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Enhancement of the Heat and Mass Transfer in Compact Zeolite Layers

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Abstract. Heat and mass transfer during the adsorption of water on zeolite has been studied both theoretically and experimentally. A dynamic simulation model of a zeolite layer has been developed to estimate the predominant transport resistances and calculations were carried out to assist the simultaneous experimental investigations. On one hand, a metallic matrix was added to the compact zeolite layer to improve the heat transfer. On the other hand, pore-forming materials such as melamine or tartaric acid were used. These organic components are removed during drying of the zeolite so that the mass transfer inside the zeolite is significantly enhanced compared to a granulated zeolite bed. The experimental investigations show that the theoretically deduced possibilities of improving the adsorption process can be realized in the manufactured zeolites.

The investigations described here are of interest for the development of adsorption heat pumps. Due to the thermodynamic characteristics the adsorption system zeolite-water is a promising working pair for this application. The investigations show that the main shortcoming of these machines, the thermal output, can be increased significantly.

Keywords: adsorption heat pump, experimental kinetic data, heat and mass transfer, simulation, zeolite

Introduction

The following investigations have been carried out to develop a periodically operating adsorption heat pump for domestic heating with the working pair zeolite-water. The sorbent zeolite is a very common catalyst and also displays very good characteristics for the heat pump application (Alefeld et al., 1981; Eichengrün and Winter, 1994; Restuccia et al., 1988; Jung et al., 1985). A large quantity of water of around 150 g/kg$_{\text{zeolite}}$ can be charged and discharged during the heat pump process. The useful temperature range is large and the system is thermally stable within the process temperatures (Rothmeyer, 1985). The working pair is non-poisonous, non-flammable and minimally corrosive. One disadvantage is the high freezing point of water. However, the periodic operation of the heat pump ensures that the evaporation of ice does not cause serious problems.

Different systems operating with at least two adsorbers are proposed to avoid intermittent cycles (Douss et al., 1988; Miles and Shelton, 1986; Tchernev, 1990). Such systems promise a significant improvement in the overall performance by internal heat recovery. A comparison between analytical, numerical and experimental results for the socalled thermal wave process can be found in Aittomäki and Härkönen (1992) and Miles et al. (1992).

In the investigations carried out by Maier-Laxhuber (1983), Restuccia et al. (1988), and Jung et al. (1985) zeolite pellets were used as an adsorbent. The investigations showed that the initial adsorption rate is high due to the large surface of the zeolite bed. However, the poor thermal conductivity of a zeolite bed of around 0.15 W/(mK)(Völkl, 1982) and the poor contact between the zeolite pellets and heat exchanger wall cause a steep drop in the adsorption rate. This leads to long cycle times and a low thermal output of the heat pump. Thus, granular zeolite does not promise good results.

The use of zeolite powder is also unfavorable since the coupled heat and mass transfer inside a pulverized zeolite bed is insufficient (Eichengrün and Winter, 1994).

The most promising material is compact zeolite layers, which is prepared of zeolite powder and a binder and linked directly to the heat transfer area. This produces a very good thermal contact between the compact layers and the heat transfer area, and a higher thermal conductivity than a zeolite bed is attained. One disadvantage of the compact structures is the smaller mass transfer area compared to granules. The low diffusivity in the solid may dominate the adsorption process. But whereas it is difficult to improve the thermal conductivity of a zeolite bed, the heat and mass transfer of solid zeolite structures can be enhanced by appropriate additives. Higher thermal conductivity can be achieved by the use of a metallic matrix, which is inserted in the solid adsorbent. The mass transfer can be improved by using pore-forming materials. These organic components are completely removed during drying of the zeolite so that the macropore fraction in the zeolite is enhanced. Doelle (1978) reports that the porosity of zeolite pellets can be increased from 26 vol.% to 63 vol.% by the use of melamine and tartaric acid. Guilleminot et al. (1994) used a metallic matrix and a highly conductive carbon matrix and conclude that a reduction of the adsorber size by a factor of 5 to 10 would appear feasible. Cacciola et al. (1992) developed a plate-type heat exchanger with channeled solid adsorbent in order to improve the overall heat transfer coefficient and the mass transfer to and from the solid bed.

In the studies described below different compact zeolite layers were investigated theoretically and experimentally and this was followed by a discussion of the effects created by different additions.

Properties, Structure and Calorific Data of Zeolites

Zeolites are aluminosilicates. The crystal lattice consists of AlO_4^- and SiO_4^- tetrahedrons, which form a system of regular and uniform pores, the so-called micropores. The pores vary in size between 3–5 Å for the zeolites of type A. The adsorbed water is bonded in the micropores by electrostatic forces. This causes a reduction of the vapor pressure and a high heat of adsorption. The calculations presented in this paper are based on calorific data measured in Munich by Maier-Laxhuber (1983) and Rothmeyer (1985).

The crystals are manufactured in sizes of around 0.1–10 μm and are normally bonded in granules. Typical binders are aluminum oxide or sodium water glass. A clear characterization of the bonded zeolite is impossible because of the great influence of the preparation process. The bonded crystals form a non-uniform system of channels and hollows, the so-called macropores, with a diameter of about 6000 Å. The porosity of such a solid is in the range of $\Psi_{\text{map}} = 0.45\text{–}0.65\ \text{m}^3_{\text{macropore}}/\text{m}^3_{\text{solid}}$. The structure of the manufactured solids is taken into account by the tortuosity factor μ_{map}.

