

Sorption heat storage for long-term low-temperature applications: A review on the advancements at material and prototype scale



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HIGHLIGHTS

- A review on recent advancements on sorption heat storage is provided.
- Emphasis is on adsorbents, salt hydrates and composites with water as sorbate.
- Solid sorption systems based on the reviewed materials are analyzed.
- Prototype performance and experimental conditions are specified and compared.

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ABSTRACT

Sorption heat storage has the potential to store large amounts of thermal energy from renewables and other distributed energy sources. This article provides an overview on the recent advancements on long-term sorption heat storage at material- and prototype- scales. The focus is on applications requiring heat within a temperature range of 30–150 °C such as space heating, domestic hot water production, and some industrial processes.

At material level, emphasis is put on solid/gas reactions with water as sorbate. In particular, salt hydrates, adsorbents, and recent advancements on composite materials are reviewed. Most of the investigated salt hydrates comply with requirements such as safety and availability at low cost. However, hydrothermal stability issues such as deliquescence and decomposition at certain operating conditions make their utilization in a pure form challenging. Adsorbents are more hydrothermally stable but have lower energy densities and higher prices. Composite materials are investigated to reduce hydrothermal instabilities while achieving acceptable energy densities and material costs.

At prototype-scale, the article provides an updated review on system prototypes based on the reviewed materials. Both open and closed system layouts are addressed, together with the main design issues such as heat and mass transfer in the reactors and materials corrosion resistance. Especially for open systems, the focus is on pure adsorbents rather than salt hydrates as active materials due to their better stability. However, high material costs and desorption temperatures, coupled with lower energy densities at typical system operating conditions, decrease their commercial attractiveness. Among the main conclusions, the implementation within the scientific community of common key performance indicators is suggested together with the inclusion of economic aspects already at material-scale investigations.

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Nomenclature

C	cost (€)
E	volumetric energy density (GJ/m ³)
p	pressure (mbar)
P	power (kW)
RH	relative humidity (%)
T	temperature (°C)
t	time (h)

NMR	nuclear magnetic resonance
PSD	particle size distribution
SEM	scanning electron microscopy
TGA	thermogravimetric analysis
WSS	wakkanai siliceous shale
XRD	X-ray powder diffraction

Abbreviations

CHP	combined heat and power
COP	coefficient of performance
DHW	domestic hot water
DRH	deliquescence relative humidity
DSC	differential scanning calorimetry
DTA	differential thermal analysis
ENG	expanded natural graphite

Subscripts and superscripts

ads	adsorption
des	desorption
el	electrical
sorp	sorption
th	thermal

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1. Introduction

The awareness of humankind's role into climate change [1] and the increasing energy intensity in developing and underdeveloped countries [2] are among the main drivers for a more sustainable production and use of energy. The energy grid consists of a system in which multiple carriers are produced, transported, consumed, and stored. The level of complexity of this system is constantly increasing due to technological advancements such as energy production systems with new requirements, transportation and storage methods that are more efficient, new policies, and new types of consumers and other stakeholders. The advance of renewable energy sources, cogeneration, and intermittent power sources in general, is drastically changing the requirements on the energy grid. Some of the new energy production units are characterized by relatively low and decentralized installed capacities, intermittent and often unpredictable production patterns frequently driven by the owner's needs or by the source availability, and production of multiple energy carriers. Therefore, the energy network is constantly evolving [3,4] to cope with new types of stakeholders and an increasing penetration of intermittent distributed production sources. Storage of multiple energy carriers, demand side management, exchange and relocation through conversion of energy carriers

are among the main practices that the future system will have to incorporate to gain the needed flexibility [5]. Energy storage is useful to handle fluctuations in energy demand to spread the production of energy needed during demand peaks over a different time period and to make efficient use of fluctuating production sources such as renewables, increase energy grid safety, and improve the overall system efficiency [6]. In Table 1–1, an overview of the main storage technologies, their costs, efficiencies, and typical response times is displayed.

Thermal energy storage is an attractive storage category because in principle it can be more economical than other technologies, it has a wide range of storage possibilities with storage periods ranging from minutes to months, and finally because thermal energy dominates the final energy use in sectors such as industry or household (Fig. 1–1 left). Thermal energy storage can be divided into three main categories according to how energy is stored: sensible heat (e.g. water tanks, underground storage) [11–13], latent heat (e.g. ice, phase change materials) [14–16], and sorption heat storage.

1.1. Sorption heat storage

Sorption heat storage implies the use of physical or chemical bonds to store energy. The principle of sorption occurs during a

Table 1-1

Production costs, efficiencies and response times of energy storage technologies [7–9]. Maturity levels according to [10]: 1 = research and development; 2 = demonstration and deployment; 3 = commercialization.

Storage technology	Cost (\$/kWh)	Efficiency (%)	Response time	Maturity
Pumped Hydro	5–100	75–85	s/min	3
CAES	2–100	50–89	min	2
Flywheels	5000	93–95	s	1–2
Lead Acid Batteries	400	70–90	ms	3
Lithium-ion Batteries	2500	85–90	ms	2
Sodium Sulphur	300–500	80–90	ms	2
Ni-Cd Batteries	500–1500	60–65	ms	3
Flow Batteries	150–1000	75–85	ms	1–2
Capacitors	1000	60–65	instantaneous	3
Supercapacitors	2000	90–95	instantaneous	1
SMES	10,000	95–98	instantaneous	1
Sensible Heat	0.1–10	50–90	min	3
Latent Heat	10–50	75–90	min	2–3
Chemical Reactions	8–100	75–100	min	1

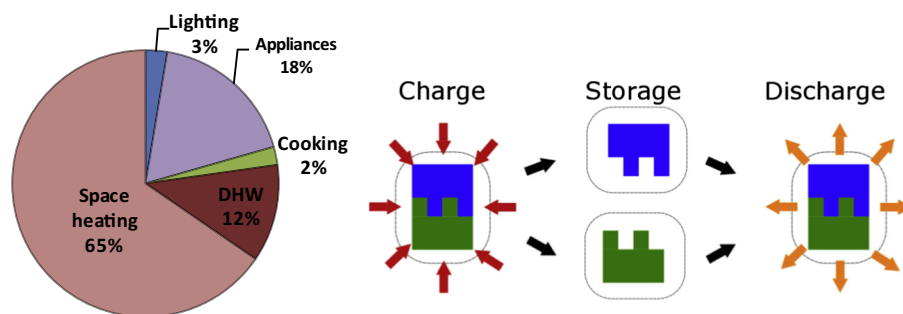


Fig. 1-1. Left: Dutch household energy consumption by end-use in 2012 [17]. Right: Sorption heat storage concept.

reaction, and in order to take place, at least two components are needed: a sorbent, which is typically a liquid or solid, and a sorbate, which is typically a vapor. During the charging process (Fig. 1-1 right), an endothermic reaction occurs, and the sorbent and sorbate are separated. The two components can then be stored separately, ideally without energy losses. During the discharging process, sorbent and sorbate react producing an exothermic reaction that releases heat. The main advantages of sorption heat storage are higher energy density and negligible heat losses compared to a conventional thermal storage based on sensible heat. A conventional water storage needs to be approximately five to ten times larger than a sorption heat storage system for storing the same energy. Since many years, the use of sorption heat storage systems for long-term storage applications is being investigated [18–22]. Previous review works on the topic are from N'Tsoukpoe et al. [23], who reviewed long-term sorption energy storage technologies; Yu et al. [18], who reviewed solid and liquid sorption materials and reactors; Solé et al. [24], who focused in particular on reactors and systems for building applications; and Xu et al. [19], who reviewed sensible, latent and chemical heat storage systems for seasonal storage applications. The aim of this work is to provide an overview on the last advancements on sorption heat storage technologies for long-term low-temperature applications based on solid/gas reactions with water as sorbate. The focus of this article is on the state of the research at material- and prototype-scale. The current work is divided into two main sections. In Section 2, the focus is on sorption materials and current advancements on their research. In Section 3, a review on the state-of-the-art research on solid sorption storage systems is carried out, and their performances are discussed and compared.

2. Materials for sorption heat storage

The terminological framework of sorption heat storage has been defined by Yu et al. [18], based on the work of many authors, and this terminology will be adopted in the present work. Sorption includes different phenomena, and it is a prerequisite for a chemical process mediated by a surface. Sorption reactions can be divided into two categories according to the sorption mechanism: absorption and adsorption.

Absorption is defined as “the process of one material (absorbate) being retained by another (absorbent)” [25]. It occurs at the sorbent molecular level, and it alters the composition and morphological structure of a solid sorbent. Therefore, during the process, a material expansion typically occurs and significantly higher activation energy than for adsorption is present. This energy is mainly related to covalent bonding of atoms and molecules. Absorbents can be liquids or solids, and the main difference is that their concentration during the reaction process varies stepwise for solids or continuously for liquids. Absorbates can be liquids or gases, which have a different amount of binding energy released as heat of reaction. If the absorbate is in liquid state, part of the binding energy is needed to break the bonds within the liquid, therefore, only part of it will be released as heat of reaction. For absorbents in vapor state, all the binding energy is released as heat of reaction.

Adsorption is defined as “a phenomenon occurring at the interface between two phases, in which cohesive forces act between the molecules of all substances irrespective of their state of aggregation” [26]. Therefore, adsorption occurs at the surface of the adsorbent forming an extremely thin layer of atoms or molecules on the adsorbent surface, while leaving its structure unaltered. No expansion

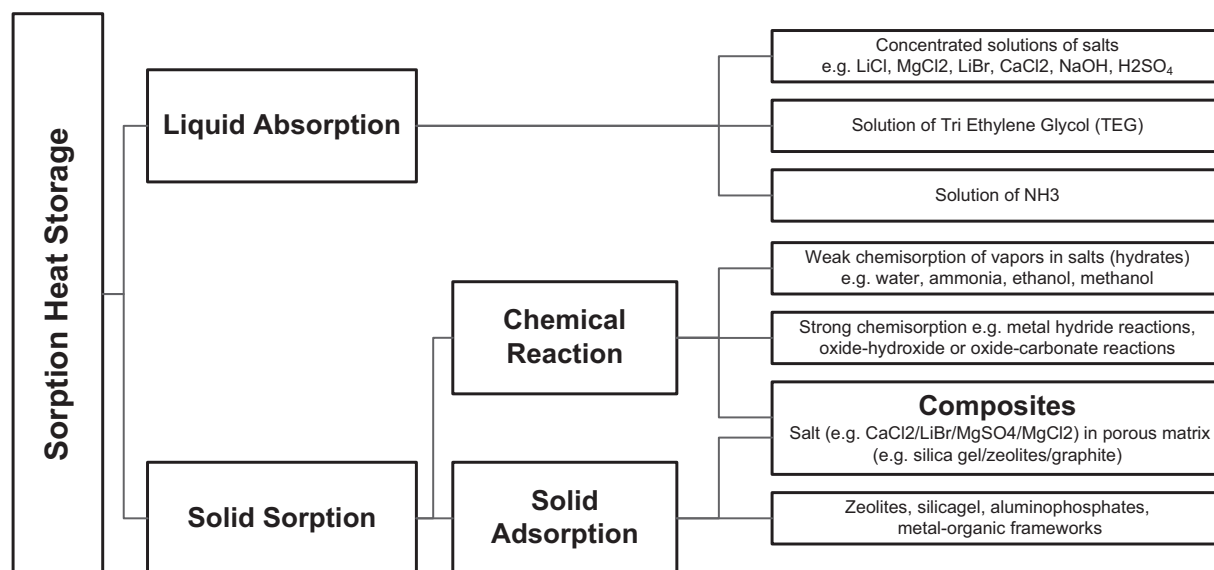


Fig. 2-1. Classification of sorption heat storage. Partially adapted from [18].

sion occurs and no or negligible activation energy is involved. A further division among sorption phenomena can be made based on the cohesive forces involved in the process: physisorption and chemisorption. In physisorption, the sorption energy is typically related to the weak intermolecular forces (Van der Waals forces) and hydrogen bonding [25] and no activation energy is required. In chemisorption, stronger covalent bonding is involved and in some cases, it can be irreversible. Often, both processes can simultaneously happen, and a clear distinction cannot be made.

Yu et al. [18] divided sorption heat storage into four main categories: liquid absorption, solid adsorption, chemical reaction and composite materials. This division emphasizes the predominant type of reaction that occurs during the sorption processes. A similar subdivision is presented in Fig. 2-1, in which the “Composites” sub-category is shared between the “Chemical Reaction” and the “Solid Adsorption” categories since both phenomena are present.

In order to use a sorption material for thermal energy storage purposes, certain criteria should be met concerning the material energy density, physical characteristics and safety. In Table 2-1, the selection criteria for a sorption material for long-term low-temperature heat storage purposes are shown. In principle, a high uptake of sorbates leads to a high energy density. However, many requirements concerning the kinetics are also present such as regeneration temperature and time. Water is the preferred sorbate because it is abundant, low cost and non-hazardous.

2.1. Solid sorption

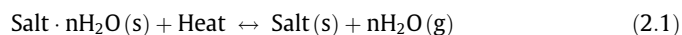
Solid sorption materials can be divided into three categories (Fig. 2-1): chemical reaction, solid adsorption and composites. The chemical reaction category includes materials undergoing solid/gas reactions in which an absorption process is predominant but, in principle, also adsorption may be occurring. The solid adsorption category includes purely adsorbent materials. Finally, composite materials can be a combination of the abovementioned categories including also inert components.

2.1.1. Chemical reaction

In the following paragraph, the chemical reaction materials category is discussed. In particular, salt hydrates, hydroxides, carbonates and ammoniates are presented. The emphasis is on materials that can be suitable for long-term low-temperature heat storage

purposes. Therefore, materials with too high desorption temperatures or too many unmet requirements from Table 2-1 are marginally discussed.

2.1.1.1. Salt hydrates. Extensive research on salt hydrates is being carried out for thermal storage purposes. The main reasons are a high theoretical energy density of the materials, desorption temperatures achievable with waste heat sources and solar thermal collectors, and discharge temperatures useful for low-temperature heat applications such as space heating and domestic hot water production. Currently, research at material level is still ongoing due to technical drawbacks of salt hydrates, which are further discussed in the following paragraphs. The general reversible reaction of a salt hydrate can be written as follows:



The reversible reaction can take place in different steps at different desorption temperatures, and intermediate hydrates of the salt can appear in the system. This is because the binding energy of the water molecules increases with the decrease of the water molecules into the salt molecular structure. For some practical

Table 2-1
Selection criteria for suitable sorption materials [20,27–29].

Sorption materials selection criteria		
• High uptake of sorbate	• High energy density at system operating temperatures	• Small molar volume of the products to minimize storage volume
• Regeneration at relatively low temperature	• Short regeneration time	• Small volume variation during reaction
• Good mass transport of the sorbate	• Good heat transport from/to the sorbent	• High thermal conductivity
• Reactions completely reversible without secondary reactions	• High yield of reaction at charge and discharge temperatures	• Rapid separation of products during storage
• Large reaction enthalpy to maximize storage capacity	• Preferably components non-reactive to O ₂	• Reaction compounds easy to handle
		• Non-toxic
		• Non-flammable/explosive
		• Non-corrosive
		• Low-cost
		• Material commercially available

applications of salt hydrates for sorption heat storage, only part of the reversible reaction is considered. The reason can be that in order to have a certain salt in its anhydrous form, a too high desorption temperature is required. Conversely, by having a completely hydrated form, deliquescence might occur and the sorbate mass transfer into the system will be blocked causing issues such as high pressure drops and ultimately system failure.

2.1.1.1.1. Magnesium sulfate. De/hydration reactions for $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ were investigated by van Essen et al. [30,31] due to its suitability in a seasonal storage system operating at 13 mbar of water vapor pressure achievable in a low temperature reservoir. TGA/DSC/SEM/XRD and particle size distribution measurements were carried out. A melting process for large particles ($>200 \mu\text{m}$) at heating rates higher than $1^\circ\text{C}/\text{min}$ was present at 52.5°C , reducing the effective bed porosity. During the second reaction step of the experiment ($55\text{--}265^\circ\text{C}$), the material released $5.9 \text{ H}_2\text{O}$ molecules with an energy density of $2.2 \text{ GJ}/\text{m}^3$ based on the solid density of the heptahydrate form, resulting in $\text{MgSO}_4 \cdot 0.1\text{H}_2\text{O}$. The largest amount of energy could be stored below 90°C , since a sharp mass loss took place below that temperature. Particle size had a very limited effect on hydration. Therefore, the vapor mass transfer resistance was not limiting the reaction for the investigated particle sizes ($20\text{--}500 \mu\text{m}$). Layer thickness, on the other hand, strongly affected the hydration time: smaller thicknesses implied a faster reaction. During dehydration/hydration cycles, cracks were formed, and there was a formation of smaller particles. Material pulverization is a typical and main issue occurring in salt hydrates, since active material can be removed from the system thereby reducing its energy density. Experiments under vacuum conditions evidenced a maximum hydration temperature step of 4°C with a water vapor pressure of 13 mbar. The main conclusion of the authors was that a heat release above 50°C was not feasible for this material. Ferchaud et al. [32,33] studied the material crystal and grain-scale properties. $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ was able to release six molecules of water in two different reaction steps, at $30\text{--}45^\circ\text{C}$ and $60\text{--}75^\circ\text{C}$, respectively. However, the formation of the monohydrate occurred gradually up to a temperature of 150°C under a water vapor pressure of 13 mbar. At $60\text{--}75^\circ\text{C}$ probably $\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$ was present, as expected by van Essen et al. [30]. The experiments were conducted with a moist air flow of $100 \text{ ml}/\text{min}$ and a water vapor pressure of 13 mbar. Concerning the material kinetics, Ferchaud [34] reported very slow reaction rates at the abovementioned operating conditions. The author concludes that MgSO_4 is not indicated for seasonal heat storage applications since slow kinetics lead to too low power delivery, especially in a full-scale reactor. An improvement in reaction kinetics was obtained by increasing the water vapor pressure up to 50 mbar. However, the material should be maintained above 36°C to avoid overhydration, and saturated air at 33°C should be provided to the system. Concerning the rehydration reaction, other previous studies showed that there was a low temperature lift under practical conditions for low-temperature heat storage. In particular, Bertsch et al. [35] measured a maximum temperature lift of 8°C , with a water vapor pressure of 12.5 mbar and an inlet hydration temperature of 23°C . During their experiments, the temperature lift was decreasing due to a decreasing reaction rate caused by the vapor transport inhibition within the crystals. Also Linnow et al. [36] analyzed the kinetics of hydration for MgSO_4 , and they found that the rate-limiting step during hydration could be due to the hydrated layer formed from outside to the inside of the particle, limiting the water diffusion into the material. The material water uptake was investigated by impregnating a solution of magnesium sulfate in various porous glasses. For large pores ($1.7 \mu\text{m}$), full hydration was not achieved. For the smallest pores (7 nm), an aqueous solution was formed resulting from capillary condensation. This phenomenon is of particular interest when

composites are used in order to consider the correct amount of salt content.

