Adsorption Heat Pumps and Chillers – Recent Developments for Materials and Components

Wittstadt, U.[a]; Füldner, G.[b]; Vasta; S.[c], Volmer, R.[b]; Bendix, P.[b]; Schnabel, L.[b]; Mittelbach, W.[a,*]

[a]*SorTech AG, Zscherbener Landstr. 17, 06126 Halle (Saale), Germany*
[b]*Fraunhofer ISE, Heidenhofstr. 2, 79110 Freiburg, Germany*
[c]*CNR-ITAE, Via Salita S. Lucia sopra Contesse n. 5 98126, Messina, Italy*

Abstract

Thermally driven heat pumps and chillers using the principle of adsorption have been developed over the last decades. The recent developments have focused on units (adsorption modules) that comprise efficient materials in contact with adsorption heat exchangers, put together in compact modules with adequate condenser and evaporator concepts.
This contribution provides an overview on some recently presented component and module concepts that allow to build highly efficient and cost effective adsorption heat pumps and chillers.

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"adsorption; heat echanger; SAPO-34; evaporator/condenser; carbon; Al fiber; coating"

1. Introduction

The development of heat pumps and chillers that use adsorption of a refrigerant on an adsorbent material has been found an attractive possibility to use heat available at an upper temperature (HT, e.g. waste heat or solar thermal heat) either to produce cold or to convert heat from a low temperature (LT) heat source to a medium temperature level for heating.

The aspects that have to be taken into account are the following:

- Choosing the working pair (adsorption material and refrigerant) according to their adsorption equilibria considering the requirements of the application (temperature of heat sources/sinks, availability, stability).
- Design of the adsorption heat exchanger by balancing various heat and mass transfer resistances.
- Design of evaporator/condenser together with the module concept.

Criteria for optimization in terms of performance are the power density per volume or mass depending whether space or weight is the limiting factor in the application addressed and the coefficient of performance (COP) which is a measure for the efficiency of the adsorption module. As in the operation of adsorption heat pumps and chillers these two properties behave contradictory, there are many ways to find enhanced solutions.

* Corresponding author:
Phone +49 345 27980911, Fax +49 345 27980998
walter.mittelbach@sortech.de

This paper will give an overview on some recent developments in the field of adsorption modules and their components for adsorption heat pumps and chillers.

2. Materials for Heat Pumps and Chillers

Within the last ten years mainly three classes of adsorbent material have been used for adsorptive heat transformation in close-to-market applications: various silica gels, zeolites/zeotype materials (e.g. SAPO-34) and activated carbons [1], [2]. As working fluids, mainly water, methanol and ammonia [3], [4] have been used. In recent years also metal-organic framework (MOF) materials have been specifically developed for these applications, some of which are now also available on commercial scale. Another material class that received attention are salt hydrates or salt ammoniates and composite materials that incorporate these salts [5]–[7].

Shimooka et al. [8] and Aristov [9] have shown that an S-shaped isotherm is favorable for heat transformation applications. Other main parameters that have to be checked for a material to fit the application are: uptake of working fluid at cycle boundary temperatures, stability, availability, cost, form of connection with heat exchanger (pellet, gluing, coating, direct synthesis).

Special attention has been given to shaping of adsorbents and contacting them with a heat exchanger in order to get an adsorption heat exchanger. Adsorbent granules can be glued to the heat exchanger [10], or the granulation step can be skipped and adsorbent powder can be directly coated to the heat exchanger.

Coating adsorbent on the heat exchanger allows to increase the thermal contact area between adsorbent and heating surface while maintaining good accessibility from the gas phase [11], [12] A key component here is the binder that acts as a glue between adsorbent particles and the metal surface of the heat exchanger. Li compared different binders [13].

Kummer et. al. proposed the use of silicone binders for improved thermal stability [14]. Bendix et. al. compared the different types of silicone binders and investigated the effect of coating thickness on the adsorber performance [15].

