

Sorption Thermal Energy Storage



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Abstract In the present chapter, an introduction about the concept of sorption TES technology is reported. The closed and open configurations are discussed and an overview on the ongoing research and development activities for materials, components and systems is given.

1 Introduction

Sorption TES belongs to the wider class of thermochemical energy storage. The definition ‘sorption’ was first reported by McBain [1] in 1909 to describe the interaction occurring between a gaseous sorbate and a liquid or solid sorbent. The former interaction was identified as absorption while the latter as adsorption. Absorption was defined as ‘*a modified solid solution in which practically only the outer layers become saturated, owing to the difficulty of diffusion in solids*’, while adsorption was defined as ‘*condensation on the outside of the surface of the solid*’. In most of the TESs based on sorption technology, the sorbate is represented by water vapour. For this reason, a classification among the materials for sorption TES is mainly referred to the sorbent employed, as represented in Fig. 1. The classification is performed taking into account the main reaction occurring between the sorbate and the sorbent materials. The absorption into liquids relates to absorption of water vapour inside salt solutions, or ammonia inside liquid water. The solid adsorption is related to the surface interaction between the sorbate (i.e. water vapour) with the solid surface, through weak bonds, like Van der Waals and hydrogen bonds. Nevertheless, in some cases different phenomena can coexist. In particular, the sorption composites present an intermediate behaviour between physical adsorption onto the solid (i.e. the host matrix) and chemical hydration reaction (i.e. in the embedded salt).

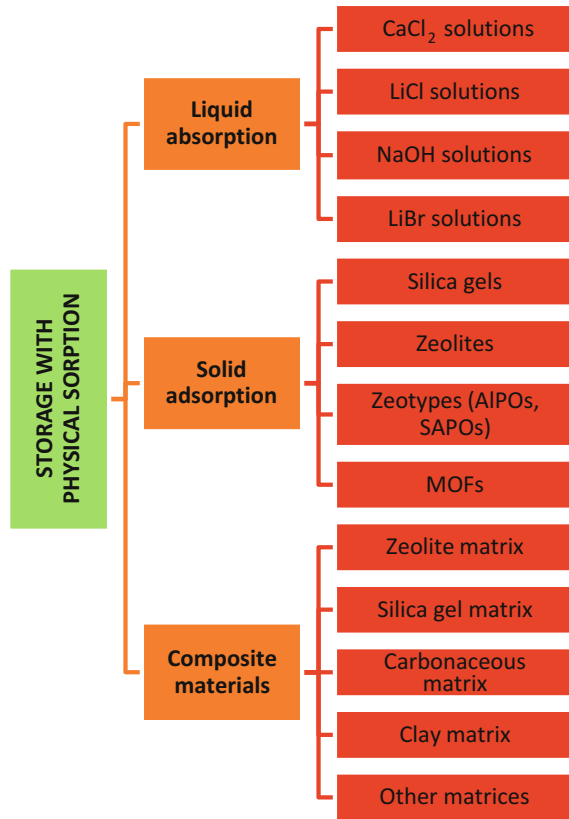
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A. Frazzica and L. F. Cabeza (eds.), *Recent Advancements in Materials and Systems for Thermal Energy Storage*, Green Energy and Technology,
https://doi.org/10.1007/978-3-319-96640-3_4

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Fig. 1 Categorisation of sorbent materials for sorption TES



Generally, there are two system configurations for sorption TES: closed and open cycle. Figure 2 reports the working phases of a closed sorption TES. During charging phase, the reactor, in which the sorbent material is saturated of sorbate (e.g. water), is regenerated exploiting heat coming from the heat source, Q_{des} . The desorbed vapour is then condensed in the condenser, and the heat of condensation, Q_{cond} , is either dissipated in the ambient or delivered to the load, if the temperature level is sufficient to satisfy it. Once the charging process is completed (i.e. the sorbent material is almost dry), the connection between the condenser and the reactor is closed. Under this condition, the system can keep the stored energy for indefinite time, since the thermal energy is stored as sorption potential between sorbate and sorbent material. In order to get back the stored thermal energy, the connection between liquid sorbate reservoir, which in this phase acts as evaporator and sorbent material in the reactor is again opened. During this discharging phase, the sorbate is evaporated by means of the heat from the ambient, Q_{evap} , then the

