

Chapter 2

Adsorption Heat Exchangers

2.1 Ideal Adsorber Design Requirements

As described in Chap. 1, one of the major adsorber heat exchanger design requirements is the reduction of the ratio between the heat capacity of the adsorber heat exchanger material as well as its heat transfer medium's holdup and the heat capacity of the applied adsorbent. This results in enhancing the coefficient of performance of the adsorption heat pump and increases the obtainable specific heating or cooling power.

Beside low cost, manufacturability including a reasonable quality assurance procedure, there are two more sets of adsorber design requirements; namely, dynamic performance and reliability design requirements.

The dynamic performance design requirements include

- (a) High overall heat transfer coefficient between the heat transfer medium and the adsorbent.
- (b) High overall (inter- and intra-particle) mass diffusion coefficient.
- (c) Keeping the refrigerant vapour velocities as low as possible (<50 m/s) in the connecting ducts between adsorber and evaporator or condenser. This implies the reduction of pressure losses, most specifically during the adsorption-evaporation phase.
- (d) In case non-return valves with floating elements are incorporated, the required force to open those valves and, consequently, the required "opening" pressure shall be minimized.

The reliability design requirements are:

- 1. High stability against hydrothermal aging.
- 2. High mechanical stability against loading, transport and operating conditions.
- 3. No corrosion potential under loading, transport and operating conditions.
- 4. No release of inert gases upon repeated adsorption-desorption cycling.

2.2 Overview on Adsorber Developments for Adsorption Heat Pumps

Considering the methodology of bringing the adsorbent on the outer surface of the adsorber heat exchanger, the following four configurations have been identified so far:

- Consolidated
- Loose grains
- In situ crystallized coatings
- Binder-based coatings

This section will focus on the first three technologies, while the binder-based technique, to whom this book is dedicated, will be described in more details in the section.

In general, the main drawbacks to overcome in the development of more efficient adsorbers are the intrinsic low heat and mass transfer efficiencies showed by these components. This is always true when the vapour pressure inside the chamber is noticeably lower than the atmospheric pressure (e.g. refrigerants like water, ethanol and methanol), while the mass transfer resistance becomes negligible where working fluids at high pressure are employed (e.g. ammonia and HFCs). Since the present book is focused on zeolite-water as a working pair, the state of the art of its adsorber heat exchanger designs will be reviewed.

Basically, the development of thermally efficient adsorbent beds has been carried out at two levels of activities:

- (i) small-scale adsorber concepts, whose thermo-physical parameters as well as dynamic performance are experimentally evaluated to verify the achievable advancement, beyond the state-of-the-art, in heat and mass transfer efficiency.
- (ii) full scale adsorbers, whose performance, in terms of specific power (massive and volumetric) and COP, are experimentally evaluated, in order to identify the most efficient configurations.

In the following, the evolution of adsorber concepts over the years is reported, by analyzing some of the most innovative researches carried out.

The first proposed idea to enhance the poor heat transfer properties of an adsorber was the development of the consolidated adsorbent bed. Early studies proposed the realization of consolidated thick beds with enhanced thermal conductivity. Guillemot et al. [1] realized consolidated cylindrical adsorbents made of compressed zeolite powder (NaX or NaA) and metal foams (copper or nickel). The resulting equivalent thermal conductivity was in the range between 1.7 (Ni foam) and 8.3 W m⁻¹ K⁻¹ (Cu Foam), which is clearly superior to that of a granular adsorbent bed. However, with this arrangement the mass transfer becomes the limiting factor, due to the high thickness and the low gas permeability of the bed (see Table 2.1). In order to reduce the mass transfer resistance, Lang et al. [2] prepared a consolidated adsorbent consisting of zeolite powder integrated into an aluminium honeycomb-like

structure, adding pore forming materials such as melanine or tartaric acid. Indeed, the organic components were completely removed during the drying process of the zeolite increasing the macro-pore fraction of the material. The same concept of using pore-forming additives to improve mass transfer was adopted by Gordeeva et al. in [3], that realized consolidated layers consisting of hydrophobic zeolite CBV901 as methanol adsorbent, aluminium hydroxide as binder and ammonium bicarbonate as pore-forming additive.

Generally, the concept of forming a consolidated layer of adsorbent was potentially interesting, but the following issues were found to negatively affect the adsorption heat pump performance:

- (i) high amount of binder/additive in the adsorbent formulation, affecting the overall adsorption capacity
- (ii) too high density of the adsorbent layer due to the compression process, affecting the mass transfer efficiency
- (iii) too thick adsorbent layers (typically 2–10 mm) affecting the vapour diffusion through the layer
- (iv) shaping of the adsorbent restricted to planar or cylindrical configuration, which limited the practical utilization in real heat exchangers

Table 2.1 summarizes some of the main activities carried out in the field of consolidated bed developments.

