1$ the difference of adsorbed amounts $\Delta a$. It corresponds for the zeolite NaX to $\Delta a = 0.182$

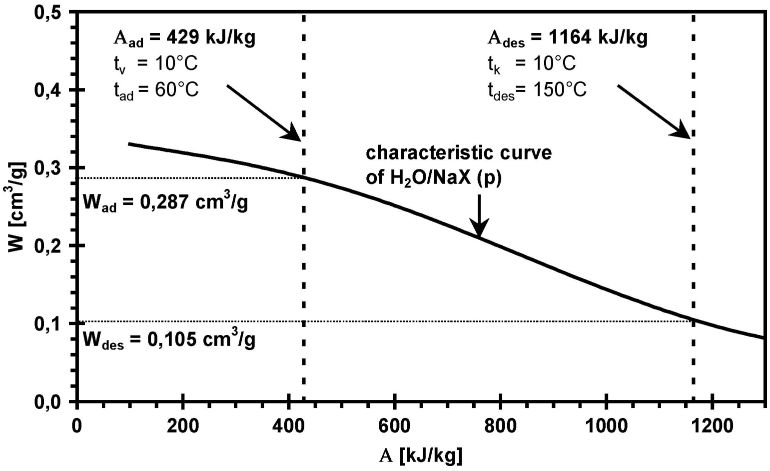

*Figure 2.* Working range of a thermochemical heat storage system with NaX (in powder form) as storage material.

[g/g]. That means the adsorption capacity of NaX in the thermochemical storage process under the given process conditions corresponds to 0.182 [g/g].

Knowing the adsorbed amount and the curve of the differential heat of adsorption in dependences on the amount adsorbed $\Delta\bar{h}_{\text{ads}} = f(a)$ the storage density $\Delta h_{\text{sp}}$ is easy to find by integration

$$q_{\text{in}} = \int_{a_{\text{des}}}^{a_{\text{ads}}} \Delta h da. \tag{8}$$

From

$$\Delta\bar{h}_{\text{ads}} = \Delta\bar{h}_e + \Delta\bar{h}_b \tag{9}$$

($\Delta\bar{h}_e$ - evaporation enthalpy, $\Delta\bar{h}_b$ - binding enthalpy) and

$$\Delta\bar{h}_b = \Delta f - T\Delta s \tag{10}$$

follows

$$\Delta\bar{h}_{\text{ads}} = \Delta\bar{h}_e + \Delta f - T\Delta s \tag{11}$$

and

$$\begin{aligned}\Delta h_{\text{sp}} &= \int_{a_{\text{des}}}^{a_{\text{ads}}} \Delta\bar{h} da = \int_{a_{\text{des}}}^{a_{\text{ads}}} \Delta\bar{h}_e(T) da \\ &\quad + \int_{a_{\text{des}}}^{a_{\text{ads}}} \Delta f da + \int_{a_{\text{des}}}^{a_{\text{ads}}} T\Delta s da. \end{aligned} \tag{12}$$

In the paper presented all storage energy values were found by integration of the curve of the differential heat of adsorption between the limits $a_{\text{ads}}$ and $a_{\text{des}}$. As an example in the following Fig. 3 the specific storage energy density of water on the zeolite NaX is presented. It corresponds to the hatched area in the shown figure. Increasing the desorption temperature the numerical value of $a_{\text{des}}$ becomes smaller and the specific density larger.

### *Experimental results and discussion*

In Fig. 4 and Table 1 the results of the TG- and DSC-measurements on the pure $Na^+$-form and with $Mg^{2+}$-cation exchanged zeolites of the types NaA, NaY and NaX are presented. From Fig. 4 follows a linear increase of the water adsorption with rising number of $Mg^{2+}$-ions replacing $Na^+$-ions. Though in all systems studied an increase of water adsorption with the number of the bivalent cation is found the numerical values are different reflecting the diverse field strength in the voids and pores of the various crystal structures of the zeolites.