Thermal Conductivity

The thermal conductivity depends on the porosity of the solid. Due to the very low thermal conductivity of the water vapor most of the heat has to be conducted by the solid, e.g. the zeolite crystals. A conductivity of 0.58 W/(mK) has been quoted for the crystals by Kast (1988). Furthermore, thermal radiation may support the heat transport at high temperatures. The temperatures are too low for a significant heat transport by radiation during the adsorption phase and the majority of the desorption phase. Thus, the radiation, the heat conduction in the gas phase, and the dependence of the thermal conductivity of the crystals on the temperature will be ignored. The effective thermal conductivity of the zeolite solid therefore only depends on the porosity Ψ_{map} of the zeolite structure:

$$\lambda_z = \lambda_{\text{crystal}}(1 - \Psi_{\text{map}}) \tag{1}$$

Mass Transfer in the Zeolite Structure

Mass transfer of pure water vapor in a zeolite crystal is divided into three phases. Firstly, the vapor has to be transported to the zeolite layer. It reaches the sodalite cages, where the adsorption finally takes place, by passing through the intercrystalline macropores and the system of micropores. The first part of the mass transfer depends on pressure differences between the evaporator and the adsorber. The two other phases are influenced by the structure of the zeolite layer. In accordance with other authors, the mass transfer resistance in zeolite structures is mainly influenced by the macropores if the size of the zeolite crystals is small compared to the size of the zeolite structure (Kast, 1988; Ruthven and Lap-Keung, 1981). If the diameter of the zeolite crystals is only a few micrometers and the typical thickness of the zeolite layers several millimeters, the mass transfer resistance in the micropores is negligible (Mersmann, 1989). Therefore, only the mass transfer in the macropores has to be described.

Different transport mechanism influence the mass transfer in the macropores depending on the pressure, temperature and diameter of the macropores. The determining mechanism can be estimated with the Knudsen number, which describes the ratio of the free length of path Λ_g of the gas molecules to the diameter of the macropores:

$$\text{Kn} = \frac{\Lambda_g}{d_{\text{map}}} \tag{2}$$

If the Knudsen number is less than one, free mass flow takes place. If Kn is greater than one, the mass transfer is characterized by the Brownian movement of the vapor molecules. The share of free mass flow only exceeds that of the Brownian movement if Kn is less than 0.1. With a diameter of the macropores of around 6000 Å and typical process pressures and temperatures, the Knudsen number is always greater than 0.5, so that the Brownian movement is the determining mechanism of the mass transfer in the zeolite structures.

In accordance with the laws of the kinetic gas theory, the following relationship can be deduced for the mass transport in the macropores:

$$\dot{m}_D = -A_{\text{map}} \cdot \frac{D_{\text{Kn}}}{\mu_{\text{map}}} \cdot \frac{dp}{ds} \tag{3}$$

with

$$A_{\text{map}} = A \cdot \Psi_{\text{map}} \tag{4}$$

$$D_{\text{Kn}} = \frac{4}{3} \cdot d_{\text{map}} \cdot \sqrt{\frac{M_g}{2 \cdot \pi \cdot R_m \cdot T}} \tag{5}$$

The mass flow is proportional to the pressure gradient, the cross-sectional area of the macropores and a diffusion coefficient D_{Kn}, which has to be divided by the tortuosity factor μ_{map} (also called labyrinth factor). This factor depends on the structure of the pore system of the zeolite. The diffusion coefficient is described by the diameter of the macropores and by the Brownian movement of the vapor molecules. Since it is very difficult to determine the diameter of the macropores and the tortuosity factor, both parameters and the porosity are combined in the geometrical diffusion coefficient, D_{geo}:

$$D_{\text{geo}} = \frac{\Psi_{\text{map}} \cdot d_{\text{map}}}{\mu_{\text{map}}} \tag{6}$$

D_{geo} depends on the preparation of the zeolite layers and has to be adapted to the experimental data of adsorption kinetic experiments.

Numerical Simulation of the Adsorption Process

The complete adsorption heat pump can be seen as a network of capacities and resistances. A single unit can store mass and energy. The connections between these balance units describe the heat and mass transfer resistances.

The energy-balance for each unit can be formulated as:

$$\frac{dU}{dt} = \sum \dot{Q} + \sum \dot{m}_i \cdot h_i + \sum \dot{m}_o \cdot h_o \tag{7}$$

The total mass balance is:

$$\frac{dm}{dt} = \sum \dot{m}_i + \sum \dot{m}_o \tag{8}$$

The mass balances for each component can be described as:

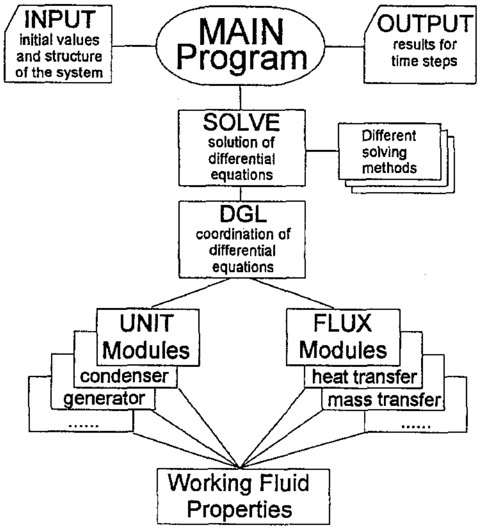
$$\frac{dm_i}{dt} = \sum (\dot{m}_i)_i + \sum (\dot{m}_i)_o \tag{9}$$

Finally, the boundary conditions can be expressed as a function of time. A very common boundary condition is constant volume, e.g., the adsorber material or the zeolite layer. With this condition, the following equation can be formulated:

$$\frac{dV}{dt} = 0 \tag{10}$$

The balances, Eqs. (7–10), are formulated for each unit of the periodically operating adsorption heat pump. This leads to a system of first order differential and algebraic equations depending on time.

