On the Effect of Grain Size on the Kinetics of Water Vapor Adsorption and Desorption into/from Loose Pellets of FAM-Z02 under a Typical Operating Condition of Adsorption Heat Pumps

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The kinetics of water vapor adsorption/desorption under quasi isobaric conditions have been studied on one layer of loose pellets of FAM-Z02 placed on a metal plate. Temperature of the sample holding plate has been changed as it takes place in real adsorption heat pumps (AHPs), while the vapor pressure over the adsorbent was maintained almost constant (saturation pressures corresponding to an evaporator temperature of 5°C and a condenser temperature of 35°C). Adsorption- and desorption-end temperatures have been adjusted to 35 and 90°C, respectively. Measurements have been carried out on grains having the following size distributions: 0.7 to 1.0 mm, 1.4 to 1.6 mm and 2.0 to 2.6 mm. An average equilibrium differential water loading of 19.2 g/100 g has been measured during desorption compared to 16.4 g/100 g during adsorption. The adsorption/desorption rates have been characterized by the times required to reach 50, 80 and 90% of the equilibrium loading. It has been found that the adsorption kinetics are mainly dominated by inter-crystalline diffusion, while the desorption kinetics are mostly influenced by surface resistance to the heat and mass transfer. Average specific evaporator cooling/condenser heating capacities in the order of 1 kW/kg have been estimated for the grain size 0.7 to 1.0 mm, putting in evidence the possibility of developing highly compacted AHPs with FAM-Z02 for heating and cooling applications. The influencing parameters on the combined heat and mass transfer process have been discussed.

Introduction

One of the methodologies to apply zeolite on adsorber heat exchangers is to locate it in form of loose pellets between the fins of finned-tube heat exchangers (Lang et al., 1999; Stricker, 2003; Núñez et al., 2005; Dawoud et al., 2007). This methodology offers the maximum adsorbent surface area for mass transfer. However, the point contacts between the pellets and the fins limit the heat transfer process. It follows that, the smaller the pellet size the higher the surface area per unit mass available for mass transfer and, in the same time, the smaller the heat and mass transfer paths inside each adsorbent grain. This implies that an adsorber heat exchanger with the lowest possible grain size would be the most effective design. As the main idea of applying loose pellets was to allow only one layer of adsorbent grains between two successive fins (Lang et al., 1999; Stricker, 2003; Dawoud et al., 2007), the lowest possible grain size would require an infinite number of fins. This indeed increases the thermal capacity ratio between the adsorber heat exchanger and the adsorbent leading to a poor heat pump performance (Westerfeld, 1996). Accordingly, the proper grain size has to be defined for each new adsorbent under typical operating conditions of AHPs. The first step towards defining the proper grain size is to study the sorption kinetics on one layer of loose pellets under typical working conditions of AHPs.

Dawoud and Aristov (2003) has introduced and applied a constant volume-variable pressure setup to measure the adsorption kinetics of loose pellets of two porous host materials (meso-porous silica gel KSK and alumina A1) in comparison with the two selective water sorbent (SWS) composites namely, SWS-1L and SWS-1A (Aristov et al., 1996) formed by impregnating these two host matrices with CaCl₂. Dawoud et al. (2003) have applied the same setup to investigate the grain size effect on the adsorption kinetics of SWS-1L. At the beginning of the experiments the loose grains of the sample were almost completely dry (residual uptake \( x_o = 0.17 \) g/100 g) and maintained at initial adsorption temperature 35°C (or 50°C). After that, the sample was subjected to a step change of the vapor pressure up to 40 mbar (or 60 mbar), which initiated the sorption process in the constant volume apparatus.
The vapor pressure was decreasing due to water sorption. Depending on the size of the grains and the configuration of the sorbent layer (single or multi layer) the sorption process can be isothermal or non-isothermal. Measuring the temporal evolution of pressure \( p(t) \), the time variation of the water loading was calculated. The sorption of water lasted some tens of minutes until the equilibrium was reached. As the pressure jump was large (non-isothermal adsorption) and the pressure was not constant during the water adsorption, no simple kinetic models could be applied for extracting kinetic parameters from the experimental curves. However, this simple qualitative procedure could be used for comparative study of various sorbents under the prescribed boundary conditions.

