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# Technologies for Seasonal Solar Energy Storage in Buildings

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## Abstract

Thermochemical heat storage is a very promising technology that enables us to save the excess heat produced during summer time for the needs in the winter, when we have higher heating needs. Thermochemical heat storage bases and an overview of thermochemical materials (TCMs), suitable for the solar energy storage, are given. Choosing a suitable adsorbent and adsorbate is very important. The most important properties of the substance are high energy density for high thermal storage, low charging temperature for low energy consumption, high uptake of sorbate kg(sorbate)/kg(sorbent) and environmental safety and easy to handle-nonpoisonous. The paper also presents the differences between the closed and the open sorption system. The biggest difference between those two systems is the importance of sorbent, which in case of open systems means that sorbent must be environmentally friendly. Also, various closed and open systems are presented.

**Keywords:** thermochemical heat storage, adsorption, solar energy, open and closed systems

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## 1. Introduction

In 2030 Energy Strategy, European Union (EU) set a goal to achieve the following 3 major targets by 2030:

- To reduce at least 30% of greenhouse gas (GHG) emissions, compared to 1990 levels
- 27% increase of the share of renewable energy sources in final energy consumption
- To achieve at least 27% increase of energy efficiency

The key to achieve these goals is improving the building energy performance, because buildings are responsible for 36% of CO<sub>2</sub> emissions and 40% of energy consumption in the EU [1, 2]. Since solar energy has a lot of potential, it would be smart to use more of it. Because of the mismatch between the availability of the source and the energy needs of the building, the use of heat storage technologies is needed to realize its potential.

Heat storage can be achieved by different chemical or physical processes. Depending on how heat is stored, we distinguish two basic methods: sensible and latent physical heat storage. Sensible storage is achieved by the temperature change of the storage material. The amount of energy stored depends on the temperature rise and specific heat of the storage material (stored energy per unit volume or mass). Latent heat storage depends on heat interactions associated with phase change of the material (at constant temperature), usually from liquid to solid, and vice versa. Due to higher thermal energy change during phase change, compared to temperature rise of storage material in sensible heat storage, latent heat storage allows higher heat densities. Nevertheless, in practice, the use of sensible heat storage systems predominates due to better and higher thermal stability and cheaper storage materials, compared to phase change materials (PCMs).

In addition to these two storage methods, we also know thermochemical heat storage systems, which are not yet available on the market. In thermochemical heat storages are involved reversible chemical reactions. During the charging stage, heat is usually from the collector supplied to the storage material, which triggers desorption of the water vapor, which is endothermic reaction. As long as the products of endothermic reaction are separated, the supplied heat can be stored for an arbitrary time (almost) without losses. This and a several times higher stored thermal energy density (Figure 1) make thermochemical materials (TCMs) a promising option for mid- and long-term heat storage.

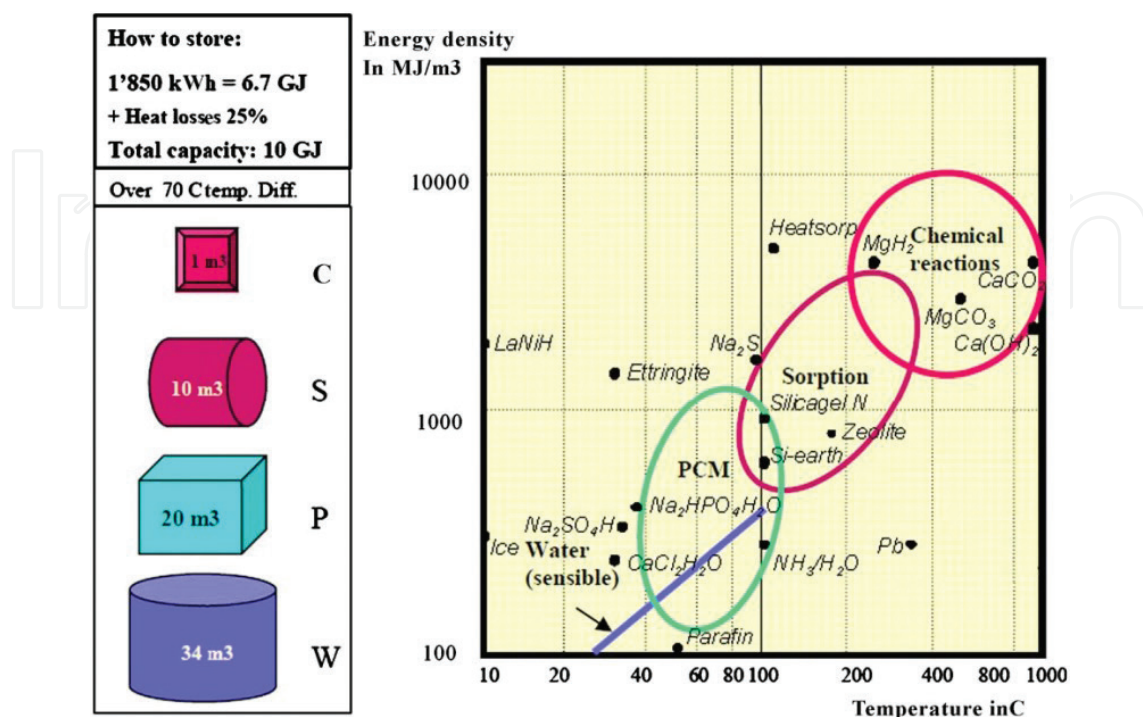


Figure 1. Energy density of thermal storage technologies [4].

In this paper, a review of thermochemical heat storage technologies and systems with solar energy utilization in buildings, regarding TCMs with a charging temperature below 140°C, is presented [3]. The paper is organized as follows: Section 2 sums up the fundamentals of thermochemical heat storage and contains an overview of TCMs suitable for solar energy storage. Section 3 presents possible system configurations for thermochemical heat storage and evaluates applications appropriate for reducing the energy needs of buildings. An overview of models for predicting and optimizing the performance of thermochemical storage systems is included in Section 4. Section 5 concludes the paper.

## 2. Thermochemical heat storage

### 2.1. Basics

Thermochemical heat storage is generally classified under chemical heat storage processes (Figure 2). Under the term thermochemical heat storage, we usually summarize sorption heat storage processes. Some authors (e.g., [4]) also mention thermochemical storage without sorption but with no exact definition of the latter. Sorption can be defined as a phenomenon of fixation of a gas by a substance in solid or liquid phase [5]. We differ between absorption and adsorption. Absorption is used when we have substance in gas phase and substance in liquid (usually) or solid phase. The substance in gas phase enters a liquid or solid and in the process changes the composition of the liquid or solid [6], while adsorption is defined as a gaseous substance that binds to the surface of a solid or porous material [4]. Further, adsorption is divided into chemical adsorption or chemisorption and physical adsorption or physisorption. The attraction between substances is caused by different forces, in physisorption by Van der Waals forces and in case of chemisorption by valence forces, which create stronger bonds. Because of stronger bonds, the chemisorption processes are able to reach higher thermal energy densities than physisorption. Chemisorption processes are also reversible, which makes them suitable for heat storage applications. In the following section, only reversible sorption processes are presented.

Reversible sorption heat storage processes can be written in the following way:

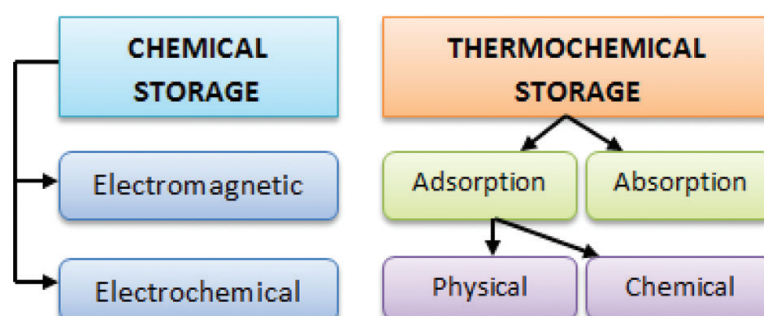
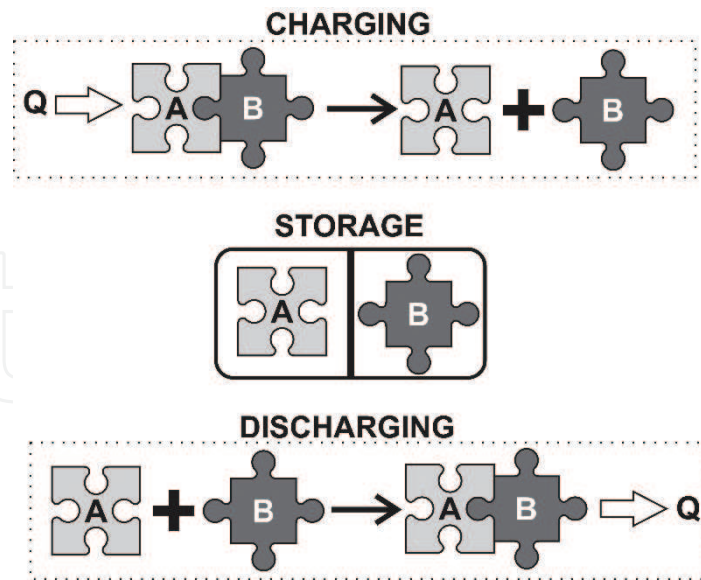


Figure 2. Classification of chemical heat storage.