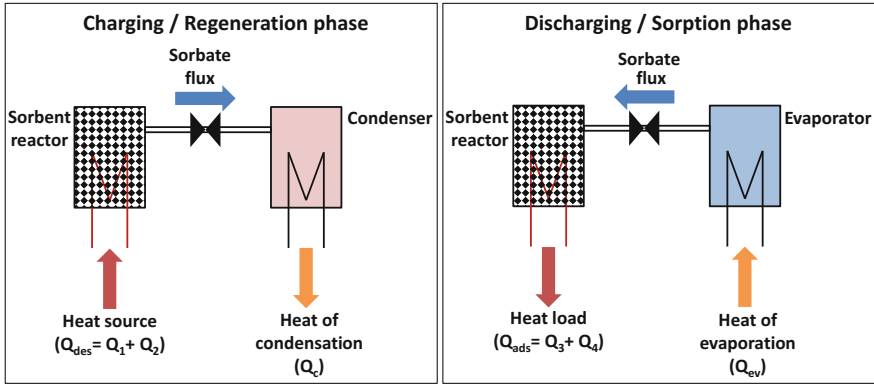


Fig. 2 Closed sorption TES cycle: charging and discharging phase

vapour fluxes to the sorbent material, since the sorption process is exothermic, heat is released to the load, Q_{sorp} . Clearly, this process is defined closed since the sorbate is continuously condensed/evaporated in a closed system without any mass exchange with the ambient.

Differently, the open sorption TES system, represented in Fig. 3, continuously exchanges mass (sorbate) with the ambient. Actually, the two charging/discharging phases are similar to the ones already described for the closed cycle. Main difference is that, in this case, heat is provided and extracted by fluxing air through the sorbent material contained in the reactor. Particularly, during charging/regeneration phase, a hot and dry air flux enters the storage, causing the desorption of sorbate (i.e. water), and exiting at lower temperature and higher humidity content. During discharging/sorption phase, the humid and cooled air flux is provided to the dry sorbent material, which triggers the sorption and the consequent release of stored heat, which reflects on the exiting hot and dry air flux.

In the literature, several reviews focus on the analysis of the peculiarities of each class of sorbent materials for TES applications, some suggested readings are [2–6]. The following sections focus on the most recent advancements achieved in the sorption TES technology during last years.

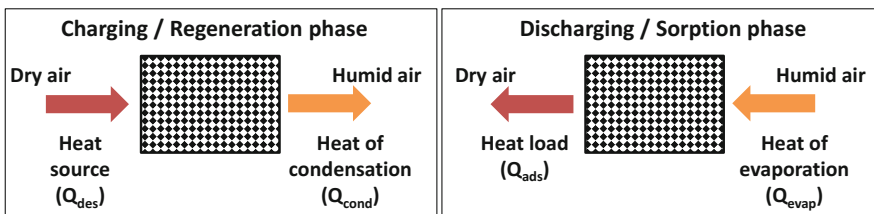


Fig. 3 Open sorption TES cycle: charging and discharging phase

2 Sorption Materials for TES Applications

2.1 Liquid Absorption

Liquid absorption technology was mainly investigated for absorption heat pumps and chillers applications [7]. In such a context, LiBr-water and ammonia-water are the working pairs commonly used for these applications, thanks to their good thermodynamic properties as well as their high cycling stability [7]. This technology has been proposed also for long-term thermal energy storage, investigating different possible salt solutions as sorbent. In the literature, the ones that showed the most attractive features are the aqueous solutions based on LiBr [8] and NaOH [9].

An interesting comparison among possible candidates for liquid absorption thermal energy storage was presented by [10]. They investigated seven working pairs, (aqueous solutions of CaCl_2 , Glycerine, KOH, LiBr, LiCl, NaOH and water/ammonia working pairs) analysing also the effect of allowing partial crystallisation of the salt inside the solution. In the paper, different features were analysed, taking into account optimal charging temperatures, cost of the materials and corrosion resistance. In Table 1 the achievable TES densities, minimum charging temperatures required, the storage system efficiency and the absolute pressure of the system are summarised. The data are reported for both solutions working without any crystallisation and solutions achieving a crystallisation up to a solid salt mass four times higher than the salt solution mass.

