Survey Summary on Salts Hydrates and Composites Used in Thermochemical Sorption Heat Storage: A Review

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Abstract: To improve the proficiency of energy systems in addition to increasing the usage of renewable energies, thermal energy storage (TES) is a strategic path. The present literature review reports an overview of the recent advancements in the utilization of salt hydrates (single or binary mixtures) and composites as sorbents for sorption heat storage. Starting by introducing various heat storage systems, the operating concept of the adsorption TES was clarified and contrasted to other technologies. Consequently, a deep examination and crucial problems related to the different types of salt hydrates and adsorbents were performed. Recent advances in the composite materials used in sorption heat storage were also reviewed and compared. A deep discussion related to safety, price, availability, and hydrothermal stability issues is reported. Salt hydrates display high theoretical energy densities, which are promising materials in TES. However, they show a number of drawbacks for use in the basic state including low temperature overhydration and deliquescence (e.g., $MgCl_2$), high temperature degradation, sluggish kinetics leading to a low temperature rise (e.g., $MgSO_4$), corrosiveness and toxicity (e.g., Na_2S), and low mass transport due to the material macrostructure. The biggest advantage of adsorption materials is that they are more hydrothermally stable. However, since adsorption is the most common sorption phenomenon, such materials have a lower energy content. Furthermore, when compared to salt hydrates, they have higher prices per mass, which reduces their appeal even further when combined with lower energy densities. Economies of scale and the optimization of manufacturing processes may help cut costs. Among the zeolites, Zeolite 13X is among the most promising. Temperature lifts of 35–45 °C were reached in lab-scale reactors and micro-scale experiments under the device operating settings. Although the key disadvantage is an excessively high desorption temperature, which is problematic to attain using heat sources, for instance, solar thermal collectors. To increase the energy densities and enhance the stability of adsorbents, composite materials have been examined to ameliorate the stability and to achieve suitable energy densities. Based on the reviewed materials, $MgSO_4$ has been identified as the most promising salt; it presents a higher energy density compared to other salts and can be impregnated in a porous matrix to prepare composites in order to overcome the drawbacks connected to its use as pure salt. However, due to pore volume reduction, potential deliquescence and salt leakage from the composite as well as degradation, issues with heat and mass transport can still exist. In addition, to increase the kinetics, stability, and energy density, the use of binary salt deposited in a porous matrix is suitable. Nevertheless, this solution should take into account the deliquescence, safety, and cost of the selected salts. Therefore, binary systems can be the solution to design innovative materials with predetermined sorption properties adapted to particular sorption heat storage cycles. Finally, working condition, desorption temperature, material costs, lifetime, and reparation, among others, are the essential point for commercial competitiveness. High material costs and desorption temperatures, combined with lower energy densities under normal device operating conditions, decrease their market attractiveness. As a result, the introduction of performance metrics within the scientific community and the use of economic features on a material scale are suggested.

Keywords: sorption; heat storage; thermo-chemical; energy; adsorbent materials; salts; composite

1. Introduction

From 2005 to 2030, global energy demand is projected to increase by 50% due to population growth and economic development [1]. Energy policy production is now at a crossroads due to decreasing fossil fuel supplies, growing energy demand, and rising greenhouse gas emissions [2]. The current energy policy aims to decarbonize the energy system by switching to alternative energy sources, developing new energy production technologies, and increasing energy efficiency [3–6]. One of the aims of the Paris Agreement is to migrate entirely away from fossil fuels and toward renewable energy sources. However, the world's renewable energy potential has yet to be fully realized; only 23% of these energy sources have been used [7]. This opens up a lot of space for strengthening and innovating clean energy policies.

Fossil fuels release greenhouse gases (for instance, CO_2, NO_x, and others), which are damaging the atmosphere. The U.S. Energy Information Administration's Annual Energy Outlook (AEO) report forecasted that by the end of 2020, energy generated from renewable energy sources such as solar, wind, and geothermal will rise to 20 percent. The key problem related to solar and wind energy is their intermittent nature and the lack of ability to generate energy 24 h a day. Consequently, renewable energy storage technologies (REST) that allow for a stable supply chain of energy are crucially required.

There are different approaches to storing energy, comprising the following: electrical energy storage (EES), mechanical energy storage (MES), chemical energy storage (CES), and thermal energy storage (TES) [8,9]. For instance, about 39% of the total energy is used by residential and industrial buildings in the United States; the majority of this energy is used for cooling and heating applications [10]. Batteries are the most popular electricity storage technology, but TES may be the ideal choice when dealing with heating and cooling [2,11,12]. TES devices store energy extracted from the sun, helping to minimize the costs, improve demand-side control with an overall performance improvement, provide improved reliability, and diminish the carbon footprint. District heating/cooling, seasonal storage for commercial and private buildings heating, time-shifting of energy demands, and waste heat recovery are the main applications of TES. Systems designed for TES-based heating or cooling applications have the promising economic advantage of minimizing the cost of capital and maintenance that can satisfy average demand, and not just peak and cycling requirements.

Solar energy, by its nature, is intermittent (day/night), random (thunderstorms and cloud passages), diluted, and delayed on daily or seasonal energy demand. Moreover, its exploitation requires the deployment of high-performance storage systems. In contrast, thermal energy storage technology has reached maturity, which makes it ready to be harnessed for the efficient use of renewable energies. To store energy in the form of heat, there are three basic principles: sensible heat storage (SHS), latent heat (LHS), and thermochemical storage (TCES) [13]. The importance of thermal energy storage compared to other existing technologies is illustrated in Figure 1 [14]. It shows that thermal energy storage allows for the management of high power over long periods of time.

Energy storage is about saving a quantity of the stored energy for later use. By extension, the expression also refers to the storage of matter containing energy, therefore, the storage material. This sector continues to be the subject of research, whether for sensible, latent, or thermochemical storage applications, always looking for promising materials having both ecological and economic criteria and good thermal conductivity [15–20]. The storage of thermal energy mainly concerns the heat coming from the sun. More recently, the storage of the waste heat produced by certain industries (metallurgical industry, gas plant, incineration plant and others) has also been investigated. Thermal energy storage technologies can be classified into various categories according to different criteria (see Figure 2). If the criterion is the temperature range, storage systems are divided into "heat storage" and "cold storage" [21,22]. In the case where the criterion is the duration of storage, two classes are considered: "long-term storage" and "short-term" storage. On the other

hand, if the criterion is the condition of the storage material, there are three main types: "sensible heat storage", "latent heat storage", and "thermochemical heat storage" [23].
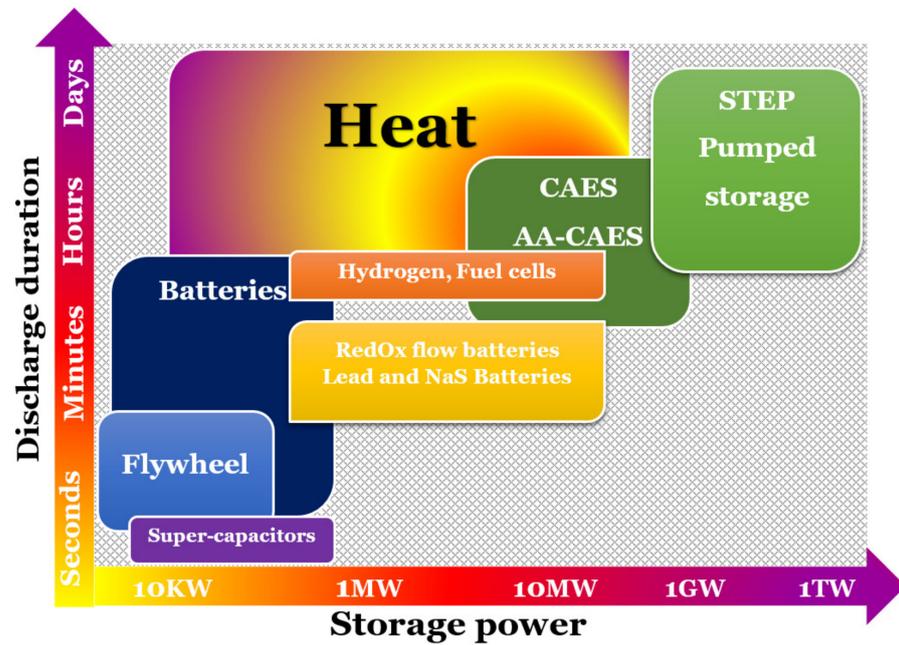

Figure 1. Different storage technologies depending on their storage power and discharge time.
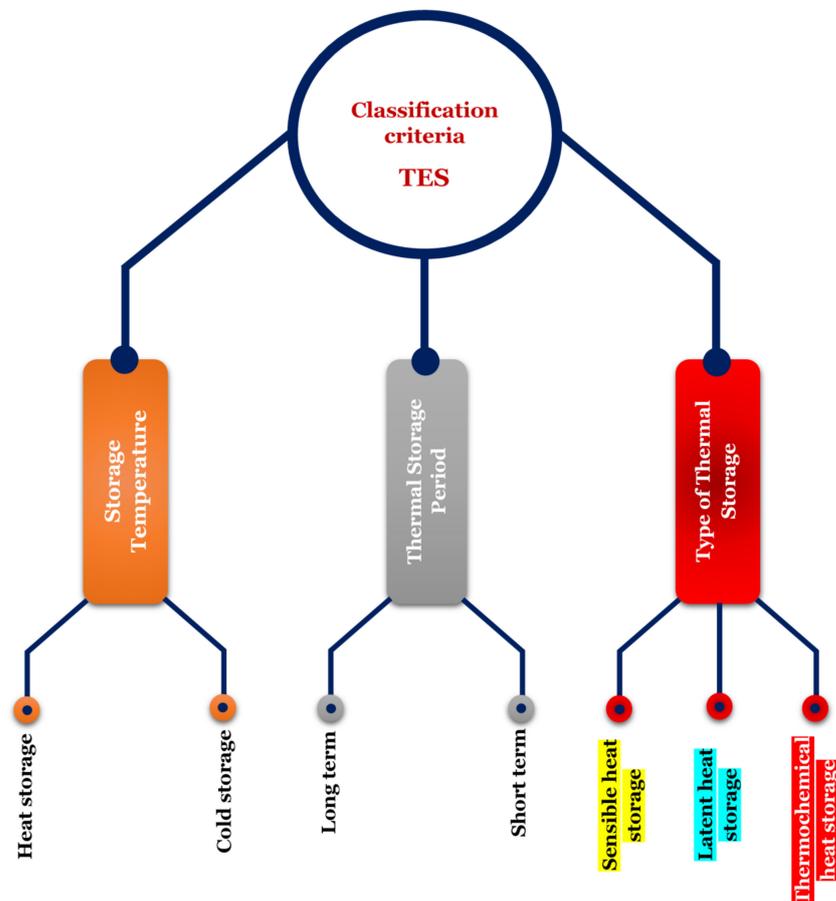

Figure 2. Classification of thermal energy storage systems.

Table 1 lists the characteristics of the three types of thermal energy storage presented. Six fundamental parameters were chosen: energy density, storage temperature, storage time, energy transport, system maturity, and system implementation complexity. Currently, SHS is the most mature thermal energy storage process. Without changing the phase of a material, the SHS system stores energy, and the energy storage density depends on the material's specific heat, mass of the heat storage medium, and the increase in temperature. Low cost and thermal stability are desirable characteristics of heat storage in the SHS system, while the SHS system's drawbacks are the need for a larger volume, higher thermal loss, unbalanced discharge temperature, and smaller energy storage density than the LHS and TCES systems. During the phase change of a material, the LHS system stores heat. Solid–solid, solid–liquid, or solid–gas can be the phase transition [24,25]. The quantity of heat retained depends on the latent heat of the material in the LHS method.

The LHS system has a higher heat storage density compared to the SHS, is dense, and has a steady discharge temperature. Low thermal conductivity, flammability of certain organic materials, and corrosiveness are the main drawbacks of the LHS system [13,26]. Via the sorption process and chemical reaction, a thermochemical energy storage (TCES) system stores energy. Endothermic and exothermic reactions are the chemical reactions for charging and discharging heat, respectively.

Table 1. List of thermal energy storage systems and their characteristics.