The loose grains adsorbent bed represents the opposite concept of the consolidated one. In this case, grains or pellets are embedded inside a heat exchanger without any kind of additional binder. Such a configuration allows to reach optimal mass transfer properties, thanks to the high void fraction existing between the grains. Clearly, on the opposite side, the heat transfer results to be strongly limited, due to the point contacts between heat exchanger and grains as well as to the thermal insulating properties of the adsorbent material itself. Activities devoted to the development of this adsorber concept have been mainly oriented towards the optimization of the adsorbent grains' integration within the heat exchanger by the identification of optimal grain sizes as well as the employment of highly efficient heat exchangers. Figure 2.1 reports some concepts of loose grains adsorbers.

Aristov et al. [12] have performed a deep analysis on the heat and mass transfer phenomena affecting the performance of loose grains adsorbers. They analysed the influence of heat transfer surface to adsorbent mass ratio, as well as the grain size, on the dynamic behaviour of adsorber configurations. Starting from the simple flat plate adsorber, they verified that, under certain conditions, the kinetics of isobaric ad-/desorption is invariant with respect to the ratio (S/m) "heat transfer surface"/"adsorbent mass". In particular, they identified two different regimes: lumped regime and grain sensitive regime. The former one is established under certain combinations of grain sizes and S/m ratios. Under these conditions the dynamic performance is affected by the heat transfer efficiency, while the mass transfer effect is negligible. The latter one, on the contrary, is realized for large adsorbent grain size. In these conditions, the kinetic is mainly affected by intra-grain diffusion resistance, while the heat transfer plays a minor role. Similar conclusions were

Table 2.1 Summarizes some of the main activities carried out on in the field of the consolidated bed development

Authors	Adsorbent configuration/ adsorbate	Eq. thermal conductivity, $\text{W m}^{-1} \text{K}^{-1}$	Thickness, mm	Wall heat transfer coeff. $\text{W m}^{-2} \text{K}^{-1}$	Binder content or $m_{\text{ads}}/m_{\text{additive}}$	Gas permeability, m^2
Guilleminot et al. [1]	Consolidated NaA or 13X zeolite powder in metal foam/ water	1.7 (Ni foam) 8.3 (Cu foam)	20	110 (Ni foam) 180 (Cu foam)	35 wt%	10^{-13}
Guilleminot et al. [4]	Consolidated 13X zeolite powder in expanded natural graphite/water	4–17	75	200–3000	30 wt%	10^{-13}
Wang et al. [5]	Consolidated activated carbon in expanded natural graphite/ ammonia	2.5	12	n.a.	$m_{\text{ads}}/m_{\text{GNE}} = 0.5\text{--}2$	10^{-12}
Tamainot- Tello and Crittoph [6]	Consolidated monolithic activated carbons/ammonia	0.34–0.44	10	350–800	0	10^{-14}
Pino et al. [7]	Consolidated 4A zeolite powder with different binders and additives/water	0.12–0.43	30	n.a.	20–40 wt%	n.a.
Restuccia et al. [8]	Consolidated 4A zeolite powder and $\text{Al}(\text{OH}_3)$ on aluminium sheets/water	0.43	2	120	40 wt%	10^{-12}
Lang et al. [2]	Consolidated zeolite powder in aluminium honeycomb matrix/ water	0.4	3	1000	25 wt%	10^{-9}
Gordeeva et al. [3]	Consolidated hydrophobic zeolite powder and $\text{Al}(\text{OH}_3)$ / methanol	0.4	5	55	20–30 wt%	10^{-12}

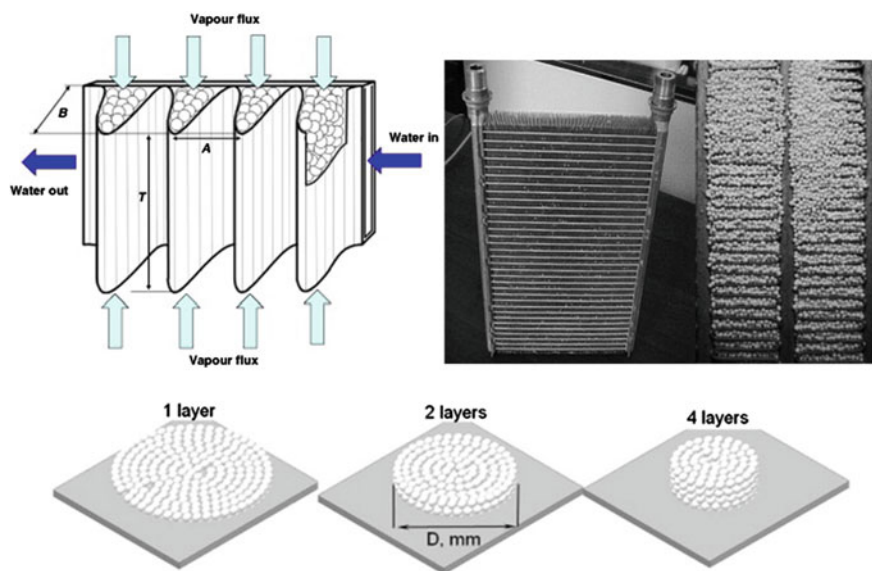


Fig. 2.1 Schematic of the loose grains arrangement within a finned flat-tube heat exchanger, proposed in [9], on the *left hand side*. Example of the integration of loose grains within a finned tube heat exchanger [10], on the *right hand side*. Schematic of flat plate loose grains adsorber concept, with different layers of adsorbent grains [11]

recently drawn for more complex configurations by Santamaria et al. [9] and Gordeeva et al. [13].

