

## Review

## Sorption thermal storage for solar energy



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## ABSTRACT

Sorption technologies, which are considered mainly for solar cooling and heat pumping before, have gained a lot of interests for heat storage of solar energy in recent years, due to their high energy densities and long-term preservation ability for thermal energy. The aim of this review is to provide an insight into the basic knowledge and the current state of the art of research on sorption thermal storage technologies. The first section is concerned with the terminology and classification for sorption processes to give a clear scope of discussion in this paper. Sorption thermal storage is suggested to cover four technologies: liquid absorption, solid adsorption, chemical reaction and composite materials. Then the storage mechanisms and descriptions of basic closed and open cycles are given. The progress of sorption materials, cycles, and systems are also reviewed. Besides the well-known sorbents like silica gels and zeolites, some new materials, including aluminophosphates (AlPOs), silico-aluminophosphates (SAPOs) and metal-organic frameworks (MOFs), are proposed for heat storage. As energy density is a key criterion, emphasis is given to the comparison of storage densities and charging temperatures for different materials. Ongoing research and development studies show that the challenges of the technology focus on the aspects of different types of sorption materials, the configurations of absorption cycles and advanced adsorption reactors. Booming progress illustrates that sorption thermal storage is a realistic and sustainable option for storing solar energy, especially for long-term applications. To bring the sorption storage solution into market, more intensive studies in fields of evaluation of advanced materials and development of efficient and compact prototypes are still required.

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## 1. Introduction

With the depletion of fossil fuels and the challenge of global warming, the world community has taken initiatives to steer energy sources toward renewable energy. Solar energy is regarded as one of the most promising substitutes for traditional energy resources; however, its intermittent and unstable nature is a major drawback, which leads to a disparity between supply and demand. Energy storage is an appropriate method of correcting the disparity [1]. To enhance the fraction of energy utilization and make solar energy products more practical and attractive, thermal storage systems today are perceived as crucial components in solar energy applications.

Methods of solar thermal energy storage are mainly divided into three types: sensible, latent and thermochemical [2]. Sensible and latent thermal storage are the most studied technologies in recent decades. Most thermal storage devices applied in practical solar driven systems employ sensible and latent storage methods. For sensible storage, heat is stored by the temperature difference of the storage medium; the value of its storage density closely depends on the product of its specific heat and the temperature difference. Water, brick, rock and soil are the most common materials in sensible energy storage applications.

In the latent thermal storage method, heat is stored through the phase change process of a material at a constant temperature. The materials are often referred to as Phase Change Materials (PCMs). These storage substances are generally ice, paraffin, fatty acids, salts and other mixtures [3]. Compared with sensible thermal storage, latent heat has greater storage density with a much smaller temperature interval; but it still involves many drawbacks, such as long-term stability of storage properties, low thermal conductivity, phase segregation and subcooling during the phase change process [4].

Thermochemical storage can be divided into chemical reaction (should be called “chemical reaction without sorption” strictly) and sorption [2]. Large amounts of heat can be stored in reversible chemical reactions and sorption processes. In a sorption process, heat is stored by breaking the binding force between the sorbent and the sorbate in terms of chemical potential. The features of sorption thermal storage method are illustrated as follows:

- Desorption (charging) process requires the supply of heat to expel the sorbate from the restriction of the sorbent. The heat required is higher than that associated with the evaporation (or condensation) heat of pure sorbate (such as water). Large integral heat of desorption involved in the desorption (or sorption) process causes high energy densities of sorption

materials, in theory, only next to chemical reaction (see Fig. 1). Thus a smaller volume is needed for a given storage capacity for sorption thermal storage, according to Hadorn [2], only one-third of that required for sensible heat storage system with water.

- A sorption process will not occur until the sorbent contacts with the sorbate, so the binding energy can be stored, independent of the time span between the desorption process and the sorption process. Thus, sorption storage is also called an “indirect” thermal storage approach from the view of thermodynamics, distinguished from other “direct” sensible and latent methods [5]. The heat and entropy is not stored in the storage vessels but released to the environment for the indirect storage. This feature makes sorption thermal storage a promising solution for long-term solar energy storage applications, where solar energy is stored in summer to meet heating demands in winter [6].
- Conventional heat storage materials, such as PCMs, can only be applied at specific temperature levels as their phase transition temperatures are definite, which imposes restrictions on the temperature ranges of their applications. However, input and output temperature levels of a sorption thermal storage system are determined by practical demands and working conditions. The discharging process could be operated to provide cooling effect from the evaporator in summer or heating effect from the reactor in winter, exhibiting some extent of flexibility.

Although sorption thermal storage systems offer some benefits, there are still critical drawbacks, such as great complexity in the system configuration (for closed systems), expensive investment, poor heat and mass transfer ability (for chemical reaction) and low heat storage density in actual systems. To overcome these barriers, extensive academic efforts are now being carried out worldwide. The past and present studies on sorption thermal storage are mainly related to the search and evaluation of sorption storage materials [7–11], proposal of sorption cycles [12–21], and development of reactors [22,23]. This review presents the state of the art of sorption thermal storage technology for solar energy, including terminology of some basic terms and concepts, fundamentals, energy densities of diverse sorbents in varied temperature ranges, progress in different configurations of liquid absorption cycles, and new concepts concerning the design of reactors in solid adsorption systems. Some of the typical past and present projects for both short-term and long-term applications are presented. These cases could be served as important references for future endeavors. Major conclusions and perspectives are pointed out at the end of this review.

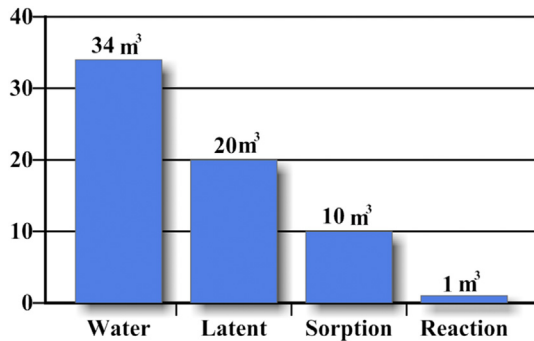


Fig. 1. Volume required to store 1850 kWh (With consideration of 25% heat losses, based on a 70 °C temperature increase for water) [2].

## 2. Fundamentals

### 2.1. Terminology

“Sorptions” is first proposed by McBain [24] as a general term to cover both adsorption and absorption. Sorption of molecules on a surface is prerequisite to any surface mediated chemical process. The expressions “chemical”, “thermochemical”, “thermochemical sorption”, “compact” and “sorption” have all been used in previous papers regarding sorption thermal energy storage [25–32]. Each term carries its own connotation and scope concerning which kind of phenomenon it encompasses and it seems difficult to distinguish clear boundaries between these terms. In most cases, these expressions are employed without special statements. Some attempts have been made in the literature to elucidate their definitions [6,26,33]. N’Tsoukpoe et al. [6] identified thermochemical storage as a part of chemical storage excluding electrochemical and electromagnetic (see Fig. 2). Thermochemical storage was further classified into chemical adsorption, chemical absorption and thermochemical without sorption—the first two also belonged to sorption storage and the exact definition of “thermochemical without sorption” wasn’t given by the authors. In this review, according to storage mechanisms and established customs, sorption thermal storage is suggested to be distributed into four categories: liquid absorption, solid adsorption, chemical reaction and composite materials (see Fig. 3).

According to the definition recommended by IUPAC (International Union of Pure and Applied Chemistry) [34,35], adsorption is the enrichment or depletion of one or more components in an

interfacial layer. The material capable of adsorbing other components is called the adsorbent. The material in the adsorbed state is denoted the adsorbate, while that present in one or other (or both) of the bulk phases and capable of being adsorbed may be distinguished as the adsorptive (so are the definitions of adsorbate, adsorptive, sorbate and sorptive). When adsorbate and adsorptive can be easily distinguished—for example, in cases of chemisorption—they may be chemically different species. However, in most cases, especially in physisorption, the chemical structures of adsorbate and adsorbent are almost the same, so they can be collectively called adsorbate. For simplicity sake, some studies related to sorption cooling, heat pump and thermal storage [36–38] only use adsorbate instead of telling adsorptive from adsorbate, so is this article.

Depending on the interface between adsorbent and adsorbate, adsorption can be divided into four types: solid/gas, solid/liquid, liquid/liquid, liquid/gas. The solid/gas adsorption has been widely used and studied, playing a pivotal role in interface chemistry. As a rule, when talking about adsorption or solid adsorption, it is referred in particular to solid/gas adsorption.

Based on the cohesive force between the two phases, adsorption is further divided into two types: physical adsorption (physisorption) and chemical adsorption (chemisorption) [34,38]. Physical adsorption is a general phenomenon whenever an adsorbate is brought into contact with the surface of the adsorbent. The forces involved are intermolecular forces (Van der Waals forces) of the same kind as those responsible for the imperfection of real gases and the condensation of vapors. Chemical adsorption is due to covalent forces of the same kind as those operating in the formation of chemical compounds. There are certain differences in the properties of the two kinds of adsorption, which can be used as experimental criteria for deciding the adsorption type. The best single criterion is the magnitude of the heat of adsorption [39]. Because chemical forces are normally stronger than physical forces, heat of chemical adsorption should therefore be larger than heat of physical adsorption. In addition, as a chemical reaction, chemical adsorption requires appreciable activation energy, resulting that it can only proceed at a reasonable rate above a certain minimum temperature. In contrast, physical adsorption needs no activation energy, leading to a rapid adsorption speed. Though these features will help to recognize physical adsorption and chemical adsorption, there are many cases where it is uncertain which kind of adsorption is operating or both of them may be taking place at different moments and sites. Silica gel and zeolite are widely studied and applied as common adsorbents using water as working fluid. Some new classes of materials, including aluminophosphates (AIPs), silico-aluminophosphates (SAPOs) and metal-organic frameworks (MOFs), have recently emerged as promising porous materials for heat storage, as shown in Fig. 3.

The term absorption is used when the molecules of the adsorbate penetrate the surface layer and enter the structure of the bulk solid/liquid, causing the change of the composition of one or both bulk phases [34]. If the adsorbent is liquid and the adsorbate is gas, the process can be named liquid–gas absorption or liquid absorption. As the liquid–gas absorption process has been applied in refrigeration industry for a long time, sometimes absorption is specially referred to liquid/gas absorption. The most familiar liquid absorption working pairs encompass LiBr/H<sub>2</sub>O and H<sub>2</sub>O/ammonia, which have been successfully applied in commercial absorption chillers and heat pumps. Conventionally, liquid absorption is referred to as two-phase absorption. Another innovative kind of absorption thermal storage process, using lithium chloride crystals to increase energy density, is called “three-phase absorption” [40,41].

Chemical reaction corresponding to sorption mainly consists of two kinds of reactions: coordination reaction of ammoniate with

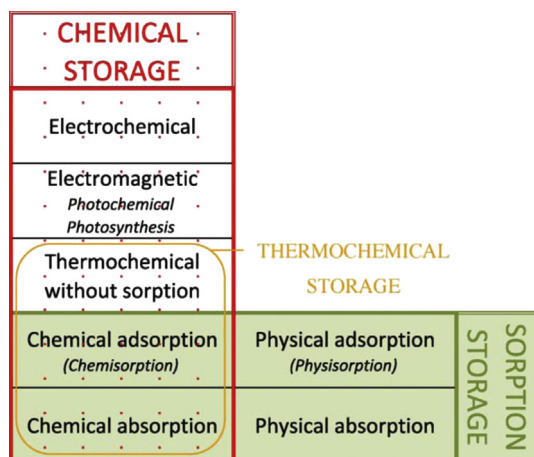


Fig. 2. Chemical storage and sorption storage classification [6].

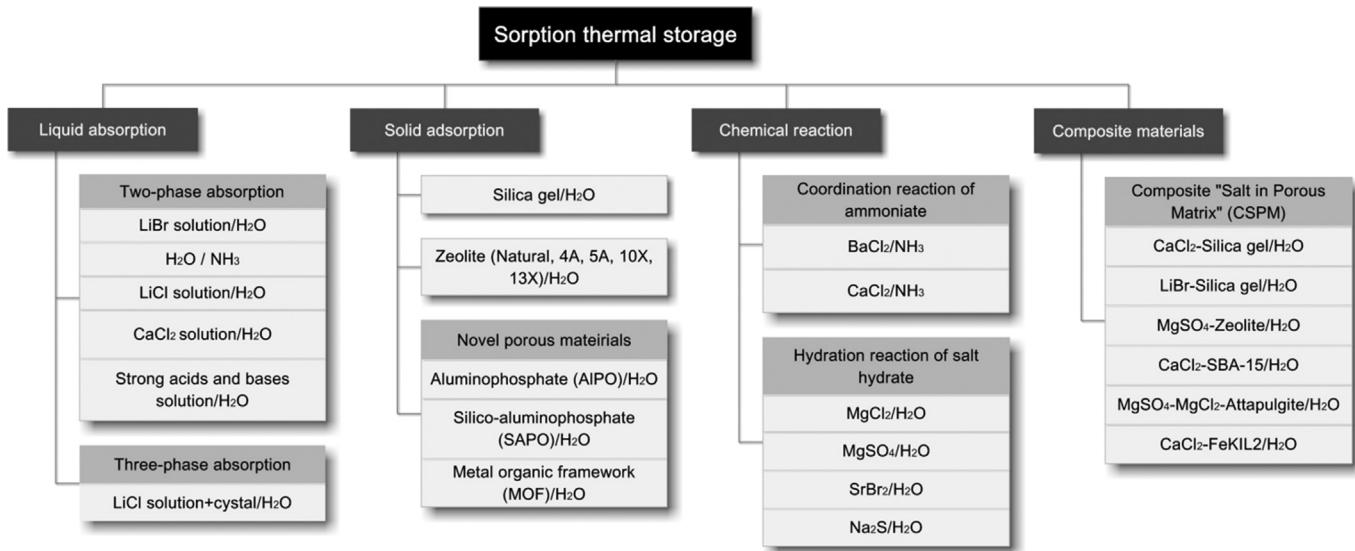


Fig. 3. Sorption thermal storage classification.

ammonia and hydration reaction of salt hydrate with water. Strictly speaking, both the two reactions can be regarded as coordination reactions—molecules of ammonia or water vapor are attracted by metal ions to form coordinate bonds. There still exists a controversy about whether the coordination reaction should be classified into solid adsorption or solid absorption. Wang et al. [38] and N'Tsoukpoe et al. [6] were inclined to use chemical adsorption (chemisorption) to describe the coordination reactions, possibly due to importance of the part played by the solid surface in these solid/gas reactions. Cot Gores [25] recognized them as solid/gas absorption because of the change of molecular structure. To avoid any possible dispute, the term “chemical reaction” has generally been conceded as an adequate description [9,28] and it will be used here.

To improve sorption properties, a new family of composite sorbents, called composite “salt porous matrix” (CSPM) [42–46] has recently been adopted for sorption cooling, heat pump and energy storage applications. If the sorbate is water, these materials are called selective water sorbents (SWS) [47–52]. They are two-component sorbents: one component is a host matrix (silica gel, alumina, expanded vermiculite, aerogel etc.), the other is an inorganic salt (LiCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>, MgSO<sub>4</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>, LiNO<sub>3</sub> etc.), placed inside the matrix pores. In fact, the water sorption process, which takes place on selective water sorbents, contains two main mechanisms: chemical reaction between salt and water, and liquid absorption [53,54]. Adsorption on the matrix surface is responsible for 3–5% and can be neglected in the first approximation [53]. The scheme of water interaction with SWSs is displayed in Fig. 4; it indicates the consequent formation of various crystalline hydrates and then the concentration of salt solution. Thus the sorption processes of composite materials such as SWSs cannot be simply grouped into either absorption or adsorption, but should be regarded as a combination process.

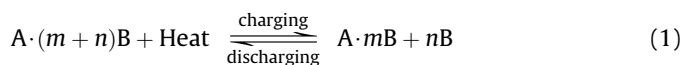
The concept of long-term energy storage or seasonal energy storage has become a fairly hot research topic in recent decades [3,6,55]. Conventional storage methods can be sorted as short-term storage since heat input and output occur within an interval of several hours or days. Long-term energy storage is defined as storage systems designed to store energy for a few months or even a whole season to compensate for the seasonal offset of energy demand. Long-term solar energy storage is regarded as an efficient approach for making rational use of solar energy to achieve a

considerable reduction of fossil fuel consumption and emission of CO<sub>2</sub>. For this reason, since the 1980s, several large-scale solar heating plants have been constructed across Europe—especially in Germany—based on the concept of long-term energy storage [56,57]. Comparisons between short-term and long-term solar storage systems are listed in Table 1.