	SHS System	LHS System	TCES System
Principle description	SHS storage involves increasing the temperature of an element and recovering this energy by dropping its temperature during the discharge phase. Then, we use the heat capacity, Cp, of the element, which is the amount of energy needed, per unit mass, to increase (or decrease) its temperature by 1 °C. The discharge temperature cannot be higher than the charge temperature. For applications where the operating temperature is between 0 and 100 °C, the most widely-used material is water, for example, in the domestic hot water tank of a home. Indeed, it is a non-toxic and inexpensive product. There is also the use of certain rocks or concrete. Beyond 100 °C, it is possible to use solid elements such as concrete at high temperatures or refractory ceramics, but the necessary volumes are important. Generally, we can find liquid storage systems for molten salts, pressurized water, or organic oils. For high temperature applications, molten salts are the most widely used material. This is due to their high volumetric heat capacity, a high boiling point, high temperature stability, and their vapor pressure being close to zero. Additionally, they are relatively cheap, readily available, neither toxic nor flammable, and can act as a heat transfer fluid as well as a TES material. However, they have certain disadvantages: they have a relatively high melting point (generally >200 °C), which results in them solidifying in pipes in the absence of a heat source and thus necessitates the installation of antifreeze systems; they also have high viscosity and low thermal conductivity compared to other fluids [27].	LHS is the amount of energy required to change the state of a solid, liquid or gas, called phase change material, PCM. In LHS systems, common transformations are from solid to liquid or from liquid to gas. The temperature range corresponding to the phase change of a PCM should be relatively small (20 to 80 °C). The materials used in LHS are numerous and allow working over a wide temperature range (example: 0 °C for water; 318 °C for sodium hydroxide). Latent heat storage in 'low' temperature range below 220 °C, 'medium' range up to 420 °C, and 'high' range greater than 420 °C is associated with a solar power tower as the point focus system. Materials for potential use as PCMs are mostly organic compounds, inorganic salts, and their eutectics. Inorganic materials such as salt hydrates, metals, and eutectics as well as organic compounds such as paraffin waxes, esters, acids, and alcohols have been studied [28]. According to the literature, molten salts have received more attention for heat storage applications than molten metals and alloys [29].	TCES involves reversible reactions, endothermic in one direction and exothermic in the other direction. These may be physical or chemical phenomena, described as follows: A + ΔH ⇔ B + C During the storage process, the charging phase corresponds to an endothermic decomposition reaction of a chemical element A into two products B and C stored separately at room temperature. The phase of discharge corresponds to the exothermic synthesis of the chemical element A by association of the two components B and C. It can correspond to physisorption or chemisorption phenomena, but in all cases, the heat released comes from the breaking of the bonds between the various components. TCES can be applied to energy storage at less than 100 °C and between 100–400 °C, the physisorption being characterized by a low enthalpy (<50 kJ/mol of material) and chemisorption, by a high enthalpy (>100 kJ/mol of material). TCES is defined according to two criteria: is the process open or closed, and is the reactor integrated or separate from the storage system. In a closed circuit, the storage of the sorbate is an internal element of the process. In an open circuit, in contrast, there is a transfer of material with the outside of the process in order to supply the sorbate to the reactor. In both cases, sorbent storage is a component of the system.

Table 1. *Cont.*

	SHS System	LHS System	TCES System
Volumetric energy density storage	Small (15–50 kWh/m³)	Medium (50–100 kWh/m³)	High (100–700 kWh/m³)
Gravimetric energy density storage	Small (0.02–0.03 kWh/kg)	Medium (0.05–0.1 kWh/kg)	High (0.5–1.0 kWh/kg)
Capacity	10–50 (kWh/t)	50–100 (kWh/t)	120–250 (kWh/t)
Power	0.001–10.0 (MW)	0.001–1.0 (MW)	0.01–1.0 (MW)
Efficiency	50–90%	75–90%	75–100%
Cost	0.1–10 (€/kWh)	10–50 (€/kWh)	8–100 (€/kWh)
Storage temperature	Charging step temperature	Charging step temperature	Ambient temperature
Storage period	Limited due to thermal losses to surroundings	Limited due to thermal losses to surroundings	Theoretically unlimited
Energy transport	Shorter distance	Shorter distance	Theoretically long distance
Maturity	Industrial scale	Pilot-scale	Laboratory and pilot-scale
Technology	Simple	Simple	Complex

In the literature, two types of TCES systems are addressed: sorption-based TCES and reaction-based TCES. High energy storage density and the ability to store energy with minor losses for longer periods are the two key advantages of a TCES approach. For these reasons, TCES has attracted the interest of researchers around the world.

2. Philosophies and Concept of Sorption Heat Storage

The term "thermochemical" storage, which often replaces heat storage by sorption, designates the process during which the molecules (adsorbate) of a fluid (generally a gas) are fixed on a solid or a liquid (adsorbent/absorbent) [30–32].

Two types of "sorption" can then be distinguished (Figure 3):

- Adsorption, a surface interaction phenomenon generally between a solid and a gas.
- Absorption, a volume interaction phenomenon in which the adsorbate molecules diffuse into the adsorbent volume (e.g., a gas or a liquid that goes into solution in another liquid).
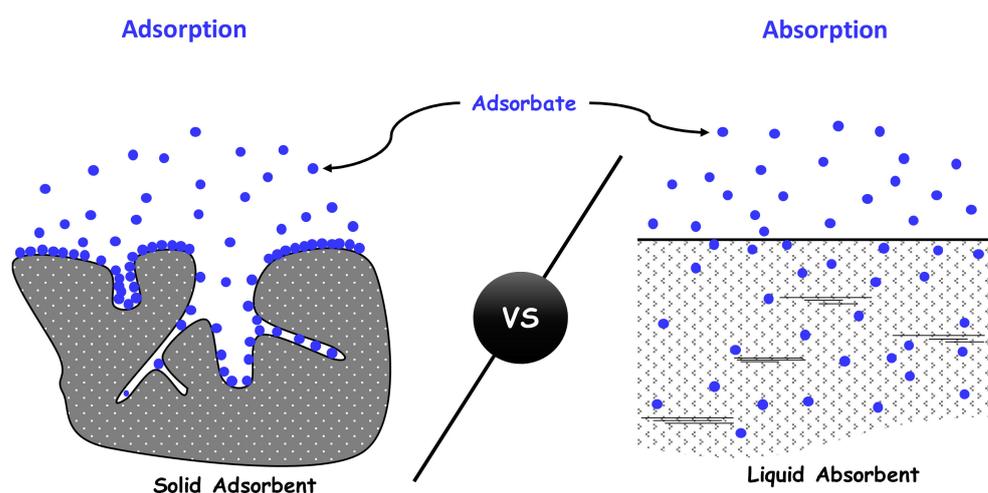
Figure 3. Adsorption vs. absorption: difference and comparison.

In the latter case, an additional differentiation is related to the nature of the bonds:

- Physical adsorption or physisorption: the fixation of adsorbate molecules to the adsorbent surface is done primarily by van der Waals forces (10–100 meV) and the forces due to polarization electrostatic interactions for adsorbents with an ionic structure (e.g., zeolite). It occurs without changing the molecular structure and is generally

reversible: the adsorbed molecules can be desorbed by reducing the pressure or increasing the temperature.

- The chemical adsorption or chemisorption: the process is the result of a chemical reaction with the formation of chemical bonds between the adsorbate and adsorbent surface. The binding energy (1–10 eV) is much stronger than that of physical adsorption and the process may be irreversible.

Due to its high energy density and low heat loss, the sorption-based heat storage TCES system has gained substantial consideration [33]. This reversible energy storage mechanism is commonly referred to as the process of charging for energy storage and discharging for the use of the stored energy. For different applications, the concept of sorption-based TCES can be practical: short/long-term energy storage, cooling systems, domestic supply of hot water, industrial heat/cooling, and space heating.

Sorption-based TCES charge, storage, and discharge processes are presented in Figure 4. Charging is an endothermic process in which heat is externally supplied and the adsorbent and adsorbate are dissociated as a consequence. At room temperature, the dissociated materials can be stored separately. The adsorbent and adsorbate are transported together during the discharge process to form the original substrate. During this exothermic step, the heat is released [34].
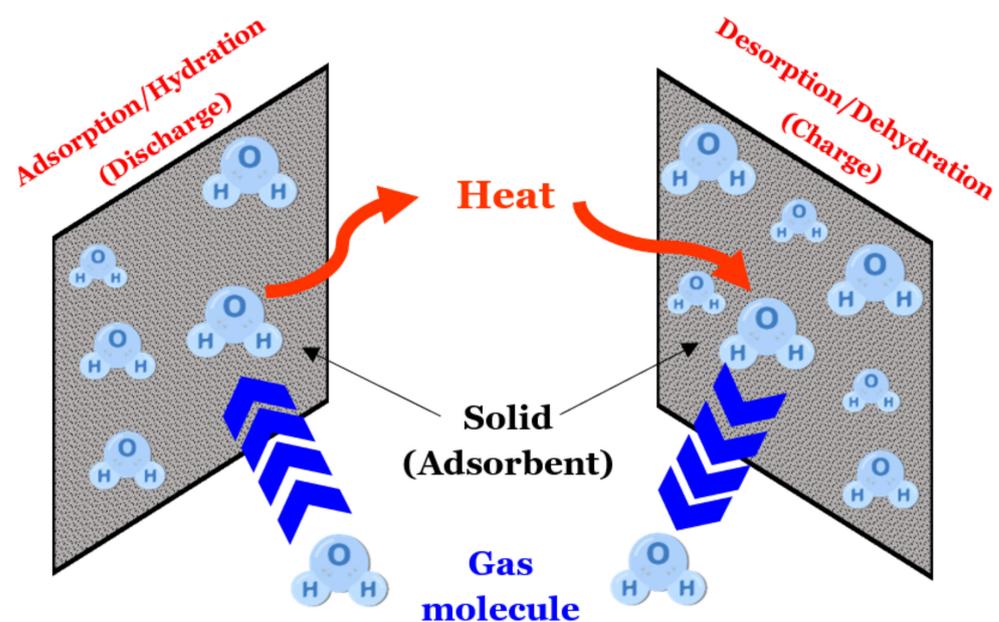

Figure 4. TCES principle of sorption (charge and discharge).

An energy storage system can be categorized based on the following features [35–38]:

- The storage period (hours, days, or weeks) determines the time-consumption of the energy stored.
- The word "power" refers to how easily energy stored in a device can be charged and discharged. Expressly, power capacity (W) refers to the maximum amount of power that the storage device can produce during discharging. The power density (W/L) is the ratio of the power capacity to the energy storage system's capacity.
- The amount of energy absorbed in the storage device throughout the charging process under nominal conditions is known as the energy storage capacity or energy capacity. The amount of stored energy in a device after it has been charged is determined by the storage process, storage medium, and system size.
- Energy density, also known as volumetric heat power, is the ratio of stored energy to the volume of the energy storage unit.

- The time required to charge or discharge the device is determined by the charge and discharge time. The cycling capacity, or number of cycles, is defined as the maximum number of charge–discharge cycles possible under the given conditions.
- Self-discharge is the amount of energy initially accumulated and dissipated over a given non-use time.
- The ratio of energy delivered and the energy required to charge the storage device is known as efficiency. It takes into account the energy losses that occur during storage and the charge/discharge cycle.
- The rate at which energy is adsorbed or released is known as the response time [h].
- The time needed for the storage device in order to release energy after each recharge is referred to as the cycle life.
- Cost is a metrics that describes the overall cost in terms of total capacity (€/kWh) or power (€/kW). These are the storage equipment's capital costs as well as the operating and repair costs over its lifetime.
- The cost per unit of energy divided by the storage efficiency ratio is recognized as cost per output (useful) energy.
- The cost per cycle is calculated by dividing the cost per unit of energy by the cycle life.

Table 1 shows the typical values for the above-mentioned parameters for thermal energy storage technologies. When it comes to the storage duration, TCES approaches are classified as short-term when the heat input and output occur within a few hours or days, and as long-term when the time duration corresponds to a few months or even a whole season [39]. TCES, in comparison to SHS and LHS, are well-suited to long-term storage [40]. The explanation for this is that there are no major energy losses (no self-discharge) during the storage process [41]. Heat cannot be stored for a long time because SHS and LHS require isolation systems during storage to prevent thermal losses [36]. TCES for hot/cold request, despite its seasonal storage capacity, is still in the primary stages of production, with only a few prototype setups [35].

To select a thermal energy storage device for a specific application, the storage energy density is the most critical parameter [42]. TCES technology has fascinated and attracted attention in many domains [43] due to its potentially higher energy storage density, which is five to 10 times higher than LHS and SHS systems, respectively [44]. Because of its high energy density, thermochemical thermal energy storage systems (TCES) are more compact energy systems, and their usage, which decreases the system's volume, may be very efficient in circumstances where space is restricted [35]. In term of capital costs, SHS is less costly than LHS and TCES, according to a simplified economic comparison. TCESs are not commonly available in the market because of their high capital costs [40].

The key advantages of TCES technology are the high storage density, the low heat loss, the absence of self-discharge and long charge/discharge, the broad availability, and the suitable temperature ranges. However, due to the high complexity and cost of these technologies, only a few prototype-scale systems have been investigated. Comprehensive evaluations and investigations are expected to enhance their implementation. Thermochemical storage, on the other hand, is commonly used in the heat-to-power industry. The heat-to-power and power-to-heat industries are two of the most important choices for balancing renewable energy sources and, as a result, the power grid. This unique relationship between the electricity and heat sectors will be crucial in achieving a cost-effective transition to a low-carbon energy system with strong renewable generation diffusion.

The use of sorption thermal energy storage systems for long-term storage applications has been studied for several years [42,45–48]. Earlier review papers on this subject focused on sensible, latent, and chemical heat storage systems for seasonal storage applications [45], long-term sorption energy storage technologies [2], solid and liquid sorption materials and reactors [47], and systems for building applications [18].

