

Chapter 2

State-of-Art of Thermochemical Heat Storage Systems

2.1 Short Review of Thermal Energy Storage System with Cogeneration System

A combined heat and power (CHP) or cogeneration plant simultaneously produces thermal and electrical energy, primarily to meet industry and household demand. As we focus on household's application, we talk about a residential micro-CHP. Micro-CHP plants have a higher energy efficiency than conventional (without coupling thermal and power) thermal power systems, leading to a decreased environmental impact, in other words, reduced greenhouse gas emission (CO_2 , N_2O , CH_4) and a significant increase of economic profitability (Yusta et al. 2008). They can also decrease fuel consumption by 30 % compared with decoupled production in conventional power plants (Lund et al. 2005). The use of micro-CHP plants has been recognised as crucial by the European Parliament for the achievement of the Kyoto Protocol objectives, and consequently, legislation to encourage the use of cogeneration has been approved. These regulations dictate the parameters that define a plant as a cogeneration power plant (Tina and Passarello 2012). Installation of thermal energy storage systems, particularly thermochemical heat storage systems (THSS) allow heat accumulation, which increases the flexibility of heat and electricity production in the power plant (Katulić et al. 2014). In a micro-CHP with regulated steam extraction turbines, at constant load, an increase in thermal energy production reduces the amount of electrical energy production. The main objective of THSS in a micro-CHP system is to support the simultaneous of thermal and electrical energy production. A THSS can store thermal energy during phases when it can be produced in excess for use when it cannot be produced to meet the heat demand or when its production is not a priority. Figure 2.1 shows an example of such system.

Using THSS, thermal energy can be accumulated while electricity market prices are low and discharged while prices are high (i.e., when it is more profitable to produce and sell larger quantities of electrical energy) (Katulić et al. 2014) via a

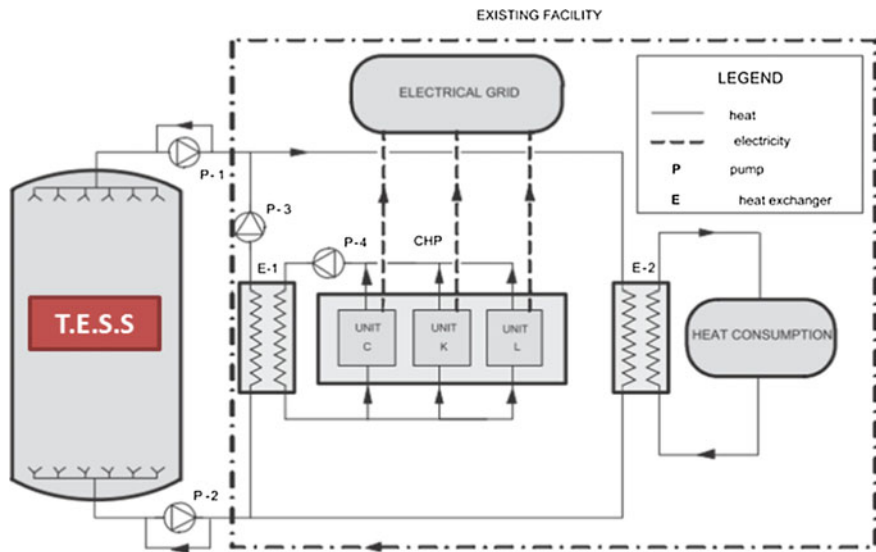


Fig. 2.1 Scheme of a combined heat and power plant with a thermal energy storage system (TESS) where C, K and L are steam turbines (adapted from Katulić et al. 2014)

conversion chain-like electricity \rightarrow heat \rightarrow chemical \rightarrow heat \rightarrow electricity. Heat storage system also makes it possible to operate production units at more efficient loads. There are three mechanisms of heat accumulation in THSS: (a) increasing the temperature of a working fluid (heat carrier) within the THSS (sensible heat accumulation), (b) changing phase of a working fluid (latent heat accumulation) and (c) thermochemical heat accumulation (Paksoy 2005). The latter is the most appropriate, though not yet commercialized. It is important to note that the design of market regulations play a major role in defining the optimal performance of a micro-CHP plant when maximizing the income from electricity sales. Optimising the operation mode of a micro-CHP plant coupled with a THSS can lead to significant financial savings and more stable and secure thermal energy supply. The benefits of THSS systems are recognised in large scale residential micro-CHP systems (Arteconi et al. 2013).

Since 2006, there are some studies considering energy storage system and cogeneration plant, but mostly on optimisation process. However, using THSS and closed systems (will be explained in section §2.2) with a micro-CHP for household's application is quite new. Though on CHP plant, some studies focusing on modelling approaches show considerable results. Some authors (Bogdan and Kopjar 2006), while considering CHP plant and hot water tank for district heating and steam for industry and electric power (trigeneration), noted both, the economic and environmental benefits of using an energy storage system in a CHP plant.

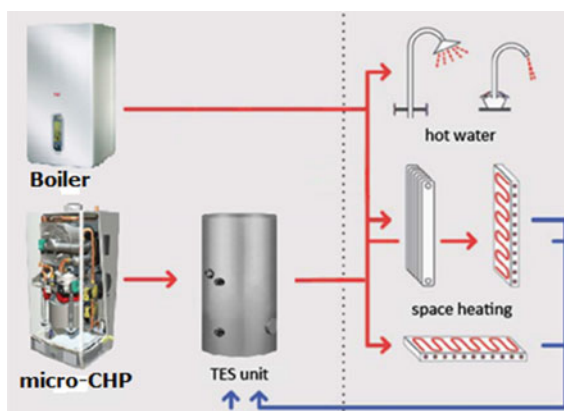
Khan et al. (2007) presented a feasibility study, both technical and economical, of cogeneration coupled with a THSS intended for energy conservation in

institutional buildings. They conclude that the use of THSS can provide a 23 % reduction in peak demand and 21 % savings in energy consumption. Some authors (Haeseldonckx et al. 2007) analysed the environmental impact of micro-CHP facilities and concluded that using a small or compact THSS device causes a net reduction of CO₂ almost three times higher than a cogeneration plant without a THSS. Barbieri et al. presented a model (Barbieri et al. 2012) for the calculation of the profitability of micro-scale combined heat and power systems consisting of a CHP unit, heat boiler and thermal energy storage (TES) unit for residential building applications (Fig. 2.2).

Siddiqui et al. (2007) demonstrated the effects of using a thermal energy storage system by analysing five commercial buildings in San Francisco, California. Pagliarini and Rainieri (2010) presented an analysis of a CHP system coupled with a TES which matched the heating load of the campus of the University of Parma. These authors concluded that a TES facility can effectively reduce the auxiliary boiler contribution, leading to a proportional decrease of CO₂ emission. (Chesi et al. 2013) showed that to allow high energy efficiencies, smart systems like small-size combined heating and power units should be coupled with thermal energy storage devices instead of the conventional energy supply from boilers. The authors focused on the effect of different volumes of the storage device when coupling to a micro-CHP. They concluded that a thermal storage system of 10.7 m³ reduces the heater (own thermal system of the micro-CHP) contribution to a third and allows a year-round reduction in fuel consumption of approximately 12 %, which is a big step towards reducing use of fossil energies. Making the TES system, compact, reduces the space but it remains the challenge to keep the performances.

Few et al. (1997), Smith and Few (2001) introduced the innovative concept of heat pump incorporation into a domestic scale cogeneration plant (called the CHP/HP plant). Further works were led by them, using computer modelling, to demonstrate the potential of such systems and how heat pump incorporation overcomes many problems associated with domestic-scale cogeneration (micro-CHP). Their results show an energy upgrade of the combined system.

Fig. 2.2 Energy system sketch of micro-CHP with a TES unit (Barbieri et al. 2012)



However, their heat pump was water-based with a lower energy density. Years ago, (Kato 2000) has shown the contribution of chemical heat storage process to a cogeneration system. Kato first analyses a conventional cogeneration system (Fig. 2.3a) from a shaft work and an exhaust heat of a gas, then, a diesel engine or micro gas turbine for electrical and heat output, respectively. The exhaust gas of the engine is generally used to generate steam at an exhaust gas boiler. However, since demand for electrical output is generally inconsistent with that of the heat output, a large amount of surplus heat output is occasionally discharged into the atmosphere as shown in Fig. 2.3a. Chemical heat storage has a possibility to enhance the energy use efficiency of a cogeneration. Kato proposed then a system as shown in Fig. 2.3b. The system consists of a cogeneration engine and a chemical heat storage system. With this system, the exhaust heat at 70 °C was reheated to 200 °C, showing an impressive heat upgrade. (Streckienė et al. 2009) study the feasibility of a coupled CHP with a thermal energy storage system in the German energy market. The drawn conclusions from their work was that coupling a TES with a CHP could reduce the CHP-plant investment and reduce the simple payback time from 9 to 10 years down to 5 years.

The notion of incorporating or associating a thermal energy storage system to an existing micro-CHP or CHP to upgrade the energy efficiency existed decades ago. Some attempts on the size reduction of the storage system were performed, but not enough to have a compact device. The research goal of the project “Thermal Battery” in which this thesis is performed, is to minimize the thermal heat storage component through an optimised integration into the micro-CHP system, as well as the targeted optimisation of the process and appropriate storage materials to reduce