It should be noted that this comparative study uses water as the storage medium. It is shown that the minimum sizes of long-term storage systems are much larger than those of short-term systems. The collector area and the total investment increase due to the size effect. Short-term solar heating systems are usually designed to cover 10–20% of the total yearly heat demand for both heating and domestic hot water. Nevertheless, solar heating systems with long-term storage can increase the solar fraction up to more than 50%. Today, all the large-scale solar heating projects employ four types of materials as storage mediums: hot water, gravel water, duct and aquifer [57]. Compared with these existing storage techniques, sorption thermal storage with high heat storage capacity and without significant direct heat losses in the storage state seems to be another possible option. Except for the time span between heat input and heat output processes and system scales, there is basically little essential difference between short-term and long-term systems. For this reason, both of them are examined together in the fundamental part.

## 2.2. Description of basic cycles

The mechanism of sorption thermal storage process can be represented by the following equation:



A is the sorbent and B is the sorbate. A/B is called a sorption working pair or sorption couple. For a chemical reaction process, A·(m + n)B and A·mB signify a compound of one mole A with (m + n) mole B and m mole B respectively; for a liquid absorption process, A·(m + n)B represents a solution with a lower concentration of A then A·mB; for a solid adsorption process, A·(m + n)B denotes the enrichment of B on the surface of A as (m + n) mole B is adsorbed. During the charging process, when heat is added to A·(m + n)B, the binding force between A and B is broken and a part



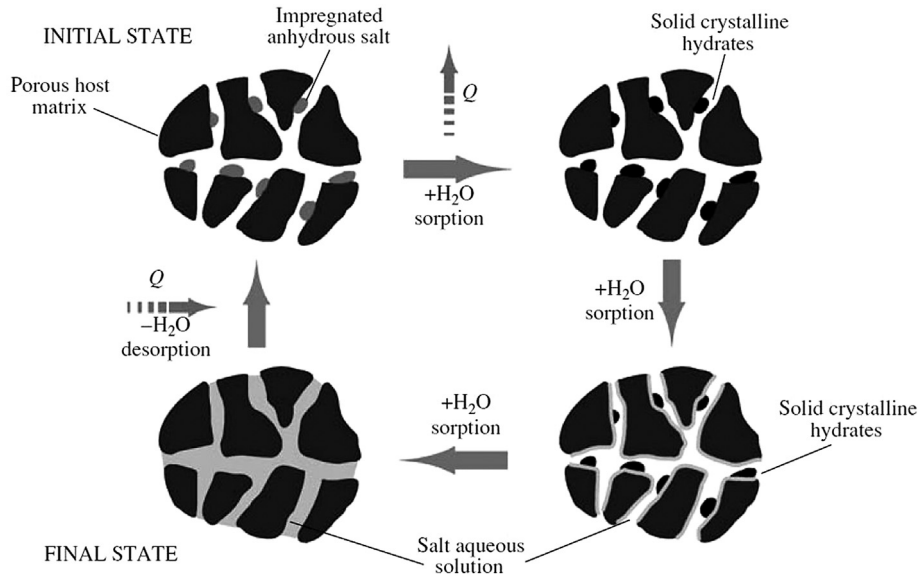


Fig. 4. Scheme of water sorption on SWS [53].

of B is released from A. Energy is stored in terms of chemical potential which the mass fraction of B decreases. During the exothermal discharging process,  $A \cdot mB$  contacts with B to form  $A \cdot (m + n)B$  again and the chemical potential is transferred into thermal energy. In short, sorption technology owes its storage function to a difference in the amount of the sorbate attracted onto/into the sorbent, accompanied by vast amounts of heat.

According to the system configurations, sorption storage systems can be divided into open and closed systems [40,58,59]. Closed sorption systems, which are isolated from the atmospheric environment, have long been studied for refrigeration, heat pump and energy storage applications [60–62]. Closed systems are attractive choices in small-scale applications where compact and highly efficient devices are needed. In closed systems, not the sorbate itself but the entropy is released/absorbed to the environment via a heat exchanger [36]. Operation principle of closed sorption thermal storage system is presented in Fig. 5. The system is mainly composed by two vessels: a reactor where reactive sorbent is located and a condenser/evaporator where liquid water is collected. The vessels are connected by a conduct as a passage for vapor. The charging process consists of a desorption reaction in the reactor and a gas–liquid phase change reaction in the condenser. When a high temperature heat collected by a solar collector, is added to the reactor, the sorbate which clings to the liquid or solid sorbent, starts to escape from the binding force between the sorbate and the sorbent. Through the duct, the vapor turns into its liquid state in a condenser at a low temperature level. The heat of

condensation is taken away and released to the heat sink. After the charging process is finished, the reactor and the condenser are separated from each other. If heating or cooling demands are needed, the reactor and the condenser/evaporator are connected again. The discharging process works in a reverse direction: it includes a sorption reaction in the reactor and a liquid–gas phase change reaction in the evaporator. Depending on the practical requirement, a cooling effect can be produced by the evaporator or a heating effect can be created by the reactor. This feature makes the sorption thermal storage processes able to offer “cold storage” function in summer and “heat storage” function in winter.

Discharging of closed sorption systems requires an additional heat source to provide the heat of evaporation, making choosing of heat sources a critical issue. Air is normally proposed as a heat source for it is always available, easy to design heat exchanger and free of location restrictions [63]. However, when the ambient temperature is too low to drive the evaporation, it will be quite formidable for the discharging process to proceed. Thus, air source is suitable for areas with warm climate in winter. Compared with air, temperature of ground is higher and more stable. Ground source heat exchangers are adopted in some sorption storage projects [19,64,65] to extract heat from the earth. The main drawback of ground source is that construction of heat exchangers is time-consuming and costly. If the storage system is just near waters or swimming pools, water source is a decent option. Sorption storage systems using water as the sorbate are unable to operate under 0 °C, so ammonia or methanol should then be considered for cold areas.

Open systems, as the name implies, are connected with the ambient environment to allow the release and sorption of the sorbate. Thus, only water can be used in those systems. Fig. 6 depicts the operation principle of open sorption thermal storage system. In charging process, a dry air stream, after heating by an heat source like solar energy, becomes dry hot stream and enters a reactor filled with sorbent. Water adsorbed/absorbed by the sorbent is extracted by the hot air and exits the bed. The air then becomes wetter and cooler. During discharging, a humid, cool air stream goes into the previously desorbed reactor. Part of the water vapor in the air is attracted by the sorbent. The released heat of sorption makes the air become hotter and the hot air could be used for heating. In case of a liquid absorption, the dehumidification of

Table 1

Comparisons between central solar heating systems with short-term and long-term storage (adapted from [57])

	Short-term storage	Long-term storage
Time span	Several hours or days	3–6 months
Minimum size	More than 30 apartments or more than 60 persons	More than 100 apartments (each 70 m <sup>2</sup> )
Yearly solar fraction	10–20%	Over 50%
Costs in Germany	0.08–0.15 Euro/kWh	0.17–0.40 Euro/kWh/year
Collector area	0.8–1.2 m <sup>2</sup> FC <sup>a</sup> per person	1.4–2.4 m <sup>2</sup> FC per MWh annual heat demand
Storage volume	0.05–0.1 m <sup>3</sup> water/m <sup>2</sup> FC	1.4–2.1 m <sup>3</sup> water/m <sup>2</sup> FC

<sup>a</sup> FC: flat plate collector.

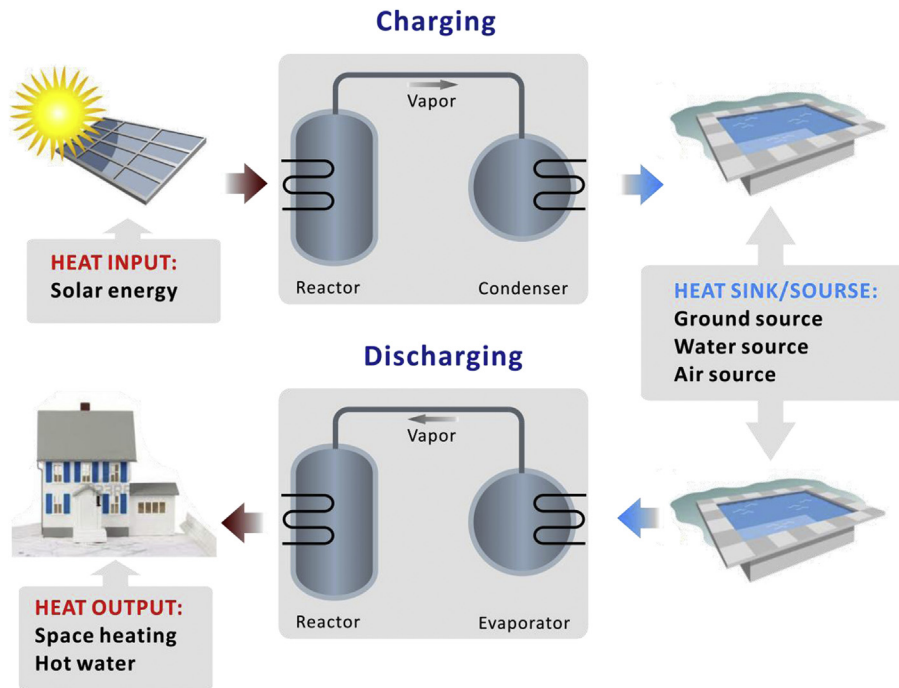


Fig. 5. Operation principle of closed sorption thermal storage system.

the air is the main purpose [66–71]. The lower cost of investment, coupled with better heat and mass transfer conditions (compared with closed systems), provide compelling reasons for practical projects employing open sorption systems to store thermal energy [58,59]. However, before employing the open systems, an analysis should be carried out to define whether the ambient moisture is sufficiently high for a good discharging rate. Otherwise, an additional humidifier is required to make the air wet enough. Furthermore, care has to be taken to reduce or to limit the pressure drop when blowing humid air through the reaction system, to keep the electricity demand for the blower on a low level [72].

From the design point of view, in contrast with closed sorption, open sorption has many benefits—free of many troubles like condensers, evaporators, water storage reservoirs, maintenance of system pressure and complex process control strategy. Therefore, open systems are considered in many recent research related to sorption thermal storage [8,32,73–77]. Abedin et al. [78] carried out a comparison study between closed and open thermochemical energy storage systems, based on an energy and exergy analysis. The calculation results showed that the overall system energy and exergy efficiencies were determined to be 50% and 9% for closed systems and 69% and 23% for open systems. Since the obtained exergy efficiencies of both closed and open systems are a bit low, more effort should be directed toward reducing losses and improving the exergy efficiencies of these systems.

### 2.3. Thermodynamics

For sorption thermal storage systems, the energy for charging  $Q_{\text{char}}$  includes three different parts:

$$Q_{\text{char}} = Q_{\text{sens}} + \underbrace{Q_{\text{cond}} + Q_{\text{bind}}}_{Q_{\text{des}}} \quad (2)$$

The sensible heat  $Q_{\text{sens}}$  is a prerequisite energy to heat up the reactor to a required desorption temperature. This heat is subject to the temperature difference, heat ratio between thermal mass of

sorbent and auxiliary components, and heat losses. The sensible heat can be partially retrieved for short-term thermal storage, but not for long-term storage due to thermal losses. The heat of condensation  $Q_{\text{cond}}$  is defined as the heat of liquid–gas phase change at a specific temperature (normally condensation temperature at the condenser), which is assumed constant. The heat of binding  $Q_{\text{bind}}$  is used to denote the difference between the heat required for desorption  $Q_{\text{des}}$  and the condensation heat  $Q_{\text{cond}}$ . The binding heat  $Q_{\text{bind}}$  is contributed by the sorption forces between the sorbent and the sorbate, and when referred to the unit mass of sorbate it is often called the differential heat of sorption. The definitions of  $Q_{\text{cond}}$  and  $Q_{\text{bind}}$  are illustrated in Fig. 7.

For liquid absorption and solid adsorption, the differential heat of absorption/adsorption is affected by many factors, such as temperature, pressure and sorbate concentration (sorbate uptake on/in the sorbent in g/g) [80,81]. But it is generally accepted that sorbate concentration plays the most significant part and the differential heat of sorption can be seen as a function of the sorbate concentration over some range of temperature [81,82]. As a rule, the differential heat will increase as the concentration decreases, in accordance with the fact that more heat is required for desorption at a low sorbate concentration. For a chemical reaction, the value of reaction heat is always presumed invariable, calculated from the formation enthalpies of materials involved in the reactions, the reaction equilibrium equations or measured from calorimetric methods [29,63,83].

As shown in Fig. 7, integrating the curve of the differential heat of adsorption from the lowest concentration at desorption process to the highest concentration at the end of the adsorption process gives the integral heat of adsorption/desorption ( $Q_{\text{des}}$ ).  $Q_{\text{char}}$  is the sum of  $Q_{\text{des}}$  and  $Q_{\text{sens}}$ . The ratio of heat of condensation to the total charging heat ( $Q_{\text{cond}}/Q_{\text{char}}$ ) is an important parameter to show the contribution of the heat of condensation and then to evaluate the thermal storage potential of sorption materials. Higher values of  $Q_{\text{cond}}/Q_{\text{char}}$  mean lower contributions of the binding heat, coming along with lower desorption temperatures, as it is the case for zeolite/water [36]. For cold storage, the value of  $Q_{\text{cond}}/Q_{\text{char}}$  almost

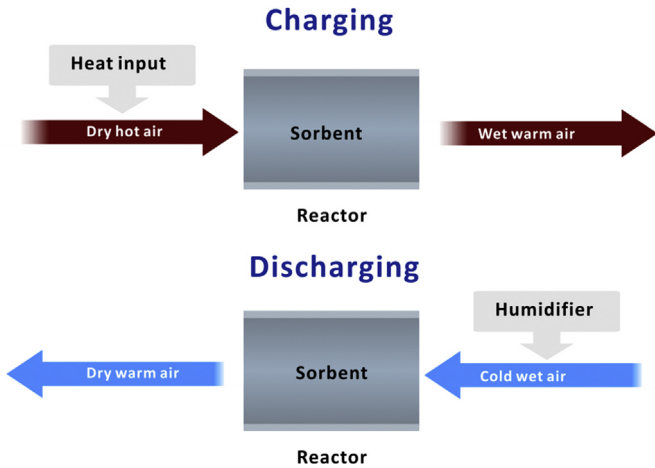


Fig. 6. Operation principle of open sorption thermal storage system.

equals the cooling coefficient of performance ( $COP_c$ ). Therefore, greater  $COP_c$  could be expected with higher  $Q_{cond}/Q_{char}$ .

The characteristics of storage materials—especially the energy density—are prerequisite to obtaining compact and efficient sorption thermal storage applications. Energy density is defined as the amount of energy stored in a given system or region of space per unit volume or per unit mass. It can be calculated based on mass or on volume, depending on which measure makes the most sense for each situation. Energy density of sorption materials in terms of mass and volume are both widely applied in previous works. In the preliminary search of advanced sorption materials, energy density by mass ( $\rho_{Q-m}$ ), is adopted to evaluate the investment on storage materials, defined as follows:

$$\rho_{Q-m} = \frac{\text{heat storage capacity output}}{\text{mass of storage material}} \quad (3)$$

For absorption systems, mass of the storage material is related to the concentration of the salt solution. Therefore, it is suggested that calculation of energy density by mass should be based on the pure mass of solid salt.

The volume of the storage material could also be considered to achieve a compact thermal storage system. Since most of sorption systems include several essential components, energy density by

volume ( $\rho_{Q-v}$ ), is a more practical parameter to calculate the heat storage potential of prototypes.

$$\rho_{Q-v} = \frac{\text{heat storage capacity output}}{\text{volume of storage material or prototype}} \quad (4)$$

### 3. Storage materials

#### 3.1. Selection criteria

Storage materials play a crucial role in the development of sorption thermal storage systems. Key principles for selecting appropriate materials include [6,55,60]:

- High energy storage density (Wh/kg or kWh/m<sup>3</sup>)
- Low charging temperature.
- High uptake of sorbate (g sorbate/ g sorbent).
- Appropriate heat and mass transfer properties to ensure designed output power.
- Easy to handle—nonpoisonous.
- Low cost—low price per kWh heat energy stored.
- Thermal stability—no deterioration.