The replacement of two large monovalent sodium cations (1.02 Å) by one smaller bivalent magnium ion (0.72 Å) (for charge compensation) enlarges the adsorption volume giving more place for the water molecules and rises the adsorbed amount. Quite similiar linear relations are found between the number of exchanged $Mg^{2+}$-ions and the integral heats of water desorption. In Table 1 these integral heats of the Na-form of the different zeolite types are compared with the (extrapolated) data for the fully exchanged Mg-type

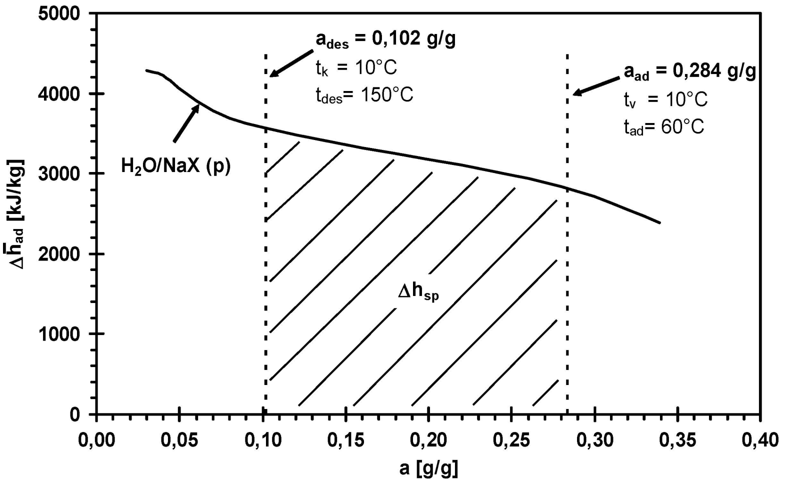

*Figure 3*. Specific storage density of water on zeolite NaX.

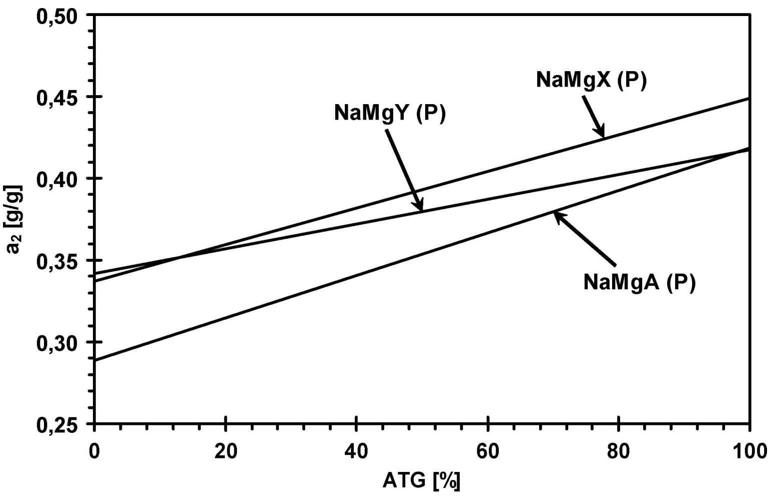

*Figure 4.* Adsorbed amount of water vs Mg ion exchange degree (ATG) for zeolite NaA and NaX at 293 K and 10.5 mbar equilibrium pressure.

of the correspond molecular sieves. It is seen that in all systems investigated the exchange of $Na^+$-against $Mg^{2+}$-ions rises the energetic interaction by a factor between 1.4 and 2.1. In a first approximation the integral heat of adsorption/desorption may by regarded as a storage density. The ion exchange rises the storage density of the exchanged material up to 100%.

From Table 1 follows further that the heat of vaporization contributes to a large extent to the storage density (last column). It corresponds to about 66% for the sodium forms of the three zeolites and becomes reduced to nearly 40% to 60% for the magnesium form of the molecular sieves. However, high heats of desorption demand also high temperatures for the removal of the water molecules from the pore system. For example $T \geq 623$ K are needed to remove 95% of the adsorbed water amount in NaMgA-zeolites.

