

## Adsorption dynamics of MOF coatings for waste heat driven cooling

Eric LAURENZ<sup>(a)</sup>, Andreas VELTE<sup>(a)</sup>, Harry KUMMER<sup>(a)</sup>, Gerrit  
FÜLDNER<sup>(a)</sup>, Lena SCHNABEL<sup>(a)</sup>

<sup>(a)</sup> Fraunhofer Institute for Solar Energy Systems ISE  
79110 Freiburg, Germany, [eric.laurenz@ise.fraunhofer.de](mailto:eric.laurenz@ise.fraunhofer.de)

### ABSTRACT

Adsorption chillers are a promising option for environmentally friendly data centre cooling allowing for high energy efficiency. Waste heat from liquid cooled CPUs (~60 °C) drives the cooling for auxiliary loads (~20 °C) with heat rejection around 30 °C. Adsorption properties of the metal-organic frame work (MOF) aluminium fumarate largely outperform the state-of-the-art material silica gel at these temperatures. With adsorbent coatings, volume and mass specific cooling power may be increased to reduce specific costs.

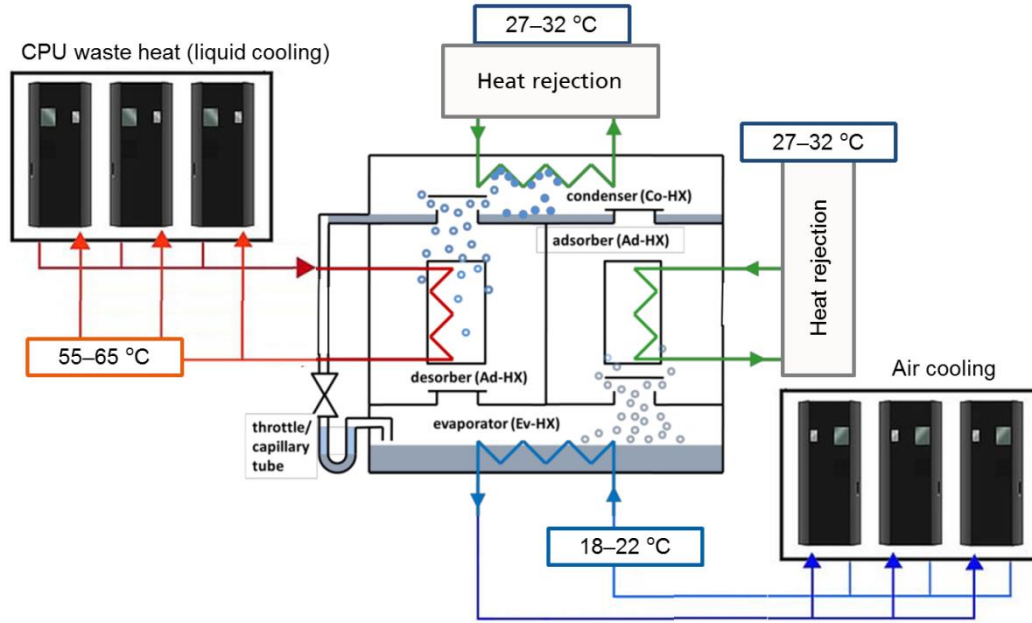
Samples were prepared with a binder-based aluminium fumarate coating in three different thicknesses (140–610 µm) and measured for adsorption dynamics with large-temperature-jump-experiments. Uptake-times (15–85%) are in the range of 9–78 s. On a full scale heat exchanger expected volume and adsorbent mass specific cooling powers are 200–700 W l<sup>-1</sup> and 1.3–14 kW kg<sup>-1</sup> – an increase to state-of-the-art of 3–10 times and >10 times at reasonable cooling COPs of 0.47–0.57.

Keywords: Adsorption Cooling, Data Centre Cooling, Energy Efficiency, Metal Organic Frameworks, Aluminium Fumarate, Adsorbent Coating

### 1. INTRODUCTION

Adsorption chillers are an environmentally friendly solution for the valorisation of waste heat for cooling demands. The working principle allows a simple, robust and scalable design. Adsorption chillers and heat pumps have been applied successfully for different applications like solar thermal cooling of buildings (Meunier, 2013) or gas adsorption heat pumps (Metcalf et al., 2012). A possible application that has attracted rising interest in recent years is the provision of data centre cooling driven by heat yielded from water cooled CPUs. Current high performance CPUs allow cooling water temperatures of up to 60 °C or more (Wilde et al., 2017; Zimmermann et al., 2012) that can be used to drive adsorption chillers.