In fact, no material currently available could satisfy all listed requirements. Therefore, the available material selection should be screened and optimized. Sorption properties are the foundations to find suitable storage materials. The comprehensive evaluation of sorption properties of a mass of available sorbents is a time-consuming task as it requires precise measurements of a set of sorption isobars, isosters and isotherms under a wide range of temperature and pressure. Recently, Aristov [11,42] proposed an alternative way, named a target-oriented design (or tailoring), to seek suitable adsorbents for adsorption heat transformation (AHT) cycles—adsorption cooling, heating and storage cycles. The main idea of the approach is that there is an optimal adsorbent for each AHT cycle with particular climatic and boundary conditions. The target-oriented design includes two steps: the first step is formulating the temperature requirements for particular application; the next step is synthesis of the adsorbent whose properties can fit the requirements. Using a fast experimental method based on the Polanyi potential theory [84,85], a conclusion was drawn that the optimal adsorbent for AHT should have step-wise sorption isobars in theory and for real adsorbents, S-shaped isobars were more realistic. Modification of composites “salt inside porous matrix” was perceived as a good example for nanotailoring the sorption properties according to practical demands. Aristov [21,43,86] also described a novel experimental approach (LTJ) to find optimal adsorbents under conditions typical for AHT from the dynamic point of view. Effects of the adsorbent nature, grain size, residual non-adsorbable gas, heating rate, local shape of adsorption isobar were studied. Mugnier and Goetz [9] compared the cold storage potentials of a series of sorption materials, under both freezing and air conditioning situations. Under solar cooling conditions, with an evaporation temperature of 5 °C and a heating temperature of 120 °C, their calculations showed that chemical reactions were the best choice in sorption thermal storage. Working pairs of inorganic salts with water such as Na<sub>2</sub>S/H<sub>2</sub>O (353 Wh/kg), CaCl<sub>2</sub>/H<sub>2</sub>O (271 Wh/kg), MgCl<sub>2</sub>/H<sub>2</sub>O (233 Wh/kg), and LiCl/H<sub>2</sub>O (197 Wh/kg) possessed the greatest storage capacities. It is worth noting that in this calculation, the results of these hygroscopic salts—Na<sub>2</sub>S, LiCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>—may be wrong, because the authors didn’t consider the possibility of the formation of salt solutions.

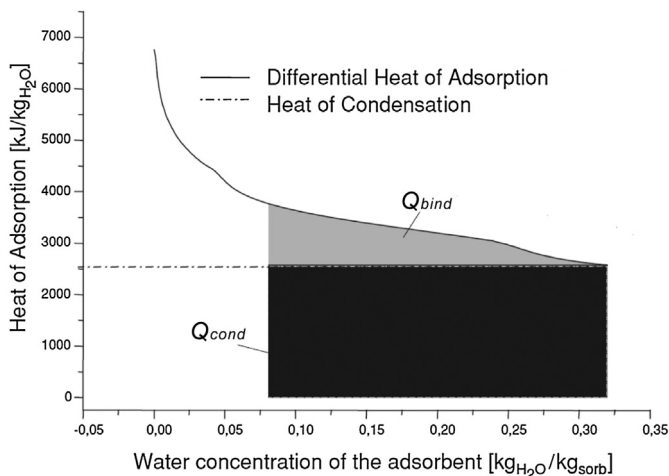


Fig. 7. Definitions of  $Q_{cond}$  and  $Q_{bind}$  for zeolite/water as an example [79].

Compared with selections of sorbents, those of sorbates are limited. Different working pairs, or materials considered mainly employ water as the sorbate, due to its environmentally friendly properties and high evaporation heat. Methanol and ammonia should be considered if the environment temperature is lower than 0 °C.

As part of the energy is released to or extracted from the environment, the performance of a sorption system is closely linked with many factors. Charging conditions (charging temperature and pressure) and discharging conditions (discharging temperature and pressure) determine the energy storage density together. Therefore, when referring to a value of storage density for a sorbent, its relevant conditions should be pointed out. Among all the effect factors, charging temperature is the most prominent one since it tells the requirement of heat source. Sorption materials with high energy storage densities and low charging temperatures seem the most attractive choices.

Some of literature data for typical sorption couples are selected and summarized in Fig. 8, to give an overview of relations between energy densities and charging temperatures. Their related detailed information is given in the following Table 2. The dates listed in Fig. 8 are based on experiment results with a small amount of sample, or theoretical calculations with other known thermal properties. For silica gels, though the required charging temperatures are lower than 100 °C, their storage densities are even lower than sensible heat method of water, making application prospect of silica gel/water in sorption storage obscure. Zeolites (type 4A, 13X,Y) and other modified zeolites (via ion exchange of Na by Li, Ca, Mg) shows varied and moderate storage densities (71–225 Wh/kg) with charging temperatures higher than 150 °C. Required charging temperatures for most liquid absorption couples, including LiCl/

H<sub>2</sub>O, LiBr/H<sub>2</sub>O, KOH/H<sub>2</sub>O, NaOH/H<sub>2</sub>O, CaCl<sub>2</sub>/H<sub>2</sub>O, are lower than 100 °C. It is a bit surprising to find that LiCl/H<sub>2</sub>O presents the best energy storage density (1219 Wh/kg)—even higher than the densities obtained from chemical reactions—with a charging temperature of only 66 °C. All kinds of chemical reactions provide superior storage potentials within a wide range of temperatures. Their storage densities range from 408 Wh/kg (BaCl<sub>2</sub>/NH<sub>3</sub>) to 1067 Wh/kg (Na<sub>2</sub>S/H<sub>2</sub>O). The composite materials, such as the well-know SWS-1L, exhibit intermediate densities between the salt and the matrix (silica gel or zeolite), as expected. In Table 2, it should be specially mentioned that the fractions of condensation heat in the total charging heat ( $Q_{cond}/Q_{char}$ ) for chemical reactions are lower than those for adsorption, generally around 0.5, confirming strong binding energy between chemical sorbents and sorbates. Further discussions about the recent progress in these sorption materials will be carried out in the following section.

### 3.2. Working pairs for liquid absorption

Many kinds of absorption materials have been considered in energy storage systems but only a few have been implemented in practical prototypes and projects. LiBr/H<sub>2</sub>O single effect absorption machines are suitable for solar cooling applications due to good performance at the temperatures available from conventional collectors. Berlitz et al. [93] compared three storage techniques—external storage of driving heat by means of thermal oil, external storage of cold with sensible heat of cold water and internal storage with latent heat of the refrigerant water and LiBr solution—for a double effect LiBr/H<sub>2</sub>O absorption chiller with a cooling capacity of 20 kW and a need for cold storage of 3.3 kWh. A less-than-thorough comparison proved that the required amount

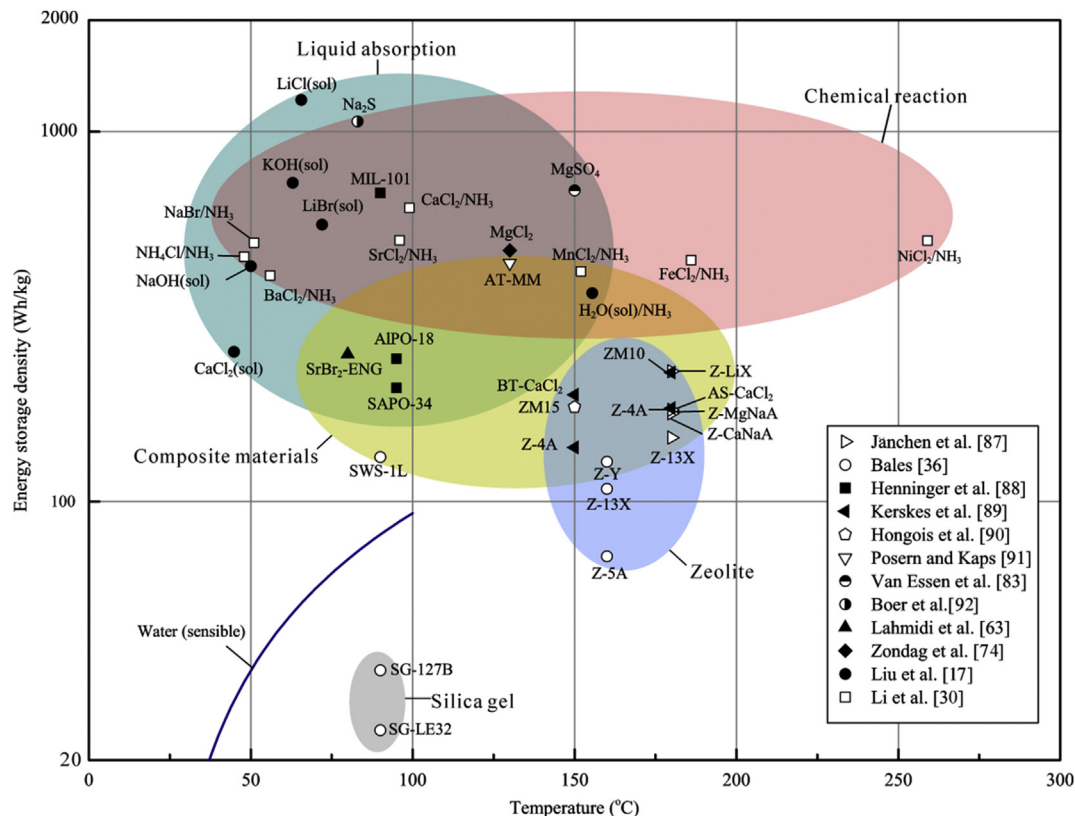


Fig. 8. Energy storage densities of sorption materials. The default sorbate is water and it is omitted, details of the data are shown in Table 2. The reference temperature of sensible heat storage of water (the blue curve) is 20 °C.



**Table 2**  
Details of literature data shown in Fig. 8.

Reference	Label	Couple	Description	Operation conditions	Storage density (Wh/kg)	Storage density (kWh/m <sup>3</sup> )	$Q_{\text{cond}}/Q_{\text{char}}$ *	Density** (kg/m <sup>3</sup> )	
Jänchen et al. [87]	Z-13X	Zeolite type 13X	Experimental, closed system, with sensible heat	Charging: 180 °C	149	110	0.84	739	
	Z-MgNaX	Zeolite type MgNaX			175	128	0.81	732	
	Z-LiX	Zeolite type LiX			225	160	0.72	711	
	Z-CaNaA	Zeolite type CaNaA-60			173	116	0.64	671	
Bales [36]	AS-CaCl <sub>2</sub>	Aluminosilicate impregnated with 30% CaCl <sub>2</sub>	Theoretical, closed, without sensible heat	Charging: 90 °C; condensation: 40 °C; discharging: 40 °C; evaporation: 15 °C	177	172	0.68	972	
	SWS-1L	Mesoporous silica gel impregnated with 33.7 wt.% CaCl <sub>2</sub>			132	85	0.89	646	
	SG-127B	Microporous silica gel			35	25	0.91	710	
	SG-LE32	Macroporous silica gel			24	15	0.89	620	
	Z-13X	Zeolite type 13X			108	97	0.73	896	
	Z-5A	Zeolite type NaCa 5A			71	57	0.72	801	
Henninger et al. [88]	Z-Y	Zeolite type Y	Experimental, TG/DSC, with sensible heat, charging at 1.2 kPa discharging at 5.6 kPa	Charging: 95 °C; discharging: 40 °C	128		0.76		
	SAPO-34	Silico-aluminophosphate type 34			203		0.78		
	AIPO-18	Aluminophosphate type 18			243		0.79		
	MIL-101	Metal-organic framework type MIL-101			684		0.85		
Kerskes et al. [89]	Z-4A	Zeolite type 4A	Experimental, open system, with sensible heat	Charging: 180 °C	179	125	0.67	700	
	Z-4A	Zeolite type 4A			140	98	0.67	700	
	ZM10	Zeolite 4A impregnated with 10 wt.% MgSO <sub>4</sub>			223	178	0.69	797	
	BT-CaCl <sub>2</sub>	Bentonite impregnated with 40 wt. % CaCl <sub>2</sub>			194	135	0.69	695	
Hongois et al. [90]	ZM15	Zeolite 13X impregnated with 15 wt.% MgSO <sub>4</sub>	Experimental, open system, calorimeter	Charging: 150 °C; discharging: 30 °C	180	166	0.53	922	
Posern and Kaps [91]	AT-MM	Attapulgite impregnated with MgSO <sub>4</sub> and MgCl <sub>2</sub> (mass ratio 20/80)	Experimental, open system, calorimeter	Charging: 130 °C; discharging: 30 °C at 85% RH	442				
Van Essen et al. [83]	MgSO <sub>4</sub>	MgSO <sub>4</sub> ·7H <sub>2</sub> O ↔ MgSO <sub>4</sub> ·0.1H <sub>2</sub> O	Experimental, open system, TG and DSC	Charging: 150 °C	694	924	0.48	1330	
Boer et al. [92]	Na <sub>2</sub> S	Na <sub>2</sub> S·5H <sub>2</sub> O → Na <sub>2</sub> S·1/2H <sub>2</sub> O	Experimental	Charging: 83 °C	1067	990	0.66	928	
Lahmidi et al. [63]	SrBr <sub>2</sub> -ENG	Consolidated SrBr <sub>2</sub> with expanded natural graphite, SrBr <sub>2</sub> ·6H <sub>2</sub> O → SrBr <sub>2</sub> ·H <sub>2</sub> O,	Experimental, closed system	Charging: 80 °C	250	175	0.48	700	
Zondag et al. [74]	MgCl <sub>2</sub>	MgCl <sub>2</sub> ·6H <sub>2</sub> O → MgCl <sub>2</sub> ·2H <sub>2</sub> O	Experimental, DSC	Charging: 130 °C	477	556	0.50	1165	
Liu et al. [17]	CaCl <sub>2</sub> (sol)	CaCl <sub>2</sub> (solution)/H <sub>2</sub> O	Theoretical, closed, long-term storage charging at 4.2 kPa; discharging at 1.2 kPa	Charging: 44.8 °C	254	119		469	
	KOH(sol)	KOH(solution)/H <sub>2</sub> O			Charging: 63 °C	727	313		430
	LiBr(sol)	LiBr(solution)/H <sub>2</sub> O			Charging: 72 °C	561	313		557
	LiCl(sol)	LiCl(solution)/H <sub>2</sub> O			Charging: 65.6 °C	1219	400		328
	NaOH(sol)	NaOH(solution)/H <sub>2</sub> O			Charging: 50 °C	433	154		355
	H <sub>2</sub> O/NH <sub>3</sub> (sol)	H <sub>2</sub> O(solution)/NH <sub>3</sub>			Charging: 155.5 °C	366	98		268
	NH <sub>4</sub> Cl/NH <sub>3</sub>	NH <sub>4</sub> Cl·3NH <sub>3</sub> → NH <sub>4</sub> Cl			Charging: 48 °C	459	351	0.66	351
	NaBr/NH <sub>3</sub>	NaBr·5.25NH <sub>3</sub> → NaBr			Charging: 51 °C	501	802	0.55	802
	BaCl <sub>2</sub> /NH <sub>3</sub>	BaCl <sub>2</sub> ·8NH <sub>3</sub> → BaCl <sub>2</sub>			Charging: 56 °C	408	787	0.51	787
	SrCl <sub>2</sub> /NH <sub>3</sub>	SrCl <sub>2</sub> ·8NH <sub>3</sub> → SrCl <sub>2</sub> ·NH <sub>3</sub>			Charging: 96 °C	509	776	0.47	776
Li et al. [30]	CaCl <sub>2</sub> /NH <sub>3</sub>	CaCl <sub>2</sub> ·8NH <sub>3</sub> → CaCl <sub>2</sub> ·NH <sub>3</sub>	Theoretical without sensible heat charging at 1167 kPa	Charging: 99 °C	623	673	0.47	673	
	MnCl <sub>2</sub> /NH <sub>3</sub>	MnCl <sub>2</sub> ·6NH <sub>3</sub> → MnCl <sub>2</sub> ·2 NH <sub>3</sub>			Charging: 152 °C	419	624	0.41	624
	FeCl <sub>2</sub> /NH <sub>3</sub>	FeCl <sub>2</sub> ·6NH <sub>3</sub> → FeCl <sub>2</sub> ·2NH <sub>3</sub>			Charging: 186 °C	450	711	0.38	711
	NiCl <sub>2</sub> /NH <sub>3</sub>	NiCl <sub>2</sub> ·6NH <sub>3</sub> → NiCl <sub>2</sub> ·2NH <sub>3</sub>			Charging: 259 °C	508	488	0.33	488

\*  $Q_{\text{cond}}/Q_{\text{char}}$ : the fraction of condensation heat in the total charging heat.

\*\* Density data for salts are based on pure salts (without water or ammonia) with 50% porosity.

of water and strong LiBr solution were 4.8 l and 42 l for internal storage method, which was less than 10% that of external storage. Thus, it was concluded that the internal absorption thermal storage was a better choice than external storage methods. Simulations made by N'Tsoukpoe et al. [19], based on an evaporation temperature of 5–10 °C to produce heat at 25–33 °C in winter, showed long-term storage densities between 180 and 310 kWh/m<sup>3</sup>. A solar powered absorption refrigeration system with an energy storage function using LiBr solution, proposed by Xu et al. [18], achieved a storage density of 102.36 kWh/m<sup>3</sup>. Rizza [94] analyzed a cascade absorption system with aqueous LiBr thermal energy storage and R-123 chiller in series, and a storage density of 90.9 kWh/m<sup>3</sup> was obtained; the volume was based on the volume of a mass concentration of 59% LiBr solution.