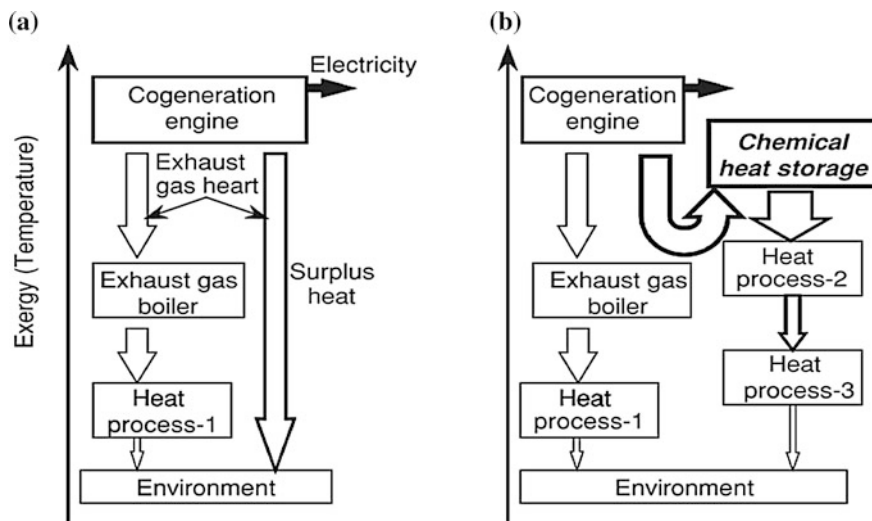


Fig. 2.3 Contribution of chemical heat storage on cogeneration; **a** conventional cogeneration system, **b** combined system with chemical heat storage system (Paksoy 2005)

costs. However, the previous authors were not focusing on the idea to have a more compact and powerful storage system oriented to micro-CHP upgrading. Energy storage has been identified as an important solution for decentralized energy systems. Storage is particularly crucial for thermal energy systems based on renewable energy, which often offer their highest potential during low demand periods. On the other hand, energy storage helps improving the performance of combined heat and power (CHP), which is considered as a fundamental principle or practice of decentralized energy. Indeed, during off-peak electricity periods, the CHP can switch off while heat is supplied by the storage, and provide the energy demand mainly in periods of high market price. However, there is not always a sufficiently space when the thermal storage has to be installed in family houses or urban areas where the space may be restricted or expensive (Ibrahim et al. 2008). That is why a compact TESS should be constructed. In addition, Raine et al. (2014) mentioned three main advantages such as increase of running time of a CHP, reduction of payback period of the system and reduction of carbon dioxide emissions, of using heat storage in a classic CHP as summarized above by previous authors. Furthermore, volume of an energy storage unit affects the cost of such a project when considering for instance the containers (which may have to be maintained under vacuum or insulated) and the size of heat exchanger. Thermochemical heat storage appears to be relevant towards these problems because they promise high energy density (specific thermal storage capacity) and an negligible heat loss (Ding and Riffat 2012; Tatsidjodoung et al. 2013). Thermochemical heat storage review is presented in the following section.

2.2 Review of Thermochemical Heat Storage Systems

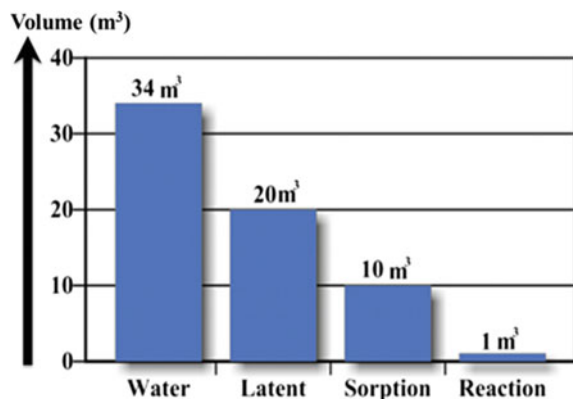
Talking about thermochemical always refer to sorption and chemical reaction phenomena (Tatsidjodoung et al. 2013). Large amounts of heat can be stored in reversible chemical reactions and sorption processes. In a sorption process, heat is stored by breaking the binding force between the sorbent and the sorbate in terms of chemical potential. The term “Sorption” was first proposed by McBain in 1909 (McBain 1909) as a general expression covering both adsorption and absorption. He reported that the uptake of hydrogen by carbon appeared to occur in two stages: a rapid process of adsorption appeared to be followed by a slow process of absorption into the interior of the solid. Sorption of molecules on a surface is a prerequisite to any surface mediated chemical process. The expressions “chemical”, “thermochemical”, “thermochemical sorption”, “compact” and “sorption” have all been used in different contexts by many authors regarding thermal energy storage (Chan et al. 2013; Cot-Gores et al. 2012; Ding and Riffat 2012; Li et al. 2013; Meunier 2013; Neveu and Castaing-Lasvignottes 1997). 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 (Cot-Gores et al. 2012; Ding and Riffat 2012; N'Tsoukpoe et al. 2009). Research works regarding sorption thermal energy storage in which chemical reaction coexists are well mentioned in Refs. (Abedin and Rosen 2011; Chan et al. 2013; Cot-Gores et al. 2012; Ding and Riffat 2012; Mette et al. 2012; Tatsidjoudoung et al. 2013).

The sorption thermal storage method is as follows:

1. **Desorption** (charging) process, which requires the supply of heat to remove the sorbate from 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 during the desorption (or sorption) process causes high energy densities of sorption materials in theory, only next to chemical reaction (see Fig. 2.4). Thus a smaller volume is needed for a given storage capacity for sorption thermal storage. For example, only one third of the volume is required for sensible heat storage system with water (Yu et al. 2013).
2. **Sorption** (discharging) 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. The sorption can be of adsorption or absorption depending on the 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 (Gil et al. 2010). 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 energy storage applications, where solar energy is stored in summer to meet with heating demands in winter (N'Tsoukpoe et al. 2009). The discharging process could be operated to provide a 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. Among them, are the great complexity in the system configuration (for closed systems),

Fig. 2.4 Volume to store 1850 kWh with 25 % heat losses consideration (Yu et al. 2013)



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.

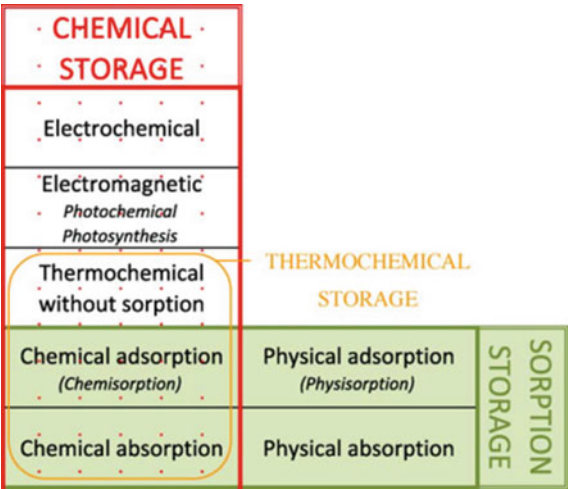
N'Tsoukpoe et al. (2009) identified thermochemical storage as a part of chemical storage disregarding electrochemical and electromagnetic storage (see Fig. 2.5). Thermochemical storage was further classified into chemical adsorption, chemical absorption and thermochemical without sorption. The first two also belonged to sorption storage and the exact definition of “thermochemical without sorption” was not given by the authors. This was corrected by Yu et al. (2013). They suggested sorption thermal storage to be distributed into four categories:

- 1. liquid absorption,
- 2. solid adsorption,
- 3. chemical reaction,
- 4. and composite materials as illustrated in Fig. 2.6.

Thus, the term “sorption thermal energy storage” in this thesis will refer to these four categories. It can be only one or two of them processing simultaneous.

The term adsorption is universally understood (Rouquerol et al. 1999) as the enrichment of one or more of the components in the region between two bulk phases (i.e. the interfacial layer), in which cohesive forces including Van der Waals and hydrogen bonding act between the molecules of phase substances. If the solid is ionic, we will also have cation-water and anion-water interactions. In the present context, one of these phases is necessarily a solid or liquid (called sorbent) and the other a fluid (i.e. gas called sorbate, see Table 2.1). With a certain system (like some salt hydrates exposed to water vapour), the adsorption process is accompanied by absorption, i.e. the penetration of the fluid into the solid phase. The International Union of Pure and Applied Chemistry (IUPAC) also gives some definitions in the

Fig. 2.5 Chemical storage and sorption storage classification (N'Tsoukpoe et al. 2009)



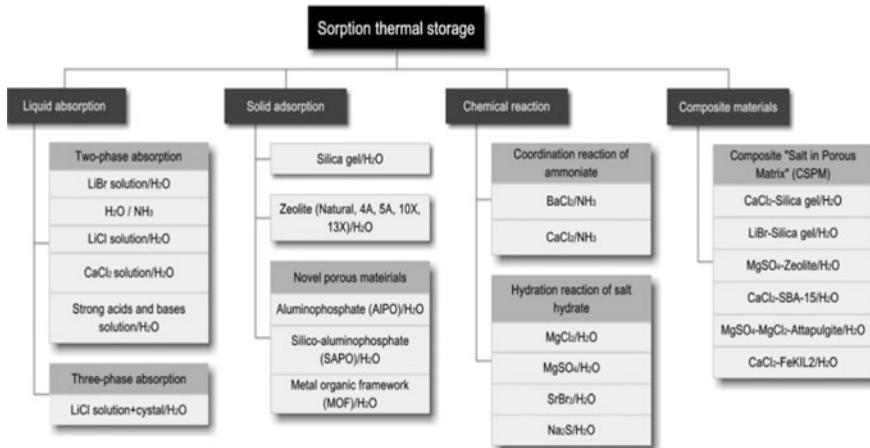


Fig. 2.6 New sorption thermal storage classification (Yu et al. 2013)

Table 2.1 Definition of different adsorption terms (Rouquerol et al. 1999)

Term	Definition
Adsorption	Enrichment of one or more components in an interfacial layer
Adsorbate	Substance in the adsorbed state
Adsorptive	Adsorbate substance in the fluid phase
Adsorbent	Solid material on which adsorption occurs
Chemisorption	Adsorption involving chemical bonding
Physisorption	Adsorption without chemical bonding

same way (Robert and Burwell 1976; Sing 1985). Depending on the interface between sorbent and sorbate, adsorption can be divided into four types: solid/gas, solid/liquid, liquid/liquid, and liquid/gas. The solid/gas adsorption has been widely used and studied, playing a pivotal role in interface chemistry. As a rule in this chapter, 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) (Wang et al. 2009, 2010). 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 vapours. 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 (Bolis et al. 2003, 2006). Because chemical

forces are normally stronger than physical forces, the released heat of chemical adsorption should therefore be larger than the 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 recognise 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. Chemisorption processes provide high energy of sorption than physisorption, but may be irreversible. Silica gel and zeolite are widely studied and applied as common adsorbents using water as working fluid. Some new classes of materials (Duquesne 2013), including aluminophosphates (AlPOs), selective water sorbents (SWS), salts in porous matrix (CSPM) (Gordeeva and Aristov 2012; Tanashev and Aristov 2000), silico-aluminophosphates (SAPOs) and metal-organic frameworks (MOFs), have recently emerged as promising porous materials for thermal energy storage. More description on those porous materials will be presented later.

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 (Robert and Burwell 1976). If the absorbent is a liquid and the absorbate is a 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/H₂O (N'Tsoukpoe et al. 2013) and H₂O/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" (Yu et al. 2013).

A chemical reaction corresponding to sorption mainly consists of three kinds of reactions:

1. coordination reaction of ammoniate with ammonia,
2. hydration reaction of salt hydrate with water,
3. hydration reaction of salt hydrate with alcohol (Douss and Meunier 1989; Li et al. 2004).