An adsorption chiller (Figure 1) consists of two adsorption heat exchangers, a condenser and an evaporator in a pure working fluid atmosphere. If temperatures below 0 °C can be excluded, usually water is used as working fluid due to its high evaporation enthalpy. The adsorption heat exchangers (Ad-HX) have a heat transfer fluid on the primary and a stationary adsorbent material or composite on the secondary side. The process is cyclic: In the first half-cycle the CPU's waste heat is used to regenerate the first Ad-HX. The desorbed working fluid is condensed in the condenser which is cooled to the ambient at e.g. 30 °C. In the second half-cycle working fluid is adsorbed on the Ad-HX which is again cooled to the ambient. The resulting pressure drop induces the evaporation in the evaporator at about 20 °C. For continuous provision of cold, two Ad-HXs are operated alternately.



**Figure 1: Working principle of an adsorption chiller for data centre cooling**

Aluminium fumarate, a metal-organic framework (MOF) that attracted increasing interest for thermal applications in recent years, exhibits adsorption equilibrium properties that fit well to the boundary conditions of this cycle. Compared to the state of the art material silica gel it allows considerably more efficient cycles with a good hydrothermal cycle stability (Jeremias et al., 2014; Kummer et al., 2017). The material is potentially a low cost material due to widely available educts (Al-salts and fumaric acid) and water based synthesis route (Kiener et al.).

The increase of volume specific cooling power (VSCP) – thus reduction of specific costs – while keeping a reasonably high COP is one of the major development challenges for adsorption chillers (Schnabel et al., 2018). Typical values for COPs of market available adsorption chillers are in the order of 0.5 to 0.65 (ASUE, 2017). In the case of data centre cooling the target COP is determined by the ratio of low temperature cooling demand and available waste heat from CPUs which typically is in the same range (Wilde et al., 2017). A promising approach to increase VSCP is to use binder based adsorbent coatings to allow for a substantially better heat transfer to the heat exchanger structure in comparison to loose grain bed, the state of the art solution (Freni et al., 2015).

The aim of this study is to evaluate the potential of binder based aluminium fumarate coatings in adsorption chillers for data centre cooling. Based on a variation of the coating thickness particular attention will be paid to the effect of this key design parameter.

## 2. MATERIAL

The aqueous dispersion (26.8 wt% aluminium fumarate Basolite® A520, BASF; 17.9 wt% SilRes® MP50E, Wacker Silicones) was processed by a knife coating applicator on 50x50x2 mm AlMg3 sample plates. The wet film thickness was varied by an octagonal stainless steel mask with a defined thickness (200, 350, 600  $\mu\text{m}$ ) and constant coating surface  $A_{\text{ct}}$  (18.7  $\text{cm}^2$ ). Samples were oven dried at 200 °C for 3 h before measuring coating thicknesses  $d_{\text{ct}}$  of final samples (Table 1, Figure 2) at five points with a probe indicator. Total dry adsorbent content  $w_{\text{s,dry}}$  and sample adsorbent dry mass  $m_{\text{s}}$  were calculated based on experimentally determined dry mass of dispersion components and final samples, as shown by Kummer et al. (2015).

**Table 1: Sample properties**

Sample	$m_s$ (mg)	$d_{ct}$ ( $\mu\text{m}$ )	$w_{s,dry}$ (-)
Ct_140	100	$140\pm40$	0.749
Ct_240	163	$240\pm50$	0.749
Ct_610	422	$610\pm70$	0.749

**Figure 2: Sample with 610  $\mu\text{m}$  coating**

### 3. EXPERIMENTAL

The measurement set-up for the experiments carried out is described in detail in recent publications by Sapienza et al. (2017) and Velte et al. (2017). It consists mainly of two vacuum chambers with pressure sensors (MKS Baratron 627B), an infrared temperature sensor (Heitronics KT15.82 IIP) for sample surface temperature, and three Pt-100 temperature sensors to measure the vapour temperature in the dosage chamber and the carrier plate temperature, respectively. The samples are placed on the carrier plate with thermal grease (TG20032) for a good thermal contact. Two independent thermostats are operated in parallel and each of them can be coupled to the carrier plate via the hydraulic circuit. The switching between the two thermostats is very fast (switching time  $< 0.5$  s) due to pneumatically actuated valves. For the large temperature jump (LTJ) experiments the sample is heated up while the measurement chamber is connected to the vacuum pump. After this pre-conditioning dosage chamber and measurement chamber are filled with water vapour at a certain pressure. After reaching equilibrium, the thermostats are switched. The sample starts to ad- or desorb water vapour to reach the new equilibrium. The mass of water vapour that is ad- or desorbed can be calculated by applying the law of the ideal gas to the closed system (volumetric measurement).