As can be highlighted in Table 1, when no crystallisation is allowed, the most attractive solution is the one employing LiCl as salt, presenting also low charging temperature and good efficiency. Similar result is obtained when the crystallisation happens. Clearly, neither glycerine/water nor water/ammonia working pairs can allow any crystallisation under the operating conditions typical of the TES. Generally, crystallisation improves the storage density, lowering at the same time the efficiency of the system. More discussions on the proper selection of liquid absorption working pairs can be found in [11, 12].

2.2 Solid Adsorption

In the solid adsorption TES, the adsorbate molecules interact with the solid on the external surface of the adsorbent by means of physical bonds. The adsorbent materials usually employed in solid adsorption TES are zeolites [13], silico-aluminophosphates [14] and silica gels [15]. Recently, also activities on Metalorganic Frameworks (MOFs) are under development for this purpose [16].

Zeolites are crystalline aluminosilicate adsorbents with microporous structure able to host molecules of different nature. Several different structures exist, but, for sorption TES applications with water as sorbate, the most commonly employed are 4A, 5A, 13X and Y [17]. These materials are quite well established and investigated

Table 1 Main features of investigated working pairs for liquid absorption TES

Crystallisation ratio	Parameter	CaCl ₂ /H ₂ O	Glycerine/H ₂ O	KOH/H ₂ O	LiBr/H ₂ O	LiCl/H ₂ O	NaOH/H ₂ O	H ₂ O/NH ₃
0	Storage density (kWh/kg)	0.254	0.053	0.727	0.56	1.218	0.432	0.365
	Minimum charging temperature (°C)	44.8	53.0	63.0	72.0	65.6	50.0	155.5
	Efficiency	0.909	0.545	0.830	0.850	0.950	0.750	0.665
	Absolute pressure (kPa)	1.2-4.2	1.2-4.2	1.2-4.2	1.2-4.2	1.2-4.2	1.2-4.2	615-1167
4	Storage density (kWh/kg)	0.562	-	0.916	0.723	1.425	0.661	-
	Minimum charging temperature (°C)	54.2	-	84.0	93.3	77.6	57.0	-
	Efficiency	0.885	-	0.586	0.835	0.923	0.767	-
	Absolute pressure (kPa)	1.2-4.2	-	1.2-4.2	1.2-4.2	1.2-4.2	1.2-4.2	-

Adapted from [10]

in the literature. Nevertheless, still some activities are currently performed. For instance, in [18], a comparison between commercial 13X with Na^+ as cation and exchanged samples with Mg^{2+} and Ca^{2+} was performed. It demonstrated that the effect of the cation allows obtaining higher storage density when the Mg^{2+} cations replace the Na^+ in the zeolite structure. Another analysis performed on the exchanged cations in 13X samples was recently reported in [19]. In this case, different cations were employed, demonstrating that the increasing trend of the storage density depends on the exchanged cations (i.e. $\text{Zn} > \text{Sr} > \text{Cd} > \text{Na}$). This confirms the possibility of tuning it by properly varying the exchanged cations. In general, zeolites are characterised by high charging temperatures (i.e. above $150\text{ }^\circ\text{C}$), which make them suitable for industrial TES applications but less attractive for low temperature solar TES.

Aluminophosphates (AIPOs) and other derived structures like silico-aluminophosphates (SAPOs) are characterised by a crystalline and porous structure, similar to the classical zeolites. For this reason they are often referred as zeotypes [20, 21]. These materials are usually characterised by an adsorption isotherm V according to IUPAC classification [22], showing a partially hydrophobic behaviour at low relative pressure and a partially hydrophilic behaviour at high relative pressure. This isotherm is sometimes defined as ‘S-shaped’ since a high water vapour exchange can be achieved in a narrow relative pressure range, making these materials suitable for sorption TES applications [21, 23]. Recently, Brancato and Frazzica [21] comparatively analysed the achievable performance of three among the most attractive zeotypes for adsorption heat transformation, namely, AIPO-18, SAPO-34 and FAPO-34. In particular, for TES application, they demonstrated that the storage density achievable by these materials, when heat source at $90\text{ }^\circ\text{C}$ is available, can reach up to 0.14 kWh/kg , to provide space heating, which represents a promising performance indicator for sorption TES application. Nevertheless, the available micro pores volume typical of these materials, which cannot allow further increasing the sorption capacity and thus the related TES density, limits this value. Some other papers dealing with the analysis of these materials are the following [14, 24].