**Figure 3.** Thermochemical heat storage cycle has three stages: charging stage, storage stage and discharging stage.

where, AB is a compound of components A and B. When AB is split into A and B with energy input (Q)-this is called a “charging stage.” Then, A and B are stored separately (storage state). At a discharge when A and B are in contact, they form AB with energy released (Q)-this is called “discharging state” (**Figure 3**). Storage materials consist of component A also called adsorbent and component B also called adsorbate. In charging stage, adsorbate is desorbed from adsorbent, and then in discharging stage, adsorbate is adsorbed on the surface of adsorbent. For adsorbate in desorbed state, term adsorptive is also used. In heat storage applications, mainly water (vapor) is used as adsorbate because of its availability (i.e., cheap) and nontoxicity.

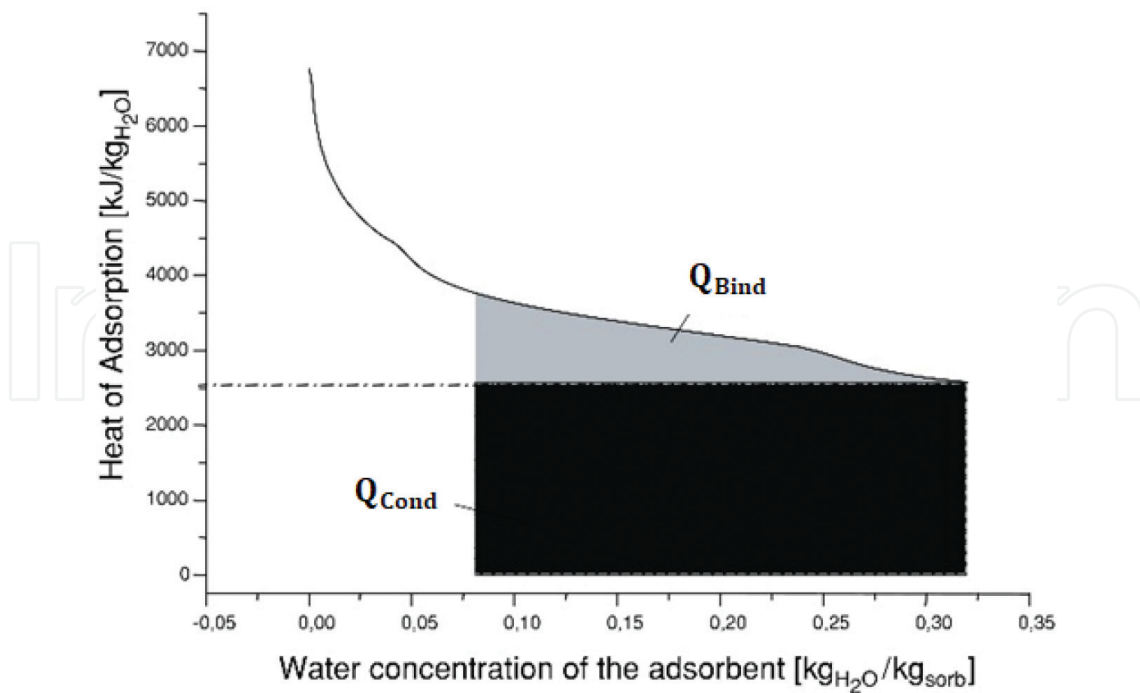
The heat needed for desorption can be divided into three parts [5]:

$$Q = Q_{sens} + Q_{cond} + Q_{bind} \quad (2)$$

here,  $Q_{sens}$  represents the sensible heat needed to heat the absorbent to the temperature needed for desorption.  $Q_{cond}$  is the heat needed to vaporize the adsorbate, while  $Q_{bind}$  is the heat required to overcome the sorption forces. The latter is therefore usually termed as binding heat. As seen from **Figure 4**,  $Q_{bind}$  decreases with the increase of sorbate concentration. This means that more is needed at the beginning of the charging process when the sorbate concentration is low. For heat storage applications, the contribution of  $Q_{bind}$  must be as low as possible compared to  $Q_{cond}$  since it results in lower temperatures required for desorption [7].

## 2.2. Reactants

Knowledge on materials is a prerequisite to design thermal storage systems and their components. Different sorption working pairs or reactants have been studied for thermal energy



**Figure 4.** Break down of the required heat for desorption for zeolite as an example [5].

storage applications. The sorbents with the highest potential in sorption storage systems are crystalline and amorphous materials and their composites with hygroscopic inorganic salt hydrates. But the abovementioned materials do not meet the requirements for large-scale applications yet [3]. Through the literature [4, 7–11], the following requirements for materials have been exposed:

- High energy density for high thermal storage-thermal energy density at the operating temperature (kWh/m<sup>3</sup>, Wh/kg)
- Low charging temperature for low energy consumption
- High uptake of sorbate kg(sorbate)/kg(sorbent)-if water is the sorbate, a high selectivity for water
- Thermal and chemical stability-no deterioration
- High thermal conductivity for high heat transfer
- High heat and mass transfer of the working fluid to the sorbent
- Moderate operating pressure range
- Low regeneration time
- Noncorrosive
- Environmental safety and easy to handle-nonpoisonous
- Low cost-low price per kWh heat stored



The abovementioned material requirements of sorption properties represent the foundation of selecting appropriate TCM for application. But complete evaluation of sorption material properties demands precise measurements of sorption isotherms, isobars and isosteres under a wide range of pressures and temperatures [9]. The energy storage densities and charging/discharging temperatures of some materials suitable for thermochemical heat storage are listed in **Table 1**. The most promising materials have low charging temperatures and high energy storage densities.

Phenomena	Sorbent	Sorbate	Charging temperature (°C)	Discharging temperature (°C)	Energy density (kWh/m <sup>3</sup> )
Adsorption					
	silica gel	H <sub>2</sub> O	88	32	50–125
	zeolite 13X	H <sub>2</sub> O	160–180	20–40	97–160.5
	zeolite 4A	H <sub>2</sub> O	180	65	130–148
	zeolite 5A	H <sub>2</sub> O	80–120	20–30	83
	zeolite MSX	H <sub>2</sub> O	230		154
	APO-n	H <sub>2</sub> O	95–140	40	240
	SAPO-n	H <sub>2</sub> O	95–140	40	—
	MeAPO-n	H <sub>2</sub> O	95–140	40	—
Absorption					
	CaCl <sub>2</sub>	H <sub>2</sub> O	45–138	21	120–381
	LiCl	H <sub>2</sub> O	66–87	30	253–400
	LiCl <sub>2</sub>	H <sub>2</sub> O	46–87	30	253
	LiBr	H <sub>2</sub> O	40–90	30	252–313
	NaOH	H <sub>2</sub> O	50–95	70	154–250
	SrBr <sub>2</sub>	H <sub>2</sub> O	80	—	60–321
Chem. react.					
	BaCl <sub>2</sub>	NH <sub>3</sub>	56–70	40	787
	CaCl <sub>2</sub>	NH <sub>3</sub>	95–99	—	673
	CaSO <sub>4</sub>	H <sub>2</sub> O	—	89	390
	CuSO <sub>4</sub>	H <sub>2</sub> O	92	—	575
	Li <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> O	103	—	255
	MgCl <sub>2</sub>	H <sub>2</sub> O	130–150	30–50	556–695
	MgSO <sub>4</sub>	H <sub>2</sub> O	122–150	120	420–924
	MnCl <sub>2</sub>	NH <sub>3</sub>	152	—	624
	Na <sub>2</sub> S	H <sub>2</sub> O	80–95	80–110	780

**Table 1.** Materials used in thermochemical heat storage studies.

Because of good properties, water is the most used sorbate for seasonal solar energy storage in buildings. Water is environmentally friendly and cheap, which satisfies most conditions. Hence, hydrophilic materials such as silica gels are appropriate for the counterpart reactant or the sorbent. Silica gels have high affinity to water vapor, large water sorption capacity at low humidity, easy regeneration and low cost, but they provide low material energy densities, because of the low hydrophilic characteristic within the working window [10]. Therefore, the application prospect of silica gels in solar energy storage is obscure. Because of the strong interaction between electrostatically charged framework and the water molecules, zeolites are more hydrophilic than silica gels [12]. Because of that, their desorption or charging temperature needs to be higher, which can be altered with dealumination, ion exchange or the variation of the aluminum-silicon ratio [12–14]. Impregnated mesoporous silicates with hygroscopic salts are another option [15–19] to increase performance of the sorption reaction and enhance heat and mass transfer. Nevertheless, these composite materials have some disadvantages such as they suffer from leakage of salt species and are also corrosive due to the contained salts [20].

