

**REPORT ON STATE OF THE DATABASE OF SORPTION MATERIALS AS INHERITED FROM
ANNEX 34 WITH PROVISIONAL PLANS FOR EXPANSION AND IMPROVEMENT**

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Executive Summary

Annex 34 of the IEA Heat Pump Programme, entitled 'Thermally Driven Heat Pumps for Heating and Cooling' ran from 2009 to 2012. Its scope was the use of thermally driven heat pumps and chillers in domestic and small commercial buildings and industrial applications, such as:

- Larger district heating systems with cooling and/or heat pumping
- Small thermally driven heat pumps for domestic heating and cooling
- Small Absorption/Adsorption chillers driven by heat from combined heat and power (CHP) units
- Small Absorption/Adsorption chillers driven by solar heat
- Industrial processes using waste heat

The five Tasks within it were:

- A) Market overview / state of the art
- B) Performance evaluation
- C) Apparatus Technology
- D) System Technology
- E) Implementation / Market transfer activities

Under Task 'C', WP2 was to set up an adsorbent materials database and to devise standardised testing methods that could be used in many laboratories. All of the systems studied under Annex 34 were sorption heat pumps or chillers that use the affinity of chosen refrigerant and sorbent (liquid or solid) pairs to form the basis of a 'heat driven compressor' rather than the electrically driven compressors that are the heart of conventional electric heat pumps. In order to develop improved systems it is essential to have reliable data on (in particular) the adsorption characteristics of a whole range of existing and novel solid adsorbents with refrigerants such as water, methanol, ethanol or ammonia. Measurement of the quantity of uptake with varying pressure and temperature can be problematic and data measured for the same materials in different laboratories can differ widely. The challenge under WP2 was to standardise testing methods and produce a robust database of results for different sorbent pairs. This was to be evaluated by round-robin tests of the same materials in different laboratories.

This work is of continuing importance to the new Annex 43 – 'Fuel Driven Sorption Heat Pumps' and part of its programme is to expand and improve on the previous database. This report explains what was achieved under Annex 34 and how the task will continue. In Annex 34, two laboratories in Germany and Italy agreed testing protocols and compared results on several pairs with some success. The refrigerant was water in all cases and eventually nine different adsorbents were tested. The intention had been to include a much wider range of refrigerants and adsorbents and this challenge will be taken up by Annex 43 in the coming three years.

1 General overview

For further improvement of adsorption heat pumps it is of importance to identify useful working pairs of adsorbent and refrigerant and to measure their physical properties. Many groups in different research institutes are working in this field. In order to compare their materials characterisation results and to find the best working pair for any given application it is of importance to have common testing methodology. Within Annex 34 such a methodology was proposed and work initiated, but much remains to be done in Annex 43.

The characterisation of adsorption materials has been the focus of many publications e.g. (Srivastava and Eames 1998), (Aristov, Restuccia et al. 2002), (Janchen, Ackermann et al. 2002), (Critoph and Zhong 2005), (Henninger, Schmidt et al. 2010). Three main methods are used to measure adsorbent uptake of refrigerant:

- a) The classical and most frequent measurement method used to assess porosity where water is the refrigerant is thermogravimetry (TGA) and volumetry using nitrogen as inert gas under a well-defined temperature-scanning rate in the TGA equipment. However, the material has to be carefully prepared before the measurement takes place and results are very sensitive to the heating rate used to desorb water from the sample. Comparison of materials measured with this method leads to large discrepancies as the initial state, which is room temperature, is not well defined and therefore difficult to reproduce. In addition without the ability to perform adsorption curves, possible hysteresis effects cannot be detected. The method is not recommended for adsorbent pair characterisation.
- b) Another possibility in case of open systems is to use a well-defined humidified carrier gas (e.g. Setaram WetSys) which flows around the sample. To prevent condensation, the transfer line and the measurement cell has to be temperature controlled in an accurate way.
- c) The third range of possibilities are systems with closed working fluid atmosphere. As shown in (Henninger, Schmidt et al. 2010) measurements with open and closed systems are comparable if using the same reference conditions. These influencing factors have to be taken into account in order to define a common procedure (Fig. 1).



Fig. 1: Influencing factors for thermal analysis of the adsorption characteristics.