Strictly speaking, the three reactions can be regarded as coordination reactions. Molecules of ammonia, water vapour or alcohol 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. In order to homogenize the appellation, all are called chemical reactions. Unlike a chemical reaction, there is no change in molecular configuration of the compound in the sorption process. The term composite materials enclose sites where chemical reaction and ad/absorption takes place.

Among the three reaction partners mentioned in the above paragraph, water has been chosen since the storage is suitable for building application. Not only for this reason, water has presented many valuable assets for this application. Besides the fact that water vapour transport does not need electrical energy, it is a non-corrosive and chemically inert component, it is non-flammable, and has the thermodynamic requirements: high specific enthalpy of vaporization (Radermacher and Hwang 2005) and high polarity for its use in a sorption system (Dinçer and Rosen 2002). Compared with other adsorbates such as ammonia or methanol, water achieves highest energy densities. Besides the high enthalpy of vaporization, water provides the following benefits: it is chemically stable, it is ecologically and physiologically harmless, it is available and it is economical. However due to the low vapour pressure of water, desorption and particularly the lower pressure adsorption processes can be limited by mass transfer.

According to the system configurations, thermochemical and sorption systems dedicated to storage can be sorted as open and closed systems (Bales 2008; Hauer 2007). Whether close or open, the system can have separate or integrate (compact) reactors (Zondag et al. 2008). The authors suggested that separate reactors are most appropriate for seasonal storage (Fig. 2.7). However, the authors clearly stated that integrated reactors are for solid sorption material because the transport of the solid material is not necessary although they exhibit heat loss to the ambient during and after discharging. Which is what we are aiming for in the present application: that means this heat lost to the ambient, here the space to be heated. Furthermore, the reactor can be easily insulated. By contrast, only little amounts of sorbent and sorbate are to be heated up in a separate reactor, according to the desired reactor power so that the system is more efficient (N'Tsoukpoe et al. 2009). The Table 2.2 shows a few comparisons.

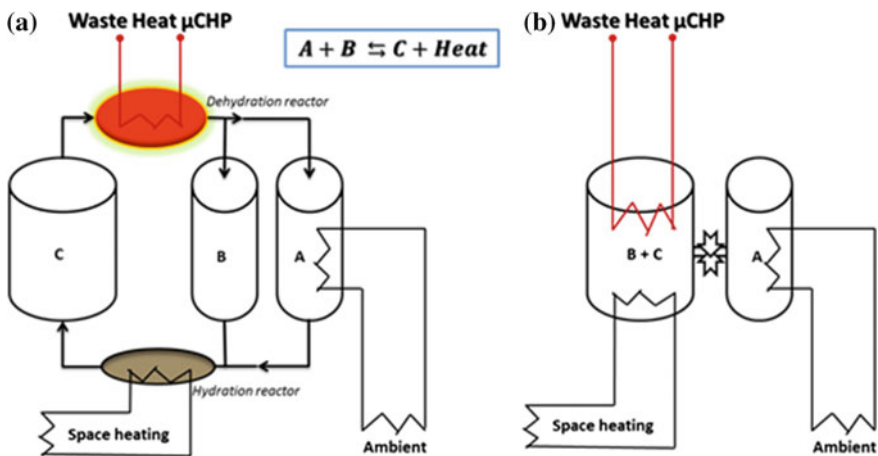


Fig. 2.7 Modes of closed systems **a** Separate reactor and **b** Integrated reactor (adapted from Zondag et al. 2008)

Table 2.2 Short comparison between open and closed systems

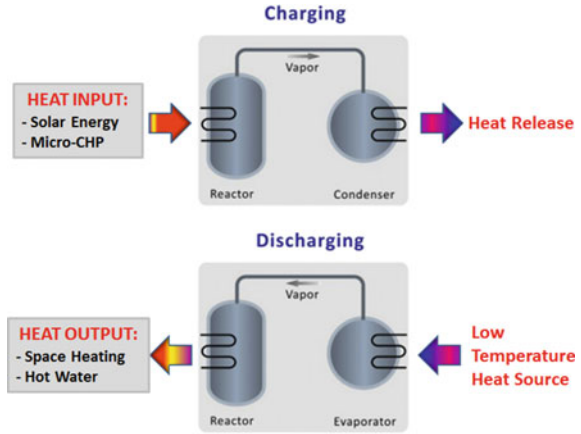
Type	+	–
Closed systems (vacuum conditions)	Small and compact design Low pressure Higher reaction power	Presence of non-condensable gases Tightness Good heat transfer, mass transfer need to be worked out
Open systems (atmospheric conditions)	Non-compact and easy design Better heat and mass transfer	High pressure Low reaction power Additional humidifier to wet enough air Limitation of pressure drop

Closed sorption systems have long time been studied for refrigeration, heat pump and energy storage applications (Wongsuwan et al. 2001). They are able to supply higher output temperatures for heating applications than open systems (Hauer and Avemann 2007; Michel 2012; Michel et al. 2014). In closed systems, not the sorbate itself but the energy is released/absorbed to/from the environment via a heat exchanger (Bales 2008). The process is alike chemical heat pumps with a major difference. The purpose of a heat pump is to absorb heat in one place where it is plentiful, then to transport and release it in another location where it can be used in a continuous process. The need of a condenser and an evaporator is therefore required. Additionally to the desorber and the ab/adsorber, a heat storage system is a batch process and the desorber might be used as an ab/adsorber and the condenser also as an evaporator (N'Tsoukpoe et al. 2009).

The operating principle of a closed sorption thermal storage system is presented in Fig. 2.8. The system is mainly composed by two vessels: a reactor where the reactive sorbent is located and a condenser/evaporator where water is collected or condensed and later evaporated. The vessels are connected by a conduct or a pipe as a passage for vapour. The charging process consists of a desorption reaction in the reactor and a gas-liquid phase change reaction in the condenser. Once the collected waste heat (from the micro-CHP) is added to the reactor, the sorbate which cleaves to the solid sorbent, starts to break loose from the binding force between the sorbate and the sorbent. Through the pipe, the vapour 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 (here the water in the condenser). Besides, the heat of condensation is also absorbed by the thermal mass of the reactor (reactor metal, heat exchanger metal). After the charging process is finished, the reactor and the condenser are separated from each other.

Separation here, means close the connecting valve. 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

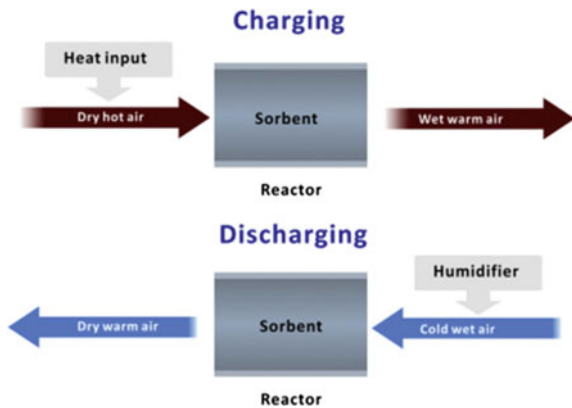
Fig. 2.8 Operating principle of closed sorption thermal storage system (adapted from Yu et al. 2013)



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 the choice of heat sources a critical issue. Yu et al. (2013) showed that by designing an efficient heat exchanger, air can be an additional heat source. He also suggested geothermal source heat exchangers which are unfortunately time-consuming and costly. However, for houses or buildings with an already existing solar system, the heat of evaporation would not be a problem. A connection from the solar panel can be made to provide the low temperature heat source.

Open systems operate at the atmospheric pressure to allow the release and sorption of the sorbate. Thus, only water can be used in those systems to preserve or not to harm the environment. The operation principle of open sorption thermal storage system is shown in Fig. 2.9. In charging process, a dry air stream, after heating by an external heat source, becomes a dry hot stream and enters a reactor filled with sorbent. Water adsorbed/absorbed by the sorbent is extracted by the hot

Fig. 2.9 Operating principle of open sorption thermal storage system (Yu et al. 2013)



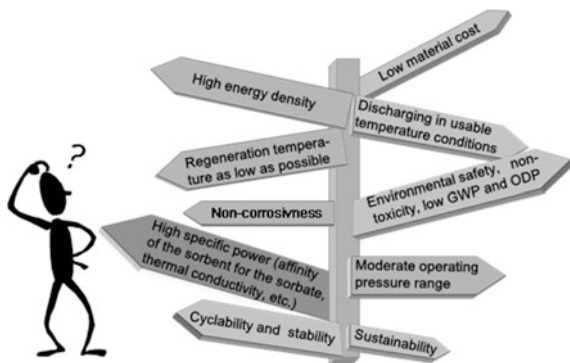
air and leaves the bed. The air then becomes wetter and cooler. During discharging, a humid, cool air stream goes into the previously desorbed reactor. Part of the water vapour in the air is pulled in by the sorbent. The released heat of sorption warms up the air so that it could be used for heating. 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 (Paksoy 2005). Moreover, strategy need to be considered 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.

Once a system classification, a reactor configuration and a design are known or decided, the material selection fulfilling the required operating conditions should be processed. The storage material strongly affects the performance and cost of such a heat storage system according to some economical studies for various applications (typically, about 30 % of the total investment cost) (Hauer 2007; Kerkes and Drück 2011; Krönauer et al. 2012). Therefore, the material selection is a critical point in an energy storage unit development. Material selection for a given application is often conflicting when it is not simply profoundly antagonistic (N'Tsoukpoe et al. 2014b). The Fig. 2.12 shows what we face when considering material selection for thermal energy storage systems. However a few investigations (Courbon et al. 2011; Visscher and Veldhuis 2005) have considered a comparison of several materials under operating conditions but most of them were theoretically conducted.

Numerous salt hydrates have been reviewed for thermochemical storage in the literature (N'Tsoukpoe et al. 2009; Tatsidjodoung et al. 2013; Yu et al. 2013). However, almost all of these salt hydrates fail to meet the great expectations to cover both space heating and DHW. Therefore, in the framework of the large-scale EU-funded project “Thermal Battery”, devoted to micro-CHPs efficiency improvement (mainly economic savings) using thermochemical storage (Schmidt et al. 2012), a systematic evaluation of the potential of salt hydrates for low temperature thermochemical heat storage have been considered. N'Tsoukpoe et al. (2014b) performed a rough evaluation of the suitability of salt hydrates for a low temperature thermochemical heat storage application below 105 °C based on theoretical and experimental approaches. The authors concluded that $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ are the most promising materials for this application, disregarding an economic analysis.