Finally, Donkers et al. [37] performed cyclability studies (7–13 cycles) on 1–2 mm grains of four salt hydrates: CuCl_2 , CuSO_4 , MgCl_2 , and MgSO_4 . The experimental procedure consisted in performing temperature cycles over a range of $20\text{--}150^\circ\text{C}$. NMR is used in order to measure the amount and location of water in the samples. The authors suggested that the production of pore water affected the material performance over the cycles. Moreover, grain fracturing over the first cycles, as found also by Ferchaud [34], caused by the sample volume change, increased the water mobility through the grains thus increasing the dehydration/hydration rates. On the contrary, during the rehydration phases, the hydrated layer on the outer part of the grain reduced the water mobility thus leading to partial hydration of the samples. MgSO_4 showed a decrease in the kinetics and a final rehydration level of 15% after 7 cycles.

2.1.1.1.2. Sodium sulfide. The first studies on Na_2S for heat storage purposes are from Brunberg et al. [38–40], who studied the potential of this material to store thermal energy in a domestic environment. The authors built different prototypes (0.6 kg, 500 kg, and 7000 kg of salt) to demonstrate the proof of concept and its applicability in a domestic environment.

De Boer et al. [41,42] characterized sodium sulfide for a solid/gas reaction chemical heat pump to be used in buildings for space cooling purposes. The aim of the authors was to prove the existence of a phase close to $\text{Na}_2\text{S} \cdot 2\text{H}_2\text{O}$, and to determine its p-T equilibrium line. During dehydration, with 17 mbar of water vapor pressure, the first reaction step was not completed before the melting point of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (49°C). Thus, partial melting occurred. The second dehydration step, from the pentahydrate to a lower water content form, started at 60°C up to approximately $90\text{--}100^\circ\text{C}$. High heating/cooling rates limited heat and mass transfer, and a hysteresis effect was observed. In addition, the melting of the material formed a more compact structure causing the same consequences. Subsequently, cellulose was added to prevent porosity loss during the melting process. An energy density of approximately $1.93 \text{ GJ}/\text{m}^3$ referred to the anhydrous salt was measured. Operating conditions under vacuum, a high corrosiveness of the material and potential production of toxic H_2S are the main drawbacks for the utilization of this material [43].

2.1.1.1.3. Magnesium chloride. Magnesium chloride has been largely investigated as a promising sorption material due to its relatively high energy density. Huang et al. [44] investigated the decomposition mechanism of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ up to the anhydrous phase, at 600°C with TGA/DSC/SEM/XRD measurements. Five distinct endothermic peaks were identified during the dehydration process. HCl formation below 203°C was impeded by immersing the sample into an HCl atmosphere. For heat storage at low-temperature purposes, the most interesting hydration states are the dihydrate, tetrahydrate and hexahydrate forms. The main issue of this material, and for chlorides in general, is its instability at both low and high temperatures [32]. Therefore, controlled operating conditions in terms of water vapor pressure and temperature are required. At low temperature, approximately below 40°C , and ambient humidity, overhydration and deliquescence occur, causing the formation of an outer layer on the material grains. This impedes the mass transfer and causes the formation of a salt solution, which leads to irreversible changes in the material porosity. At high temperature, above 100°C formation of HCl can be an issue and causes material degradation. Ferchaud et al. [45] confirmed the promising characteristics of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, which was tested in rehydration mode in an experimental open system reactor of 20 l at 12 mbar of water vapor pressure and 10°C of inlet airflow temperature. The system was able to deliver heat at temperatures higher than 60°C for 20 h, with preheated air at 50°C and a maximum temperature lift of 15°C . Van Essen et al. [31], in a closed

system configuration, measured a temperature lift of 63 °C and 19 °C for an hydration temperature of 25 and 50 °C and water vapor pressures of 31.6 and 12.8 mbar, respectively. After dehydration and after the material exposure to ambient air at room temperature, a gel-like formation was present, supporting the fact that a minimum temperature of 30–40 °C has to be maintained in the system if certain chlorides are used. The same operating boundary conditions and material issues were found also by Zondag et al. [46], in particular HCl formation above 135 °C and over-hydration at the end of the hydration process. Rammelberg et al. [47] investigated the kinetics, reaction enthalpies of water uptake/release, and the related hydration/dehydration power of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ with a TGA/DSC setup. The experimental conditions consisted in a temperature program with temperature gradients of 1–5–10 °C/min and –5 °C/min, hydration at 30 °C or 35 °C, nitrogen flow at 25–150 ml/min with water pressure during hydration at of 12–22 mbar. The desorption process of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ started immediately above room temperature and it had a three-step reaction at 82, 116, and 145 °C, in which the last step was the conversion to monohydrate and a parallel decomposition reaction in which HCl was formed.

Donkers et al. [37] in their study investigated MgCl_2 performing two temperature programs up to 100 °C and 150 °C of maximum dehydration temperature. The sample with a maximum dehydration temperature of 150 °C, after 8 cycles, showed a decrease in the rehydration level of 32%. The sample with a maximum dehydration temperature of 100 °C has been tested for 11 cycles, and the final rehydration level was less than 10% lower compare to the initial one. The authors stated that the performance difference between the two MgCl_2 is due to the pore water production in the sample with the highest dehydration temperature.

2.1.1.1.4. Copper sulfate. Copper sulfate was also studied for its suitability as sorption heat storage material. Bertsch et al. [35] tested the material in an open system configuration in a lab reactor with 100 g samples and a previous dehydration at 200 °C. With a volumetric flow of 25 l/min, a maximum temperature lift of 11 °C was present for a hydration temperature of 40 °C and 69.2 mbar of water vapor pressure. During hydration/dehydration, crystals expansion/shrinking formed a fine powder, documented also by Ferchaud et al. [32]. The authors reported that the materials were stable during the experiment and cyclability was possible. Assuming a water vapor pressure of 13 mbar, the authors considered the temperature lift (~5 °C) too low for thermal storage. Concerning the material stability over the cycles, also Ferchaud [34] reported a good mechanical stability at crystal level. At grain-scale, the crack formation process, which is a typical result of the volume change over the cycles, did not result in an improvement in the reaction rates. The reason suggested by the author is that the rate limiting factor is the material conversion, which involves complex crystal structure reorganization.

Concerning the material stability over the cycles, Donkers et al. [37] showed that CuSO_4 had a remarkable decrease in the kinetics after 13 cycles, and a final rehydration level of 35%. To conclude, an additional material drawback is its toxicity, which would imply additional safety measures for its integration in a commercial application.

2.1.1.1.5. Strontium bromide. Strontium bromide was also investigated as possible candidate in some system prototypes. In particular, the reaction from the hexahydrate to the monohydrate is of interest. A relatively high energy density at reactor level was measured in certain experiments [48]. A temperature of approximately 80 °C was sufficient to dehydrate the material. Moreover, in certain systems even lower dehydration temperatures were applied [49,50]. A crystal energy density of 2.02 GJ/m³ [43], and reactor energy densities of approximately 1.44 GJ/m³ were reached [48]. Finally, the stability of the salt was promising for certain investiga-

tions [51], since this salt showed good stability over multiple dehydration/hydration cycles. However, its high price compared to other salt hydrates [43] make this material less attractive from a commercial point of view, especially in systems that require large amounts of active material and perform few cycles per year.

The main findings on the utilization of pure salt hydrates as sorption materials for a long-term low-temperature heat storage are presented in Table 2–2. In particular, their energy density measured during the experiments at different operating conditions and their main advantages and issues are displayed. The reported desorption temperatures are the maximum desorption temperature in the experiments at which the material was subjected, while the water vapor pressure reported was present during hydration phases. It has to be stated that, in some cases, the experimental conditions were not clear in the scientific literature. Therefore, it is advisable to interpret the data with caution. A proper material characterization at system operating conditions is always advisable before experimentation at larger scales in order to avoid misleading results and indications [54]. Due to the intrinsic disadvantages of every material, their utilization in pure form for sorption heat storage is challenging. Despite the high energy densities measured, they can have hydrothermal stability problems at system operating conditions, slow kinetics, problems with corrosiveness and toxicity, or too high costs.

2.1.1.1.6. Additional studies on salt hydrates. Other examples of salt hydrates studied for their use in pure form for sorption heat storage systems are aluminum sulfate (Al_2SO_4) and calcium chloride (CaCl_2). However, at typical operating conditions¹ of a low-temperature heat storage system, a too low temperature lift (1–2 °C) has been measured for the former and a high deliquescence for the latter [31]. An extensive material screening process has been carried out by N'Tsoukpoe et al. [55], in which more than one hundred salt hydrates were analyzed. The authors' main objective was to find a suitable working pair to be used in a system able to store approximately 0.3 GJ/m³ of heat generated by a micro-CHP system with a maximum desorption temperature of 105–115 °C. The most suitable candidates were SrBr_2 , MgSO_4 and LaCl_3 . However, the authors highlighted that parameters like materials cost, effective reactor bed porosity, system components, sensible thermal losses and kinetic limitations at reactor level were not considered as investigation parameters. Therefore, a techno-economic analysis on the most suitable materials is needed, in which parameters at reactor and system levels are considered.

Finally, Donkers et al. [37] investigated the hydrothermal stability of CuCl_2 . The authors reported that this salt performed best among the salts investigated in their study. It had an almost constant rehydration level after 9 cycles, and no pore water generation was observed.

2.1.1.2. Hydroxides, oxides and carbonates. These material categories have a stronger bonding energy in the formation of their products compared to hydration reactions. Examples of materials used for hydroxide reactions are $\text{CaO}/\text{Ca}(\text{OH})_2$ [56], which have equilibrium temperatures of approximately 500 °C at standard conditions, or $\text{MgO}/\text{Mg}(\text{OH})_2$ [57–62] with a dehydration temperature of 250 °C and a discharge temperature of 200 °C. Concerning carbonate reactions, equilibrium temperatures can vary from 160 °C to 1300 °C at standard conditions, and system pressures are usually much lower compared to hydroxide systems, often in the range of few millibar. Materials examples are CaO/CaCO_3 and PbO/PbCO_3 . High temperatures and low pressures make this reac-

¹ Dehydration temperature of 150 °C and hydration conditions at 25–50 °C and 13 mbar of water vapor pressure.

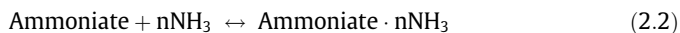
Table 2-2

Summary of main advantages and disadvantages of the investigated pure salt hydrates.

	E (GJ/m ³)	T _{des} (°C)	p _{H₂O} (mbar)	C (€/t) [43,52]	Main issues	Advantages	Refs.
MgSO ₄	1.8–2.2	150	12.5–13	77	Heat release above 50 °C not possible; low temperature lift	Most of the energy stored below 90 °C	[30–33,35,36]
Na ₂ S	1.93–2.66	100	19	348	Melting reduced mass transfer; operation under vacuum required; highly corrosive; formation of H ₂ S	High energy density	[41,43]
MgCl ₂	1.89–1.94	150	11.8–31.6	154	Deliquescence and overhydration below 40 °C; thermal decomposition and HCl formation above 110–130 °C	Relatively large temperature lifts	[31,32,43–47,53]
CuSO ₄	1.93	150	2.13–69	134	Low temperature lift; environmental toxicity		[32,35]
SrBr ₂	2.02	80	9.7–17.5	2400	High cost	High stability and energy density	[43,48–50]

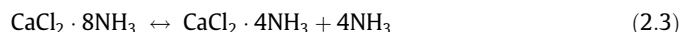
tions category more suitable for chemical heat pumps for medium- to high-temperature applications rather than for low-temperature heat storage. A comprehensive review is carried out by Pardo et al. [63].

2.1.1.3. Ammoniates. Ammoniates react with ammonia to form complex compounds in which coordination bonds are present. The general reaction can be written as:



Metal halides such as NH₄Cl, PbCl₂, NaBr, BaCl₂, LiCl, CaCl₂, NaI, BaBr₂, SrCl₂, CaCl₂, SrBr₂, MnCl₂, CaBr₂, FeCl₂, MnBr₂, CoCl₂, MgCl₂, FeBr₂, CaI₂, CoBr₂, NiCl₂, MnI₂, FeI₂, MgBr₂, NiBr₂ and NiI₂ are used in ammoniation/deammoniation reactions. Equilibrium temperatures of reaction and energy densities are in the range of 48 (NH₄Cl) – 334 (NiI₂) °C and 563 (BaBr₂) – 2341 (MgCl₂) kJ/kg, respectively [64]. This materials category has been mainly investigated for chemical heat pumps and sorption cooling applications [18]. Cot-Gores et al. [65] presented a summary of the thermal performances of chemical heat pumping systems based on the solid-gas de/ammoniation reaction. The systems applications were mainly refrigeration, ice making, air conditioning and heat transformation. Recently, applications for thermal storage purposes are being investigated. Li et al. [64,66] proposed a dual mode device for low temperature heat upgrade and energy storage. The selection of the working pairs allows to control the temperature

of the upgraded heat; e.g. 87–171 °C using MnCl₂–CaCl₂–NH₃ or 130–282 °C with NiCl₂–SrBr₂–NH₃. During the discharge phase, if the ambient temperature is not high enough, the system could internally upgrade the heat by using a heat recovery technique (Fig. 2-2), allowing its operation at winter ambient temperatures of –30 to +15 °C. For ambient temperatures of 0 °C, a COP in heating mode of 0.6 was measured by the authors. The system pressures and temperatures were between 1.8–11.3 bar and –20 to 99 °C for the NaBr–CaCl₂–NH₃ working pair. Sakamoto et al. [67] developed an energy storage lab-scale reactor based on the following ammoniation/deammoniation reaction using calcium chloride as ammoniate:



The system operating pressure was kept at approximately 5 bar, while ammoniation and deammoniation temperatures were 30 and 80 °C, respectively. In order to increase the heat transfer rate, a titanium sponge was added with different Ti/CaCl₂ ratios (0:1/1:1/3:1/5:1). The addition of Ti decreased remarkably the reaction time halving the duration of the de/ammoniation processes. The system filled with 110 g of CaCl₂ with a Ti/CaCl₂ weight ratio of 5:1 was able to deliver energy reaching a peak power of 25 W. System cyclability is claimed after 30 ammoniation/deammoniation cycles without observation of materials decomposition and reaction rate decrease.

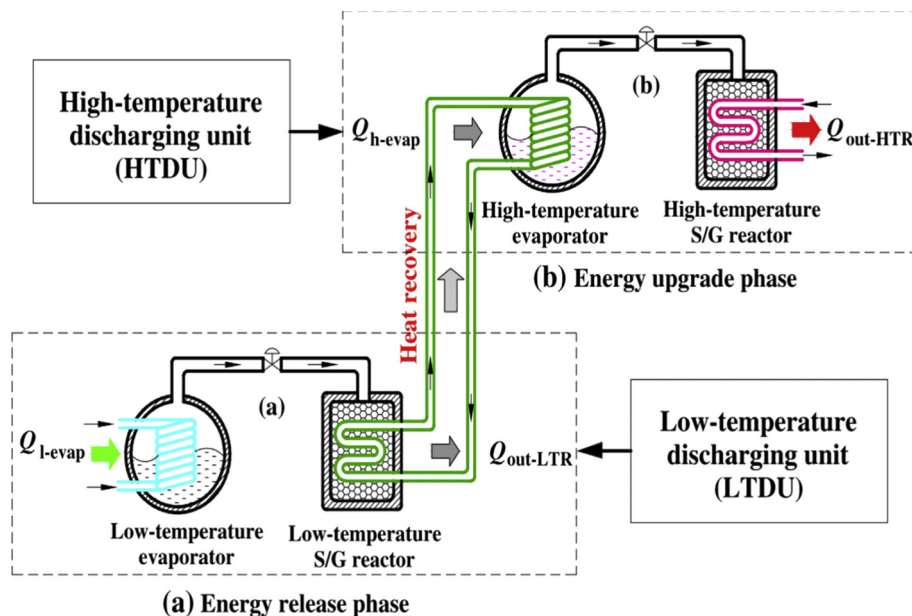


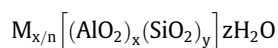
Fig. 2-2. Schematic diagram of the integrated energy storage and energy upgrade solid/gas sorption system for seasonal storage of solar thermal energy [66].

To conclude, research on ammoniates/ammonia systems for long-term low temperature thermal energy storage is still at early stages. Actual disadvantages of these systems are operating pressures above the standard conditions, and the use of ammonia as sorbate, which can represent a drawback for a possible domestic system by considering the criteria in Table 2-1.

2.1.2. Solid adsorption

In general, since adsorption reactions have weaker bonding forces than absorption reactions, the energy density of these materials is lower compared to e.g. salt hydrates. Moreover, for certain adsorbents such as zeolites, the water uptake is relatively low due to the structural limitations of the matrix itself. On the other hand, heat and mass transport are improved compared to salt hydrates due to a better hydrothermal stability of the materials. Typically, adsorption materials should have a large internal pore volume and surface area for a large adsorption capacity, fast adsorption kinetics, good mechanical strength and they should be easily regenerable [68].