Direct crystallization of adsorption material onto heat exchanger surfaces has been shown for different substrates and adsorbents [11], [16]–[18]. With this method, synthesis of adsorbent and coating of the heat exchanger can be done in only one step but changes in material combination are much more difficult to realize. The resulting coatings are limited in thickness (4- 230 µm [19]) but show higher densities than binder based ones. In the following section recent developments of adsorption heat exchangers with both, binder based and direct coating will be presented.

3. Heat exchanger concepts

Adsorption heat pumps and chillers apply heat exchangers for different purposes, evaporation/condensation and adsorption/desorption of the working fluid, respectively. These phase change processes require different characteristics for the heat exchangers. Therefore, an overview on the heat exchanger concepts will be given for evaporator/condenser and sorption heat exchanger separately.

3.1 Adsorption Heat Exchanger

For the development of adsorption heat exchangers (AdHEX) many requirements have to be taken into account to meet the goal of high power density and COP within the cyclic operation between high and medium temperature level. Standard tube-fin heat exchangers are used in commercial products which use a loose bed configuration, have pellets glued onto the fin surface or coated fins in order to combine the adsorption material with the heat exchanger. An overview on different concepts can be found in [20].

The "perfect" heat exchanger used as an adsorber would be one with an infinite surface area for the contact to the adsorbent, no heat transfer resistance within the heat exchanger itself and to the heat transfer fluid combined with zero thermal mass and the mechanical strength to withstand the pressures occurring in the system as well as the temperature changes during cycling. The following sections give examples of recent developments to come closer to this perfect configuration.

3.1.1 Flat tube fin heat exchanger with binder based coating

As explained above, a binder-based coating can significantly enhance the heat transfer while maintaining good accessibility for the water vapor. A major advantage over loose grain configurations is the mechanical stability of the coating, which does not need any surrounding structure to keep the adsorbent in place [21].

Recently, several fluid-to-air heat exchangers (plate-fin heat exchanger, see Figure 1), have been coated with binder-based coatings of different thicknesses and investigated for their dynamic properties.

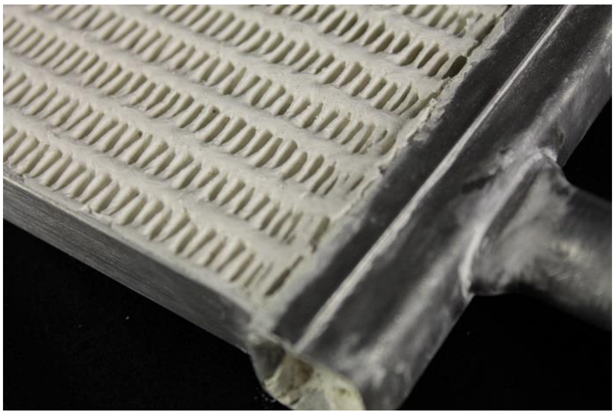

Figure 1: Plate-fin heat exchanger coated with a binder-based coating (Figure taken from [21]).

From the performance measurements, a similar power density has been found as also known from other research both on binder coated adsorption heat exchangers [20], [22] as well as from configurations with small loose grains [9], [23]. The adsorbent coating thickness can be increased up to almost complete filling of the heat exchanger, without significantly reducing the volume-specific power. Only when the accessibility of the coating's surface for the vapor becomes a limiting factor (clogging of vapor distribution paths), the power density starts to drop.

3.1.2 Fiber heat exchanger with direct adsorbent coating

A direct coating method of SAPO-34 on aluminum by a partial support transformation (PST) process 1 leads to very compact layers of adsorbent with a density of 1500 kg/m³ and a layer thicknesses of around 20 – 100 µm [24]. Thus, the main requirement for a heat exchanger with such a coating is a high surface area in order to get a high enough adsorbent mass within the adsorption heat exchanger. Sintered aluminum fiber structures [25] with a surface area of 6,000 – 9,000 m²/m³ have been found a promising substrate for this coating technique. With a porosity of 70 – 80 % and a heat conductivity of 8 – 10 W/mK.