The aim of this review paper is to provide an overview of the most recent developments in sorption heat storage technologies based on solid/gas reactions with water as the sorbate. This work focuses on the current state of science at the material scale. The

current project is divided into eight major parts. A systematic analysis of the various hydrated salts and their properties in relation to their use in thermochemical heat storage is presented in Section 3. An analysis of current research on salt hydrate materials is conducted in Section 4, and their classification outputs are discussed and compared. Different composite-based mono salt hydrates and binary salt hydrates in sorption-based TCES are discussed and compared in Sections 5 and 6. Section 7 discusses safety, corrosion effects, and recommendations, while Section 8 concludes with a detailed overview, the challenges, and potential scope of the discussed adsorbent materials. This will serve as a roadmap for the development and optimization of target-oriented adsorbent materials for TCES systems in the future. In Table 2, the main contributions of numerous reviews published on TCES are summarized and compared.

Table 2. Summary of the latest review papers on low and medium temperature TCES systems.

Author(s)	Highlights	Ref.
Fopah-Lele and Tamba (2017)	$SrBr_2 \cdot 6H_2O$ was chosen for its thermal properties and sorption characteristics in heating and cooling applications. Several studies on $SrBr_2 \cdot 6H_2O$ were conducted at the laboratory and prototype scales.	[49]
Krese et al. (2018)	The use of solar energy in TCES technologies and systems for building applications was highlighted. The numerical modeling of device design for open and closed sorption storage systems was the focus of this project.	[50]
Lizana et al. (2018)	An analysis of recent developments in thermal energy storage technology for zero-energy building applications was presented. Sensible, latent, and thermochemical thermal energy storage systems were used to investigate different types of materials and mechanisms for heat storage.	[51]
Kuznik et al. (2018)	The idea of a building-based physisorption heat storage system was introduced. Concentrated on physisorption materials (activated carbon, silica gel, zeolites, and composite salts), reactors (fixed bed and fluidized bed), and experimental prototypes.	[52]
Sunku Prasad et al. (2019)	Reviewed TCES systems operating over 300 °C. Under the category of solid–gas reactions, authors discussed carbonates, hydroxides, metal hydrides, and redox reactions; Under the category of gas–gas reactions, authors discussed ammonia synthesis/dissociation, methane reforming, and the $SO_3/O_2/SO_2$ TCES system. A variety of reactor designs for solid–gas and gas–gas reactions were described. Cyclic experiments on solid–gas reaction materials were described.	[53]
Palomba et al. (2019)	A review of the most recent developments in the field of sorption TES. The results of activity analysis at the materials and device levels are presented. In addition, the most recent events and sponsored programs in the field of sorption TES are highlighted.	[54]
Fumey et al. (2019)	Open fixed, open transported, closed fixed, and closed transported are the four basic sorption thermal energy storage processes. Temperature effectiveness is a universal metric for comparing the efficiency of sorption heat storage systems. In terms of temperature effectiveness, closed transported sorption thermal energy storage systems perform much better.	[55]
Wu et al. (2019)	In light of space heating applications, a critical review of solid materials for low-temperature thermochemical storage of solar energy based on solid-vapor adsorption. The current report is about low-temperature thermochemical storage for space heating, which is dependent on vapor adsorption into solid adsorbents.	[56]
Desai et al. (2021)	For cooling and process heating applications, a thermochemical energy storage device is used. Metal hydride-based cooling and heating systems are defined in detail. For medium-temperature applications, salt hydrates are discussed. Solar-powered cooling and heating systems conceptual designs.	[13]
Lin et al. (2021)	Based on material classification, applications of low-temperature thermochemical energy storage systems for salt hydrates. This review established a fair classification of salt hydrates for TCES systems, summarizing material properties, appropriate reactor types, applications, and device prototype optimization based on material properties.	[57]
Present review	The materials, mechanisms, and storage principles of sorption and reaction-based TCES systems are discussed in this study. TCES materials and applications at low and medium temperatures are the focus. A comprehensive review of recent research on the use of mono and binary salts imbedded in host matrixes. The safety of various materials is discussed.	

3. An Overview about the Use of Salts

Salt hydrates, with the formula salt. xH_2O, were thought to be a common solid crystal made up of inorganic salt and water. There were different types of hydrates: into certain hydrates, water is organized around the positively charged (cation) elements of the salt. This is a chemisorption phenomenon and these hydrates contain coordinating water molecules. In other types of hydrates, water fills the interstitial void in the salt structure. This is a phenomenon of physisorption (adsorption) and these hydrates contain structural water molecules [58]. In chemisorption (the reaction enthalpy is superior than in physisorption), the thermodynamic and kinetic properties of the components were directly related to the modifications of their crystal structures during hydration and dehydration reactions. These modifications were controlled by the vapor pressure, operating temperatures, and heating and cooling rates (related in practice to the characteristics of the heat exchangers) [59]. A systematic analysis of 125 hydrated salts was published by N'Tsoukpoe et al. [60] in 2014. The work focused on the characterization and evaluation of the various salts in terms of their suitability for energy thermochemical storage processes. The first evaluation allowed for the exclusion of compounds with a certain toxicity or even explosion risk from the list. Table 3 lists the different pairs of hydrated salts studied for thermal energy storage applications as well as their thermochemical properties.

Table 3. Hydrated salts and their properties.

Hydrated Salt	Dehydrated Salt	T_{fusion} (°C)	Density (kg/m³)	Reaction Enthalpy (kJ/mol$_{mat}$)	Energy Storage Density (kWh/m³$_{mat}$)
$Al_2(SO_4)_3.18H_2O$	$Al_2(SO_4)_3.8H_2O$	88	1690	554.5 [61]	391 [60]
$CaBr_2.6H_2O$	$CaBr_2.0.3H_2O$	38.2	2295	353.9 [61,62]; 372.6 [61,63]	732 [60]
$CaCl_2.2H_2O$	$CaCl_2.H_2O$	176	1850	47 [58]	167 [64]
$CaCl2.6H2O$	$CaCl2.H2O$	29	1710	277 [65]	601 [60]
$Ce(SO_4)_2.4H_2O$	$Ce(SO_4)_2.2H_2O$	180	3910	58 [60]	156 [60]
$K_2CO_3.1.5H_2O$	K_2CO_3	891	2155	95.5 [61]; 96.7 [61]	346 [60]
$LaCl_3.7H_2O$	$LaCl_3.H_2O$	91	2223	355.5 [61]	591 [60]
$La(NO_3)_3.6H_2O$	$La(NO_3)_3.1.5H_2O$	40	2347	260.4 [61]	392 [60]
$LiCl.H_2O$	$LiCl$	99	1700	62.2 [61]	486 [60]; 253 [2]
$LiNO_3.3H_2O$	$LiNO_3$	29.9	1550	165.8 [61]	580 [60]
$MgBr_2.6H_2O$	$MgBr_2.4H_2O$	152–165	2000	144.9 [61]	-
$MgBr_2.6H_2O$	$MgBr_2$	152–165	2000	439.7 [61]	276 [60]
$MgCl_2.6H_2O$	$MgCl_2.2H_2O$	117	1569	255 [65]; 220.02 (183.83 [i]) [59]	-
$MgSO_4.7H_2O$ [ii]	$MgSO_4.H_2O$	49.2	1680	335.7–336 [58,66]	547 [60]; 556 [60,67]
$MgSO_4.7H_2O$ [ii]	$MgSO_4$	49.2	1680	411 [58]	632 [60]; 639 [60,64]
$MgSO_4.H_2O$	$MgSO_4$	200	2570	75 [58]	780 [2]; 760 [59]
$Na_2S_2O_3.5H_2O$	$Na_2S_2O_3$	48.3	1690–1580	279.9 [61,68]; 312.2 [61,69]	361 [64]
$SrBr_2.6H_2O$	$SrBr_2.H_2O$	88.6	2386	337 [70–72]	529 [60]
$SrCl_2.6H_2O$	$SrCl_2$	61	1960	342 [65]; 348,962 [61,66]	628 [60]; 400 [72]
$Zn(NO_3)_2.6H_2O$	$Zn(NO_3)_2$	36.4	2067	372 [61]; 376.9 [61]	698 [60]
$CaSO_4.2H_2O$	$CaSO_4$	128	2320	105 [61]	817 [60]

Remarks on Hydrated Salts for Heat Storage Applications		
Hydrated salt	**Dehydrated salt**	**Remarks**
$Al_2 (SO_4)_3.18H_2O$	$Al_2 (SO_4)_3.8H_2O$	Low level of corrosiveness; very small temperature difference during hydration of $Al_2(SO_4)_3.5H_2O$ (ΔT = from 1 to 10 °C) [67,73]
$CaCl_2.2H_2O$ $CaCl_2.6H_2O$	$CaCl_2.H_2O$ $CaCl_2.H_2O$	Hydration of the anhydrous to dihydrate results in the formation of a gel, which reduces the porosity of the bed and the rehydration capacity of the material [73]. Cost = 0.11 €/kg [69]
$K_2CO_3.1.5H_2O$	K_2CO_3	The rate of dehydration was strongly affected by the presence of water vapor [74]
$LiCl.H_2O$	$LiCl$	Lithium resources tend to be depleted which could result in additional material costs in the future. Cost = 3600 €/m³ [2]
$LiNO_3.3H_2O$	$LiNO_3$	Lithium resources tend to be depleted which could result in additional material costs in the future. Cost = 3600 €/m³ [2]
$MgCl_2.6H_2O$	$MgCl_2.2H_2O$	Formation of HCl above 115 °C [59,60] and decomposition of $MgCl_2.2H_2O$ into MgOHCl above 130 °C [59] ≥ material deterioration and corrosively. Over-hydration below 40 °C ≥ liquefaction consequently loss of performance [59]. Cost = 0.154 €/kg [69]
$MgSO_4.7H_2O$	$MgSO_4.H_2O$	Very low reaction kinetics. Recrystallization of $MgSO_4.7H_2O$ possible only at a water vapor pressure > 60 mbar [59]. Cost = 4870 €/m³ [2]/3.8 €/kg [69]
$MgSO_4.7H_2O$ $MgSO_4.H_2O$	$MgSO_4$ $MgSO_4$	Non-corrosive, non-toxic; Most of the energy stored at less than 90 °C. Cost = 4870 €/m³ [2],/3.8 €/kg [69]
$Na_2S_2O_3.5H_2O$	$Na_2S_2O_3$	Formation of a thin surface layer that interferes with the release of water [75]. Poor reversibility in real conditions [60].
$SrBr_2.6H_2O$	$SrBr_2.H_2O$	Total dehydration from 80 °C [69]
$Zn(NO_3)_2.6H_2O$	$Zn(NO_3)_2$	Observation of melting during tests but the reaction remains reversible. There are inconsistencies in the literature [60].
$CaSO_4.2H_2O$	$CaSO_4$	Poor reversibility in real conditions [60]

(i) For the dehydration reaction. (ii) At p_{vap} = 13 mbar, $MgSO_4.7H_2O$ was dehydrated until $MgSO_4.6H_2O$ was obtained. Beyond T = 60 °C, the salt decomposes into an amorphous phase and does not reach less hydrated crystalline forms (we then have $\Delta H_{r,V}$ = 380 kWh.m^{-3}), even at T_{max} = 150 °C. To obtain its hydrated salts, p(H_2O) must be greater than 20 mbar [59].

The list of salt hydrates and their properties shows the great diversity of this family of reagents, both in terms of storage density (156–817 kWh/m^3 $_{mat}$) and application temperature limit (T$_{fusion}$: 29–891 °C). For long-term thermal energy storage of solar energy, both open and closed systems were investigated [47]. Both sorbate and energy are exchanged between the system and the surrounding environment in an open system, while only energy is exchanged between the system and the surrounding environment in a closed system. Because of its robustness and low cost, the open system concept appears to be more promising for seasonal heat storage [76]. Mass transfer is the primary limiting factor in achieving good system efficiency in open systems [77]. As a result, the local mass transfer phenomena in the reactor, and thus the material reaction, are important parameters for the system's overall efficiency [78]. Low material stability, for example, may result in the formation of a non-diffusive layer around the material grains in the reactor, restricting vapor transport into the thermochemical material. As a result, after a few de/re-hydration cycles, the system's output drops with such unstable material. When selecting the reagent that will be used for a specific application, it is necessary to evaluate if the reactional equilibrium of the various hydrates is compatible with the system parameters (i.e., temperature of the inlet air stream), in order to know if the hydration reaction can take place and if the reaction equilibrium will allow reaching the target operating temperatures. Since each material has drawbacks and each study has its own set of device parameters and operating conditions, the best materials may not fulfill all user needs. Since these parameters cannot be explicitly compared, the properties of these materials must be described and classified in order to choose the best material for the application and the needs of the consumer.