In general, the main drawbacks related to the employment of loose grains configurations are the following:

- (i) low efficiency of secondary fins in extended surface heat exchangers, which limit the overall heat transfer coefficient.
- (ii) possible pressure drops along the packed grains, which limits the vapour diffusion and so the kinetic performance
- (iii) need of metallic net to keep the material inside the heat exchanger, which increases the complexity of the realization and can add significant mass transfer resistance.

Table 2.2 summarizes some of the most recent activities on loose grains adsorbers development, with particular attention paid to their kinetic performance.

The direct synthesis of thin zeolite coatings on heat exchanger walls has been proposed as another way to realize efficient adsorbers. Some authors consider this technology as a possible solution to achieve high heat and mass transfer efficiency through the adsorber. Indeed, the heat transfer across the interface strongly increases due to the nearly perfect contact between the heat exchanger surface and the zeolite,

Table 2.2 Relevant activities on the development of loose grains adsorbers

Authors	Adsorber configuration	Working pair	Main evaluated parameters (kW/kg _{ads})
Aristov et al. [12]	Loose adsorbent grains over flat plate HEX	SWS-1 L—water	SCP = 0.3–3.7
Gordeeva and Aristov [14]	Loose adsorbent grains over flat plate HEX	Composite LiCl/SiO ₂ —methanol	SCP = 2.5–7.9
Gordeeva and Aristov [11]	Loose adsorbent grains over flat plate HEX	Activated carbon ACM-35.4—methanol	SCP = 0.21–1.5
Santamaria et al. [9]	Loose adsorbent grains within finned flat-tube HEX	AQSOA FAMZ02—water	SCP = 1.3–2.3
Gordeeva et al. [13]	Loose adsorbent grains within finned flat-tube HEX	Composite LiBr/SiO ₂ —ethanol	SCP = 0.4–0.9

while the mass transfer resistance is substantially reduced due to the very thin zeolite layer. Tatlier and Erdem-Şenatalar [15] and Bonaccorsi and Proverbio [16] have developed methods for direct hydrothermal synthesis of zeolite NaA on stainless steel plates. Bonaccorsi et al. [17] improved the synthesis method to Y and SAPO zeolites over stainless steel and aluminum plates. Generally, homogeneous zeolite coating layers in the range of 20–150 µm in thickness firmly bonded over the metal substrate were obtained. More recently, this technique has been applied to directly crystallize the zeolite over metal or graphite foams and metal fibers, giving a relevant increase of surface area and more convenient zeolite-to-metal-mass ratio. Bonaccorsi et al. [18] obtained growth of zeolite NaA layers on open-cell copper foam by in situ hydrothermal synthesis processes. The copper foam surface was totally coated with a compact layer of zeolite NaA crystals firmly bonded to the substrate. The quantity of zeolite coating deposited was valued to be 17 % in (dry) weight. Fuldner et al. [19], proposed and numerically studied adsorbent layers (2–4 mm thick) consisting of SAPO34 directly synthesized on sintered aluminium fibers by a partial support transformation method developed in [20]. This structure presented high porosity (approx. 70 %) and enhanced equivalent adsorbent thermal conductivity (8 W m⁻¹ K⁻¹).

In general, even though zeolite direct crystallization offers the clear advantage of a high coating stability and a perfect thermal contact between zeolitic crystals and metal surface, it is characterized by some drawbacks:

- (i) production process complex and expensive, with synthesis conditions that can be rather drastic (e.g. 20 bar and 200 °C in autoclave for SAPOs zeolite)
- (ii) necessity to increase the heat exchanger surface in order to reach the needed adsorbent mass, leading to the decrease of the zeolite/metal mass ratio and a consequent reduction of the adsorption machine efficiency, COP

Table 2.3 summarizes some of the main features of the developed directly synthesized adsorber concepts.

Table 2.3 Relevant activities on the development of directly synthesized adsorbers

Authors	Adsorbent configuration/ adsorbate	Eq. thermal conductivity, $\text{W m}^{-1} \text{K}^{-1}$	Thickness, mm	Wall heat transfer coeff. $\text{W m}^{-2} \text{K}^{-1}$	Binder content or $m_{\text{ads}}/m_{\text{additive}}$	Gas permeability, m^2
Tatlier and Erdem- Şenatalar [15]	Synthesized NaA on stainless steel plates/ water	0.2	0.07–0.15	>1000	0	10^{-8}
Bonaccorsi and Proverbio [16], Bonaccorsi et al. [17]	Synthesized NaA, Y, SAPO34 on SS and Aluminum plates/water	0.15	0.02–0.08	>1000	0	10^{-8}
Bonaccorsi et al. [18]	Synthesized NaA on copper foam/water	27	5	>1000	$m_{\text{ads}}/m_{\text{metal}} = \text{n.a.}$	10^{-8}
Fuldner et al. [19]	Synthesized SAPO34 on aluminum fibers/water	8	2–4	>1000	$m_{\text{ads}}/m_{\text{metal}} = 1.3\text{--}1.5$	n.a.
Bonaccorsi et al. [21]	Synthesized SAPO on aluminum foam/water	14	2–5	>1000	$m_{\text{ads}}/m_{\text{metal}} = \text{n.a.}$	10^{-8}