Some authors [3, 13, 21–23] favor microporous aluminophosphates (APO-n) and their modified analogs (SAPO-n and MeAPO-n) to modified zeolites, because of lower discharging temperatures and higher energy densities. The main focus in research of materials suitable for heat storage applications has been to increase the uptake of sorbate (water) with incorporating silicon or metal cations in aluminophosphates [3, 24, 25]. The performance of the latter substances usually degrades after a few charging/discharging cycles because of framework structure degradation and dislodgement of incorporated cations from the framework [13, 21, 24, 25]. However, the main limitation of aluminophosphates compared to zeolites (and silica gels) is their high synthesis cost [10, 12].

As we can see in **Table 1**, mostly used sorbents in absorption heat storage studies are calcium chloride ( $\text{CaCl}_2$ ), lithium chloride ( $\text{LiCl}$ ), lithium bromide ( $\text{LiBr}$ ) and sodium hydroxide ( $\text{NaOH}$ ) and almost all use water as sorbate. Of the listed substances,  $\text{NaOH}$  is a base while the other compounds are hygroscopic salts and are thus applied in the form of solutions. Advantages of strong bases and acids are higher water uptake and low cost, but they also have disadvantages like corrosiveness, need of higher charging temperature, etc.

In contrast to sorption processes, chemical reactions are characterized by a change in the molecular configuration of the compound involved during the reactions. Based on the material, chemical reactions have great storage potential. But their performance in applications does not perform well, and after several initial cycles, the reaction is very difficult to continue due to swelling, deliquescence and agglomeration. Thus, the performance of material in applications needs further investigation [7]. Furthermore, because chemical reactions induce volume modification of the solid, an obvious hysteresis may exist.

Sorption processes are more suitable for low temperature applications such as seasonal solar energy storage, then chemical reactions, because they require lower activation energy. In the subsequent sections, only heat storage applications utilizing solid-gas adsorption processes are discussed, because liquid-gas absorption systems have limitations with corrosion and crystallization issues.

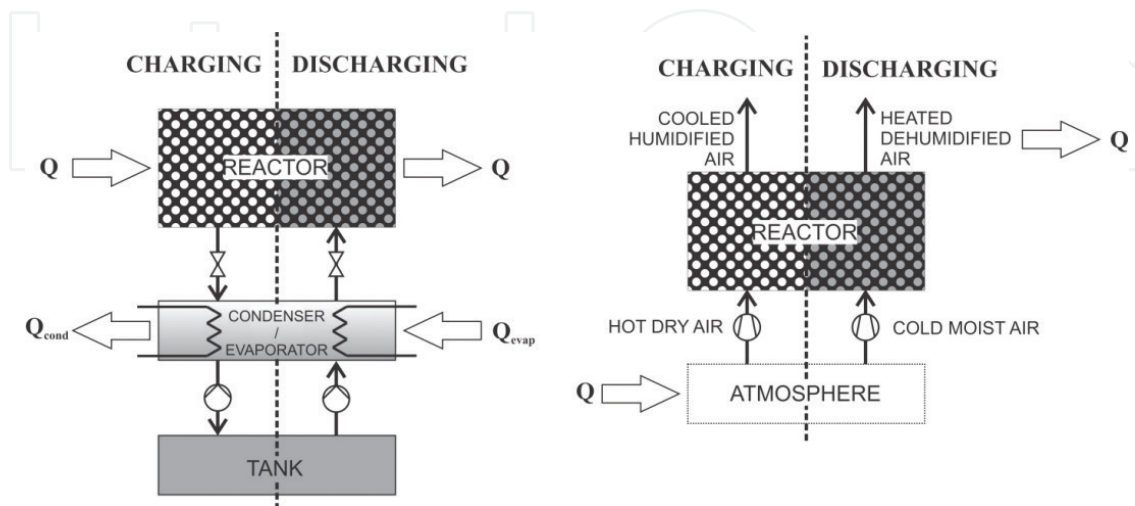


### 3. Sorption storage systems

According to the system design, sorption thermal storage systems can be divided into open and closed systems. The biggest difference between those two systems is the importance of sorbent, which is usually in gaseous phase and interacts with atmospheric environment, so it is not isolated, which means it is important that the sorbate is environmentally friendly. Meanwhile, closed system is isolated and we need storage for the storage material (sorbate). In contrast, the working fluid vapor is released to the environment in open systems, which means that only water (vapor) can be used as the sorbate.

Closed system generally consists of two vessels that are connected (**Figure 5**), namely, a condenser/evaporator where liquid water is collected and a reactor that consists of reactive sorbent. Desorption in the reactor and a phase change in the condenser take place in the charging process. Sorbate exits from the sorbent when heat source with high temperature (e.g., solar energy from solar collector) is supplied to the reactor. Low temperature level in a condenser causes liquefying of vapor where the condensation heat is released into the heat sink. The flow from reactor and the condenser is prevented with the valve after charging process is finished and in such a way the heat is stored. When head demand occurs, the flow from condenser/evaporator to the reactor is established again by opening the valve. The discharging process works in a reverse direction, whereby an additional low-temperature heat source is needed for water evaporation. Closed systems allow adjusting the operating pressure of the working fluid and are able to reach higher output temperatures for heating applications compared to open systems [7, 11]. However, the regeneration of closed systems usually requires a higher temperature level. Therefore, closed systems are appropriate especially for small-scale applications.

In open systems (**Figure 5**), a dry air stream is guided into a reactor filled with sorbent during the charging process. Water adsorbed/absorbed by the sorbent is extracted by the hot air and exits the reactor bed. Hereby, the air is adiabatically cooled. During discharging, cold humid air stream enters into the (desorbed) reactor. Part of the water vapor in the air is attracted



**Figure 5.** Operation principle of sorption storage systems: (left) closed, (right) open [11].

by the sorbent. The air temperature increases, due to the released sorption heat. Weather conditions limit the operation of open systems. For a good discharging rate, the ambient air humidity must be sufficient. Thus, the air must be additionally humidified when the ambient moisture content is insufficient. Compared to closed system, the open system has many advantages, such as the design is simpler, which in the end means cheaper, because they do not require the use of condensers, evaporators and working fluid storage reservoirs. However, the main advantage of using the open system configuration is the better heat and mass transfer conditions, because the heat transfer fluid (air) is in direct contact with the solid reactant, while closed systems require a separate heat transfer loop and hence a heat exchanger in the reactor (heat transferred mainly by conduction). On the other side, open systems may suffer from high energy consumption for overcoming pressure losses through the reactor, which is reflected in higher fan power thereby in higher electrical energy usage.

The main objective of this section is to review the available equipment used for sorption heat storage, especially concerning gas-solid reactors for solar energy utilization.

### 3.1. Closed systems

A closed adsorption system with silica gel-H<sub>2</sub>O as the working pair suitable for the long-term storage of low-temperature heat was developed within the HYDES project [26–28]. The developed storage system consists of multiple storage units combined with solar collectors (**Figure 6**). Each storage unit includes an absorber with an integrated heat exchanger, which is connected through a valve to a combined evaporator/condenser unit. Both the high-temperature heat for desorption and the low-temperature heat for evaporation heat are provided by the solar collectors. To study the performance of the proposed design, a prototype with two sorption storage units with a combined volume of 1.25 m<sup>3</sup> (1.1 m<sup>3</sup> of silica gel) connected to solar collectors with an area of 20.4 m<sup>2</sup> was installed in a low energy house to provide heating and domestic hot water production. Two heat sink options for condensation were provided, namely, a 10 m<sup>3</sup> rainwater reservoir for simultaneous condensation (with desorption) and water from the solar plant loop (as in evaporation) for asynchronous condensation. The experimentally determined storage density of silica gel was around 20% lower from the theoretically expected value (i.e., 123 kWh/m<sup>3</sup> compared to 150 kWh/m<sup>3</sup>).

The follow-up project of HYDES was called MODESTORE [26–29]. Within this project, a second-generation storage module prototype was developed (**Figure 7**). To improve the performance, the reactor and the condenser/evaporator were combined in a single casing, thereby achieving a significantly more compact design. The reactor contains a spiral heat exchanger containing the silica gel, whereby a channel in the center is left free for vapor diffusion. In contrast to the HYDES prototype, where the evaporator was submerged at the bottom of the reservoir for the entire water for adsorption, only a small amount of water was pumped into the evaporator area at the bottom of the storage module, which significantly improved the heat transfer. The volume of laboratory-tested prototype was approximately 350 L, while the reactor contained around 200 kg of silica gel. The experimental performance of the prototype was unsatisfactory, since the energy storage density of silica gel on the prototype scale was below that of water sensible storage (50 kWh/m<sup>3</sup>). The discrepancy between the material and

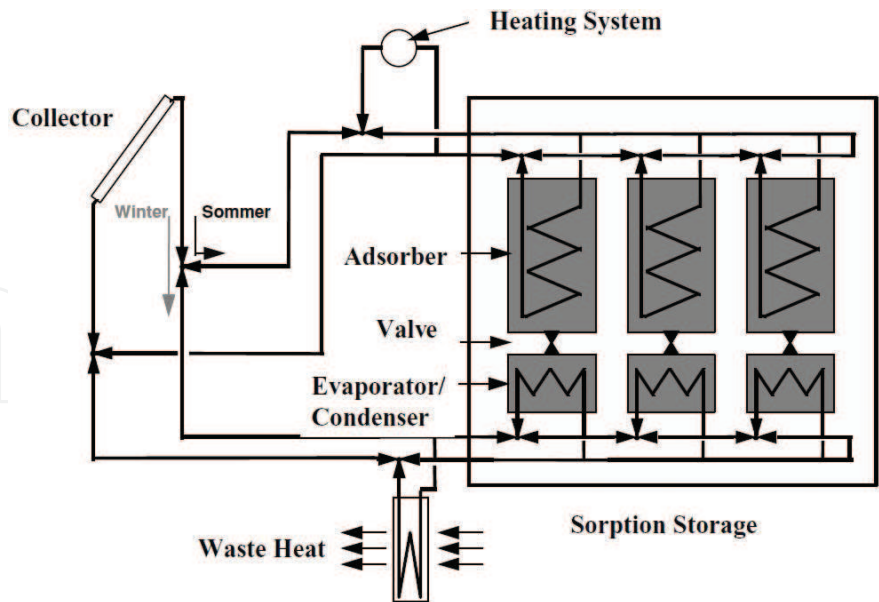


Figure 6. HYDES seasonal storage system concept [27].