A modular, dynamic simulation program to simulate periodically operating systems is required to solve these balances simultaneously. The program used was developed at the Institute for Technical Thermodynamics by H. Zerres (Knoche et al., 1990). The structure of the program is shown in figure 1. It can be divided into five levels. The main program MAIN manages the data input and output and controls the overall calculation process. The initial values, the specifications of the units and the connections between the components are determined by the input files. This enables a simple change of connections and an easy examination



level	function
1.	program control, data input and output
2.	solving the set of differential equations with special methods
3.	coordinating units and creating a set of differential equations
4.	unit and flux modules for the system description
5.	working fluid properties

Figure 1. Structure of the dynamic simulation program.

of different heat pump systems without modifying the program. The simulation models of the single components (adsorber, evaporator ...) including the energy and mass-balances are specified in the UNIT program modules (level 4). The heat and mass transfer phenomena are described in the FLUX modules. The solution and coordination of the differential equations is performed in the SOLVE and DGL-modules.

Simulation of the Zeolite Layer

The system of equations for the coupled heat and mass transfer in a zeolite layer can be developed on the basis of the energy-balance Eq. (7) and the mass-balance Eq. (8). On account of the small thickness of each layer compared to the cross-sectional area, the simulation of the adsorption process in a zeolite layer merely requires a one-dimensional concentration and temperature field. The energy balance for the incompressible zeolite layer can be formulated as:

$$\frac{dU}{dt} = A \cdot \frac{\delta}{\delta s}\left(\lambda \cdot \frac{\delta T}{\delta s}\right) ds - \frac{\delta(\dot{m}_v \cdot h_v)}{\delta_s}\, ds \qquad (11)$$

The first term describes the energy transport based on heat conduction, the second the energy transport based on mass transfer. Together with Fick's first law the energy balance is:

$$\frac{dU'''}{dt} = \frac{\delta}{\delta s}\left(\lambda \cdot \frac{\delta T}{\delta s}\right) + D \cdot \frac{\delta p}{\delta s} \cdot \frac{\delta h_v}{\delta s} - h_v \cdot \frac{\delta \dot{m}''_v}{\delta s} \qquad (12)$$

with the mass balance:

$$\frac{\delta m''_v}{dt} = -\frac{\delta \dot{m}''_v}{\partial s} \qquad (13)$$

In order to convert the differential equations into difference equations, the zeolite layer is divided into several thin layers. The model of the complete zeolite structure is shown in figure 2. Each layer (described as a unit in the simulation program) has a homogeneous condition, which changes from layer to layer. This determines the boundary conditions for Eqs. (11–13), which for the heat transfer can be formulated as:

$$s = 0\colon \quad \alpha \cdot (\vartheta_W - \vartheta_Z) = -\lambda \cdot \frac{\partial \vartheta_Z}{\partial s} \qquad (14)$$

for the conservation of energy, and

$$s = d\colon \quad \frac{\partial \vartheta_Z}{\partial s} = 0 \qquad (15)$$

for the adiabatic surface.

The boundary conditions for the mass transfer can be formulated as:

$$s = 0\colon \quad \frac{\partial p}{\partial s} = 0 \qquad (16)$$

because of the closed surface on the wall, and

$$s = d\colon \quad p = p_D \qquad (17)$$

for the defined pressure on the surface. The temperature and pressure gradient as well as the heat and mass transfer coefficients determine the heat and mass transfer between contiguous layers. The energy transport by heat transfer can be described as:

$$\dot{Q}''_{\text{Conduction}} = \frac{\lambda}{\frac{d_{n-2}}{2} + \frac{d_{n-1}}{2}} \cdot (T_{n-2} - T_{n-1}) \qquad (18)$$

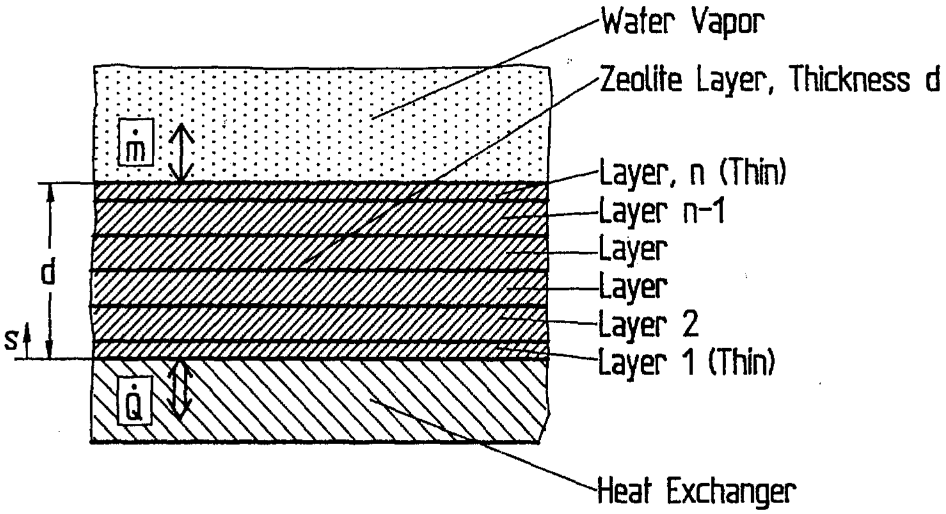


Figure 2. Simulation model of the zeolite layer.