Silica gels are porous materials with an amorphous structure, which have been historically considered for sorption TES applications, thanks to their ability as water sorbents. These materials can be synthesised under different conditions, achieving porous structure from the micro- to meso-pores [20]. They attracted a lot of attention, especially thanks to their low cost and wide commercial availability. Nevertheless, the interest towards this class of materials has been recently reduced, since outcomes of some research projects, like Modestore [25], demonstrated that they have low water vapour exchange, which limits the achievable TES density.

2.3 Composite Materials

The development of composite sorbent materials was proposed to overcome some of the main issues of the pure salt applied for sorption TES (i.e. cycling stability, low thermal conductivity and vapour transfer resistance) [26, 27]. Indeed, in these materials the salt is embedded inside a porous matrix, which disperses the salt, allowing lowering mass transfer resistance and limiting agglomeration problems. The research activity on the development and testing of this class of materials is gaining a lot of attention, thanks to high achievable TES density as well as their flexibility in terms of composition that makes them adaptable for different operating conditions.

Several salts coupled to different porous matrixes (e.g. zeolites, silica gels, carbonaceous materials) were investigated and reported in the literature. A deep literature review is reported in [6].

In Table 2, an overview of the composite sorbents developed and tested so far is reported. As can be seen, also from the storage density point of view, these materials show an intermediate behaviour between pure salts and physical adsorbents.

Table 3 reports a comparison among the average thermo-physical parameters of different sorbent materials for TES applications. As can be seen, the composites present the most attractive performance in terms of sorption capacity, which means achievable TES density. While, among the pure adsorbents, MOFs present attractive features. Nevertheless, both categories presents some open issues to be investigated, such as the cycling stability and the cost, especially for MOFs. This confirms the needs for further research and development activities.

3 Components and Systems for Sorption TES Application

Material development represents only the first stage in the design of a TES system, since the realisation of a complete system generally involves several technical challenges. Research on sorption storages, useful for application in the residential sector, still requires significant efforts for increasing the technological level. Nonetheless, during the last years, significant efforts were devoted to the study of components and prototypes, demonstrating the practical feasibility of the technology. To present a complete overview of the most recent systems reported in the literature, Table 4 summarises the relevant features and findings regarding the prototypes, while Table 5 presents the testing conditions and main experimental outcomes of a vast amount of prototypes of thermochemical storages available in the literature.

Among absorption systems, a wide experimental activity was performed on NaOH/water working pair for the development of a pilot demonstrator [42]. However, the results of the experimental campaign, despite proving the successful

Table 2 Some of the most interesting composite sorbents reported in the literature for sorption TES applications

Matrices	Salts	Salt (wt %)	Experimental conditions: temperature discharging/charging range (°C)	Experimental conditions: pressure range (kPa)	TES density (kWh/m ³ _{adsorbent}) or (kWh/kg _{adsorbent})	References
Silica gel, zeolite 13X, vermiculite	CaCl ₂ , MgSO ₄ , Ca(NO ₃) ₂ , LiNO ₃ , LiBr	2–65	30–140	–	Up to 50 (kWh/m ³)	[28]
Expanded natural graphite	KCl, CaCl ₂	63–90	25–200	2.0	Up to 175 (kWh/m ³)	[29]
Siliceous shale	LiCl, CaCl ₂	9.6	15–150	2.21	55.5 (kWh/m ³)	[30]
Graphite, zeolite A, sand	MgCl ₂	46–69	35–200	1.18–2.18	155.5 (kWh/m ³)	[31]
Activated carbon, silica solution, expanded graphite	LiCl	32–45	30–90	2.54	200–397.2 (kWh/m ³)	[32]
Silica gel	CaCl ₂	43	50–100	0–5.0	–	[33]
Zeolite 13X, silica gel	MgSO ₄	15	25–150	2.15	166.6 (kWh/m ³)	[34]
Silica gel, aluminosilicate	MgCl ₂ , CaCl ₂	30	–	–	166.6 (kWh/m ³)	[35]
Attapulgit	CaCl ₂	30	40–400	–	113.8–300 (kWh/m ³)	[36]
Attapulgit	MgSO ₄ , MgCl ₂	33	30–130	3.6	0.24 (kWh/kg)	[37]
FeKIL2	CaCl ₂	7	40–150	1.18–5.53	0.15 (kWh/kg)	[38]
Expanded natural graphite, activated carbon foam	KCl, CaCl ₂	31–90	25–200	1–2	0.36–0.40 (kWh/kg)	[39]
Multi Wall Carbon Nanotubes	LiCl, CaCl ₂	44–53	35–75	0.87–5.6	0.14–0.47 (kWh/kg)	[40]
Vermiculite	LiCl	59	35–85	0.87–5.6	0.5–0.72 (kWh/kg)	[41]