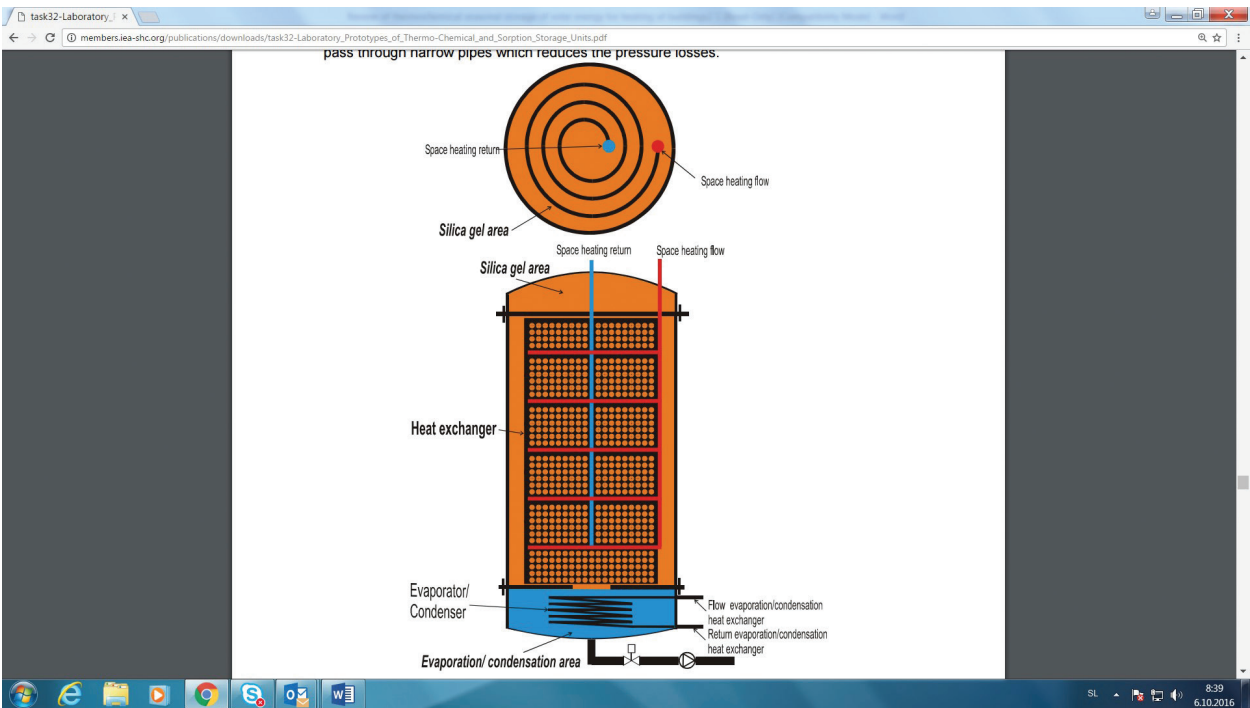
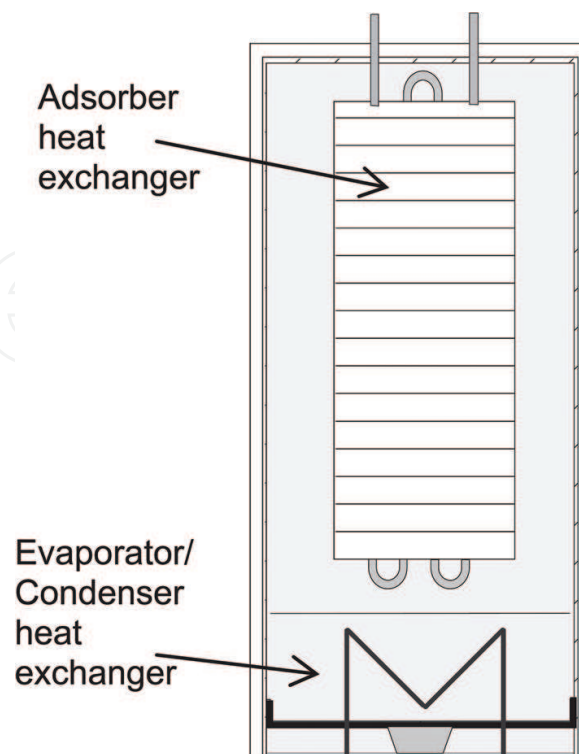


Figure 7. Scheme of the MODESTORE storage module prototype [29].

system scale energy densities was due to the adsorption conditions required to guarantee desorption under the temperature provided by the solar collectors and the heat sinks (i.e., silica gel water content between 3 and 13%). The authors therefore declared the working pair silica gel-H<sub>2</sub>O as unsuitable for solar energy storage systems for building applications. Stritih and Bombać [30] came to the same conclusion with a similarly designed closed storage unit prototype with silica gel-H<sub>2</sub>O working pair, but on a smaller scale (5.7 kg of silica gel).

Schreiber et al. [31] developed a laboratory-scale closed heat storage unit with zeolite 13X and water as the adsorption pair suitable for cogeneration in industrial batch processes (i.e., brewery). The design of the storage unit is similar to that of the MODESTORE prototype, since the absorber and evaporator/condenser unit are integrated into a single container (**Figure 8**) without valves in between. In contrast to the MODESTORE module, a lamellae heat exchanger is used in the reactor bed, while thermal oil was used as the heat transfer fluid to allow temperatures higher than 100°C. For the evaporator/condenser heat exchanger, water was used as the heat transfer fluid. The absorber contained 20 kg of zeolite. In the experiment, the heat supply was provided via an electric heater, while the heat demand was emulated using a water reservoir, which was heated during the discharging process. Measurements were conducted with constant power of the electric heater. The temperature was 120°C during adsorption, while the charging temperature was up to 200°C (i.e., too high for solar energy storage). Three temperature profiles for evaporation/condensation were tested, namely, 60/90°C, 90/60°C and 90/90°C. The results of the study showed a strong dependence between the storage unit performance and the evaporation/condensation temperatures, whereby a low evaporation temperature proved to be crucial.

Lu et al. [32] developed a closed adsorption cold storage system also using zeolite 13X and water as a working pair. The system has been installed in an internal combustion engine locomotive for producing chilled water for air conditioning the driver's cab. In contrast to the previously mentioned closed system with zeolite-H<sub>2</sub>O working pair [31], the evaporator and condenser are separate units, since the evaporator is used to absorb heat from the cabin (**Figure 9**). During charging, the adsorbent bed is heated by the locomotive's internal combustion engine exhaust gasses, while ambient air is used to cool the condenser and the adsorber



**Figure 8.** Scheme of the closed zeolite-H<sub>2</sub>O heat storage unit [31].



during discharging. The prototype system was filled with 140 kg of zeolite grains and 185 kg of water. The system reached an average cooling power of 4.1 kW, while a maximum storage capacity of 5.5 kWh was obtained at an adsorption bed temperature of 125°C. Since the expected maximal storage capacity was 23.3 kWh, the authors concluded that heat and mass transfer of the adsorber need to be improved for better performance.

Lass-Seyoum et al. [33, 34] developed a large-scale adsorption storage system (volume 750 L) with water and an unspecified porous material as the adsorption pair. The storage systems consist of two subsystems connected by a valve, i.e., the storage reactor and the evaporator/condenser unit (**Figure 10**). The reactor contains a copper matrix heat exchanger, which enables to reach a relatively uniform temperature distribution in the reactor (**Figure 10**). Solar thermal heat pipes with a capacity of 4 kW served as the high temperature source. Several dynamic performance tests were carried out. The maximum charging temperature varied between 100 and 120°C, while the maximum discharging temperatures lied in the interval 65–70°C. The daily average heat output ranged between 2.5 and 3 kW. The achieved material energy storage density was 30–40% lower than the values expected from laboratory tests due to the significantly lower charging temperatures (laboratory 220–250°C). For this reason, the authors intend to use a storage material more suitable for the available charging temperature range in the developed storage system.