The energy transport by diffusion of water vapor is:

$$\dot{H}''_{\text{Diffusion}} = \frac{D \cdot h_v}{\frac{d_{n-2}}{2} + \frac{d_{n-1}}{2}} \cdot (p_{n-2} - p_{n-1}) \qquad (19)$$

with the diffusion coefficient Eqs. (3–6):

$$D = D_{\text{geo}} \cdot \frac{4}{3} \cdot \sqrt{\frac{M_g}{2 \cdot \pi \cdot R_m \cdot T}} \qquad (20)$$

These equations can be easily described in different flux-modules of the dynamic simulation program.

The number of layers required for a proper simulation of a complete zeolite layer was determined by increasing the number of the single layers until the temperature and concentration profiles no longer changed. This condition was fulfilled when eight layers were used.

Description of the Adsorption Process

Figures 3–5 show the adsorbed amount of water, the temperature and the pressure profiles in the zeolite layer as a function of the time during the adsorption process. The zeolite layer is 10 millimeters thick and fixed on a heat exchanger, through which thermal oil passes as a heat transfer medium. The adsorber is connected to the evaporator via a check valve, so that both vessels are disconnected if the pressure in the adsorber is higher than the pressure in the evaporator. Due to the preparation of the zeolite structures a small gap of 0.1 mm is assumed between the zeolite and the heat

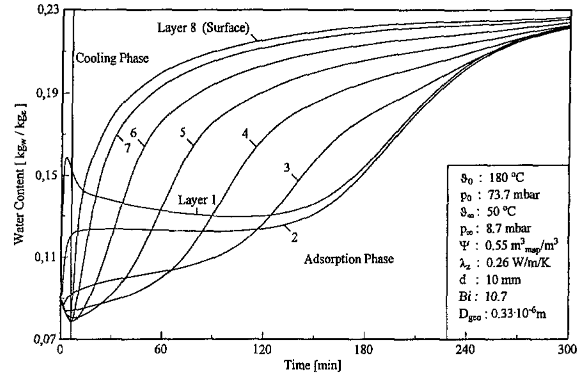


Figure 3. Water content depending on time.

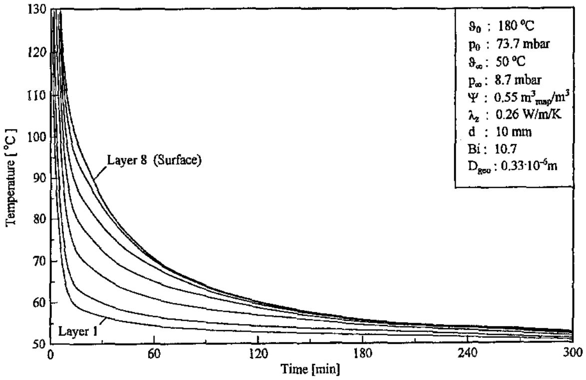


Figure 4. Temperature profiles depending on time.

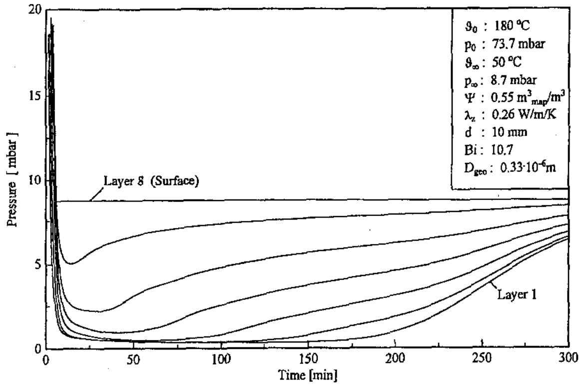


Figure 5. Pressure profiles depending on time.

exchanger wall. Thus, if one ignores the heat transfer resistance between the heat exchanger and the heat transfer medium, the heat transfer coefficient can be determined as $\alpha_w = 280$ W/(m^{2}K). The porosity of the zeolite layer is $\Psi_{\text{map}} = 0.55$, leading to a thermal conductivity of $\lambda_z = 0.26$ W/(mK), Eq. (1). Therefore, with a given thickness of the wall of $d = 10$ mm the Biot number as the ratio of heat transfer to thermal conductivity can be calculated as:

$$\text{Biot} = \frac{\alpha}{\lambda/d} = 10.7 \tag{21}$$

Finally, assuming the tortuosity factor to be $\mu = 1$ and the average diameter of the macropores to be $d_{\text{map}} = 6000$ Å, the geometrical diffusion coefficient is $D_{\text{geo}} = 0.33 * 10^{-6}$ m, Eq. (6).