Aristov et al. (2006) have reported on an isothermal, constant-pressure and thermo-gravimetrical methodology to investigate the adsorption kinetics on loose SWS-1L pellets. The tested grains have been subjected to small step changes in Pressure (2.5 mbar each), while the temporal change of the sample weight has been registered. Due to the isothermal and constant pressure conditions, analytical models (Kärger and Ruthven, 1992) could be applied to extract the diffusion coefficient from the experimental data. Aristov et al. (2004) have summarized both theoretical and experimental basics of the constant-volume variable pressure and the isothermal constant pressure methodologies and how to analyze the obtained experimental data from each method.

Schnabel and Henning (2005) and Schnabel et al. (2005) have introduced a similar test rig to that of Dawoud and Aristov (2003) for solely measuring the adsorption kinetics of adsorbent samples under constant temperature and quasi isobaric conditions. They have added a heat flux meter to measure the released heat of adsorption as well as the sample surface temperature during the adsorption process. Besides, the measuring cell can be connected to one of two vapor vessels having two different volumes, in order to be able to test samples with different masses (in the order of 0.5 or 5.0 g). Moreover, the measuring cell can be connected to an evaporator providing a constant pressure during adsorption. However, the later case means loosing the pressure signal for detecting the water loading. So the only data from such isobaric measurements are the sample temperature on the surface and the heat flux giving the heat emission of the sample.

The main drawback of the previous methodologies lies in the fact that they are carried out under different conditions compared to those of real AHPs. Accordingly, the obtained results could not be directly applied in estimating the duration of the isobaric adsorption process of AHPs. Moreover, those methodologies have concentrated on investigating only the adsorption kinetics and haven’t paid any attention to the kinetics of the desorption process.

Accordingly, Aristov et al. (2007) have modified the constant-volume, variable pressure setup presented by Dawoud and Aristov (2003) and introduced a novel experimental methodology to investigate both isobaric adsorption and desorption processes of AHPs with the sample temperature being decreased/increased as it takes place in real adsorption heat pumps. The new methodology has been applied successfully in investigating the isobaric adsorption/desorption kinetics on one layer of SWS-1L grains (1.4 to 1.6 mm size) with small (5 K) and large (35 K) temperature jumps as well as the effect of the cooling/heating rate on the dynamics of the adsorption/desorption processes.

CHA-type structure silicoaluminophosphate zeolite (SAPO-34) has been introduced recently by Mitsubishi Chemicals Corp. (Kakiuchi et al., 2003). Furthermore, adsorption equilibrium and durability of SAPO-34 with a silicon content of 7.5 mol% (Functional Adsorbent Material; FAM-Z02) have been tested (Kakiuchi et al., 2005). The water vapor adsorption isotherm of FAM-Z02 was found to be S-shaped and highly dependent on temperature. A small hysteresis has been observed and there has been almost no change observed in the adsorption equilibrium after 100,000 cycles of water vapor adsorption-desorption indicating that FAM-Z02 is durable enough for practical use in adsorption heat pumps (AHPs).

In this paper, the novel methodology of Aristov et al. (2007) has been applied to investigate the kinetics of water vapor adsorption/desorption on one layer of loose pellets of FAM-Z02 (Kakiuchi et al., 2005) of Mitsubishi Chemicals Corp. under quasi isobaric conditions. Experiments have been carried out on grains having the following size distributions: 0.7 to 1.0 mm, 1.4 to 1.6 mm and 2.0 to 2.6 mm with the main goal to define the most appropriate grain size for AHP applications. All FAM-Z02 grains have been tested under the following AHP working condition: evaporator, adsorber-end/condenser and desorption-end temperatures of 5, 35 and 90°C, respectively. The equilibrium differential water loading has been measured and compared with that of SWS-1L under the same working conditions (Aristov et al., 2007). The adsorption/desorption rates have been characterized by characteristic times. The average evaporator cooling/condenser heating capacities have been estimated and the influencing parameters on the combined heat and mass transfer process have been discussed.