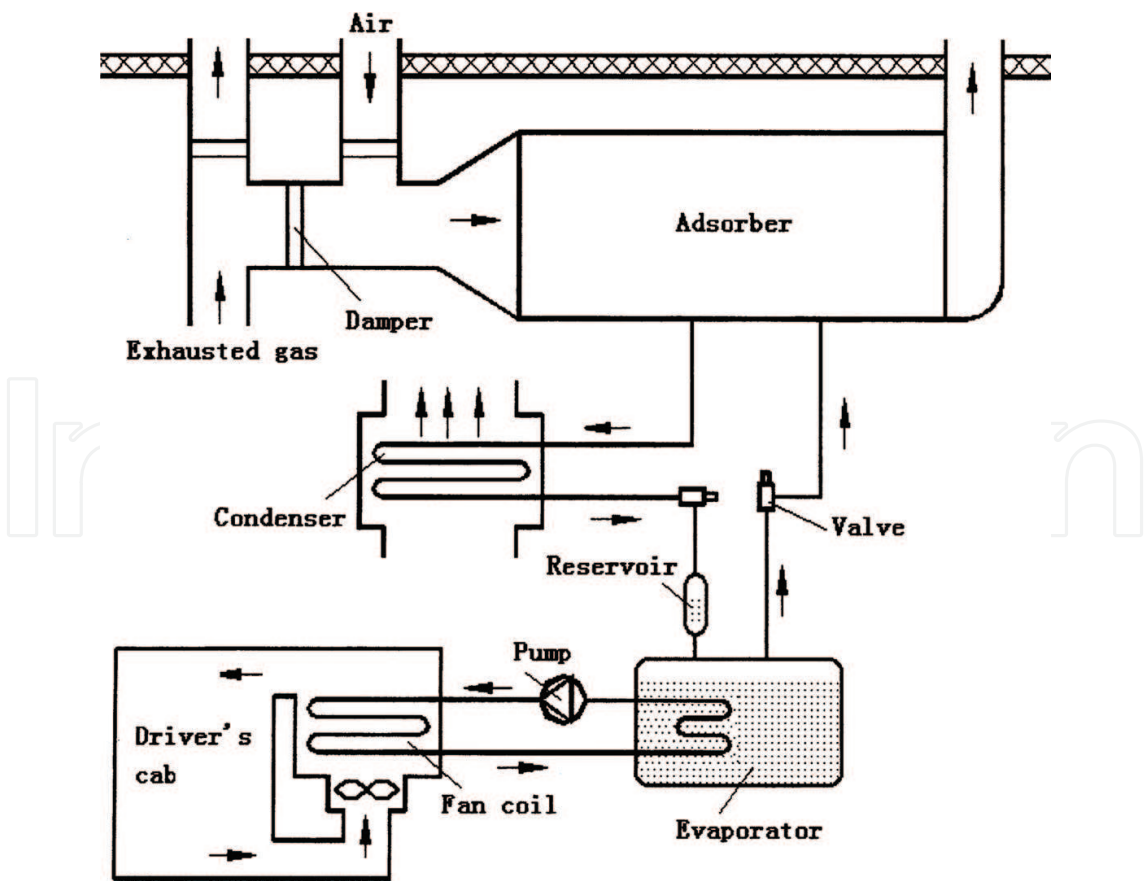
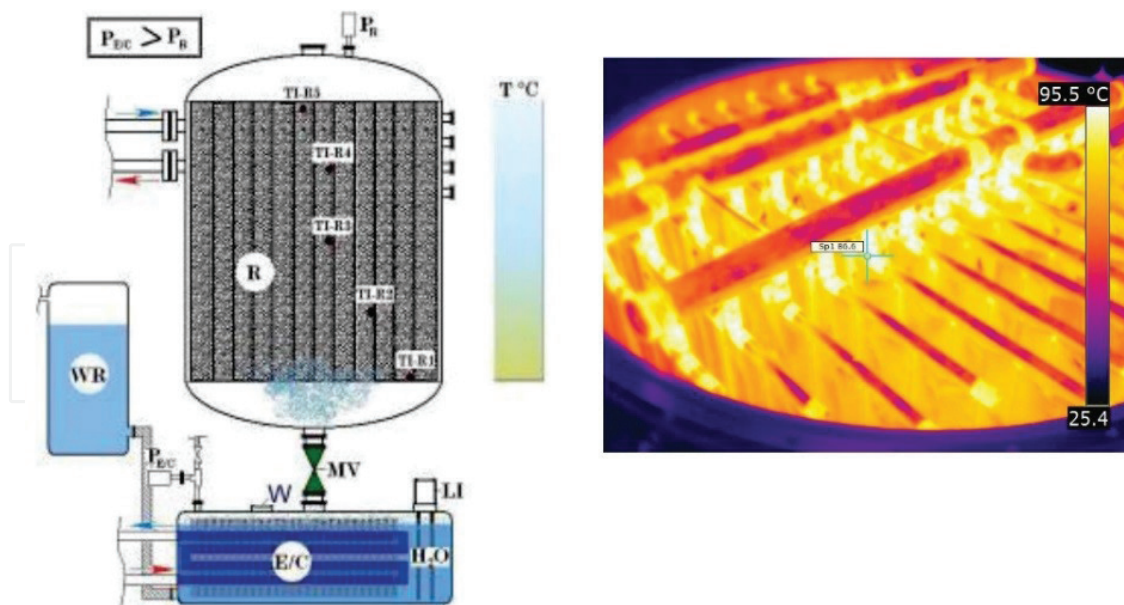


Figure 9. Closed adsorption cold storage system [32].



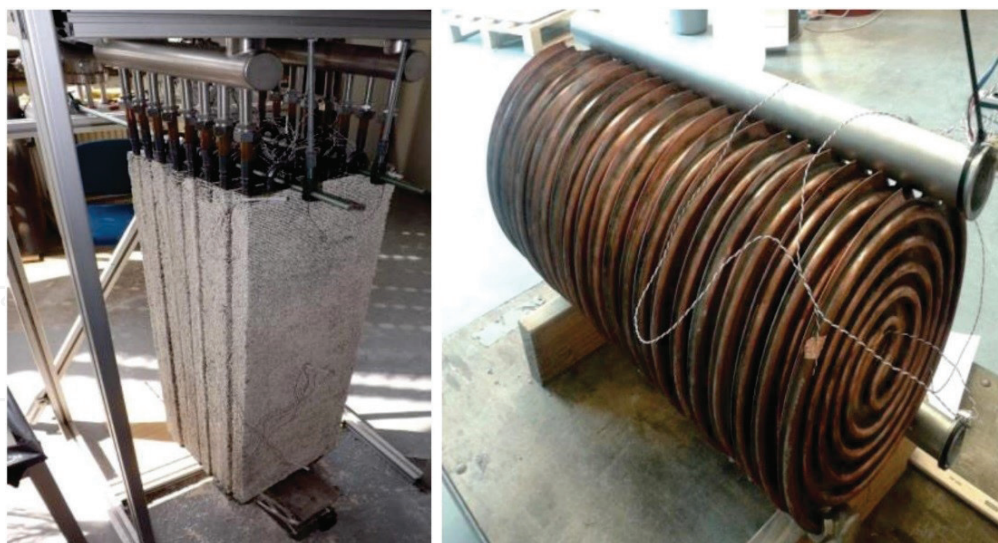
**Figure 10.** 750 L closed adsorption heat storage prototype: (left) scheme [33]; (right) temperature distribution inside the reactor [34].

TNO [35–37] developed and built modular seasonal storage system, whereby zeolite 5A and water were chosen as the reactants. The system basically consists of two separate cylindrical vessels, i.e., heat storage (reactor) and evaporator/condenser (single) unit, connected to a high- and low-temperature heat source. The reactor is built of parallel arranged and finned heat exchangers packed with zeolite (**Figure 11**), placed in a stainless steel vessel. The evaporator/condenser unit consists of a combination of a copper fin connected on one side to a copper spiral and a capillary working material on the other side with a heat exchange area of  $1.4 \text{ m}^2$  (**Figure 11**). A prototype filled with 41 kg of zeolite corresponding to a storage capacity of 3 kWh was constructed, consisting of one reactor and one evaporator/condenser unit. A 12 kW electrical heater served as the high temperature source, while thermostatic water bats were used as a low-temperature heat source (evaporator) and/or heat sink (condensation, discharging). Although the test results were in accordance with expectations, i.e., maximal heat storage 4 kWh and heat output between 0.7 and 1.6 kW, the system energy density was around 73% lower than the material energy density (22 versus  $83 \text{ kWh/m}^3$ ). The authors expect that an approximately 60% performance increase can be achieved by optimizing the system.