The adsorption behavior of different variants of the fiber structures (porosity and thickness of sintered fiber structure) as well as coating thickness have been investigated before designing an adsorption heat exchanger [26].

A flat-tube heat exchanger geometry is combined with this fiber material to form a compact adsorption heat exchanger. A standard production process (brazing) is successfully used to firmly bond the fiber mats between the flat tubes. Thus, a low heat transfer resistance between the adsorbent and the heat transfer fluid is reached. Vapor channels ensure a sufficient mass transfer during the ad- and desorption process, see Figure 2. The high surface area of the fiber structures a very high adsorbent filling ratio of 333 kg adsorbent per m³ volume of adsorption heat exchanger.

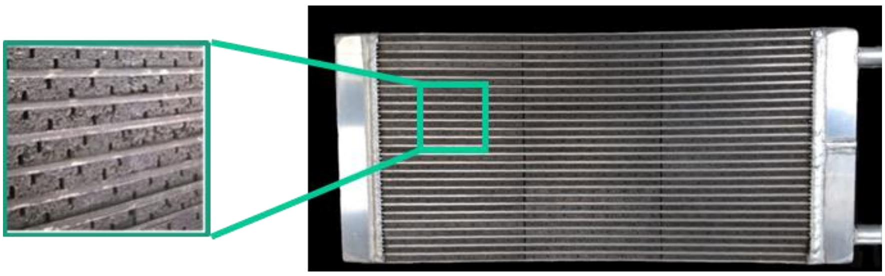

Figure 2: Fiber adsorption heat exchanger

3.1.3 Hybrid Zeolite/Graphite Adsorber

Leading principles in the design of the innovative hybrid zeolite/graphite adsorber have been the possibility to achieve high efficiency and high specific power, allowing at the same time flexibility and easy realization and assembling of the system. To evaluate the viability of the concept, a preliminary investigations have been performed on small samples, as described in [27]. Different geometries of the adsorber were studied, as shown in Figure 3, together with the mechanical and adsorption properties of the hybrid after the realization of the zeolite coating.

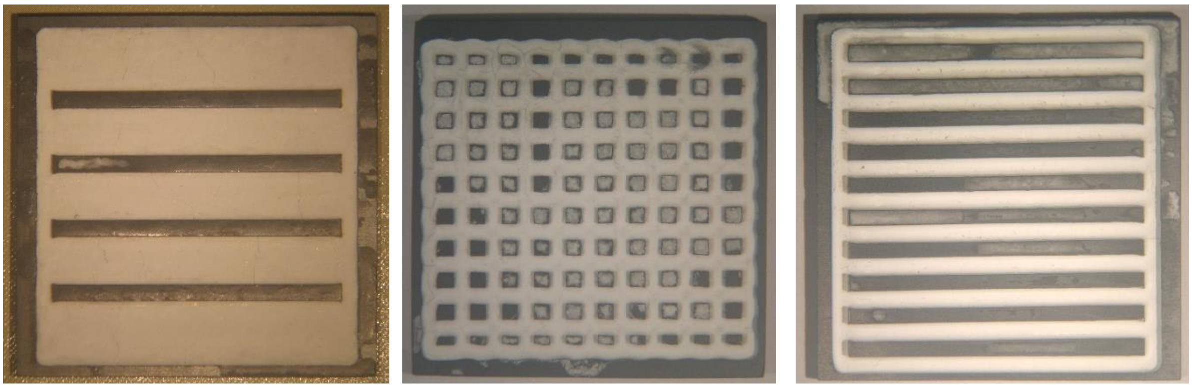

Figure 3: Three small samples of hybrid zeolite/graphite adsorbers: different coating layout

Starting from the outcomes of this analysis, a modular heat exchanger has been designed, shown in Figure 4. It consists of a certain number of assembled double-faced graphite plates, two compact manifolds, gaskets and screw clamps. Each semi-plate is composed of a process side (onto which zeolite is deposited) and a heat transfer fluid (HTF) side where a liquid medium flows to provide the needed thermal energy for desorption or to remove the adsorption heat. Eventually, two single semi-plates are bonded together to make a sealed fluid path, while the compact manifolds allow to distribute the liquid medium to each plate.