In figures 3–5 the beginning of the adsorption process is characterized by the disconnection of the heat supply. Consequently, the temperature and pressure in the zeolite layer initially decrease in the layer closest to the wall. The temperature gradient close to the wall is also great on account of the high Biot number of $\text{Bi} = 10.7$. This leads to a pressure gradient from the surface to the wall, which causes a concentration profile into the complete zeolite layer. A local maximum of the amount of water adsorbed close to the wall is reached after five minutes. The further temperature drop at the wall cannot maintain the mass flow to the layer close to the wall so that the pressure gradient is reversed. This leads to a decrease in the amount of water adsorbed in the layer closest to the wall. When the pressure in the adsorber remains under the pressure in the evaporator the check valve opens so that water vapor can be adsorbed by the zeolite. Up until now the water concentration profile inside the zeolite layer changes considerably whereas the total amount of water in the complete zeolite structure remains constant. After the check valve has opened, the water content initially rises on the surface of the zeolite. The expected concentration profile following a continuous increase in the adsorbed amount of water from the heat exchanger wall to the surface is reached after more than two hours.

The Adsorption Process as a Function of the Properties of the Zeolite Layer

The adsorption process described here is one example of a possible process, which depends on the properties of the zeolite layers. The design of an adsorber with a high thermal output requires information on the influence of the different transport mechanisms. An important fixed variable is the water content of the zeolite. The beginning and the end of the adsorption and the desorption phase determine the equilibrium of both phases. A large volume of water must be charged and discharged to achieve a high performance of the heat pump process. However, the adsorption rate decreases when equilibrium is neared so that the thermal input or output also decreases. Therefore, in practical operation the adsorption process is stopped if the charged or discharged amount of water has reached a certain share of the maximum or minimum amount of water. This can be described by the relative water content χ:

$$\chi = \frac{x - x_0}{x_\infty - x_0} \tag{22}$$

which is the ratio of the measured adsorption $(x - x_0)$ relative to the maximum adsorption at the end of the experiment $(x_\infty - x_0)$. x_0 is the initial water content of the zeolite quoted as a weight fraction.

If a state of equilibrium is changed discontinuously by a sudden change of pressure in the vapor room of the adsorber the reaction of the system is a decay process, which can be described by an exponential function (Gerlich, 1993). The following discussion explains how and at what time the different transport mechanisms influence the adsorption process. It is thus assumed that a change in one transport coefficient does not alter the other parameters, although an increase of the diffusion coefficient, Eq. (6), by a greater porosity does result in a decrease of the thermal conductivity, Eq. (1). Due to the temporal displacement of the

State variables and geometric data for zeolite structures					
wall temperature T_w [°C]	100	initial pressure p_0 [mbar]	5	final pressure p_∞ [mbar]	15
initial water content x_0 [kg_W/kg_Z]	0,113	final water content x_∞ [kg_W/kg_Z]	0,17	porosity Ψ_{map}[m^3_{map}/m^3]	0.55
thickness of layer d = 4mm			content of binder = 0		

	varied values								
Designation	0	A	B	C	D	E	F	G	H
α_w[W/m²/K]	280	280	280	28	28	280	280	28	28
λ_z [W/m/K]	0,26	2,6	0,26	2,6	0,26	2,6	0,26	2,6	0,26
D_{geo} [10^{-6}m]	0,33	3,3	3,3	3,3	3,3	0,11	0,11	0,11	0,11

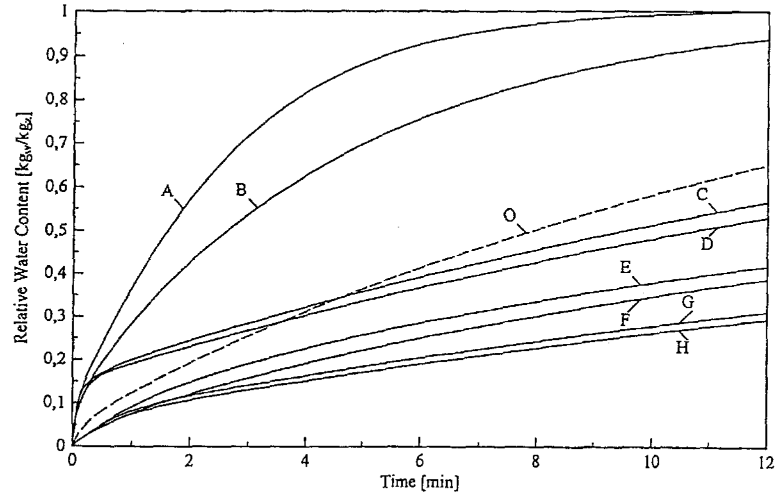


Figure 6. Profiles of the adsorption rates of the structures.

influences of the different transport coefficients on the adsorption rate, the theoretical investigations should help determine the predominant resistance in the prepared zeolite structures.

Figure 6 shows several profiles of adsorption rates depending on the heat transfer coefficient α_w, the thermal conductivity λ_z and the geometrical diffusion coefficient D_{geo}. The reference curve "O" in figure 6 is that of a compact zeolite structure without any additions.

It is obvious that the variation of each transport coefficient influences the process at a different time. The profile of the adsorption rate after a sudden change of pressure is primarily influenced by mass transfer and does not depend on heat transfer. In the case of a high permeability (curves A–D) the adsorption rate rises quickly. After a few seconds the profiles of the structures with metallic matrix, A and C, show a more rapid increase in the adsorption rate than the curves B and D. The zeolite structures with a lower heat transfer coefficient at the wall (C and D) cannot dissipate the adsorption heat fast enough, so that the layer reaches the "adiabatic state of water content" of approximately 16%. The adsorption rate consequently decreases significantly.