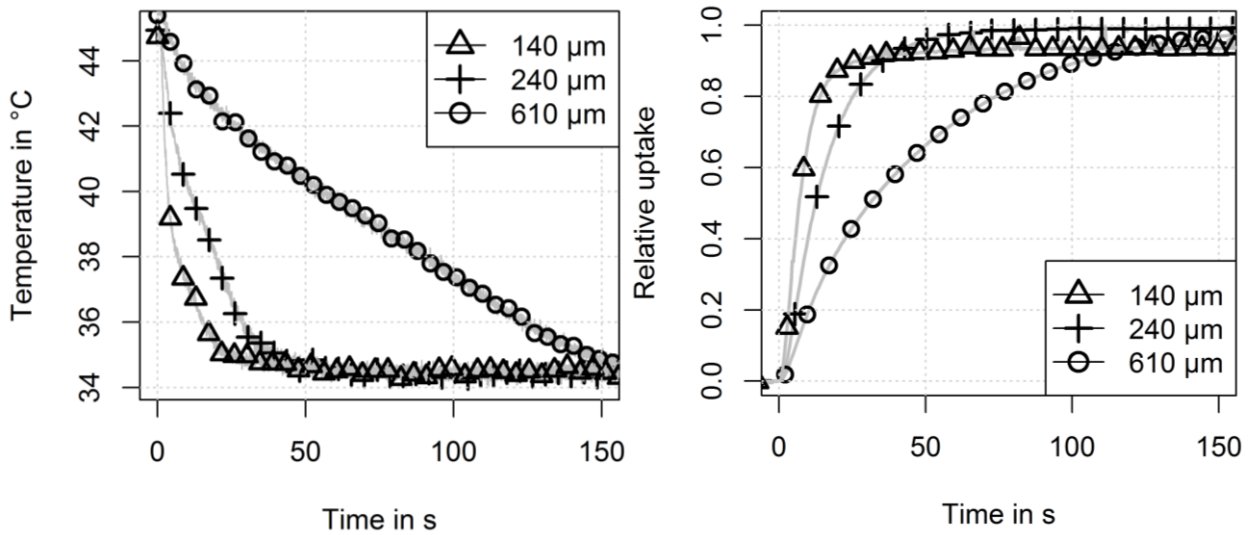
LTJ experiments from 45 to 35 °C and from 50 to 30 °C were performed (carrier plate temperatures). Given a driving temperature difference of 5 K, this simulates boundary conditions of about 60 °C for driving heat and 30 or 25 °C respectively for heat rejection. The earlier is easier met in actual application while the latter is expected to allow for better performance. To keep the average pressure at about 23.4 mbar (i.e. 20 °C evaporator temperature) for all measurements, the initial pressure in measurement chamber and dosage chamber was slightly lower for larger samples than for smaller samples.

### 4. RESULTS

In this section we first report the large temperature jump experiment results followed by an extrapolation to the performance of a full adsorber heat exchanger.