Besides the shown criteria in Fig. 2.10, a first condition “thermodynamically reasonable” for material selection should be always met. This is linked to finding a reaction which changes direction at a desired temperature so that energy is stored at higher temperatures and given off at lower temperatures. For a general thermodynamic screening of suitable processes, it has been found advantageous to use the concept of turning temperature T_t (Wentworth and Chen 1976). T_t is the

Fig. 2.10 Dilemma around material selection for thermochemical heat storage system (N'Tsoukpoe et al. 2014b). *GWP* Global warming potential; *ODP* Ozone depletion potential



temperature at which the reaction changes its direction so that at $T > T_t$ the products dominate while at $T < T_t$ the reactants dominate. A first approximation $T_t = \Delta H_r / \Delta S_r$, where ΔH_r and ΔS_r are the reaction enthalpy and the reaction entropy respectively, results from setting the equilibrium constant as unity and assuming that the heat capacity is constant during the chemical reaction. However, where only one type of gas molecule is formed, the Clausius-Clapeyron equation defines the turning temperature.

Let comeback on the criterion energy storage density which brings controversy in some storage material discussion. It is most valuable characteristic of a thermal energy storage system. In the following different used terms of energy density are clarified:

1. the *theoretical energy density* ($\text{kJ}\cdot\text{kg}^{-1}$), widely used for sorption systems, is the maximal energy density of the material considering the porosity;
2. The *mass energy density* ($\text{kJ}\cdot\text{kg}^{-1}$), which is the ratio between the reaction enthalpy and the molecular mass;
3. The *volume energy density* ($\text{kJ}\cdot\text{m}^{-3}$), depending on the highest involved hydrates in the reaction (initial salt to be dehydrated), is calculated as the product of the mass energy density and the density of the salt particles (it is not the bulk density and therefore, the required porosity is not considered here);
4. The *lean energy density* ($\text{kJ}\cdot\text{m}^{-3}$), which takes into account the stored heat and the evaporation energy, corresponds to the actual and real energy storage potential (N'Tsoukpoe et al. 2014b).

In the following, different systems (open and close) are presented where sorption and/or thermochemical phenomenon is/are involved. Technically spoken, each system is classified by the storage material. So the systems will be discussed with respect to the storage material. The aim is to show their operating conditions and performances, to address the encountered issues followed by their overcomings if possible.

2.2.1 Absorption Systems

Also called liquid-gas systems, absorption systems are promising storage option because they can be pumped and used as the working heat transfer fluid in solar collectors and heat exchangers. However, it can be defined as a process in which the sorbate diffuses into the liquid or solid sorbent accompanying a phase change and/or a chemical reaction. Faster heat and mass transfer rates are possible with liquid absorption. Materials recently investigated include aqueous solutions of Calcium Chloride (CaCl_2), Lithium Chloride (LiCl), Lithium Bromide (LiBr), Sodium Hydroxide (NaOH), Potassium Hydroxide (KOH) and Ammonia as shown in Table 2.3. Hui et al. (2011) compared absorption materials for the use in low pressure (1.2–4.2 kPa) absorption cycles and have reported theoretical material energy densities up to $476 \text{ kWh}\cdot\text{m}^{-3}$. CaCl_2 with a desorption temperature of 44°C , has an energy density of $263 \text{ kWh}\cdot\text{m}^{-3}$ and a limited absorption temperature range of $20\text{--}23^\circ\text{C}$.

LiCl with desorption temperature of 66°C , has the highest storage density of $476 \text{ kWh}\cdot\text{m}^{-3}$, but also has a high absorption temperature range, $20\text{--}35^\circ\text{C}$ (Davidson et al. 2013). NaOH with a desorption temperature of 50°C , has an energy density of $233 \text{ kWh}\cdot\text{m}^{-3}$ and the highest absorption temperature of 45°C (Weber and Dorer 2008). LiBr presenting an absorption temperature between 25 and 35°C with a desorption at 72°C (prototype value is 40°C), can store 8 kWh heat and produce 1 kW (N'Tsoukpoe 2012) and has an energy density of $400 \text{ kWh}\cdot\text{m}^{-3}$. KOH with a desorption temperature of 63°C , has an energy density of $400 \text{ kWh}\cdot\text{m}^{-3}$ and an absorption temperature of 35°C . Figure 2.11 illustrates a closed- and an open-cycle absorption system. The system comprises of multiple storage vessels, two reactors (for absorption/desorption), a condenser and evaporator, and heat exchangers. The concept with separated storage and reactor, in this case, consist of physical transport of the sorbent and heat and mass transfer in the reactors. Three and two storage vessels respectively, one each for water, diluted (discharged), and concentrated (charged) solutions, are shown in this illustration to emphasize the necessity of preventing mixing prior to discharging.

Mixing of the diluted and concentrated solutions releases the stored binding energy and converts the chemical potential into sensible energy, which is subject to thermal loss to the ambient. The use of multiple storage vessels ensures long-term storage of chemical potential but decreases the system-level energy density and increases the cost.

In an absorption system, there is one loop for concentrated solutions and diluted solutions (after the sorbate is diluted in the base solution) and another loop solely for sorbate. The strong solution becomes a weak solution after it absorbs the sorbate from the evaporator. The weak solution becomes a strong solution after it evaporates the sorbate from the base solution and condenses in the condenser after being heated up in a generator (Pang et al. 2013). These systems are very well developed and proof-tested and already on the market.

Table 2.3 Absorption systems for household application

Working pair	Characteristics	Projects	Scale level	References
H ₂ O/NH ₃	Charge: 93 °C; Discharge: 43 °C. Heat: 900 MJ·m ⁻³ of NaOH (with single stage reactor). Theoretical energy density: 119 kWh·m ⁻³ of anhydrous. Storage capacity: 40 kWh. Discharging time: 12 h for 5 kW power	Delft University of Technology—Netherlands	Reactor scale, Numerical scale and Prototype	Ruiter (1987)
NaOH/H ₂ O	Charge: 100–150 °C; Discharge: 40–65 °C. Heat: 900 MJ·m ⁻³ of NaOH (with single stage reactor). Theoretical energy density: 250 kWh·m ⁻³ of anhydrous. Storage capacity: 8.9 kWh. Discharging time: 8.9 h for 1 kW power	EMPA, COMTES	Reactor scale, Prototype, commercial	Fumey et al. (2014a, b), Weber and Dorer (2008)
LiCl/H ₂ O	Charge: 46–87 °C; Discharge: 30 °C. Heat: 910.8 MJ·m ⁻³ of LiCl (with crystallization in the storage tank). Theoretical energy density: 253 kWh·m ⁻³ of anhydrous. Storage capacity: 35 kWh. Discharging time: 4.4 h for 8 kW power	SERC	Reactor scale, Prototype	Bales (2008), Bales and Nordlander (2005)
LiBr/H ₂ O	Charge: 40–90 °C; Discharge: 30–33 °C. Heat: 907.2 MJ·m ⁻³ of solution. Theoretical energy density: 251 kWh·m ⁻³ of solution. Storage capacity: 8 kWh. Discharging time: 8 h for 1 kW power	LOCIE, LRHPT-China	Reactor scale, Prototype, commercial	N'Tsoukpoe et al. (2013, 2014a), Xu et al. (2011)

(continued)

Table 2.3 (continued)

Working pair	Characteristics	Projects	Scale level	References
CaCl ₂ /H ₂ O	Charge: 70–80 °C; Discharge: 21 °C. Heat: 428 MJ·m ⁻³ . Simulated energy density: 200 kWh·m ⁻³ of anhydrous. Prototype energy density: 116 kWh·m ⁻³ . Storage capacity: 15 kWh. Discharging time: 27–500 h for 560 W power	LOCIE, SOLVAY, BEMS	Reactor scale, Numerical scale, Prototype	Courbon et al. (2011), Hui et al. (2011)
Expanded Vermiculite + LiNO ₃	Discharge: 33–36 °C. Heat: 450 MJ·m ⁻³ of reactor	–		Tatsidjodoung et al. (2013)

2.2.2 Adsorption Systems

The field of solid adsorption started as historical curiosity and the first scientific and quantitative work was performed in 1773, by Scheele and Fontana (Critoph and Zhong 2005). It is a process where the sorbate does not diffuse into the sorbent but changes phase on the surface of the sorbent. Depending on adsorbent and adsorbate phases, adsorption systems may be classified as solid/gas, liquid/gas, solid/liquid, and liquid/liquid (Srivastava and Eames 1998). As it is a surface phenomenon, surface polarity corresponds to strong affinity with polar substances such as water in this case. Polar adsorbents are thus called ‘hydrophilic’ and aluminosilicates such as zeolites, porous alumina, silica gel or silica–alumina are examples of adsorbents of this type. On the other hand, non-polar adsorbents are generally ‘hydrophobic’. Carbonaceous adsorbents, polymer adsorbents and silicalite are typical non-polar adsorbents. In the following, talking about adsorption systems refers only to gas-solid adsorption system. These materials are the most widespread sorbents for water vapour adsorption. Their sorption behaviour is based on the presence of regular or irregular pore systems within their molecular structure. Silica gels are widely studied as hydrophilic materials due to their large water sorption capacity at low humidity, low cost, and easy regeneration (Chua et al. 2002). Surprisingly, this compound presents hydrophilic limitations for adsorption condition at 35 °C and 12 mbar and desorption condition at 150 °C and 56 mbar (Henninger et al. 2012). In the same order, several materials have been used for heat storage purpose such as: zeolites (natural and synthetics as types 4A, 5A, 13X, Y), more hydrophilic than silica gel with the major inconvenient of higher desorption temperature (>200 °C precisely in close system) although some experiment results show possibility at