Beside the differences in the apparatus used an additional difficulty is the difference in isobaric (constant pressure) versus isothermal (constant temperature) measurements. Isothermal measurement in principle allows the determination of the heat of adsorption, by calculation for at least two isotherms or direct measurement within equipment for simultaneous Thermo-Gravimetry / Differential Scanning Calorimetry (TG/DSC).

Isobaric measurement can in principle be performed in a broader temperature range therefore covering a larger range of the adsorption potential A , where

$$A = RT \ln \frac{P}{P_0}$$

Furthermore as the real cycle (ideally) consists of two isobaric phases of desorption and adsorption at condenser and evaporator pressure, the isothermal measured data is not directly adoptable to the operating device.

2 Recommended procedure

As a result of the arguments above a common method for determination of water adsorption characteristics with focus on adsorption heat pumps and chillers has been developed (Henninger, Freni et al. 2011).

The procedure consists of a pre-treatment of the sample under continuous evacuation (vacuum level: $1e^{-4}$ kPa). The optimal sample pre-treatment temperature should be selected according to the following classification.

- Strongly hydrophilic zeolites (4A, 13X): pre-treatment $T = 300^{\circ}\text{C}$.
- Hydrophilic aluminosilicates (NaY): pre-treatment $T = 200^{\circ}\text{C}$
- Hydrophobic aluminosilicates (silicalites, ZSM5): $T=150^{\circ}\text{C}$
- Aluminophosphates (AlPO, SAPO): $T=150^{\circ}\text{C}$
- Others (silica gels, activated carbons): $T=150^{\circ}\text{C}$

The sample is heated starting from ambient conditions with a heating rate of 1K/min followed by an isothermal drying step for another 8 hours. In the following step, isobar measurement at a water vapour pressure of 1.2 and 5.6 kPa takes place.

The selection of the two pressure levels is determined by the possible applications. The pressure level of 1.2 kPa corresponds to an evaporation temperature of 10°C , which marks a useful temperature level for cooling applications. The second pressure level of 5.6 kPa corresponds to 35°C which either marks the temperature where heat can be rejected (cooling application) or can be used for low temperature heating (heat pumping application). For each pressure level the sample temperature is varied in 5 or 10 K steps between 150°C and 40°C for the higher pressure and 150°C and 20°C for the lower pressure. In addition at least one adsorption and desorption measurement should be performed in order to detect possible hysteresis effects.

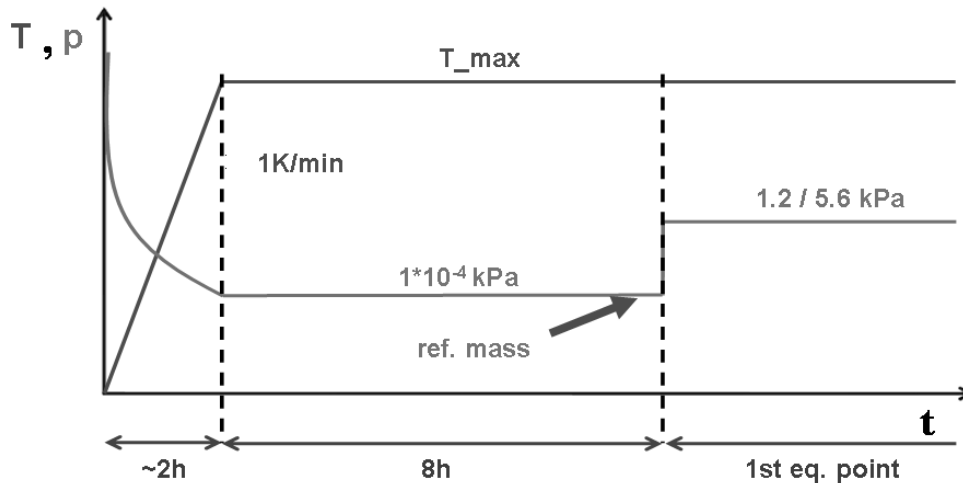


Fig. 2: Proposed measurement procedure, including sample pre-treatment and the first isobaric step.

3 Results

3.1 Comparison using Silica Gel 127 B

In a first step, the proposed procedure was successfully verified by measuring water adsorption characteristics on a standard Silica Gel 127 B manufactured by Grace. Measurement at ITAE ('Istituto di Technologie Avanzate per l'Energia' in Messina) were performed with a Cahn thermobalance whereas the measurements at ISE (Fraunhofer-Institut für Solare Energiesysteme in Freiburg) were performed using a Rubotherm thermobalance. Both sets of apparatus were connected by a heated transfer line to an evaporator in order to maintain fixed water vapour pressure over the sample.