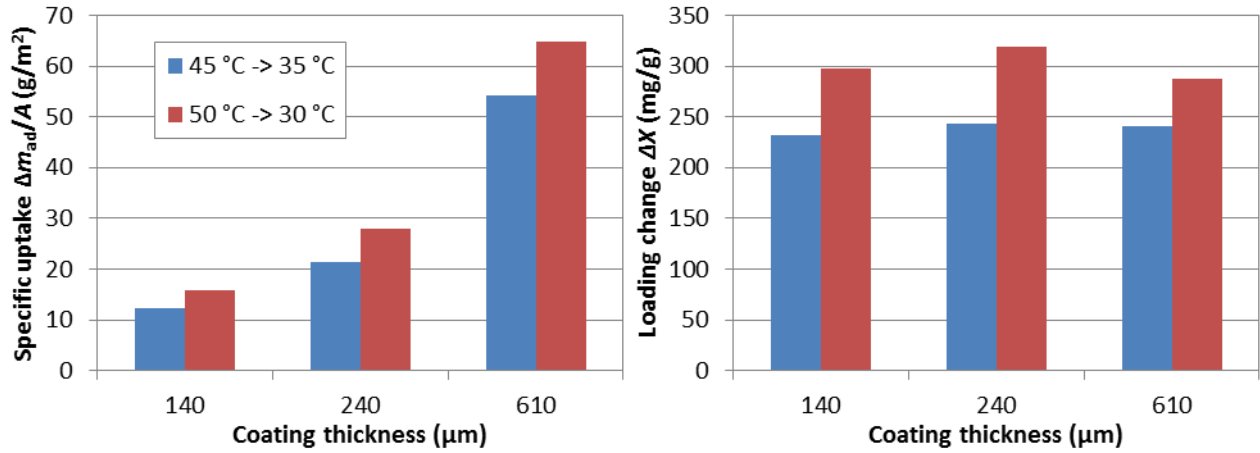
#### 4.1. Large temperature jump

The temperature jump experiments show fast adsorption kinetics of all samples with the larger temperature jumps (50  $\rightarrow$  30 °C) slightly faster than the smaller jumps (45  $\rightarrow$  35 °C). As expected the adsorption time increases with coating thickness. The uptake over time (Figure 3) shows the exponential form typical for adsorption kinetic experiments (Velte et al., 2017). The significantly delayed surface temperature response indicates heat transfer to be among the rate limiting steps, especially for thicker coatings.



**Figure 3:** Surface temperature (left) and relative uptake (right, determined volumetrically) over time after rapid jump ( $\tau < 1$  s) of the carrier plate temperature for different coating thicknesses. Here the data for the jump from 45 to 35 °C is shown.

The absolute uptake (Figure 4) does not change much with the jump temperature boundary conditions. This can be explained by the form of the isotherm with a step at about  $p_{rel} = 0.3$  (Splith et al., 2018): Both, the small and the large jump cover this step as shown by the step initial and end state in Table 2. The relative uptake shows a good comparability between the different samples. The remaining differences are due to slight deviations in experimental conditions and small errors of dry mass determination.



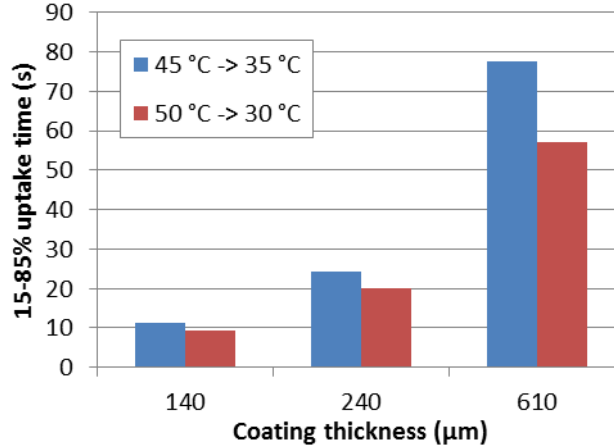
**Figure 4:** Area specific uptake and loading spread for different coating thicknesses and measurement conditions

**Table 2:** Initial (0), final ( $\infty$ ) and integral results of LTJ experiments for differently coated samples

$d_{ct}$ (μm)	$T_0 \rightarrow T_\infty$ (°C)	$p_0 \rightarrow p_\infty$ (mbar)	$p_{rel,0} \rightarrow p_{rel,\infty}$	$\Delta m_{ad}$ (mg)	$\Delta X$ (mg/g)	$\Delta t_{15-85}$ (s)
140	44.9 $\rightarrow$ 34.8	24.1 $\rightarrow$ 23.3	0.25 $\rightarrow$ 0.42	23.2	232	11
140	49.8 $\rightarrow$ 30.0	24.1 $\rightarrow$ 23.1	0.20 $\rightarrow$ 0.54	29.8	298	9.3
240	44.9 $\rightarrow$ 34.9	24.4 $\rightarrow$ 23.0	0.26 $\rightarrow$ 0.41	39.8	244	24
240	49.8 $\rightarrow$ 30.0	24.4 $\rightarrow$ 22.6	0.20 $\rightarrow$ 0.53	52.1	320	20
610	45.5 $\rightarrow$ 34.9	24.3 $\rightarrow$ 20.8	0.25 $\rightarrow$ 0.37	102	241	78
610	49.8 $\rightarrow$ 30.0	24.4 $\rightarrow$ 20.2	0.20 $\rightarrow$ 0.48	121	288	57