Adapted from [6]

Table 3 Thermo-physical parameters of different sorbent materials for TES applications

	Silica gels	Zeolites	AlPOs/SAPOs
Adsorption heat (kJ/kg)	160–180 ^a	50–300 ^a	250–300 ^a
Typical desorption temperatures (°C)	50–80	70–350	60–90
Density (kg/m ³)	650–700	650–900	800–900
Specific heat (kJ/kg K)	0.8–0.9	0.85–0.95	0.85–0.95
Thermal conductivity (W/mK)	0.15–0.20	0.15–0.25	0.15–0.25
Possible working fluids	Water	Water	Water
Amount of uptake exchanged in a typical cycle (g/g)	0.03–0.10	up to 0.2	up to 0.25
	Composites	MOFs	Activated carbons
Adsorption heat (kJ/kg)	50–250 ^a	20–200 ^b	45–900 ^c
Typical desorption temperatures (°C)	60–90	60–150	80–200
Density (kg/m ³)	300–600	1000–2000	700–750
Specific heat (kJ/kg K)	0.95–1.05	0.8–1.2	0.8–1.5
Thermal conductivity (W/mK)	0.15–0.30	0.10–0.15	0.15–0.75
Possible working fluids	Water, methanol, ethanol	Water, methanol, ethanol	Methanol, ethanol, ammonia
Amount of uptake exchanged in a typical cycle (g/g)	Up to 0.8	0.16–1.10	0.15–0.60

^athe heat of adsorption is calculated for a cycle with $T_{des} = 100$ °C, $T_{cond} = 30$ °C, $T_{ads} = 50$ °C, $T_{ev} = 10$ °C, with water as sorbate

^bthe heat of adsorption is calculated from isotherms at 298, 303 and 333 K, with water as sorbate

^cthe range of heat of adsorption is calculated with methanol and ammonia as sorbates

operation of the system, evidenced that a proper design of the components is needed to avoid low thermal power output.

In the field of solid adsorption, several prototypes were developed for space heating application, employing zeolite 13X as adsorbent within open cycles. The main peculiarity of the prototypes presented in [43–45] is their modularity, which allows parallel or series operation, to extend the time during which the useful effect is produced or increase the thermal power output. Instead, only a few prototypes were developed using zeolite (i.e. FAM Z02) for closed adsorption applications in space heating and cooling, which have further stressed the need for an optimised design of the storage unit itself and the auxiliary components, such as the evaporator.

On the contrary, during the last years, the intense activity on composite materials lead to the development of an increasing number of prototypes. Apart from the tailoring of the composite for the specific application, the main peculiarity of several of these prototypes is the use under different conditions than the standard charge/discharge cycle presented in Fig. 2. For instance, the prototypes developed

Table 4 Sorption storage systems recently presented

References	System description	Classification	Working pair	Size	Relevant results
[42]	Closed sorption heat storage for seasonal storage applications	Liquid absorption	NaOH/water	Pilot demonstrator	About 1 kW useful effect output was produced. Results of tests highlighted the need for a careful design of HEXs and the possibility to use a different solution rather than tube bundle array
[49]	Design of a spiral finned tube HEX for closed sorption heat storage	Liquid absorption	NaOH/water	Lab-scale	The tested heat exchanger guarantees large surface area, good wetting, thin film and sufficient exposure time, but the achievable thermal power is lower than with other solutions
[50]	Design of a falling film tube bundle HEX for closed sorption heat storage	Liquid absorption	NaOH/water	Prototype—10 kW nominal power	Detailed design of the absorber HEX is crucial for the correct operation of the prototype. An estimated energy density double of those of water tank was reached
[51]	Seasonal heat storage from solar collectors	Liquid absorption	KCOOH/water	Prototype—8 kWh nominal energy and 1 kW nominal power	The system can be regenerated at temperatures of 50–60 °C, but crystallisation occurred under some conditions
[43]	Open adsorption heat storage for a single family house	Open cycle adsorption	Zeolite Na-X/air	Prototype—4 kWh energy 2 kW nominal power	The system was able to provide continuous useful effect for 6 h. Air flow rate does not influence the amount of stored energy
[44]	Open adsorption heat storage for residential applications	Open cycle adsorption	Zeolite 13X/air	Prototype—2 kW nominal power	Effective regeneration of the prototype with 120–180 °C hot air from solar collectors was possible and a useful effect for 8 h was measured