H<sub>2</sub>O/NH<sub>3</sub> absorption machines are able to obtain an evaporation temperature lower than 0 °C. At low driving temperatures, efficiencies of a single effect H<sub>2</sub>O/NH<sub>3</sub> cycle are lower than those of a single effect LiBr/H<sub>2</sub>O absorption chiller [95]. So concentrating collectors are recommended to drive the single effect H<sub>2</sub>O/NH<sub>3</sub> systems. In the field of absorption thermal storage, efforts dedicated to the H<sub>2</sub>O/NH<sub>3</sub> working pair focus mainly on the function of shifting the electricity demand from peak hours to off-peak hours using an internal vapor compression heat pump [12,15,96–99]. The energy densities obtained from the calculations were somewhat low, ranging from 32.8 to 33.8 kWh/m<sup>3</sup> [97–99].

Metal chloride solutions developed for liquid absorption thermal storage mainly include LiCl and CaCl<sub>2</sub>, which have been widely applied in open desiccant dehumidification and storage systems [67,71,100,101]. The LiCl/H<sub>2</sub>O couple has shown excellent performance on storage capacity compared with the CaCl<sub>2</sub>/H<sub>2</sub>O couple. However, its high price—nearly ten times that of CaCl<sub>2</sub> by mass [17]—is a major disadvantage. Though absorption thermal storage systems using LiCl are not suitable for large-scale applications due to the high investment, they still possess great storage potential in small-scale applications, for example, a three-phase absorption heat pump developed by ClimateWell [41].

Strong acids such as H<sub>2</sub>SO<sub>4</sub> used to be considered as alternatives for absorption heat pumps or energy storage systems [102–106]. As absorption systems using H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O require extra effort to design an effective rectifying column to separate H<sub>2</sub>SO<sub>4</sub> from water vapor, this idea seems to have been abandoned these years. Strong bases, such as NaOH and KOH, are now being studied in heat transformers and long-term storage applications [55,65,107]. Strong acids and bases have the advantage of high water uptake and low cost; their disadvantage is the high temperature required for heat source and corrosivity on metal materials. Special care must be taken when working with these highly corrosive chemicals.

### 3.3. Working pairs for solid adsorption

Commonly studied adsorption materials include silica gel and zeolite, which have been successfully applied in a large number of adsorption chillers and heat pumps [108,109]. Unlike other materials, the interest in silica gel and zeolite in sorption thermal storage began as early as 1970s and many experimental data are currently available.

#### 3.3.1. Silica gel/H<sub>2</sub>O

Silica gel is the most widely used desiccant because of its low cost and low desorption temperature. Hot water lower than 100 °C provide by common solar collectors is able to charge silica gel in the desorption process. The key shortcoming with silica gel is that the water adsorption mainly occurs at too high relative pressures, which leads to a low water exchange within a typical cycle, especially for closed systems. Another shortcoming is its low

temperature-lift during the adsorption process over a limited range of sorption capacity [10,110]. These reasons give rise to a poor storage performance for the silica gel/H<sub>2</sub>O system. Close and Dunkle [111] proposed the idea of storing energy in form of heat of adsorption in beds of adsorbent material and silica gel was used to illustrate the behavior of adsorption beds. Calculation results showed that the energy density in unit of volume of silica gel was 8.2–20.2 times that of gravel, determined by the charging temperatures. Pryor and Close [112] presented data from measurements made on an open silica gel storage bed, but no results about energy density were given. Tahat [113] studied theoretically and experimentally during both heating and cooling modes in a simple closed test rig. Jaehnig et al. [114,115] developed several generations of prototypes in a series of studies and experimentally achieved about 50 kWh/m<sup>3</sup> of material storage density, which was less than water—with an energy density of 70 kWh/m<sup>3</sup> (within a temperature difference of 25–85 °C and no heat losses is considered). It seems that using silica gel in closed sorption thermal storage systems is not sufficiently competitive for short-term applications, due to its low energy density. However, when it comes to longer periods, silica gel still possesses the heat storage ability in some extent and its energy density could be higher than sensible storage of water.

#### 3.3.2. Zeolite/H<sub>2</sub>O

Zeolites are crystalline aluminosilicates of alkali or alkali earth elements, such as sodium, potassium, and calcium [116]. The term molecular sieves are usually used if zeolites are synthetic. The structures of zeolites are based essentially on the tetrahedral networks of silicon and aluminum—SiO<sub>4</sub> and AlO<sub>4</sub>, which compass channels and cavities. Different arrangements of the tetrahedrons could produce numerous possibility of some 800 crystalline structures and some of them have been found in natural deposits or synthesized [117]. Types 4A, 5A, 10X, 13X and Y remain the dominant zeolites that have been developed for commercial use. Generally, zeolites are more hydrophilic compared to silica gels, leading to the fact that desorption temperatures above 150 °C or even 200 °C are required for extensive regeneration of the materials, which is a major drawback for solar energy storage.

Many scholars [118–122] have suggested the use of natural zeolites in energy storage systems. Compared with synthesized zeolites, natural zeolites are inexpensive and easy to access. Scarmozzino et al. [123] proposed the use of natural zeolites for thermal storage. Aiello et al. [124] studied the behavior of an Italian chabazite-rich tuff in open solar energy storage systems. The dynamics of the discharge process in the zeolite bed was found to be considerably faster than the charge process in closed systems. Artificially synthesized zeolites have higher bulk specific weight and better heat transfer performance [38]. Most of the demonstration projects on sorption thermal energy storage [58,125,126] use zeolite 13X as an adsorbent, owing to its high adsorption performance. Shigeishi et al. [127] proposed the use of the latent heat of adsorption of synthetic zeolites for solar energy storage. They compared activated alumina and silica gel with synthetic zeolite 4A, 5A, and 13X and determined zeolite 13X was the best adsorbent, with a energy density of 148 Wh/kg after drying at 110 °C. Lu et al. [126] developed an adsorption cold storage system with zeolite/water working pair which was designed to provide air conditioning for the driver's cab of an locomotive. Hauer [58,128] reported an successful open sorption system using 7000 kg zeolite 13X, which was installed in a school in Munich and connected to the local district heating network to offset the peak energy demands, performing at a storage density of 124 kWh/m<sup>3</sup>. Hauer and Fischer [76] introduced zeolite 13X into a dishwasher to reduce the energy consumption by means of an open adsorption

system. Their experimental results showed that the energy consumption compared to a conventional dishwasher was reduced from 1.06 kWh down to 0.80 kWh per cycle, leading to energy savings of 24%. To reduce the strong hydrophilic character of zeolites, some modification methods, such as ion exchange, variation of the Si/Al ratio or even dealumination, can be used [87,88,129–131]. Modified zeolites present promising sorption properties, with increased water uptake and integral heat of sorption. In case of Li-exchanged type, the storage density is significantly increased from 149 Wh/kg to 225 Wh/kg [87]. An activated alumina and zeolite 13X hybrid adsorbent (AA/13X), combined with water as the adsorbate was chosen by Dicaire and Tezel [132,133] as an promising working pair. A maximum energy density of 200 kWh/m<sup>3</sup> was achieved in their tests [133].

### 3.3.3. Novel porous materials

Booming progress is reported in the materials science in recent decades, offering a huge choice of novel porous solids which may be used for sorption thermal energy storage. Several new classes of adsorption materials, namely, aluminophosphates (AlPOs), silicoaluminophosphates (SAPOs) and metal-organic frameworks (MOFs), have been proposed and investigated as promising for the use in thermal driven sorption chillers, heat pumps and heat storage [10,42,88,129,134,135]. AlPOs and SAPOs belong to zeolite-like molecular sieves as they are similar to zeolites in some properties [136,137]. These materials show S-shape isotherms, which is quite different from conventional materials (see Fig. 9). According to the theory given by Aristov [42], this unique feature of S-shape isotherms makes AlPOs and SAPOs optimal materials for heat transformation applications. Out of the classes of AlPOs and SAPOs, AlPO-18 and SAPO-34 are regarded as the most attractive choices. Jänchen et al. [138] implemented a calorimetric investigation on SAPO-34, showing that the storage density was about 290 Wh/kg at a discharging temperature of 40 °C. In a measurement reported by Henninger et al. [129], the storage densities of SAPO-34 and AlPO-18 were found to be 203 and 243 Wh/kg respectively. Beside SAPOs and AlPOs, a novel class of microporous materials termed the metal-organic frameworks (MOFs) has emerged. MOFs are described as porous solids containing metal ions linked by molecular species [139]. Due to the high porosity, large surface area and tuneable pore sizes, MOFs have attracted an increasing attention for heating, cooling, dehumidification and storage applications over the past years [10,129,134,135,139,140]. Out of this large class of porous materials, MIL-101 is identified as one of the highly interesting candidates, as it adsorbs up to 1 g of water per gram of sorbent and is stable even over several cycles [134]. MIL-101 shows low heat of adsorption, as a consequence of the high water uptake. In spite of this, a high storage density up to 680 Wh/kg would still be obtained at a charging temperature of 90 °C and a discharging temperature of 40 °C with such a high water uptake [88]. In contrast to traditional adsorbents like silica gels and zeolites, the main drawback of most of these novel materials may be their comparatively expensive production costs, yet many MOFs are of reasonable cost.

### 3.4. Working pairs for chemical reaction

In fact, there is no clear boundary between “chemical reaction with sorption”, which could be classified into sorption phenomenon and “chemical reaction without sorption”. According to past experiences and customs, solid/gas coordination reactions, mainly including coordination reaction of ammoniate with ammonia and hydration reaction of salt hydrate with water, are widely regarded as sorption [6,28,141–144]. The product of the coordination reaction of ammoniate with ammonia is called a coordinated

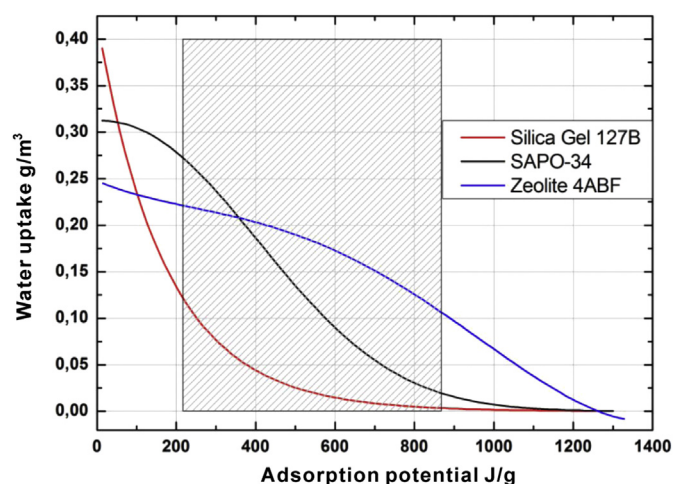


Fig. 9. Characteristic curves of three different sorption materials, Grace Silica Gel 127B, SAPO-34 and Zeolite 4ABF. The gray area represents a possible working window for adsorption chillers or heat pumps with adsorption at 35 °C/1.2 kPa and desorption at 150 °C/5.6 kPa [88].

compound or a complex compound. A coordinated bond is formed when a lone electron pair provided by a ligand (such as NH<sub>3</sub>, H<sub>2</sub>O) falls into a free hybrid orbit supplied by a center atom (such as a metal ion). Unlike the liquid absorption and solid adsorption, chemical reaction is monovariant and induces volume modification of the solid. A obvious hysteresis may exists.

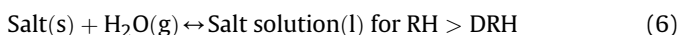
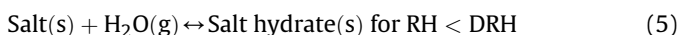
#### 3.4.1. Coordination reaction of ammoniate with ammonia

Metal halides are the most used ammoniates for the coordination reactions with ammonia. The large number of halides and different steps of coordination reactions provide vast choices of working pairs, covering a wide range of temperatures—from 48 °C (NH<sub>4</sub>Cl) to 334 °C (NiI<sub>2</sub>) at 1167 kPa [30].

Though coordination reactions of ammoniate with ammonia have long been used for sorption cooling and heat pumping systems [28,29,108,142,145], their potential for heat storage has not been extensively studied. Stitou et al. [64], constructed a solar powered BaCl<sub>2</sub>/NH<sub>3</sub> sorption pilot plant with a cooling capacity of 20 kWh, realizing a cold storage density of 114 Wh/kg material at a 60–70 °C charging temperature. The heat source is provided by flat-type solar collectors. Lépinasse et al. [146] investigated an experimental setup based on the resorption process between BaCl<sub>2</sub> and MnCl<sub>2</sub>. The experimental results showed that the resorption process was promising for energy storage use with a cooling capacity of 47 kWh/m<sup>3</sup>. Bao et al. [147] also designed a resorption system using MgCl<sub>2</sub> and NH<sub>4</sub>Cl for cold storage. The obtained cold storage densities ranged from 95 to 125 Wh/kg, as a function of evaporation temperatures. Employment of varied pairs and reaction levels also offers functions of sorption heat storage systems with great flexibility. Recently Li et al. [30,31] proposed two types of thermochemical sorption heat storage cycles for both energy storage and energy upgrade. The first one was called a target-oriented sorption heat transformer [30], using a pressure-reducing desorption (resorption) technique during charging process and a temperature-lift technique during discharging process. Theoretical analysis showed this kind of heat transformer was able to upgrade the low-grade energy from 87 °C to 171 °C, using a group of working pair MnCl<sub>2</sub>–CaCl<sub>2</sub>–NH<sub>3</sub>. The second proposed cycle was named a dual-mode heat transformer [31], mainly introducing a heat recovery process to provide heat at appropriate temperature even when the ambient temperature was very low. A test rig based on the second cycle is now being constructed in Shanghai Jiao Tong University.

### 3.4.2. Hydration reaction of salt hydrate with water

The interests in using hydration reactions for heat storage application mainly focus on the hygroscopic salts such as magnesium chloride ( $\text{MgCl}_2$ ), sodium sulfide ( $\text{Na}_2\text{S}$ ), strontium bromide ( $\text{SrBr}_2$ ) and magnesium sulfate ( $\text{MgSO}_4$ ). Usually, the products of hydration reactions of these salts are assumed to be higher hydrates with more crystal water molecules. However, in some cases, the relative humidity/pressure is so high that the product of the hydration is a saturated salt solution, rather than a salt hydrate. This process is called deliquescence, which is an important solid-water interaction phenomenon. Deliquescence is defined as a first order phase transformation of the solid to a saturated solution when the relative humidity (RH) reaches a certain threshold value, namely, the deliquescence relative humidity (DRH) [148]. DRH is also the equilibrium relative humidity above the saturated solution. The two cases can be represented by the following equations [91].



The value of DRH depends on the properties of the salt and the temperatures. Some problems will be encountered if the deliquescence phenomenon happens. The forming of liquid film on the surface of salt crystal will not only prevent the hydration reaction from proceeding, but also cause corrosion problems due to the dripping of solution to other metal components.

According to the DRH values presented by Greenspan [149], the DRH of  $\text{LiCl}$  and  $\text{LiBr}$  are only 11.3% and 6.2% at 30 °C, implying that it's very easy for their solids to form solutions in most situations. Thus  $\text{LiCl}$  and  $\text{LiBr}$  should not be considered for solid/gas hydration reactions. Though the DRH of  $\text{MgCl}_2$  (32.4% at 30 °C) is not as low as those of  $\text{LiBr}$  and  $\text{LiCl}$ , it is also regarded as a deliquescent salt, meaning that treating of  $\text{MgCl}_2$  in sorption storage systems needs special care.  $\text{MgCl}_2$  was identified by Zondag et al. [150] from ECN (Energy Research Centre of the Netherlands) as the most promising of the tested materials for seasonal heat storage, after testing a list of thermochemical materials including  $\text{MgSO}_4$ ,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{MgCl}_2$ , and  $\text{CaCl}_2$ . ECN [22,23,74,144,150,151] also raised several reactor concepts for  $\text{MgCl}_2/\text{H}_2\text{O}$  sorption thermal storage of solar energy in residential houses and built a series of lab-scale open reactors using the  $\text{MgCl}_2/\text{H}_2\text{O}$  couple. An effective energy density of 139  $\text{kWh/m}^3$  was achieved at a charging temperature of 130 °C with the open system.

Compared with  $\text{MgCl}_2$ ,  $\text{MgSO}_4$  is a hydrothermally stable salt with a high DRH (90% at 30 °C). To improve the performance and stability of heat storage materials, Posern and Kaps [91] suggested to mix  $\text{MgCl}_2$  with a small amount of  $\text{MgSO}_4$ , using attapulgite as the matrix. The measured storage density for this composite was 694  $\text{Wh/kg}$  at a charging temperature of 130 °C.