The water adsorption and desorption isobars at 1.2 kPa measured by ITAE and ISE are shown in Fig. 3. Although some points are not exactly in equilibrium, the overall agreement between ITAE and ISE isobar adsorption measurement with the above described procedure is excellent. The desorption isobars are also in good agreement for higher temperatures however for lower temperatures and higher loadings there is a significant difference. This is probably a combination of non-equilibrium state and small hysteresis.

The water adsorption and desorption isobars at 5.6 kPa in direct comparison are shown in Fig. 4. . Again the agreement between the equilibrium points measured in similar conditions at CNR-ITAE and at Fraunhofer-ISE is excellent.

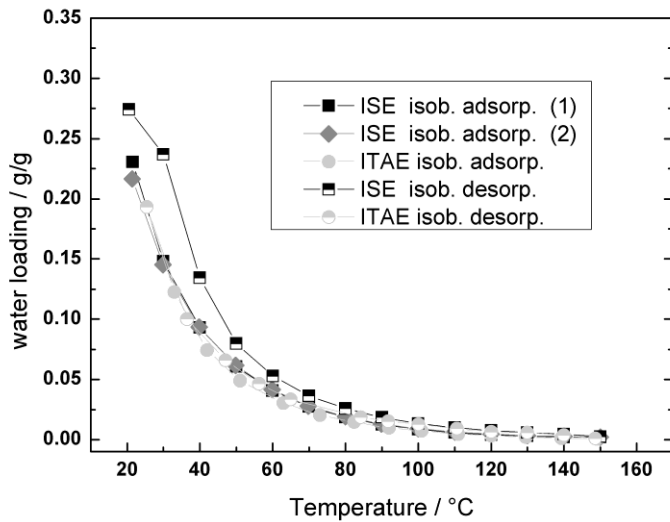


Fig. 3: Comparison of isobar adsorption measurements for Silica Gel 127 B at 1.2 kPa.

As result of these measurements, a water uptake for an adsorption chiller working under the conditions (30°C/1.2kPa adsorption versus 100°C/5.6 kPa desorption), which are typical values, can easily be taken from the measurement data and accounts to 127 g/kg.

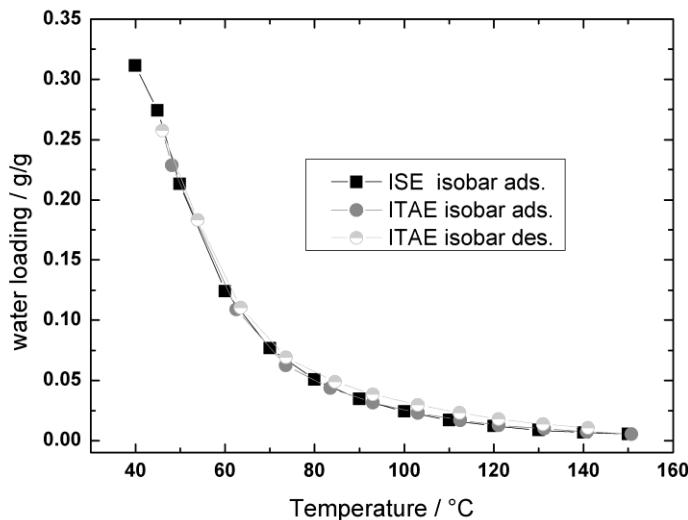


Fig. 4: Comparison of isobar adsorption and desorption measurements for Silica Gel 127 B at 5.6 kPa.

Concerning the possible utilization of the silica gel 127B as water adsorbent in adsorption chillers driven by low temperature heat ($T < 100^{\circ}\text{C}$), the following remarks can be made. First, a large part of the adsorbed water can be released at a regeneration temperature of about 100°C , without noticeable hysteresis effects. Second, a maximum water loading “at equilibrium” is rather high (0.2-0.3 g/g, depending on the imposed vapour pressure). However, a high relative pressure ($p/p_s = 0.5-0.7$) is required to reach such elevated levels of saturation, which is not favourable for application in adsorption heat transformers.

3.2 Comparison using SAPO-34

In addition to the first results on the Silica Gel another material out of the class of the silica-aluminophosphates has been used for comparison. Unlike the Silica Gel SAPO-34 shows a quite different adsorption characteristic with an S-shaped adsorption isotherm within a narrow relative pressure. This shape is advantageous for the application in adsorption heat transformers.