2.1.2.1. Zeolites. Zeolites are promising materials for heat storage and as supportive structures for composites. They consist of porous crystalline aluminosilicates of alkali or alkali earth elements such as sodium, potassium and calcium. The general formula of zeolite is [68]:



with x and y integers with their ratio larger than one; n the valence of cation M , and z the number of water molecules in each unit cell. Zeolites exist in nature, but for commercial application are commonly synthesized and defined as molecular sieves due to their well-defined pore size distribution. Their structure is typically tetrahedral made of silicon and aluminum. Different arrangements make numerous conceivable possibilities. For commercial use, the dominant types are 4A, 5A, 10X, 13X and Y [18]. Creation of defects through ions replacement with others of different size and charge improved the storage properties of zeolites. Jänchen et al. [69] tested ion exchanged NaA, NaX, and NaY zeolites. By including Li^+ ions into zeolites, the authors increased the amount of water adsorbed and the heat of de/sorption. However, a higher desorption temperature was required. Ions of Zn^{2+} , La^{3+} and Al^{3+} increased the water adsorption amount and the energy storage potential of zeolites as well. Beside the micro-scale investigations, the authors used two closed reactors with a storage capacity of approximately 1–1.5 and 20 kg of adsorbents. The maximum desorption temperature was 180 °C, and the materials energy densities were in the range of 0.4–0.6 GJ/m³. Type 13X is reported as one of the best performing zeolites for heat storage purposes due to a high water uptake and fast reaction kinetics [18,70,71]. In an open system configuration, Gantenbein et al. [72] reported experiments on zeolite 13X, in which a maximum sorption temperature of 80 °C was achieved with a water vapor pressure of 20 mbar and a hydration temperature of 35 °C. Similar results, in an open configuration, were found also by Mette et al. [70] for binder-free zeolite 13X, which measured temperatures of approximately 85 °C during hydration with a water vapor pressure of 15 mbar and an hydration inlet temperature of 50 °C. A typical drawback of synthetic zeolites is their cost, which makes them in principle unsuitable for seasonal heat storage [73] but allows shorter cycles such as in load leveling in district heating networks [74].

2.1.2.2. AlPOs and SAPOs. Two classes of promising sorption materials are aluminophosphates (AlPOs) and silico-aluminophosphates (SAPOs) [75,76]. Silicon or metal cations incorporated in aluminophosphates are beneficial for heat storage because structural

defects improve surface interactions of polar water molecules. On the other hand, dislodgment after few cycles leads to material degradation [77]. In particular, for low temperature heat storage purposes, SAPO-34 [78,79] and AlPO-18 [78] are found to have remarkable energy densities (203 and 243 W h/kg respectively), discharging temperatures approximately at 40 °C and charging temperatures of 95 °C.

In Fig. 2-3 left, a comparison among different adsorption materials considering the water uptake is made. It can be seen that AlPO-18 and SAPO-34 samples have the best performances considering the most favorable operating conditions of thermal heat storage, which are a low charging temperature and adsorption water vapor pressure similar to the saturation water vapor pressure at ambient temperature. Zeolites of types Y and X with different metal cations need higher desorption temperatures to have acceptable performances, while silica gel and type A zeolites underperform the other samples. The last group on the right is copper(II) benzene-1,3,5-tricarboxylate metal organic framework. Its performances are worse at the lowest desorption conditions compared to AlPOs and SAPOs but comparable or even better at a desorption temperature of 140 °C.

One of the most promising materials of this category, APO-Tric, was investigated by Ristić et al. [77] for energy storage purposes. Optimal sorption temperatures and maximum water uptake were the two parameters investigated. APO-Tric was able to adsorb the maximum amount of water (318 g_{H₂O}/g) at the lowest temperature (95 °C) similar to AlPO-18 (Fig. 2-3 right). However, APO-Tric was able to incorporate the water in a smaller range of water vapor pressure, which is beneficial for the system efficiency. In particular, APO-Tric incorporated most of the water within a relative pressure range of 0.1–0.15 while AlPO-18 incorporated the same amount of water in the range 0–0.55. Desorption temperatures up to 140 °C and 55.27 mbar of water vapor pressure were used, while minimum adsorption temperatures of 40 °C and 56 mbar were set. The energy density of APO-Tric was estimated to be 0.86 GJ/m³ based on the packed bed density. To evaluate the thermal stability, 50 thermal cycles were performed, and a linear decrease of performances of approximately 5% was observed. The authors justified the sudden water uptake by the exothermic formation of ordered hydrogen-bonded water clusters at low p/p_0 ratios (0.12–0.16 for APO-Tric and 0.12–0.25 for AlPO-18). Therefore, water ordering contributes to the heat storage capacity of the material. The authors observed also the typical issue of adsorption materials: larger pores into aluminophosphates (pore diameters from 0.55 to 0.75 nm) did not improve the material performance because the water-structure interactions decreased. On the other hand, higher pores connectivity improved the overall kinetics.

2.1.2.3. Metal organic frameworks (MOF). This relatively novel class of porous materials gained attention in the past years due to its high sorbate uptake potential. A metal organic framework is defined as a solid containing metal ions linked by organic species that presents certain characteristics such as strong bonding providing robustness, linking units that are available for modification by organic synthesis and a geometrically well-defined geometrical structure [80]. They are of interest for gas storage (e.g. hydrogen), and their suitability for adsorption cycles and heat storage is under investigation [80–83]. Henninger et al. [83] compared the MOF ISE-1 to silica gel and zeolites for adsorption chillers and heat transformation purposes. ISE-1 had a water uptake of 210 g_{water}/kg with desorption conditions at 140 °C/11.84 mbar and adsorption conditions at 30 °C/11.84 mbar. This value outperformed the five zeolites used for comparison (Fig. 2-4). Stability over ten cycles was assessed and the material was found to be very stable with only slight decrease of the performance.

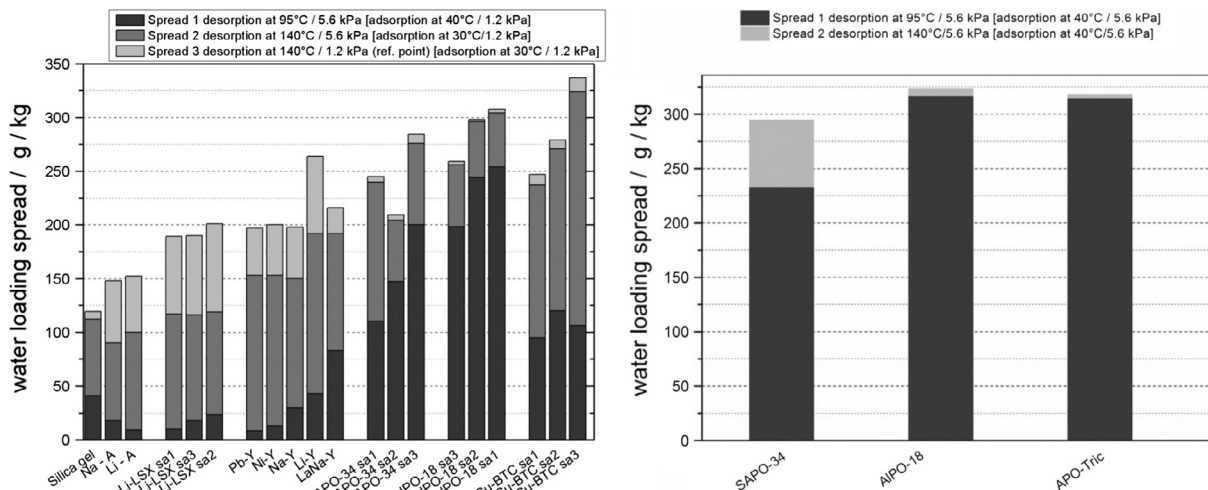


Fig. 2-3. Left: Comparison of water uptake of different adsorption material classes [79]. Right: Comparison of water uptake between SAPO-34, AlPO-18 and APO-Tric [77].

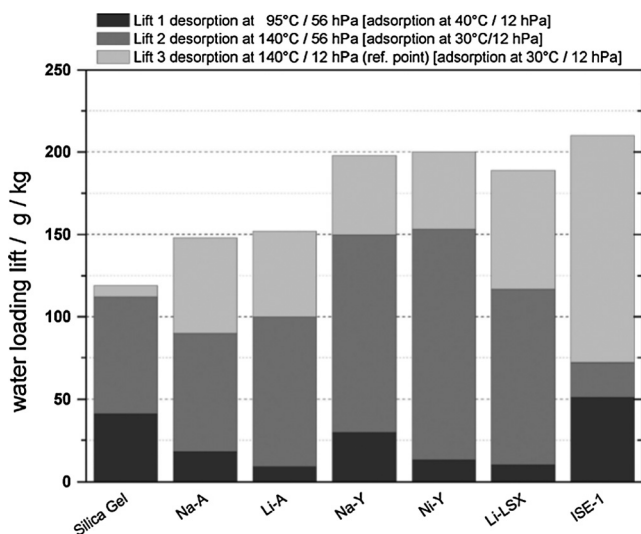


Fig. 2-4. Water uptake for various adsorbents. From left to right: Silica gel, two commercial zeolites type A normally used as desiccants, two zeolites type Y and one type X used for heat pumping and cooling cycles, and the MOF ISE-1 [83].

Ehrenmann et al. [82] reported the promising characteristics of a crystalline mesoporous metal organic framework, MIL-101 (Table 2-3), with its ability to adsorb up to $1 \text{ g}_{\text{H}_2\text{O}}/\text{g}$ between 140 and 40°C at a water vapor pressure of 55 mbar. The material presented a water uptake up to $1.01 \text{ g}_{\text{H}_2\text{O}}/\text{g}_{\text{material}}$ and it could be desorbed at 90°C . A moderate hysteresis effect between adsorption and desorption was reported. For what concerns the hydrothermal stability and the material degradation, 40 cycles were performed, and after 20 and 40 cycles, its capacity compared to the initial one was 98.1% and 96.8%, respectively. Sorption heat, including

Table 2-3

Energy density and desorption temperature ranges for the investigated adsorption material category.

Adsorption material	Energy density (GJ/m^3)	T_{des} ($^\circ\text{C}$)	T_{ads} ($^\circ\text{C}$)
Zeolites	0.4–0.6	Up to 180	Up to 80
AlPOs and SAPOs	0.61*–0.86	95–140	30–40
MOF (MIL-101)	1.6	90–140	30–40

* Assuming a packed density of $840 \text{ kg}/\text{m}^3$ for SAPO-34 [86].

sensible heat, was approximately $2588 \text{ J}/\text{g}$ ($1.6 \text{ GJ}/\text{m}^3$ assuming a density of $620 \text{ kg}/\text{m}^3$ [84]), with negligible sensible heat contribution (measured heat capacity $1\text{--}1.5 \text{ J}/\text{g}\cdot\text{K}$). It is considered as one of the most promising MOFs for heat transformation and storage. However, it has to be highlighted that the adsorption water vapor pressure of 55 mbar cannot be achieved in a low-temperature heat storage system without additional equipment for humidification. A main drawback of this material class is its current high cost of production; e.g. MIL-101 is available at approximately $52 \text{ k€}/\text{t}$ [85].

In Table 2-3, a summary of the energy densities and desorption/adsorption temperatures of the most promising adsorption materials is presented. It is evident that material energy density values are lower compared to pure salt hydrates. However, the investigated adsorption materials do not present large instability issues at system operating conditions. Moreover, corrosiveness or toxicity issues were not found. Concerning AlPOs, SAPOs and MOFs, maximum discharging temperatures of 40°C were set during tests; therefore, their ability to produce higher temperature heat is not investigated yet. Zeolites, on the other hand, presented adsorption temperatures suitable for low temperature heating and DHW production.

2.1.3. Composites

Sorption heat storage through chemical reactions, and in particular with salt hydrates, is of main interest. Chemical reactions have high theoretical energy densities, desorption temperatures achievable with solar thermal collectors or with waste heat, and discharge temperatures useful for low temperature heating. However, many issues are still present at material level like overhydration and deliquescence at low temperatures, material decomposition at high temperatures, degradation after few cycles, poor thermal conductivity and low power output [32,46,87,88]. In order to overcome these disadvantages, composite materials for heat storage purposes are being largely investigated. They consist of at least two materials in which, in general, one gives structural support (host matrix) and the other is the active material that undergoes the sorption reaction. The host matrix should have a large porosity in order to retain the largest amount of active material possible. However, a compromise between pores occupied by the active material and free pores has to be present in order not to impede the sorbate transport [88]. Other functions of the host matrix are to increase the composite thermal conductivity and stability [89]. The matrix can provide also sorption heat if the pore size is small but the amount of salt uptake decreases. On the other

hand, large pores are able to retain larger amount of salt but the host matrix will not participate in the sorption process. For example, a matrix of zeolite 13X could provide a consistent amount of sorption heat and participate in the heat storage process, however the adsorbent desorption temperature should be achieved in order to utilize its heat of sorption. The sorption process of salts hydrate/porous matrix composites includes a non-linear combination of the characteristics of an adsorption system and a chemical reaction Section 2.1.1 system [90]. The result is typically a type VI adsorption isotherm in which each sorption step reflects a chemical reaction between the salt and the sorbate [91]. It is expected that the gas–solid reaction of a confined salt is much faster than a bulk one since the rate of sorption is controlled by the intra-particle vapor diffusion [92]. A review of current studies on composite materials is hereby presented together with the experimental operating conditions and the main findings.

Casey et al. [93] characterized salt composites (CaCl_2 , MgSO_4 , $\text{Ca}(\text{NO}_3)_2$, LiNO_3 and LiBr) with matrices of silica gel, zeolite 13X and vermiculite. Pure matrices followed a type I isotherm behavior, while impregnated ones typically followed type IV isotherms with hysteresis cycles. An increased pore size distribution was observed for zeolite 13X composites, probably because of the destruction of the micro-pores network due to expansion/reduction of the impregnated salt. Matrices of silica gel and activated carbon showed less of this behavior due to a stronger pore-wall structure. For vermiculite samples, no damage of the porous structure was shown. In non-vermiculite based samples, a reduction of the meso-pores was present; therefore, less sorbate could be taken up by the material. Two composites with a matrix of vermiculite impregnated with CaCl_2 or LiBr performed best in terms of energy density (0.179 and 0.167 GJ/m^3 respectively) and moisture uptake between 30 and 140 °C. The salt content of the two composites, based on the bulk densities reported by the authors, was estimated to be approximately 56% and 65% for the sample with CaCl_2 and LiBr , respectively. However, energy density values are relatively low considering that a water storage with a temperature step of 50 °C can store approximately 0.2 GJ/m^3 .

Druske et al. [88] tested composites made by impregnation of porous matrices (carbon foam media and expanded natural graphite) into salts (KCl and CaCl_2) with the aim to prevent deliquescence and improve water transport into the materials.

Dehydrations at 200 °C and hydrations at 25 °C and 20 mbar of water vapor pressure were performed on samples of 10–20 mg. A higher salt content was achieved in graphite by impregnating molten salts rather than aqueous salt solutions. The composites showed improved heat conductivity and sorption behavior compared to pure salts. In particular, expanded natural graphite in powder and CaCl_2 showed the best performance with a water uptake/release of approximately 0.45 $\text{g}_{\text{H}_2\text{O}}/\text{g}$, a thermal conductivity in the range of 0.74–1.64 $\text{W}/(\text{m}\cdot\text{K})$, and an energy density of 1268 J/g , or 0.63 GJ/m^3 .

Liu et al. [94] developed a new composite material by impregnating the mesopores of Wakkanai siliceous shale (WSS) with 9.6 wt% of LiCl . As a comparison, a composite made of WSS impregnated with CaCl_2 was also used. Samples of the composite were tested with TGA and DTA. Next, a two liters honeycomb reactor with 36 channels/ cm^2 made of the same composite was tested in an open system with a dual chamber for desorption and sorption phases. The desorption process was performed at 150 °C and 5 mbar. The sorption process started at 35 °C while the sample was connected to an evaporator kept at 15 °C and 16.8 mbar of water vapor pressure. Isotherms measurement showed hysteresis due to capillary condensation, and no major differences have been observed between the experiments in an open and closed system. Three sorption processes were identified: heterogeneous adsorption of water onto the pores surface, adsorption (chemisorption)

of water vapor onto the salt surface, and liquid absorption into the salt. The limiting factor of the water sorption process was the formation of a hygroscopic salt solution film near the channels surface. The reactor was able to deliver hot air above 50 °C for approximately 350 min, with a desorption temperature of 120 °C and a sorption temperature and water vapor pressure of 25 °C and 22.1 mbar, respectively. By decreasing the desorption temperature, the maximum hydration temperature also decreased, together with the sorption time. The reactor energy density was approximately 0.2 GJ/m^3 for a temperature step due to sorption of 20 °C, a sorption temperature of 25 °C, and a previous desorption temperature of 120 °C. Flow rates during the sorption process influenced the peak temperatures and the sorption time: a lower flow rate implied lower temperatures maintained for longer periods, and vice versa for high flow rates. The authors assessed the system stability by performing 250 sorption/desorption cycles, and no changes in the water sorption amount were detected. However, those tests were performed with a desorption temperature of 60 °C, which implied hydration peak temperatures below 50 °C and shorter hydration times compared to a system previously regenerated at 120 °C.

Opel et al. [95] investigated composites made with physical mixtures of $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$, graphite, copper, zeolite A, and sand. Measurements at a water vapor pressure range of 12–22 mbar were performed. During hydration, a flow temperature of 35 °C was kept while for dehydration, temperature programs starting from 25–35 °C up to 130–200 °C at 0.1, 1 and 5 °C/min were performed. Materials stability was assessed by carrying out multiple dehydration/hydration cycles. The most interesting result showed that the addition of graphite to $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$ increased the overall composite conductivity allowing reactions at 10–15 °C lower. This effect was present for high heating rates (5 °C/min) and absent for low ones (0.1 °C/min). Thermal decomposition (hydrolysis) was present for temperatures greater than 125 °C, and had a peak at 160 °C. Moreover, decomposition under vacuum happened at even lower temperatures. Thermal decomposition of composite $\text{MgCl}_2\cdot 6\text{H}_2\text{O}/\text{zeolite}$ followed an almost linear behavior, similar to pure $\text{MgCl}_2\cdot 6\text{H}_2\text{O}$, indicating that zeolite was suitable as supporting agent but not as additive. Overhydration decreased the performance of $\text{MgCl}_2\cdot 6\text{H}_2\text{O}/\text{zeolite}$ after 35 cycles, which could be recovered up to 80–90% of its initial reactivity by grounding the sample with a mortar, confirming that overhydration was the main cause of its reactivity decrease.