### 3.2. Open systems

Within the project MONOSORP [38, 39], an open adsorption heat storage with zeolite 4A and water as adsorption pair was developed. The storage system was designed for the inclusion in a building ventilation system with heat recovery. During discharging, the exhaust air flow is blown through the sorption material, which leads to a rise in temperature and dehumidification. The leaving air stream is then guided into an air to air heat exchanger (**Figure 12**) where it releases heat to the fresh air stream. Because the air that exits the sorption material is not appropriate for direct ventilation of the building, the heat recovery with fresh air through the

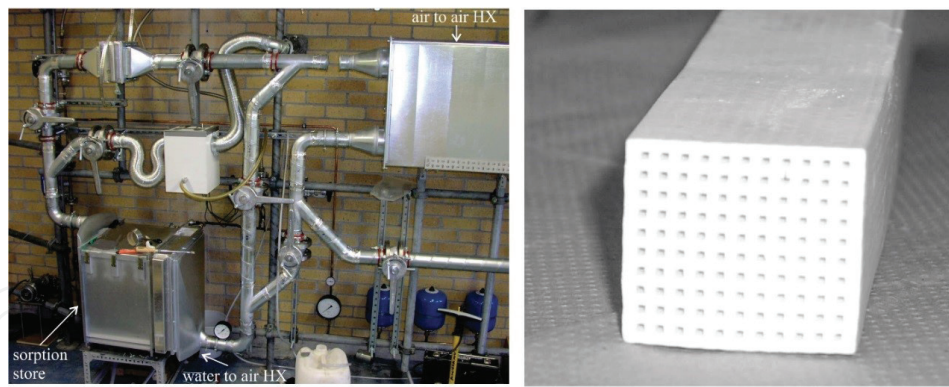




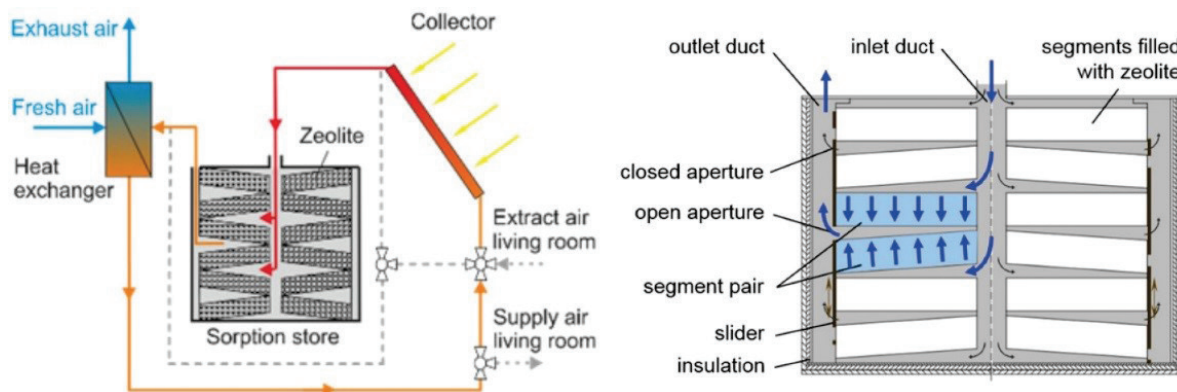
**Figure 11.** TNO adsorption storage module: (left) adsorber/desorber unit; (right) evaporator/condenser unit [37].

heat exchanger is taking place. To achieve a good heat transfer between air flow and sorption material, honeycomb monoliths with a numerous straight, small channels (large contact area) were developed and made by extrusion of zeolite 4A powder (**Figure 12**). Apart from the good heat transfer, the main advantage of these structures is the low pressure loss. The only required component aside from the monolith container is a water to air heat exchanger (**Figure 12**), which is connected to solar collectors (i.e., high-temperature heat source). Since a desorption temperature above  $160^{\circ}\text{C}$  was required, only evacuated tube collectors were suitable. The laboratory prototype (**Figure 12**) with storage volume of 100 L (62 kg of zeolite) was built and connected to  $4.4\text{ m}^2$  of collectors via a finned tube heat exchanger. For air to air heat recovery, a plate heat exchanger was used. Both heat exchangers were commercially available, not specifically designed for adsorption heat storage. The prototype performed satisfactory with an energy density of  $130\text{ kWh/m}^3$  (without sensible heat) and a heat output between 1 and 1.5 kW, whereby a maximal temperature lift of  $22^{\circ}\text{C}$  was achieved. The charging rate on the other side ranged from 2 to 2.5 kW. The discharging rate could be increased with additional humidification of the exhaust air. Apart from this, the major drawbacks of the proposed systems are the high desorption temperature and the high material and production costs.

The follow-up project of MONOSORP is called SolSpaces [40, 41]. Within SolSpaces, a new solar heating system, including adsorption storage for seasonal energy storage with binderless zeolite 13X as adsorbent, has been developed. The system concept is similar to the MONOSORP project with the difference that air solar collectors were used (**Figure 13**), therewith eliminating the need for a water to air heat exchanger. The projects also differ in the reactor design. In contrast to MONOSORP, a packed bed of zeolite spheres is used instead of honeycomb monoliths. The storage has been further subdivided into smaller segments (**Figure 13**) to improve the thermal performance (i.e., reduced heat capacities and heat losses). The developed system has been built up in full scale in a research building with vacuum tube air collectors for testing and demonstration. Although the building has an area of only  $43\text{ m}^2$ , it is comparable to larger buildings, since it has a relatively high specific heat demand due to a large surface-to-volume



**Figure 12.** MONOSORP prototype: (left) laboratory setup; (right) zeolite monolith [39].

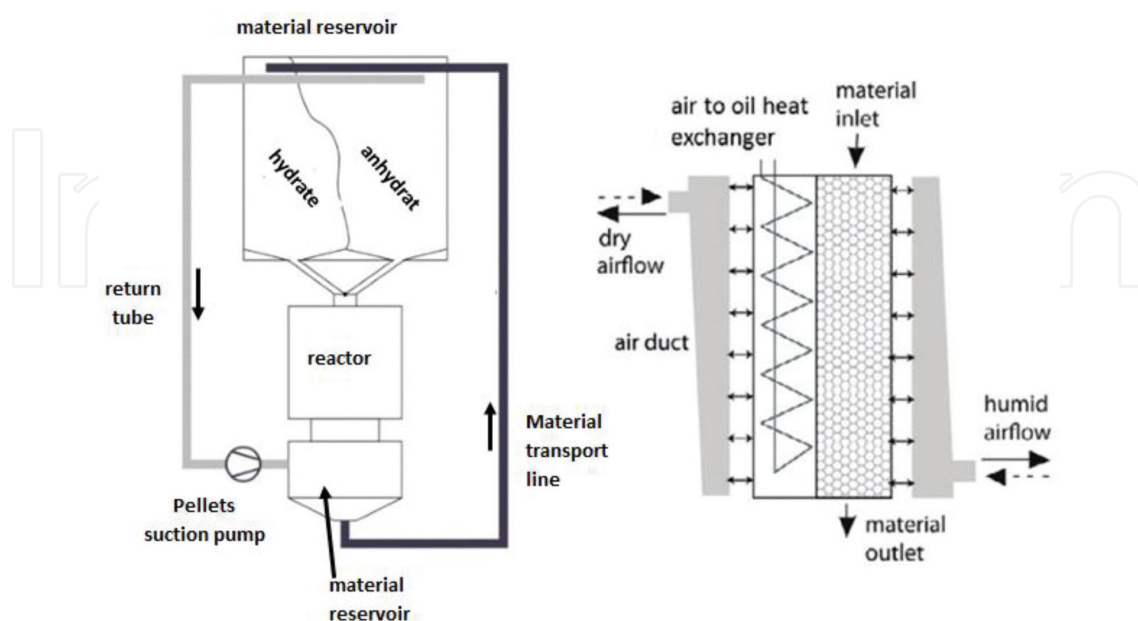


**Figure 13.** SolSpaces project: (left) heating system scheme; (right) vertical cut through the storage systems [40].

ratio. The built storage unit has a total volume of  $8 \text{ m}^3$  and is filled with  $4.3 \text{ m}^3$  of zeolite grains (diameter  $2 \text{ mm}$ ) with a heat storage capacity of around  $700 \text{ kWh}$ . The unit is divided into four quadrants according to the top view and each quadrant itself is subdivided into six segments as is shown in cross-section on right side of **Figure 13**. Each of the two stacked segments form a pair (12 pairs total). The selection of the segment pairs is realized through the opening and closure of apertures in the outlet ducts by a slider mechanism, which is the only moving part within the reactor. Airflow inlet is at the top of the inlet duct, which is placed at the center of the unit. The airflow exits the inlet duct through one of the four ducts on the vertical edges. Airflow can pass through each segment pair individually so the segment pairs can be adsorbed and desorbed separately. On the right side of **Figure 13**, the airflow through the unit is shown for a middle segment pair, which is colored blue. On an exemplary (discharging) operation day, the discharging rate varied between  $565$  and  $790 \text{ W}$ , while a temperature lift between  $22$  and  $28^\circ\text{C}$  was achieved. The experiments also showed that the flow through two segments of a segment pair is quite homogeneous, meaning that the charging and discharging process takes place simultaneously in both segments. The authors plan to further monitor the developed system also during the discharging period. Same as for the MONOSORP prototype, the heat output could be increased with humidifying the exhaust air stream before it enters the storage unit. Dividing the unit into segments gives lower pressure drop of air through the unit, greater heat transfer and no dead volume of sorption material.