1. Experimental

1.1 Apparatus

The sorption kinetics’ setup consists, as depicted in Figure 1, mainly of two compartments. The first is the measuring cell, in which a sorbent sample is placed. The temperature of the surface holding the sample can be adjusted and controlled using an oil circuit coupled
to the circulating heating thermal bath 2. The rate of oil heating and cooling can be adjusted by moderating the cooling water flux, which circulates through the plate heat exchanger, so that different cooling (heating) scenarios can be realized. The second compartment is a constant volume vapor vessel. The temperature of this vessel is controlled using a water circuit coupled to the circulating thermal bath 1. This bath 1 is also used to control the temperature of the outer surface of the connecting pipes of the setup (not shown in Figure 1) to prevent the undesired local vapor condensation.

A heating/cooling bath 3 is added to adjust the temperature, and consequently, the pressure of water vapor in the steam generator, in order to realize the equilibrium states at the beginning of the adsorption and desorption processes. In other words, the steam generator acts as an evaporator/condenser to adjust the starting points of the adsorption/desorption processes, respectively. Afterwards, it is locked by closing the regulating valve (RV) and enables the adsorption/desorption processes taking place under constant volume conditions. A three way valve (3WV) is introduced in the oil loop to bypass the measuring cell and first heat or cool the oil content of the thermal bath 2 to the desired final temperature for the desorption or adsorption processes, respectively.

By rotating the 3WV to the position, which enables the heated/cooled oil to flow into the measuring cell, either a desorption or an adsorption process can be started. The accuracy of the pressure measuring devices amounts to ±0.05 mbar. The temperature controllers of the circulating thermal baths have an accuracy of ±0.1 K. The data required for evaluating the change of water loading with time are recorded every second.

1.2 Procedure

Figure 2 depicts the idealized AHP-cycle (1-2-3-4-1) on an isobaric chart of FAM-Z02-water. The idealized AHP-cycle starts with the pre-heating process (1-2) at almost constant water loading \( x_{\text{max}} \) followed by the isobaric desorption process (2-3), during which the water loading decreases from \( x_{\text{max}} \) to \( x_{\text{min}} \) upon further heating up the adsorbent up to the desorption-end temperature (here 90°C). During the desorption condensation phase, the condenser is supposed to keep the pressure constant at the saturation pressure (here \( p_{\text{Con}} = 56.4 \text{ mbar} \)) corresponding to the condenser temperature (here 35°C). The pre-cooling process (3-4) takes place ideally at a constant water loading \( x_{\text{min}} \), where the system pressure decreases from the condenser pressure \( p_{\text{Con}} \) down to the evaporator pressure \( p_{\text{Ev}} = 8.75 \text{ mbar} \), which is the saturation pressure corresponding to the evaporator temperature of 5°C. The adsorption process starts then from state point 4 (56°C and 8.75 mbar) and proceeds under constant pressure, which is supposed to be kept constant by a proper evaporator design. During the adsorption process (4-1) the
adsorbent is cooled down to the adsorption-end temperature (here 35°C) and the water loading increases from the cycle minimum to the cycle maximum loading.

The experimental procedure lies simply in achieving first the equilibrium state points 4 and 2, in the adsorbent sample as the start points of both isobaric adsorption/desorption processes, respectively. Upon cooling down/heating up the adsorbent sample to the adsorption/desorption-end temperatures in a constant volume apparatus, the water loading increases/decreases, while the vapor pressure slightly decreases (4-1*)/increases (2-3*) compared to the isobaric processes. The magnitude of pressure reduction/increase depends on the sample weight, which has then to be minimized to minimize the deviation from the isobaric processes.

In the following paragraphs the experimental procedure for investigating the adsorption process will be explained in more detail followed by a short description for the desorption process.

The adsorbent sample is first heated up to 100°C and evacuated for one hour using a vacuum pump (valves V1–V3 are open, valve RV is closed). Valve V3 is then closed and the measuring cell is cooled down to the starting temperature (\(\vartheta_4\)) of the isobaric adsorption (point 4, Figure 2). The vapor vessel and measuring cell are charged with water vapor, from the steam generator, up to the required starting pressure for the adsorption process \(p_{Ev}\). The temperature of the connecting piping and valves is maintained at 35°C for isobaric adsorption and at 60°C for isobaric desorption. After the sample is equilibrated with water vapor at \(\vartheta_4\) and \(p_{Ev}\), the measuring cell is cooled down to the adsorption-end temperature of 35°C (\(\vartheta_1\)).