For further evaluation the 15-85% uptake time constant  $\Delta t_{15-85}$  is evaluated in Figure 5, being the range of 9 to 57 s and 11 to 78 s for the larger and the smaller jumps. The faster kinetics of the larger jump is again a result of the step like isotherm. For experiment's pressure level (23.4 mbar) the equilibrium temperature at the step position is of about 40 °C. This results in higher driving temperature differences for the larger jumps.

To what extent heat or mass transfer resistances govern the overall kinetics and whether this mass transfer is macropore diffusion in the coating or micropore diffusion in the adsorbent particle may not be answered from these results straight away. As discussed above, a tendency towards heat transfer limitations can be seen. However, for further targeted improvements this information would be highly valuable.



**Figure 5: Duration between 15% and 85% uptake for different coating thicknesses and operation conditions as basis for all power and efficiency estimations**

#### 4.2. Extrapolation to full scale adsorption heat exchanger

To judge the application relevance of results from small scale kinetic experimental they need to be extrapolated to the performance of a full scale heat exchanger (Wittstadt, 2018). In the following this will be done based on a simple adsorption cooling cycle with passive heat recovery (delayed valve switching (Wang et al., 2005)) for a fin-and-tube heat exchanger as described in detail by Wittstadt (2018, p. 141). Tubes (copper, Ø9.5×0.3 mm) have a spacing of 25×21.6 mm, fins (aluminium, 0.2 mm thickness) are arranged in spacing allowing for 2 mm free vapour channels. Headers and tube bends outside the fin package are assumed to occupy 20% of the total HX volume and to account for additional 25% of the tube's thermal mass. We assume the resistance from heat transfer in the tubes and fins as well as from the vapour flow to be negligible. Thus the expected average evaporator heat flux (per coated area) for a single Ad-HX

$$\begin{aligned} \dot{q}_{\text{evp}} &= \frac{q_{\text{evp}}}{\Delta t_{\text{cyc}}} \\ &= \frac{-(0.85 - 0.15)\Delta m_{\text{ad}}}{A_{\text{ct}} 2\Delta t_{15-85}} \left( \Delta h_v(T_{\text{evp}}) - c_w(T_{\text{cnd}} - T_{\text{evp}}) \right) \end{aligned} \quad \text{Eq. (1)}$$

can be directly deduced from the measurement results and material properties of water (Wagner et al., 2000) under the assumption that the total cycle time  $\Delta t_{\text{cyc}}$  is twice  $\Delta t_{15-85}$ . With the above mentioned geometry the volume specific cooling power can be derived straightforwardly:

$$\text{VSCP} = \dot{q}_{\text{evp}} \frac{A_{\text{ct}}}{V_{\text{HX}}} \quad \text{Eq. (2)}$$

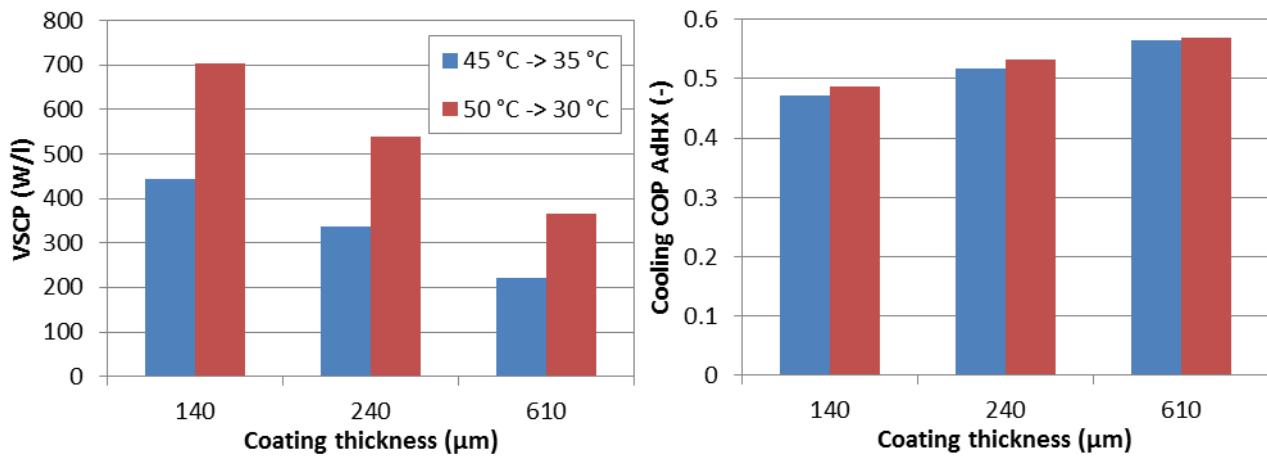
Similarly, the COP for an adsorption cooling cycle is