The adsorption and desorption measurements for 1.2 kPa are shown in Fig.5. Fig. Again there is a good agreement between the measurements although the applied pressure was slightly different (1.2 vs. 1.1 kPa). For very high loadings again there is a difference for the adsorption path, whereas the desorption path is in excellent agreement.

It has to be mentioned, that the ISE measurements have been performed in an open flow system TG-DSC by Setaram. As there is no possibility for evacuation of the system, the sample pre-treatment was different. To determine the dry mass, the sample was dried at 150°C under a pure carrier gas flow.

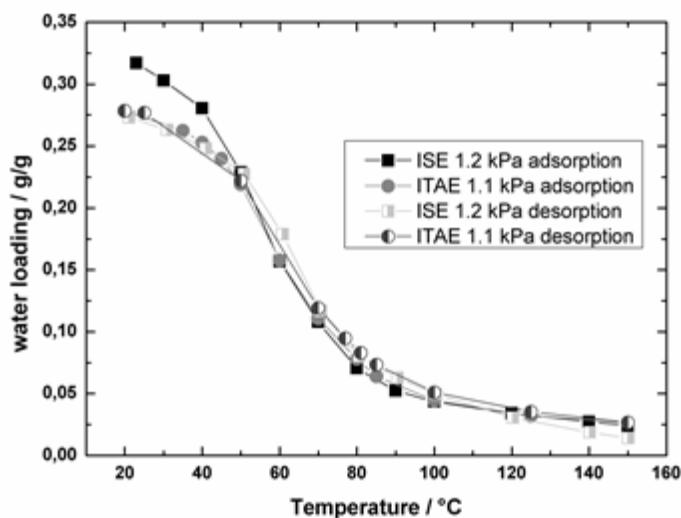


Fig. 5: Comparison of 1.1 kPa and 1.2 kPa adsorption/desorption isobars on a SAPO-34 sample. ISE measurements have been performed in an open flow system.

3.3 Influence of different measurement conditions

As stated above, the proposed procedure cannot be used in all measurement equipment. Especially using an open flow system, the drying of the sample by continuous evacuation is not possible. Also, the influence of the drying procedure is reduced, if the material can be desorbed at low temperatures, i.e. if the material is not too hydrophilic.

A first comparison between different equipment (balances) and different measurement procedures (isotherms vs. isobars) is shown in Fig. 6.

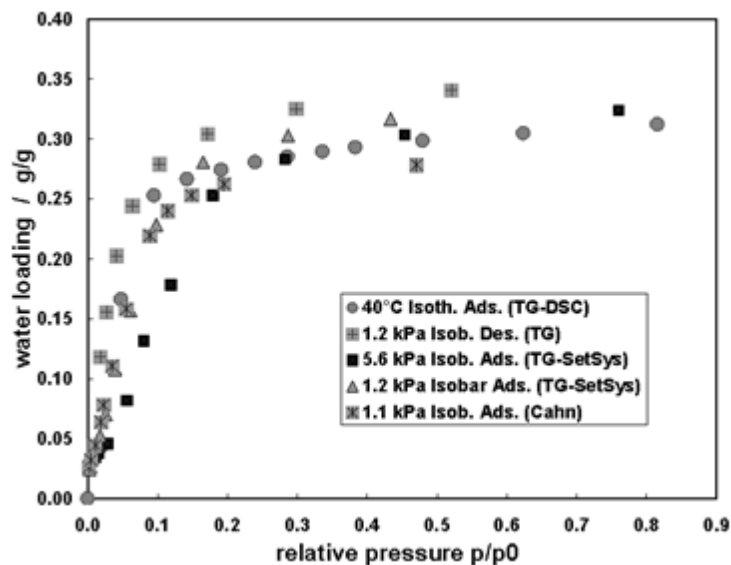


Fig. 6: Comparison of measurements for the SAPO-34 sample with different equipment and procedures.

The measurements have been performed with a Rubotherm thermobalance (TG), a Setaram SetSys Evolution (TG-SetSys), a Setaram simultaneous TG/DSC (TG-DSC) and a Cahn-balance model C2000 (Cahn). Details on the setup can be found in (Henninger, Munz et al. 2011), (Henninger, Schmidt et al. 2010), and (Restuccia, Freni et al. 1999).