The adsorption process driven by the sample cooling starts, which results in reducing the vapor pressure with time (process 4-1* schematically in Figure 2). This pressure decrement is limited to 2 to 3 mbar by limiting the adsorbent sample weight. However, the pressure decrement during the adsorption process is quite typical for adsorption heat pumps (Westerfeld, 1996), as the evaporator could not be designed to keep the pressure perfectly constant (needs to be of infinite size), most specifically, at the beginning of the adsorption process. Accordingly, the adsorption process can be considered as a quasi-isobaric one as it proceeded close to isobaric line 4-1 (Figure 2). The sorption process approaches the equilibrium state related to the final water vapor pressure \(p_f < p_{Ev}\) and the final sample temperature \(\vartheta_1\). A similar procedure is used for studying the dynamics of water vapor desorption, which is also a quasi-isobaric process following the course 2-3* close to the isobaric course 2-3 (Figure 2).

The time course of pressure variation, being measured with the two pressure transducers P1 and P2 determines the kinetics of the sorption process and is applied to determine the amount of the adsorbed/desorbed water vapor on/from the adsorbent sample (the detailed analysis of the experimental setup could be read in (Dawoud and Aristov, 2003 as well as Aristov et al., 2007). The ratio of the accumulated adsorbed/desorbed water mass, at a certain time, and the mass of the dry adsorbent sample is the instantaneous differential water loading \(x_1 - x_o\), where \(x_1\) and \(x_o\) are the instantaneous and the initial water loadings, respectively. In order to compare the results of the adsorption and desorption kinetics for the different grain sizes studied, it is reasonable to represent the time variation of the water loading in a dimensionless form. This may occur by defining the dimensionless differential water loading \(\chi\) as the ratio between the instantaneous differential water loading \(x_1 - x_o\) and the maximum differential water loading achievable at each operating condition of each adsorption and desorption process on the adsorbent sample.

\[
\chi_t = \frac{x_t - x_o}{x_f - x_o}
\]
Table 1 Measured equilibrium differential water loadings in dependence on the grain size of FAM-Z02 at evaporator, adsorber-condenser and desorber temperatures of 5, 35 and 90°C

<table>
<thead>
<tr>
<th>Grain Size [mm]</th>
<th>Adsorption/Desorption</th>
<th>( (x_i - x_c) ) [g/100 g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7–1.0</td>
<td>Adsorption</td>
<td>17.55</td>
</tr>
<tr>
<td>0.7–1.0</td>
<td>Desorption</td>
<td>20.8</td>
</tr>
<tr>
<td>1.4–1.6</td>
<td>Adsorption</td>
<td>16.1</td>
</tr>
<tr>
<td>1.4–1.6</td>
<td>Desorption</td>
<td>19.3</td>
</tr>
<tr>
<td>2.0–2.6</td>
<td>Adsorption</td>
<td>15.4</td>
</tr>
<tr>
<td>2.0–2.6</td>
<td>Desorption</td>
<td>17.4</td>
</tr>
</tbody>
</table>

1.3 Material

Functional adsorbent material (FAM-Z02 or SAPO 34) samples having the grain sizes: 0.7 to 1.0, 1.4 to 1.6 and 2.0 to 2.6 mm have been investigated. From each grain size a dry mass of 150 mg has been applied in form of one layer of loose pellets on the sample holding surface of the measuring cell.

2. Results and Discussion

Table 1 represents the obtained equilibrium differential water uptakes for the different grain sizes. In each experiment, equilibrium is supposed to be reached after a period of 2 h. It could be observed that the smaller the grain size, the larger the differential water loading in both adsorption and desorption runs. This is rather strange as the duration of two hours should be quite sufficient for establishing equilibrium, which is observed with four different grain sizes of SWS-1L (Dawoud et al., 2003). However, the systematic reduction of the differential water loading observed here with the increase in the grain size could be referred to the size of FAM-Z02 powder used in forming the pellets. Strictly speaking, if the powder applied to produce the grains is too fine, this will lead to enhancing the interparticle diffusion resistance inside each grain, leading to the requirement of very long times to establish equilibrium throughout the whole grains. Moreover, it can be observed that the differential water uptake during the desorption runs is always higher than that during the adsorption runs, which could be attributed to the slight hysteresis already observed by Mitsubishi Chemicals Corp. (Kakiuchi et al., 2005).