Yu et al. [87] proposed a method to produce a composite made of LiCl and a host matrix of activated carbon (AC) as porous matrix, a silica solution (SS) as a binder to increase mechanical strength, and expanded graphite treated with sulfuric acid ENG-TSA to enhance thermal conductivity. The composite was tested, and it was proven that the water uptake was mainly controlled by the amount of LiCl ; the other components were mainly supportive. The sample was completely dehydrated at 90 °C in two reaction steps, with the first step occurring before 50 °C. Rehydration conditions were at 30 °C and 25.4 mbar of water vapor pressure. Expanded graphite increased thermal conductivities in the range of 2–2.8 $\text{W}/(\text{m}\cdot\text{K})$, approximately 14 times higher than the pure Activated Carbon/ LiCl composite. However, it decreased the amount of water uptake due to slow kinetics caused by a worse water transport. Hysteresis was observed between sorption/desorption cycles. The expected material energy density of the composites was in the range of 0.72–1.43 GJ/m^3 , for the abovementioned temperatures and pressures, depending on the amount of LiCl .

Tanashev et al. [96] investigated the thermal conductivities of inorganic salts (CaCl_2 , MgCl_2 and LiBr) in porous matrices (silica gel and alumina) in function of the water uptake. For silica-based composites, disregarding the salt impregnated, a typical behavior

in thermal conductivity enhancement was present: a threshold was reached at a typical value, after which a steep thermal conductivity increase was present. This threshold corresponded to the complete matrix meso-pores filling (Fig. 2-5), after which the formation of a salt solution outside the pores was present. For alumina matrix, this threshold was not present probably due to the alumina matrix pores structure, which led to a uniform pore filling from the salt.

Also Fopah-Lele et al. [89] studied the thermal conductivity of composites and salt hydrates. TGA/DSC measurements were performed with 50 ml/min of N_2 flow, 100 mg samples of anhydrous material, and temperature programs ranging from 100 to 200 °C. The reaction rate increased by increasing the salt thermal conductivity, also reported by Tae Kim et al. [97], which is typically low for pure salts (0.1–0.5 W/(m·K)). Thermal conductivity of $CaCl_2$ was in average 0.39 W/(m·K), but when impregnated in silica gel or vermiculite, its conductivity increased to 0.83 W/(m·K) and 0.74 W/(m·K), respectively. Finally, the authors showed that effective thermal conductivity of both pure salts and composites was strongly dependent on material porosity.

Ponomarenko et al. [98] characterized a composite, previously dehydrated at 80–100 °C, made with a porous matrix of nano-structured mesoporous silica SBA-15 impregnated with a saturated salt solution of $CaCl_2$ (43 wt%). TGA/DSC/XRD and N_2 adsorption measurements were performed. Isotherms were measured at 50 °C and 0–50 mbar of water vapor pressure. The melting point temperature of the salt was lower for small particles confined into pores due to the Gibbs-Thompson effect: small particles melt at lower temperature than the bulk substance due to increased surface energy. The effective diffusion coefficient was found close to the Knudsen diffusion coefficient, confirming that Knudsen diffusion was the rate-limiting step. This meant that the reaction of the salt was faster than the water transport inside the pores (intra-grain diffusion). Hydration reactions were present at 2.5–4 times lower relative vapor pressure than for the bulk $CaCl_2$. Matrix pore size determined the pressure at which the salt hydrate experienced the hydration reactions. A larger pore size implied a lower relative sorbate pressure necessary for the hydration reaction.

Hongois et al. [99] tested a composite of $MgSO_4$ 10–25 wt% impregnated in zeolite 13X for long-term seasonal heat storage in which the humidity from the exhaust air of a building was used for the sorption reaction. The temperature lift comparison during sorption between a silica gel/ $MgSO_4$ composite and zeolite 13X/ $MgSO_4$ showed that a higher temperature increase could be reached with the latter (22 K and 30 K, respectively). TGA was performed to measure the water loss during dehydration, which at 150 °C resulted to be 80% of the initial water content. DSC measurements were also performed with a heating rate of 10 °C/min. The behavior of zeolite 13X/ $MgSO_4$ was very similar to pure zeolite but with higher DSC peaks at the maximum temperature, suggesting that the salt did not behave kinetically as a salt anymore. One possible hypothesis presented by the authors was a replacement of the charge balancing cations of zeolite 13X skeleton from Na^+ to

Mg^{++} . Lab-scale experiments and a sensitivity analysis were carried out in a not well-insulated reactor. Air mass flow and relative humidity were studied as parameters. At 8 l/min and 50% RH, only 45% of the theoretical energy storage density was present (648 J/g). The authors reported as possible cause the poor reactor insulation. An increase in air flow from 4 l/min to 8 l/min raised the maximum temperature lift from 15 to 26 K. The same hold for the relative humidity RH, which increased the temperature lift from 11 K to 34 K (RH 20–80%, respectively). A volumetric energy density of 0.6 GJ/m³ was measured for the composite zeolite 13X/ $MgSO_4$ 15 wt%, which is 27% more than the theoretical energy density of zeolite 13X (~0.47 GJ/m³). Concerning the cyclability, micro calorimetry experiments proved that after three cycles the amount of energy that could be extracted from the system was the same.

Jänchen et al. [69] compared the zeolites previously investigated in Section 2.1.2 with two composites of silica gel and $MgCl_2/CaCl_2$, concluding that the former had higher desorption temperatures (180 °C and 120 °C, respectively) and lower energy densities compared to the composites (0.4–0.5 and 0.6 GJ/m³, respectively). However, the authors highlighted that composites could be used only if good heat and mass transport can be achieved within the sorption bed.

In a further study, Jänchen et al. [78] found an opposite trend between pure adsorbents and composites. They used TGA/DSC, micro calorimetry and sorption isotherms to characterize low silica X zeolites, microporous aluminophosphates, and a composite of $CaCl_2$ (30 wt%) impregnated in a matrix of attapulgite. The maximum desorption temperature was 400 °C at 5 K/min heating rate in N_2 flow. LiLSX (lithium zeolite molecular sieve) showed the highest energy density for a hydration temperature of 40 °C (1184 kJ/kg_{adsorbent}), while the composite showed the lowest (871 kJ/kg_{adsorbent}). In hydrations at 60 °C, the energy density of LiLSX decreased by 7.85% while for the composite a 62% reduction was present (1091 and 330 kJ/kg_{material} respectively). AlPO₄ and SAPO molecular sieves had energy densities in between LiLSX and the attapulgite/ $CaCl_2$ composite.

Also Posern et al. [100] tested a composite material made of attapulgite and two salts, $MgSO_4$ and $MgCl_2$, with different mixing ratios. Their aim was to take advantageous properties of both materials to impede the thermal decomposition at high temperatures and deliquescence at low temperatures of $MgCl_2$. The measured energy density of the composite with a salt content of 32.8 wt% at 40 °C (80/20 wt% salts solution of $MgSO_4$ and $MgCl_2$, respectively) was 1590 kJ/kg at 30 °C and 36 mbar of water vapor pressure, with a previous dehydration at 130 °C. The more $MgCl_2$ was present in the composite, the more heat was released due to a lower deliquescence relative humidity (DRH) of the material. Therefore, more water was quickly absorbed, but a salt solution that leaked from the solid sorbent was formed. The authors did a preliminary investigation on the amount of $MgCl_2$ that could be present in the salt solution given a relative humidity value. It is noteworthy that a 10% concentration of $MgCl_2$ in a mixture of $MgCl_2/MgSO_4$ could increase the heat of sorption by 50% compared

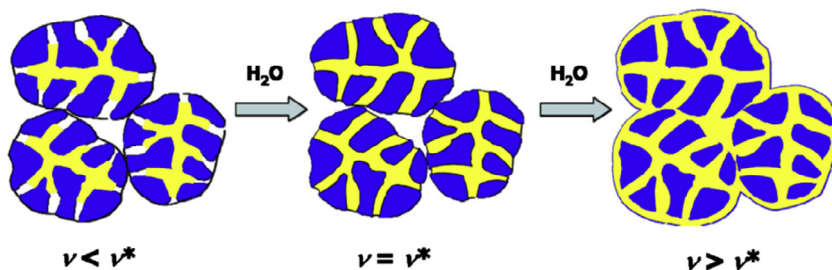


Fig. 2-5. Schematic picture of the relation between amount of salt impregnated in pores and thermal conductivity [96].

to a solution of pure MgSO_4 impregnated in the attapulgite, and the RH would be above or equal to the DRH value of the material. However, cyclability of the material, and therefore the thermal decomposition and degradation were not investigated.

Ristić et al. [101] studied the water sorption properties of a composite made of iron silicate (FeKIL2) and CaCl_2 . XRD/SEM/PSD/TGA/DSC (10 K/min, 40–150 °C)/ N_2 physisorption were performed. PSD showed a pore distribution from 5 to 30 nm, with a lower overall pore volume compared to pure FeKIL2 . The composite had a water uptake of 0.58 $\text{g}_{\text{H}_2\text{O}}/\text{g}$ referred to the dried material, more than three times compared pure FeKIL2 . Moreover, it could be almost completely dehydrated at 120 °C. Cyclability was assessed for 20 cycles with a thermal program from 40 to 150 °C, and a 3.6% linear loss of active material was measured due to degradation. After cycling, the isotherm of the composite was significantly changed by having a wider hysteresis, and the composite pores were reduced after the thermal cycles. A heat storage capacity of 560 kJ/kg was estimated with desorption and sorption conditions of 150 °C - 56 mbar and 10 °C - 12 mbar of water vapor pressure, respectively.

Korhammer et al. [102] investigated composites based on CaCl_2 with different matrices, namely expanded natural graphite in powder and pellet forms and activated carbon foam. The active material was impregnated in solution or molten form, and accounted for 31–90 wt%. TGA/DSC analyses were carried out to estimate the energy storage density and water uptake of the 10–20 mg samples. Hydration conditions were set at 25 °C with a water vapor pressure of 10, 17, and 20 mbar. Among the conclusions, composites based on CaCl_2 and expanded natural graphite resulted in water uptakes of 0.67–0.72 $\text{g}_{\text{H}_2\text{O}}/\text{g}_{\text{dried material}}$ and energy storage densities of 1451–1310 J/g for the salt impregnated in solution (87 wt%) or molten (90 wt%) form, respectively.

In Table 2-4, a summary of the performance and main findings of the literature on composite materials is presented. The water vapor pressure, when available, is referred to hydration reactions. The two values of temperature are referred to sorption and desorption, respectively. Energy densities are often the highest or most achievable ones related to the most promising composite material in the study, if more composites were investigated. It is clear that research at material level is still needed to find a suitable composite material that can satisfy the requirements of a long-term low-temperature heat storage system; in which high energy density, material hydrothermal stability at system operating conditions, and other relevant requirements (Table 2-1) need to be satisfied. It is noticeable that the research is still investigating a broad range of materials to be used as matrices and active materials; highlighting the fact that the scientific community is still in a screening phase. Moreover, further requirements have to be satisfied at technical and economic levels. For example, zeolite 13X showed good performance as host matrix beside as pure active material, leading to a 27% higher energy density of a composite impregnated with MgSO_4 (15 wt%) compared to pure zeolite 13X. However, its high cost and desorption temperatures, have to be taken into account because it will largely increase the system costs and decrease the system efficiency. Moreover, due to the small pore size, it cannot incorporate a large amount of salt.

Composite materials, compared to zeolite 13X, if stable at system operating conditions, can lead at least to lower system costs. On the other hand, compared to pure salt hydrates, composites can be stable materials. Considering a composite made by a salt and an inert matrix, the energy density might not be much higher than e.g. pure zeolite 13X, supposing suitable operating conditions. However, if the material costs are lower, the system might be able to become commercially attractive even if a relatively large volume of material is required. Ultimately, the active material selection depends on the intended application that imposes the system

operating conditions. As suggested by Aristov et al. [91], research should continue to be focused on systematic testing of novel adsorbents initially used for different purposes, and tailoring of new adsorbents/composites that can perform at their best at the selected system operating conditions.

2.2. Liquid absorption

Systems based on liquid absorption rely on a relatively established and developed technology. For example, in refrigeration units, the working fluid consists of a binary mixture of an absorbent and a refrigerant. Two of the most used mixtures are $\text{LiBr}/\text{H}_2\text{O}$ and $\text{H}_2\text{O}/\text{NH}_3$, and systems based on those working pairs have COP ranges of 0.7–1.2 [103] and 0.3–0.6 [104], respectively. The basic working principle can be explained with a thermodynamic cycle with generator, condenser, evaporator and an absorber (Fig. 2-6, left). The cycle is described assuming a salt/water working couple in which the water takes the role of the refrigerant. In the generator, high temperature heat is used to separate the refrigerant from the salt solution by evaporation. The refrigerant vapor is then condensed in the condenser and heat at intermediate temperature is rejected to the ambient. Next, the refrigerant enters into the evaporator, at a lower pressure, in which ambient heat is used to evaporate it. Then, the refrigerant vapor enters the absorber in which the strong solution from the generator is present and through an exothermic process in which heat is rejected, the strong solution re-incorporates the initial amount of refrigerant becoming weaker in salt concentration. A circulation pump is then used to bring the solution from the absorber to the generator. The heat exchanger between the generator and the absorber can increase the system COP by pre-heating of the strong solution.

Grassie et al. [107] proposed a $\text{LiBr}/\text{H}_2\text{O}$ system with absorbent and refrigerant storages. Xu et al. [108] proposed to use solar thermal collectors directly as generators in an absorption cycle powered by solar energy. In order to shift electricity demand to off-peak hours, a compressor can be added to drive an absorption machine instead of solar energy, as proposed by Voigt [109].

Liu et al. [106,110] investigated different absorption couples implemented in a system for long-term storage of domestic space heating, namely $\text{CaCl}_2\text{-H}_2\text{O}$, Glycerin- H_2O , $\text{LiBr-H}_2\text{O}$, $\text{LiCl-H}_2\text{O}$, $\text{CaCl}_2\text{-H}_2\text{O}$, $\text{NaOH-H}_2\text{O}$, and $\text{NH}_3\text{-H}_2\text{O}$. The main findings were that every working couple presented some disadvantages (e.g. low storage capacity of CaCl_2 , and high price of LiCl_2). Moreover, temperatures suitable for DHW production were not achieved. Next, the authors proposed to allow partial crystallization of the salt during the storage period thereby increasing the system energy density. During summer, the solution is concentrated by evaporating water vapor, and during the storage period, partial crystallization is allowed into the tank for certain absorption couples so that a large concentration gradient can be present, allowing a higher energy density of the process. Then, during winter, the solution absorbs water vapor and releases the stored heat. Special care has to be taken in the selection of the charging temperature to avoid crystallization during the desorption process. The system layout is displayed in Fig. 2-6 right. The operational limits of this kind of system are imposed by the crystallization of the strong solution above certain absorbent concentrations, and the maximum evaporator temperature that can be reached by the low temperature heat source.

Research on a multistage system based on $\text{NaOH-H}_2\text{O}$ has been carried out by Weber et al. [111] and it is currently under research by Fumey et al. [112–115] within the COMTES European project framework. The aim of the system is to deliver energy for space heating and domestic hot water. Due to the fact that the charging and discharging processes occur at different moments in time, condenser and evaporator are the same component. An initial system

Table 2-4
Summary of investigation on composites materials for sorption heat storage.

Authors	Matrices	Salts	Salt (wt %)	Experimental conditions		Energy density (GJ/m ³)	Main findings
				T (°C)	p _{H2O} (mbar)		
Casey et al. [93]	Silica gel, zeolite 13X; vermiculite	CaCl ₂ , MgSO ₄ , Ca(NO ₃) ₂ , LiNO ₃ and LiBr	2–65****	30–140	–	Up to 0.18	Micro-pore network of some matrices partially destroyed due to cyclical salt expansion/shrinking
Druske et al. [88]	Carbon foam; expanded natural graphite	KCl; CaCl ₂	63–90	25–200	20	Up to 0.63	Improved heat conductivity and higher water uptake
Liu et al. [94]	Wakkanai siliceous shale (WSS)	LiCl; CaCl ₂	9.6	15–150	22.1	0.2	Discharge temperature above 50 °C with 22.1 mbar of water vapor pressure at 25 °C
Opel et al. [95]	Graphite, copper, zeolite A, sand	MgCl ₂	46–69	35–200	11.8–21.8	0.56*	Cyclability assessed for a desorption temperature of 60 °C Formation of salt solution limited the sorbate sorption process Adding graphite increased conductivity and allowed reactions at 10–15 °C lower for high heating rates Salt decomposition above 125 °C did not allow zeolite to be used as active material
Yu et al. [87]	Activated carbon, silica solution, expanded graphite	LiCl	32–45	30–90	25.4	0.72–1.43	Expanded graphite increased thermal conductivity and decreased water uptake. Hysteresis present during the de/sorption cycles
Tanashev et al. [96]	Silica Gel; alumina	CaCl ₂ , MgCl ₂ and LiBr	30–75	–	–	–	Thermal conductivity of composite had a large increase after a threshold value, which coincided with the complete matrix mesopores filling of salt in silica gel For alumina, this behavior was not present probably due to the material pores structure
Fopah-Lele et al. [89]	Silica gel; vermiculite	CaCl ₂	–	–	–	–	Thermal conductivity increase up to 90–112% compared to pure salt
Ponomarenko et al. [98]	Silica SBA-15	CaCl ₂	43	50–100	0–50	–	Hydration happened at a 2.5–4 times lower vapor pressure than for the pure salt
Hongois et al. [99]	Zeolite 13X; silica gel	MgSO ₄	15	25–150	21.5	0.6	Temperature lift of 30 °C achieved with Zeolite 13X matrix; no material degradation measured after three cycles
Jänchen et al. [69]	Silica Gel; Aluminosilicate	MgCl ₂ ; CaCl ₂	30	–	–	0.6	Composites could be used only if good heat and mass transport were achieved within the material. Max discharge temperature of 40 °C for composites
Jänchen et al. [78]	Attapulgit	CaCl ₂	30	40–400	–	1.08 (40 °C) 0.41 (60 °C)**	Low energy density of the composite measured at a discharge temperature of 60 °C
Posern et al. [100]	Attapulgit	MgSO ₄ ; MgCl ₂	33	30–130	36	880 kJ/kg***	Salt solution formation due to high deliquescence of MgCl ₂
Ristić et al. [101]	FeKIL2	CaCl ₂	7	40–150	11.8–55.3	560 kJ/kg***	Stability assessed after 20 cycles: 3.6% decrease of water uptake
Korhammer et al. [102]	Expanded natural graphite; Activated carbon foam	KCl; CaCl ₂	31–90	25–200	10–20	1451–1310 kJ/kg***	Thermal conductivity tripled for sample impregnated in expanded natural graphite. Water uptake increased to 160% and 195% after dehydrations at 100 °C and 200 °C, respectively, compared to untreated CaCl ₂

* calculated for the composite MgCl₂·6H₂O/Zeolite (1:1,17) assuming material densities of 1569 and 900 kg/m³ respectively.