The profiles of a zeolite structure with low permeability (E–H) can also be classified in these two phases. The metallic matrix in the zeolite structure increases both the thermal conductivity and the heat capacity so that a higher adiabatic water content can be achieved (E, G). However, the influence of the metallic matrix on the profiles of the structures C, E, and G is almost negligible since the adsorption process is dominated by either a poor mass transfer (E–H) or by a poor heat transfer (C, D). The structures with good heat transfer characteristics and a high diffusion coefficient D_{geo} (A, B) permit higher adsorption rates. From a comparison of the profiles A and B it can be deduced that the adsorption process can be significantly improved by adding a metallic matrix.

Though the calculations described here are only valid for compact layers, the results can be transferred to a zeolite bed. Due to the large free surface of a zeolite bed, the mass transfer is not impeded at the beginning of the adsorption process, so that the initial adsorption rate is very high. However, the poor heat transfer between the bed and the heat exchanger wall inhibits the further adsorption of water. This was also discovered by Doelle (1978) and Busweiler (1984) and is demonstrated by the profiles C and D. According to these results, it can be concluded that the predominant resistance can be determined by comparing the theoretical and experimental results. This resistance has to be reduced by a suitable variation during the preparation of the zeolite samples.

Design of the Adsorption Module

An experimental set-up has been developed to investigate various zeolite structures with different additions and is shown in figure 7. The adsorption module essentially consists of an ad-/desorber and an evaporator/condenser connected by a gas channel. Each vessel is integrated into a temperature-controlled, heat transfer medium circuit. The volume flow of each heat transfer medium is measured with an oval disk meter. All temperatures are measured by NiCr-Ni-thermocouples. The evaporator is designed as a tube evaporator integrated in a glass vessel so that evaporation can be observed. The design of the adsorber allows an easy change of the different zeolite samples to be examined. Thus the geometry and, our main goal, the specific thermal output of the adsorber (thermal output related to the mass of zeolite) will be improved in further investigations. The adsorber consists of an inner and an outer cylinder as shown in figure 7. The heat transfer

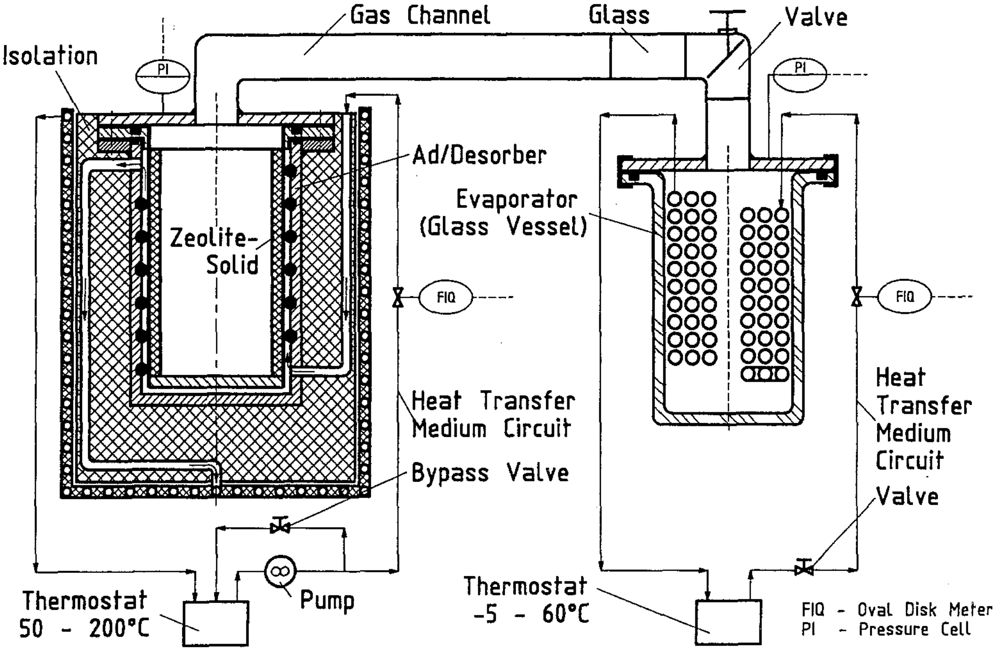


Figure 7. Experimental set-up of the adsorption module.

medium flows in a spiral from the bottom to the top of the adsorber between the two cylinders. The zeolite layer is fixed directly to the inner surface of the inner cylinder. The contact between the zeolite and the inner cylinder has an important influence on the transfer characteristics in the adsorber. Three thermocouples are placed at the boundary of zeolite and the wall to determine the heat transfer coefficient between the zeolite layer and the heat exchanger wall.

The experimental investigations focused on a study of the dynamic adsorption process of water in zeolite. The system presented here determines the following characteristics:

- temperature profile in the zeolite, in the refrigerant and in the heat transfer medium circuits during the adsorption phase
- time dependent thermal output of both vessels
- time dependent adsorption of water in zeolite

The inlet temperature of the heat transfer mediums of adsorber and evaporator are kept constant in all experiments. In accordance with typical operating conditions for a heating device the adsorber temperature is 50°C and the evaporator temperature is 10°C. Before starting the experiment the adsorption module is heated until stationary conditions are achieved. The adsorption process starts when the vapor valve is opened. It stops when equilibrium conditions are reached.