The following Fig. 5 compares by means of an example the characteristic curves of the water adsorption on the zeolite NaY and NaMgY (degree of ion-exchange = 67%).

From the picture follows that the experimental points are well described by a single curve showing the temperature invariance of the characteristic curves. The characteristic curves were calculated from measured adsorption isotherms using higher polynomials. At very low and rather high adsorption work deviation of the calculated values from the smooth curve were

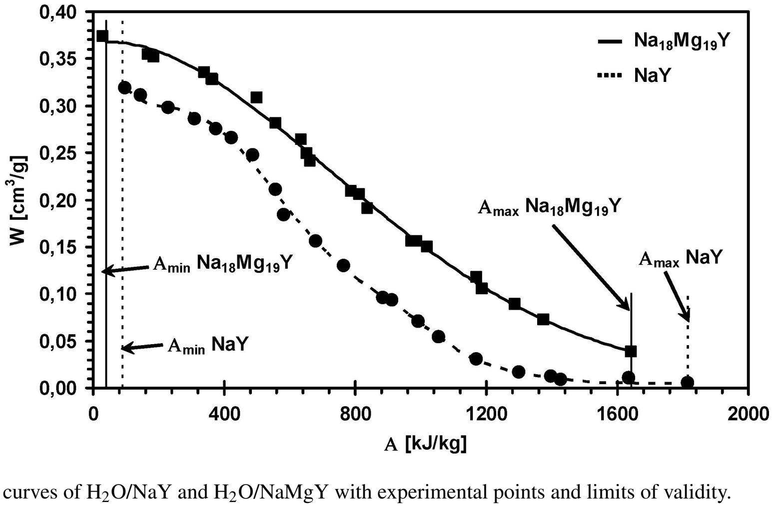

*Figure 5.* Characteristic curves of $H_2O$/NaY and $H_2O$/NaMgY with experimental points and limits of validity.

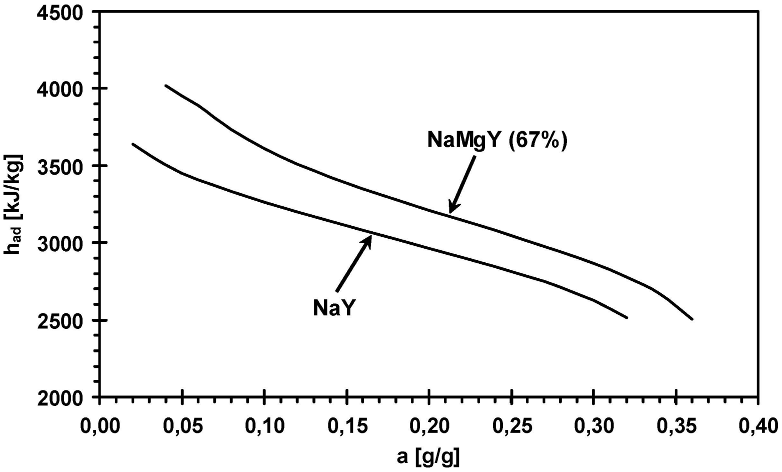

*Figure 6.* Differential heat of water desorption on NaY and NaMgY.

found thus reflecting regions of non-validity of the Dubinin equation. The limits of the characteristic curves are expressed by vertical lines and the symbols $A_{\min}$ resp. $A_{\max}$ $A_{\min} = 31$ [kJ/kg] and $A_{\max} = 1642$ [kJ/kg] with the adsorption volumes $W_{\text{ads}} = 0.371$ [cm$^3$/g] and $W_{\text{des}} = 0.037$ [cm$^3$/g].

As can be seen from Fig. 5 the regions of non-validity of the Dubinin equation for both zeolites studied are rather small. These limitation of the validity region of the charactristic curve are not critical because in practical application of heat storage by water adsorption in zeolites the working range of the function W = f(A) is found within the shown limitation (Hauer, 2002).