** Calculated by assuming densities of attapulgit and calcium chloride of 854 and 2150 kg/m³ respectively.

*** Composite density not available.

**** Estimated from the bulk densities of the materials given by the authors.

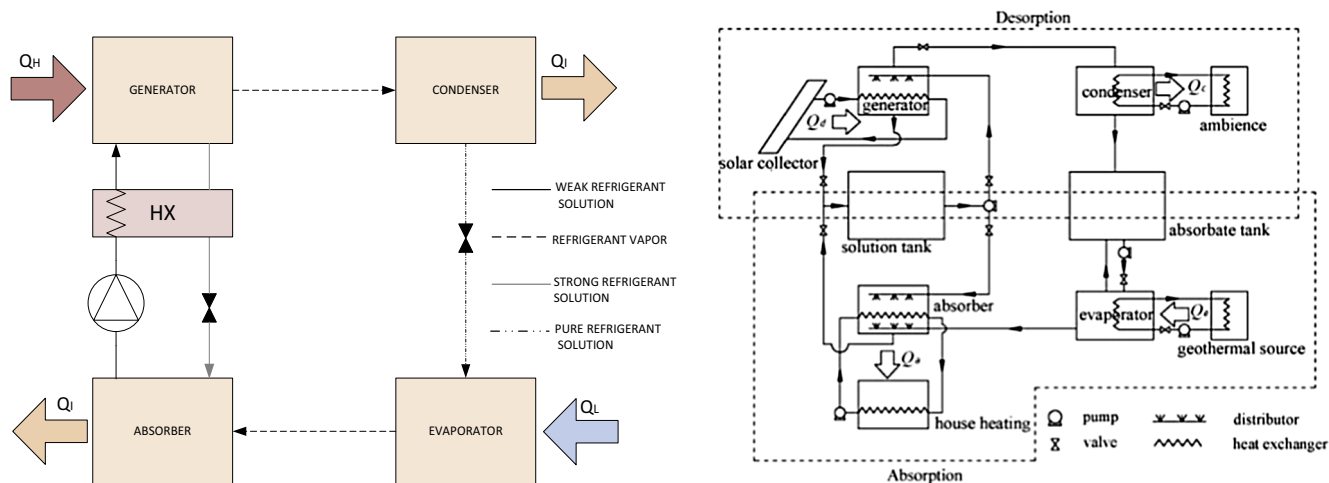


Fig. 2-6. Left: Single stage scheme of an absorption refrigeration system; adapted from [105]. Q_H = high temperature heat, Q_i = intermediate temperature heat, Q_L = low temperature heat, HX = heat exchanger. Right: Seasonal heat storage system based on liquid absorption [106].

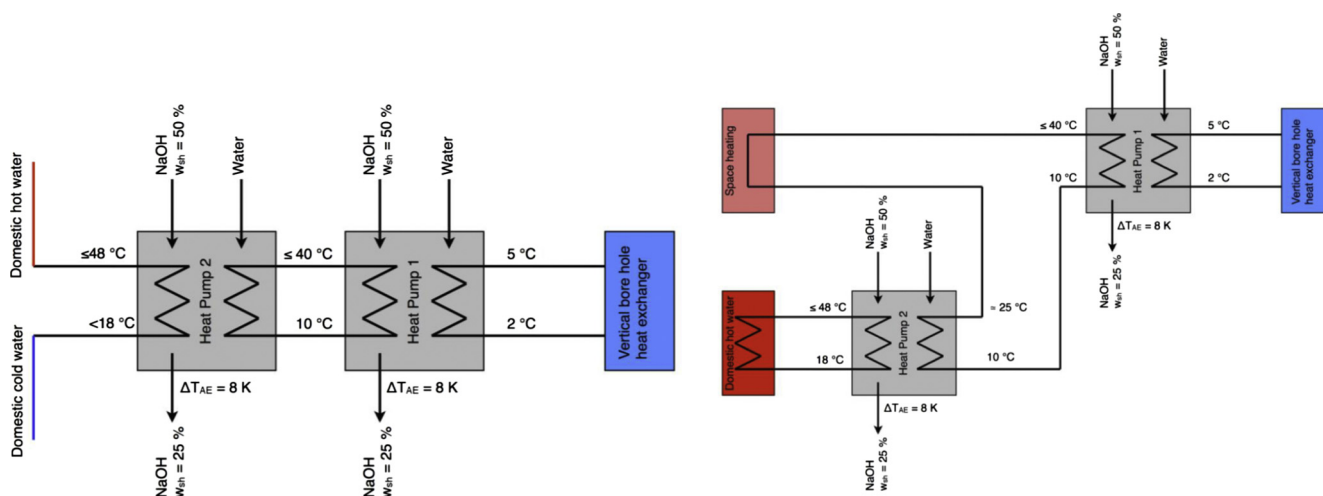


Fig. 2-7. Left: Series connection of two stages. Right: Series connection of two stages with space heating implemented in between [114].

layout [114] consisted of connecting two single system stages in series, resulting in a double stage heat pump system (Fig. 2-7 left). However, this configuration led to a substantial decrease in the system energy density. The authors proposed a possible solution to optimize the system performance by using the water after the first stage for space heating, and then use it in the evaporator of the second stage (Fig. 2-7 right).

In both setups, the required return temperature of 10 °C in the first heat pump limited the maximum achievable DHW temperature of the second heat pump. Moreover, a larger amount of solution was necessary to deliver the same final energy, decreasing the system energy density. To avoid the abovementioned design issues and increase the system flexibility, a prototype was realized connecting the components in parallel [112]. A single absorber/desorber and evaporator/condenser were implemented. Three storage tanks were used as buffer storage at three different temperature levels for the evaporator at low temperature, space heating, and DHW. With this system, single charging of different storage tanks was possible.

In order to have a larger concentration difference and to increase the absorption cycle energy density, Lourduoss et al. [116] investigated a three-phase system in which during the charging process solid crystals were also formed. Different working

pairs were investigated for this purpose. In particular, with a LiCl/H₂O system, an energy density of 1.1 GJ/m³ and a COP of 1.58 were obtained. A similar work was also carried out by Bales et al. [117] at SERC (Solar Energy Research Center) in Sweden. The authors achieved an energy density of 0.91 GJ/m³ with heat released at approximately 30 °C. Since the focus of this work is on solid-gas reactions with water as sorbate, liquid absorption systems will not be investigated further. Literature suggestions on liquid absorption systems for thermal energy production and storage are [105,118,119].

2.3. Conclusions on materials review

In the first part of this work, a review of the sorption materials categories is performed. Special focus is on promising materials for long-term low-temperature sorption heat storage applications based on solid/gas reactions.

Promising materials of the chemical reaction category are salt hydrates, which possess high theoretical energy densities. However, they present several issues for their implementation in pure form such as overhydration and deliquescence at low temperatures (e.g. MgCl₂), decomposition at high temperatures, slow kinetics leading to a low temperature lift (e.g. MgSO₄), corrosiveness and

toxicity (e.g. Na_2S), low mass transport due to the material macrostructure and, if used in closed systems, low heat transport because of a typically low thermal conductivity.

Adsorption materials have the main advantage of a more hydrothermally stable behavior. However, since the main sorption phenomenon is adsorption, lower energy content is intrinsic in those materials category. Moreover, they have typically higher costs per mass compared to salt hydrates, which further decreases their attractiveness if coupled with the fact that they have lower energy densities. Costs reduction could be achieved by optimizing manufacturing processes and by economies of scale. Zeolite 13X is considered as one of the most promising materials among the zeolites. Experiments achieved temperature lifts of 35–45 °C in lab-scale reactors and micro-scale experiments at system operating conditions. However, the main drawback is a too high desorption temperature, which are difficult to achieve by heat sources such as solar thermal collectors at a reasonable efficiency.

Silico-/Aluminophosphates and metal organic frameworks presented also a promising performance in terms of water uptake relative to the amount of sorbent. Moreover, they require lower desorption temperatures compared to zeolites. APO-Tric and MIL-101 resulted to have the most promising performances among these materials categories, with measured energy densities, at adsorption temperatures of 30–40 °C, of 0.86 and 1.6 GJ/m³, at water vapor pressures of 12 and 55 mbar, respectively. Moreover, DHW production would not be possible at the previously mentioned heat release temperatures. Research on this kind of materials for thermal storage is still at material-scale stages, and a proper experimentation at prototype-scale is required. From the economic perspective, the utilization of the abovementioned materials for seasonal heat storage would drastically increase the system costs.

Composite materials are being researched with the aim to reduce instabilities at material levels of salt hydrates. The host matrices can be made of a porous material that could be also used as active adsorption material if a sufficiently high desorption temperature is achieved. However, small pore sizes necessary for the matrix to be involved in the sorption process lead to low salt filling in the matrix. However, also inactive materials such as expanded graphite, sand, silica gel and vermiculite have been tested for solely structural support. Several studies have been reported but research of promising working pairs is still ongoing. General issues are a reduced mass transport within the matrix pores and salts deliquescence or overhydration with possible leaking of the active material. Finally, the experimental conditions of the investigated studies are heterogeneous and some of them are far from typical conditions of low-temperature heat storage.

Regarding liquid absorption for heat storage, several materials and system layouts are under investigation for space heating and domestic hot water production. Among the issues, temperatures high enough for DHW production were hard to achieve with an acceptable energy density. Several studies investigated the possibility to allow partial recrystallization of the active material within the storage tank, thereby increasing the system energy density. However, additional complexity is added to the system.

3. Sorption heat storage systems

In designing a low-temperature long-term sorption heat storage, materials investigation is only one of the challenging fields to be tackled. The main criteria for the suitability of a material for sorption heat storage purposes (Table 2-1) have to be satisfied also at system-scale. The focus of this section is on the current state of the art of sorption systems for long-term low-temperature heat storage purposes using solid/gas reactions with water as sorbate. The main system layouts, reactor arrangements, system param-

eters, and performances of the existing prototypes are presented and discussed in the next paragraphs.

3.1. System design

3.1.1. Open and closed systems

Sorption systems can be divided into open and closed systems (Fig. 3-1). An open system exchanges mass and energy with the environment, and operates typically at ambient pressure. The sorbate is transported together with other species, e.g. water vapor into the airflow. The main disadvantages of these systems are that a fan is needed to drive the moist flow through the reactor, a humidifier can be required to reach the desired sorbate vapor pressure, and the temperature step over the reactor is limited by the thermal mass of the flow, which requires a heat recovery unit to obtain temperatures useful for space heating and DHW production. Moreover, due to the fact that mass is also exchanged with the environment, hazardous materials and components cannot be employed. The main advantage is that the system is generally simple, not pressurized, it has a good and controllable heat transfer, and requires less components compared to a closed one. Closed systems exchange only energy with the environment, and are normally evacuated in order to have a satisfactory sorbate transport between the reactor and the sorbate reservoir.

The main system advantage is that a fan is usually not needed since the sorbate is driven by the vapor pressure difference between the system components, a faster transport mechanism compared to diffusion in open systems [120]. On the other hand, main disadvantages are that, often, the system needs to be periodically evacuated due to the formation of incondensable gases that block the sorbate flow to the condenser. Moreover, the presence of the adsorbate storage, condenser and evaporator decrease the overall system energy density. A conceptual scheme of open and closed systems is shown in Fig. 3-1 while the main advantages and drawbacks of both options are shown in Table 3-1. Abedin et al. [121] performed an energy and exergy analysis on open and closed systems. The main findings were that the investigated open system had higher overall efficiencies compared to the closed ones. However, system basic parameters like sorbate flows, discharge temperatures and pressures had major influence on the analysis. Therefore, a universal conclusion on the better performance of an open or closed sorption system could not be drawn.

3.1.2. Reactors design and issues

3.1.2.1. Reactor layout. Reactors for sorption heat storage systems can be divided into two main categories from the active material location perspective: integrated and separate. Integrated reactors contain the total amount of the system active material. Therefore, the material does not have to be moved once placed inside it. The main disadvantage is that a large reactor able to handle the de/sorption conditions has to be built.

Separate reactors require the material to be injected and extracted from it; therefore, a material transport system has to be present resulting in a more complex design. However, the material storage can be made of cheaper materials since it does not have to withstand the reaction operating conditions, and a smaller reactor has to be designed compared to the integrated one, which results also in a smaller thermal mass [123].

Modular reactors can be considered a sub-category of the integrated reactors, since the active material is not transported, nor does the entire amount of material have to be flushed by the sorbate flow during system operation, causing large pressure drops. The material is stored into several smaller reactors with smaller thermal mass that have a volume optimized for the system purpose. Modular reactors have the advantage that an extension/reduction of the system-scale needs low technical effort and can

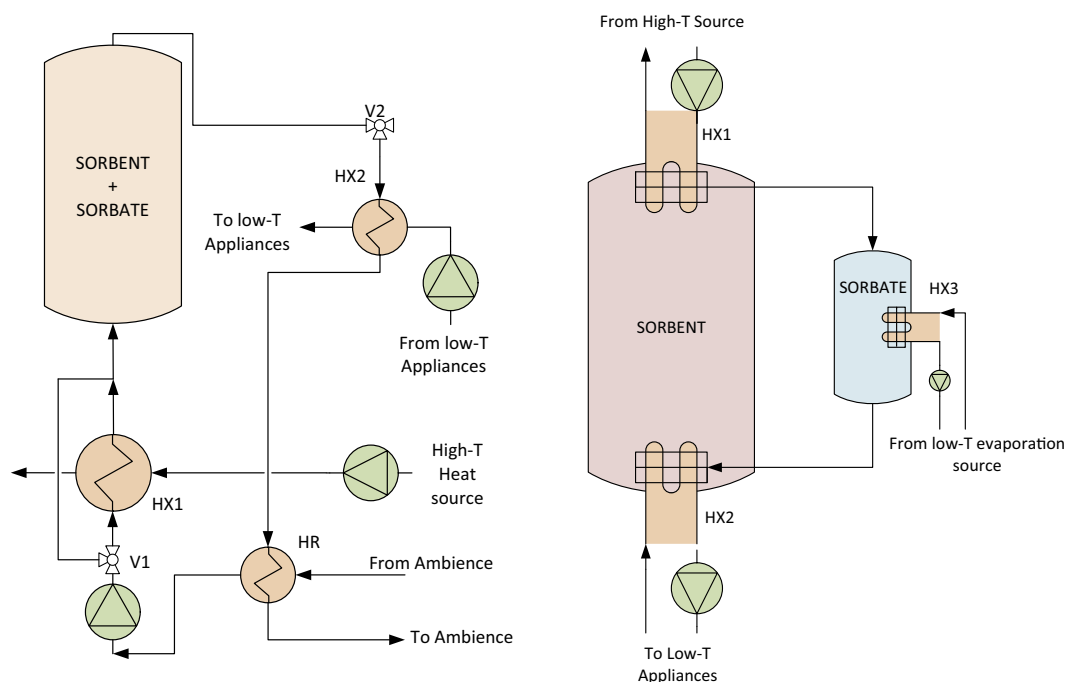


Fig. 3-1. Left: Open system design concept. During desorption, valve V1 directs the flow through the heat exchanger HX1 to be heated from a high-T source, and valve V2 bypasses HX2. During sorption, valve V1 bypasses HX1 and valve V2 directs the heated flow after sorption into the heat exchanger HX2 to transfer heat to the appliances and then to the heat recovery unit HR. Right: Closed system design concept. During desorption HX1 is used to separate sorbent and sorbate with a high-T heat source. Sorbate is then condensed in the sorbate tank in which HX3 used to remove the condensation heat. HX2 is not in function. During sorption, a low-T source evaporates the sorbate through HX3, which is transported by pressure difference back into the sorbate tank. The heat of reaction is removed through HX2. HX1 is not in function.

Table 3-1
Advantages and drawbacks of open and closed systems, partially from [122].

Type of system	Advantages	Drawbacks
Open	<ul style="list-style-type: none"> Atmospheric pressure Simple system Less components than close system Heat transfer increased by forced circulation 	<ul style="list-style-type: none"> Fan and humidifier often needed to drive the sorbate flow and provide partial humidification Sorbate safety requirements High sorbate flow leads to high pressure drops Mass transfer limiting step
Closed	<ul style="list-style-type: none"> Higher discharging temperature compared to open system at similar water vapor pressure No mass exchange with environment Can be used as an adsorption heat pump for cooling and heating 	<ul style="list-style-type: none"> Complex system Condenser/evaporator required Heat transfer limiting step Sorbate needs to be stored Periodical evacuation to avoid non-condensable gases Sorbate evaporation energy always to be provided

be done using standard procedures, achieving competitive prices compared to other solutions. A disadvantage of modular reactors is that each module might need additional volume for its own components leading to higher system costs.

De Jong et al. [120] suggested a possible operational strategy for modular reactors. Instead of on-demand delivery, which would require a reactor design for high peak powers, it is an option to discharge, e.g. daily, one module to heat up a conventional sensible storage system, and then provide the thermal power required with a mature and well-known technology. Some of the operational considerations were the following: the water storage has to store the sorption heat of at least an entire module; conventional storage has to afford the daily demand fluctuations; when the conven-

tional storage needs to be charged, an entire module is discharged. Another alternative considered was an open system with separate reactor and a periodical refilling of dried material and removal of hydrated material, which will be dried elsewhere e.g. where waste heat is available [124]. However, transportation costs have to be taken into account. In 2006, a preliminary investigation [125] for waste heat transportation modes in the industrial area of Nyköping (Sweden) showed that transportation of dried zeolites by train was the most cost effective solution.