Within the CWS [42–46] project, a seasonal solar storage system for a composite material of zeolite and salt was developed. The system was designed for integration in a solar combi-system, i.e., solar collectors alternatively heat the combined storage tank or supply the heat required for desorbing the storage material. The main difference from the previously mentioned projects lies in the design of the sorption storage unit. In contrast to the MONOSORP and SolSpaces units, where sorption reactions occur within the storage vessel, the CWS storage unit consists of an external reactor in which the adsorption/desorption takes place and a separate storage vessel for hydrated and dehydrated storage material as well as a material transport system (**Figure 14**). The reactor consists of two chambers: one chamber to load the material and one chamber to regenerate it. Both chambers are separated by an air to HTF (e.g., water, oil) heat exchanger (**Figure 14**). During the reaction, the material is filled into the reactor from the top and emptied through the outlet at the bottom, driven only by gravity. The air enters the reactor from the side. The laboratory prototype reactor with a storage volume of 20 L was built with the flow cross-section area of  $0.25 \text{ m}^2$  and length of 80 mm. A thermostat connected to an air to oil heat exchanger in the reactor was used alternately as heat source or heat sink. The experiment was carried out with zeolite 13X as the adsorbent. Although the prototype suffered from significant heat losses (37% of released heat) due to the uninsulated reactor, the prototype achieved a satisfactory heat output of 750 W and a  $30^\circ\text{C}$  temperature lift.

ZAE Bayern designed and installed an adsorption storage system with zeolite 13X as adsorbent for providing space heating and cooling to a school and jazz club connected to district heating system [27, 47]. The built storage system contains 7000 kg of zeolite and consists of three cylindrical storage modules connected in series: a humidifier, water reservoir (for humidification) and a control unit (**Figure 15**). The storage units are connected to the district heating system via a heat exchanger on the supply side and a combined air/radiator/floor heating system on the demand side. The storage system is used as a buffer between the district heating system and space heating

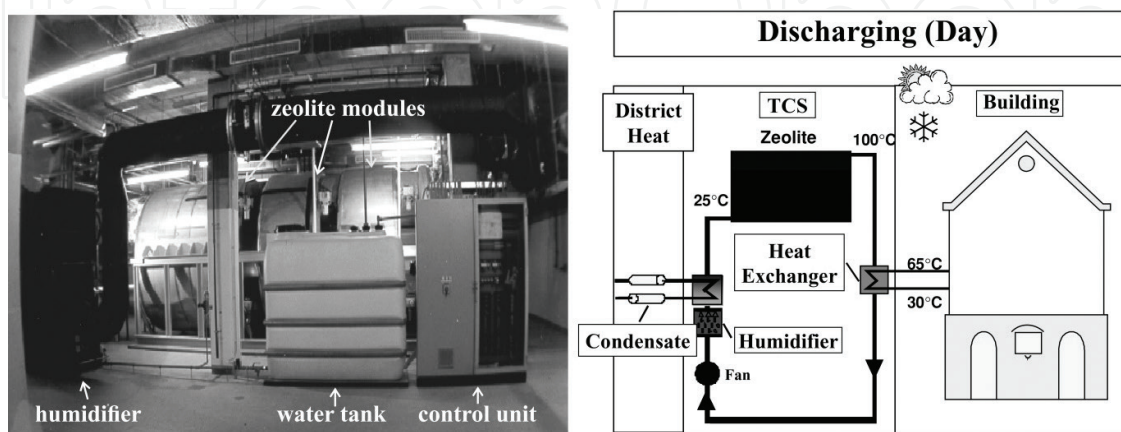


**Figure 14.** Separate adsorption storage: (left) unit concept; (right) reactor design [45].

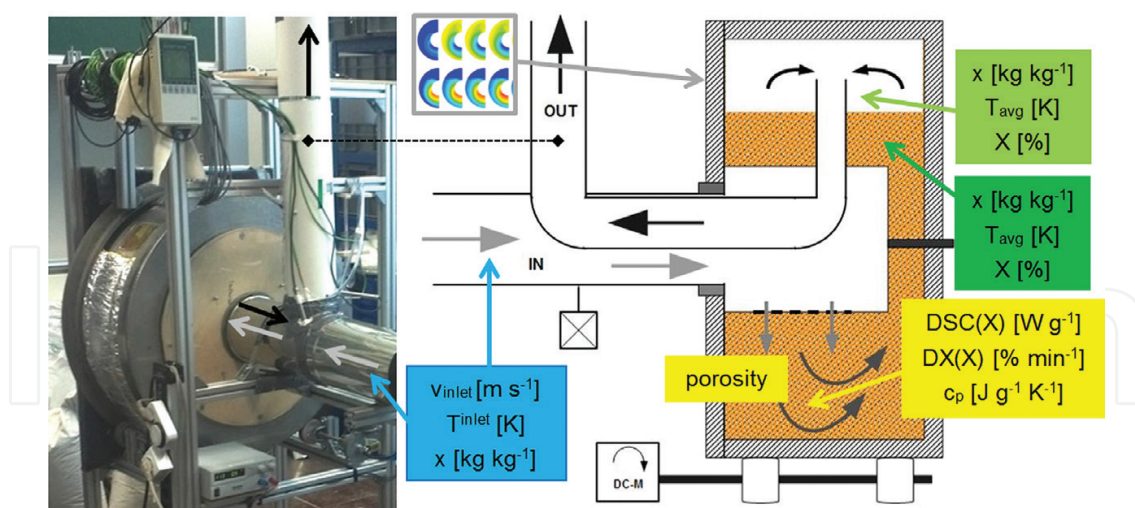


system of the school. The storage is charged by the district heating system during off-peak periods (desorption temperatures between 130 and 180°C), while during peak hours, the building heating system can be powered only by the energy stored in the zeolite, thereby reducing the peak power demand of the district heating system. During monitoring, the system reached a 19% lower energy density than the theoretical maximum value, namely 124 kWh/m<sup>3</sup>. In order to use the storage system as a desiccant cooling device for the mentioned jazz club, the system was additionally upgraded with a heat recovery device (exhaust air) to cool the dried supply air exiting the zeolite modules and a supply air humidifier to adiabatically cool the air afterward. The heat recovery device consisted of an exhaust air humidifier with an integrated heat exchanger and the supply air heat exchanger, which were connected by a fluid circuit. Three desorption temperatures were tested, namely 130, 100 and 80°C. The corresponding achieved energy densities (in the same order) are as follows: 168, 105 and 100 kWh/m<sup>3</sup>. Although higher energy densities were achieved at higher desorption temperatures, the best overall system performance (COP) was achieved at the lowest tested desorption temperature (i.e., 0.87). The rough economic analysis showed that the payback time of the installed adsorption storage system was estimated to be 7–8 years and is dependent on the price reduction for the off-peak thermal energy, the investment costs and the number of storage cycles. The authors concluded that the system performance could further be enhanced with an improvement and simplification of the operation control strategies.

Zettl et al. developed a revolving drum reactor for open adsorption heat storage systems [48, 49]. The reactor was designed as a slowly rotating cylindrical drum to enable a steady mixing of the storage material in granular form in order to reach homogeneous temperatures and to avoid overhydration of the storage material. Air is supplied/extracted from the reactor through pipe-in-pipe air inlet/outlet construction, whereby the supply air is blown through the outer part while the extracted air leaves the reactor through the central pipe (**Figure 16**). The main advantage of this design is that in contrast to fixed bed reactors no reaction front is formed, since adsorption takes place throughout the whole storage material volume due to bed rotation. The laboratory prototype reactor with a maximum design heat output of 1.5 kW was built (**Figure 16**). It was filled with 70 L of a granular storage material, i.e., alternately zeolite 4A (53 kg) and zeolite MSX (50 kg), covering a volume fraction of about 80% of the interior.