(continued)

Table 4 (continued)

References	System description	Classification	Working pair	Size	Relevant results
[52]	Open adsorption seasonal heat storage for residential applications	Open cycle adsorption	Zeolite 13XBF/air	Prototype—4 kW nominal power	The reactor was divided into 4 segments of 62.5 l each. A maximum output power of 0.9 kW per segment was achieved. About 75% of total discharge is obtained in the first 10 h.
[53]	Adsorption storage for refrigeration purposes	Open cycle adsorption	Zeolite 13XBF/air	Prototype—3 kWh nominal energy	Design of the adsorber proved to be a critical issue, especially in terms of heat transfer and vacuum tightness
[54]	Closed seasonal adsorption storage to cover domestic hot water and space heating demand of a single family house	Closed cycle adsorption	Zeolite 13X/water	Pilot demonstrator	The system proved to be reliable and able to work with a solar fraction of 83.5%. A charge boost mode operation was tested, that allowed increasing energy density. Vacuum tightness was a critical issue to be addressed during design
[55]	Adsorption seasonal heat storage for solar heat systems in residential applications realised through a segmented reactor	Closed cycle adsorption	Zeolite 13XBF/water	Pilot demonstrator	The reactor was divided into 12 segment pairs that can be adsorbed and desorbed separately. Adjustment of flow rate to keep a constant outlet power was suggested
[24]	Adsorption closed storage for heat and cold applications	Closed cycle adsorption	Zeotype FAM Z02/water	Lab-scale	The system was tested as short-term heat storage, long-term heat storage and cold storage. An increase of energy density of about 100% with respect of water under the same boundaries was measured
[56]	Evaporation systems for application in closed sorption storages	Closed cycle adsorption	–	Lab-scale	Measurements on a falling film tube bundle to be used as evaporator in sorption storages, assessing the effect of geometrical parameters, such as tube spacing and irrigation density

(continued)

Table 4 (continued)

References	System description	Classification	Working pair	Size	Relevant results
[57]	Storage for space heating applications	Chemical reaction	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$	Lab-scale	The prototype is realised embedding the salt in an aluminium honeycomb structure to prevent agglomeration. 13 cycles were realised, showing a good cycling stability. Some design issues were evidenced, such as evapo-condenser unsteadiness, aluminium corrosion, and salt leaving the cells
[58]	Storage for space heating applications	Chemical reaction	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$	Prototype—100 kWh nominal storage capacity	The system was tested several times, showing a stabilisation of the thermal power output after the first cycle, with an average value of 0.3 kW. Furthermore, ways to control this storage system in order to meet user demand were investigated by changing the equilibrium drop and the air flow rate
[59]	Heat storage with gas–solid reaction	Composite materials	$\text{MnCl}_2\text{-ENG/NH}_3$	Lab-scale	Expanded graphite was used to increase the thermal conductivity of the salt. High maximum power (up to 50 kW) was measured, but the need for further improvements was evidenced, in particular towards the reduction of heat losses and the increase in filling ratio
[60]	Modular open sorption pipe reactor for solar thermal energy storage	Composite materials	Vermiculite- CaCl_2/air	Lab-scale	The system was regenerated with temperatures as low as 80 °C. The reactor consists of an outer and an inner (perforated) cylindrical shell and the sorption material filled in between. Results indicated an increase of storable energy up to 6 times that of water

(continued)

Table 4 (continued)