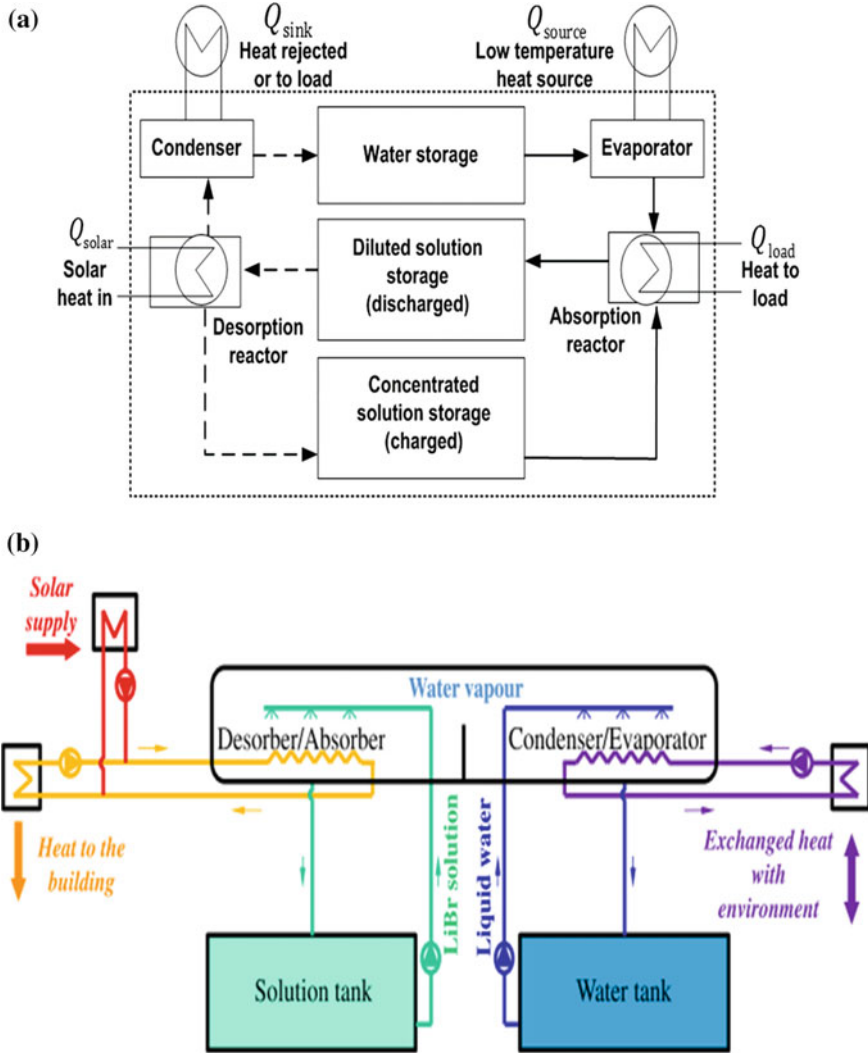


Fig. 2.11 Scheme of a closed (Quinnell and Davidson 2012) (a) and an open (N'Tsoukpoe et al. 2013) separate absorption storage system (b)

120 °C (Steiger et al. 2008). Aluminophosphates (AlPO₄-34 or AlPO-Tric) (the most promising) and silica-aluminophosphates (SAPO-34). Metal-organic-frameworks (MOFs) but still with hydro-thermal instability (Henninger et al. 2012; van Helden and Hauer 2013a), materials with crystalline open porous structure. Salts and composites (Hongois et al. 2011; Lahmidi et al. 2006; Mauran et al. 2008; Mette et al. 2013; Zondag et al. 2013). These materials have been theoretically and experimentally studied, and some were prototyped and commercialized as resume in Table 2.4. Composites based on those materials have also been developed

Table 2.4 Adsorption systems for household application

Materials	Characteristics	Projects	Scale level	References
Silica gel/H ₂ O (Close system)	Charge: 88 °C at 1.5 kW; Discharge: 32–42 °C at 1–2.87 kW for 9.5 h. Theoretical energy density: 50 kWh·m ⁻³ of anhydrous. Experimental energy density: 300 kWh·m ⁻³ of material. Prototype energy density: 33.3 kWh·m ⁻³ . Storage capacity: 13 kWh	AEE-INTEC, Austria	Reactor scale, Numerical scale and Prototype	Bales (2008), Ng and Mintova (2008)
Zeolites 13X/H ₂ O (Open system)	Charge: 130–180 °C; Discharge: 55–65 °C at 1.8 kW. Experimental energy density: 124–180 kWh·m ⁻³ of material. Prototype energy density: 57.8 kWh·m ⁻³	ZAE-Bayern, Germany. SPF, Switzerland	Reactor scale, Prototype	Bales (2008), Hauer (2007)
Zeolites 13X/H ₂ O (Close system)	Charge: 350 °C; Discharge: 15 °C at 4.1 kW (cold storage). Theoretical energy density: 167 kWh·m ⁻³ of material. Storage capacity: 5.5 kWh	SJTU, China	Reactor scale	Lu et al. (2003)

(continued)

Table 2.4 (continued)

Materials	Characteristics	Projects	Scale level	References
Zeolites 4A/H ₂ O (Open system)	Charge: 180 °C at 2.5 kW; Discharge: 35 °C at 1.5 kW. Experimental energy density: 160 kWh·m ⁻³ of material. Prototype energy density: 120 kWh·m ⁻³ Storage capacity: 12 kWh	ITW, Germany	Reactor scale, Prototype	Bales (2008), Kerkes (2006)
Metal-organic-framework (MOFs)	Charge: 45–50 °C; Discharge: 15 °C for cooling. Very low affinity to water. Up to 1.4 g·g ⁻¹ as sorption capacity	USA, NJNU, China. BIC, Russia	–	Aristov (2013), Li and Xu (2013), Ng and Mintova (2008), Rowsell and Yaghi (2004)

in order to behave as shape-stabilized material at macroscopic scale and Tatsidjodoung et al. emphasized them in his review (Tatsidjodoung et al. 2013).

These systems can be designed in the open or closed mode. In the closed mode (under vacuum), the principle is similar to absorption system with the difference that the sorbate diffuses only at the surface of the solid sorbent and the solution tank and water tank are the same. However, the inconvenient of the closed system remains the low pressure for water. In the open mode, water is of course the perfect sorbate candidate and air plays the role of heat transfer fluid. So, partial pressures are taking into account and there is not need a condenser and a water tank any more.

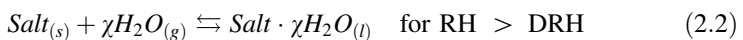
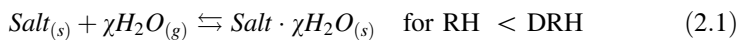
2.2.3 Thermochemical Systems

As mentioned before, thermochemical storage is in general, a simultaneous chemical reaction and sorption. Yu et al. argue that there is no clear boundary between them anyway (Yu et al. 2013). Although it can be noticed that chemical materials present higher heat capacities than sorption materials. In this section we focus only on hydration reaction (disregarding coordination reaction with ammonia) at low-temperature application for environmental reasons (Introduction, Sect. 1.1).

For thermochemical energy storage units, the choice of the storage material is critical (Fig. 2.10). A complete couple of the material properties and working conditions could allow significant improvements in the thermal performances of the

system. According to Gordeeva and Aristov (2012), the common way to select the best adsorbent for a given application is to screen the properties of available adsorbents in order to select which meet the application demands. The previous authors argued that this method is difficult and time-consuming and usually results in a compromise choice rather than in the ultimate one. One smart and more precise method, namely the target-oriented design, was proposed and Gordeeva and Aristov (2012) describes it as follows: (1) determining the demand (based on thermodynamic analysis of the cycle efficiency) of the application for the required storage material properties, (2) choice of the candidate material (based on equilibrium sorbent-sorbate), whose properties precisely or nearly fit these demands. Based on a similar method, Ma et al. (2009) investigated more than two hundred salt hydrates (for adsorption) and recently N'Tsoukpoe et al. (2014b) screened 125 hygroscopic salts leading to 17 possible candidates for low temperature thermochemical energy storage (Table 2.5) and from which prototype a maximal energy density of 60 kWh could be obtained.

Among the 17 materials for heat storage application, only magnesium chloride (MgCl_2), sodium sulfide (Na_2S), strontium bromide (SrBr_2) and magnesium sulphate (MgSO_4) are of great interest and were applied in many works and research projects (Table 2.6). The products of hydration reactions of these salts are generally assumed to be hydrates with a high number of 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 process by which a substance sorbs water vapour from the environment and gradually dissolves in the sorbed water to form a solution at a critical relative humidity (RH) value, namely, the deliquescence relative humidity (DRH) (Mauer and Taylor 2010). The water intake or uptake strongly depended on the deliquescence relative humidity (DRH) and this latter on the properties of the salt and the temperatures. If the relative humidity (RH) of the environment exceeded the DRH, the salt absorbs water and dissolved until reaching the equilibrium, i.e. until the water activity of the solution equaled the relative humidity. At relative humidity below the DRH, the salt lifts up water vapour forming a higher hydrated state but no solution. Both cases are shown in the following equations (Posern and Kaps 2010):



The deliquescence phenomenon favours some issues such as chemical instability. The forming of a liquid film on the surface of salt crystal will not only forbid the occurring hydration reaction, but also cause corrosion problems due to the dripping of solution to other metal components (in case of the LiCl , LiBr , CaCl_2 , showing why it was used in absorption systems).

Table 2.5 Suitable thermochemical materials for household applications at low temperature (from N^oTsoukpo et al. (2014b))

Hydrated salt	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	$\text{CaBr}_2 \cdot 4\text{H}_2\text{O}$	$\text{Ce}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	$\text{K}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}$	$\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$	$\text{La}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$
Dehydrated salt	$\text{Al}_2(\text{SO}_4)_3 \cdot 8.5\text{H}_2\text{O}$	$\text{CaBr}_2 \cdot 3\text{H}_2\text{O}$	$\text{Ce}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$	$\text{K}_2\text{CO}_3 \cdot 0.8\text{H}_2\text{O}$	$\text{LaCl}_3 \cdot \text{H}_2\text{O}$	$\text{La}(\text{NO}_3)_3 \cdot 1.5\text{H}_2\text{O}$
$T_{\text{melting}} [^\circ\text{C}]$	88	80–110	180	> 80	91	86–95
$d_s [\text{t} \cdot \text{m}^{-3}]$	1.69	2.2	3.91	2.15	2.223	2.459
N	9.5	1	2	0.7	6	2.5
$\Delta H_r [\text{kJ} \cdot \text{mol}^{-1}]$	526.8	59.7	58.0*	44.6	355.5	158.6
$\Delta H_{r,m} [\text{kWh} \cdot \text{kg}^{-1}]$	0.220	0.061	0.040	0.075	0.266	0.111
$\Delta H_{r,v} [\text{kWh} \cdot \text{m}^{-3}]$	371	134	156	161	591	273
$\Delta H_{\text{lean}} [\text{kJ} \cdot \text{mol}^{-1}]$	103.1	15.1		13.4	88.0	47.1
$\Delta H_{\text{lean},v} [\text{kWh} \cdot \text{m}^{-3}]$	73	34		48	146	81
$\eta [\%]$	19.6	25.3		30.0	24.7	29.7
$\Delta H_{r,v}^* [\text{kWh} \cdot \text{m}^{-3}]$	259	117		138	359	213
$\Delta H_{\text{lean},v}^* [\text{kWh} \cdot \text{m}^{-3}]$	51	30		41	89	63
Hydrated salt	$\text{LiCl} \cdot \text{H}_2\text{O}$	$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$	$\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$	$\text{Na}_2\text{S}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$	$\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$	$\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$
Dehydrated salt	LiCl	$\text{MgCl}_2 \cdot 4.7\text{H}_2\text{O}$	$\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$ ^a	$\text{Na}_2\text{S}_2\text{O}_3$	$\text{SrBr}_2 \cdot \text{H}_2\text{O}$	$\text{SrCl}_2 \cdot \text{H}_2\text{O}$
$T_{\text{melting}} [^\circ\text{C}]$	99	117–118	88.5–93 ^a	–	88	100
$d [\text{t} \cdot \text{m}^{-3}]$	1.7	1.569	2.04	1.69 ^b	2.386	2.672
N	1	1.3	4	2	5	1
$\Delta H_r [\text{kJ} \cdot \text{mol}^{-1}]$	62.2	71.5	225.1	110.3	337.0	59.0
$\Delta H_{r,m} [\text{kWh} \cdot \text{kg}^{-1}]$	0.286	0.098	0.274	0.158	0.263	0.061
$\Delta H_{r,v} [\text{kWh} \cdot \text{m}^{-3}]$	486	153	558	267	628	164
$\Delta H_{\text{lean}} [\text{kJ} \cdot \text{mol}^{-1}]$	17.6	13.5	46.8	21.2	114.0	14.4
$\Delta H_{\text{lean},v} [\text{kWh} \cdot \text{m}^{-3}]$	137	29	116	51	213	40
$\eta [\%]$	28.3	18.9	20.8	19.2	33.8	24.4
$\Delta H_{r,v}^* [\text{kWh} \cdot \text{m}^{-3}]$	322	130	340	203	392	139
$\Delta H_{\text{lean},v}^* [\text{kWh} \cdot \text{m}^{-3}]$	91	25	71	39	133	34