Ucar and Pounder from Syracuse University [152] gave a proposal of utilizing hygroscopic properties of  $\text{Na}_2\text{S}$  for thermal storage in 1982. Two key problems met in their experimental research are the high cost of the vacuum system and the possibly toxic emissions from the vacuum pump ( $\text{H}_2\text{S}$ ). The thermochemical properties of the  $\text{Na}_2\text{S}/\text{H}_2\text{O}$  working pair have been determined by Boer et al. [92]. The melting temperature of the salt hydrate in the composition range between  $\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$  and  $\text{Na}_2\text{S} \cdot 0.5\text{H}_2\text{O}$  is 83 °C, and the heat storage capacity related to the dehydration reaction, is approximately 1.07  $\text{kWh/kg}$   $\text{Na}_2\text{S}$ . The storage density obtained from the SWEAT prototype [143] was almost 1.1  $\text{kWh/kg}$  for heat and 0.7  $\text{kWh/kg}$  for cooling with COP of 0.84 and 0.57, respectively. Chiang Mai University (Thailand) [153] developed several generations of modular chemical energy storage prototypes to improve the system performance. A COP for both heating and cooling of 1.11

was finally achieved. The main challenge for  $\text{Na}_2\text{S}$  is its rigorous requirement for high vacuum conditions, due to much lower pressure levels than other hygroscopic materials like  $\text{SrBr}_2$ ; in case of  $\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$ , the equilibrium pressure is only 1.24 kPa at 64.8 °C, corresponding to a condensation temperature of 10.2 °C for saturated water. According to the analysis of thermodynamic constraints conducted by Mauran et al. [154], salt hydrates  $\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O}$  and  $\text{Na}_2\text{S} \cdot 2\text{H}_2\text{O}$  could not be dehydrated in summer, with an outside temperature of 35 °C and a heat source below 80 °C.

As the working pair  $\text{SrBr}_2/\text{H}_2\text{O}$  only needs a charging temperature lower than 80 °C, it is regarded as a promising alternative for the direct heating of residential homes working with classic flat-type solar collectors [63]. The experimental tests demonstrated that the power level in the range of 40  $\text{kW/m}^3$  could be reached with reactive composites ( $\text{SrBr}_2$  and expanded graphite), having a heating storage capacity of higher than 250  $\text{kWh/m}^3$ . A prototype at the scale of 60 kWh for heating and 40 kWh for cooling was set up and tested under conditions representative of summer or mid-season [154].

$\text{MgSO}_4$  was selected by Van Essen et al. [83,155], based on results from theoretical and experimental study on promising materials for compact seasonal heat storage. Experiments indicated that the second step ( $\text{MgSO}_4 \cdot 6\text{H}_2\text{O(s)} \rightarrow \text{MgSO}_4 \cdot 0.1\text{H}_2\text{O(s)} + 5.9\text{H}_2\text{O(g)}$ ), of the three dehydration steps had a high energy density ( $611 \pm 28 \text{ kWh/m}^3$ ), which primarily occurred in a temperature range that can be covered by medium temperature collectors. Due to its high heat storage potential,  $\text{MgSO}_4$  are considered as the preferred sorption material in many recent studies [89,156–160].  $\text{MgSO}_4$  in the form of fine powder seems impossible to be directly used in a practical storage system due to its poor mass transfer ability. To overcome possible deliquescence problem, a family of composite materials have been developed by confining magnesium sulfate into a porous matrix, providing a large specific area for hydration reaction [90,91].

### 3.5. Composite materials

Though chemical reactions possess excellent storage potential based on the analysis on the material level, their performance in actual systems requires further research. Due to the deliquescence, swelling and agglomeration phenomena after several incipient cycles, the reaction is very difficult to continue. An additive with a porous structure and high thermal conductivity could be used to improve such problems in some extent.

According to Aristov et al. [50] and Levitskij et al. [161], the energy storage ability of the SWSs materials is similar to that of the metal hydrides and crystalline hydrates, ranging on a scale from 390 to 780  $\text{kWh/m}^3$  with a temperature range of 30–150 °C. Hongois et al. [90] prepared a zeolite/ $\text{MgSO}_4$  composite (ZM15) for low temperature heat storage applications. The optimum mass percentage of  $\text{MgSO}_4$  in the composite was founded to be 15%. An energy density of 166  $\text{kWh/m}^3$  was obtained with an airflow rate of 8 L/min and inlet air RH of 50% in an open cycle. Jänchen et al. [87] performed a comparative study of several types of composite storage materials and the material of 30 wt.%  $\text{CaCl}_2$  impregnated in aluminosilicate was found to have a storage density of 172  $\text{kWh/m}^3$ . The  $\text{CaCl}_2$ -silica gel composite has been extensively studied by Wu et al. [162,163] and Zhu et al. [164] for thermal energy storage. The composite sorbent prepared by impregnating of silica gel with a 30 wt.%  $\text{CaCl}_2$  solution, showed the highest and most stable storage capacity of 283  $\text{Wh/kg}$  at the relatively low charging temperature of about 90 °C [162]. An approximately stable energy storage density of 264  $\text{Wh/kg}$  could be obtained from the sorption thermal storage experiments over multiple repeated sorption/desorption cycles [164]. The study of Tokarev et al. [165] showed that the composite



material based on  $\text{CaCl}_2$  and MCM-41 was able to absorb up to 0.75 g of  $\text{H}_2\text{O}$  per gram of the dry sorbent, which contributed to a high thermal storage capacity (583 Wh/kg). As reported by Sapienza et al. [166], a new composite sorbent  $\text{LiNO}_3/\text{vermiculite}$  (SWS-9V), was specifically developed to operate at low regeneration temperature ( $<65\text{--}70\text{ }^\circ\text{C}$ ), and demonstrated a remarkable heat storage capacity of 250 Wh/kg.

One advantage of using composite materials for water sorption is that the large pore volume of the porous matrix allows existence of some amount of salt solution in it. However, the pore volume is limited and leakage of the salt solution during sorption is still the most worrying issue in some extreme cases. Once the liquid drops out of the matrix, it's hard for it to come back to the original position. With regard to this problem, Gordeeva and Aristov [44] proposed several solutions: a proper selection of salt content in the composite, which has been used in some researches [167,168]; an anchoring the salt cations to the matrix surface by means of enhanced adsorption of the metal cations on the pore surface at increased pH of the impregnating solution; covering the external surface of the grains with a hydrophobic coating which is only penetrable for vapor but not for liquid.

#### 4. Progress in liquid absorption cycles

Absorption refrigeration is a relatively mature and reliable technique for utilizing low-grade thermal energy such as solar energy. Up until now, various kinds of single effect, double effect, even triple effect absorption chillers and heat pumps are available in international markets. The search for new absorption couples for thermal storage needs much basic research, which will take a long time and great effort. Compared with this, modification of the configuration of existing absorption cycles, based on familiar absorption couples, seems more attractive and realistic. Many efforts focus mainly on presenting and analyzing various types of absorption thermal storage cycles, including long-term storage cycles, solar driven cycles, compression combined cycles, double-stage cycles, three-phase cycles.

##### 4.1. Long-term cycles

Liu et al. [17,169] proposed an long-term absorption energy storage cycle for house heating. The charging of solar energy takes place in summer and heat is released in winter. The unique feature of this cycle is the fact that it allows the solution to reach the crystallization point in the storage tank. Fig. 10 (a) describes the working principle of the long-term absorption thermal storage cycle, using  $\text{LiBr}/\text{H}_2\text{O}$  as an example. Fig. 10(b) gives the operation principle of the cycle. In Fig. 10(a), the high pressure level (HP) and low pressure level (LP) depend on the condensation temperature (point C) in summer and the evaporation temperature (point E) in winter respectively. From point 2 to point 3 or 3', solar heat is continually collected from solar collectors to heat the solution. The absorbate is driven out of the  $\text{LiBr}$  solution and then transferred to the condenser. The strong solution at point 3 or 3' flows back to the storage tank. Line 3–5 or 3'–5 represents the transition storage period during the summer to the winter, when the solution is kept in the tank and separated from other vessels. In winter, the absorbate is evaporated and then absorbed by the solution at point 5. The pressure of the solution increases at the beginning session of the absorption process until it arrives at point 6, where the pressure is equal to the low pressure level (LP). Path 1–2–3–5–6–7–1 refers to a conventional long-term absorption storage cycle, in which point 3 should be carefully designed to avoid the formation of crystal from point 3 to point 5. For the proposed cycle 1–2–3'–4–5–6–7–1, the mass fraction of the salt solution at point 3' can be higher than that

at point 3. The crystal form of the salt is allowed to appear in the end of the storage period in the solution tank. Whereas, a note must be made concerning this cycle that the charging temperature (temperature at point 3') is still restrained as crystallization is only permitted in the storage tank, rather than in the reactor/desorber during the desorption process. It is claimed that this improvement greatly enhances the storage density of the solution because of the increase of the interval of mass fraction between the weak and strong solutions.

##### 4.2. Solar driven cycles with integrated heat storage

Absorption chillers and heat pumps with integrated heat storage function are mainly proposed to compensate for the solar heat offset, by storing more solutions and absorbates. The more solutions are charged when the solar energy is available, the longer time the absorption system can export cooling or heating effect without solar heat. Grassie and Sheridan [170] proposed a  $\text{LiBr}/\text{H}_2\text{O}$  absorption cooling cycle with absorbent and absorbate storage. Compared with conventional cycles, the condenser and the absorber are associated with a refrigerant store and an absorbent store respectively. Weak solution and strong solution is stored in one tank to reduce the storage volume. Results of the simulation showed that absorption thermal storage was indeed thermodynamically feasible and it could offer considerable advantages for solar cooling application. However, no data about energy densities of the solution were offered through this model. Kaushik et al. [96] presented a similar water/ammonia absorption thermal storage cycle for space heating. Xu et al. [18] proposed a direct solar powered absorption refrigeration system (SPAR) with an energy storage function, as shown in Fig. 11. In this cycle, the solar collector actually acts as a generator. Energy collected from the solar radiation is transformed into the chemical potential of the  $\text{LiBr}$  solution directly in the solar collectors. After being heated by solar radiation, the temperature of the  $\text{LiBr}$  solution rises and reaches the saturation point. The vapor-liquid mixture flows into the solution tank where they are separated. The vapor is cooled in the condenser and collected in the water storage tank. Other processes of the SPAR system are similar to traditional absorption thermal storage systems. A dynamic model for the system was developed and simulation example was offered to evaluate the performance of the presented SPAR system. The simulation results indicated that COP of the system was 0.75 and the storage density was  $102\text{ kWh}/\text{m}^3$ .

##### 4.3. Compression combined cycles

When solar energy is not available, or the heat source temperature of the solar collectors cannot drive absorption machines, internal or external compressors can be used [12,14,15,94,97–99,171,172]. The common ground of different compressor combined cycles is that they all include a compressor for the absorbate vapor—such as water or ammonia—to transfer electricity into the internal energy of the absorbate vapor, which will be added to the desorber/generator in the following condenser. These cycles aim to shift electricity demand from peak hours to off-peak hours as the compressor is driven by electricity.

Hans [12] introduced the concept of combining a compressor (for the charge process) with an absorption heat pump (for the discharge process). The circuit diagram of the cycle is shown in Fig. 12. During the charging phase, vapor from the strong solution is regenerated and sucked in by the compressor. The temperature and pressure levels of the vapor are considerably increased through the compression process. Then the hot vapor is condensed and stored in an absorbate tank. The heat of condensation and the waste heat of the compressor are used to generate the weak solution in the

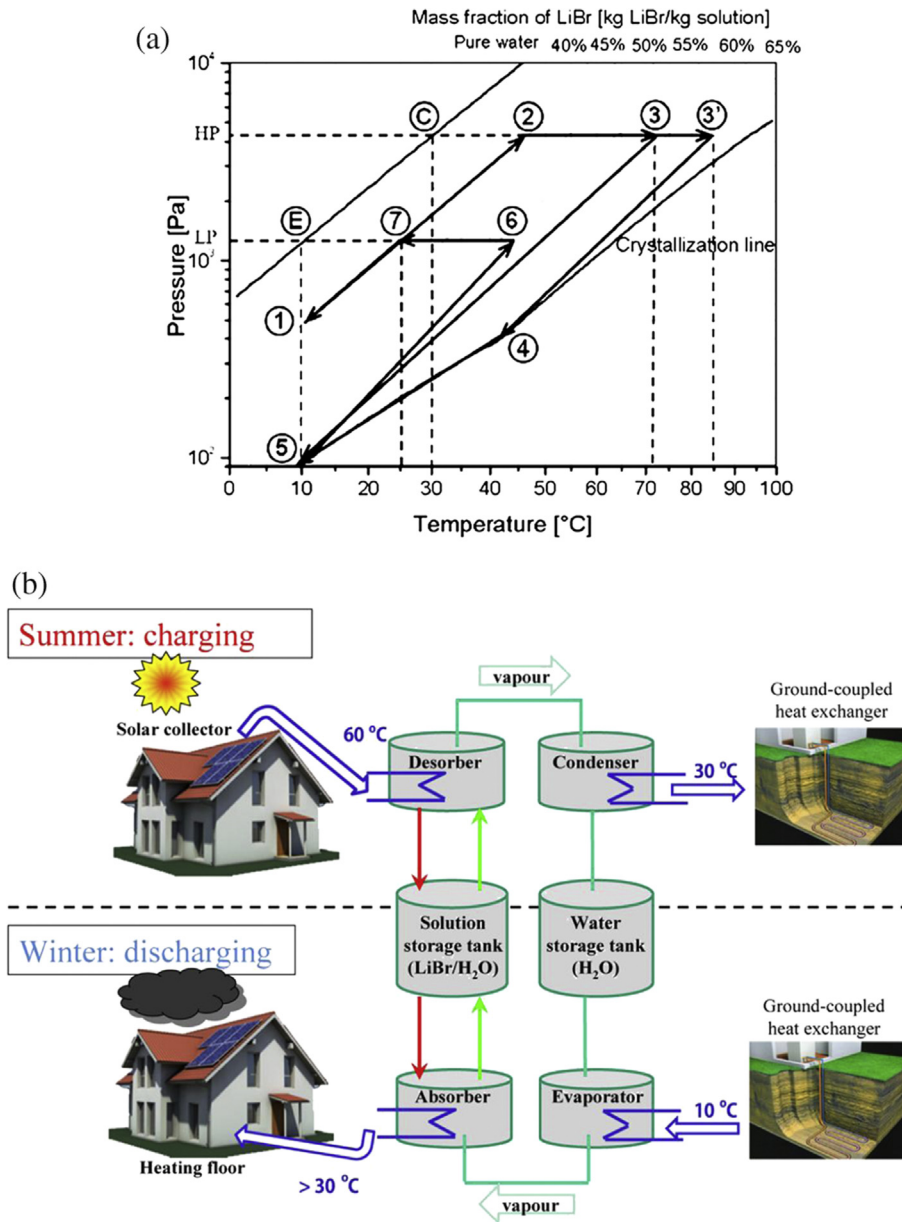


Fig. 10. Long-term absorption storage cycle: (a) working principle in pressure-temperature-concentration diagram [17]; (b) operation principle [19].

desorber. No heat is exchanged with the environment during this charging phase and only electricity power is supplied to the system by the compressor. The discharge phase is triggered by opening the expansion valve. The compressor and condenser are not in operation. Hans [12] also presented a double-stage absorption thermal storage system combined with a compressor (Fig. 13). The charging process of the double-stage system is similar to that of the single stage system. Unlike conventional absorption thermal storage systems, the absorber in the charging phase is no longer inactive. The so called “absorber” can act as either an absorber or a desorber, according to the heating or cooling capacity. The most striking advantage of the system is claimed to be that cooling capacity and heating capacity can be controlled independently, continuously from zero to full power, and the compressor power does not need to be controlled. Xu et al. [98,99,171,172] presented a similar compression combined absorption system as Fig. 12. Based on a dynamic model, a numerical simulation is implemented to investigate system performances when it operates to provide combined

air conditioning and hot water for a hotel located near the Yangzi River in China.

#### 4.4. Double-stage cycles

For lower charging temperature, or higher condensation temperature during the charging process, and for higher discharging temperature or operating with lower solution concentration during the discharging process, a double-stage cycle was presented by Weber and Dorer [55] using the NaOH/H<sub>2</sub>O couple, as illustrated in Fig. 14. The overall working principle is similar to the common system (single stage process), except for an added absorber/desorber 2, an evaporator/condenser 2 and a heat exchanger. In the double-stage cycles, the discharging process of the NaOH solution is divided into two steps within different pressure levels. The maximum concentration interval of the NaOH solution is increased from 22% (mass fraction of NaOH in single stage) to 37% (mass fraction of NaOH in double-stage). The heat generated in absorber 1

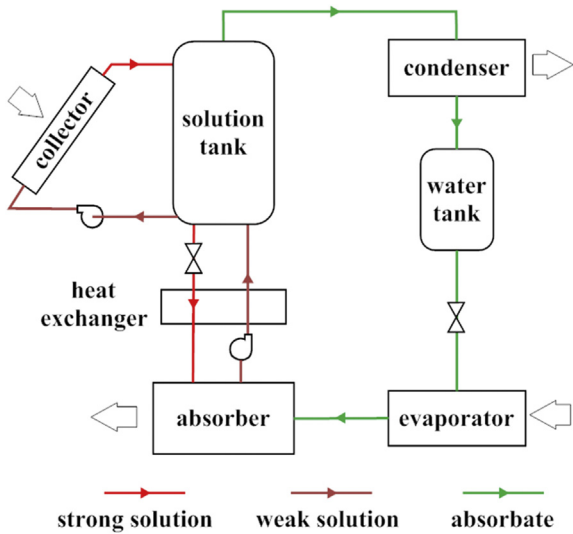


Fig. 11. Solar driven LiBr/H<sub>2</sub>O absorption thermal storage cycle [18].

is used to produce vapor in evaporator 2. The main drawbacks of the double-stage cycles are diminution of storage density and the complexity of the system, because of the requirements for more vessels and heat exchangers.