References	System description	Classification	Working pair	Size	Relevant results
[61]	Short and long-term heat storage	Composite materials	Vermiculite-LiCl/water	Lab-scale	Tests were done under seasonal storage boundary conditions. Average power of 0.5 kW and energy density of 330 kWh/kg _{material} were measured
[46]	Thermal battery for deep-freezing cold energy storage and heat energy storage	Composite materials	MnCl ₂ -EG/NH ₃	Lab-scale	Cold and heat energy densities measured are 600 kJ/kg and 1498 kJ/kg, respectively However, the benefits are more marked for heat energy storage when compared with cold energy storage
[47]	Seasonal solar heat storage for space heating applications	Composite materials	StCl ₂ -EG/NH ₃	Prototype	The system consists of two storage units, that can work in series or in parallel. For the two modes, energy storage densities of 706 kJ/kg and 305 kJ/kg were measured. Optimization of the HEXs is indicated as the possibility to increase salt conversion and improve system performance
[62]	Open sorption heat storage	Composite materials	Na-X zeolite-CaCl ₂ /air	Lab-scale	The composite adsorbent is realised by impregnation of the zeolite with the salt. The system consists of an external reactor and a moving material bed. Steady-state power output was 1.2 kW
[63]	Heat storage for domestic hot water and space heating	Composite materials	LiCl-EG/water	Prototype—1 kWh nominal stored energy	The sorption reactor consists of 25 identical sorption bed units, which are connected by manifold tubes in parallel. Stored energy density is compared to that of a water tank and is found to be double that of water

(continued)

Table 4 (continued)

References	System description	Classification	Working pair	Size	Relevant results
[64]	Open sorption thermal storage for space heating	Composite materials	LiCl-activated alumina/air	Prototype—1 kWh nominal stored energy	The reactor is designed as a modular system. However, due to different air inlet conditions, the various modules have different performance. Useful effect (warm air at 30 °C) was supplied for 7 h
[48]	Seasonal resorption energy storage for space heating	Composite materials	MnCl ₂ -CaCl ₂ /NH ₃ , MnCl ₂ -CaCl ₂ -ENG/NH ₃	Prototype	Different operating modes are evaluated, based on winter external conditions. Despite the typical operation with a high temperature and low temperature unit, coupling of two sets of high temperature and low temperature units and a sorption-compression mode are tested
[65]	Hybrid “solid sorption heat storage/air sourced heat pump” system for energy efficient	Composite materials	Vermiculite-CaCl ₂ /air, Vermiculite-MgCl ₂ /air, Vermiculite-LiCl-CaCl ₂ /air, Vermiculite-LiCl-MgCl ₂ /air,	Prototype—full scale domestic size	The reactor is a multilayer fixed bed. Among the composites, Vermiculite-CaCl ₂ and Vermiculite-LiCl-CaCl ₂ performed better. Under the best conditions, a useful effect for 1200 min, corresponding to 170 kWh could be obtained

Table 5 Boundary conditions and main results of the prototypes of sorption storages presented in literature

References	Classification	Working pair	Experimental conditions			Energy density	Max power (kW)
			T_{charge} (°C)	$T_{\text{discharge}}$ (°C)	$p_{\text{discharge}}$ (kPa)		
[66]	Liquid absorption	CaCl ₂ /water	95	47	–	380 kW/h/m ³ _{material}	–
[67]	Liquid absorption	LiBr/water	95	22	1.6	–	5.0
[42]	Liquid absorption	NaOH/water	95	25	2.6	–	1.0
[49]	Liquid absorption	NaOH/water	70	30–55	1.8	435 kW/h/m ³ _{material}	0.2
[50]	Liquid absorption	NaOH/water	70	50	5–12	74 kW/h/m ³ _{system}	1.2
[51]	Liquid absorption	KCOOH/water	50–70	30	4	–	0.4
[68]	Open cycle adsorption	Zeolite 4A/air	120–180	20–25	Atmospheric	130 kW/h/m ³ _{material}	–
[43]	Open cycle adsorption	Zeolite Na-X/air	180	20	Atmospheric	0.3 kW/h/kg _{material}	2.2
[44]	Open cycle adsorption	Zeolite 13X/air	120–180	20	8	–	–
[52]	Open cycle adsorption	Zeolite 13XBF/air	180	30	Atmospheric	198 kW/h/m ³ _{material} , 109 kW/h/m ³ _{system}	0.9
[69]	Closed cycle adsorption	Zeolite 13XBF/water	180	65	–	95 kW/h/m ³ _{material}	–
[70]	Closed cycle adsorption	Zeolite 13X/water	175–250	70	7	20.4 kW/h/m ³ _{system}	–
[53]	Closed cycle adsorption	Zeolite 13XBF/water	220	20	1.2	–	0.5
[54]	Closed cycle adsorption	Zeolite 13X/water	180	25	1.8	178 kW/h/m ³ _{material}	4.6