In order to be able to compare isotherms and isobars even at different pressures, the water loading is shown versus the calculated relative pressure in case of the isobars, or the measured relative pressure in case of the isotherm.

At first view, there is a more or less broad scattering of the data points. Taking into account, that four different balances have been used, that the material shows a slight hysteresis between adsorption and desorption, and in addition that the stability of the materials is a critical issue, the agreement is good.

4 Characterising equations

In order to use the above measurements in engineering design and optimisation it is necessary to be able to calculate the concentration of refrigerant in the adsorbent at any desired temperature and pressure, i.e. to have a mathematical equation or algorithm that relates the three parameters when the material is in equilibrium.

Several theoretical models and phenomenological laws have been applied to the adsorption data in order to provide an analytical expression describing the sorption characteristics, i.e. the adsorption equilibrium, and to allow interpolation and extrapolation of the measured data.

In case of the working pair water/silica gel there exist various models based on the Langmuir equation, like the modified Freundlich's equation used by (Saha, Koyama et al. 2003) or the related Toth equation used by Chua and co-workers (Chua, Ng et al. 2004). A different equilibrium equation, developed by Boelman is used in (Zhang, Liu et al. 2005). (Aristov, Tokarev et al. 2006) proposed a simple polynomial expression in which the equilibrium uptake is expressed as a function of the Dubinin–Polanyi adsorption potential. A

phenomenological law derived from the Clausius-Clapeyron equation has been used by (Cacciola and Restuccia 1995).

4.1 Dubinin Equation

As a first step, analysis and characterisation of measured data according to Dubinin's theory of pore volume filling (Dubinin 1975) has been used for describing the physical properties of the adsorption characteristics regarding temperature (T), pressure (p) and load (x). Although this theory was originally used for methanol/activated carbon it has been showed that it can be used for silica gel (Núñez, Henning et al. 1999) , (Schicktanz and Nunez 2009).

The theory is based on the concept of the differential work of adsorption A, defined by

$$A = -\Delta G = RT \ln \left(\frac{p_s(T)}{p} \right) \quad 1)$$

where p is the equilibrium pressure, p_s the saturated vapour pressure G the Gibbs free energy and R the specific gas constant.

According to the Polanyi, Dubinin and co-workers adopted the thermodynamic interpretation of the Polanyi adsorption potential as the negative differential free energy of adsorption (ΔG), that is a variation in Gibb's free energy. The second characteristic quantity is the adsorption volume (W) defined as

$$W = \frac{X(T, p)}{\rho_{ads}(T)} \quad 2)$$

with X denoting the amount adsorbed at a given temperature and pressure and ρ_{ads} describing the temperature-dependent density of the adsorbate.

The theory states that all relevant thermodynamic properties can be derived from one equation

$$W = f(A) \quad 3)$$

expressed as the characteristic curve. Several different functional relation $W = f(A)$ have been proposed, whereof the Dubinin-Astakhov (D-A) and Dubinin-Radushkevitch (D-R) are the best known. A brief overview on extensions of the classical D-A and D-R equations as well as a theoretical basis can be found in (Hutson and Yang 1997).

As can be seen in, the resulting characteristic curve for the working pair water/silica gel 127B according to Dubinin's approach is quite smooth, so the equation seems to give reasonable results.

It has to be mentioned, that the fundamental condition of the temperature invariance of the characteristic curve for using Dubinin's approach cannot be guaranteed, as there are small discrepancies between different temperatures. However, in a first instance, the resulting curve and furthermore the analytical expression of the fit curve reflects the adsorption characteristics well. For the functional relation a classical D-A equation in reduced form is as shown in Fig. 7.

$$W = W_0 \exp \left[(bx)^n \right] \quad 4)$$

Of course, the main advantage for using this approach is the fact, that a single curve contains all thermodynamic information, compared to the parameterization of isobars or isotherms.