One of the key features of the innovative hybrid adsorber is the possibility to study and design a proper HTF path: the high machinability of the graphite allows to realize, in a simple and cheap way, an extremely complex fluid path, with the final aim of assuring a uniform temperature distribution on the surface plate. Indeed, uniform distribution of temperature in the zeolite layer and a reduced temperature difference between coolant inlet and outlet can guarantee optimal conditions for the adsorption/desorption phenomenon.

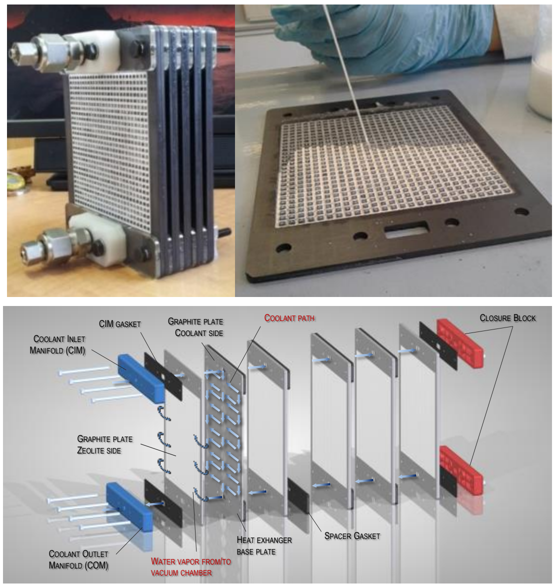

Figure 4:- Concept of the graphite/zeolite adsorber: assembled prototype (upper left); Coating with adsorbent (upper right), exploded view (bottom).

Outcomes of the analysis has been the choice of a double mirrored multiple serpentine flow field as distributor for the heat transfer fluid. The number of parallel serpentines have been designed to reduce the liquid medium´s pressure drop as well. The design has been completed by testing different bonding possibilities and realizing the components for the connection of the plates [28]. The prototype realized is shown in Figure 4, together with the coating process. In a reference test under controlled working conditions (90°C/35°C/15°C) performed at ITAE a power density of 280 – 470 W/kg at cycle times from 200 to 500 s are reported.

3.2 Evaporator /Condenser

The development of more efficient thermally driven adsorption heat pumps or chillers also leads to a need for improved evaporator concepts [29]. Many of the commercially available adsorption systems use water as refrigerant which requires – considering the temperature conditions between 3 and 20 °C – an evaporation pressure between 0.76 and 2.34 kPa. These sub-atmospheric pressure conditions involve different evaporation characteristics compared to common pressure ranges and thus require an appropriate evaporator design.

Existing evaporators in commercially available machines often use pool boiling or falling film concepts (e.g. Vaillant, Viessmann). Pool boiling solutions with for instance a tube coil or tube-fin heat exchanger, partly or completely immersed in a refrigerant pool, often suffer from the fact that the efficient nucleate boiling regime is hard to be reached with the small driving temperature differences that can be supplied. Partially flooded variants are quite sensitive on filling level and only the three phase contact line regions of the heat exchanger significantly contribute to evaporation. Falling film concepts result in highly effective thin film evaporation due to a very small thermal resistance of the refrigerant film, but they need an additional circulation pump. Since an important advantage of adsorption technology is the lack of any moving parts, an additional pump should be avoided.

Several recent research activities in research institutes and industry aim at overcoming the limitations of state-of-the-art evaporators:

In the field of nucleate boiling Giraud, Toublanc et al. [30], [31] investigate bubble formation characteristics for the evaporation of water at sub-atmospheric pressures in order to implement knowledge on basic boiling mechanisms in an advanced evaporator design.

To enhance evaporation heat transfer in partially flooded evaporators both Lanzerath et al. [32] and Schnabel, Witte et al. [29] use finned tubes or tubes with a microstructured / porous surface layer. In that way the capillary effect can be exploited to spread the refrigerant into a thin film which results in a significantly increased heat transfer coefficient.