^aThe $\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$ is metastable according to (Grevel and Majzlan 2009). 88.5–93 °C correspond to the phase transition point for crystalline modification of the $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$ (Kandiner 1970)

^bThis is the density of the $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$

Table 2.6 Most used thermochemical materials in projects followed with some prototypes

Material (TCM)	Characteristics	Research level	Projects/Institutions	References
$\text{SrBr}_2 \cdot 6\text{H}_2\text{O} \leftrightarrow \text{SrBr}_2 \cdot \text{H}_2\text{O} + 5\text{H}_2\text{O}$ (Additive: Expanded Natural Graphite in proportion 6 and 8 %)	Charge: 70–80 °C at 4.4 kWh of HX for 840 min; Discharge: 35 °C at 2.2 kWh of HX for heating and evaporator at 12 °C, during 15–24 h. Theoretical energy density: 628 kWh·m ⁻³ of salt. Prototype energy density: 60 kWh·m ⁻³ . Storage capacity: 60 kWh	Reactor scale, Numerical scale and prototype	PROMES, CEA-INES/LITEN; SOLUX prototype 170 kg of SrBr ₂ ·H ₂ O. IEC-Leuphana	Lahmidi et al. (2006), Mauran et al. (2008), Tanguy et al. (2010), Marias et al. (2014)
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O} \leftrightarrow \text{MgSO}_4 + 7\text{H}_2\text{O}$ (Pure and Zeolite 13X impregnated with 15 wt%)	Charge: 122–150 °C; Discharge: 30 °C. Theoretical energy density: 0.76–1.5 GJ·m ⁻³ of salt. Total hydration energy density: 476 kWh·m ⁻³	Reactor scale, Numerical scale (Balasubramanian et al. 2010) and prototype	ECN-Netherlands, IWT-Bremen, INSA-Lyon, Bauhaus-Universität Weimar-Germany.	Bales (2008), Ferchaud et al. (2012a, b), Hongois et al. (2011), Steiger et al. (2008); van Essen et al. (2009a, b), Posern (2012)
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \leftrightarrow \text{MgCl}_2 \cdot 2\text{H}_2\text{O} + 4\text{H}_2\text{O}$	Charge: 117 °C; Discharge: 35 °C. Theoretical energy density: 2.17 GJ·m ⁻³ of MgCl ₂ ·2H ₂ O	Reactor scale (labscale experiment).	ECN-Netherlands, IEC-Leuphana	Ferchaud et al. (2012a, b), Opel et al. 2011)
$\text{MgCl}_2 \cdot 6\text{H}_2\text{O} \leftrightarrow \text{MgCl}_2 \cdot \text{H}_2\text{O} + 5\text{H}_2\text{O}$	Charge: 150 °C; Discharge: 60 °C at 50 W. Prototype density: 0.5 GJ·m ⁻³ . Thermal power: 150 W after 25 h	Reactor scale, prototype (17 l of salt).	ECN-Netherlands	Zondag et al. (2013)
$\text{CaCl}_2 \cdot 2\text{H}_2\text{O} \leftrightarrow \text{CaCl}_2 \cdot \text{H}_2\text{O} + \text{H}_2\text{O}$	Charge: 95 °C; Discharge: 35 °C. Theoretical energy density: 0.72 GJ/m ³ of CaCl ₂ . Prototype energy density: 60 kWh·m ⁻³ (40 m ³)	Reactor scale, (theoretical study)	SOLAUTARK project (BEMS-Liège, Belgium)	Courbon et al. (2011), Hennaut et al. (2014)

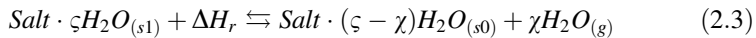
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Table 2.6 (continued)

Material (TCM)	Characteristics	Research level	Projects/Institutions	References
$\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O} \leftrightarrow \text{Na}_2\text{S} \cdot 1.5\text{H}_2\text{O} + 3.5\text{H}_2\text{O}$ (ECN) $\text{Na}_2\text{S} \cdot 5\text{H}_2\text{O} \leftrightarrow \text{Na}_2\text{S} \cdot 1\text{H}_2\text{O} + 4\text{H}_2\text{O}$ (MCES Project)	Charge: 72–83 °C and at 180 °C at 2.5 kW; Discharge: 35 °C at 0.7–1.5 kW for 4.6 h. Theoretical energy density: 2.8 GJ·m ⁻³ of Na ₂ S·5H ₂ O. Experimental energy density: 780 kWh·m ⁻³ of Na ₂ S·5H ₂ O. Storage energy density: 990 kWh·m ⁻³	Reactor scale, SWEAT-prototype (3 kg of salt)	ECN-Netherlands, Chiang University, MCES Project)	de Boer et al. (2002, 2004, 2006), Wongsuwan (2004)
$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} \leftrightarrow \text{Al}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O} + 13\text{H}_2\text{O}$	Charge: 150 °C; Discharge with temperature lift at a variation of 9.8 °C, reactor and evaporator both at 25.1 °C	Reactor scale (40 g of salt)	ECN-Netherlands	van Essen et al. (2009a)
$\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O} \leftrightarrow \text{Al}_2(\text{SO}_4)_3 \cdot 3\text{H}_2\text{O} + 9\text{H}_2\text{O}$	Charge: 60 °C during 18 h; Discharge: 15 °C during 81 h. Experimental energy density: 0.86 GJ·m ⁻³ of KAl(SO ₄) ₂ ·3H ₂ O	Reactor scale, prototype (25 kg of KAl(SO ₄) ₂ ·12H ₂ O)	PROMES, CEA-INES-project (ANR-08-STOCK-E-04 ESSI)	Marias et al. (2014)

All those performances stand for the heating only

Thermodynamically spoken, thermochemical systems are based on reversible reaction between a solid and a gas (here water vapour) as shown in Eq. (2.3), where ΔH_r is the reaction enthalpy, standing for every specie enthalpy in the reaction and strongly depends on the melting temperature of phase transition ($\text{J}\cdot\text{mol}^{-1}$ of water) and x, y the stoichiometric coefficients.



In contrast to absorption and adsorption equilibria, the thermodynamic equilibrium of thermochemical reactions is monovariant (Stitou 2013) and therefore follows the Clausius-Clapeyron relationship. This relationship is obtained by using the fact that, for this transformation, the Gibbs free energy is equal to zero at the thermodynamic equilibrium (Levine 2002). Assuming constant heat of reaction ΔH_r and pure ideal gas phase, the thermodynamic equilibrium results in the Van't Hoff equation (Raldow and Wentworth 1979) since vapour is far from ideal:

$$\ln\left(\frac{p_{eq}}{p^0}\right) = \frac{-\Delta H_r^0}{R \cdot T_{eq}} + \frac{\Delta S_r^0}{R} \quad (2.4)$$

with p_{eq} : equilibrium pressure (Pa). ΔS_r^0 : formation entropy ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ of water) of reaction at reference pressure p^0 (Pa) and R : ideal gas constant ($\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$). Equation (2.4) ordinarily stands for pure vapour system and for a corresponding pressure; the equilibrium temperature can be deduced. That equilibrium temperature allows to evaluate the temperature in the reactor during the whole cycle and consequently to perform the energy and exergy analysis of the process (Hongois et al. 2011). Energy analysis is related to the first law of thermodynamics through energy balances and energy efficiencies. Additionally, energy analysis is the evaluation method on how energy is used in a process, involving the physical or chemical processing of materials and the transfer or conversion of energy. However, it is not sufficient to evaluate all the aspects of energy utilisation in the process. So, the exergy analysis method, which is based on the first and second laws of thermodynamics, is a supplement for full understanding and is used to improve the real efficiencies of the system. Exergy is also defined as potential or quality of energy. With exergy analysis it is possible to make a sustainable quality assessment of energy for any thermodynamic system (Caliskan et al. 2012).

In the Clausius-Clapeyron diagram, the thermodynamic equilibrium of the reaction in Eq. (2.3) is plotted as a nearly straight line, by neglecting the enthalpy and entropy variation of the process with the temperature (Fig. 2.12). This is due to the fact that reaction enthalpy varies slightly when temperature interval is not large. Below the equilibrium line of the solid/gas reaction, the salt is in its desorbed solid form or less hydrate form (s0). Conversely, above the equilibrium line, the salt is in its solid form (s1).