$$\text{COP} = \frac{-q_{\text{evp}}}{(0.85 - 0.15)\Delta m_{\text{ad}}/A_{\text{ct}}\Delta h_s + c_{\text{A,HX}}(T_{\text{des}} - T_{\text{ads}})} \quad \text{Eq. (3)}$$

Where the specific heat capacity (per coated area) of the Ad-HX is  $c_{A,HX}$  derived from the geometry and material properties of the heat exchanger metals ( $(\rho c_p)_{Al} = 2.43 \text{ MJ m}^{-3}\text{K}^{-1}$ ,  $(\rho c_p)_{Cu} = 3.42 \text{ MJ m}^{-3}\text{K}^{-1}$ ) and the adsorbent coating ( $\rho = 400 \text{ kg m}^{-3}$ ,  $c_p = 2.27 \text{ kJ kg}^{-1}\text{K}^{-1}$ ). The adsorption enthalpy is approximated following Dubinin and Astakhov (1971) for the steepest position in the isotherm ( $\Delta h_s = 2.51 \text{ MJ kg}^{-1}$ ).

The expected VSCP of a supposed coated Ad-HX is in the order of 200 to 700  $\text{W l}^{-1}$  for the different coatings and temperature conditions (Figure 6). With respect to the cost relevant aluminium fumarate input the expected adsorbent mass specific cooling power (MSCP) ranges between 1.3 and 14  $\text{kW kg}^{-1}$ . The dependency on coating thickness and temperature conditions reflects mainly the results for uptake time and total uptake (Table 2) damped by the decreased volume usage of the thin samples (less sorption material per HX volume).

Measurements with state of the art silica gel loose grains (single layer) as described by Aristov et al. (2012) at conditions comparable to the larger jump (LTJ 48  $\rightarrow$  30  $^{\circ}\text{C}$ , evaporator temperature: 20  $^{\circ}\text{C}$ ) results in expected values of 70  $\text{W l}^{-1}$  and 0.11  $\text{kW kg}^{-1}$  for VSCP and MSCP. This underlines the high performance of the aluminium fumarate coating for data centre cooling applications. With the same material Kummer et al. (2017) reported values of 100  $\text{W l}^{-1}$  and 1.4  $\text{kW kg}^{-1}$  indicating the potentially high performance increase from coating and heat exchanger optimization.



**Figure 6: Expected volume specific cooling power and COP with respect to adsorber heat exchanger volume and thermal mass for different coating thicknesses and operation conditions with 20  $^{\circ}\text{C}$  evaporation temperature under assumption given in the text**

The expected COP is between 0.47 and 0.57 – the required order for data centre cooling (Wilde et al., 2017). As expected (Schnabel et al., 2018) thicker coatings are more preferable in terms of efficiency due to a better mass ratio between sorption material and heat exchanger metal. For the temperature conditions, the difference vanishes. The positive effect of higher uptakes is compensated by larger temperature differences between de- and adsorption (25 and 30 K for small and the large temperature lift, respectively) which increases the amount of heat required for sensible heating.

It should be noted that the assumption are rather conservative. In practise thinner fins with narrower vapour channels might prove to be preferable as the increased transport resistance could be balanced out by the gains in volume and thermal mass. However, for this kind of targeted design and optimization a more detailed understanding and modelling of the underlying heat and mass transfer resistances is necessary in order to avoid costly and time consuming parameter variations on prototype level.