Another novel approach in evaporator/condenser development for adsorption modules is the periodic use of only one heat exchanger as condenser and evaporator. Refrigerant vapor is condensed on the heat exchanger in the desorption phase and subsequently evaporated in the adsorption phase by the same heat exchanger. Advantage of this approach is the reduction of module volume and complexity since two heat exchangers are replaced by one and internal valves etc. can be avoided. On the other hand this concept involves certain challenges concerning heat exchanger design and refrigerant supply: Since the heat exchanger periodically oscillates between evaporator and condenser temperature level a reduction of the thermal masses (of heat exchanger and refrigerant) to a minimum is essential for retaining a satisfactory module power and efficiency. Furthermore, especially when working with small amounts of refrigerant, it is important to guarantee good contact conditions between refrigerant and evaporator. The accumulation of water without contact to the heat exchanger should be as it would not be available for evaporation anymore.

One way to tackle these challenges is operating the evaporator/condenser in a dynamic thin film evaporation mode and providing a large surface area. During condensation refrigerant is stored directly on the heat exchanger surface by means of surface tension which ensures favorable wetting conditions for the evaporation phase. By employing porous structures the refrigerant storage capacity can be enhanced due to capillary action. The thin refrigerant films represent very small thermal resistances which potentially entails a high heat transfer coefficient and thereby the possibility to design a compact and effective evaporator/condenser. However, the dynamic evaporation characteristics are very sensitive on heat exchanger geometry, material and surface properties and operation conditions, as investigations by Volmer et al. [33] on fin-tube heat exchangers demonstrated. Therefore a sophisticated design of the heat exchanger is crucial. First evaporator/condenser prototypes based on fiber structures (identically constructed as the AdHEX shown in Figure 2) were developed and tested by SorTech AG, Fraunhofer IFAM and Fraunhofer ISE within the project ADOSO, yielding promising results.

3.3 Integration of heat exchangers to a module

The functionality of a heat pump or chiller can only be achieved with the combination of both, the heat exchangers for ad-/ desorption and evaporation/condensation. The combination is then called an “adsorption module”. There are different possibilities for their combination, see Figure 5.

The first possibility is to have different housings for all heat exchangers (ad/desorption, evaporator, condenser), see Figure 5. The connection is done by valves (active or passive) that control the vapor flow during the different phases of the adsorption/desorption cycle. A second option is the integration of both heat exchangers into one housing. In this concept one single heat exchanger serves as evaporator and condenser in the module. This compact construction implies that both the thermal mass of the adsorption and the evaporator/condenser heat exchanger becomes important for the performance of the system, as now the latter has to be cycled between evaporation and condensation temperature as well.

The operation of a machine can be done either with one module operating alternatingly in adsorption and desorption mode or with two modules in parallel. As the operation with a single module provides continuous production of heat but not of cold, this concept is used for heat pumps only. It offers the possibility to use different duration for the adsorption and desorption process which can be beneficial as the speed of desorption usually is faster than the one of adsorption. This operation strategy leads to an increase in power densities [34]. Additionally, heat recovery can be done much easier within a two module concept.