2.3 Introduction to the Concept of Coated Adsorbers

The idea of developing binder-based coated adsorbers originated by the need to overcome the drawbacks showed by the techniques reported in the previous paragraph:

- high heat and mass transfer resistance, respectively for loose grains and consolidated configurations,
- complex and expensive preparation procedure in the case of directly synthesized adsorbers.

Generally, coating methods (e.g. dip coating, spray coating) offer the potential benefit of mild reaction conditions, easily variable coating thickness (up to 0.5 mm) and, in principle, easier implementation in serial production lines. Adsorbent coatings can be realized by gluing the adsorbent grains on the metal surface or by dip coating technique where the metal substrate is immersed into a liquid solution made of active powder and an organic (e.g. resins) or inorganic binder (e.g. clays, etc.). Usually, a proper thermal treatment is carried out to remove the excess solvent, so obtaining a compact adsorbent layer.

According to the former approach, Jaeschke and Wolf from Sortech AG, patented a method for realizing a silica gel coating on the heat exchanger surface using a resin as gluing agent [22], as showed in Fig. 2.2.

Dawoud et al. [23] realized and numerically studied an adsorbent coating based on the special Y-type zeolite DDZ70, attached on the metal substrate by a proper adhesive. A wall heat transfer coefficient of $230 \text{ W m}^{-2} \text{ K}^{-1}$ has been estimated.

Following the dip-coating approach, Restuccia et al. [24], developed and numerically studied a NaA zeolite coating (4 mm thick) on a stainless steel tube. Alumina gel precipitated in situ was used as binder. This configuration of the adsorbent bed allowed to obtain a slight increase of the thermal conductivity of the adsorbent and a strong rise of the metal/adsorbent wall heat transfer coefficient.

Van Hayden et al. [25] developed ALPO18-coated aluminum plates using Polyvinyl alcohol as binder. An optimal layer thickness of 0.2 mm was found.

Waszkiewicz et al. [26] developed a heat exchanger with coated annular fins of CBV901 hydrophobic zeolite for methanol adsorption. Cellulose methyl ether was



Fig. 2.2 Three examples of dip coated adsorbers, employing a binder: silica gel coating, by Sortech [22], on the *left hand side*, AQSOA Z01 coating, by Mitsubishi [27], *central*, SAPO 34 coating, by CNR ITAE and University of Messina [28], on the *right hand side*

used as binder and a noticeable increase in thermal conductivity and wall heat transfer coefficient was found.

Recently, Okamoto et al. [27] presented a coating technique based on an organic binder for the AQSOA materials (Z01, Z02, Z05), focusing mainly on the performance achievable by the AQSOA Z01. Figure 2.2 reports a picture of the coating realized. The procedure allowed to coat lamellas of a heat exchanger with an average coating thickness of 0.3 mm. Interestingly, they found a clear increasing in thermal conductivity passing from powders (0.113 W/m K) to coating (0.36 W/m K). Moreover they proved the physical durability of the coating itself by performing up to 200,000 ad/desorption cycles.

In [28] Freni et al. introduced a new coating composition, employing SAPO 34 powder as adsorbent and silane as binder, see Fig. 2.2. The complete thermo-physical characterization was presented, confirming the goodness of the developed technique. Moreover, kinetic characterization of small scale coated samples with a thickness of 0.3 mm, by means of the Isothermal Differential Steps Method, was performed. The results showed only slight lowering in kinetic performance, if compared to pure adsorbent material, which confirmed that the presence of the binder does not heavily affect the water vapour transport through the layer.

Another coating methodology proposed by Freni et al. [29] consists in the employment of an inorganic clay as binder for AQSOA Z02 adsorbent material. Also in this case, the coated samples were prepared by dip coating technique, reaching thicknesses variable between 0.2 and 0.8 mm. Their hydrothermal as well as mechanical stability were tested, proving sufficient performance, even if the layer resulted to be not strong enough.

A patent by Sauer et al. [30], defined a procedure for realization of coated adsorbents. In this case, they proposed to employ inorganic binders, in order to reduce the thermal degradation of the layer during operation as well as to avoid releasing of non-condensable gases. Moreover, they described the beneficial effects related to the employment of fibres (carbon, carbon nanotubes), which allows to increase the elasticity and strength of the layer, thus avoiding shrinkage cracks and increasing the overall thermal conductivity of the coating itself.