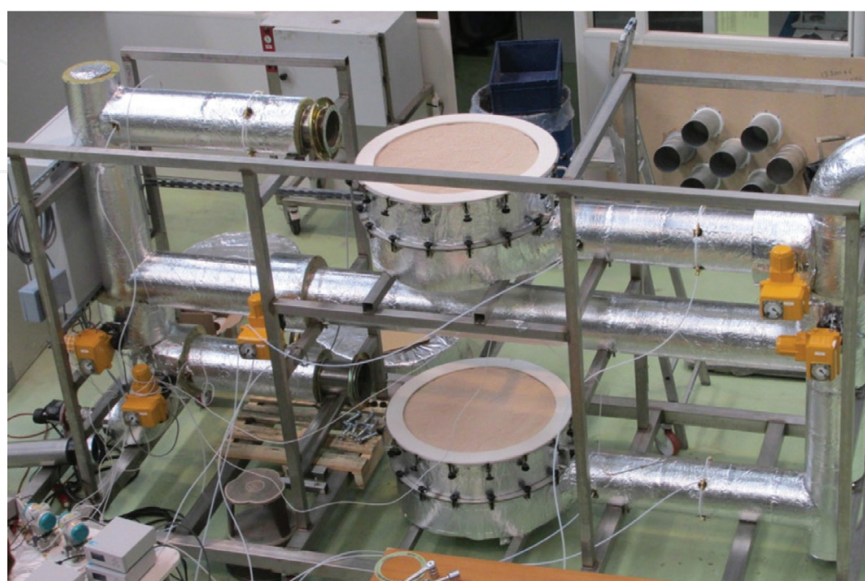


**Figure 15.** Large-scale open adsorption storage system connected to district heating system [47].



**Figure 16.** Revolving drum reactor: (left) laboratory setup; (right) cross-section sketch [49].

Special care was taken in the design of the reactor interior to avoid abrasion of the storage material (e.g., no sharp edges). Only adsorption was monitored in the reactor, desorption took place in a conventional drying oven prior to the adsorption tests. During the adsorption tests, the inlet air was adiabatically humidified. Both materials reached a comparable maximum temperature lifts of  $36^{\circ}C$ . The test with zeolite 4A generated 10.5 kWh of heat and 11.9 kWh was reached with zeolite MSX, which correspond to a stored energy density of 148 kWh/m<sup>3</sup> for zeolite 4A and 154 kWh/m<sup>3</sup> for zeolite MSX. The average heat output during the tests was 1.2 kW, while the combined electric energy use for drum rotation and fan operation was around 100 W. The authors plan to upscale the developed reactor to a realistic size, with which airflow velocity, pressure drop of airflow and specific fan power will be reduced. Special care will be taken on the containment material to guarantee loss-free storage. With upscaling of the storage unit, 16 m<sup>3</sup> storage volume filled with zeolite and material dehydration at  $180^{\circ}C$  would be required

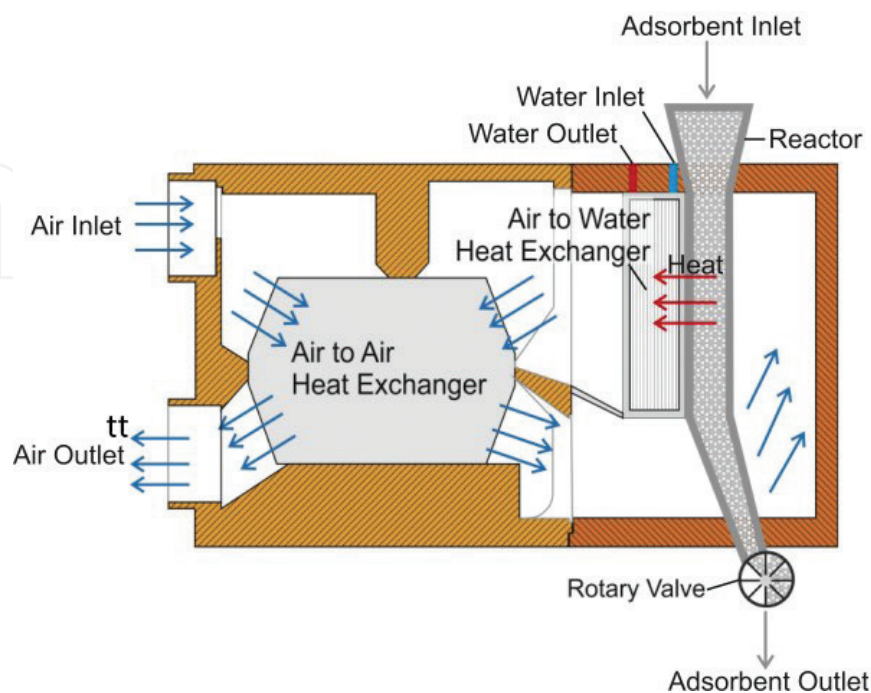


**Figure 17.** Experimental setup of an open adsorption storage system with reactors in parallel configuration [50].

to achieve energy savings of 80%. But for realistic evaluation, other aspects of investigation needs to take place like efficient desorption and building integration.

Johannes et al. [50] designed a high-powered energy-dense zeolite heat storage system with the intention to shave the electricity peak loads in a house by reducing the heating part of the demand. A packed bed reactor system was built containing 80 kg of zeolite 13X, which was split into two equal-sized reactors, in order to test serial and parallel configurations of reactors. The whole system consists of two reactors and ducts to drive the airflow into the reactors (**Figure 17**). An air treatment system was used to prepare (i.e., heat and/or humidify) the airflow during the experiments. Several tests have been carried out both during discharging and charging at various flow rates, relative humidity and temperatures of hydration. The experiments revealed that serial configuration of reactors is unsuitable because the thermal mass of the second reactor draws heat from the first one in serial configuration, which results in a unstable maximum heat output during discharging. For parallel configuration, the results show that the reactor is able to supply a constant power of 2.25 kW for more than 2 hours, while the COP varied between 1.7 and 6.8 depending on the air temperature during charging and air humidity during discharging. For the next step, the authors plan to validate a numerical model of the system to further optimize the developed storage system as well as to numerically asses the performance when coupled to a building.

Within the FlowTCS project [51], an open adsorption storage system with an external reactor configuration has been developed, whereby zeolite and salt-impregnated zeolite were used as the sorbent. The storage system consists of a reactor with approximately 30 L of zeolite and the adsorbent storage reservoir with a volume of 200 L, thereby achieving a high flexibility regarding both storage capacity and heat output. The reactor is designed as a quasicontinuous cross-flow reactor, i.e., the adsorbent flows down through the reactor led by gravity and controlled by a rotary valve through which it is discharged out of the reactor (**Figure 18**).



**Figure 18.** External reactor concept during discharging [51].



The heat released during discharging is transported to the heating system/buffer store via an air to water heat exchanger. During charging, the air is heated up in the air to water heat exchanger. For heat recovery, an air to air heat exchanger was additionally integrated into the reactor unit. The storage system was experimentally tested by varying the air humidity and the heating demand. The system performance was in compliance with the theoretically expected thermal power and temperature lift based on the heat storage density of the adsorbent. The developers further plan to increase the system compactness, reduce heat losses and lower the charging temperature and also to test the concept in an in situ setup.

## 4. Conclusions

Thermochemical heat storage is considered as the only storage concept with a potential for long-term low-temperature heat storage of high enough storage density to be also economically attractive. In this paper, thermochemical heat storage technologies and systems were reviewed. The studies were reviewed based on used storage materials, system configuration as well as models to predict and optimize system performance. Emphasis was placed on systems suitable for solar energy utilization in buildings.

In the paper, an overview of working pairs studied for thermochemical heat storage and transformation applications was given, but none of the presented materials meet the requirements for large-scale low-temperature heat storage applications due to unsuitable operating conditions (i.e., too high charging temperature), too low energy density and discharging temperature, corrosiveness, thermal/chemical instability, environmentally unfriendly production or high cost. The most promising are solid materials that participate in reversible chemical and physical sorption processes with water vapor as sorbate. The focus of material research has been on zeolites and their composites with hygroscopic inorganic salt hydrates and on microporous aluminophosphates. Nevertheless, one issue is common to all sorption storage materials, i.e., the discrepancy between the material and system energy storage density.

One of the main reasons that the prototypes do not achieve the storage capacity expected based on the material energy storage density is insufficient heat and mass transfer inside the reactor. In this regard, open reactor concepts have an advantage over closed reactor configuration, since the heat transfer fluid is in direct contact with the solid reactant, while closed systems require a separate heat transfer loop and hence a heat exchanger in the reactor. Additionally, the design of open systems is much simpler and consequently cheaper compared to closed systems, because they do not require the use of condensers, evaporators and working fluid storage reservoirs.

However, weather conditions are limiting the operation of open systems, i.e., supply air must be humidified when the ambient moisture content is insufficient (e.g., during winter). Another issue limiting the performance of sorption storage systems is the sensible heat loss during charging and discharging as a consequence of heating up the sorbent material and consequently the reactor to the charging/discharging temperature. Therefore, modular, moving beds and fluidized bed reactors are favorable. Also, attention should be paid on building reactors from materials with lower thermal mass, yet with comparable thermal conductivity, than the usually used steel alloys.

Since seasonal storage requires a steady and continuous heat output when discharging, the reactor bed must be optimized in such a way that it guarantees a constant flow rate to enable stable heat output during discharging. In order to achieve this without sacrificing the heat storage unit, compactness numerical modeling techniques have to be employed in the reactor design phase. The review of literature indicates that in the majority of solid-gas adsorption processes modeling efforts, the Dubinin-Polanyi theory is applied for describing adsorption equilibria, while Darcy's law and LDF model are used to predict the pressure gradient inside the adsorbent bed and the adsorption rate.

To conclude, the storage materials represent a bottleneck for the development of thermochemical heat storage systems. Therefore, in order to achieve the commercial breakthrough of thermochemical heat storage systems, a bottom-up approach of storage material engineering is needed, i.e., during material development, the required material characteristics have to be redefined according to the dynamics of the thermochemical process in the particular storage design, thereby obtaining a better understanding of the relations between material synthesis procedures, structural properties and system-level properties. In addition, a significant performance increase can also be expected from the optimization of the storage system's control strategies.

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