(continued)

Table 5 (continued)

References	Classification	Working pair	Experimental conditions			Energy density	Max power (kW)
			T_{charge} (°C)	$T_{\text{discharge}}$ (°C)	$P_{\text{discharge}}$ (kPa)		
[55]	Closed cycle adsorption	Zeolite 13XBF/water	180	30	–	163 kWh/m ³ _{material}	0.8
[24]	Closed cycle adsorption	Zeotype FAM Z02/water	90	5–20 (cold storage) 30–45 (heat storage)	1.2	0.8 kWh/kg _{material} (cold storage) 1.6 kWh/kg _{material} (short-term heat storage) 2.8 kWh/kg _{material} (long-term heat storage)	0.6
[56]	Closed cycle adsorption	–	–	–	–	–	–
[71]	Chemical reaction	Na ₂ S·5H ₂ O	80	20	1.8	1.7 kWh/kg _{material} (heat) 0.7 kWh/kg _{material} (cold)	0.5 W/kg
[72]	Chemical reaction	MgCl ₂ ·6H ₂ O	130	60	1.2	140 kWh/m ³ _{material}	0.15
[58]	Chemical reaction	SrBr ₂ ·6H ₂ O	80	25	Atmospheric	203 kWh/m ³ _{material}	0.8
[57]	Chemical reaction	SrBr ₂ ·6H ₂ O	100	20	1.5–3.2	213 kWh/m ³ _{material}	–
[59]	Composite materials	MnCl ₂ -ENG/NH ₃	174	50	90	179 kWh/m ³ _{material}	9.9
[73]	Composite materials	BaCl ₂ -ENG/NH ₃	60–70	4	–	114 kWh/kg _{material}	5.0
[60]	Composite materials	Vermiculite-CaCl ₂ /air	80	20	Atmospheric	290 kWh/m ³ _{material}	0.6
[61]	Composite materials	Vermiculite-LiCl/water	75–90	35	1.2	2330 kWh/kg _{material}	–

(continued)

Table 5 (continued)

References	Classification	Working pair	Experimental conditions			Energy density	Max power (kW)
			T_{charge} (°C)	$T_{\text{discharge}}$ (°C)	$P_{\text{discharge}}$ (kPa)		
[46]	Composite materials	MnCl ₂ -EG/NH ₃	150	112 °C (heat storage) -10 °C (cold storage)	-	167 kWh/kg _{material} (cold storage) 417 kWh/kg _{material} (heat storage)	-
[47]	Composite materials	SrCl ₂ -EG/NH ₃	90	45	-	196 kWh/kg _{material} (parallel operation) 85 kWh/kg _{material} (series operation)	643 W/kg _{material}
[62]	Composite materials	Na-X zeolite-CaCl ₂ /air	180	30	1.5	260 kWh/m ³ _{material}	1.5
[63]	Composite materials	LiCl-EG/water	85	40	1.5	65 kWh/m ³ _{material}	11
[64]	Composite materials	LiCl-activated alumina/air	110	20	Atmospheric	190 kWh/m ³ _{material}	0.13
[48]	Composite materials	MnCl ₂ -CaCl ₂ /NH ₃ , MnCl ₂ -CaCl ₂ -ENG/ NH ₃	50	30	-	1047 kJ/kg _{material}	402 W/kg _{material}
[65]	Composite materials	Vermiculite-CaCl ₂ /air, Vermiculite-MgCl ₂ / air, Vermiculite- LiCl-CaCl ₂ /air Vermiculite- LiCl-MgCl ₂ /air	85	30	Atmospheric	170 kWh/m ³ _{material}	

in [46, 47] are used as ‘sorption thermal battery’ for cold and heat energy storage: based on user request (i.e. cold or heat) connection to the evaporator or to the sorption bed of the thermal battery can be selected, even to achieve contemporary heat and freezing useful effect. The prototype reported in [48] is a resorption thermal battery that can be operated in different modes according to the external ambient temperature.

A common outcome of many experimentations is the need to address design issues, either to increase the achievable storage capacity or, in the case of the prototypes containing salts, to avoid salt leakage and increase the thermal conductivity of the system. It is however possible to foresee that, thanks also to the increasing number of projects involving sorption storages, a technological growth will be achieved within the next years.

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