In general, the advantages related to the employment of dip coating methods are:

- (i) possibility of easily coat complex heat exchanger geometries with an adsorbent layer, maintaining a uniform thickness
- (ii) large coating thicknesses, up to 0.5 mm, obtainable by properly changing the preparative parameters (e.g. slurry viscosity, temperature)
- (iii) reduced heat and mass transfer resistances, thanks to the good contact between adsorbent layer and heat exchanger surface and to the controlled thickness

Nevertheless, still some issues have to be systematically analyzed and solved in order to obtain reliable and marketable products, like:

- (i) the poor mechanical strength of the coating layer,
- (ii) possible adsorbent pores occlusion by the employed binder,
- (iii) possible production of volatile compounds from organic binders.

2.4 Methodologies for the Experimental Characterization of Zeolites

Structural and chemio–physical properties of zeolites are commonly investigated by a variety of characterization techniques normally adopted for porous solids. A general description of most common characterization technique is reported elsewhere [31]. Many of such techniques can be also applied for chemio–physical characterization of adsorbent coatings based on zeolite as active material, however taking into account that organic compounds are often employed as binding agent. Herein below, a short overview of the most common techniques specifically applied for zeolite characterization is reported.

Infrared and Raman molecular spectroscopy are major tools for obtaining information regarding the zeolite structure. Indeed, each chemical structure has specific frequencies associated with internal vibrations of group of atoms, which yield unique IR spectra, i.e. “fingerprints” for each zeolite.

Magnetic resonance (NMR) spectroscopy is a useful technique to provide information on the state of the water molecules in hydrated zeolites and can be applied to measure diffusion mechanisms in the porous media, as widely discussed in [32].

X-Ray Analysis (XRD) has been widely used to obtain information about the structure, composition and phase purity of crystalline zeolites. Each zeolite exhibits a typical XRD pattern, so that several zeolites that belong to various structural groups have been precisely identify and classified. The International Zeolite Association (IZA) published online a wide database, which provides structural information on all of the Zeolite Framework Types [33].

X-Ray Fluorescence (XRF) is another useful and non-destructive spectroscopic technique for quantitative analysis of elemental composition of zeolites.

Atomic Absorption (AA) and *Inductively Coupled Plasma (ICP)* spectroscopy are other powerful tools for elemental analysis in zeolites.

Scanning Electron Microscopy (SEM) is the preferred microscopy method to study the habit, crystal growth and surface topography of zeolitic crystals. SEM are usually equipped with electron probe microanalysis for X-ray spectroscopy.

Differential Thermal Analysis (DTA) coupled with *Thermogravimetric Analysis (TGA)* are useful methods for thermal characterization of zeolites and are usually used to study the dehydration behaviour of the zeolite which may involve major structural changes, as reported in [34].

X-Ray Photoelectron Spectroscopy (XPS) is a surface-sensitive spectroscopic tool that can be used to collect information about the chemical state and the concentration of elements comprising the surface layers of the zeolite.

Physical gas adsorption techniques (Langmuir, BET methods) are used to determine the pore volume, pore size distribution and surface area of solids by physical gas (e.g. nitrogen, helium, argon) adsorption at low temperature. No universal adsorption equations exists for zeolites. Since many zeolites exhibit the

classical type I isotherm according to the IUPAC classification, the monolayer adsorption Langmuir model has been successfully applied. The classical BET theory, which was developed for multilayer adsorption, can hardly be applied on zeolites, as reported in [35].

Equilibrium adsorption curves. This is the most important characterization for the evaluation of the most suitable adsorbent for a practical application. The amount of a given gas or vapour which is adsorbed by a dehydrated crystalline zeolite depends in the equilibrium pressure, on the temperature, the nature of gas or vapour and the nature of pores in the zeolite crystal. Considerable experimental data for adsorption of gases and vapours on several zeolites are widely available. Usually, equilibrium data are presented in tabular form or graphically summarized with isothermal, isobaric or isosteric representation. Adsorption equilibrium curves are generally determined by volumetric or gravimetric method. The volumetric method determines the quantity of gas or vapour present in the system by measuring the pressure, volume and temperature. After exposing the dry adsorbent to a quantity of gas in the closed system, the adsorbed amount is indirectly determined from pressure, temperature and volume when equilibrium is reached. The gravimetric method directly measure the amount of gas or vapour adsorbed by weighing the sample in a closed system on a balance. McBain adsorption balance using a quartz spring type and Cahn balance using a force-to-current converter are the most common types of microbalance adopted. In the gravimetric method, the buoyancy correction must normally be applied, which involves the determination of the volume occupied by sample.

Recently, Henninger et al. proposed in [36] a standardized procedure for determination of the water adsorption equilibrium on adsorption materials to be used in an adsorption heat pump or chiller. The procedure consists of a pre-treatment of the sample under continuous evacuation (vacuum level: $1\text{e-}4$ kPa). The optimal sample pre-treatment temperature should be selected according to the following classification.