All temperatures are recorded during the experiment by means of data acquisition. A computer program for energy balances determines the thermal output, the accumulated amount of heat exchanged during the experiment, the amount of water adsorbed in zeolite and the heat transfer coefficient. If one performs a total balance for the evaporator the adsorbed amount in each measuring interval Δt_k can be determined as:

$$x(t_n) = x_0 + \frac{\sum_{k=1}^{n} (\dot{Q}_{\mathrm{eva},t} \cdot \Delta t_k)}{r_{d,\mathrm{wat}} \cdot m_{\mathrm{zeo,dr}}} \tag{23}$$

whereby x_0 is the initial water content of the zeolite, $r_{d,\mathrm{wat}}$ is the heat of evaporation of the refrigerant depending on the evaporation temperature, $m_{\mathrm{zeo,dr}}$ is the mass of dry zeolite and n is the number of measuring intervals.

Preparation of Zeolite Samples

Zeolite is available as granular or pulverized material. Solid layers can be formed with the zeolite powder by using additives and a special drying process. In order to achieve a high specific thermal output the heat and mass transfer of pure zeolite has to be increased. One possible method of increasing the heat transfer in a zeolite layer is to use metallic, matrix-like honeycomb structures. These structures are available in various designs. A hexagonal aluminum honeycomb with the following specifications was used for the problem on hand:

- cell depth: 3 mm
- cell size: 4.8 mm
- foil thickness: 38 μm

This structure was clamped to the inside of the inner cylinder and filled with zeolite.

The mass transfer in zeolites can be improved significantly by using pore-forming materials such as melamine or tartaric acid. These organic components are added to the mixture of zeolite, distilled water and binder and are completely removed during the drying process of the zeolite at around 500°C. This leads to a significant increase of the macropore fraction Ψ_{map}.

Different zeolite layers of 3 mm thickness were manufactured and investigated using these methods:

- zeolite layer without additives
- zeolite layer with 5 wt.% melamine
- zeolite layer with 10 wt.% melamine
- zeolite layer with 5 wt.% melamine and honeycomb matrix
- zeolite layer with 5 wt.% melamine, 5 wt.% tartaric acid and honeycomb matrix

Furthermore, a layer of granular zeolite was investigated to determine the specific thermal output of a granular zeolite bed compared to a compact zeolite structure with a similar geometry. The thickness of the layer was 3.5 mm, the diameter of the granules was 1–2 mm.

Before starting the experiment the adsorber with the zeolite is evacuated at a temperature of 150°C for 24 hours. In this way the zeolite is activated and the inert gases removed from the adsorber. The refrigerant in the evaporator is degassed at a temperature of 50°C.

Experimental Results

Figure 8 shows the measured adsorption rates of the compact zeolite layers as well as those of the granular

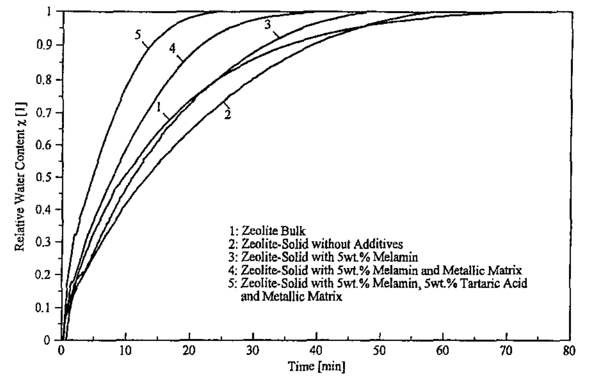


Figure 8. Measured adsorption rates.

zeolite. The adsorption rate is described by the relative water content χ, Eq. (22). Curve 1 demonstrates the adsorption characteristics of granular zeolite. Due to the large surface of the granular zeolite the adsorption rate at the beginning of the adsorption process is better than that of the compact zeolite samples 2 and 3. However, having adsorbed 75% of the maximum amount of water the surface of the granular zeolite is saturated with water vapor. According to the theoretical investigations it can be concluded that the limited heat transfer inside the granular zeolite layer inhibits further adsorption of water. The improvement in the heat and mass transfer of pure zeolite through the use of pore-forming materials and a metallic matrix becomes obvious if one compares curves 1 and 5. This is illustrated in Table 1, which shows the average adsorption rates of the granular zeolite and the zeolite-solid with pore-forming material and metallic matrix. Compared to the results quoted by Eichengrün and Winter, (1994), who investigated the adsorption of water in pulverized zeolite, the adsorption rates of the compact zeolite structures are significantly higher. Additional experiments proved that an increase of the melamine and tartaric acid mass fraction to over 5% does not cause a further improvement of the adsorption rate.

Table 1. Average adsorption rates of the zeolite samples.

	Sample 1	Sample 5
	$\Delta x/\Delta t[\%/\text{min}]$	
$\chi = 0,85$	0, 62	1, 85
$\chi = 0,95$	0, 43	1, 45

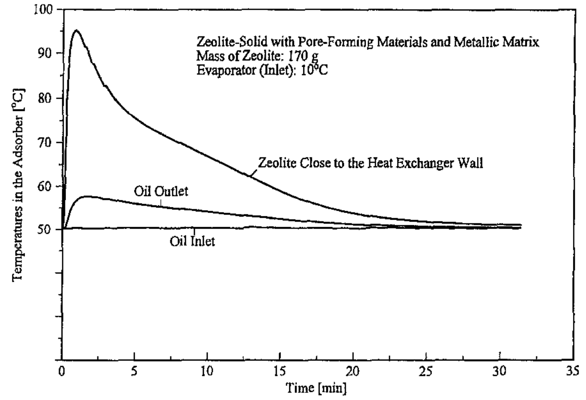


Figure 9. Temperature profiles of the adsorber.