Concerning the reactor charging strategy, Mette et al. [126] proposed a method to reduce the charging temperature of an open system by pre-drying the air at the inlet of the sorption reactor. In the system investigated based on zeolite 13X (CWS-NT, see Fig. 3-4 right), normally a dehydration temperature of 180 °C was applied. The authors proposed an additional adsorption unit based on the same sorption material to reduce the water content of the supply air during the desorption phase, before the air-to-air heat exchanger. With a reduced water content in the supply air, a desorption temperature of 130 °C was able to remove more water from the sorption reactor compared to the supply air at 180 °C without pre-drying. The additional adsorption unit was also regenerated at 130 °C. For the pre-drying process, additional sorption material and energy are required. The authors assumed that solar energy during summer was used for the desorption process. Therefore, the solar thermal collectors have to be sized to provide both desorption energy for the main sorption reactor and the additional adsorption unit.

3.1.2.2. Reactor design. The most common reactor configurations are packed bed for solid reactors and separate reactors for liquid reactors. However, different reactor designs were investigated for sorption heat storage systems in order to tackle main system issues such as control of the system heat capacity, heat losses reduction, and heat and mass transfer improvement [18]. Zondag et al. [127]

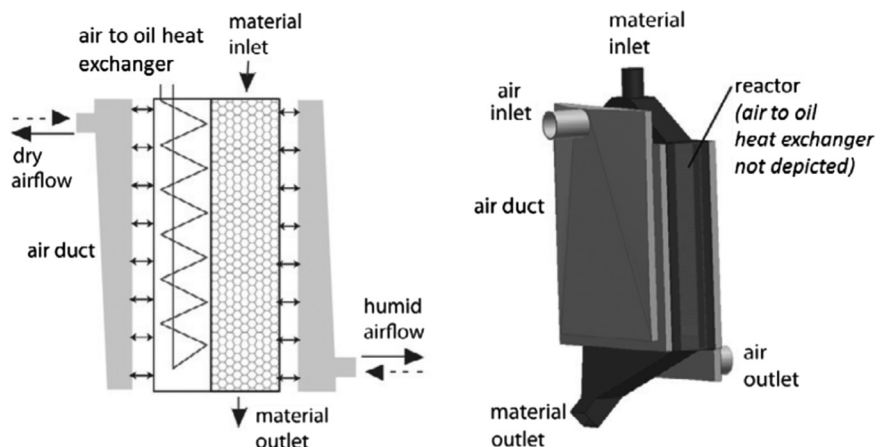


Fig. 3-2. Schematic of a separate reactor design [128].

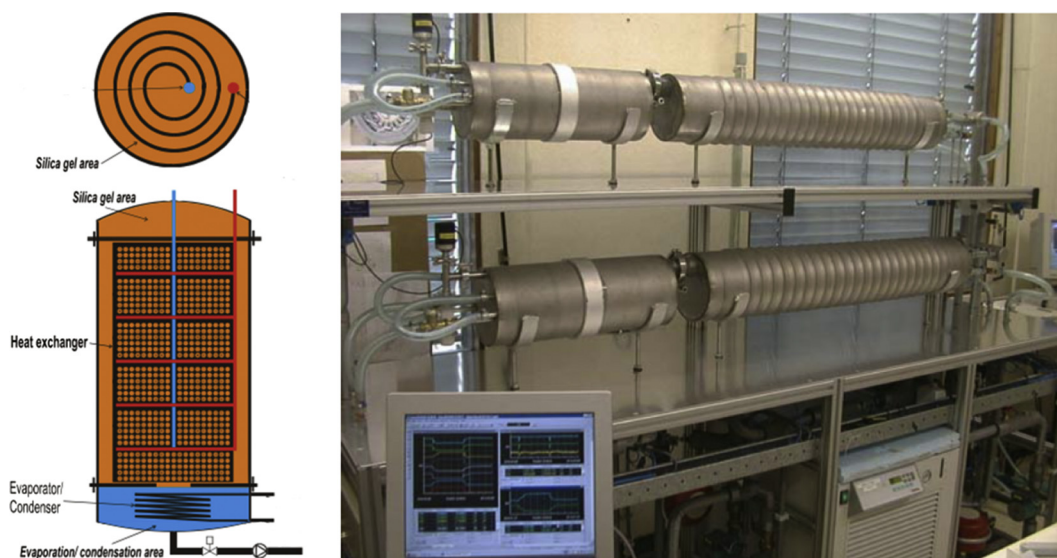


Fig. 3-3. Left: MODESTORE project reactor layout [131]. Right: SWEAT prototype [42].

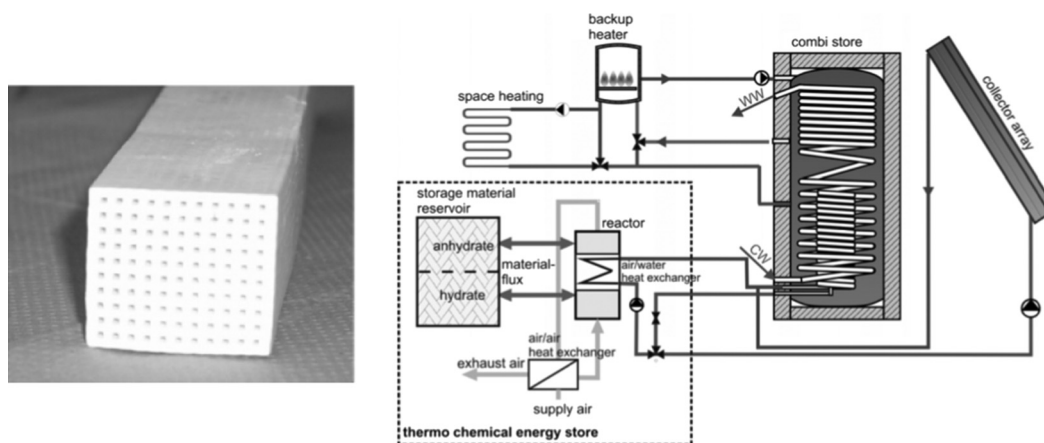


Fig. 3-4. Left: zeolite 4A monolith from the MonoSorp project [117]. Right: CWS-NT System layout [133].

investigated three reactor layouts: agitated reactor, fluidized bed reactor and gravity-assisted bulk flow reactor. The authors' conclusion was that an agitated reactor, and in particular a screw reactor, was the best option because active material stirring greatly

improved the system performances in their preliminary experiments. However, a main drawback of this option was that mechanical stirring could irreversibly damage the active material and might reduce reliability and increase maintenance costs for the

system. The use of layouts with extended surfaces increase heat transfer areas and guarantee a better heat transport from and to the active material, which has a generally low thermal conductivity. Finned tubes [120], plate heat exchangers [49], plate-fin heat exchangers and coated spiro-tubes [42] were possible design options. Extended surfaces are suitable if the volume change between de/sorption cycles is not significant. Large cross-flow areas with a minimum bed length [123] or porous matrices could be used to achieve a low pressure drop for the air flow. For example, Mette et al. [123] developed a reactor that could be operated both in fixed bed and quasi-continuous mass flow configurations. For the reactor concept, three considerations were decisive: large cross flow section area for the airflow and minimal material width in flow direction for pressure losses minimization; material transport to be realized in a reliable and technical inexpensive way with low material losses; a compact construction with short distance between heat source and heat removal in order to minimize heat losses. In the quasi-continuous flow configuration, the material moved from the top to the bottom driven by gravity (Fig. 3-2).

Air was fed from one lateral side and exited from the opposite side, in a crossflow configuration. The main advantages of this design were a constant power output and a stationary reaction zone. The main challenge was to maintain a uniform material flow through the reactor. Moreover, well-defined hard spherical particles might be necessary for this reactor concept. On the other hand, the fixed bed reactor had the advantage of a stationary material. However, reaction front, temperature, and grade of conversion were moving. After that the sorption reaction was completed, the material inside the reactor had to be replaced. No constant thermal power could be provided and power reduction at start-up and end of conversion took place.

3.1.2.3. Reactor heat and mass transfer. In closed systems, heat transfer is often the limiting step while in open systems the mass transfer is the main issue. This is often the combination of unfavorable material and system characteristics. Material coagulation can happen due to contact with liquid water, local deliquescence and swelling. Material pulverization can occur due to the periodical material expansion/shrinking [120]. Beside the already mentioned instabilities, the choice of the materials particle size within the system is often a compromise to have a sufficient amount of active material with good kinetics, and sufficient effective bed porosity and permeability that allow good sorbate transport and acceptable pressure drops. To this regard, N'Tsoukpoe et al. [122] reviewed different studies to investigate how heat and mass transfer were influenced by the particle size distribution of the sorbents. They found that adsorption kinetics were influenced by particle size until the “grain size insensitive regime” was achieved, below certain particle dimensions. In other words, the particle size has to be small enough to achieve this regime, but large enough to avoid large pressure drops. The ratio between the heat transfer surface area and the amount of adsorbent was detected as an important parameter for system optimization in a packed bed reactor. As an example, a ratio in the range of 1–5 m²/kg, characterized the grain size insensitive regime for silica gel, activated carbon and SAPO-34. Typically, the reviewed studies evidenced the use of pellets in the range of 0.2–0.6 mm for closed systems. The authors stated that, in principle, it is not necessary to select a precise grain size as long as the insensitive regime is reached. On the other hand, for every specific application there is an optimal combination of parameters that are also dependent on the particle size (e.g. effective thermal conductivity, permeability, etc.) that have to be optimized. For open systems, powders and pellets were equally considered. However, by using powders, low power output and high pressure drops were found in the reported studies. This indicated that higher flow rates might have been required to provide higher thermal powers;

however, higher pressure drops would have resulted and the use of larger particles could have been necessary. The authors stated that the contact between the heat exchanger and the active material could be another issue if salt hydrates are used because their cyclical expansion and shrinking during system cycles varies the contact area. A permeability of $1\text{--}5 \cdot 10^{-12} \text{ m}^2$, effective thermal conductivity of 1 W/(m·K), and heat transfer coefficients between heat exchangers and adsorbent of 200 W/(m²·K) were suggested for closed evacuated systems. To conclude, the authors suggested to include the method based on the determination of the grain size insensitive regime in the design optimization of packed bed reactors, and that results based solely on TGA/DSC analyses can be misleading due to the small amount of material involved. Influence of grain size on heat and mass transfer was discussed also by Michel et al. [48]. They tried to enhance the mass transfer by adding a gas diffuser in form of a foam up to the mid-height of a fixed bed reactor. This solution increased the system permeability by 1.7 times and provided slightly higher specific power without affecting the energy density. Another option to decrease pressure drops within the reactor was used in the MonoSorp project [117]. The authors used honeycomb structures (monoliths) made out of a zeolite that could be placed in different configurations so that a modular, simple, and flexible system could be designed.

3.1.2.4. Components corrosion. Side reactions can produce corrosive or toxic byproducts together with the depletion of the active material. For example, a system based on Na₂S can produce H₂S if the sorbent is in contact with liquid water but also, at lower pace, with water vapor. Then, H₂S can dissolve into liquid water and cause metal corrosion and H₂ formation. With an undesirable gas production, the system condenser can be blocked, reducing the sorption reaction rate. This is why periodical system evacuation is needed. To prevent this, corrosion resistant coatings, H₂S and H₂ getters or the addition of hydroxides can be supportive [120].

To this regard, Solé et al. [129] tested four common metals: copper, aluminum, stainless steel 316 and carbon steel against five salt hydrates: CaCl₂, Na₂S, MgSO₄ and MgCl₂. Immersion tests were performed at the operating conditions that simulate an open system: immersion temperature of 60 °C and humidity at 99%. The metal samples were removed after one, four, and twelve weeks. The results are visible in Table 3-2.

3.2. Existing prototypes review

In the following section, a review of existing sorption systems for low-temperature sorption heat storage is presented. The focus is on open and closed systems with water vapor as sorbate and solid adsorbents, salt hydrates or composites as active materials.

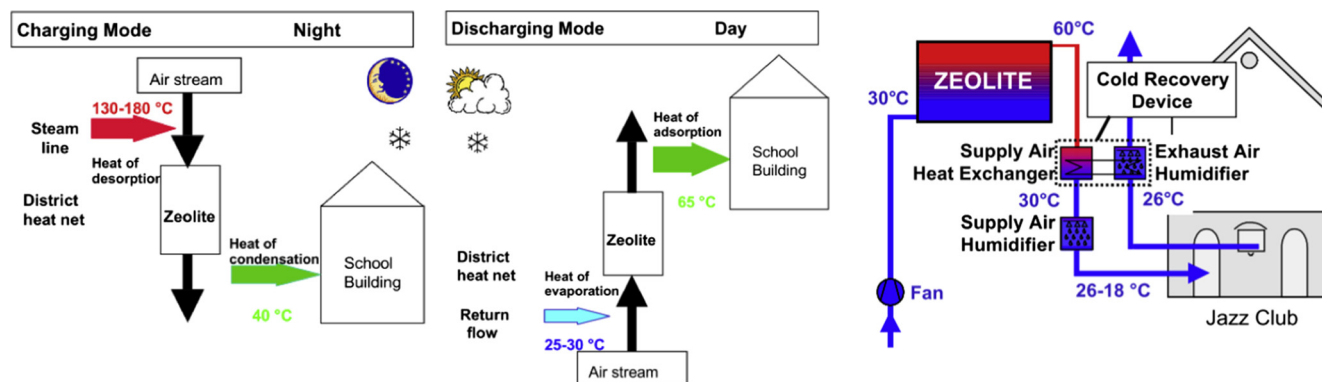
3.2.1. Open systems

3.2.1.1. ZAE Bayern (1997). One of the first and largest prototypes of a sorption storage system was built in Munich [74,130] by ZAE Bayern (Fig. 3-5). It was an open system designed for peak shaving of the heating load of a school in winter and cooling load of a Jazz club in summer. The active material was zeolite 13X. The system reactor consisted of three connected horizontal cylinders containing a total of 7000 kg of zeolite 13X with an energy density of approximately 0.45–0.36 GJ/m³ and 130–50 kW of discharging power for heating and cooling mode, respectively. A district heating network running on steam was used as desorption heat source, and the return line of the network consisted of condensate steam, used as low temperature source for water evaporation in sorption mode. Moreover, during desorption at night, residual heat was injected into the school heating system to avoid a peak of the heating load in the early morning. Cooling mode consisted in the air dehumidification of the Jazz club (latent cooling). A desorption

Table 3-2

Corrosion tests results from Solé et al. [129].

Salts	Copper	Stainless Steel 316	Carbon Steel	Aluminum
CaCl ₂	Recommended with caution	Recommended for long-term service	Recommended with caution	Recommended with caution
Na ₂ S	Destroyed	Recommended for long-term service	Recommended with caution	Destroyed
MgCl ₂	Recommended with caution	Recommended for long-term service	Not recommended (>1 year)	Recommended with caution
MgSO ₄	Not recommended (>1 year)	Recommended for long-term service	Not recommended (>1 month)	Recommended with caution

**Fig. 3-5.** ZAE Bayern zeolite 13X system for peak shaving of a heating system and latent cooling in Munich [74].

temperature of 80 °C during cooling mode showed the best COP, and a temperature of approximately 25.5 °C was successfully kept during concerts in the Jazz club only with desiccant cooling and ventilation instead of 29 °C without air conditioning, as previously measured. A rough economic analysis highlighted that the payback costs strongly depended on energy price reduction during off-peak hours, investment costs and number of storage cycles. A payback time of 7–8 years was found assuming 40 and 60% price reduction during winter and summer respectively, 60 k€ of investment costs, and 100–150 yearly heating and cooling cycles.

3.2.1.2. MonoSorp. In the MonoSorp project framework, the research carried out by Kerskes and Sommer and reported by Bales [117], aimed at the development of an open sorption heat storage system regenerated by solar thermal energy for space heating in buildings. A sorption storage was built, consisting of 70 kg of zeolite 4A honeycomb structures divided in monoliths (Fig. 3-4 left). A regeneration temperature of 180 °C and a sorption temperature of approximately 20 °C were used during the experiments. A maximum temperature lift of 22 °C and discharging powers of 1–1.5 kW were measured with an inlet water vapor pressure of 8.7 mbar and an inlet air temperature of 19 °C.

3.2.1.3. SPF. The Institut fuer Solartechnik SPF [117] tested a lab-scale open sorption storage with 7 kg of Zeolite 13X. Desorption temperatures of 180 °C and sorption temperatures of 20 °C with a sorption water vapor pressure of 23.4 mbar were applied. A maximum temperature lift of 70 °C was reached during the sorption phase, and 0.8 kW of discharging power at temperatures above 55 °C.

3.2.1.4. ECN. Zondag et al. [46] tested a lab-scale reactor filled with 3.6 kg of MgCl₂·6H₂O in an open system configuration. A temperature rise of 15 °C was found and a discharge time of 25 h was measured. A system charging storage density of 0.14 MJ/kg was measured but the value was expected to be higher since the material hydration was not complete.

Next, Zondag et al. [132], developed a lab-scale sorption reactor with a volume of 17 l, in which the MgCl₂–H₂O working pair was tested at realistic system operating conditions (evaporator at 10 °C and reactor at 50 °C assuming a heat recovery unit). The reac-

tor was designed to produce 150 W of heating power with airflow of 510 l/min at a water vapor pressure of 12 mbar. A charging temperature of 130 °C was used. A temperature rise of 14 °C (up to 64 °C) was measured, together with a thermal power of 50 W. Consistent heat losses in the air-to-air heat exchanger used as heat recovery unit have been identified as the cause of the 100 W power drop and 9 °C temperature drop between the reactor outlet and the system outlet. An effective energy density of 0.5 GJ/m³ was measured. A pressure drop increase in the hydration reactor was identified and probably caused by the material deliquescence within the reactor, causing in turn mass transfer problems. An instant COP of 12 was measured considering 4 W_{el} of consumption for the sorbate fan.