Initially, in the state (s1) (in the reactor), the material in the reactor is heated up through a heat exchanger (in case of a closed system) via heat loss from the

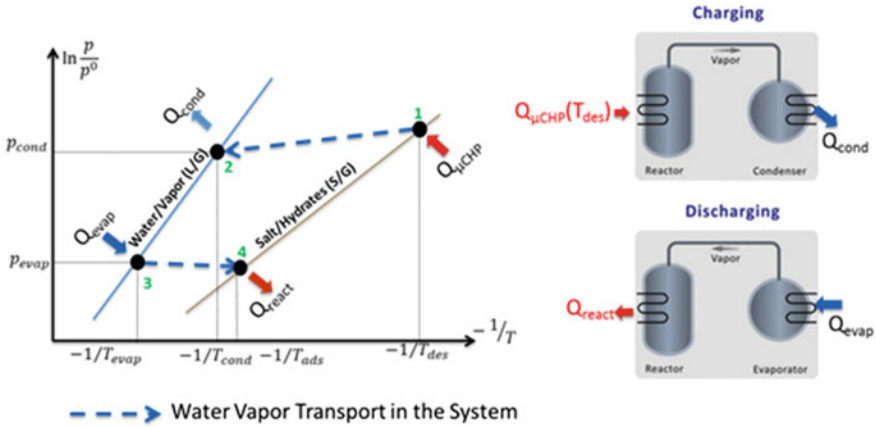


Fig. 2.12 Theoretical thermodynamic equilibrium of a thermochemical system in the Clausius-Clapeyron diagram. 1 decomposition; 2 condensation; 3 evaporation; 4 synthesis

micro-CHP. The desorbed water is then condensed at condensation conditions (p_{cond} and T_{cond}) followed by an endothermic heat release (Q_{cond}).

This is called the charging phase or charge mode. The endothermic heat release or energy of condensation can be used in the existing DHW (domestic hot water) system or stored elsewhere. In the discharging phase, water in the house system is heated up via a low energy source, so that water can evaporate and flow through the salt bed in the reactor. The transport is favoured by a pressure difference in the reactor and in the evaporator (p_{evap} and T_{evap}). The occurring exothermic reaction releases a higher heat (Q_{react}) that can be used for both space heating and DHW again.

In practise, Fig. 2.12 does not proceed as shown, since it is ideal. Though Sharanov et al. showed and confirmed that the efficiency equal to the Carnot efficiency can, in principle, be obtained for a chemical heat pump that results from a monovariant equilibrium of a gas–solid reaction (Sharanov and Aristov 2008). However, according to the principle of Le Chatelier's, by increasing or decreasing the temperature during the thermal decomposition or synthesis, the process shifts towards vapour formation or absorption and an increase or decrease of the vapour pressure. This shifts of the equilibrium to the formation of the anhydrous salt by imposing a deviation from the thermodynamic equilibrium as shown in Fig. 2.13. In addition, a synthesis or decomposition reaction can only take place if the reagent equilibrium is deviated to allow a reaction kinetic (Stitou 2013). This deviation is defined for the decomposition as the difference between the temperature T_{des} imposed to the reactor and the solid/gas equilibrium temperature $T_{eq}(p_{cond})$ at the reactor pressure. For the synthesis, it is the difference between the temperature T_{ads} imposed to the reactor and the solid/gas equilibrium temperature $T_{eq}(p_{evap})$ at the reactor pressure. Figure 2.13 explained the shifted equilibrium. Such of studies have been performed by many authors (Castets and Mazet 2000, 2001; Mazet et al. 1991;

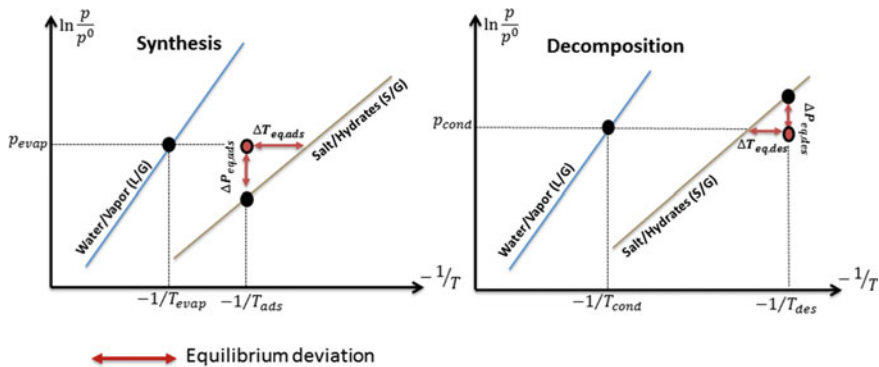


Fig. 2.13 Shifted thermodynamic equilibrium of a thermochemical system in the (left) synthesis and (right) decomposition phase

Stitou 2013) and they showed that there is an important effect on the reaction kinetics due to those deviations. However, in a closed system, the system pressure is imposed by the evapo-condenser pressure (Michel 2012). So the shifted equilibrium (pressure and temperature) for decomposition and synthesis respectively are defined as:

$$\Delta T_{eq,des} = T_{des} - T_{eq}(P_{cond}) \text{ and } \Delta P_{eq,des} = P_{eq}(T_{des}) - P_{cond} \quad (2.5)$$

$$\Delta T_{eq,ads} = T_{ads} - T_{eq}(P_{evap}) \text{ and } \Delta P_{eq,ads} = P_{eq}(T_{ads}) - P_{evap} \quad (2.6)$$

Returning to these salts of great interest, $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ was identified at the Energy research Centre of the Netherlands (ECN) (Ferchaud et al. 2012a, b; Zondag et al. 2013) as the promising material for a heat storage application in a 50 W power prototype. This material was also investigated in our Lab. To reach a tetra-hydrate form of MgCl_2 , a 120 °C source was needed depending on the water vapour pressure which would have been difficult to obtain from the micro-CHP heat losses. Other studies (Ferchaud et al. 2012a, b; Opel et al. 2011; Van Essen et al. 2009a) showed that a quasi-complete dehydration was possible for a temperature higher than 125 °C but cycle stability was not very good. Complete dehydration is not possible since it leads to the formation of hydrochloric acid and magnesium oxide (Sugimoto et al. 2007). Hongois (Hongois et al. 2011) has clearly demonstrated that $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ also was worthy using for heating purpose. At the ECN, they identified $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ as one of the most interesting salt hydrates for compact seasonal heat storage. Van Essen et al. stated that first experiments performed in a closed system at low pressure indicate that a small amount of heat can be released at 50 °C with a water vapour pressure of 1300 Pa. If a heat storage system has to operate at atmospheric pressure, then the application of $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ for seasonal heat storage is possible for space heating operating at 25 °C, a water vapour pressure of 2100 Pa and a dehydration temperature of 150 °C which is difficult to

reach with micro-CHP heat losses. However, this salt is corrosive, has a bad kinetic, and is expensive. Additionally, the release power is small when considering an evaporation temperature of 10 °C (the power for evaporation should be less to be provided naturally or economically).

The couple $\text{Na}_2\text{S}/\text{H}_2\text{O}$ (with 9-, 5-, 2-hydrates) has also attracted the ECN interest, but the kinetic is relatively slow and during decomposition, the structure pattern is modified showing simultaneous region of higher and slower hydration (de Boer et al. 2002, 2004). However this salt can not allow sufficient release temperature for heating purpose and has a low melting temperature of 49 °C. The salt which seems to fit our need is $\text{SrBr}_2 \cdot 6\text{H}_2\text{O}$ according to the Table 2.5. At the Institute of Science and Materials Processing (PROMES) in France, this well investigated salt, showed good results followed by a 1 m³ prototype development which can store 60 kWh in heating capacity and a water flow rate of 0.1 l·s⁻¹ (Mauran et al. 2008). The only inconvenient is the irritation and the price which is around 195 €/kg for 95 % purity (<http://www.alfa.com/>). It however shows good cycle stability over >20 cycles.

Once the above-mentioned salts have been identified, the first tests in a close heat storage system (pure salts in powder form), always presented, transfer problems such as agglomeration, swelling, expansion and phase change. During the hydration, to bring the water vapour in contact with the salt, it was sometimes difficult. Small deliquescence can be noticed, in fact a skin of hydrated salt is sometimes formed on the surface of the bulk powder and strongly limits the diffusivity of the water vapour within the unreacted part of the sorbent (Tatsidjodoung et al. 2013). Since the performance of the system depends on heat and mass transfer, this had to be improved within the reactive bed, and therefore composites have been developed over the past two decades. They combine the heat storage capacity of the salt and the heat storage capacity of the host. This hybrid character of composites provides to the material some physical and chemical properties (large sorption area, hydrophobic character) between the salt and the host. The hosts (Aristov 2013; Critoph and Zhong 2005) can be in porous sorbent materials such as silica gel (Aristov et al. 2000; Fopah Lele et al. 2013; Gordeeva and Aristov 2012), vermiculite (Fopah Lele et al. 2013; Michel et al. 2012) and zeolites (Hongois et al. 2011). Furthermore, they can be in nonreactive host materials, such as expanded natural graphite (Jiang et al. 2014; Li et al. 2011; Oliveira and Wang 2007; Wang et al. 2006), metal foam (Guilleminot et al. 1993; Haije et al. 2007; Thapa et al. 2014), carbon fiber (Fukai et al. 2000; Wu and Chou 2012), or activated carbon (Tamainot-Telto and Critoph 2001; Wang et al. 2012; Ye et al. 2013) to improve the heat and mass transfer performance of the composites. The host/carrier matrix fulfils different functions: it defines the stability, the shape and the size of the material, which can be specially adapted for the application (van Helden and Hauer 2013b). The use of composite materials as well as the reactor design has been found to considerably improve the heat and mass transfer within thermochemical processes, though the use of a host matrix strongly affects the sorption equilibrium of the salt with the sorbate (Gordeeva et al. 2013). So a compromise has to be found when performing synthesis of composites.

Azoumah et al. showed that an optimum value can be obtained by playing on the bulk density (Azoumah et al. 2004). Porosity of the composite or the bed is also an optimum parameter to overcome the heat and mass transfer issue (Dawoud and Aristov 2003). The previous both authors show that water vapour sorption in the composite is quicker (reducing the hydration time) than in pure salt due to the host sorption properties. The composite materials are obtained using different methods: mixture based salts (Rammelberg et al. 2013) and minerals (Druske et al. 2013), salt impregnation or a mixing/impregnation and consolidation (Wang et al. 2009), synthesizing (Gordeeva et al. 1999).

2.3 Thermal Management and Chemical Reaction in Heat Storage Systems

Thermochemical heat storage system based on the heat of reversible reactions between a solid and a gas allows efficient energy management. The first results of laboratory research, the performance of early prototypes and the versatility of their uses promise significant developments. However, the knowledge and understanding of transport phenomena, the nature of the media exchange is not yet complete. General literature (Azoumah et al. 2004; Ghommem et al. 2011; Ishitobi et al. 2013; Lahmidi et al. 2006; Lu et al. 1996; Mazet et al. 1991; Neveu et al. 2013) on the study of solid-gas reaction media revealed a great interest of research: mastering and transport optimisation via the use of a solid-gas reaction to store energy and recover it through the reaction enthalpy. This implies heat and mass exchange in the system, as it is related to transport phenomena.