4. Recent Research of Salt Hydrate Material in TCES Applications

In order to build systems such as reactors, heat exchangers, and solar collectors, thermochemical material properties are a prerequisite. The energy storage capability, operating conditions, and costs of TCES systems are determined by these properties.

New materials matching the criteria need to be developed (i.e., high energy density, thermal conductivity, specific heat capacity, and desorption rate) [18,79–81] to enhance the TES proficiency of the system.

The optimal material (Figure 5), however, differs based on different perspectives. For instance, the Energy Research Center of the Netherlands (ECN) has decided that for seasonal heat storage systems, $MgSO_4 \cdot 7H_2O$ was the most promising material after performing a theoretical evaluation of about 90 materials [82]. According to Bertsch et al., $MgSO_4$ and $CuSO_4$ have the ideal theoretical heat storage densities [83]. With a high energy density and well matched to low temperature and low water vapor pressure (~13 mbar) heat storage systems, the $MgSO_4/H_2O$ pair has attracted the attention of several authors [84–86]. The maximum energy density for total magnesium sulfate heptahydrate dehydration is in the range of 2.8 GJ.m^{-3} [87]. It is possible to divide the dehydration reaction into three stages: the loss of a water molecule and the formation of $MgSO_4.6H_2O$ around 30–45 °C; during the second stage between 55–265 °C, the loss of 5.9 molecules of water was observed; and finally, the crystalline anhydrous $MgSO_4$ was formed by the removal of the last water residues [88]. Assuming that a solar collector is used to dehydrate the material, the temperature will be a maximum of 150 °C. Dehydration therefore takes place from $MgSO_4 \cdot 6H_2O$ to approximately $MgSO_4 \cdot 1H_2O$ [89]. Under these conditions, the energy density was 1.83 GJ.m^{-3}, or 77% of the theoretical maximum capacity (2.8 GJ.m^{-3}). Moreover, this material was non-toxic, non-corrosive, and relatively inexpensive, which is indispensable for systems.

Despite these advantages, some studies have shown that the restitution power is very low and the increase in air temperature at the outlet of the reactor ΔT is +10 °C under realistic conditions, which is not sufficient for real heating applications [85,86]. The formation of hydrated salt agglomerates during cycles may explain this phenomenon. These limit the access of the reactive gas inside the reactor. The mechanical instability of the grains during cycles, which contributes to the formation of small particles, is another

drawback. This can be detrimental to the process as these particles can be carried by the air flow, thus leading to a decrease in the mass of salt over time.

A cyclability investigation on a 1–2 mm crystal was conducted by Donkers et al. [90]. They demonstrated that water could not easily diffuse out from the crystal during the first step of dehydration and that it tended to concentrate in the pores created by the fracturing of the grains. The aqueous solution formed by the crystal dissolution strongly influences the dehydration process. A decrease in the degree of rehydration to 15% was observed after seven cycles.

The other salts were also examined and tested. The $MgCl_2/H_2O$ pair has been the subject of considerable research [86,87,91–93]. This pair is highly relevant in heat storage systems since it presents the highest energy density, a low charging temperature, and high heat release. The dehydration reaction of $MgCl_2 \cdot 6H_2O$ occurs in three stages, forming $MgCl_2 \cdot 4H_2O$ at 70–75 °C, $MgCl_2 \cdot 2H_2O$ at 105 °C, and $MgCl_2 \cdot 1H_2O$ at 150 °C, respectively. The theoretical energy density in the $MgCl_2 \cdot 6H_2O/MgCl_2 \cdot 1H_2O$ system was 2.5 GJ.m^{-3} [88]. However, an undesirable reaction occurs at about 140 °C, producing MgOHCl and HCl acid. The latter substance was highly corrosive to the system and the formation of MgOHCl decreased the active amount of material [86]. Consequently, to avoid this phenomenon, the maximum operating temperature was fixed at 130 °C. Under such conditions, an energy density of 1.89 GJ.m^{-3} can be reached, which corresponds to 88% of the theoretical value (2.5 GJ.m^{-3}). This value remains higher than the value obtained for magnesium sulfate. The performances of hydrated $MgCl_2$ were measured under a humid atmosphere for the following pressure/temperature conditions: 32 mbar, 25 °C and 12 mbar, 50 °C. The results show an increase in temperature of about 60 °C and 20 °C, respectively. These restitution temperature values were higher than those obtained for $MgSO_4$ (6 °C and 4 °C, respectively), which makes it a very promising candidate for real applications [67].
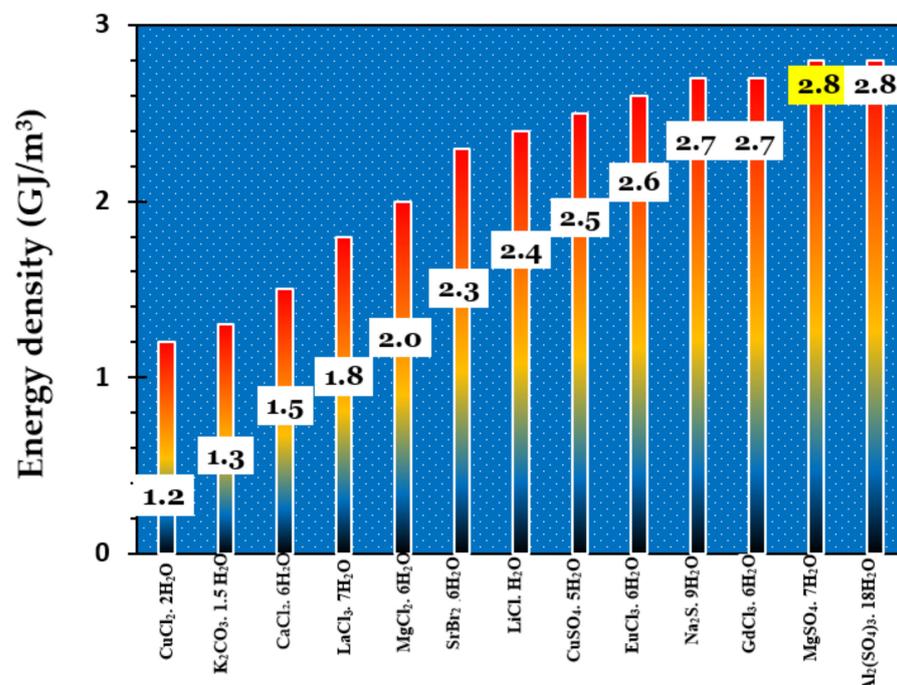
Figure 5. Energy densities of pure salt for the TCES system [94].

A laboratory prototype based on the $MgCl_2/H_2O$ pair was developed and tested in a Dutch laboratory (Energy Research Center of the Netherlands, ECN). The prototype was an open system constituted of a 20 L reactor. The obtained results demonstrate the ability to provide, in winter conditions, a high restitution temperature and indicate the importance

of the use of this material for seasonal storage [86]. However, for domestic heat storage systems, many factors make this material inappropriate such as instability during cycling, overhydration, and therefore the formation of agglomerates and even the gel structure, which blocks heat and mass transfer and decreases system efficiency, hydrochloric acid formation, and consequently material deterioration, corrosion, and safety issues.

The NaS_2/H_2O pair had a large storage capacity of 2.7 $GJ.m^{-3}$ (theoretical value) and a great heat of restitution [92]. A prototype of a closed system of 3 kg of NaS_2 has been tested for long-term heat storage, but also as a cooling source [93]. A temperature of 83 °C was chosen to load the system, because the melting process takes place above this temperature. An energy density of 1.93 $GJ.m^{-3}$ was expected. However, this material is very corrosive and the release of H_2S may occur. All these drawbacks limit the practical use of this material.

N'Tsoukpoe et al. [60] carried out a study from the point of view of input temperature, concluding that when the maximal desorption temperature was 105–115 °C, $SrBr_2. 6H_2O$, $MgSO_4.7H_2O$, and $LaCl_3.7H_2O$ were the most promising salt hydrates for both heating and domestic hot water heat demand. $MgCl_2$ was found to be the most talented candidate if the cost was used as a parameter, though if energy density was used as an indicator, Na_2S, $GdCl_3$, and $EuCl_3$ were the favorable absorbents. However, after establishing additional screening criteria for thorough consideration, the optimal materials were Na_2S, $LiCl$, $EuCl_3$, and $GdCl_3$ [94].

Thermochemical heat storage systems display promising potential compared to sensible heat, latent heat, and sorption heat storage systems. However, its performances such as energy density and restitution capacity remain high at the laboratory scale, but, on a large scale, these systems require more research and improvement. Usually, this phenomenon is caused by the swelling and agglomeration of grains during cycles, the super-saturation and formation of aqueous solutions, which limit mass and heat transfer within the reactive salt bed. It turns out that the use of a porous matrix can improve the performance of the systems, as some of these problems can be overcome. This type of new composite material will be discussed in more detail in the next section.

5. Composites Based Salt Hydrates

As previously reported, chemical heat storage materials, particularly hydrates, are promising materials. The well-known studied salts are mainly sulfates (e.g., $MgSO_4$ [73,88,95–97] and $Al_2(SO_4)_3$ [73,88]), chlorides (e.g., $CaCl_2$ [98–100], $MgCl_2$ [59,86,89,101], and $LiCl$ [102]), and bromides (e.g., $LiBr$ [49] and $SrBr_2$ [49]).

Despite the high theoretical energy density of certain salt hydrates, a number of related issues remain unsolved [103–108] (see Figure 6).

These characters make it problematic for salt hydrates to be used in TCES systems in a single form [109–111]. Consequently, several authors have developed an approach for improving the efficiency of these systems [112–122]. It consists of preparing a composite material by combining a porous matrix (structural support) with an active material (inorganic salt).

In addition to these drawbacks, the use of solar low-temperature type collectors as heat sources showed a higher temperature limit in thermochemical energy storage (TCES) systems for the desorption (storage) temperature of adsorbent materials. Hence, researchers have assessed the performance of materials that encounter these temperature restrictions and were given the selection criteria [15–20]. With the aim of using a sorption material for thermal energy storage purposes, the fulfillment of certain criteria such as the material energy density, the required physical characteristics and safety is mandatory. For long-term low-temperature heat storage purposes, the selection criteria for a sorption material are shown in Figure 7. The high adsorption of adsorbates, in general, leads to a high energy density. However, certain kinetic criteria are also present such as time and regeneration temperature. The preferred adsorbate was water because it is abundant, low-cost, and non-hazardous.
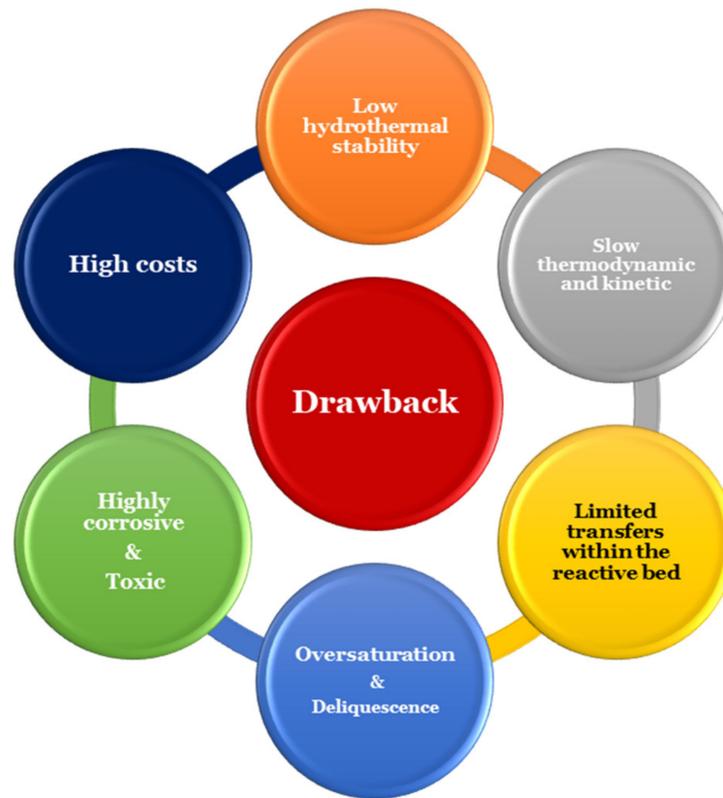
Figure 6. Drawback of using salts in TCES systems.

High sorption of adsorbate

High energy density at system operating temperatures

Regeneration should takes place at low temperature

Regeneration time is short.

Adsorbate mass transport is good.

Heat transfer from/to the adsorbent is excellent.

Reactions totally reversible and do not produce secondary reactions

At charge and discharge temperatures, the reaction yield is high.

Small molar volume of the products to minimize storage volume

During the reaction, there is just a small volume difference.