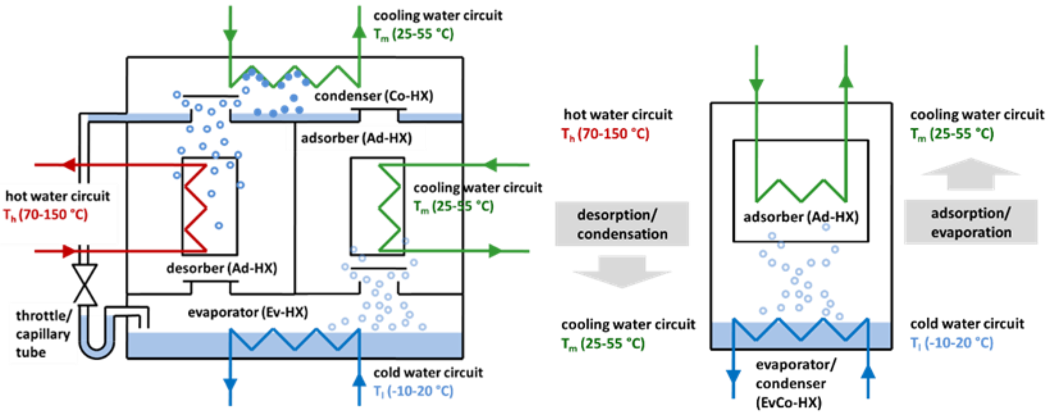

Figure 5: Adsorption module concepts (taken from [21])

From the heat exchanger developments described in Section 3 only the fiber heat exchanger concept combined with the direct coating of SAPO-34 as developed in the project ADOSO has been built up as a complete adsorption module so far. Two identically constructed fiber heat exchangers are set into one housing (as shown in Figure 5, right) using a patented concept of SorTech AG that allows a very thin wall thickness, which results in low costs and thermal mass for the housing. First measurements of a prototype for a single module without heat recovery are presented in [35]. A double module set-up with a standard heat recovery method has shown twice the power density of the product eZea of the SorTech AG without reducing the COP, see Table 1. The two modules (eZea and fiber) are shown in Figure 6.

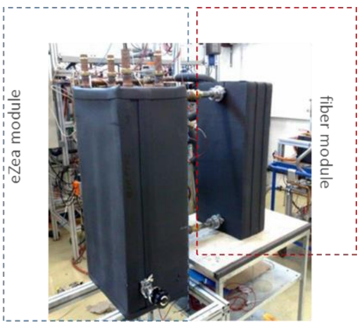

Figure 6: Adsorption modules of product “eZea” and prototype of the fiber module

Table 1: Characteristic and performance figures of a double adsorption module (with standard heat recovery developed for the eZea module, measured at SorTech AG)

	eZea module	Fiber module
Size module /mm	800x417x267	730x320x147
Volume module / m³	0,89	0,34
Dry mass sorbent (SAPO-34) / kg	9	3
Temperature conditions	85 °C / 27 °C / 19 °C	
Nominal cooling power / kW	9.1	6.7
COP (at nominal conditions) / -	0.48	0.47
Volume specific cooling power (W/l)	50	100

4. Conclusions

The design of adsorption heat pumps and chillers rely on efficient heat exchanger concepts and adsorption materials that show high refrigerant uptake within the temperature and pressure range of the application. Some recent developments with a focus on heat exchanger concepts show promising results which are now available for further development into an adsorption module.

A comparison of the concepts is given in Table 2. The fiber adsorber can reach the same amount of adsorbent mass per volume as the plate-fin-adsorber with the thickest coating whereas the graphite adsorber concept holds even more adsorbent. The mass ratio between heat exchanger and adsorbent is around the same for the two binder coated concepts, the construction of the fiber adsorber is not yet optimized in terms of metal mass. The firmly bonded thin adsorbent layer on the fibers results in a compact construction with a high volume specific power density. Together with new concepts for evaporator/condenser operated in dynamic thin film evaporation and heat exchangers with high surface areas, compact adsorption modules can be provided for adsorption heat pumps and chillers.

Table 2: Comparison of the presented adsorption heat exchangers

Exchanger Type	**Plate-fin heat exchanger with binder based coating**	**Fiber adsorber with direct coating**	**Hybrid zeolite/graphite adsorber**
Exchanger Mass [kg]	0.465	8.5	0.478
Adsorbent mass, dry (kg)	0.062 – 0.543	3.3	0.5
Exchanger Material	aluminum	aluminum	graphite
Adsorbent material	TiAPSO	SAPO-34	SAPO-34
Overall Volume [dm3]	1.4	9.9	1.2
Total mass per volume (kg/dm³)	0.38 – 0.72	1.19	0.81
Mass ratio (kg_{ad}/kg_{HX})	0.01 – 1.17	0.39	0.96
Adsorbent filling factor (kg_{ad}/m^3)	44 – 388	333	416

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