In Fig. 6 the curves of the differential water adsorption heats in dependence on the adsorbed amount for the zeolites NaY and NaMgY are presented. They were calculated from the data of the characteristic curves (Fig. 5) via the isosteres.

Curve fitting by higher polynominals allows a good description of the function $\Delta\bar{h} = f(a)$ and its integration to get the integral heat of adsorption (Eq. (8)). From Fig. 6 follows that the ion-exchanged Y-zeolites exhibit higher differential desorption heats than the NaY-molecular sieve. For the integral heats of desorption this was already shown in Table 1.

Using the characteristic curve of the system $H_2O$/KG5-88 ($CaCl_2$) the water adsorption isotherms and isobares on the composite material were calculated. They are presented in the following figures.

Figure 7 shows the isotherms for the temperatures form 273 to 353 K. Included are the experimental points for three temperatures. As can be seen the measured points are well reproduced. All isotherms are characterized by a pronounced step. The adsorbed amount of water at the step corresponds to a molar ratio N of $N_{H_2O} : N_{CaCl_2} = 2$, in accordance with (Aristov et al., 1996).

That is in accordance with the formation of a dihydrate i.e. $CaCl_2 \times 2H_2O$. With rising temperature the width of the steps become smaller but it still exists up to 353 K. The water adsorption at 293 K rises after the step very strongly and reaches at $p = 10$ mbar a value as high as 1 [g/g]. By reducing the water pressure to 0.1 mbar (at the same temperature) almost all of the adsorbed water can be removed. This adsorption equilibrium makes the composite material very interesting for the storage of low temperature heat especially for solar energy.

In Fig. 8 the water isobars of the same system are plotted. They give additional evidence for the favourable range of water adsorption equilibrium on the calciumchloride silica gel composite.

At an equilibrium pressure of water vapour p $\sim$ 10 mbar and a desorption temperature of 323 K about 80% of the adsorbed water are removed. The desorption of the remaining two dihydrate water molecules is possible rising $T_{\text{des}}$ to 373 K. This temperature is easily to be reached by solar collectors.

The most important properties of an adsorption system for thermochemical storage are the temperature lift ($T_{\text{lift}}$) and the energy density of the storage material ($\Delta h_{\text{sp}}$). The temperature lift is the temperature difference between the adsorber and evaporator (adsorption phase) or adsorber and condensator (desorption phase). The energy density is the energy per unit volume and

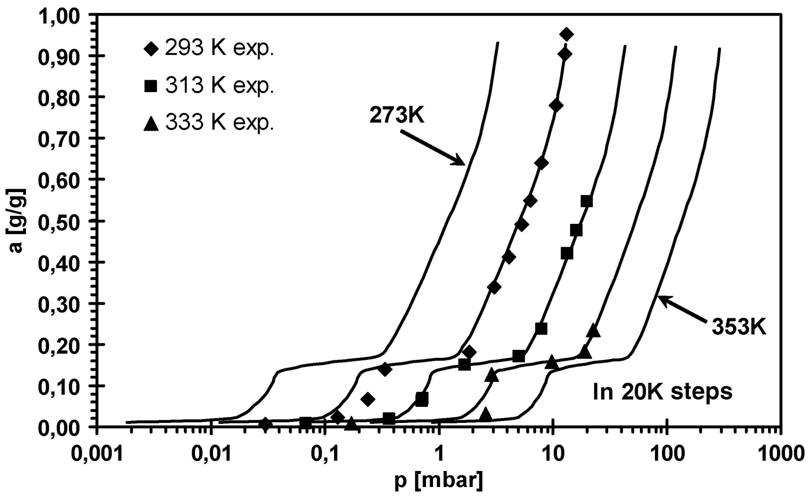

*Figure 7.* Calculated water isotherms of the system $H_2O$/KG5-88 ($CaCl_2$), symbols experimental points.