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

The sample is heated starting from ambient conditions with a heating rate of 1 K/min followed by an isothermal drying step for another 8 h. 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 motivated with respect to the possible applications. The pressure level of 1.2 kPa corresponds to an evaporation temperature of $10\text{ }^{\circ}\text{C}$, which marks a useful temperature level for cooling applications. The second pressure level of 5.6 kPa corresponds to $35\text{ }^{\circ}\text{C}$, which either marks the temperature where heat can be rejected (cooling application) or can be used for low

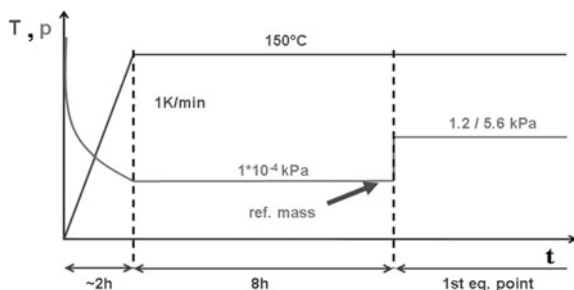


Fig. 2.3 Proposed measurement procedure, including sample pre-treatment and the first isobaric step

temperature heating (heat pumping application). For each pressure level the sample temperature is varied in 5 or 10 K steps between 150 and 40 °C (for 5.6 kPa 9 or 20°C (for 1.2 kPa) respectively. The water uptake is calculated as $w = m(p_{\text{H}_2\text{O}}, T)/m_0$ where m_0 is the dry weight of the sample. In addition at least one adsorption and desorption measurements should be performed in order to detect possible hysteresis effects. Schematic representation of the procedure is reported in Fig. 2.3.

Heat of adsorption. Adsorption process is exothermic, involving heat production. The heat of adsorption is commonly derived from the isosters by the use of the well-known Clausius–Clapeyron equation, as reported in [35].

Adsorption rate. Isothermal Differential Step (IDS) method is considered as the most reliable for the kinetic characterization of the adsorbent material itself. Indeed, such thermogravimetric approach allows the identification of several kinetic parameters like the diffusion constant and the adsorbate diffusivity, as the analytical solution under these testing conditions is well known since long time [37]. An example of application of the IDS method for studying the kinetics of water adsorption on silica Fuji Davison RD under typical adsorption cooling operating conditions is reported in [38].

Hydrothermal stability. Plenty of studies about thermal stability of zeolites for various applications (gas separation, drying, etc.) are available in literature, while only a limited number of studies were dedicated to heat transformation applications. As far as the authors know, first systematic study of hydrothermal stability on 22 commercial zeolites for heat pumping applications was carried out by Rothmeyer [39] in his PhD thesis (1985). Other authors determined the stability of adsorbents for heat storage or dessicant open-cycles systems [40–42].

Mechanical stability. Generally, few information are available concerning the mechanical properties of adsorbents. A hardness of crystals of zeolites of 100–400 HV (Vickers hardness) and a crush strength of 2.5–10 kg for commercial pellets or extrudates are reported in [35].

2.5 Experimental Methodologies to Verify the Performance of Adsorbers

One of the key points in the development of advanced adsorber concepts is related to the experimental methodologies to be employed to verify their performance. In fact, in the past, several studies were oriented towards the adsorbent material characterization and full scale prototype testing, while, only during last years a systematic experimental study of adsorber concepts has been developed. Such an evolution has been guaranteed by the design and realization of proper setups. Usually, they are mainly focused on the analysis of the adsorber dynamic behaviour, thus allowing the evaluation of the achievable specific power. Nevertheless, also test rigs dedicated to the characterization of full-scale adsorbers, both in terms of efficiency (COP) and cooling power, have been developed.

In general, the experimental methodologies for adsorber performance evaluation can be distinguished considering the scale of the tested adsorber: small scale, which allow to test small but representative piece of adsorber concepts, and full scale, where the entire adsorber can be tested under almost-realistic boundary conditions. In the following, the main apparatuses realized for this purpose are described, putting in evidence the working principles and peculiarities of each one.

2.5.1 *Small Scale Large Pressure Jump (LPJ)*

The first version of Large Pressure Jump (LPJ) kinetic characterization of small scale adsorbers was proposed by Dawoud et al. in [43]. The adsorption/desorption process is triggered by a sudden jump/drop in absolute vapour pressure over the adsorber kept at almost constant temperature.

The adsorption kinetics test-rig is depicted in Fig. 2.4. It comprises mainly two compartments. The first compartment is the measuring cell, in which the small scale adsorber is placed. The temperature of the holding surface of the sample is adjusted and controlled using an oil circuit coupled to the circulating thermal bath 2. The second compartment is a constant volume vapor vessel. A water circuit coupled to the circulating thermal bath 1 allows the management of the temperature of this vessel.

The typical test procedure is the following: regeneration of the adsorbent material, heating up to 150 °C the measuring cell under continuous evacuation for 2 h. Subsequently, establishing of the adsorption temperature inside the measuring cell and charging of the water vapour inside the vapour vessel, by means of the steam generator. Once reached the initial conditions, the connection between vapour vessel and measuring chamber is opened and the adsorption phase starts, followed by the pressure decreasing inside the system. The pressure decreasing recorded is then used to determine the amount of vapour adsorbed.