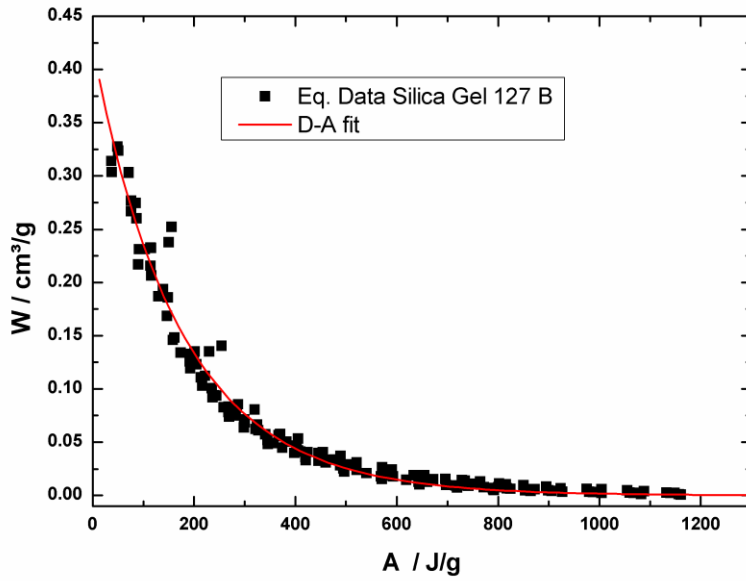


Fig. 7: Transformation according to D-A equation of the equilibrium points for water/Silica Gel.

4.2 Other relationships

In case of the SAPO-34 the situation changes. As illustrated in Fig. 8, the transformation leads to a more scattered plot of data points. This is due to some hysteresis effects, which can be identified between the 1.2 kPa and 5.6 kPa adsorption measurement. In addition the shape of the characteristic curve is not a good match to the D-A fit equation. Consequently the D-A fit leads to significant deviations. However, a similar transformation can be used, based on the following equilibrium relationship (Cacciola and Restuccia 1995).

$$\ln(p) = A(w) + B(w)/T \quad 5)$$

with the pressure (p) in mbar, temperature (T) in K and loading (w) as weight per cent. The parameters $A(w)$ and $B(w)$ are polynomial functions.

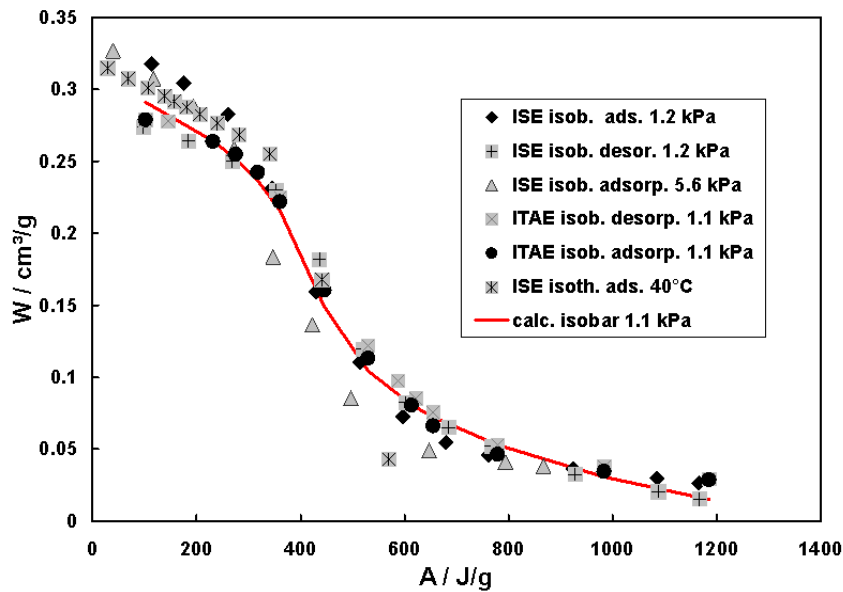


Fig. 8: Transformation of equilibrium point for water /SAPO-34 according to Dubinin's theory.

This expression is directly derived from classical Clausius-Clapeyron equation. The fundamental assumptions are a) the heat capacity of the adsorbate is equal to that of the liquid phase; b) the enthalpy of adsorption therefore is a function of the amount adsorbed; c) the enthalpy is independent of the temperature; d) the equilibrium conditions can be represented by a set of isosteres (lines of constant concentration). Under these assumptions, the isostere on a diagram of $\ln(p)$ versus $1/T$ are straight lines. The slope is proportional to the enthalpy of adsorption.

It has to be mentioned that this is only one possible thermodynamic expression for the adsorption characteristics. With regard to classical adsorption materials like zeolites a great variety of well-known models is available in literature and has been used for description of the adsorption of water, e.g. Langmuir, Sips, Toth and Dubinin-Astakhov.