Thermal conductivity is high

During storage, products separate quickly

Reaction compounds easy to handle

Preferably component non-reactive to O_2

Non-toxic

Non flammable

Non-corrosive

Non expansive
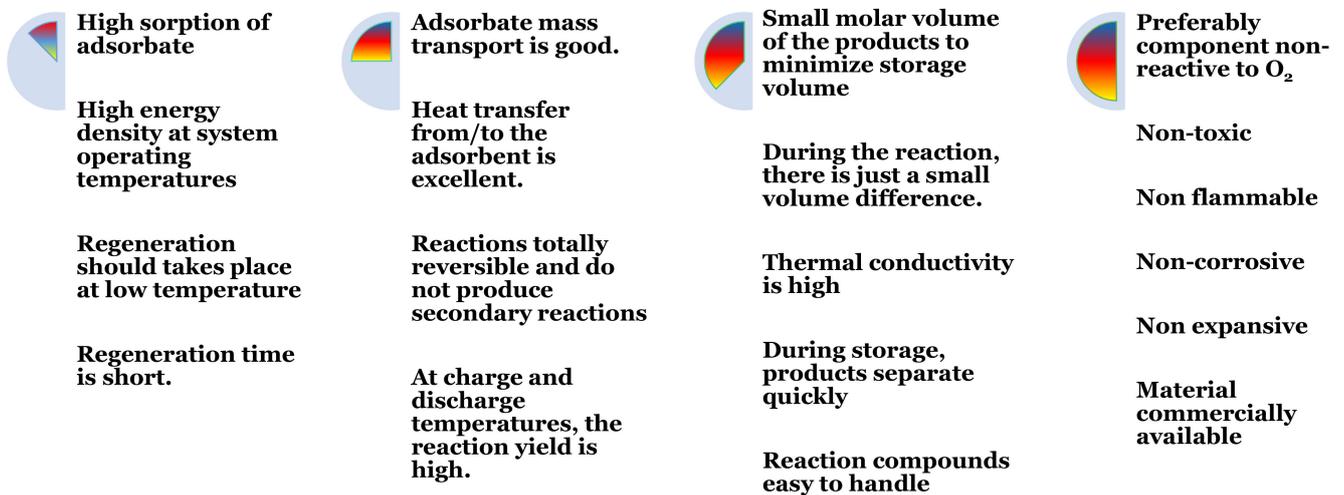
Material commercially available

Figure 7. Criteria for selecting appropriate sorption materials.

Materials based on solid/gas reactions for low-temperature TCES applications have received a lot of attention. Since 2008, salt hydrates and salt hydrate-based composite adsorbents have been the preferred building materials for TCES. In comparison to phase-change and physically adsorbed materials, they have a higher energy storage density and thermal conductivity, are relatively inexpensive, and can release heat at a more suitable temperature. They can also achieve their desorption temperatures by using waste heat sources and low-temperature solar collectors. Their exothermic reaction can be used for low-temperature thermal applications including building space heating and domestic hot

water production. This means that they are extremely appropriate for TCES systems in buildings [47,123].

The choice of the adsorbent and the reactive salt is an indispensable step in the production of the composite material. An adsorbent with heat storage capacity can be the matrix material itself, for instance, zeolite [124,125] and silica gel [126,127]. Otherwise, it may be a non-absorbent substance that has strong properties for heat and mass transfer such as expanded graphite [70,128–131], which has high thermal conductivity, or activated carbon [132] and activated carbon fibers [133–136], which have high porosity, surface area, and thermal conductivity. Natural rocks [137–139] and metal foams [140,141] such as expanded vermiculite are also frequently used as matrix materials for composite adsorbents. Through extensive experimental indication and theoretical study, the advantages of composite adsorbents have been found to be as follows [80,122,142]:

- Due to their high and well-developed porosity, these adsorbents can contain significant quantities of salt hydrate.
- During the hydration process, water vapor can adsorb on the porous matrix by van der Waals forces, and on the anhydrous salt by chemisorption to form salt hydrates.
- The saturated salt solution on the surface of the salt hydrates may be stored in a porous matrix without leakage of the solution, even though excessive water sorption and deliquescence occur. This increases the mechanical strength and overall ability of the products to be sorted.
- The efficiency of heat and mass transfer can be increased by the use of abundant channels.
- The swelling of adsorbents decreases the transfer of heat and severe agglomeration decreases the transfer of mass.
- A porous matrix allows salt hydrates to be confined into pores on a micrometer scale, resulting in a larger specific surface area and more gas diffusion pathways.
- Reasonable drop in pressure to speed up the reaction. In addition, the porous matrix has a great thermal conductivity.
- Composite properties help prevent salt hydrates from swelling and agglomerating, and enhance the heat and mass transfer and the stability of the cycle.
- The mixing parameters can be adjusted to change the properties of the materials.
- The properties of salt hydrates in composite adsorbents and change monomeric materials.
- Changing factors such as material type, pore size, mixing ratio, and preparation conditions can modify the adsorption properties within a certain range.

Generally, the porosity of the porous matrix plays an important role in the properties of the composite. High porosity allows adsorption materials to retain a large amount of active salt as well as provide stability during cycling. As stated above, an adsorption material having small pores (Less than 2 nm) exhibits a greater adsorption capacity. However, the addition of hygroscopic salt risks clogging the micropores during crystallization and in the worst case, destroying the porous structure due to the expansion of the salts during their hydration. The purpose of using a porous matrix is to disperse the hygroscopic salt within the pores in order to increase mass and heat transfer. However, the study of the sorption kinetics carried out on the silica gel/hydrated salt composite material revealed slower kinetics compared to pure silica gel [143]. The authors explain this phenomenon by the increased resistance of water vapor diffusion due to the film formation of the adsorbed solution on the surface.

The use of composite materials for thermochemical storage operations presents a higher storage density than other thermal energy storage techniques for comparable efficiency [93]. Hydrated salts are deliquescent substances that have a very strong affinity with the absorbed humidity to the point of dissolving in it. Thus, the relative humidity of deliquescence (RHD) of the salt is an important element to consider when dealing with composite materials. The RHD is the humidity limit at which the salt will dissolve in the adsorbed water, the phenomenon of absorption into the material then occurring. Exceeding this limit allows more water to be absorbed and thus increases the amount of heat provided by the reaction, however, the formation of saline solution can degrade the

porous matrix containing the salt [144]. This phenomenon also impacts the evolution of the thermal conductivity of the composite material depending on the nature of the matrix (its structure and humidification capacity) [71,145,146]. Indeed, we can discern three phases in the evolution of thermal conductivity (λ) with respect to mesoporous matrices such as silica gel (Figure 8):
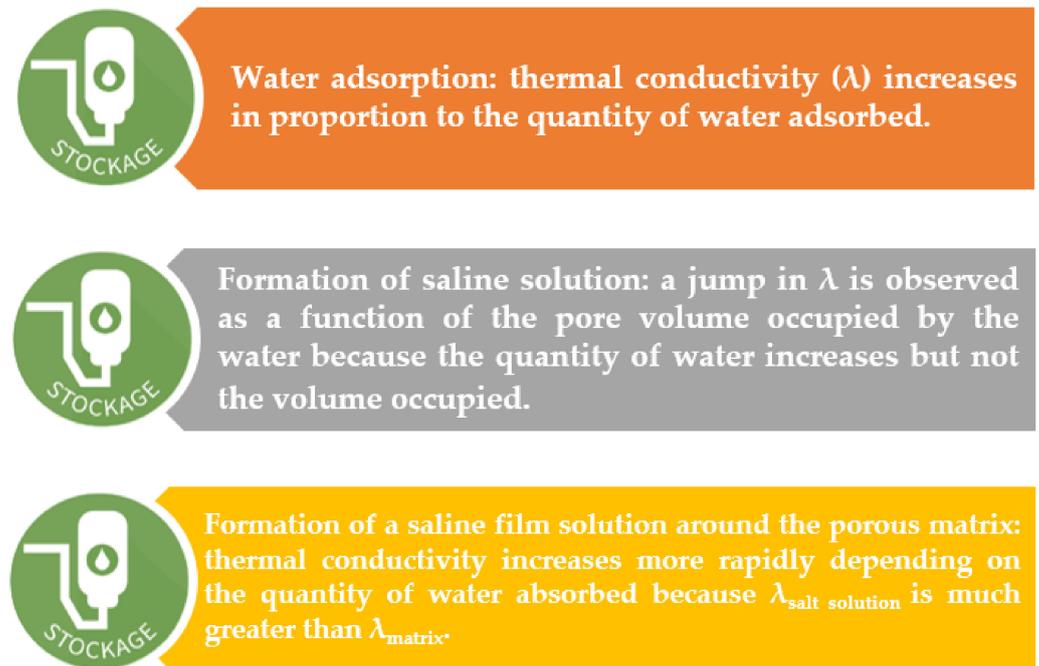

Figure 8. Phase evolution of the thermal conductivity of the composite material.

Tanashev et al. [145] reported that silica impregnated with $CaCl_2$, $MgCl_2$, and LiBr showed, at lower water uptake, a smooth rise in thermal conductivity. At this stage, the dispersed salts were transformed into solid crystalline hydrates salt.nH_2O. The authors concluded that the specific heat conductivity of the hydrated salts was lower than that of the anhydrous salts. The salt solution occurred within the silica pores as adsorption increased, and its thermal conductivity was at least twice lower compared to the crystalline hydrates. As a result, the composite thermal conductivity was decreased. However, this decline was entirely or moderately compensated by the evolution of conductivity, which was explained by the increase in the composite density caused by air extrusion from the pores and the increase in the conductivity of the saline solution during dilution.

In the case of alumina modified by $CaCl_2$, Tanashev et al. [145] identified that the thermal conductivity progressively augmented without any jump. Meanwhile, the confined salt was similar to the salt used for the preparation of the silica based composite, and the dissimilarity in behavior was recognized as due to variations in the pore structure and/or chemical composition of the two host matrices, silica and alumina. The average pore size of alumina (7 nm) was two times smaller than that of silica (17 nm). According to an earlier study [147], this can result in a bi-variant type of water sorption equilibrium for $CaCl_2$–alumina rather than a mono-variant type of water sorption equilibrium for $CaCl_2$–silica gel. During water sorption, the bi-variant type of equilibrium was signified by the fact that a liquid salt solution formed in the alumina pores. The authors stated that if the exterior and interior surfaces of alumina particles are highly wetted by the solution, the latter will form a continuous film that is dispersed within and outside the primary particles. With water sorption, the film thickness was steadily augmented, resulting in a steady rise in composite thermal conductivity. There was no threshold effect since the solution occupied both the meso- and macropores of alumina at the same time. Due to the pores filling with a salt

and the formation of a saline solution, the resistance to water diffusivity in the material increases and thus decreases the absorption kinetics of the water vapor [148]. However, the adsorption rate was still sufficient to consider a heat storage application.

Several hygroscopic salts as well as their quantity of impregnation and various porous matrices have been the subject of several studies. Composites based on silica-alumina with three different hygroscopic salts such as $CaCl_2$, $Ba(OH)_2$, and $LiNO_3$ have been developed by Jabbari-Hichri et al. [149]. Different compositions of these three salts in the composite were tested. The results show that the energy density of the composites impregnated with $LiNO_3$ and $CaCl_2$ was increased by approximately 1.5 to 2 times, respectively, compared to pure silica–alumina. These results are remarkable, especially for the composite with 30–40% by mass of $CaCl_2$ because this allows the volume of the reactor for heating a habitat to be considerably reduced. In this work, the impregnated silica–alumina by $CaCl_2$ (SACax) showed high dehydration heat (656–886 kJ/kg_{sample}) compared to other composites based $CaCl_2$ reported in literature with much higher amounts of salt from 30 to 40 wt.% $CaCl_2$. Ristić et al. [150] obtained a heat storage capacity of 560 J/g by using a $CaCl_2$–FeKIL2 composite and a value of 637 J/g was reached by $CaCl_2$–alumina–silica [151]. The incorporation of $CaCl_2$ on alumina–silica allows for the formation of a salt surface layer, which increases hydration without allowing the salt to dissolve.

Other composites based on zeolite, silica gel, activated carbon, and vermiculite with different salts such as $CaCl_2$, $LiNO_3$, $MgSO_4$, $Ca(NO_3)_2$, and LiBr have been tested and characterized [138]. The sorption capacity for each composite was measured at 23 °C. The highest values were observed for vermiculite-based composites with respective masses of $CaCl_2$, LiBr, $LiNO_3$, and $Ca(NO_3)_2$ of 1.45 $kg.kg^{-1}$, 0.9 $kg.kg^{-1}$, 0.8 $kg.kg^{-1}$, and 0.45 $kg.kg^{-1}$ at 15 mbar while the sorption capacity of pure vermiculite was 0.05 $kg.kg^{-1}$. The two composites based on vermiculite impregnated with $CaCl_2$ and LiBr showed the best performances at 0.18 and 0.17 $GJ.m^{-3}$, respectively.