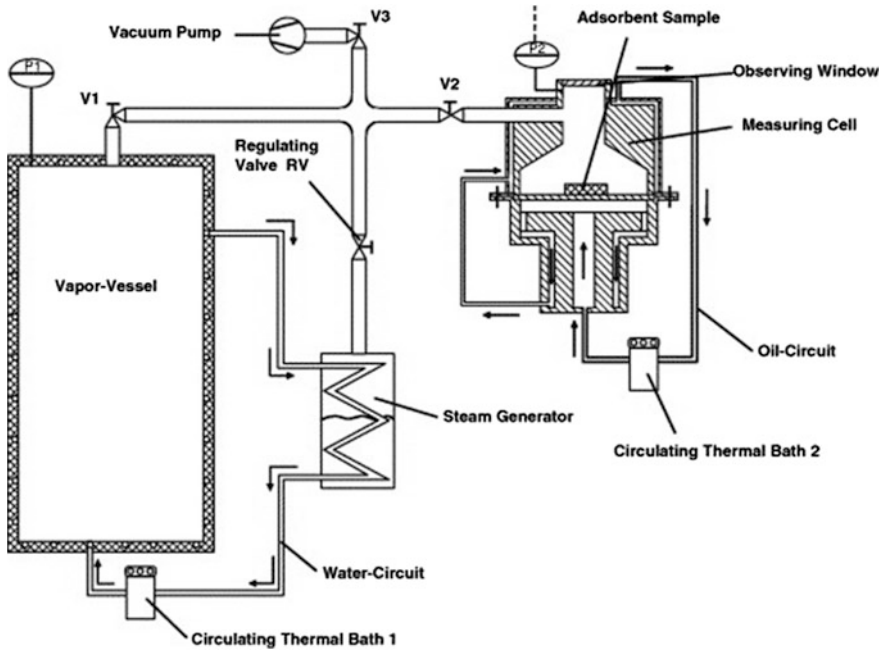


Fig. 2.4 Test-rig for measuring the kinetics of small scale adsorbers, according to the LPJ procedure, as reported in [43]

Such an approach, is useful to give a comparative estimation of the achievable dynamic performance of adsorber configurations, in terms of characteristic times of ad/desorption. Nevertheless, since the working boundary conditions are completely different from the ones typical of adsorption machines (i.e. temperature jump/drop over the adsorber), it doesn't allow to directly evaluate achievable performance, like specific powers.

2.5.2 Small Scale Large Temperature Jump (LTJ)

In order to overcome the main limitation of the LPJ approach, the Large Temperature Jump (LTJ) technique, in its volumetric version, was developed by Aristov et al. [44]. Clearly, in this case the adsorption/desorption stages are promoted by a sudden drop/jump in temperature over the adsorber under almost-isobaric conditions, thus closely replicating the active phases of an adsorption machine.

The kinetic setup, depicted in Fig. 2.5, has a structure similar to the LPJ one. The main difference is related to the introduction of a second heat source in the oil loop connected to the measuring chamber, which allows to fix the final temperature for the adsorption or desorption phases.

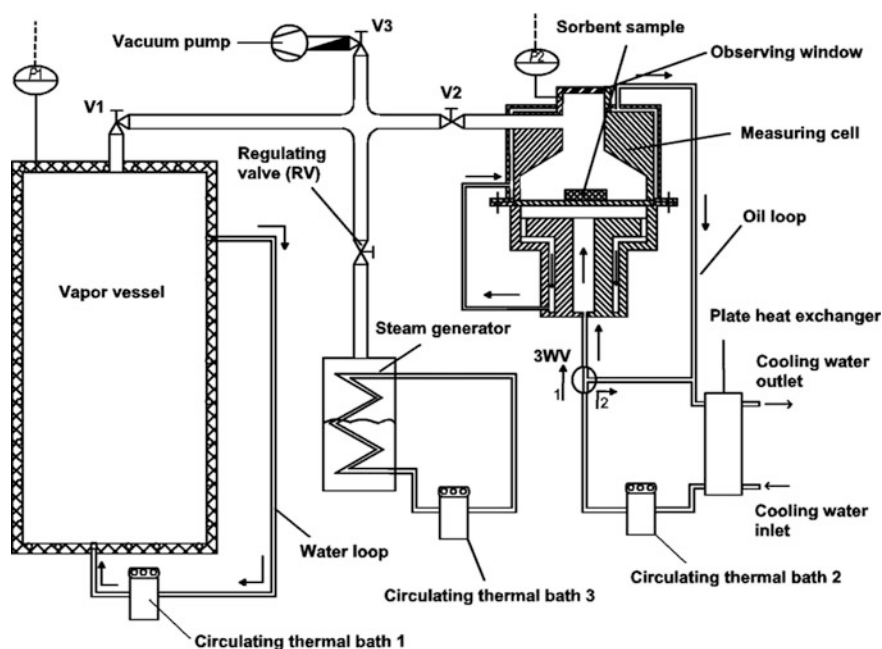


Fig. 2.5 Test-rig for measuring the kinetics of small scale adsorbers, according to the volumetric LTJ procedure, as reported in [44]