5 Conclusions of IEA Heat Pump Programme Annex 34, Thermally driven Heat Pumps for Heating and Cooling, Task C (Apparatus Technology) WP2, Characterisation of adsorption materials and materials database

A standard measurement procedure for adsorption material properties with water sorbate was adopted. First results with a good agreement between measurements performed at Fraunhofer ISE and at CNR-ITAE, using different techniques were demonstrated. As the first two candidates of a standard material to be used in a round robin test, a silica gel 127 B and a SAPO-34 were selected. Whereas measurement results for the silica gel according to the proposed procedure are in a very good agreement, comparison of the results for SAPO-34 is revealing some discrepancies. It has to be mentioned, that SAPO-34 is a quite interesting but difficult material to be used, as the adsorption characteristic shows a steep adsorption

in a very narrow relative pressure range. Therefore, small deviations in temperature or pressure lead to a large error.

6 New developments on adsorption materials and material database

Annex 34 aimed to undertake verifiable round robin testing of materials in other laboratories apart from the two mentioned and also to create a database of many more materials. Unfortunately this did not prove possible within the time and resource limitations of the Annex. Nine different water adsorbents were characterised at the two laboratories.

Novel adsorbents were investigated during the life of the project and were reported on but a true database of these materials with properties confirmed by more than one laboratory was not created. The discovery of new microporous materials for the use in adsorption heat pump processes is still a fundamental research topic with exciting improvements and numerous publications. (Aristov, Restuccia et al. 2002), (Jänchen, Ackermann et al. 2004), (Ng and Mintova 2008), (Henninger, Schmidt et al. 2010).

With regard to the well-known zeolites, the main focus was on optimization and adjustment to the given boundary conditions through the use of different cations and/or lower alumina content. In (Henninger, Schmidt et al. 2010) samples of the faujasite framework type with different cations have been evaluated. Amongst different possible cations, the lithium and especially the rare-earth LaNa exchanged form has been selected as the most promising one for the use in heat transformation applications based on water adsorption.

In addition novel sorption materials with higher surface area, larger pore volume and higher working fluid uptake have been developed and reported in the last years. Closely related to the zeolites new materials like the aluminophosphates (AIPOs) and the silica-aluminophosphates (SAPOs) have been successfully adapted to the use in adsorption heat pumps or chillers (van Heyden, Munz et al. 2009), (Ristić, Henninger et al. 2010).

The newly developed materials like SAPO-34 and AIPO-18 show up to six times higher working fluid exchange compared to the silica gel reference.

With regard to new adsorber concepts, based on these materials or composites and faster cycling times an intense investigation of the stability under application conditions, which is continuous cycling between high and low temperatures under pure adsorptive atmosphere is needed. Especially with regard to market entrance of these systems intensive investigations on hydrothermal stability are essential (Henninger and Munz 2009), (Henninger, Munz et al. 2011).

Beside the inorganic materials like zeolites and aluminophosphates a new class of microporous materials known as Porous Coordination Polymers (PCPs) or Metal-Organic Frameworks (MOFs) has emerged. With regard to water adsorption capacity, porous coordination polymers (PCPs) are the most promising materials identified so far (Henninger, Habib et al. 2009), (Ehrenmann, Henninger et al. 2011). Like zeolites and aluminophosphates, metal organic frameworks are crystalline open porous materials with a one, two or three-dimensional framework. In contrast to the zeolites MOFs are not purely inorganic but inorganic-organic hybrid materials based on metal atoms or metal clusters as nodes, which are linked by organic ligands.

Within Annex 43 it is hoped both to increase the number and type of water sorbents within the database and to extend the coverage to adsorption of other sorbates such as methanol and ammonia. Plans to do this are still at a very early stage but it is hoped that the data gathered will be considerably larger in scope and made available to Annex partners via the web site. Information that is not commercially confidential will be publicly available.

7. References

Aristov, Y. I., G. Restuccia, et al. (2002). "A family of new working materials for solid sorption air conditioning systems." Applied Thermal Engineering **22**(2): 191-204.

Aristov, Y. I., M. M. Tokarev, et al. (2006). "Kinetics of water adsorption on silica Fuji Davison RD." Microporous and Mesoporous Materials **96**: 65-71.

Cacciola, G. and G. Restuccia (1995). "Reversible Adsorption Heat-Pump - a Thermodynamic Model." International Journal of Refrigeration-Revue Internationale Du Froid **18**(2): 100-106.