4.5. Three-phase cycles

It is a general rule that a larger difference in concentration often leads to greater energy density for liquid absorption couples. In conventional absorption systems, the process of crystallization is perceived as a major barrier to further expand the concentration difference between the strong solution and the weak solution.

Lourdudoss and Stymne [13] presented an idea of using crystals of hydrophilic salts to enhance storage density. This novel cycle was named the “super solution field system” by the authors. This absorption process is reversible and monovariant with a wide solution concentration interval. To distinguish the cycle from common two-phase absorption cycles, it is suggested to be termed “three-phase absorption cycle”. A major difference between this three-phase cycle and the long-term storage cycle mentioned in Section 4.1 is that the former allows existence of crystals in the charging process but the latter only permits crystals in the storage tank. That is to say charging temperature in the three-phase cycle could be higher than other cycles, as it is free of the crystallization problem.

The principle of the three-phase absorption thermal storage system is shown in Fig. 15. The design includes only two vessels, which serve as a condense/evaporator and a desorber/absorber reactor respectively. During the charging process, the weak solution stored at the bottom of the reactor is pumped and sprayed over the heat exchanger. The solution is heated until it achieves the saturation point at the charging temperature. As the water vapor is released from the solution, solid crystal is formed continuously, flushed to the bottom of the vessel and stopped by a sieve. Three phases, including vapor, liquid solution and solid crystal coexist simultaneously, so a monovariant process is ensured. The process is reversed during the discharge process, during which the solution turns again into an unsaturated state at a lower temperature by absorbing the water vapor produced in the evaporator. The unsaturated solution falls and contacts with the solid crystal collected at the bottom; there the crystal dissolves into the solution. In the three-phase absorption cycle, salt crystals have been transformed from an obstacle to an enhancement to increase the energy density of the salt. Energy is stored efficiently and with practically no thermal loss in the dried salt. Six working pairs, including LiCl·H<sub>2</sub>O/H<sub>2</sub>O, LiBr·H<sub>2</sub>O/H<sub>2</sub>O, LiBr/CH<sub>3</sub>OH, CaCl<sub>2</sub>·H<sub>2</sub>O/H<sub>2</sub>O, LiBr/C<sub>2</sub>H<sub>5</sub>OH and KOH·H<sub>2</sub>O/H<sub>2</sub>O, were considered by making use of their enthalpy–

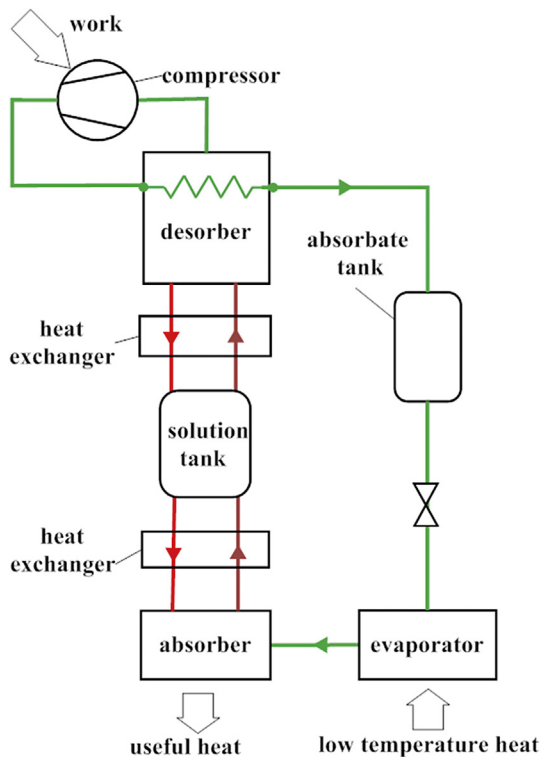


Fig. 12. Compression combined absorption thermal storage cycle [12].

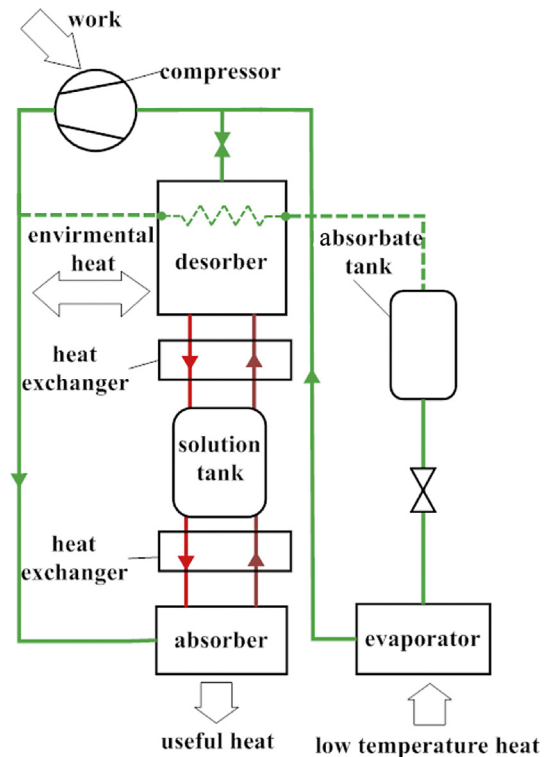


Fig. 13. Compression combined double-stage absorption thermal storage cycle (dashed lines only operate in charging) [12].

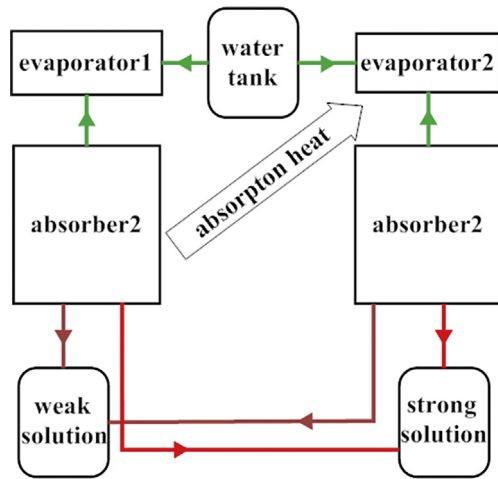


Fig. 14. Discharging process of double-stage absorption thermal storage cycle [55].

concentration diagrams [13]. It was found that the proposed three-phase process was superior due to its high storage density. For example, the obtained COP of heat pumping was 1.58 and corresponding storage densities are 340 Wh/kg by the mass of salt and 300 kWh/m<sup>3</sup> f by the volume of rich solution for LiCl.

## 5. Advanced concepts of adsorption reactors

Sorption working pairs with high energy densities on material level cannot guarantee efficient storage performance in practical applications. After screening of storage materials, more detailed issues regarding design of reactors have to be considered in order to build up efficient and compact thermal storage systems. Some of the past research activities in the field of sorption thermal heat storage [6,110] have proven the importance of some critical aspects, mainly including control of heat capacity, reducing heat losses, improving heat and mass transfer property. These problems have also been encountered in the development of solid adsorption refrigerators. Since the solid adsorption cooling technology has been extensively researched, the experiences for it could serve as useful references for developing adsorption heat storage. Advanced

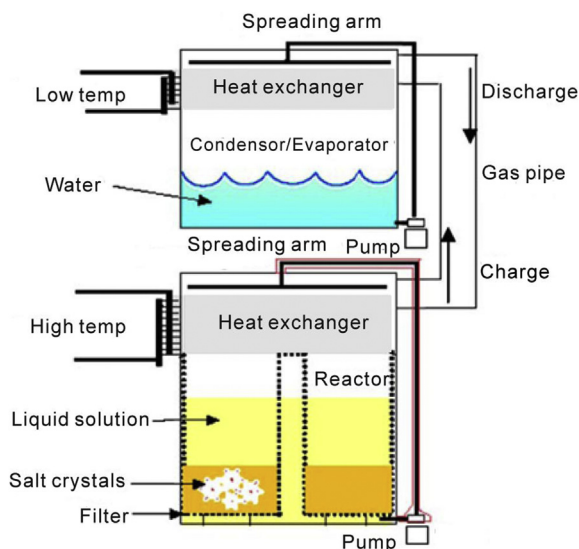


Fig. 15. Schematic of discharging process of three-phase cycle [41].

concepts of adsorption reactors are mainly related to extended surfaces, separate reactors and module reactors.

### 5.1. Extended surfaces

Extended surface heat exchangers have been extensively applied in common closed adsorption chillers, and heat pumps [173–175]. For closed adsorption systems, especially for water systems, heat conduction is the major way to transfer heat from the heating fluid to the adsorbent in the reactor. So extended surfaces are required to ensure sufficient heat transfer areas. A number of different types of extended surfaces have been studied, such as finned tubes [126], plate heat exchangers [154], plate-fin heat exchangers [175] and coated Spiro-tubes [143]. This solution is suitable if the wall heat transfer coefficient is not low and if there is no swelling or shrinking of the sorbent, which could produce considerable alteration in this coefficient [108]. One shortcoming related to this technology is that the thermal capacity of the reactor increases with the augmentation of the surface area of the heat exchanger, causing low storage efficiency. During the design of reactors, special attentions should be paid to the thermal capacity ratio between the metallic extended surfaces and the adsorbents.

For open systems, the problem of heat transfer is not so urgent as for closed systems, but a large contact surface area between the air flow and the sorbent is still necessary to realize good heat and mass transfer property. Some optimized measures such as a large cross-flow area with a minimal bed length or a porous matrix with large surface area could be used to obtain a low pressure drop for the air flow.

### 5.2. Separate reactors

There are two types of adsorption thermal storage reactors, the integrated reactor and the separate reactor. The integrated reactor, in which reaction occurs within the storage vessel, is widely applied in solid adsorption systems. For a separate reactor when the reaction is complete, the sorbent is fed back to the storage vessel. Schematic representations of the types of systems are presented in Fig. 16.

Optimization of the mass transport ability, and the reduction of heat required for inert metallic components are the main advantages of separate reactors; an integrated system has the advantage of simple construction. Zondag et al. [22] concluded that separate reactors were more suitable than integrated reactors for large-scale storage applications. The investigation on possible layouts of reactors for a sorption thermal storage system indicated three types of reactors as potentially interesting: an agitated reactor, a fluidized bed reactor and a gravity-assisted bulkflow reactor (Fig. 17). A separate reactor system needs additional electrical energy to drive the powder transport as well as the handling of the powder within the reactor. An energy analysis revealed that the screw reactor was the more promising choice as their preliminary experiment proved that active stirring significantly improved the heat transfer property of the material. A big problem associated with the influence of standing stirring on the mechanical stability of the sorbent should be further investigated though more experiments. The concept of separated reactors has been adopted in a joint project named CWS-NT [32].

### 5.3. Modular reactors

The modular concept is a popular method of designing and manufacturing industrial products, which indicates that numbers of modules are chosen according to practical requirements. Modular reactors have been widely employed in some systems



[143,154,176,177]. Design using the modular concept has the following advantages [143,154]: (1) The extension or reduction of the scale of a reactor needs less technical efforts; though it still needs some consideration on the system and control strategies as well as for scaling of exterior components. Changing the number of modules to adapt the power and storage capacity of the system to the practical requirement offers considerable adaptability for modular reactors. (2) The ratio of the volume of sorbent to the volume of reactor largely determines the performances of sorption thermal storage systems—especially for solid adsorption systems—due to the large amount of heat wasted on metallic components during the alternate heating and cooling processes. The size of modular reactors is discreetly chosen to minimize the heat transfer distance and the thermal capacity of metallic components. Sometimes, for smaller modules, it is still hard to get a good thermal capacity ratio since surface/volume ratio is worse and some parts cannot be scaled linearly. Therefore, an optimization design should be conducted to obtain the best parameters. (3) Modular reactors can be manufactured using standard procedures. This future low-cost serial production enables competitive prices in comparison to conventional machines.

## 6. Typical prototypes and projects

Interests in the sorption thermal storage technique began in the 1970s [111,170,178–180], as a result of the oil crisis; by the 1980s and 1990s interests had waned and few projects for demonstration could be found. Because of the rapid increase in solar energy development in recent decade, finding energy storage solutions to increase the fraction of solar utilization has become an urgent necessity. Thus, there has been renewed and growing interest in sorption thermal storage technology because of its high storage density and capability for long-term thermal storage of solar energy. Some prototypes and projects have been constructed. The most significant achievements for sorption thermal storage are summarized in Table 3; some of these are related to Task 32 of IEA (International energy agency)-SHC (solar heating and cooling), which has been completed, and SHC Task 42 and ECES (Energy Conservation through Energy Storage), Task 24 (SHC-ECES), which is now under way.

To date, few actual applications using the liquid absorption thermal storage technique have been implemented. As early as 1987, Ruitter [15] investigated an absorption thermal storage cycle using  $\text{H}_2\text{O}/\text{NH}_3$  for three different storage alternatives. In the first alternative the components are separated by the supply of heat. The

heat of condensation of the gaseous component is transferred to the environment. The energetic efficiency of this cycle is less than 100%. In the second storage alternative, the heat of desorption is supplied by a heat pump that used the heat of condensation as a heat source. In the third alternative, the heat of condensation is produced at such a high temperature that this heat could be used for the desorption directly. To achieve this higher temperature, the gaseous component is condensed at a higher pressure; a compressor is applied for this purpose. An experimental installation was built for the purpose, with a net heat output of 5 kW and a storage capacity of 40 kWh. The experimental results showed that the working performance of the prototype was efficient and nearly met the design objectives. The energy density reached 111.1 kWh/kg (based on the total mass of absorbate and weak solution).

The merits of low cost and high selectivity for water make NaOH a good theoretical alternative for energy storage. Weber and Dorer [55] from EMPA built a single stage closed absorption prototype in 2008 for long-term heat storage using NaOH/ $\text{H}_2\text{O}$ . The prototype compasses three storage tanks for water, strong solution and weak solution, a reactor with two integrated heat exchangers, solution pumps, connections pipes, and a hot water storage tank for the consumer. As the flow is driven by gravity in the integrated reactor, the configurations of the two dish-shaped heat exchangers are both arranged in a cascade pattern. Calculation results from a simplified static model illustrated that at a charging temperature of 70 °C, the energy storage density was three times higher compared to traditional hot water storage and about six times higher at a discharging temperature of 40 °C for low temperature space heating. The single stage NaOH prototype requires a charging temperature of 150 °C if taking all kinds of heat losses into account. To reach higher concentrations of the lye at lower temperature levels in the desorber, a double-stage cycle is suggested (see Section 4.4). As shown in Fig. 18, the second stage is constructed and directly connected to the original first stage to obtain a double-stage system [65]. The heat exchanger in the second stage is changed from an integrated heat exchanger—which is used in the first stage—to a separate heat exchanger, to reduce heat losses caused by the radiation between the hot and cold heat exchangers. With a 3 kW heat input, a heat output of 600 W could be obtained in the discharge process. The drawbacks of the double-stage cycle included a low discharging rate, crystallization of NaOH solution and overheating of the ground heat exchanger.

Based on the three-phase absorption cycle mentioned in Section 4.5, a Swedish company named ClimateWell [41,184–186] has developed several generations of prototypes which target the

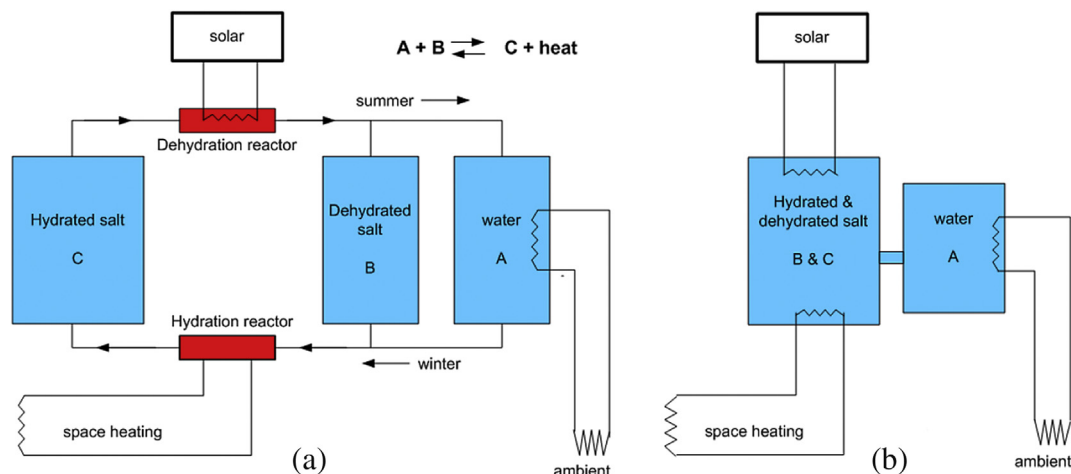


Fig. 16. Two types of reactors: (a) separate reactor and (b) integrated reactor [22].