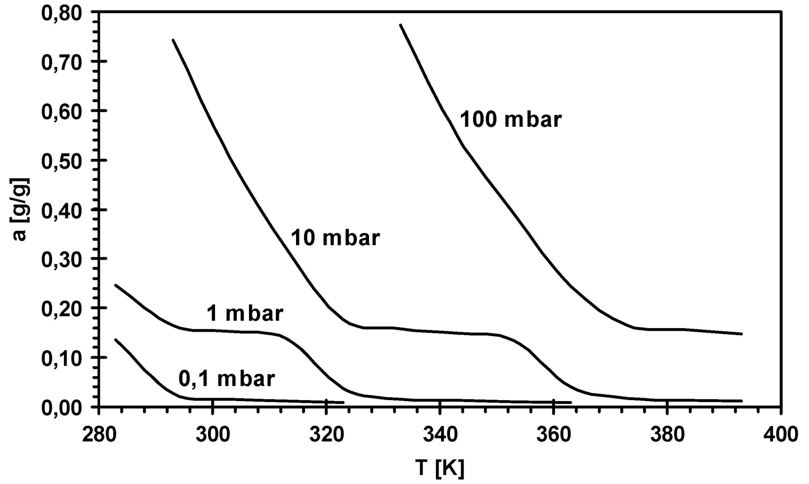

*Figure 8.* Calculated water isobars of the system $H_2O$/KG5-88 ($CaCl_2$).

may be calculated as product of the specific energy (energy per unit mass) and the bulk density $\rho_g$ (Nuñez et al., 1999).

In order to show the influence of the desorption temperature on the specific water adsorption volume for NaY and NaMgY in dependence on the adsorption work the characteristic curves were calculated. In Fig. 9 the results are plotted for the following cycle temperatures: $T_{ev} = 283$ K, $T_{co} = 283$ K, $T_{ads} = 313$ K, $T_{des} = 363$ K. It can be seen, that the adsorption potential $A_{ads}$ correspond to 259 [kJ/kg] and the desorption potential $A_{des} = 678$ [kJ/kg]. The relevant specific adsorption volumina are $W_{NaY} = 0.140$ [cm$^3$/g] and $W_{NaMgY} = 0.105$ [cm$^3$/g] i.e. the specific adsorption volume of the zeolite NaY is higher than the value of NaMgY. The consequence of this result is that the specific storage density of NaY ($\Delta h_{sp} = 406$ [kJ/kg]) is as well higher than $\Delta h_{sp}$ for the zeolite NaMgY ($\Delta h_{sp} = 307$ [kJ/kg]).

This is surprising because the differential heat of water adsorption on molecular sieve NaMgY ($\Delta h_{ads}$) is in whole range of the heat curve larger than the relevant $\Delta h_{ads}$ values of NaY. The reason for that unexpected behavior of both zeolites is the stronger desorption of water form NaY due to the weaker interaction of water at this temperature.

The following picture shows the specific water adsorption volumina of the same adsorption systems but

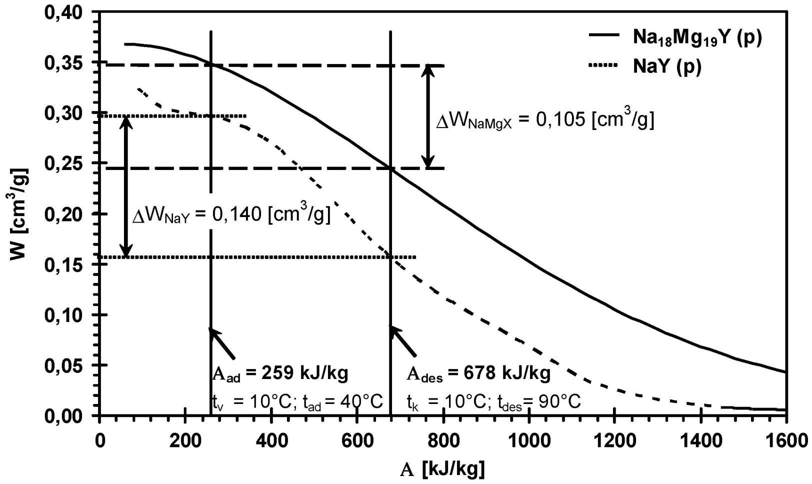

*Figure 9.* Specific adsorption volumina in the systems $H_2O$/NaY and $H_2O$/NaMgY for a desorption temperature of 363 K.