In this case, after the regeneration of the adsorber at high temperature and under continuous evacuation, the vapour vessel and measuring cell are charged with water vapour, from the steam generator, up to the required starting pressure for the adsorption process (i.e. evaporator pressure). Once that the system is in thermal equilibrium, a sudden drop in temperature is applied to the adsorber. The adsorption process driven by the sample cooling started, results in reducing the vapour pressure inside the system with time. This decrease did not exceed 2–3 mbar, which is quite typical for adsorption heat pumps, as the evaporator could not be designed to keep the pressure perfectly constant, most specifically, at the beginning of the adsorption process. Accordingly, the adsorption process can be considered as a quasi-isobaric one. The pressure variation, being measured with two pressure transducers P1 and P2 is used to determine the amount of the adsorbed water vapour on the sorbent sample.

This experimental setup allows to evaluate achievable dynamic performance, in terms of specific power, of small scale adsorber configurations. Still, some limitations are present, namely, the possibility of testing only flat plate adsorber configurations and the reduced quantity of adsorbent that can be loaded inside the measuring cell, in order to keep the pressure decreasing within the range of 2–3 mbar, to consider the test almost isobaric.

Accordingly, more recently, a new version of the LTJ approach has been developed by Sapienza et al. [45]. In this case, the evolutions of the adsorption/desorption phases are directly followed by measuring the weight of the adsorber. This is why it is referred as Gravimetric Large Temperature Jump (G-LTJ). It allows to overcome the limits showed by the volumetric LTJ version. Indeed, it can be employed to test more complex small scale adsorber configurations, as reported in [9] and in [13], while, virtually, there is no limitation in adsorbent amount to be tested.

A LTJ-like approach has been developed also by Wittstadt et al. [46] to test full scale adsorbers. Also in this case the adsorption/desorption phases are followed directly weighting the adsorber by means of a proper identified balance. The pressure inside the testing chamber is kept constant by means of an oversized evaporator/condenser.

2.5.3 Full Scale Experimental Setup for Cycling Characterization

A different approach for the characterization of full scale adsorbers have been developed at the CNR ITAE laboratory [10]. It consists in the evaluation of both efficiency (i.e. COP) and specific powers by the energy balance of each component of the test rig: evaporator, condenser and the adsorber itself. In particular, the amount of heating and cooling energy provided or removed from a single component is calculated considering the energy transferred between the external heat transfer fluids and the components during the thermodynamic cycle described.

The experimental test facility as well as the layout of the test rig are represented in Fig. 2.6. The system consists of two separated and interconnected units: an intermittent single bed adsorption chiller able to deliver a maximum cooling power of about 1 kW and a test bench. The lab-scale adsorption chiller consists of the

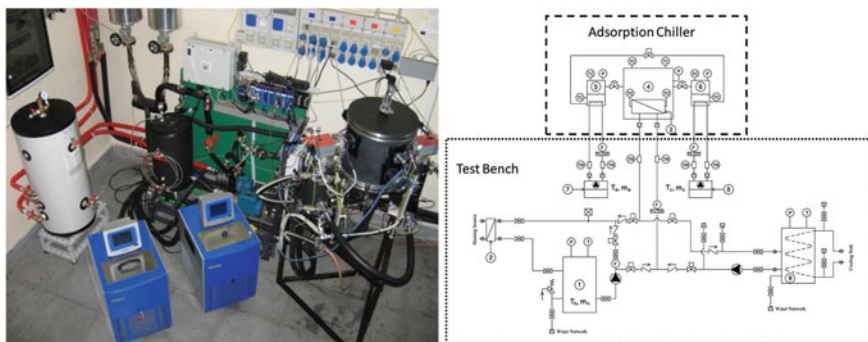


Fig. 2.6 Experimental test-rig for full scale cycling characterization, on the *left-hand side*, and schematic layout, on the *right hand side* [10]

single adsorber connected to a single evaporator and a single condenser operating with an intermittent mode. The vacuum chamber, where the adsorber is placed, was designed to allow the test of different kinds of adsorbers. The evaporator and the condenser consist of two vacuum vessels, in which the thermal energy is supplied/removed by the heat transfer fluid flowing into finned-tubes copper coils. In Fig. 2.6, also the test bench, which supplies the external heating and cooling energy to the adsorption chiller and guarantees the automatic control and management of the system is represented. A similar approach has been employed by Dawoud [47] to test adsorbers for heat pumping applications.

The present technique is of primary interest, as it allows to completely characterize an adsorber, evaluating both efficiency as well as achievable power density. Nevertheless, since it relies on the indirect measure of external heat carrier fluids, a high accuracy in temperatures and flow rates measurements is requested, in order to keep the uncertainty as low as possible.

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