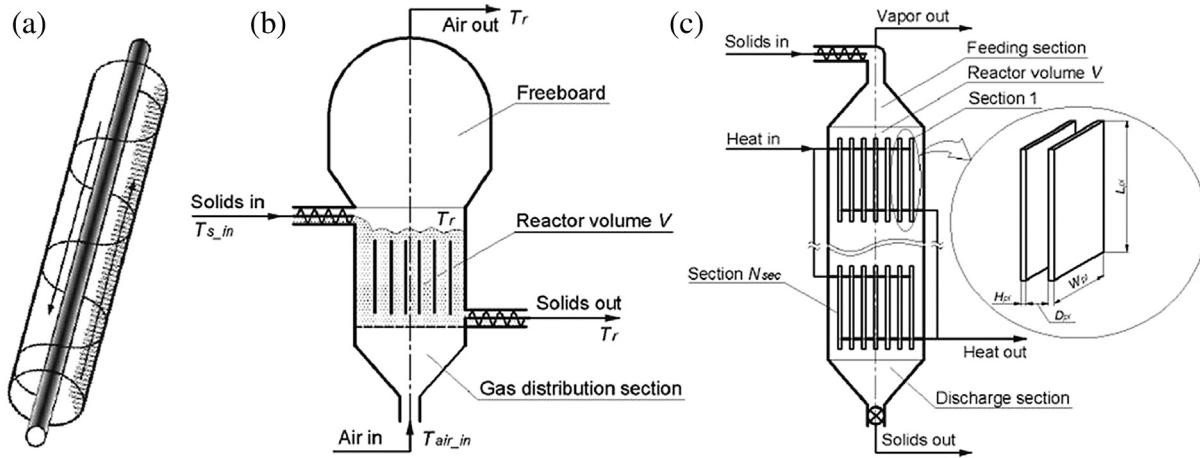


Fig. 17. Three types of separate reactors: (a) screw reactor (b) fluidized bed reactor (c) gravity-assisted bulkflow reactor [23].

Mediterranean heating and cooling market; it is regarded as one of the most achievable prototypes, combining short-term absorption thermal storage and solar cooling technologies. Test of the original prototype named TCA (Thermo-Chemical Accumulator), as shown in Fig. 19, was accomplished in the framework of IEA-SHC Task 32 [41,114]. Some fundamental test results demonstrated that with a

35 kWh heat input, a cooling storage capacity of 22 kWh could be obtained. Calculated energy density for LiCl salt was equivalent to 253 kWh/m<sup>3</sup>, 3.6 times that of water (25–85 °C). Considering the volume of other indispensable heat exchangers, connection pipes and storage vessels, the energy density of this prototype was only 1.2 times that of water. Enlargement of the scale of storage systems

**Table 3**  
Typical prototypes and projects for sorption energy storage.

Type of technology	Working pair	Charging rate	Discharging rate	Storage capacity	Storage density	Institute	Ref.
Closed liquid absorption	H <sub>2</sub> O/NH <sub>3</sub>	8 kW at 93 °C	5 kW at 43 °C	40 kWh	M <sup>a</sup> : 119 kWh/m <sup>3</sup>	Delft University of Technology, the Netherlands	[15]
Closed liquid absorption	NaOH/ H <sub>2</sub> O <sup>b</sup>	1 kW at 95 °C	1 kW at 70 °C	8.9 kWh	M: 250 kWh/m <sup>3</sup> P <sup>c</sup> : 5 kWh/m <sup>3</sup>	EMPA, Switzerland	[181]
Closed three-phase absorption	LiCl/H <sub>2</sub> O	15 kW at 87 °C	8 kW at 30 °C	35 kWh	M: 253 kWh/m <sup>3</sup> P: 86 kWh/m <sup>3</sup>	SERC, Sweden	[181]
Closed liquid absorption with one integrated storage tank	CaCl <sub>2</sub> / H <sub>2</sub> O <sup>b</sup>	At 138 °C	–	–	M: 381 kWh/m <sup>3</sup>	University of Minnesota, USA	[182]
Closed liquid absorption	LiBr/H <sub>2</sub> O	2–5 kW at 75–90 °C	At 30–40 °C	13 kWh	–	LOCIE-CNRS, France	[183]
Closed solid adsorption	Silica gel 127B/H <sub>2</sub> O	1.0–1.5 kW	0.5–1.0 kW	13 kWh	M: 50 kWh/m <sup>3</sup> P: 33.3 kWh/m <sup>3</sup>	AEE-INTEC, Austria	[181]
Open solid adsorption	Zeolite 13X/H <sub>2</sub> O	At 180 °C	0.8–1.8 kW at 55 °C	1 kWh	M: 180 kWh/m <sup>3</sup> P: 57.8 kWh/m <sup>3</sup>	SPF, Switzerland	[181]
Open solid adsorption	Zeolite 4A/H <sub>2</sub> O	2.0–2.5 kW at 180 °C	1.0–1.5 kW 35 °C	12 kWh	M: 160 kWh/m <sup>3</sup> P: 120 kWh/m <sup>3</sup>	ITW, Germany	[181]
Closed solid adsorption	Zeolite 13X/H <sub>2</sub> O	At 350 °C	4.1 kW at 15 °C (cold <sup>d</sup> )	5.5 kWh (cold)	M: 167 kWh/m <sup>3</sup> (cold)	SJTU, China	[126]
Open solid adsorption	Zeolite 13X/H <sub>2</sub> O	135 kW at 130 °C	130 kW at 65 °C 50 kW (cold) at 11 °C	1300 kWh 1751 kWh (cold)	M: 124 kWh/m <sup>3</sup> M: 168 kWh/m <sup>3</sup> (cold)	ZAE Bayern, Germany	[58]
Closed composite sorption	Na <sub>2</sub> S-graphite/H <sub>2</sub> O	3.8 kW at 80–95 °C	0.15–0.24 kW	0.56 kWh	M: 2240 Wh/kg	Chiang Ma University, Thailand	[153]
Closed composite sorption	Na <sub>2</sub> S- cellulose /H <sub>2</sub> O	0.2–1.0 kW	0.5–0.7 kW at 5–20 °C	3.2 kWh 2.1 kWh (cold)	M: 1070 Wh/kg M: 700 Wh/kg (cold)	ECN, the Netherlands	[143]
Closed composite sorption	SrBr <sub>2</sub> -ENG <sup>e</sup> /H <sub>2</sub> O	At 80 °C	2.5–4.0 kW	60 kWh <sup>b</sup> 40 kWh (cold) <sup>b</sup>	M: 321 Wh/kg <sup>b</sup> M: 214 Wh/kg (cold)	PROMES-CNRS, France	[154]
Closed composite sorption	BaCl <sub>2</sub> -ENG/NH <sub>3</sub>	7 kW at 60–70 °C	5 kW (cold) at 4 °C	20 kWh (cold)	M: 114 Wh/kg (cold)	PROMES-CNRS, France	[64]
Open composite sorption	MgCl <sub>2</sub> /H <sub>2</sub> O	–	0.15 kW at 64 °C	2.4 kWh	M: 139 kWh/m <sup>3</sup>	ECN, the Netherlands	[74]
Open sorption combisystem (CWS-NT concept)	Zeolite-salt/H <sub>2</sub> O	At 130 °C	–	–	–	ITW, Germany	[73]

<sup>a</sup> M denotes energy density based on material.

<sup>b</sup> Calculated values.

<sup>c</sup> P denotes energy density based on prototype.

<sup>d</sup> Cold denotes parameters related to cold storage, others are related to heat storage.

<sup>e</sup> ENG denotes expanded natural graphite.

could somehow increase the ratio. Unwanted crystallization problem, which occurred around the pumps, resulted in blocked pipes and long swap periods. After several improvements, the ClimateWell company [187] has developed a type of commercial heat pump with integrated energy storage, called “Coolstore”, using the three-phase absorption technology. The Coolstore heat pump consists of two barrels/reactors that work independently to supply continuous cooling or heating output (see Fig. 20). Each barrel is claimed to possess a cold storage capacity of 30 kWh and a heat storage capacity of 38 kWh [188]. This type of machine has been extensively applied and analyzed in some demonstration projects in Europe [189–191].

Quinnell [182,192] presented a novel concept of using a single storage vessel for storing liquid calcium chloride in a closed liquid absorption system. The system schematic is presented in Fig. 21(a). During the charging process in summer, diluted  $\text{CaCl}_2$  solution is circulated to the solar collector where it boils at 117–138 °C. The concentrated  $\text{CaCl}_2$  solution and condensed water are stored until the winter. When the collector temperature is not high enough—below the boiling point, the stored solution can be heated to provide sensible energy storage; when the required temperature is satisfied, the solution can be discharged directly. Design and operation of the storage vessel is crucial for this system to prevent mixing of solutions. As shown in Fig. 21(b), the storage system uses an internal heat exchanger to add and discharge thermal energy and help manage the mass, momentum, and energy transfer in the tank. In particular, a heat exchanger and a stratification manifold are immersed in the storage tank to thermally stratify the solution and minimize mixing between regions of different  $\text{CaCl}_2$  mass fractions. The storage tank is specially designed to provide higher energy density and decrease thermal loss during the storage process, with a combination of sensible and chemical binding energy of the liquid desiccant. Firstly, the feasibility of the proposed concept was demonstrated via a computational fluid dynamic study of heat and mass transfer in the system [192]. A 1500-l storage tank was built to elucidate mixing of solutions. Stable density interfaces and confined natural convection flows were observed via transient experiments, as shown in Fig. 21(c) [182].

Based on the long-term absorption storage cycle (see Section 4.1), a demonstrative  $\text{LiBr}/\text{H}_2\text{O}$  prototype with a heat storage capacity of 8 kWh and a discharging rate of 1 kW has recently been set up by N'Tsoukpoe et al. [183] in LOCIE-CNRS. The prototype (Fig. 22) mainly consists of two storage tanks and a reactor with



Fig. 18. Double-stage  $\text{NaOH}/\text{H}_2\text{O}$  prototype [65].



Fig. 19. TCA prototype developed by ClimateWell [41].

two identical vertical falling film exchangers. Although the obtained heat transfer coefficients in the desorber were less than expected, the charging process of the prototype was proved satisfactory with a charging power of 2–5 kW and heat storage up to 13 kWh. Crystallization phenomenon was observed in several cycles. The discharging process was verified a failure due to an inadequate design of the absorber. Different approaches such as use of a heat and mass transfer additive or the reversal of fluids flow direction failed to solve this problem. New configuration of the absorber should be considered to improve the discharging process.

Positive points of the silica gel/ $\text{H}_2\text{O}$  couple are that it is environmentally harmless, relatively cheap and low desorption temperatures. Within the framework of the EU-project MODESTORE [115,181], a prototype storage module was developed using silica gel/ $\text{H}_2\text{O}$ . The silica gel used in this prototype was microporous silica gel Grace 127B. As shown in Fig. 23, a spiral heat exchanger containing approximately 200 kg of silica gel is connected to an evaporator/condenser at the bottom of the vessel. Operating between a water content interval 3–13%, a storage capacity of the lab-scale unit was only 13 kWh—significantly lower than initially expected. Thus, the author concluded that silica gel was not suitable for long-term sorption thermal storage and the task of future projects was to find other advanced materials to fulfill the requirements of sorption systems for storage purpose.

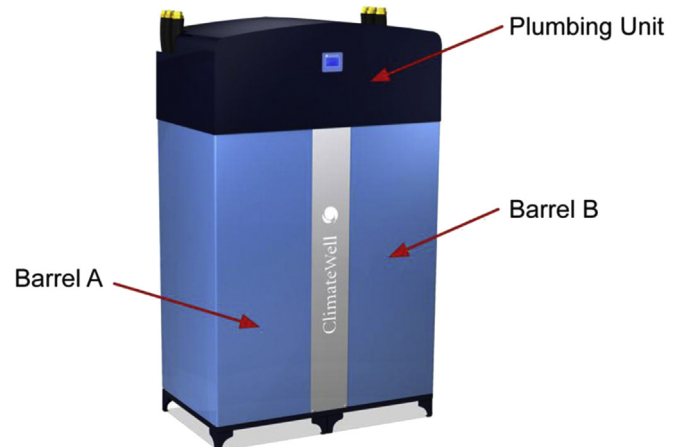


Fig. 20. ClimateWell Coolstore machine [188].



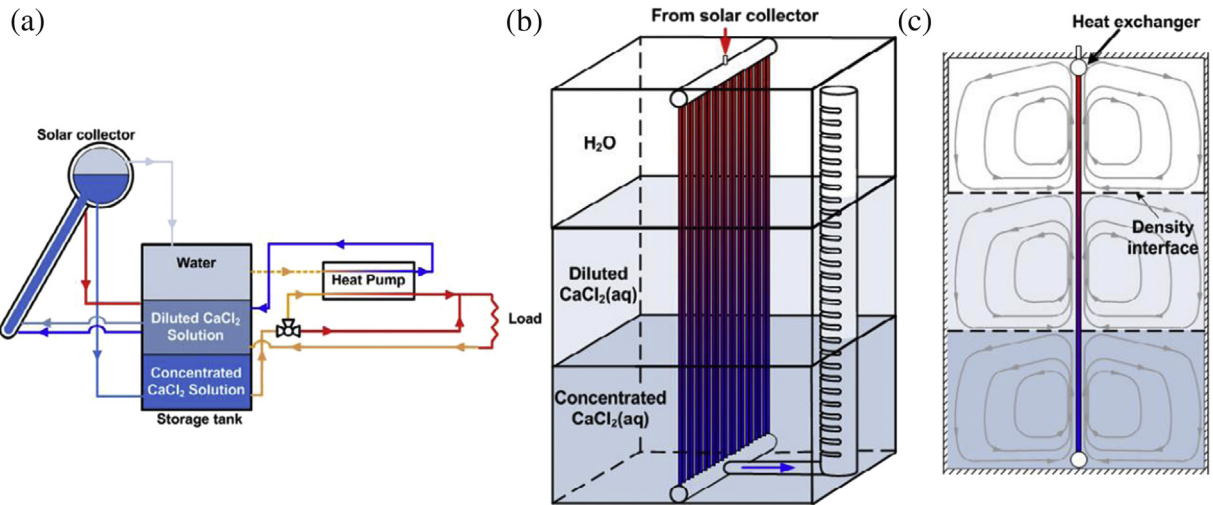


Fig. 21. Closed  $\text{CaCl}_2/\text{H}_2\text{O}$  absorption heating system with a single storage vessel: (a) system schematic [182]; (b) storage tank schematic [192]; (c) anticipated convective flow patterns during sensible charging [192].

In Shanghai Jiao Tong University, Lu et al. [126] presented a closed adsorption cold storage system with a zeolite 13X/water working pair, which is designed for locomotive air conditioning. This system is driven by exhaust gas from a locomotive. This system (Fig. 24) is used to refrigerate the driver's cabin of a locomotive that ran in the Zhejiang Province, East China. This prototype comprises only one adsorber and a cold storage tank. The operating test starts running with the adsorption process after the valve between the adsorber and the evaporator is open. The adsorber is cooled by ambient air and a cooling effect is transferred to the cabin by chilled water. The adsorber is heated by high temperature gas exhausted from an internal combustion engine. The averaged cooling power was about 4.1 kW. The total experimental capacity of the cold storage was 5.5 kWh when the temperature of adsorption bed reached its maximum value of 125 °C.

In the SWEAT (Salt-water Energy Accumulation and Transformation) project, Boer et al. [143] developed a prototype of a modular chemical adsorption cooling system using  $\text{Na}_2\text{S}/\text{H}_2\text{O}$  as the working pair. The scheme of the prototype is illustrated in Fig. 25. The shell and tube design of the module consists of sorbent-filled copper-wire-fin tubular heat exchangers, a condenser and an evaporator coil. The vessel of the accumulator/reactor is connected through a vapor channel with another vessel of the evaporator/condenser. There are six Sipro-tubes in hexagonal packing and one diffuser tube located in the accumulator. Test results showed that a

cold storage capacity of 2.1 kWh and a cooling COP of 0.56 were achieved by inputting a heat capacity of 3.7 kWh with 3 kg of  $\text{Na}_2\text{S}$  in one module.