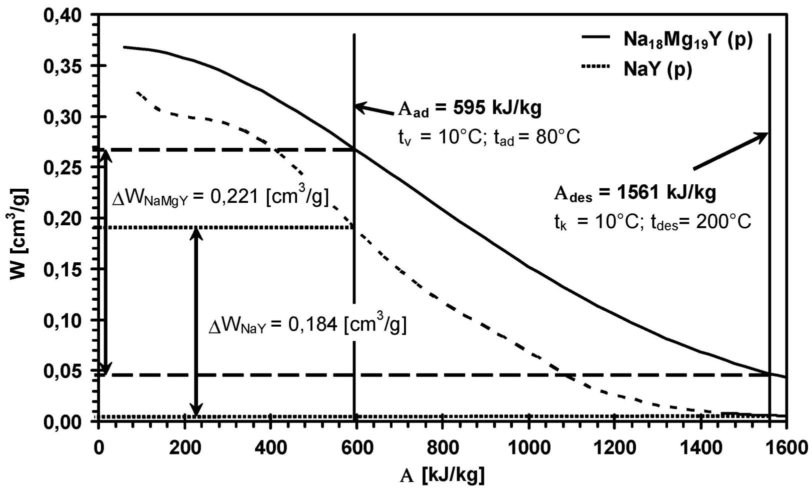

*Figure 10.* Specific adsorption volume in the systems $H_2O$/NaY and $H_2O$/NaMgY for a desorption temperature of 473 K.

with changed cycle temperatures (see Table 2). In contrast to the foregoing Fig. 8 the desorption temperature amounts to 473 K. The consequence of the increased temperature are changed adsorption volumina ($W_{NaY} = 0.184$ [cm$^3$/g] and $W_{NaMgY} = 0.221$ [cm$^3$/g]) and specific storage densities ($\Delta h_{sp}$ for NaY = 599 [kJ/kg] and $\Delta h_{sp}$ for NaMgY = 778 [kJ/kg]). The specific heat storage density of the zeolite NaMgY is under these conditions higher as for the molecular sieve NaY. This is in agreement with expectations derived from the curves of the differential adsorption heats as function of coverage. The main conclusion which can be drawn from the last consideration of the influence of desorption temperature on heat storage density is, that knowing the differential heat of adsorption is not sufficient for an assessment concerning the storage density. It is on the contrary necessary to calculate the specific storage density for the given process temperatures for every adsorbent in order to decide which is the best suited heat storage material for that particulary heat transformation process.

The following Fig. 11 compares the specific heat storage density of a microporous (NaLiX) and a mesoporous composite adsorbent (Silica Gel + 50% $CaCl_2$) in dependence on the desorption ($T_{des}$) and the adsorption temperature ($T_{ads}$). The temperatures of the heat