An average equilibrium differential water loading of 19.2 g/100 g has been measured during desorption compared to 16.4 g/100 g during adsorption under the tested boundary condition of AHPs. This differential water loading is superior and amounts to 3 to 5 times that of traditional adsorbents (silica gel and NaY-Zeolite) under the tested boundary conditions.

Similar experiments on SWS-1L grains of 1.4 to 1.6 mm size showed differential water loading of 11.8 g/100 g during adsorption and 19 g/100 g during desorption tests under the same boundary conditions (Aristov et al., 2007). It is clear that the degree of hysteresis is higher with SWS-1L and that FAM-Z02 offers 36% higher differential water loading than SWS-1L during adsorption and almost the same water loading during desorption.

Typical evolution of the dimensionless loading, the vapor pressure over the sample and the measuring cell surface is presented in Figure 3 for the adsorption run on the grain size 0.7 to 1.0 mm. The time axis is presented as a square root of time just to show the details of the characteristic curves during the first 10 min. of adsorption, during which more than 90% of the adsorption process is almost accomplished. It can be easily noticed that the effective cooling of the sample holding surface of the measuring cell begins after 2 s and that the cell temperature reaches 38°C after 1 min, which could be considered as quite fast. However, within the first minute, the vapor pressure over the sample is still high indicating that the adsorption process hasn’t been started yet effectively.

The dimensionless water loading after 1 min amounts to only 15%, which can be attributed to the relatively slower kinetics of water adsorption influenced mainly by the heat transfer characteristics of the applied kinetic setup. After 6 min the dimensionless water loading (\( q \)) reaches 80% of its final value. We named the time required for the dimensionless water loading to change from 15 to 80% as the rise up time. The characteristics of this rise up time for all adsorption and desorption runs have been compared and discussed in details later on in this communication.

Table 2 depicts the dependency of the first characteristic time (\( \tau_{0.5} \)), that is the time required to reach 50% of the final differential water loading (\( x_i - x_c \)) on the grain size. It is evident from Table 2 that the evaporator-adsorption process is always slower than the desorption-condensation process, a phenomenon that becomes more pronounced as the grain size decreases.
The influencing factors on the combined heat and mass transfer process under study are, among others, the grain size, which in turn influences the surface area to volume ratio and the heat and mass transfer paths, as well as the mean process temperature, which influences the water vapor diffusivity. The higher mean process temperature during desorption compared to that during adsorption is responsible for a higher water vapor diffusivity and, consequently, for the faster kinetics of the desorption process. The higher surface area to volume ratio and the shorter heat and mass transfer paths are responsible for enhancing the adsorption and desorption kinetics as the grain size decreases.

In addition the rate of adsorption/desorption, especially at the first stage of the process, which mainly determines its kinetics, is dependent on the instantaneous mass transfer driving force (the difference between the equilibrium loading on the surface of the pellet at the surface temperature and the gas phase pressure) and the average loading inside the pellet in case of adsorption and vice versa in case of desorption. Besides, the combined effect of the process temperature and the gas phase pressure on the adsorption/desorption kinetics depends on the relative enhancement/reduction of both diffusivity and the mass transfer driving force. Moreover, the rate of heat transfer inside the grains as well as between the adsorbent grains and the holding surface of the measuring cell influences the adsorbent temperature and, accordingly, both the instantaneous diffusivity and the mass transfer driving force.

To quantify the sorption kinetics the term sorption speed \( V_S \) is introduced. This is defined by Eq. (2) as the ratio between the half time differential water loading divided by the half time \( \tau_{0.5} \).

\[
V_S = \frac{x_{0.5} - x_0}{\tau_{0.5}} \tag{2}
\]

Examining the values given in the right-most column of Table 2 reveals that the sorption speed increases almost linearly with decreasing the average pellet radius. Moreover, it could be observed that the desorption speed amounts to 172\% of the adsorption speed for the grain size 0.7 to 1.0 mm and reduces to almost 152\% for the two other grain sizes.