Chua, H. T., K. C. Ng, et al. (2004). "Transient modeling of a two-bed silica gel-water adsorption chiller." International Journal of Heat and Mass Transfer **47**(4): 659-669.

Critoph, R. E. and Y. Zhong (2005). "Review of trends in solid sorption refrigeration and heat pumping technology." Proceedings of the Institution of Mechanical Engineers, Part E: Journal of Process Mechanical Engineering **219**: 285-300.

Dubinin, M. M. (1975). "Physical adsorption of gases and vapors in micropores." Progress in Surface and Membrane Science **9**: 1-70

Ehrenmann, J., S. K. Henninger, et al. (2011). "Water Adsorption Characteristics of MIL-101 for Heat-Transformation Applications of MOFs." European Journal of Inorganic Chemistry **2011**(4): 471-474

Henninger, S. K., A. Freni, et al. (2011). Unified water adsorption measurement procedure for sorption materials. International Sorption Heat Pump Conference, April 6-7-8 2011; Padua, Italy.

Henninger, S. K., H. A. Habib, et al. (2009). "MOFs as Adsorbents for Low Temperature Heating and Cooling Applications." Journal of the American Chemical Society **131**(8): 2776

Henninger, S. K. and G. Munz (2009). HYDROTHERMAL STABILITY OF SORPTION MATERIALS AND COMPOSITES FOR THE USE IN HEAT PUMPS AND COOLING MACHINES. Heat Powered Cycles Conference, 7 to 9 September 2009; Berlin, Germany

Henninger, S. K., G. Munz, et al. (2011). "Hydrothermal Treatment of Sorption Materials - Implications on Adsorption Heat Pumps." Renewable Energy **36**: 3043-3049

Henninger, S. K., F. P. Schmidt, et al. (2010). "Water adsorption characteristics of novel materials for heat transformation applications." Applied Thermal Engineering **30**(13): 1692-1702.

Hutson, N. D. and R. T. Yang (1997). "Theoretical basis for the Dubinin-Radushkevitch (D-R) adsorption isotherm equation." Adsorption-Journal of the International Adsorption Society **3**(3): 189-195.

Janchen, J., D. Ackermann, et al. (2002). "Adsorption properties of aluminophosphate molecular sieves - Potential applications for low temperature heat utilisation." Proceedings of the International Sorption Heat Pump Conference: 635-638.

Jänchen, J., D. Ackermann, et al. (2004). "Studies of the water adsorption on Zeolites and modified mesoporous materials for seasonal storage of solar heat." Solar Energy **76**: 339-344.

Ng, E.-P. and S. Mintova (2008). "Nanoporous materials with enhanced hydrophilicity and high water sorption capacity." Microporous and Mesoporous Materials **114**: 1-26

Núñez, T., H.-M. Henning, et al. (1999). Adsorption Cycle Modelling: Characterization and Comparison of Materials. International Sorption Heat Pump Conference.

Restuccia, G., A. Freni, et al. (1999). Adsorption beds of zeolite on aluminium sheets. International Sorption Heat Pump Conference. Munich, Germany: 343-347

Ristić, A., S. K. Henninger, et al. (2010). Microporous aluminophosphates: Promising materials for heat transformation applications. Eurosun. Graz, Austria

Saha, B. B., S. Koyama, et al. (2003). "Performance evaluation of a low-temperature waste heat driven multi-bed adsorption chiller." International Journal of Multiphase Flow **29** 1249-1263.

Schicktanz, M. and T. Nunez (2009). "Modelling of an adsorption chiller for dynamic system simulation." International Journal of Refrigeration-Revue Internationale Du Froid **32**(4): 588-595.

Srivastava, N. C. and I. W. Eames (1998). "A review of adsorbents and adsorbates in solid-vapour adsorption heat pump systems." Applied Thermal Engineering **18**(9-10): 707-714.

van Heyden, H., G. Munz, et al. (2009). "Kinetics of water adsorption in microporous aluminophosphate layers for regenerative heat exchangers." Applied Thermal Engineering **29**(8-9): 1514-1522.

Zhang, Y. H., Q. H. Liu, et al. (2005). "Properties and crystallization kinetics of poly(ether ether ketone)-co-poly(ether ether ketone ketone) block copolymers." Journal of Applied Polymer Science **97**(4): 1652-1658

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