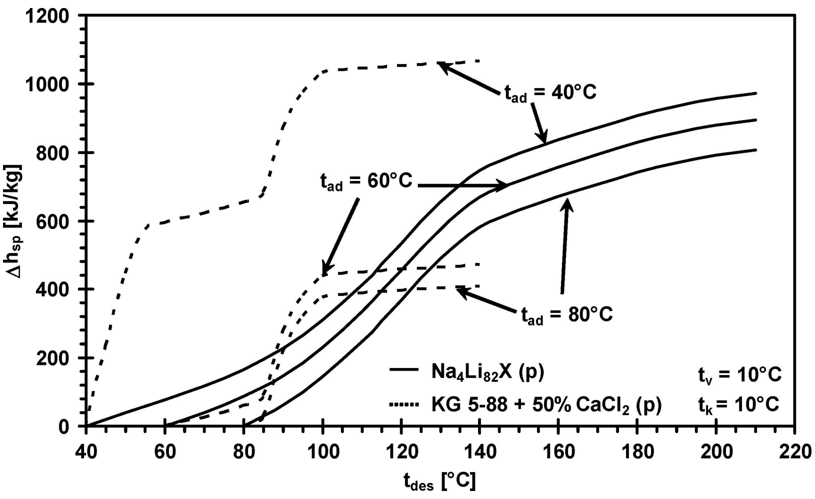

*Figure 11.* Specific heat storage density of the water adsorption on $Na_4Li_{82}X$ and KG5-88 + $CaCl_2$ in dependence on the desorption temperature.

transformation process $T_{ev}$ and $T_{co}$ are constant and correspond to 283 K.

Some important conclusions follow from the Fig. 11:

1. For desorption temperatures of 373–413 K which are easily reached by solar collectors and low application temperature (for instance 313 K used as ceiling temperature) the mesoporous composite adsorbent possess a larger storage density than the microporous zeolite.
2. With rising adsorption temperature (in the same desorption temperature region) the storage density of the composite becomes smaller and is comparable with the storage densities of the zeolite.
3. At heating temperatures of $T > 413$ K and adsorption temperatures $T > 313$ K the zeolite demonstrates larger storage densities than the composite adsorbent.

*Table 2.* Temperatures and adsorption potentials for two cycles of heat storage in the systems $H_2O$/NaY and $H_2O$/NaMgY.

| Zeolite | $T_v$ [K] | $T_{ads}$ | $T_{ev}$ | $T_{des}$ | $A_{ads}$ [kJ/kg] | $A_{des}$ [kJ/kg] |
|---|---|---|---|---|---|---|
| NaY | 283 | 313 | 283 | 363 | 259 | 678 |
| NaMgY | 283 | 353 | 283 | 473 | 595 | 1561 |

The conclusions were valid for all studied microporous zeolites and mesoporous adsorbents of different composition.

Not only from a scientific point of view but also for practical reasons the comparison of the common heat storage by water tanks with the thermochemical heat storage is of high interest. Therefore in the following Table 3 this comparison is demonstrated.

In Table 3 the specific heat storage densities were calculated for a desorptions temperature of 483 K in the case of the zeolite and for 413 K in the case of the composite material (the condensation and evaporation temperature being the same −283 K). The

*Table 3.* Comparison of the specific heat storage density of the systems $H_2O$/NaLiX and $H_2O$/KG5-88 + $CaCl_2$ with the heat capacity of water at different temperatures

| Storage material | $\Delta h_{sp}$ [kJ/kg] | | | $\Delta h_{sp}/\Delta h_{spH2O}$ [%] | | |
|---|---|---|---|---|---|---|
| | 313 K | 333 K | 353 K | 313 K | 333 K | 353 K |
| Water | 125 | 210 | 294 | 100 | 100 | 100 |
| $H_2O$/NaLiX [1] | 972 | 893 | 807 | 778 | 425 | 274 |
| $H_2O$/KG5-88 + $CaCl_2$ [2] | 1064 | 470 | 409 | 851 | 224 | 139 |

[1] $T_{des} = 483$ K; [2] $T_{des} = 413$ K.

given temperatures are working temperatures for different practical applications. From the table can be seen that at a storage temperature of 413 K the specific heat storage density of the composite adsorbent is the highest and corresponds to 8.5 fold of the hot water storage system. For a given heat storage capacity the volume requirement of the thermochemical storage system is much smaller than that for a water storage. With rising storage temperatures the quotient of $\Delta h_{\text{sp}}$ becomes rapidly smaller. The reason for this behavior is easily found by the fact that with rising storages temperature the heat capacity of water increases but the specific heat storage density decreases.