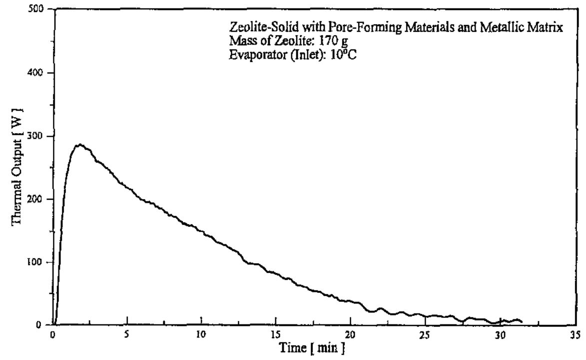


Figure 10. Thermal output of the adsorber.

Figure 9 shows a typical temperature profile in the adsorber during the adsorption phase. The start of adsorption is characterized by a temperature rise in the zeolite. It is obvious that the heat transfer between the zeolite and heat exchanger wall is insufficient. This results in a very high temperature difference between the zeolite and heat transfer medium at the beginning of the adsorption phase. Consequently, the thermal output of the adsorber as shown in figure 10 is limited. The heat transfer coefficient between zeolite and heat exchanger wall was determined as $\alpha_w = 26$ W/(m^{2}K) for the zeolite without additives and $\alpha_z = 112$ W/(m^{2}K) for the zeolite with pore-forming materials and a honeycomb matrix. The heat transfer coefficient for a laminar flow inside the oil channel in the adsorber was calculated at $\alpha_{\text{oil}} = 350$ W/(m^{2}K) for all experiments.

The heat transfer on both sides of the heat exchanger wall has to be increased to further improve the adsorption rate and, consequently, the thermal output of the adsorber.

Summary

The investigations carried out by different authors using granular zeolite as an adsorbent and water as a refrigerant for an adsorption machine show an insufficient thermal output. The adsorption rates of different compact zeolite layers were investigated and compared to the adsorption rate of granular zeolite in this paper.

The main problem of granular zeolite is the very low heat transport, which leads to long process cycle times in periodically working machines. Compact zeolites have better heat transport characteristics, though the mass transfer of pure zeolite is insufficient. Whereas it is impossible to improve the heat transfer characteristics of granular zeolite, the heat and mass transfer of compact zeolites can be enhanced. A dynamic simulation model of a zeolite layer has been developed to estimate the predominant transport resistances and calculations were carried out to assist the simultaneous experimental investigations.

The investigations described in this paper show that in a comparison of different compact zeolite layers, the use of pore-forming materials and a metallic matrix can improve the adsorption rate by up to 110%. The adsorption rate can be almost tripled compared to granular zeolite by the use of the described additives.

Thus, the thermal output of an adsorption machine working with zeolite-water can be increased significantly. The heat transport characteristics between zeolite and heat transfer medium have to be improved if used in a periodically working adsorption heat pump. Therefore, further experiments with compact heat exchanger technology and compact zeolite layers with enhanced heat and mass transfer are to be conducted. The dynamic simulation program will be expanded in order to calculate the new geometry of the compact zeolite structures.

Nomenclature

A_{map}	cross-sectional area of the macropores	m^2
d	thickness of zeolite layer	m
d_{map}	diameter of the macropores	m
D_{geo}	geometrical diffusion coefficient	m
D_{Kn}	Knudsen diffusion coefficient	s
$\dot{m}$	mass flow	kg/s
H	enthalpy	J
h	specific enthalpy	J/kg
M_g	molecular weight	kg/mol
$m_{\text{zeo,dr}}$	mass of dry zeolite	kg
p	pressure	Pa
$\dot{Q}$	heat flow	W
$\dot{Q}_{\text{eva},t}$	thermal power of the evaporator	W
$r_{d,\text{wat}}$	heat of evaporation of water	J/kg
R_m	gas constant	J/(mol K)
s	length of path	m
t	time	s
Δt_k	measuring interval	s
T	temperature	K
U	energy	J
V	volume	m^3
x	adsorbed amount of water	—
α_{oil}	heat transfer coefficient between wall and thermal oil	$\text{W/(m}^2\text{K)}$
α_w	heat transfer coefficient at the wall	$\text{W/(m}^2\text{K)}$
α_z	enhanced heat transfer cofficient at the wall	$\text{W/(m}^2\text{K)}$
λ_z	thermal conductivity of the zeolite structure	W/(mK)
λ_{crystal}	thermal conductivity of the zeolite crystal	W/(mK)
Λ_g	free length of path	m
μ_{map}	tortuosity factor	—
Ψ_{map}	porosity of the zeolite	$\text{m}^3_{\text{macropore}}/\text{m}^3_{\text{solid}}$
χ	relative water content	—
Kn	Knudsen number	—
Bi	Biot number	—

Indices:

w	wall
0	initial value
∞	final value
i	input
o	output
v	vapor
n	number of zeolite layer
$'''$	per volume
$''$	per cross sectional area

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