3.2.1.5. CWS-NT/ITW. Mette et al. [123] aimed at the development of an open sorption energy storage integrated into a complete system within the CWS (Chemische WärmeSpeicherung mittels reversibler Feststoff-Gasreaktionen) project framework. The concept consisted of an open sorption storage integrated with a water storage (combi-store) and solar thermal collectors. Solar collectors were used to charge the storage. The reactor concept in this system consisted of a quasi-continuous mass flow/fixed bed previously introduced in Section 3.1.2.

An open system was selected because of a lower technical effort due to standard pressure operating conditions and the absence of evaporator and condenser. An external reactor concept was adopted with an air-to-air heat exchanger for optimal power output. Material transport was driven by gravity from the storage to the reactor with continuous or quasi-continuous mass flow, while a vacuum blower was used to transport the material in the opposite direction. A daily reservoir between the reactor and the large storage was used. The hydration reaction happened at ambient conditions by using the humidity of a building. An air-water heat exchanger was used to remove or add heat into the reactor for de/hydration. A composite material was used because pure salts showed low reaction rates and high pressure drops due to small salt particles in the reactor. Material experiments in a fixed bed layout have been performed with a sorption temperature of 35 °C and 20 mbar of water vapor pressure, and a desorption temperature of 180 °C. A composite made of zeolite 13X and LiCl was

tested, and 20% more heat was released in the composite compared to pure zeolite. However, similar water uptake was present. This may be due to the competing effects of a decreased amount of free pores in which adsorption can take place, and the presence of reacting salt filling those pores. A 2D numerical model was developed to simulate the reactor, which had a good agreement with experimental data.

A quasi-continuous cross flow reactor concept was developed with the aim to use the strong points of a fixed bed reactor and a separate reactor. At the material outlet, the reactor width was reduced allowing a faster flow. After a certain fixed period, part of the material was removed from the bottom of the reactor. Kerskes et al. [133] developed further the work resulting in the CWS-NT (Chemische WärmeSpeicherung – Niedertemperatur) system concept (Fig. 3–4 right). A TRNSYS model was used to have a simpler version of the CFD model developed by Mette et al. [123], so that it could be integrated into a model for long-term performance assessment at system level. The results of the system simulation, compared to a similar system based on sensible heat storage with water, showed an increase of yearly fractional energy saving up to approximately 15% for various collector areas. For example, for a collector area of 28 m², the system had a yearly fractional energy saving of approximately 74%. An equivalent system with a water storage installed instead of a sorption reactor would have led to a yearly fractional energy saving of approximately 61%. During experiments investigating the active material flow, dead zones were identified in the reactor. This issue was fixed by installing guiding components at the bottom of the reactor, in order to prevent a centered core flow. The authors reported a temperature lift of approximately 20 °C, and they found that 30% of the heat of reaction was lost after the air-to-air heat exchanger. A ratio of electric consumption of the solid material transportation to useful thermal power of 13 W_{el}/kW_{th} was measured assuming an energy density of approximately 0.67 GJ/m³.

3.2.1.6. E-HUB/ECN (2013–2014). In the framework of the European project E-hub (2010–2014), two open sorption heat storage systems were developed. The project aim was to demonstrate the full potential of a smart grid concept and to provide 100% on-site renewable energy to the community members (households, power plants, offices, etc.) with energy and data exchange [134–136]. Long-term sorption heat storage concepts were developed, in particular an open and a closed sorption system [136].

After the first prototype previously described, based on MgCl₂, the material instabilities led to a second prototype [136,137] in which zeolite 13X was employed (lower energy density but similar kinetics). The new prototype was made of two packed bed modules for a total of 150 kg of zeolite, and had a material energy density of approximately 0.21 GJ/m³. During the sorption phase, a heat recovery unit increased the inlet temperature up to 40 °C, allowing higher outlet temperatures. The maximum system desorption and sorption temperatures were approximately 185 and 70 °C (temperature step of 30 °C), respectively, and the discharging power and discharging time were 400 W (flow rate of 80 m³/h) and 30 h, respectively.

3.2.1.7. ASIC. Zettl et al. [138], from the Austrian Solar Innovation Center (ASIC), studied an open system consisting of a rotating drum reactor with a diameter of 0.7 m and 0.3 m depth made of stainless steel, and filled with 50–53 kg of zeolite 4A or zeolite type X in spherical grains with diameters of 1.6–2.5 mm. The materials were desorbed at temperatures of 230–180 °C. During adsorption, humid air was blown into the reactor at 25 °C with a water content of 9–19 g_{H2O}/kg_{air}. The authors reported an initial sorption phase in which the material is heated, lasting 1–3 h depending on the initial hydration level of the material. Energy densities were calculated

considering the energy released from the reactor at a minimum temperature step of 10 K between inlet and outlet. Values up to 0.55–0.53 GJ/m³ were measured for zeolite 4A and type X, respectively, with maximum temperature lifts of approximately 36 K. However, those values were achieved with desorption temperatures higher than 230 °C with a very low initial water content in the material (<3%). The energy density measured, with a previous desorption temperature of 180 °C and humid air with a water content of 9 g_{water}/kg_{air}, was 0.34 GJ/m³ for zeolite 4A referred to the dry material, with an achieved maximum temperature step of 19 K (inlet temperature of 25 °C).

3.2.1.8. ESSI. Michel et al. [51], within the ESSI project, investigated a modular open system based on 400 kg of SrBr₂ with an estimated energy density of 0.73 GJ/m³ corresponding to 0.38 GJ of storage capacity. The system was tested for five months performing seven de/hydration cycles with moist air flow rates of 313–270 m³/h and de/sorption temperatures of 80 and 25 °C, respectively. During sorption, water vapor pressures of 10–9.6 mbar were applied. A maximum output temperature of approximately 32 °C was reported for the last sorption phase. Concerning the system control, the inlet moist air content and the equilibrium drop, defined as the difference between the equilibrium thermodynamic conditions and the system operating conditions, resulted to have a strong influence on the reactor performance. Thermal powers measured in the middle of the sorption and desorption phases were in the order of 0.8–0.3 kW and 1.6–0.4 kW, respectively, depending on the cycle.

3.2.1.9. ZAE Bayern (2015). One of the most recent and largest sorption heat storage systems is described by Kronauer et al. [124]. ZAE Bayern developed a demonstration open system for transportable sorption heat storage purposes. Two storages with 14 t of zeolite 13X were desorbed with 130 °C waste heat from an incineration plant. The storages were then transported by trailer (Fig. 3–6 right) for 7 km and discharged at the customer point with saturated humid air at 60 °C. A storage capacity of 0.6 MJ/kg_{dryzeolite} was measured, corresponding to 0.37 GJ/m³ assuming a material density of 630 kg/m³ [2]. The authors calculated that, for every cycle, 616 kg/CO₂ was saved. Flow misdistribution through the storage, and humidity variation in the airflow during sorption were observed. Material degradation was assessed with visual inspections but, after 99 cycles, no material decomposition due to mechanical stresses was detected. Primary energy costs of 73 €/MWh were determined. The authors claimed that, in order to decrease those costs to 30 €/MWh and become competitive with oil or gas primary energy costs, a storage handling system optimization and transportation of higher amounts of material, in the order of 50 t, are necessary.

3.2.1.10. STAID (2015). Johannes et al. [139] developed an open sorption heat storage system, STAID (Stockage Inter Saisonnier de l'Énergie Thermique dans les Bâtiments), based on two modules containing 40 kg of zeolite 13X each. The aim of the experimental system, supposed to be integrated in a domestic ventilation system, was to provide thermal energy for space heating during peak hours. In terms of operational requirements, the system had to deliver at least 4 kW h in a 2 h period, and the water vapor of the humid air in the building was supposed to be used as a sorbate. Several tests have been run with dehydration temperatures of 180–120 °C and flow rates of 180–120 m³/h, while the hydration temperature was kept at 20 °C with a sorbate vapor pressure of approximately 16.3–15.8 mbar. A maximum hydration temperature of 57 °C was reached during the operation of the two modules, which were tested both in parallel and serial configurations. During tests, hydration powers in the range of 2.25–1.41 kW and



Fig. 3-6. Left: 3 kW h closed system by Finck et al. [145]. Right: Sorption storage reactors of zeolite 13X transported by truck [124].

COP values of 6.8–1.7, considering the power consumption of the fan and the humidifier, have been reached, respectively. The minimum hydration time during the tests was 6 h, largely exceeding the minimum requirement of 2 h of operation. Assuming a material density of 1100 kg/m^3 [140], and an average bed porosity of 0.38 according to the authors, a maximum bed energy density of approximately 0.41 GJ/m^3 was reached. Concerning the system configuration, the authors found that series configuration of the modules was providing an inconstant thermal power compared to the parallel configuration.

3.2.2. Closed systems

3.2.2.1. HYDES. From 1998 to 2001, the European Union funded the project HYDES (High Energy Density Sorption Heat Storage for Solar Space Heating) with the aim to develop a long-term low-temperature seasonal storage of solar thermal energy for space heating purposes. Silica Gel was the chosen active material [130,141]. The closed adsorption system used solar thermal collectors also as low temperature heat source for the evaporator. A partial system charging did not give optimal results, and an energy density 20% lower than the expected was measured (0.43 GJ/m^3). The project time schedule did not allow a proper system monitoring during the entire sorption period.

3.2.2.2. MODESTORE. Jähnig et al. [131], in the framework of the MODESTORE project, tested a new concept for a closed system with a spiral heat exchanger layout (Fig. 3-3 left) charged with approximately 200 kg of silica gel. The reactor consisted of a perforated copper sheet with copper pipes soldered to it. A vertical channel in the center was used for vapor diffusion. The heat exchanger used as evaporator and condenser was placed at the bottom of the reactor to have a compact design. Experimental results during the adsorption phase showed a temperature increase of only 5 K, and a maximum transferred power of 400 W, highlighting the bad thermal conductivity of silica gel and the limited temperature increase achievable by the material. As main conclusion, the authors stated that silica gel was not suitable for heat storage purposes.

3.2.2.3. SWEAT/ECN. De Boer et al. [42] presented the results of the SWEAT (Salt Water Energy Accumulation and Transformation) prototype (Fig. 3-3 right) for solid-sorption cooling based on the $\text{Na}_2\text{S-H}_2\text{O}$ working pair. The closed system required vacuum conditions, and the smallest amount of non-condensable gases would have heavily affected the system performances, which is a typical issue for this system configuration. Stainless steel was selected as reac-

tor material, which gives sufficient protection from corrosion (Table 3-2). The heat exchanger consisted of a copper wire-fin heat exchanger (spiro-tube). Coating was crucial, and the coating material had to have zero defects to be chemically inert to $\text{Na}_2\text{S-H}_2\text{O}$ and have a 100% barrier function. In order to keep the sorbent in place, cellulose was used as support.

3.2.2.4. MCES. Iammak et al. [142] developed a closed chemical energy storage (MCES) consisting of a stainless steel reactor and an evaporator/condenser placed in line. The materials used were 175 g of $\text{Na}_2\text{S-9H}_2\text{O}$ and 75 g of graphite used as additive. The desorption temperature was in the range of 80–95 °C while the maximum sorption temperature reached was 65.1 °C. An energy density of approximately $8 \text{ MJ/kg}_{\text{composite}}$ was measured.

3.2.2.5. SOLAR-STORE. Lahmidi et al. [50] developed a closed system, in the framework of the EU project SOLAR-STORE, using SrBr_2 and expanded natural graphite. The system consisted of a plate heat exchanger with nozzles spraying the sorbate above the material. Heating and cooling powers in the order of 47–49 and 27–36 kW/m^3 have been measured, respectively.

3.2.2.6. SOLAR-STORE (Solux). Mauran et al. [49], within the SOLAR-STORE project, tested a closed system prototype (Solux) of chemical heat pump to store thermal energy based on the solid-gas reaction of the $\text{SrBr}_2\text{-H}_2\text{O}$ working pair with expanded natural graphite (ENG) as supportive material. The prototype had a volume of 1 m^3 and stored 0.22 and 0.14 GJ/m^3 for heating and cooling, respectively, with charging powers of 2.5–4 kW. Low heat transfer between the reactive layer and the wall of the heat exchanger limited the system efficiency. The de/hydration equilibrium conditions in the system during winter were 43 °C and 1000 Pa. During summer, two temperature and pressure levels were used: 66 °C/5600 Pa and 52 °C/2000 Pa for dehydration and hydration, respectively. The reactor was modular with stacking of modules consisting of plate heat exchangers between two layers of reagent, and two diffusers at the ends. The strong points of this layout, according to the authors, were a high ratio of reagent volume over the reactor volume, high exchange surface related to volume, and easy reactor scaling. The authors highlighted that the use of an additive material could be beneficial since, being a closed system configuration, the reactor power was an increasing function of the ENG apparent density, while the energy density had an opposite trend. Therefore, trying to maximize the energy density with an acceptable reactor power was one of the optimization objectives. The heat transfer coefficient between wall and material

depended on how the composite was placed and maintained, but a correlation for its prediction was missing.

3.2.2.7. Fraunhofer. Lass-Seyoum et al. [143] investigated the sorption/desorption dynamics of a closed system concept. First, material characterization was performed by screening of micro- and meso- porous materials. Zeolites and salts in porous matrices (e.g. attapulgite/30 wt% CaCl_2) were tested as materials. Both zeolites and composites were tested for cyclability by performing five thermal cycles up to a temperature of 200 and 120 °C, respectively. A 1.5 l reactor was first used to investigate the heat storage process and the maximum desorption temperatures ranged from 90 to 120 °C depending on the material. Next, a 15 l reactor was built to investigate the process conditions and to test different heat exchanger concepts with the aim to optimize the thermal conductivity and the heat transport within the system. A 750 l reactor was then built and used to test 510 kg of an unspecified type of zeolite dried to less than 1% of water content. During desorption, a maximum temperature of 200 °C was used. In the 15 l reactor, two heat exchangers were tested with three and seven fins. The heat exchanger with seven fins showed better heat and mass transport, stable heating power, and good performances during desorption due to a better thermal conductivity within the reactor. Tests in the 750 l reactor were not completed at a steady state, but interrupted when the outlet temperature was almost at 60 °C. The estimated heat storage capacity was estimated to be in the range of 0.54–0.79 MJ/kg.

3.2.2.8. TNO. Cuypers et al. [144] aimed to develop a closed sorption heat storage system starting from lab-scale prototypes and material investigations. Adsorption experiments with zeolite in a glass reactor reached maximum temperatures of 85–88 °C and maximum specific powers of 164 W/kg. In this experiment, the authors were not removing heat from the glass reactor. Numerical investigations on the adsorption/desorption processes were carried out. The results led to the development of a reactor made by 2 mm copper foils with zeolite spheres glued to them. This reactor layout can maximize the reactor power, but the heat exchanger area per material mass can be relatively high. In general, the reactor power is increased by increasing the heat transfer area in the reactor design, but the energy density decreases. Experimental results on this setup showed a maximum temperature increase of approximately 9 °C and maximum specific powers of 0.6 kW/kg in the first 1000 s of the experiment. Differently from the first experiment, the heat was removed from the reactor flowing water in the heat exchanger pipes. The authors investigated also an unspecified composite material with an energy density approximately 50% of the theoretical energy density of CaCl_2 , and a water uptake of approximately 0.4 $\text{g}_{\text{water}}/\text{g}$. After five de/sorption cycles up to 250 °C, no material deterioration was observed.

3.2.2.9. EHUB/TNO. Finck et al. [145], in the E-Hub project framework, developed a 3 kW h closed sorption heat storage with 41 kg of zeolite 5A for space heating at 40 °C. Zeolite was selected for its hydrothermal and mechanical stability, safety, and minimization of heat exchangers corrosion. Eight finned heat exchangers with glued zeolite 5A on the outer surface (Fig. 3-6 left) were packed in a parallel configuration in a cylindrical vessel of stainless steel. A single unit fulfilling the function of evaporator and condenser was built. A desorption temperature of 103 °C and an adsorption temperature of 20 °C were applied. The maximum temperature lift was 31.2 °C with an average of 20 °C in the first hour and eighteen minutes. An average heating power of 0.8 kW was measured during adsorption. After approximately 14 h of adsorption and a final temperature difference between system inlet and outlet of less than 0.5 K, a material and system energy densities

of 0.17 and 0.045 GJ/m^3 were measured. Assuming a minimum useful temperature difference of 20 °C, a material and system energy density of 0.068 and 0.018 GJ/m^3 would be present, respectively. An up-scaled version of the 3 kW h prototype with 175 kg of zeolite 5A was also planned with an expected system energy density of approximately 0.13 GJ/m^3 resulting from the system optimization [136].

3.2.3. Prototypes performance

In Table 3-3, energy densities, maximum desorption and sorption temperatures of the reviewed studies are shown. It has to be pointed out that all the values used are those reported by the references. Moreover, the energy density is reported based on the volume of the active material, or on the system volume, if this information was present in the references. The energy density based on the system volume, can be based on the reactor volume, or including also the system components. For more information, the reader is invited to consult the references for each prototype. Investigations on both open and closed systems were carried out without a clear preference for one of the two systems. On the material level, especially for open systems, the choice of adsorbents or composites rather than pure salts is evident. This is because large open systems with pure salt hydrates will face the hydrothermal stability problems mentioned in Section 2.1.1. Therefore, more stable materials with a lower energy density are often preferred for systems development, waiting for new inputs from the materials research. It can be also observed that, often, performance parameters such as the energy density are not uniformly referred to e.g. the system volume or the material volume. This makes the systems comparison difficult. In Fig. 3-7, the energy density of some prototypes is related to their maximum desorption temperature. The graph can give an indication on the systems performance but cannot demonstrate the better suitability of one system compared to another, and they have to be interpreted with caution. The main reason is that energy density is only one of the important system performance indicators. Deliverable and stable thermal power, system thermal losses, material stability within the system, system size and scalability, sorption temperature and water vapor pressure during sorption are other useful indicators that describe the system performance and suitability for a specific application. For example, the HYDES project indicated that silica gel was not suitable as active material since a limited temperature step was achievable at the operating conditions of that system. ZAE Bayern projects are in a relatively advanced stage of development (TRL 5 [146]) compared to the analyzed prototypes. They consist of two large systems with an energy density of 0.37–0.45 GJ/m^3 already implemented in real case scenarios. Moreover, at their operating conditions, they reach the highest adsorption temperatures among the investigated systems (Fig. 3-8). In order to achieve adsorption temperatures suitable for space heating and domestic hot water production, relatively high desorption temperatures are needed. Most of the systems able to deliver temperatures above 40 °C are based on zeolites, and they need desorption temperatures of 180 °C or higher. The system from ZAE Bayern of 2015 achieved an adsorption temperature of 160 °C. However, during discharge, the system was flushed with humid air at 60 °C from a drying plant, and due to the high water vapor pressure (~200 mbar), a very high adsorption temperature was achieved. Therefore, the application was not for space heating and DHW production, but it demonstrated how sorption heat storage could be integrated in an industrial process operating at specific temperature ranges and with the possibility to generate the required water vapor pressure. Finally, it is noticeable that all the systems with a sorption temperature suitable for DHW production, higher than 60 °C, are based on zeolite 13X. As already mentioned in Section 2.1.2, systems based on these materials would result particu-

Table 3-3

Summary of the sorption heat storage systems based on solid/gas reaction with water vapor as sorbate investigated for long-term low-temperature heat storage.