## 5. CONCLUSIONS

In this study we evaluated the potential of a novel adsorbent coating for waste heat valorisation in data centre applications. The metal organic framework aluminium fumarate could be applied in stable coating from a water based suspension in different layer thicknesses between 140 and

610  $\mu\text{m}$ . The results from large temperature jump experiments under two different temperature boundary conditions showed time constants (15-85% uptake) of 9 to 78 s for different coating thicknesses. Extrapolation to full scale heat exchanger reveals a high potential for application with adsorber volume specific cooling power between 200 and 700  $\text{W l}^{-1}$  and adsorbent mass specific cooling power between 1.3 and 13  $\text{kW kg}^{-1}$ . Compared to state of the art silica gel loose grain configurations this means an increase of about 3 to 10 times for volume and more than 10 times for mass specific cooling power at reasonable COPs.

From a qualitative assessment of surface temperature and uptake over time there is evidence that heat transfer in the coating becomes more relevant for thicker layers. For further optimisation a more detailed quantitative understanding of the underlying heat and mass transfer limitation appears necessary.

## ACKNOWLEDGEMENTS

Funding of the project HARVEST from Fraunhofer-Zukunftsstiftung and the PhD scholarship for Eric Laurenz from Heinrich-Böll-Stiftung is gratefully acknowledged. The authors thank Raffael Wolff for practical support in preparation and characterisation of the samples.

## NOMENCLATURE

$A_{\text{ct}}$	coated area ( $\text{m}^2$ )	$\dot{q}$	heat flux ( $\text{W}\times\text{m}^{-2}$ )
$c_A$	heat capacity per coated area ( $\text{J}\times\text{m}^{-2}\times\text{K}^{-1}$ )	$t$	time (s)
$d_{\text{ct}}$	coating thickness ( $\mu\text{m}$ )	$T$	temperature ( $^{\circ}\text{C}$ )
$m_{\text{ad}}$	adsorbed mass (kg)	$V$	volume ( $\text{m}^3$ )
$p$	pressure (kPa)	$V_{\text{HX}}$	heat exchanger volume
$p_{\text{rel}}$	relative pressure (-)	$X$	loading ( $\text{kg}_{\text{ad}}\times\text{kg}_{\text{dry}}^{-1}$ )
$q$	amount of heat per cycle per coated area ( $\text{J}\times\text{m}^{-2}$ )		
Ad-HX	adsorber heat exchanger	MSCP	adsorbent mass specific cooling power ( $\text{W}\times\text{kg}_{\text{dry}}^{-1}$ )
COP	coefficient of performance (-)	VSCP	volume specific cooling power ( $\text{W}\times\text{l}^{-1}$ )
MOF	metal-organic framework		

## REFERENCES

- Arbeitsgemeinschaft für sparsamen und umweltfreundlichen Energieverbrauch e. V., 2017. Marktübersicht Gaswärmepumpen 2017/18. [https://asue.de/sites/default/files/asue/themen/gaswaermepumpe\\_kaelte/2017/broschueren/ASUE\\_Marktuebersicht-Gaswaermepumpen\\_2017.pdf](https://asue.de/sites/default/files/asue/themen/gaswaermepumpe_kaelte/2017/broschueren/ASUE_Marktuebersicht-Gaswaermepumpen_2017.pdf). Accessed 6 February 2019.
- Aristov, Y.I., Glaznev, I.S., Girnik, I.S., 2012. Optimization of adsorption dynamics in adsorptive chillers: Loose grains configuration. *Energy* 46, 484–492. 10.1016/j.energy.2012.08.001.
- Dubinin, M.M., Astakhov, V.A., 1971. Description of Adsorption Equilibria of Vapors on Zeolites over Wide Ranges of Temperature and Pressure, in: Flanigen, E.M., Sand, L.B. (Eds.), *Molecular sieve zeolites. 2. International conference on molecular sieves 2*, vol. 102. American Chemical Society, Washington, D.C., pp. 69–85.
- Freni, A., Dawoud, B., Bonaccorsi, L., Chmielewski, S., Frazzica, A., Calabrese, L., Restuccia, G., 2015. Adsorption Heat Exchangers, in: Freni, A. (Ed.), *Characterization of zeolite-based coatings for adsorption heat pumps*. Springer, Cham, pp. 35–53.
- Jeremias, F., Fröhlich, D., Janiak, C., Henninger, S.K., 2014. Advancement of sorption-based heat transformation by a metal coating of highly-stable, hydrophilic aluminium fumarate MOF. *RSC Adv.* 4, 24073. 10.1039/C4RA03794D.
- Kiener, C., Müller, U., Schubert, M. Organometallic Aluminum Fumerate Backbone Material.