## Conclusions

1. The water adsorption capacities at different temperatures and the water adsorption heats are the most important properties for adsorbents in thermochemical heat storage systems. In order to estimate these quantities the water adsorption equilibrium was measured for three commercially available zeolite powders (NaA, NaY, NaX) and for their modified forms of the named zeolites. The modification was performed with different amounts of $Mg^{2+}$-cations (and other). The results show that with rising content of $Mg^{2+}$-cations of the zeolites the water adsorption capacity and integral adsorption heat also increase up to 100%. The ion exchange allows to tailor zeolites for special applications in heat transformation applications.
2. As an example for a composite adsorbent a mesoporous silica gel KG5-88 with impregnated $CaCl_2 \times 6H_2O$ was investigated. It shows at room temperature and an equilibrium pressure of about 20 mbar a higher adsorption capacity than the best zeolites and as well a higher integral heat of water adsorption. In contrast to the zeolites the necessary desorption temperature of the composites are about 373 K. The water/composite adsorption systems should therefore be particularity interesting for solar application.
3. Often in the literature the integral heat of adsorption is identified as heat storage density of the adsorbent. The investigations showed that these considerations are misleading. The thermochemical heat storage density depends on four the storage process describing temperatures for adsorption, desorption, condensation and evaporation. To consider all of the temperatures is necessary to calculate comparable storage densities of different adsorbents.
4. For the description of the water adsorption equilibrium on the microporous adsorbents the Dubinin theory of pore filling was used. The measured and calculated water adsorption isotherms showed a good coincidence and the characteristic curves proofed a temperature invariance. Though the Dubinin equations were derived for microporous solids they describe as well the mesoporous and composite adsorbents.
5. On the basis of the characteristic curves and using standard temperatures of heat supply for small houses the correct specific heat storage densities and the specific adsorption volume were calculated in dependence on the adsorption and desorption temperatures for microporous and mesoporous adsorbents. The comparison of both types of adsorbents shows that

   - mesoporous adsorbents (composites) need relatively low desorption temperatures and posses a small temperature lift.
   - microporous adsorbents (zeolites) need relatively high desorption temperatures and produce high temperature lifts.

## Nomenclature

| | |
|---|---|
| $A$ | adsorption potential (kJ/kg) |
| $a$ | adsorbed amount of water per mass unit of dry adsorbent (g/g) |
| $\Delta f$ | specific free energy (kJ/kg) |
| $\bar{h}$ | differential specific enthalpy (kJ/kg) |
| $\Delta \bar{h}_{\text{ads}}$ | differential specific isosteric adsorption enthalpy (kJ/kg) |
| $\Delta h_{\text{sp}}$ | specific heat storage density (kJ/kg) |
| $\Delta h_{\text{v}}$ | volumetric heat storage density (kJ/m$^3$) |
| $m$ | mass (kg) |
| $N$ | material amount (mol) |
| $p$ | water partial pressure (mbar) |
| $p_{\text{s}}$ | water saturation pressure (mbar) |
| $q$ | heat of desorption (kJ/kg) |
| $q_{\text{in}}$ | integral heat of water desorption (kJ/kg) |
| $q_{\text{v}}$ | heat of water vaporization (kJ/kg) |
| $R$ | gas constant (kJ/(kg K)) |
| $s$ | specific entropy (kJ/(kg K)) |
| $T$ | temperature (K) |
| $T_{\text{ads}}$ | adsorption temperature (K) |
| $T_{\text{des}}$ | desorption temperature (K) |

| | |
|---|---|
| $T_{ev}$ | evaporation temperature (K) |
| $T_{co}$ | condensation temperature (K) |
| $V$ | volume ($m^3$) |
| $W$ | specific adsorption volume ($cm^3/g$) |
| $A_{min}$ | minimal adsorption potential (kJ/kg) |
| $A_{max}$ | maximal adsorption potential (kJ/kg) |
| $N_{H_2O}$ | mol number of $H_2O$ (mol) |
| $N_{CaCl_2}$ | mol number of $CaCl_2$ (mol) |
| $T_{lift}$ | temperature lift (K) |
| $\rho_{ads}$ | water density (g/mL) |

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