If the sorption rate is limited by the surface resistance to the heat or mass transfer the value of effective rate constant \( k_{eff} \) that in first approximation is proportional to \( \tau_{0.5}^{-1} \) should be proportional to the specific external surface area of grains (that means the surface related to the grain volume), that means increases as \( R_p^{-1} \) (or \( \tau_{0.5} \sim R_p \) ) (Kärger and Ruthven, 1992). If the water diffusion inside a grain (inter-crystalline diffusion) is the slowest (or dominant) stage, the relation should be \( k_{eff} \sim R_p^{-2} \) (or \( \tau_{0.5} \sim R_p^2 \)). The dependence of \( \tau_{0.5} \) on the average radius of the grains \( R_p \) is best fitted with a polynomial of 2nd degree with different contributions of the 1st and 2nd order terms. Figure 4 depicts that the 2nd order term sharing has been found to be dominating for adsorption, while the 1st order term dominates the relation for desorption. Similar results have been obtained also for the dependence of \( \tau_{0.8} \) and \( \tau_{0.9} \) on the average particle radius. This puts an additional interpretation for the slower kinetics of the adsorption process compared to that of the desorption process, as it has to do predominantly with the intercrystalline diffusion at lower average temperature and, accordingly, with smaller mass diffusivity. Accordingly, it could be concluded that the adsorption kinetics are dominated by inter-crystalline diffusion, while the desorption kinetics are mostly influenced by surface resistance to the heat and mass transfer.

As discussed before, to reach the equilibrium state a very long time is required. Accordingly, assigning the time required to reach equilibrium to the adsorption heat pump’s phase change time (from adsorption...
to desorption and vice versa) implies a very low cooling/heating power. It has been a common practice to assign the time required to reach 80% or at most 90% of the equilibrium differential water loadings to the phase change time.

Table 3 presents both adsorption and desorption characteristic times (\(\tau_{0.8}\) and \(\tau_{0.9}\)) for tested grain sizes of FAM-Z02. Based on \(\tau_{0.8}\) as a phase change time, the cycle time of an AHP ((\(\tau_{0.8}\)\(_{\text{ads}}\) + \(\tau_{0.8}\)\(_{\text{des}}\)) utilizing 0.7 to 1.0 mm loose pellets would be 10.2 minutes. The cycle time increases to 14.3 and 22.3 min. for the grain sizes 1.4 to 1.6 and 2.0 to 2.6 mm, respectively. If \(\tau_{0.9}\) is taken as a phase change time, the cycle time of the AHP ((\(\tau_{0.9}\)\(_{\text{ads}}\) + \(\tau_{0.9}\)\(_{\text{des}}\)) utilizing 0.7 to 1.0 mm loose pellets would be 13.8 min and increases to 21.3 and 30 min for the other tested grain sizes.

It is a common knowledge that, in AHPs, an evaporation process through which a certain cooling capacity can be achieved accompanies each adsorption process. On the other hand, each desorption process is accompanied with a condensation process, through which a certain heating capacity could be obtained. The intensity of those cooling (heating) capacities depends mainly on the refrigerant latent heat of vaporization \((h_{fg})\), the differential water loading \((\chi)\) and the time required to realize this differential water loading in the adsorbent \((\tau)\). Equation (3) defines the specific evaporator cooling or condenser heating capacities \(((q_s)_x)\) per kg of FAM-Z02.

\[
(q_s)_x = \frac{\chi (x_f - x_o) \cdot h_{fg}}{100 \cdot \tau_x}
\]

(1) Evaporation; (2) Condensation

Table 3 Specific evaporator-cooling and condenser-heating capacities at the dimensionless loadings of 0.8 and 0.9 under the tested AHP boundary condition