Mauran et al. [154] set up a storage prototype using the reversible reaction between  $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{SrBr}_2 \cdot \text{H}_2\text{O}$ . The solid/gas reactor, which integrates an evaporator/condenser, has a volume of 1 m<sup>3</sup>. It was designed at a scale of a heat storage capacity of

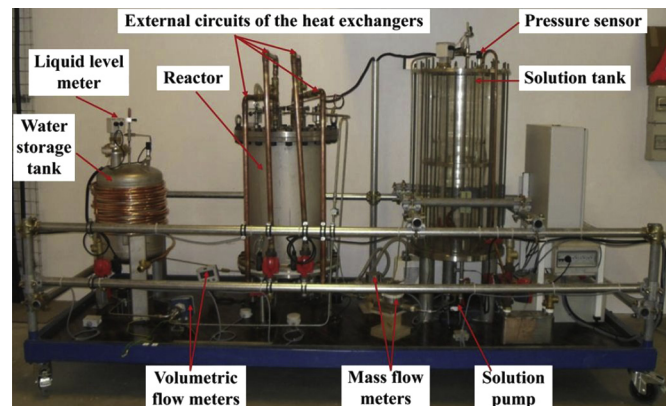


Fig. 22.  $\text{LiBr}/\text{H}_2\text{O}$  absorption prototype for long-term energy storage [183].

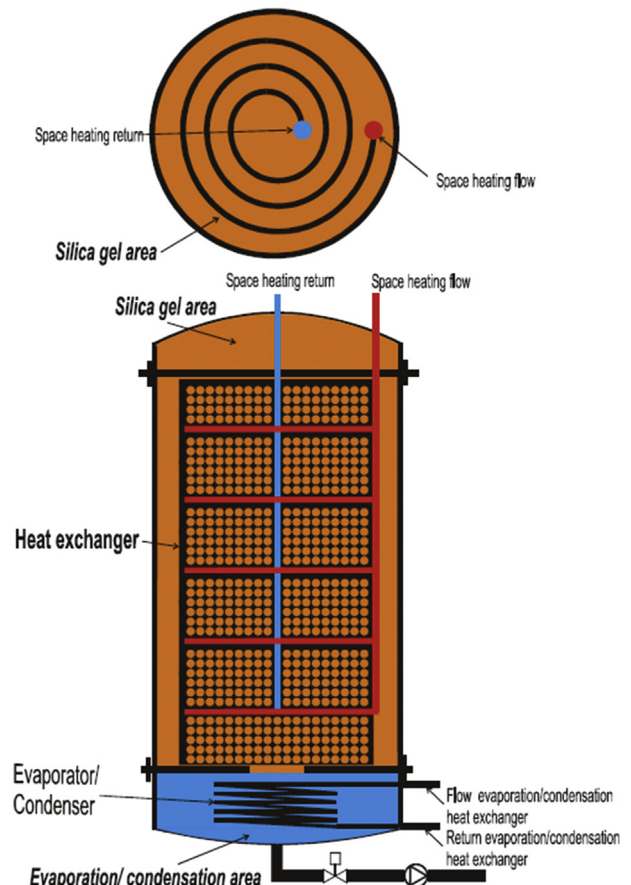


Fig. 23. Schematic of Silica gel/ $\text{H}_2\text{O}$  thermal storage prototype [115].



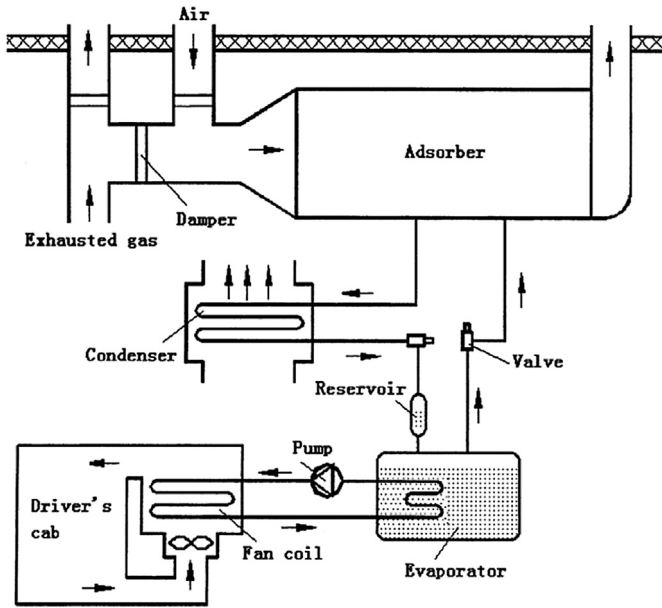


Fig. 24. Zeolite/H<sub>2</sub>O adsorption cold storage system powered by exhausted heat [126].

60 kWh at 35 °C and a cold storage capacity of 40 kWh at 18 °C. The reactive salt SrBr<sub>2</sub> is mixed with an expanded natural graphite, serving as a consolidated composite to improve heat and mass transfer properties. The prototype has a modular structure in which thin layers of reactive composite (12 mm) are laid out in alternation with plates of a heat exchanger and steam diffuser that are also thin (5–6 mm). The obtained heating and cooling power of the prototype proved to be discouraging due to heat transfer problems.

A solar air conditioning pilot plant was installed in PROMES laboratory in 2006 [64]. This pilot, with a daily cooling capacity of 20 kWh, consists of four subsystems: a solar heating loop, a thermochemical unit using the working pair BaCl<sub>2</sub>/NH<sub>3</sub>, a ground cooling loop and a chilled water production loop (Fig. 26). The

thermochemical process is powered at 60–70 °C by 20 m<sup>2</sup> of flat plate solar collectors. The reactive sorbent, which consists of a compressed mixture of 140 kg of anhydrous BaCl<sub>2</sub> and 35 kg of expanded natural graphite, is loaded into a set of 19 tubes in the thermochemical sorption unit. The hot PCM storage enables the storage of excess solar heat if the desorption reaction in the reactor is completed and the cold PCM storage makes a supply of cooling effect possible when the sorption reaction is not available. Two years of experimental operation illustrated an average yearly efficiency of solar collectors and a COP ranging from 0.4 to 0.5 and 0.3 to 0.4, respectively. A daily cold storage capacity is about 0.8–1.2 kWh/m<sup>2</sup> plate solar collector at 4 °C.

A large-scale open adsorption thermal storage system employing zeolite 13X/H<sub>2</sub>O, was installed in Munich by ZAE Bayern (Center for Applied Energy Research) [58,128] to heat a school building in winter and to cool a jazz club in summer. The school (with a heating load of 130 kW) and the club (with a cooling load of 50 kW) are connected to the local district heating system of Munich. Fig. 27(a,b) shows heat flux during charging and discharging modes. At night, zeolite is charged by the hot steam from the district heating system and heated to about 130–180 °C. During the day, the zeolite bed is discharged in times of peak power demand. An additional cold recovery device, consisting of an exhaust air humidifier with an integrated heat exchanger and the supply air heat exchanger, are required in the cooling process for the jazz club. The cold recovery device can exchange 83% of the maximum enthalpy difference from the exhaust air to the supply air. The obtained storage densities were 124 kWh/m<sup>3</sup> for heating and 100 kWh/m<sup>3</sup> for cooling with COP of 0.9 and 0.86, respectively.

ITW has recently proposed a new design, namely CWT-NT concept [32,72,73], for a long-term thermochemical energy storage integrated into a solar thermal combisystem for the composite

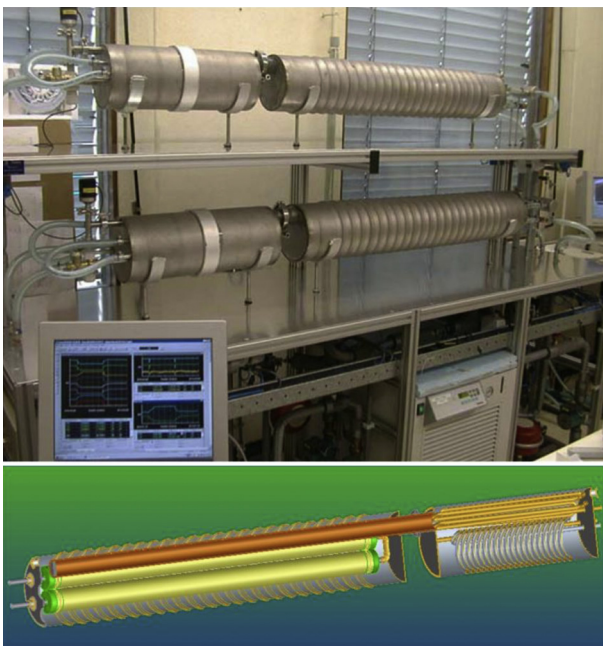


Fig. 25. SWEAT storage module [143].

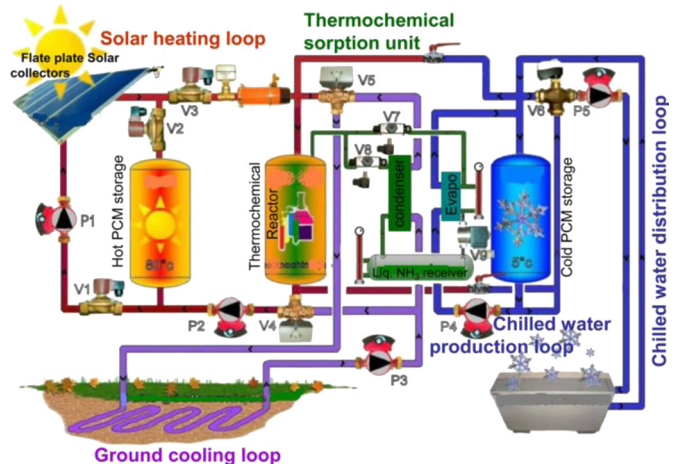


Fig. 26. Solar sorption pilot plant for air conditioning [64].

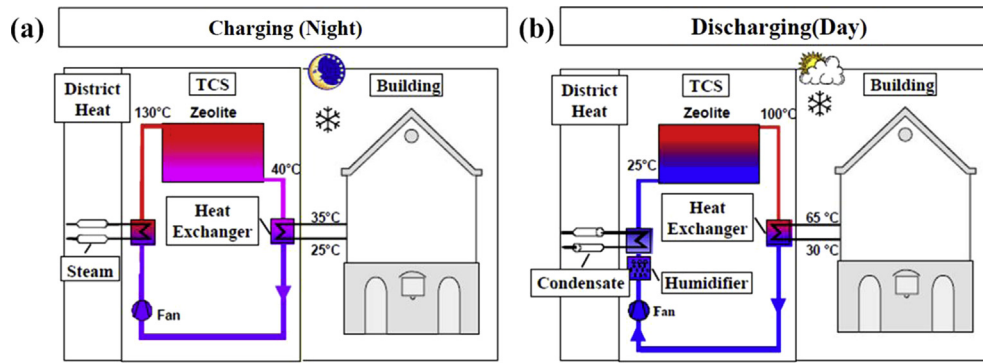


Fig. 27. Open adsorption thermal storage system on district heating net in Munich: (a) charge mode for heating; (b) discharge mode for heating [128].

material of zeolite and salt. A detailed description of the concept is presented in Fig. 28. The thermochemical storage operates as a low power heating system and is connected to the combistore of the solar thermal system. It is designed as an open system using ambient or exhaust room air for charging and discharging process. The separate reactor concept is realized, meaning that the sorption material is put into another vessel during storage process and is pumped to the reactor when the desorption/sorption process takes place. Thermal heat capacities and heat losses could be significantly reduced though this separate design. A recent progress of this project [73] was referred to a proposal of a new highly efficient regeneration process, reducing the regeneration temperature from 180 °C to 130 °C due to a decrease of humidity of air flow. Additional desiccants and dehumidification devices are needed to dry the air flow before it enters the reactor.

## 7. Conclusions and perspectives

Sorption technology, including liquid absorption, solid adsorption chemical reaction and composite materials, with potentially high energy density and without significant heat losses over long periods, is regarded as one of the promising approaches for heat

storage of solar energy. The main objective for using sorption materials is to develop compact and low cost systems to store solar heat efficiently for longer periods. In the way to obtain reliable and compact sorption thermal storage systems, some challenges still remain:

- Energy density is a key criterion for storage materials and systems. Unlike sensible and latent materials, energy densities of sorbents greatly depend on working conditions, such as temperatures of charging, discharging, evaporation and condensation for closed systems; however, little attention has been given to this aspect in previous research. Another issue concerning calculation of energy density is the inconsistency of volume. Different authors have examined different volumes in their calculations, making it hard to define and compare performances of different systems; so it is suggested that system comparisons based on storage density should take all the vessels into account; storage density will be reduced if all the components, including vessels and heat exchangers, are considered with the volume basis.
- Due to some auxiliary and indispensable components, such as evaporators and condensers, sorption thermal storage systems

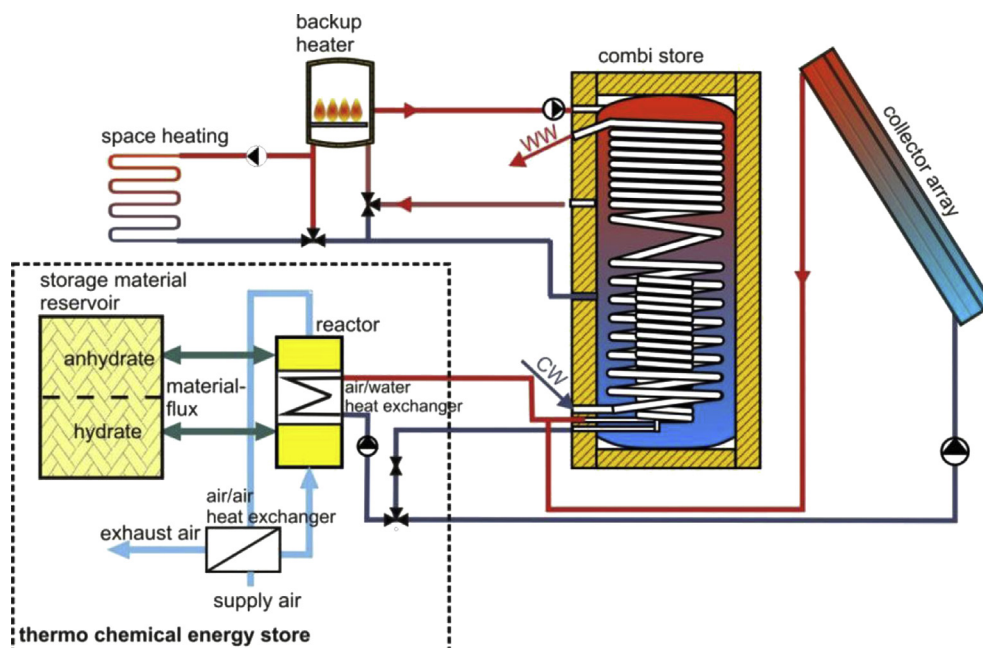


Fig. 28. Fig. 28. CWS-NT concept schematic [32].

appear to be more complex than conventional sensible and latent methods. Though some sorption systems with novel designs show excellent thermal storage performance theoretically, their experimental results are far from satisfactory, mainly owing to complicated structures and operating procedures. According to these experiences, simple design is recommended for sorption thermal storage systems; it will not only improve system performance and reliability but also reduce the high cost of production and maintenance for complex machines.

- The operational concentration differences among common absorption cycles are not sufficient for competitive high storage densities, because of crystallization problem at high concentrations. Thus, some cycles are proposed to allow the appearance of salt crystals to expand the bottleneck, for example, the long-term storage cycles and the three-phase cycles. Nevertheless, because pumps in absorption cycles are in danger of being blocked by them, crystals should be treated with great discretion.
- Heat capacity, heat losses, heat and mass transfer property are critical points concerning the design of highly efficient sorption reactors. Extended surfaces of heat exchanger can be considered a useful way to improve heat transfer within the closed reactors. New types of reactors, such as agitated reactors, fluidized bed reactors and gravity-assisted bulkflow reactors have been proposed, whose feasibility must be verified through experimental testing. It is expected that separate reactors will yield improved performance by minimizing the thermal mass which needs to be heated during both charging and discharging. Modular reactors have been adopted in some sorption systems to realize simple and compact design and low cost serial production.
- Composite water sorbents, such as SWSs which present intermediate behavior between solid adsorbents, salts hydrates and liquid absorbents, offer new opportunities for designing advanced sorption thermal storage systems. However, in closed systems, excess solution dripping from matrix pores may lead to corrosion of metal components in storage units and emission of non-condensable gas. Even in open systems, draining of salt solution will cause degradation of sorption properties. More modification and prevention attempts should be taken to overcome this shortcoming in order to make SWSs more reliable for heat storage.

The challenges mentioned here show not only that solar energy storage through sorption technology is far from a significant state of efficiency, but they also point the directions toward future investigation. Right now research activities devoted to sorption thermal energy storage are extensively increasing. As a positive outcome, all kinds of storage cycles and system designs using different storage materials have been developed and tested. These projects confirm that the idea of using sorption thermal storage for solar energy is a realistic and sustainable option. To bring this sorption storage solution into the market, more intensive studies in fields of evaluation of advanced materials and development of efficient, compact prototypes are still required.

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