Project name/ institution	Year	Scope	Active material	Amount (kg)	Additive material	Type	E (GJ/m ³)	E (MJ/kg)	P _{ch} (kW)	P _{disch} (kW)	T _{des} (°C)	T _{sorp} (°C)	Max ΔT _{sorp} (°C)	Max T _{sorp} (°C)	p(H ₂ O) (mbar)	t _{ch} (h)	t _{disch} (h)	Cost (ke)	Refs.
ZAE Bayern	1997	HS & CS	Zeolite 13X	7000	–	O	0.45 ^{MH} 0.36 ^{MC}	–	135 ^H	130 ^H 50 ^C	130 ^H 80 ^C	25–30	80	110	42	6.5 ^H 9.5 ^C	6 ^H 12 ^C	60 ^S	[74,117,130]
HYDES	1998	HS	Silica Gel	~1600	–	C	0.43 ^M	–	1.7	2.87	82	–	–	32	–	29	9	–	[117,130,141,147]
SWEAT/ECN	2004	CS	Na ₂ S	3	Cellulose	C	2.81 ^{MH} 1.84 ^{MC}	–	1.2	0.5–0.7	86–77	25–15	–	–	12–17	4	4	–	[23,42]
MCES	2004	HS & CS	Na ₂ S	–	Graphite	C	–	8	–	0.15–0.24	95–80	–	–	–	–	–	–	–	[117,142]
SOLAR-STORE	2006	HS	SrBr ₂	–	ENG	C	–	–	–	~48 ^{VC} 27–36 ^{VH}	70 ^H 80 ^C	–	–	35	23	14	4	–	[50]
MonoSorp	2006	HS	Zeolite 4A	70	–	O	0.58 ^M 0.43 ^S	–	2–2.5	1–1.5	180	20	22	42	9	–	–	2.5–3.5 ^{MV}	[117]
SPF	2006	HS	Zeolite 13X	7	–	O	0.65 ^M 0.21 ^S	–	–	0.8–1.8	180	–	–	70	23	–	–	2–3 ^{MV}	[117]
MODESTORE	2006	HS	Silica Gel	200	–	C	0.18 ^M 0.12 ^S	–	1–1.5	0.5–1	88	–	–	–	19–35	–	–	4.3 ^{MV}	[117,131,147]
SOLAR-STORE (Solux)	2008	HS & CS	SrBr ₂	171.3	ENG	C	0.22 ^{SH} 0.14 ^{SC}	–	2.5–4	–	80–70	–	–	35 ^H 18 ^C	10 ^H 20 ^C	6–8	6–8	–	[49]
CWS-NT/ITW	2011	HS	LiCl	–	Zeolite 13X	O	0.67 ^{MA}	–	–	0.4	180	35	20	55	20	–	–	–	[123,133]
Fraunhofer	2012	HS	Zeolites/ CaCl ₂	Various	Attapulgit Poolkohl	C	–	0.54–0.79 ^A	–	0.019–0.05 ^W	90–200	30	–	–	42	–	–	–	[143]
TNO	2012	HS	Zeolites/ Composite	–	–	O	–	–	–	0.6 ^W	–	–	9	29	–	–	–	–	[144]
ECN	2013	HS	MgCl ₂	9	–	O	0.5 ^S	–	–	0.15	130	–	–	64	12	–	40	–	[132,136]
E-HUB/TNO	2014	HS	Zeolite 5A	41	–	C	0.17 ^M 0.045 ^S	–	12	0.8	103	20	31.2	51.2	23	–	14	–	[136,145]
E-HUB/ECN	2014	HS	Zeolite 13X	150	–	O	~0.21 ^{M*}	–	2	0.4	185	25–60	–	70	12	48	30	–	[136,137]
ASIC	2014	HS	Zeolite 4A/X	53–50	–	O	0.55–0.34 ^S	–	–	1.5	>230–180	25	36–19	84–44	25–12	–	~10	–	[138,148]
ESSI	2014	HS	SrBr ₂	400	–	O	0.73 ^S	–	1.6–0.4	0.8–0.4	~80	25	7	32	10	75–95	60–250	–	[51]
ZAE Bayern	2015	HS	Zeolite 13X	14,000	–	O	~0.37 ^{M*}	0.6	255	125	130	60	–	160	199	12	16	89.5 ^S –324 ^S	[124]
STAID	2015	HS	Zeolite 13X	80	–	O	~0.41 ^M	–	–	2.25	180–120	20	37	57	16	6	6–14	–	[139]

• **Type:** O = Open system; C = Closed system • **Purpose:** HS = heat storage; CS = Cold storage.

• **Superscripts:** A = Assumed by the authors; M = Material-based; S = System-based; H = Heating mode; C = Cooling mode; W = per kilogram; V = per m³; *Assuming a material density of 630 kg/m³ [149].

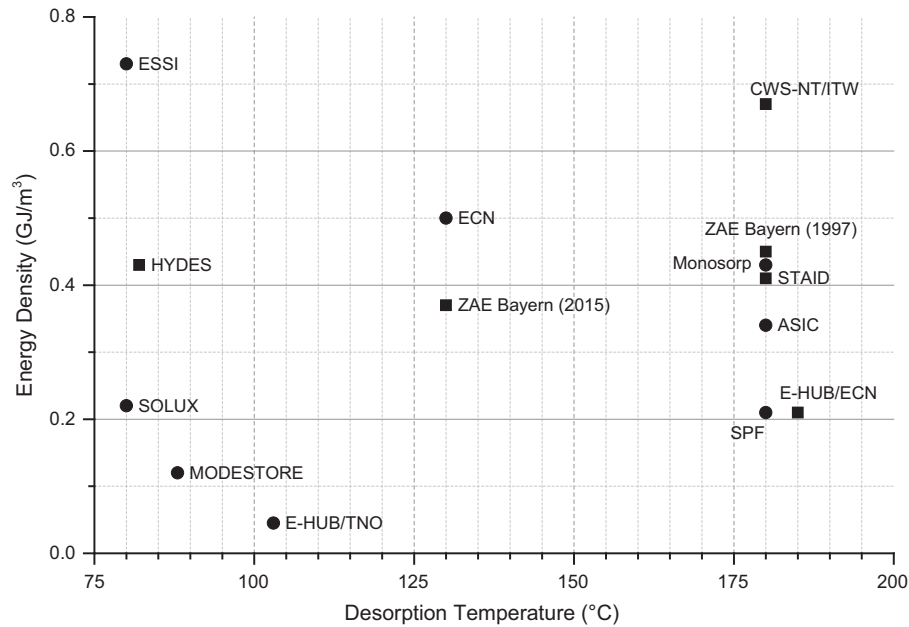


Fig. 3-7. Prototypes max desorption temperature vs energy density. Square marker: Energy density based on system/reactor volume. Circle marker: Energy density based on material volume.

larly expensive due to the relatively high specific cost of the active material. An exception was the lab prototype from ECN based on MgCl_2 , which reached a maximum temperature of 64 °C (temperature step of 14 °C), but as already mentioned, the material hydrothermal instability was a main issue.

3.2.4. Ongoing research

Beside the abovementioned systems, research on long-term low-temperature sorption heat storage is ongoing in various projects.

3.2.4.1. COMTES (2012–2016). In the COMTES (Combined Development of Compact Thermal Energy Storage Technologies) framework [150–153], the development of liquid and solid sorption

systems for seasonal heat storage purposes is carried out. In particular, a closed modular solid sorption system with a fixed bed layout based on the MODESTORE project is designed. The active material is zeolite 13XBF. The system is designed to supply heat for space heating and DHW with an additional backup heater. A prototype with a reactor of approximately 300 l and 164 kg of zeolite produced a maximum sorption temperature of 75 °C and had a measured energy density of 0.4 GJ/m³. The main issue was a too high pressure drop over the evaporator. The output power was controlled through vapor flow control. A further prototype with 2 t of zeolite is being tested.

3.2.4.2. SOTHERCO (2012–2016). The main project objective is to develop a compact and modular sorption storage system [151,154]. First, composite materials were studied [155] with the

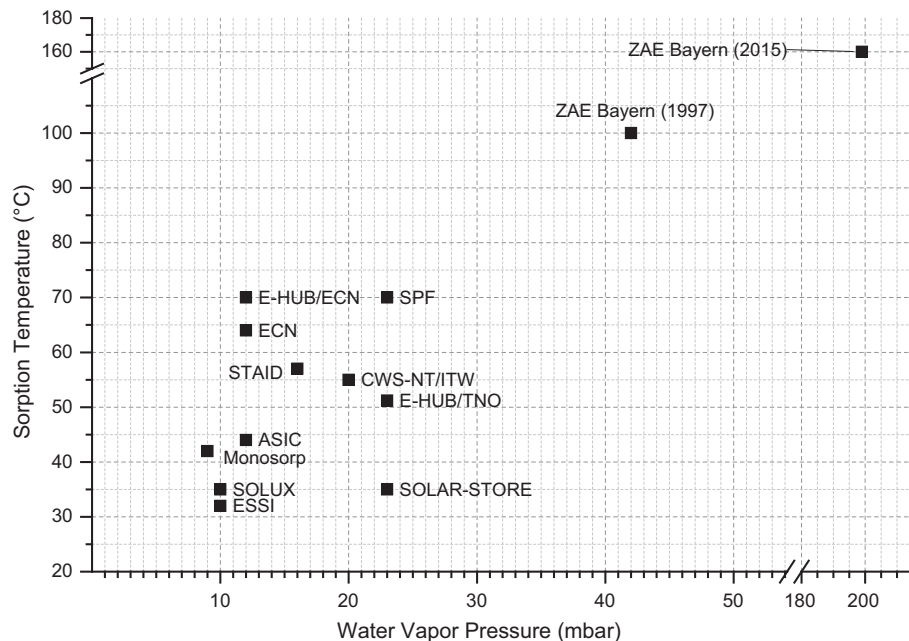


Fig. 3-8. Prototypes sorption water vapor pressure vs max sorption temperature.

aim to identify the most promising options in terms of stability and energy density. Then, the reactor development took place, and a modular configuration was developed. Currently, upscaling of the system is being investigated and a real scale unit with a separate reactor layout has been developed together with the sorbent transport system. The reactor uses vibrating beds for sorbent transport within the reactor.

3.2.4.3. MERITS (2012–2016). The MERITS consortium aims to develop a compact rechargeable heat battery to optimize the use of renewable energy sources for heating, cooling and domestic hot water in new and existing dwellings [156]. A closed modular sorption system using Na_2S is used as long-term storage, and desorption heat is provided by solar thermal collectors. The reactor consists of air/water finned tubes heat exchangers with active material present on the finned surface [120]. Currently, a real scale prototype has been built and it is tested in various European locations.

3.2.4.4. SolSpaces and EnErChem. The Institute of Thermodynamics and Thermal Engineering (ITW) at the University of Stuttgart, after the MonoSorp project experience, is continuing the research on sorption energy storage with two projects. SolSpaces [157–159] deals with the development of an open sorption system that is tested in a prefabricated compact house of 43 m². The active material is zeolite, which is desorbed at 180 °C during summer by the solar thermal collectors. EnErChem [160] follows the research of the CWS project, an open sorption system with separate reactor, with the aim to integrate it with CHP and photovoltaic plants.

3.3. Conclusions on prototypes review

Concerning sorption heat storage prototypes, research is addressing both open and closed systems. Modular or separate reactors are the concepts towards which the research is directing, especially for open systems. This is due to the better sorbate transport achievable in these layouts, implying lower pressure drops and energy consumption of auxiliary systems. However, especially for separate reactors, only few prototypes are currently studied. Further investigations on separate reactors should be done to assess which materials and materials shapes are suitable for this kind of reactor concept.

As active materials for systems prototypes, zeolites are typically used, especially in open systems where mass transport is the limiting step and it could be heavily reduced by the material instabilities. Regarding closed systems, beside adsorbents, also sodium sulfide and strontium bromide have been investigated. In particular, sodium sulfide is promising in terms of energy density but it requires materials resistant to corrosion. Performance in terms of energy density, sorption and desorption temperatures have been reported for the investigated prototypes. Often, the energy density was referred to the active material volume or to the system volume. This aspect has to be carefully considered since the energy density can seriously drop by considering the volume of all the system components. To conclude, further considerations on the prototypes comparison was not possible due to a lack of homogeneous data, also due to the intrinsic differences within each prototype investigated.

4. Discussions and conclusions

4.1. Discussions

Sorption heat storage for long-term low-temperature applications has still challenges to face at both micro- and macro-scale levels. Research is still ongoing in order to find unhazardous and low cost sorbent materials with a hydrothermal stability at system

operating conditions and a sufficiently high energy density to make a system commercially feasible. Currently, composite materials are investigated because they have the potential to overcome the disadvantages of pure salt hydrates by increasing their hydrothermal stability. This is done by mixing or impregnating salt hydrates with highly porous host matrices or powders. However, problems in heat and mass transport still can arise due to the reduction of empty pores, possible deliquescence and leakage of the salt from the composite, and degradation. To this regard, further research is needed to overcome these problems and to understand extensively the kinetics of a composite material, which does not follow a typical behavior of a salt hydrate nor of an adsorbent. Various prototype reactors and systems were developed by the scientific community to study the performances of sorption materials at macro-scale. Open and closed solid sorption systems have been analyzed and compared. Among the reviewed prototypes, mostly systems based on zeolites were able to achieve temperatures suitable for space heating or DHW production. For these systems, relatively high desorption temperatures were required, unachievable, for example, by conventional solar thermal collectors.

To make future research comparable, the development of uniform key performance indicators for compact heat storage to be used by the entire scientific community would be a consistent step towards understanding what are the optimal choices and performances from the material and system points of view. For example, a consistent way to define energy density is advisable. Due to the presence of different system layouts and various levels of development, it can be useful to define multiple energy densities related to different investigation scales. At material-scale, beside the crystal energy density, often used for salt hydrates, experimental energy density should be always measured through TGA/DSC experiments on material samples in which the macro structure and operating conditions are taken into account (sorbate pressure, temperature cycles, etc.). This first indicator (E_m) can give information about the material suitability and stability at chosen operating conditions. In this case, the energy density is referred to the material weight, or if measurable, to the volume occupied by the sample. At reactor-scale, the effective energy density is influenced by additional phenomena related to heat loss, uniformity of reaction and power distribution over time. Therefore, a second indicator (E_r) can be useful to define the energy density taking into account the reactor domain. This energy density value is often based on the volume of the active material in the reactor, but should be based on the overall reactor volume including walls and insulation. At this stage of development, auxiliary systems are simulated by the lab equipment, and do not have to be taken into account. At system-scale (E_s), the volume of auxiliary components (e.g. heat exchangers, fans, humidifiers, etc.) should be included in the energy density calculation together with their eventual energy consumption. The domain boundaries are the system inlets and outlets i.e. from and to other applications and infrastructures. In calculating energy density indicators, temperatures and sorbent vapor pressure at charging and discharging conditions should be always mentioned. By comparing the energy densities at different scales, it is also possible to identify what are the system components that decrease most the system performance.

It has to be pointed out that a decrease in the energy density by increasing the research scale is inevitable because more system components are taken into account while the energy potentially stored in the active material remains the same.

Future research on sorption heat storage systems at different scales could make use of similar indicators to compare experimental studies in a more homogeneous way.

Finally, only in few studies considerations about the economic feasibility of the systems were made. This is mainly because the research is still at material- and lab-scales; therefore, wide eco-

conomic investigations would probably lead to misleading results. However, where possible, basic key performance indicators related to e.g. materials cost, system complexity and system ancillary energy consumption can be drawn with the aim to have a first rough estimation of the system profitability. When working prototypes almost at commercial-scale are developed, additional economic considerations related to system operation, such as lifetime and operation and maintenance costs, could be included with the aim to define and evaluate a business case. By considering economic aspects at the earliest stages of the research, the scientific community can focus its efforts on research paths considering technical and economic feasibilities.

4.2. Conclusions

To conclude, further research on long-term low-temperature sorption heat storage should take into account the following considerations:

- Research at material level is still needed to find a suitable active material with sufficient energy density, hydrothermal stability and cyclability at system operating conditions. Composite materials are promising but further research on host/active material working pairs is still necessary.
- Modular reactor layouts, especially in open systems, have to be preferred to limit the pressure drops that in turn increase the auxiliary systems consumption. Separate reactors with efficient material transport systems can further increase the system performance by decreasing the overall reactor thermal mass.
- To make future research on sorption heat storage comparable, common key performance indicators should be adopted by the research community. For example, energy density at different research stages should be calculated defining a common reference temperature. Moreover, together with the energy density, the appropriate volume should be specified, which depends on the research scale (material, reactor, system).
- Economic considerations should be taken into account from the earliest stages of the research. Materials cost can already provide indications on the profitability of a future system in an intended application. When increasing the scale, all the components and auxiliary systems should be taken into account for the cost estimation.

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