<table>
<thead>
<tr>
<th>Grain Size [mm]</th>
<th>Process ((1)/(2))</th>
<th>(\tau_{0.8}) [s]</th>
<th>((q_s)_{0.8}) [kW/kg]</th>
<th>(\tau_{0.9}) [s]</th>
<th>((q_s)_{0.9}) [kW/kg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.7 – 1.0</td>
<td>(1)</td>
<td>369</td>
<td>0.974</td>
<td>489</td>
<td>0.808</td>
</tr>
<tr>
<td>0.7 – 1.0</td>
<td>(2)</td>
<td>245</td>
<td>1.702</td>
<td>336</td>
<td>1.393</td>
</tr>
<tr>
<td>1.4 – 1.6</td>
<td>(1)</td>
<td>477</td>
<td>0.676</td>
<td>660</td>
<td>0.549</td>
</tr>
<tr>
<td>1.4 – 1.6</td>
<td>(2)</td>
<td>383</td>
<td>1.012</td>
<td>619</td>
<td>0.702</td>
</tr>
<tr>
<td>2.0 – 2.6</td>
<td>(1)</td>
<td>764</td>
<td>0.398</td>
<td>1014</td>
<td>0.342</td>
</tr>
<tr>
<td>2.0 – 2.6</td>
<td>(2)</td>
<td>575</td>
<td>0.619</td>
<td>785</td>
<td>0.499</td>
</tr>
</tbody>
</table>

(1) Evaporation; (2) Condensation

The equilibrium differential water loadings \((x_f - x_o)\) are listed in Table 1 and the time \((\tau)\) required to reach a certain dimensionless differential water loadings of 0.8 and 0.9 as well as the corresponding evaporator cooling/condenser heating capacities. As the differential water uptake increases and the kinetics of adsorption/desorption becomes faster if the grain size decreases, the estimated evaporator cooling/condenser heating capacities increases remarkably. Estimated specific evaporator cooling and condenser heating capacities of 0.97 and 1.7 kW/kg with the grain size 0.7 to 1.0 mm put in evidence the feasibility of developing highly compacted adsorption heat exchangers with FAM-Z02 for heating and cooling applications. Combining the results on both cycle time and specific evaporator cooling as well as condenser heating capacities leads to the conclusion that loose grains in the order of 0.7 to 1.0 mm is the best among the tested three sizes. Rapid increase of \(\tau_{0.8}\) and \(\tau_{0.9}\) and the corresponding reduction in the specific evaporator cooling and condenser heating capacities for pellets larger than 1.4 to 1.6 mm select this size as the upper limit for applying in adsorption heat pumps with loose adsorbent layers.
It is worthy to mention here that the obtained specific evaporator cooling or condenser heating capacities are valid only as a maximum for the designs of Lang et al. (1999), Stricker (2003) and Dawoud et al. (2007) who made use of one single pellet layer between the fins of finned tube adsorber heat exchangers. For the common packed bed heat exchanger design, these results are not valid and further investigations are required. However, the introduced methodology could be simply applied for multi-layer grain tests by, e.g., making use of different metal rings having different diameters to assure two, three or more grain layers from the same sample mass. The rings have to be placed on the sample holding surface of the measuring cell and then filled in with the samples before the investigations are carried out. Doing so, the packed bed design parameters, most specifically the bed porosity depending on the pellet size and the expected change of the dominating heat and mass transfer mechanisms could be intensively investigated.

As a further future work, it is worthy to carry out similar tests on smaller grain sizes than the 0.7 to 1.0 mm size and accompanying the tests with an analytical estimation to the expected loss on coefficient of performance due to the increased heat capacity ratio between the adsorber heat exchanger metal and the adsorbent.

As mentioned before in commenting on Figure 3, we named the time required for the dimensionless water loading to rise from 15 to 80% as the rise up time. This rise up time \((t_{0.8} - t_{0.15})\) is taken as a quantitative measure for the adsorption/desorption kinetics. Table 4 depicts the values of the rise up time for the tested grain sizes as well as for the adsorption and desorption tests. The adsorption rise up time increases by 36% as the average particle radius increases from 0.43 to 0.75 mm. The desorption rise up time amounts to 66.67% of the adsorption rise up time for the grain size 0.7 to 1.0 mm.

A further quantitative measure for the adsorption/desorption kinetics is the rate of change of the differential water loading \((\Delta \chi/\Delta \tau)\) between \(\chi = 0.15\) and \(\chi = 0.8\), which is found to be inversely proportional to the average particle radius according to Eq. (4).

\[
\Delta \chi/\Delta \tau = \frac{K_{v}}{R_{p}}
\]

The average values of the adsorption and desorption velocity constants amount to \((1.08 \times 10^4 \pm 14\%)\) and \((1.45 \times 10^4 \pm 3.6\%)\) m/s, respectively. In that sense, it could be concluded that the desorption process is, in average, 34% faster than the adsorption process within the tested range of grain sizes and under the studied AHP working condition.