The water sorption properties of a composite made from iron silicate (FeKIL2) and $CaCl_2$ were studied by Ristić et al. [150]. The FeKIL2 showed a disordered mesoporous structure with a high surface area of 712 m^2/g and mesopore distribution between 4 and 29 nm, while the composite prepared by wet impregnation of $CaCl_2$ displayed a lower surface area (418 m^2/g) and the same range of pore distribution. Furthermore, the existence of dispersed $CaCl_2$ nanoparticles on FeKIL2 resulted in a decrease in mesopore volume (from 1.656 to 1.286 cm^3/g) as well as a significant tailing of the hysteresis loop, highlighting the formation of material with $CaCl_2$ clogs in the pores. There was also a variation in the nitrogen isotherm of the composite. The composite isotherm's desorption branch was divided into two stages. The first desorption step was close to that observed in pure FeKIL2 due to N_2 desorption from open pores, and the second desorption step was due to $CaCl_2$ nanoparticles (plugs) inside the mesopores (narrowed mesopores). As a result, it is safe to assume that $CaCl_2$ nanoparticles have dispersed within the pores of FeKIL2. In addition, the external surface of the composite also contained $CaCl_2$. This was shown by the fact that the hysteresis loop caused by textural porosity narrowed in the relative pressure range of 0.95 to 1. The pore size distribution (PSD), according to the BJH model (Figure 9), showed two clear maxima after impregnation, signifying open and narrowed mesopores, while in the pore size distribution of FeKIL2, a smaller peak appeared just like a shoulder of the main peak (17.6 nm), whereas the composite maximum characteristic for open mesopores shifted to a larger pore size (17.9 nm), while the composite maximum characteristic for narrowed mesopores shifted to a smaller pore diameter (11.7 nm).
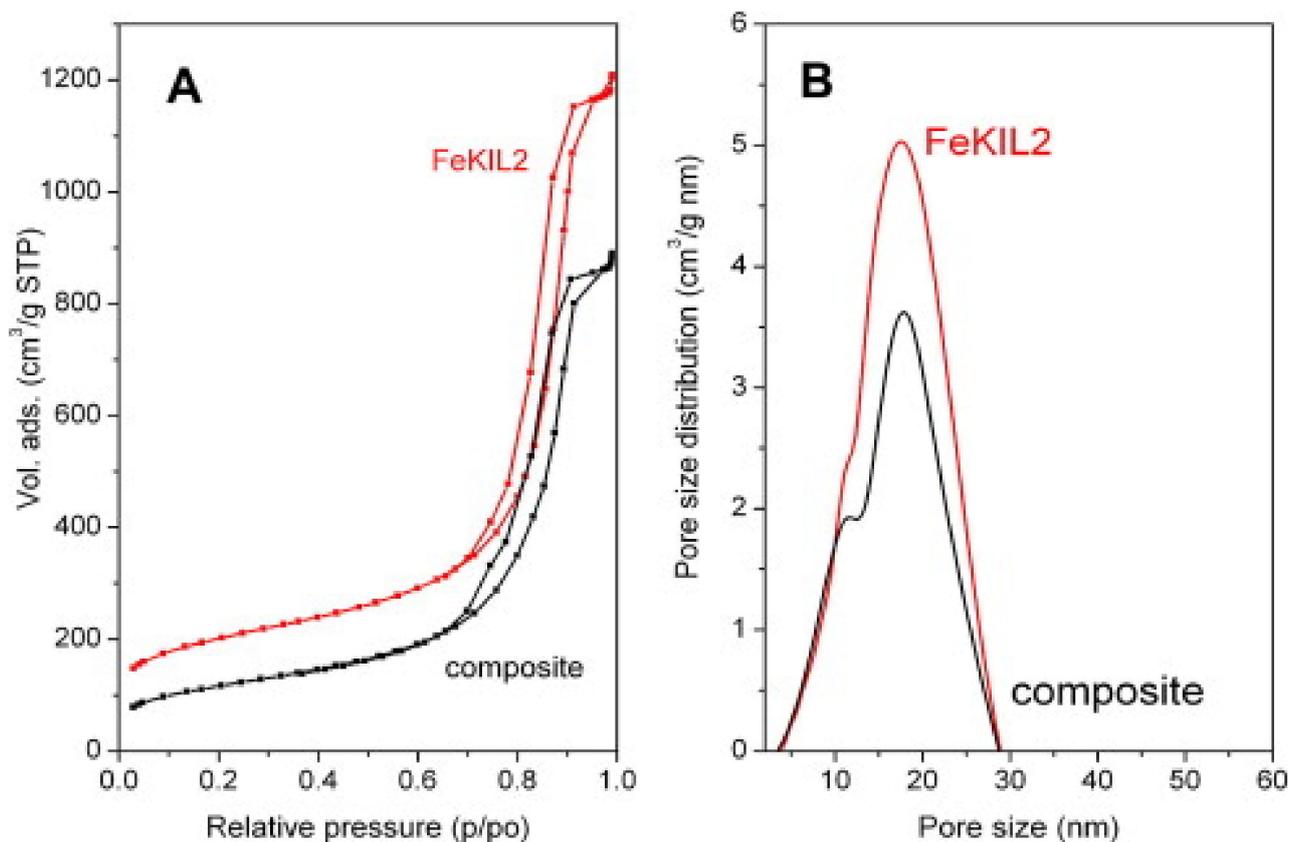
Figure 9. (**A**) Nitrogen sorption isotherms and (**B**) pore size distributions of the mesoporous FeKIL2 and the composite CaCl$_2$-FeKIL2. (Reprinted from [150], copyright (2012), with permission from Elsevier.)

The authors found that the composite had a 0.58 gH$_2$O/g water uptake linked to the dehydrated adsorbent, more than three times the pure FeKIL2 equivalent. In addition, at 120 °C, it may be practically entirely dehydrated. With a thermal program from 40 to 150 °C, cyclability was tested for 20 cycles and a 3.6 percent linear loss of active adsorbent was estimated due to degradation. Regarding porosity after the cycling test, FeKIL2 displayed a sorption isotherm that was identical to the FeKIL2 sample before the cycling test (Figure 10). The adsorption and desorption hysteresis were nearly vertical and parallel, demonstrating an adsorbent with uniformly sized pores operating in a small pressure range. This finding allowed the authors to conclude that FeKIL2 was a hydrothermally stable porous matrix. The shape of the composite isotherm was greatly changed. The intensity of the isotherm after cycling was decreased and the hysteresis loop was expanded. Authors observed after the cycling test that CaCl$_2$ was still present in the mesopores of FeKIL2 because the two-step desorption remained unchanged. Two well defined PSD maxima were noticed in the composite after the cycling test related to open mesopores and narrowed pores (Figure 10). The open mesopore limit of composite was broader and moved to a larger pore size (20.4 nm) with low intensity. Simultaneously, the limit for narrowed mesopores moved to a smaller pore diameter (11 nm). The composite specific surface area was decreased by 10% after the cycling test. In addition, the total pore and mesopore volume was decreased. After the cycling test, no direct leaching of CaCl$_2$ was observed, as is common for these materials [152]. It was assumed that the FeKIL2 matrix can prevent CaCl$_2$ leaching from the matrix's mesopores in the first step. For the first 20 cycles between temperatures of 150 and 40 °C and a water vapor pressure of 5.6 kPa, the composite CaCl$_2$–FeKIL2 exhibited promising hydrothermal stability. A heat storage capacity of 560 J/g was gained using desorption and adsorption conditions of 150 °C–56 mbar and 10 °C–12 mbar water vapor pressure, respectively.
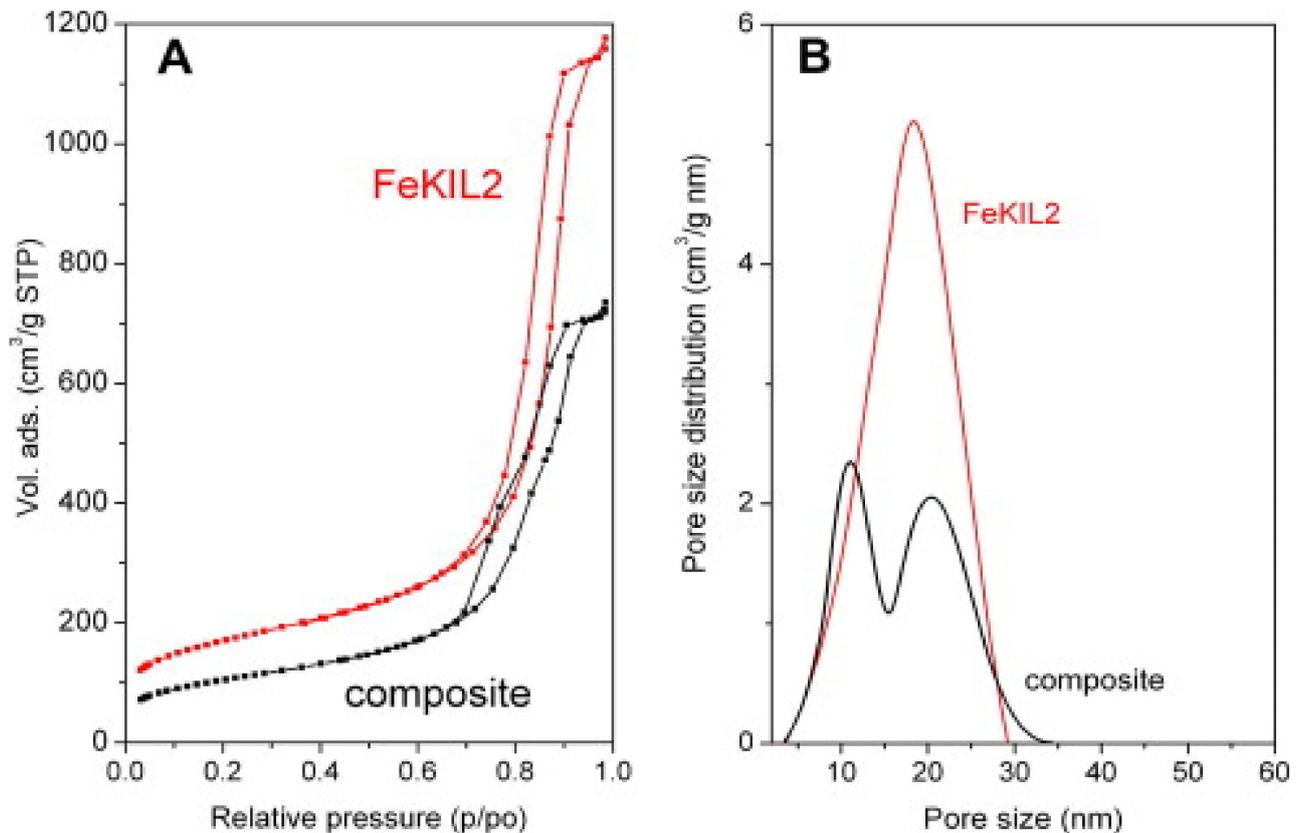
Figure 10. (**A**) Nitrogen sorption isotherms and (**B**) pore size distributions of FeKIL2 and the composite $CaCl_2$–FeKIL2 after the cycling test. (Reprinted from [150], copyright (2012), with permission from Elsevier.)

Both the adsorption enthalpy of the zeolite and the absorption enthalpy of the salt can be used when zeolites and hygroscopic salts are combined. Numerous research on these so-called salt/zeolite composites have recently been published [138,153–165]. Hongois et al. also prepared and tested microporous composites based on zeolite 13X and silica gels, impregnated or not with $MgSO_4$ [114]. The $MgSO_4$-containing composite prepared on zeolite guaranteed a higher temperature increase for similar conditions than the bare zeolites, and even higher ΔT than that measured for the silica gel composite. The temperature gains for air flow out stream from the reactor containing the zeolite and silica gel composites were respectively of 30 °C and 20 °C. The optimum quantity in the composite of 15 percent by mass of $MgSO_4$ was established, making it possible to achieve 0.6 $GJ.m^{-3}$. This value was about 27 percent higher than that of pure zeolite. Later, up to 25% wt.% $MgCl_2$, $CaCl_2$, or $MgSO_4$ was impregnated into mostly synthetic faujasite-type zeolites.

A research study on zeolite type A containing $MgSO_4$ was carried out by Kerskes et al. [112]. On the composite containing 5 percent $MgSO_4$ by mass, the volume of water adsorbed was greater than on the bare zeolite. In both cases, the increase in temperature reached +70 °C. The duration of the reaction on the composite, on the other hand, was longer and the temperature level reached was higher than on the zeolite. This was due to a higher adsorption capacity. These results led to the conclusion that an increase in energy density of 20 and 40% was possible for composites containing respectively 5 and 10% by mass of $MgSO_4$. Whiting et al. prepared and characterized zeolite/$MgCl_2$ composites [166]. The composites based on NaY and HY zeolites attained a higher heat of sorption values than those obtained on pure zeolites. These results were explained by the large volumes of pores presented in the porous matrix that permitted the deposition of the salt without pore-blocking. The NaY and HY zeolites containing 15 percent by mass of $MgCl_2$ offered heats of sorption of 1173 and 970 $J.g^{-1}$, respectively, while the zeolites alone had capacities of

980 and 830 J.g^{-1}. By comparing the composites NaY and HY/MgCl$_2$ and the composites NaY and HY/MgSO$_4$ containing 15% by weight of salt each, it was shown that during hydration, the MgCl$_2$ composites offered higher sorption heats. This was explained by the fact that the level of deliquescence was low for the MgCl$_2$ system, while MgSO$_4$ blocks the zeolite pores and therefore limits the access of water molecules.