- Kummer, H., Földner, G., Henninger, S.K., 2015. Versatile siloxane based adsorbent coatings for fast water adsorption processes in thermally driven chillers and heat pumps. *Appl. Therm. Eng.* 85, 1–8. 10.1016/j.applthermaleng.2015.03.042.
- Kummer, H., Jeremias, F., Warlo, A., Földner, G., Fröhlich, D., Janiak, C., Gläser, R., Henninger, S.K., 2017. A Functional Full-Scale Heat Exchanger Coated with Aluminum Fumarate Metal–Organic Framework for Adsorption Heat Transformation. *Ind. Eng. Chem. Res.* 56, 8393–8398. 10.1021/acs.iecr.7b00106.
- Metcalf, S.J., Critoph, R.E., Tamainot-Telto, Z., 2012. Optimal cycle selection in carbon-ammonia adsorption cycles. *International Journal of Refrigeration* 35, 571–580. 10.1016/j.ijrefrig.2011.11.006.
- Meunier, F., 2013. Adsorption heat powered heat pumps. *Appl. Therm. Eng.* 61, 830–836. 10.1016/j.applthermaleng.2013.04.050.
- Sapienza, A., Velte, A., Girnik, I., Frazzica, A., Földner, G., Schnabel, L., Aristov, Y., 2017. “Water - Silica Siegel” working pair for adsorption chillers: Adsorption equilibrium and dynamics. *Renewable Energy*, 40–46. 10.1016/j.renene.2016.09.065.
- Schnabel, L., Földner, G., Velte, A., Laurenz, E., Bendix, P., Kummer, H., Wittstadt, U., 2018. Innovative Adsorbent Heat Exchangers: Design and Evaluation, in: Bart, H.-J., Scholl, S. (Eds.), *Innovative Heat Exchangers*. Springer International Publishing, Cham, pp. 363–394.
- Splith, T., Fröhlich, D., Henninger, S.K., Stallmach, F., 2018. Development and application of an exchange model for anisotropic water diffusion in the microporous MOF aluminum fumarate. *Journal of magnetic resonance* 291, 40–46. 10.1016/j.jmr.2018.04.009.
- Velte, A., Földner, G., Laurenz, E., Schnabel, L., 2017. Advanced Measurement and Simulation Procedure for the Identification of Heat and Mass Transfer Parameters in Dynamic Adsorption Experiments. *Energies* 10, 1130. 10.3390/en10081130.
- Wagner, W., Cooper, J.R., Dittmann, A., Kijima, J., Kretzschmar, H.-J., Kruse, A., Mareš, R., Oguchi, K., Sato, H., Stöcker, I., Šifner, O., Takaishi, Y., Tanishita, I., Trübenbach, J., Willkommen, T., 2000. The IAPWS Industrial Formulation 1997 for the Thermodynamic Properties of Water and Steam. *Journal of Engineering for Gas Turbines and Power* 122, 150. 10.1115/1.483186.
- Wang, X., Chua, H.T., Ng, K.C., 2005. Experimental investigation of silica gel–water adsorption chillers with and without a passive heat recovery scheme. *International Journal of Refrigeration* 28, 756–765. 10.1016/j.ijrefrig.2004.11.011.
- Wilde, T., Ott, M., Auweter, A., Meijer, I., Ruch, P., Hilger, M., Kuhnert, S., Huber, H., 2017. CoolLMUC-2: A supercomputing cluster with heat recovery for adsorption cooling, in: *Thirty-third Annual Semiconductor Thermal Measurement and Management Symposium. Proceedings 2017, San Jose, CA, USA, March 13-17, 2017. 2017 33rd Thermal Measurement, Modeling & Management Symposium (SEMI-THERM), San Jose, CA, USA. IEEE, Piscataway, NJ, U.S.A., pp. 115–121.*
- Wittstadt, U., 2018. Experimentelle und modellgestützte Charakterisierung von Adsorptionswärmeübertragern. Dissertation. Technische Universität Berlin, Berlin.
- Zimmermann, S., Meijer, I., Tiwari, M.K., Paredes, S., Michel, B., Poulikakos, D., 2012. Aquasar: A hot water cooled data center with direct energy reuse. *Energy* 43, 237–245. 10.1016/j.energy.2012.04.037.