### Conclusions

A new experimental methodology for studying the kinetics of water vapor adsorption/desorption under quasi-isobaric conditions has been introduced. Measurements have been carried out on one layer of loose pellets of FAM-Z02 of Mitsubishi Chemicals Corp. placed on a metal plate. Temperature of the sample holding plate has been changed as it takes place in real adsorption heat pumps (AHPs), while the vapor pressure over the adsorbent was maintained almost constant. The influence of grain size on both adsorption and desorption kinetics has been measured under evaporator, adsorption-end and condenser as well as desorber-end temperatures of 5, 35 and 90°C, respectively. Measurements have been carried out on three grain sizes; namely, 0.7 to 1.0 mm, 1.4 to 1.6 mm and 2.0 to 2.6 mm. An average equilibrium differential water loading of 19.2 g/100 g has been measured during desorption compared to 16.4 g/100 g during adsorption, which amounts to 3 to 5 times of the common adsorbents silica gel and NaY-zeolite under the same tested boundary conditions. The adsorption/desorption rates have been characterized by times \(t_{0.5}, t_{0.8}\) and \(t_{0.9}\) for reaching 50, 80 and 90% of the equilibrium loading. The dependence of the characteristic times on the average particle radius showed that the adsorption kinetics are dominated by inter-crystalline diffusion, while the desorption kinetics are mostly dominated by surface resistance to the heat and mass transfer. The time required for the dimensionless water loading to rise from 15 to 80% has been termed as the rise up time. The slope of the dimensionless water loading variation with time, during this rise up time, has been found to be inversely proportional to the average particle radius. The constant of proportionality is termed as adsorption/desorption velocity constant and has been estimated for both adsorption and desorption processes. This approach enables a quantitative comparison between adsorption and desorption kinetics. Strictly speaking, the desorption kinetics have

### Table 4: Dependence of the kinetics’ rise up time and the velocity constant on the average particle radius

<table>
<thead>
<tr>
<th>Process</th>
<th>((t_{0.8} - t_{0.15}))</th>
<th>(10^4 \times (\Delta \chi/\Delta \tau))</th>
<th>(10^4 \times K_v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)/(2)</td>
<td>[s]</td>
<td>[s(^{-1})]</td>
<td>[m(^{-1})]</td>
</tr>
<tr>
<td>0.43</td>
<td>302</td>
<td>2.152</td>
<td>0.926</td>
</tr>
<tr>
<td>0.75</td>
<td>411.5</td>
<td>1.58</td>
<td>1.185</td>
</tr>
<tr>
<td>1.15</td>
<td>664.5</td>
<td>0.978</td>
<td>1.125</td>
</tr>
<tr>
<td>0.43</td>
<td>200</td>
<td>3.25</td>
<td>1.398</td>
</tr>
<tr>
<td>0.75</td>
<td>341</td>
<td>1.906</td>
<td>1.43</td>
</tr>
<tr>
<td>1.15</td>
<td>495.5</td>
<td>1.312</td>
<td>1.51</td>
</tr>
</tbody>
</table>

(1) Adsorption process; (2) Desorption process

\[ R_{p} \]
been found to be 34% faster than the adsorption kinetics within the tested range of grain sizes and under the studied AHP working condition. Average specific evaporator cooling/condenser heating capacities in the order of 1 kW/kg have been estimated for the grain size 0.7 to 1.0 mm, putting in evidence the possibility of developing highly compacted AHPs with FAM-Z02 for heating and cooling applications.

Nomenclature

- $h_v$ = latent heat of vaporization [kJ/kg]
- $k$ = rate constant [s$^{-1}$]
- $p$ = pressure [mbar]
- ($q_{i}$)$_x$ = specific evaporator cooling/condenser heating capacity [kW/kg]
- $R_t$ = average particle radius [m]
- $V_S$ = sorption speed [g/(s·100 g)]
- $x$ = water loading [g/100 g]
- $\tau$ = characteristic time [s]
- $\chi$ = dimensionless differential water loading

<Subscript>
- 1–4 = state points in Figure 2
- $\text{Ev}$ = evaporator
- $f$ = final value
- $o$ = initial value
- $t$ = instantaneous value

Literature Cited