On the other hand, Jänchen and coworkers [167] established an asymmetrical relationship between pure adsorbents and composites. They investigated silica X zeolites, microporous aluminophosphates, and a CaCl$_2$ (30 wt.%) composite imbedded in an attapulgite matrix. In N$_2$ flow, the desorption temperature was set to 400 °C. LiLSX (lithium zeolite molecular sieve) displayed the maximum energy density for a hydration temperature of 40 °C (1184 kJ/kg$_{adsorbent}$), though the composite exhibited the lowest (871 J/g$_{adsorbent}$). The energy density of LiLSX diminished by 7.85 percent (1091 J/g) during hydrations at 60 °C, while the composite's energy density diminished by 62 percent (330 J/g). The energy densities of AlPO$_4$ and SAPO were comparable to LiLSX and the attapulgite/CaCl$_2$ composite. Because of its high water adsorption and quick reaction kinetics, zeolite type 13X has been described as one of the greatest performing zeolites for heat storage [47,124,125]. Gantenbein et al. [168] published studies on zeolite 13X in an open system configuration, achieving a supreme sorption at 80 °C with a water vapor pressure of 20 mbar and a hydration temperature at 35 °C. Mette et al. [124] observed similar results for binder-free zeolite 13X in an open configuration at around 85 °C during hydration by using a water vapor pressure of 15 mbar and a hydration inlet temperature of 50 °C. Synthetic zeolites have a number of drawbacks including their high cost, which makes them inappropriate for seasonal heat storage [169], but can be adapted to shorter cycles for load leveling in district heating networks [123].

Due to the various methods and conditions for the characterization and application of the materials, a direct quantitative comparison of the findings published in the literature is difficult. Furthermore, the effects of salt loading on zeolites have been stated to be contradictory. The salt-loaded zeolites were found to have better water loading uptakes and heat storage densities [114,156,157,159,161,163,164,166], whereas in other studies, the composite material was found to be less performant then the bare zeolite [138,154,156,165]. Many research studies [156,157,166] have shown that, depending on the salt/zeolite mixture, the water loading uptake decreases when the salt contents is in the 5–10 wt.% range, but increases again at higher salt loadings of 10–15 wt.%.

The adsorption ability of zeolite 13X remains high at low water vapor pressure and its $\Delta\omega$ is high [164]. The equilibrium water uptake of zeolite 13X remained high up to 100 °C. Therefore, zeolite 13X is quite suitable for adsorption cooling systems. Impregnating zeolite 13X with CaCl$_2$ should increase the adsorption capacity and increase the difference in equilibrium water sorption between the adsorption and desorption steps. However, zeolite 13X has Na$^+$ ions in its structure. When the zeolite is placed in an aqueous solution of CaCl$_2$, ion exchange may take place between the Na$^+$ ions in the zeolite and Ca^{2+} ions in the solution. Ca-ion-exchanged zeolite is formed, and this will possibly alter the properties of the composite and affect its proficiency.

Cation exchange must be considered when interpreting the data provided in these works [114,138,154,157,165,166]. Chan et al. [164], Mahon et al. [159], and Nonnen et al. [156] have all demonstrated this issue experimentally, while Hongois et al. [114] did not take it in consideration.

Mahon et al. [159] reported that the thermochemical storage potential of the 13X sieve was boosted following a Mg^{2+} ion exchange process, resulting in a maximum augmented energy storage by 14% (65 J/g) compared to non-treated 13X pellets. The cause for the augmented dehydration enthalpy and the mass loss of the 13X ion exchanged samples was linked to the connection of H$_2$O to the Mg^{2+} ions within the 13X pellets. Due to the high hydration energy of Mg^{2+} ions, the altered 13X pellets had more bonded H$_2$O around the Mg^{2+} ion sites and a higher hydration energy. In contrast, the Na$^+$ ion sites had an inferior hydration energy. Other works have also reported an upsurge in hydration heat from

zeolites after a Mg ion exchange [170,171]. Ion exchange alters the zeolites' water sorption, according to research [172]. Nonnen et al. [156] concluded that the Ca^{2+} ion exchange raised the zeolite (CaX) heat storage density by 15% over the entire water vapor pressure range, to 143–179 kWh/m^3. This was slightly less than the estimated 73 percent rise, which was achieved by exchanging Na^+ ions for Mg^{2+} ions [151,173]. Mg^{2+} ions, on the other hand, had a higher ionic potential than Ca^{2+} ions, resulting in higher adsorption enthalpies.

Aluminophosphates (AlPOs) are a type of porous material that shares the same structure as zeolites and are also known as zeotype materials [174]. Their potential in thermal energy storage is due to their structural defects incorporated with silicon and aluminum metal cations, which improves the interactions on the surface of polar water molecules. Nonetheless, they also have a moderately good water sorption ability and, most of the time, they exhibit intermediate comportment between hygroscopic and hydrophilic materials, allowing for a high water vapor exchange in a narrow temperature range, which is a valuable feature in STES applications [175]. The AlPO-8, along with SAPO-34, have remarkable energy storage densities (243 and 203 Wh/kg, respectively) at an adsorption temperature of 40 °C and desorption temperature of 95 °C. The supreme promising aluminophosphate material is a porous, zeolite like aluminophosphate with LTA ($AlPO_4$-LTA) topology that was examined by Krajnc and coworkers [176], which was prompted by the high predicted pore volume of the material. The aluminophosphate outperformed all other zeolite-like and metalorganic porous materials studied so far in sorption and calorimetric studies. It showed superior water absorption (0.42 g/g) and energy storage potential (527 kWh/m^3) and adsorbed water in an exceptionally small relative pressure interval (0.10 < p/p^0 < 0.15). It also exhibited exceptional cycling stability, with capability dropping by less than 2% after 40 cycles of adsorption/desorption. This material's desorption temperature, which is one of the most important parameters in applications, was 10–15 °C lower than that of the other tested materials. Furthermore, its heat-pump efficiency was excellent, allowing efficient cooling in difficult conditions (cooling power up to 350 kWh/m^3 even at a temperature difference of 30 °C between the evaporator and the environment). On a microscopic scale, x-ray diffraction, nuclear magnetic resonance measurements, and first-principles calculations have been used to deduce the sorption process in $AlPO_4$–LTA. Energy is stored primarily by a hydrogen-bonded network of water molecules within the pores of this aluminophosphate. The authors also reported that $AlPO_4$–LTA water sorption mechanism was very close to that of $AlPO_4$_34, another porous aluminophosphate that has been extensively studied. Because of its greater pore depth, $AlPO_4$–LTA outperformed $AlPO_4$-34 as an energy storage material. The aluminophosphates showed a higher heat storage performance than zeolites. However, the high cost synthesis of SAPOs and AlPOs limits their applications in TCES [123].

Other composites based on $CaCl_2$ with diverse matrices, specifically expanded natural graphite in powder and pellet forms and activated carbon foam, were examined by Korhammer et al. [172]. The support material was impregnated with 31–90 wt.% of salt in solution or molten form. Hydration experiments were studied at 25 °C to avoid condensation with a water vapor pressure of 10, 17, and 20 mbar. The outcomes showed that composites based on $CaCl_2$ and expanded natural graphite led to 0.67–0.72 $g_{H2O}/g_{dried\ material}$ in water adsorption with an energy storage density of 1451–1310 J/g by using 83 wt.% of salt deposited by wet impregnation and 90 wt.% of salt impregnated in molten form, respectively.

The performances of certain types of composites have been summarized in Table 4. It is obvious that research on composites is still ongoing in order to find a new high performance adsorbent/composites. Moreover, these studies showed that composite materials were interesting materials for the application of long-term thermal energy storage and at low temperature. Henceforth, the optimization at the material level must be undertaken through the development of novel composite adsorbents. High energy storage density, low regeneration temperature, good cycle stability, and cost reduction should be the focus of optimization. For the efficient future expansion of TCES applications, such optimization is necessary.

Table 4. List of salt hydrates composites for TCES system.

Matrix	Salt	Salt Content/wt.%	Energy Storage Capacity	Adsorption T (°C)	Desorption T (°C)	Relative Humidity RH%	Ref.	Years
Silica gel	$CaCl_2$	43	1080 J/g	30	80	32	[177]	2017
MIL-101(Cr)–NH_2	$CaCl_2$	45	1205 J/g	30	120	30	[178]	2019
Bentonite	$CaCl_2$	40	700 J/g	25	150	65	[112]	2010
Silica gel	$CaCl_2$	15	746 J/g	20	150	30	[179]	2017
Bentonite	$CaCl_2$	15	719 J/g	20	150	30	[179]	2017
Aluminum oxide	$CaCl_2$	15	576 J/g	20	150	30	[179]	2017
Silica gel	$CaCl_2$	35	1000 J/g	30	90	80	[180]	2006
FeKIL2	$CaCl_2$	7	560 J/g	40	150	75	[150]	2012
Expanded natural graphite	$CaCl_2$	63	1268 J/g	25	200	63	[109]	2014
Activated carbon foam	$CaCl_2$	90	701 J/g	25	200	63	[109]	2014
Expanded natural Graphite; Activated carbon foam	KCl; $CaCl_2$	31–90	1451–1310 J/g	25	200	31–63	[172]	2016
Zeolite	$MgCl_2$	24.5	1368 J/g	30	300	68	[181]	2019
Zeolites Na–Y	$MgCl_2$	15	1173 J/g	20	150	55	[166]	2014
Zeolites H–Y	$MgCl_2$	15	970 J/g	20	150	55	[166]	2014
Zeolites Na–Y	$MgSO_4$	15	1090 J/g	20	150	55	[157]	2013
Zeolites H–Y	$MgSO_4$	15	867 J/g	20	150	55	[157]	2013
Wakkanai siliceous shale (WSS)	LiCl; $CaCl_2$	9.6	0.2 GJ/m^3	25	150	69	[182]	2015
Silica gel, zeolite 13X; vermiculite	$CaCl_2$, $MgSO_4$, $Ca(NO_3)_2$ $LiNO_3$ LiBr	2–65	0.18 GJ/m^3	30	140	-	[138]	2014
Graphite, copper, zeolite A, sand	$MgCl_2$	46–69	0.56 GJ/m^3	35	200	21–39	[183]	2006
Activated carbon, silica solution, expanded graphite	LiCl	32–45	0.72–1.43 GJ/m^3	30	90	60	[111]	2015
Zeolite 13X; silica gel	$MgSO_4$	15	0.6 GJ/m^3	25	150	68	[114]	2011
Attapulgite	$CaCl_2$	30	1.08 (40 °C) 0.41 GJ/m^3 (60 °C)	40	400	-	[167]	2005
MIL-101(Cr)	$SrBr_2$	63	375 Wh/Kg	30	80	-	[184]	2019
vermiculite	K_2CO_3	69	0.9 GJ/m^3	30–50	75–95	-	[185]	2020
activated alumina	LiCl	14.68	1041.5 J/g	20	120	80	[186]	2018
Zeolithe 13X	$MgSO_4$	15	550.8 J/g	25	250	-	[162]	2018
Expanded clay	$SrCl_2$	40	29 kW/m^3	20	110	71	[187]	2018
Pumice	$SrCl_2$	14	7.3 kW/m^3	20	110	71	[187]	2018
3D-nickel-carbon nanotubes	LiOH	14	3935 J/g	30	150	64	[188]	2018
Zeolite 13X	LiOH	80	1949 J/g	30	150	70	[189]	2018
Plugged hexagonal templated silicate (PHTS)	$CaCl_2$	20	1199 J/g	30	120	-	[190]	2019
SBA-15	$Al_2(SO_4)_3$	7	334 J/g	22	150	30	[191]	2016
MCM-41	$CaCl_2$	37.7	2.1 kJ/g	-	150	-	[115]	2002
MCM-41	$Al_2(SO_4)_3$	7	612 J/g	22	150	30	[191]	2016

6. Composites Based Binary Salts

Any material has its advantages and drawbacks. The combination of two suitable materials to form a binary salt can therefore enhance the efficiency and stability of the TCES material. In order to achieve favorable performance, for instance, a hydrothermal stable salt with a high deliquescence relative humidity (DRH) and a small amount of deliquescence salt were combined. Mixing sulfate and chloride was the most remarkable example of this. Chloride has a high hygroscopicity and is easy to overhydrate to form a solution in the hydration reaction; this drastically decreases the hydration reaction stability. In comparison, sulfate, due to weak reaction kinetics and insufficient transfer water vapor, experiences an incomplete reaction [57]. By combining these two salts (sulfate and chloride), the dehydrated sulfate was partly dissolved in a solution of chloride hydrated salt to form a higher hydrate state. This prevents the instability of excessive chloride hydration and

increases the hydration kinetics of the sulfate salt. To avoid the reactor corrosion by chlorides, a mixture with a high sulfate ratio and low desorption temperature need to be combined [57]. In order to prepare various binary salts, Rammelberg et al. [192] mixed $MgCl_2$, $MgSO_4$, $MgBr_2$, $FeSO_4$, and $CaCl_2$, examined the properties and circulation stability of each binary salt via a continuous process of hydration/dehydration. Surprisingly, the mixture of calcium chloride and magnesium chloride showed good cycle stability without reaction control to prevent overhydration and showed superior kinetic properties. Similarly, Rammelberg et al. [193] mixed $MgSO_4$, $MgCl_2$, and $CaCl_2$ salt hydrates in pairs in order to obtain three binary salt hydrates. At a constant vapor pressure of 21 mbar, the results of the hydration and dehydration reactions showed that the cycling capability of all three mixed materials was enhanced. The mixture of $CaCl_2$ and $MgCl_2$ showed an optimal cycling stability and, after 55 cycles, showed almost no diminution. Ejeian et al. [194] prepared $MgSO_4$-based composites on activated carbon fiber ((ACF)–LiCl–$MgSO_4$). $MgSO_4$ was selected as salt in order to avoid solution leakage due to the excessive hydration and increase the composites' mass transfer capability and density of adsorption.

Gordeeva et al. [117] stated that embedding two salts that affect each other into a porous material provides another "way" to control the sorption properties of composites. The formation of LiCl and LiBr solid solutions within the silica gel pores results in the shifting the equilibrium temperature (or pressure) of the salt solvation. The solvation temperature change did not exceed 5–15 °C due to the low mutual solubility of the lithium halides, thus limiting the probability of varying the composite sorption equilibrium.

Posern and Kaps [101] used attapulgite as the host material for adding $MgCl_2$ to $MgSO_4$ to produce binary salt for use in TCES systems. The sorption heat was measured at different conditions obtained by adjusting the mixing ratio and the temperature of adsorption/desorption. For composite adsorbents with a salt content of 32.8 wt.% (80/20 wt.% salt solutions of $MgSO_4$ and $MgCl_2$, respectively), an energy density of 1590 J/g was reached under 30 °C (hydration temperature) and 36 mbar (water vapor pressure). A higher content of $MgCl_2$ in the composite adsorbent corresponded to a higher water uptake and, consequently, to the increase in heat produced. In these conditions, the risk of salt solution leakage was present. The sorption heat could be boosted by 50% compared to pure $MgSO_4$ salt when the concentration of $MgCl_2$ in the mixture was 10%. The recyclability of composite adsorbents has not been studied yet.

The binary blending of other materials has also been studied by other researchers. The binary hydrated salt composite adsorbents composed of KCl and $CaCl_2$ salts were prepared by Korhammer et al. [172]. They concluded that during the hydration process, the water adsorption of binary salt was two times higher than that of the single $CaCl_2$ salt, whereas during the dehydration process, the water removal was 1.3 times higher than that of the single $CaCl_2$ salt. The highest water uptake was obtained by KCl/$CaCl_2$ in the 2:1 ratio, and KCl/$CaCl_2$ in the 1:2 ratio showed lower energy loss and higher energy storage density. The adsorption properties of LiCl/LiBr binary salts in silica gel were studied by Entezari et al. [195], showing that the addition of a small amount of LiBr to LiCl significantly improved the water adsorption of the composite, whereas the addition of LiCl to LiBr reduced the adsorption of water. Accordingly, the method of preparation and the mixing ratio were deliberately critical to the properties of the binary salt material. Gordeeva and coworkers [117] investigated the phase composition of LiCl/LiBr binary salt succeeding complex formation with silica and its sorption. They debated the effect of diverse ratios on the properties of composite adsorbents and proposed that by developing new materials with different ratios, the melting point and formation temperature of the complex salt could be controlled. A mixture of $SrBr_2$ and $MgBr_2$ was prepared and developed by Bissell et al. [196] by the impregnation technique to resolve the inconsistent melting in the 76–88 °C range. It was found that the melting temperatures of the composite adsorbents varied depending in the proportions of the two salts. By monitoring the mixing quantity, the most favorable heat storage effect was attainable within a reasonable temperature range.

For upcoming work into TCES systems based on binary salt impregnated in a porous matrix, there is a prerequisite of controlling the maximum salt content and optimum mixing ratio appropriate to the operating conditions of the reactor or system. Moreover, it is important to evaluate the variations in the process parameters that will affect the properties of the binary salt mixture and push research at the level of the reactor and overall system.

7. Safety, Corrosion Effect, and Recommendations

Safety is a significant feature in the salt selection process as the thermochemical material will be implemented in the domestic environment involving all stages of the heat storage system life cycle (installation, repair, operation, dismantlement, and accidents). Safety impact is linked to health effects or environmental damage that may be caused by a chemical.

During the TCES process, it can be possible that corrosion or toxic by-products are produced along with the reduction in the active storage material. For instance, if the adsorbent is in interaction with liquid water but not with water vapor, a device based on Na_2S will generate H_2S. H_2S can dissolve in liquid water at that stage, causing metal corrosion and the formation of H_2. With undesirable gas output, it is possible to block the machine condenser, decreasing the rate of adsorption reaction. This is why a periodic clearing of the system is obligatory [92]. Solé et al. [197] investigated four metals for the reactor supposed to contain five salt hydrates ($CaCl_2$, Na_2S, $MgSO_4$, $Ca(OH)_2$, and $MgCl_2$): copper, aluminum, stainless steel 316, and carbon steel. Immersion experiments have been carried out under operating conditions that simulate an open system: 60 °C immersion temperature and 99% humidity. After one, four, and twelve weeks, the metal samples were removed. The outcomes showed that $CaCl_2$ and $MgCl_2$ were recommended with caution for copper and also for aluminum. The same remark referred to when using $CaCl_2$ and Na_2S for carbon steel, and $MgSO_4$ for aluminum, whereas, Na_2S strongly impacted copper and aluminum. Moreover, the use of $MgCl_2$ and $MgSO_4$ was not recommended (>1 year) in carbon steel reactors, and in the same way, $MgSO_4$ was not compatible with copper reactors. $Ca(OH)_2$ can be only endorsed with stainless steel and endorsed with caution with aluminum. However, all studied salts can be recommended for long-term service for stainless steel 316.

Concerning the health effect, the lethal dose for 50% of subjects (LD50-values) of different salts is summarized in Table 5, in which LD_{50} is divided into three classes: inferior to 25 mg/kg as highly toxic; between 25 and 200 as toxic, and between 200 and 2000 as harmful [198]. This taxonomy showed that $GdCl_3$ and $NiCl_2$ were toxic, and Na_2S was harmful. Particular attention must be taking in consideration to the following hydrates, which were clearly mentioned as toxic or acute toxic in the Material Safety Data Sheet (MSDS). On other hand, there are some possible side reactions due to degassing, and the catalytic effect of salts must be considered definitely. For instance, the formation of H_2S and HCl in the case of Na_2S and $MgCl_2$, respectively. $Ca(ClO_4)_2$ is a powerful oxidizing agent that is a major concern in the incident of a fire [94].

Table 5. LD_{50}-values and chemical stability of salts [94].

Salt	LD_{50} (mg/kg)	Chemical Stability	Point of Concern
$GdCl_3$	102		Rare earth
$EuCl_3$	3527		Rare earth
$CrCl_2$	1870	Instable Cr^{2+}	Instable
LiCl	1629		Price
LiBr	1800		Price
$FeCl_2$	895	Instable Fe^{2+}	Instable
CsF	N/A		Price
$Ca(ClO_4)_2$	4500	Explosive	Safety

Table 5. *Cont.*

Salt	LD$_{50}$ (mg/kg)	Chemical Stability	Point of Concern
CuCl$_2$	584		Price
Na$_2$S	208	H$_2$S formation	Safety/Instable
RbF	N/A		Price
CrCl$_2$	1870	Instable Cr^{2+}	Instable
CaCl$_2$	1940		Deliquescence and higher hydrates
Mg(NO$_3$)$_2$	5440	Loss of N$_2$	Instable
LiNO$_2$	N/A	Loss of N$_2$	Price
Mg(NO$_3$)$_2$	5440	Loss of N$_2$	Instable
LiI	6500		Price
LaCl$_3$	2370		Rare earth
KAl(SO$_4$)$_2$	6986		Kinetics
MnI$_2$	N/A		Safety
VOSO$_4$	N/A		Price/Safety
K$_2$CO$_3$	1870		
MgCl$_2$	3800	HCl formation	Instable
Na$_2$S	208	H$_2$S formation	Safety/Instable
Na$_2$S	208	H$_2$S formation	Safety/Instable

8. Conclusions and Outlook

Research on sorption heat storage still needs more in-depth investigation at the micro- and macro-scale levels. Much research is continuing in this subject to propose and find a suitable adsorbent material for commercial application. The current review paper summarized the use of salts, composites, and binary salt as sorbents for sorption heat storage by questioning its production status from various points of view. Research work is still in progress in the effort to address the strategic issues associated with this technology. At present, researchers are proposing a new promising approach to solve the disadvantage of pure salt hydrates in the TES system by using some composite materials based salts. However, heat and mass transport problems can also occur due to:

- Decrease of unoccupied pores;
- Probable deliquescence;
- Leakage of salt from the composite; and
- Degradation.

Major conclusions of study and issues that should be addressed in future with recommendations are mentioned as follows in order to reach commercial application:

- In terms of material, the strategic task is to decrease the prices of the available materials, with the aim to make TES sorption systems more competitive. At this stage, many efforts are devoted to the use of cheaper raw materials and diminishing the hydrophilicity of traditional zeolites, which needs high energy consumption (desorption temperature) that is unattainable, for instance, by traditional solar thermal collectors.
- A deep examination on sorption heat storage is strongly required at diverse scales and several conditions can help to compare experimental studies in a standardized way. Recently, metal organic frameworks (MOFs) and aluminophosphates have shown a remarkable result that needs more focus, thanks to their promising features. Materials for TES sorption systems require more research to discover an appropriate active material with acceptable energy density, hydrothermal stability, and cyclability under the operating conditions of the device.
- Composite materials are being studied in order to diminish the instabilities at salt hydrate material levels. If a high enough desorption temperature is achieved, the host matrices can be made of a porous material that can also act as an adsorbent. Small pore sizes, which are needed for the matrix to participate in the sorption process, result in little salt impregnated in the matrix. Ineffective materials including expanded graphite, sand, silica gel, and vermiculite, on the other hand, have been studied solely

for structural support. Numerous studies have been published, but further work is being done to find promising working pairs. Diminished mass transport inside the matrix pores as well as salt deliquescence or overhydration can lead to active material leakage. Finally, the experimental conditions of the examined studies are heterogeneous and some of them are far from the characteristic conditions of low-temperature heat storage. Furthermore, more research is required to fully and deeply comprehend the kinetics and mechanisms that have occurred by using composite materials in TES sorption systems.

- For upcoming studies on sorption heat storage systems, some critical points also should be considered: For instance, the energy density at different stages of the search need to be determined by setting a common reference temperature. In addition, along with the energy density, the required volume used must be defined.

- Only a few studies have concentrated on the economic viability of the systems. This is partly due to the fact that analysis is always at the material and laboratory scale; thus, broad economic surveys will possibly lead to misleading results.

- The economic feasibility of the system has not been well examined because there are many challenges not yet achieved at material and lab-scales. Consequently, broad economic surveys would likely lead to ambiguous outcomes. Nevertheless, the central indicators allied to material cost, system complexity, and auxiliary energy consumption system should be considered in order to have an idea about the estimation of system cost-effectiveness.

- The cost of materials will already give an idea of how profitable and potential the system will be in a given application. For cost estimation, all components and auxiliary systems must be considered when increasing the scale. Supplementary economic considerations that can be highlighted at commercial scale (Prototype) linked to system operations such as lifetime and maintenance costs may perhaps also be involved to evaluate the rentability analysis.

Nomenclature

TES	Thermal energy storage
AEO	Annual energy outlook
REST	Renewable energy storage technologies
EES	Electrical energy storage
ECES	Electrochemical energy storage
MES	Mechanical energy storage
CES	Chemical energy storage
SHS	Sensible heat storage
LHS	Latent heat storage
TCES	Thermochemical energy storage
CAES	Compressed air energy storage

AA-CAES	Advanced adiabatic compressed air energy storage system
STEP	Pumping energy transfer stations
Cp	Heat capacity (J/(kg K))
PCM	Phase change material
ΔH	Standard reaction enthalpy (J/mol)
T_{fusion}	Fusion temperature (°C)
ΔT	Temperature difference (°C)
p_{vap}	Vapor pressure (mbar)
ECN	Energy Research Center of the Netherlands
RHD	Relative humidity of deliquescence
λ	Thermal conductivity (W/m °C)
PSD	Pore size distribution (nm)
ACF	Activated carbon fiber
LD50	Lethal Dose for 50% of subjects
MSDS	Material Safety Data Sheet
MOFs	Metal organic frameworks

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