Whether the chosen process (chemical or/and sorption) or the sorbent material state (liquid or solid), researchers and engineers face the heat and mass transfer issues at different scales: the material itself, the reactor and the whole system. In general and especially in a solid-gas thermochemical system, the solid is under porous media. Because, its structure will receive or reject a gas in order to fulfil the thermochemical reaction. As a first requirement, the solid should possess a higher energy density, since this is well reduced when putting together with all the reactor components (observation from Table 2.5). Among others, the material density is another requirement which needs to be high. Unfortunately, when the material density is high, porosity is reduced and favours mass transfer limitation for the thermochemical reaction. Heat transfer can also be the transfer limitation since heat exchanged involves different phenomena depending on operating conditions. The presence of heat exchanger in the reactor, which represents thermal mass, thermal contact, can be a heat transfer limitation. The fact that the gas is pure (water vapour) or mixed (air), the material configuration (size, particle size of the solid, presence of the binder, compaction, texture, etc.) are among many things that influence heat and mass transfer and must be therefore handled in order to optimise the transport phenomena. In the following a short bibliography is given at the material or reactive bed level.

2.3.1 Heat Transfer in the Material/Reactive Bed Process

A porous material is a body consisting of a solid matrix having pores with irregular shape, different size and random distribution that are filled with one or more fluids. Usually, some pores are interconnected and another disconnected. The interconnection of the pores allows the heat and mass transfer and fluid flow through itself that is accompanied with heat transfer into the solid matrix (Delgado 2012). Depending on the physical problem, the following phenomena may mainly occur between the phases into the solid at the pore and bed level: heat transfer by convection, diffusion (conduction) and radiation. As already mentioned, the fluid for synthesis reaction here is the water vapour. Water vapour (no air) is the reactive gas and the salt hydrate the reactive solid. Both are considered as pseudo-homogeneous media at the same temperature and only the solid heat capacity will be assumed in the energy balance.

Olives and Mauran (2001) showed that the thermal radiation is neglected since the working temperature range of a thermochemical heat storage system is between 10 and 90 °C. Michel (2012) mentioned in his thesis that, for a system with water vapour, the prevailing heat transfer is the conduction (convection is very small to be considered, hence neglected). Therefore, heat in a porous medium with water vapour is transferred by conduction according to Fourier's law. One of the heat transport problems in the reactive bed or material lies in the fluid phases, there is always non-condensable water which remains at the pore-level (Fig. 2.14). This has been confirmed on silica gel for a specific pore (2–50 mm) (Zhang et al. 2014). That is why the introduction of the local-equilibrium (will be developed later) is one important assumption to reduce the complexity of the model development (avoiding three phases problem) to understand and/or optimise the lab-scale experiments.

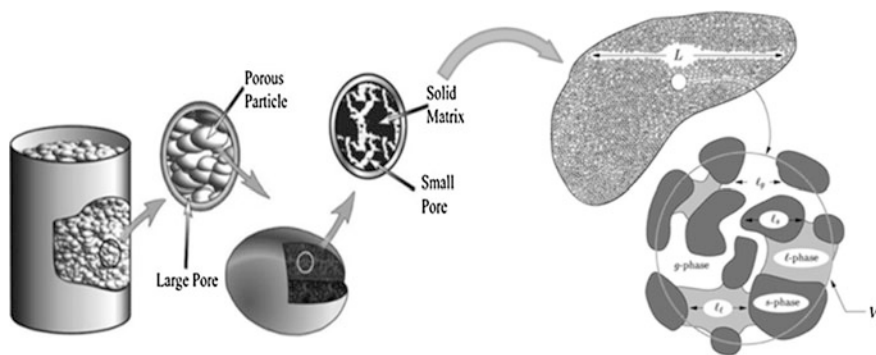


Fig. 2.14 Schematic description from the packed bed to the solid matrix where process (sorption and chemical reaction) is performed (adapted from Delgado 2012; Duval et al. 2004). g gas; l liquid; s solid

The mastering of problems of heat transfer (and mass transfer) in these porous reactants bed or material is done through mathematical models knowledge. Three approach levels can be considered to achieve these models as raised decades ago by Ajzoul (1993): molecular, microscopic and macroscopic. The molecular approach has no practical value, because it is difficult to describe the movement of molecules, properly. The microscopic approach allows developing the general equations of transfers, but at this level of analysis, it is impossible to set the boundaries conditions of these equations. However, the results obtained in this approach are the starting point for the macroscopic approach, which allows to achieve the desired model. Then, resolution of the model equations is then possible after the introduction of simplifying assumptions that experiments can justify. This is the adopted strategy in this thesis to go forward on thermal management of the TESS.

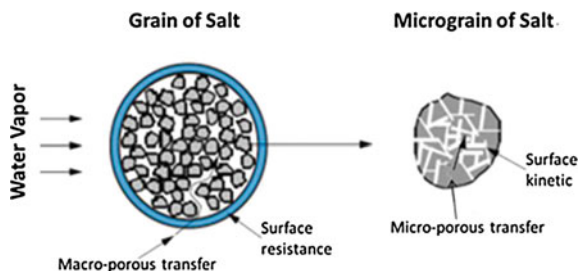
Here, important points to mention in thermal management are the thermal properties related to heat transfer such as thermal conductivity and specific heat capacity of the material (defining the suitability of a material for TESS). The storage capacity need to be known and the thermal conductivity imposes charging and discharging rates and affects the complexity and cost of the heat exchanger design (Maru et al. 1976). Therefore these properties will be determined in Chap. 4, and in the Chap. 3 the adopted model for theoretical effective (accounting for bed porosity) thermal conductivity will be presented (actually, reminded).

2.3.2 Mass Transfer in the Material/Reactive Bed Process

In the storage and release of energy process, two main phenomena are involved: chemical reaction and sorption. During desorption/dehydration or sorption/hydration, mass transfers of gas-solid phase occur in different ways according to many parameters. For example, in a fixed-bed sorption, the concentration of the gas phase and of the solid phase change with time as well as with position in the bed. Most of the time, mass transfer takes place near the inlet of the bed, where the gas contacts immediately the sorbent. If the solid contains no solute at the start, the concentration of the gas drops exponentially with distance essentially to zero before the end of the bed is reached. After some time, the solid situated at the inlet becomes slightly saturated, and most of the mass transfer takes place farther from the inlet (Benitez 2009). In short, this explains the reaction front procedure and highlights how mass transfer can be limited.

In his thesis, Michel (2012) principally studied mass transfer as a limiting factor for thermal efficiency by using modelling approach and experiments with the focus on the permeability of the salt hydrate. In fact the permeability (Sun et al. 1995) is one of the most important parameters to study mass transfer (diffusion, transport) by accounting to the material (salt hydrate) structure (texture, tortuosity, porosity, vapour flow regime, etc.). Hence the use of correlations in modelling is mandatory. Mauran et al. (2001) used such a permeability correlation in his work, showing the porosity effect on the gas flow.

Fig. 2.15 Mass transfer mechanisms in salt hydrates with porosity (adapted from Duquesne 2013)



The diffusion of gases through consolidated media is viewed as a three-step process: (1) At a high-pressure interface, gas dissolves or condenses in the solid matrix. (2) Following dissolution or condensation, gas diffuses along a solid-phase concentration gradient in accordance with Fick's law to the low-pressure interface. (3) On arrival at the low-pressure gas—solid boundary, the dissolved gas is desorbed or released to the gaseous medium.

One important feature of chemical and sorption processes is the strong relation between mass and heat transfer characteristics. Low temperature boots the sorption/hydration while high temperature promotes desorption/dehydration (called adsorbent regeneration). Thermochemical reactors are characterised by a strong coupling between kinetics and thermal transfers. Anyway, simultaneous heat and mass transfer occur in a natural way whenever the transport of mass is accompanied by the evolution or consumption of heat. As an example of strong dependence, the way to fill the salt in the reactor bed, may have a profound impact on thermal performances of the system (Mauran et al. 1993). The resistance at the salt surface (Fig. 2.15) is a limiting factor. In a heat exchanger, the number of plates and distance between them, can be limited. Numerical studies help to determine with configuration could be of interest. The knowledge at which reaction rate the mass transfer occurs is a hint of starting overcoming thermal transfers limitations in the system (Sieres and Fernández-Seara 2007). In the following Chaps. 3 and 5, numerical studies are performed to attempt understanding of such phenomena and optimise them as possible as it can.

2.3.3 Reaction/Sorption Kinetics

Reaction kinetics refers to chemical reaction mechanism and its evolution in terms of reaction rate (meaning the changes in concentration of reactants and products with time), reaction advancement/conversion. Reaction kinetics deals to a large extent with the factors which influence the reaction velocity. Those effects are concentration, temperature, reaction order, phase and surface area, solvents and catalysts. In this thesis solvent and catalyst effects will not be evocated or taken into consideration. One of the important reasons of studying chemical reaction rate is for

practical reasons. The aim is to determine at which rate the solid-gas reaction approaches the equilibrium state. Due to the complexity (Frost and Pearson 1961) of chemical phenomena (every elementary reaction has its own reaction mechanism), Asperger (2003) affirmed that complete knowledge of a reaction mechanism is rarely attained. Most of the time, modelling based on experimental data helps for rate determination. Another way of studying kinetics is through reaction advancement, which characterises the rate of the reacted salt during the decomposition or synthesis to the total salt hydrate (initial salt state).

Several models concerning the sorption kinetics have been developed over the past decades such as linear drive force (LDF), solid diffusion and equilibrium models (Chahbani et al. 2002; Ilis et al. 2010). These previous authors compared the three models. From their analysis, the equilibrium model uses the assumption where mass transfer is not a limiting factor due the slowness of intra-particles diffusion through micro- and macropores. It is however recommended when pore-diffusion are higher. The solid diffusion model has been extensively used (Chan et al. 1981; Inaba et al. 2004; Yong and Sumathy 2002) and is the more accurate, but more cumbersome one. Concerning the LDF model (Sircar and Hufton 2000), it is derived from the solid diffusion model adopting a simplifying mathematical assumption and this latter model tends to underevaluate the system performances as demonstrated by Chahbani et al. (2002). Figure 2.16a shows that an instantaneous equilibrium model is preferred for a low-pressure system. Concerning that pressure, it does not increase much. Figure 2.16b reveals an overestimation when using the equilibrium model, leading to an surestimation of system performance. However results are acceptable over a long time process and recommended for chemical processes having an adsorbate dimensionless concentration below 0.2.

On thermochemical kinetics, a phenomenological modelling requires good knowledge of the structure of the mixture and especially the mechanisms of ab/adsorption and desorption together with chemical reaction. This knowledge is still imperfect and insufficient to build a sufficiently representative model of the phenomenon. As ideal is only hypothetical, a semi-empirical law identified from

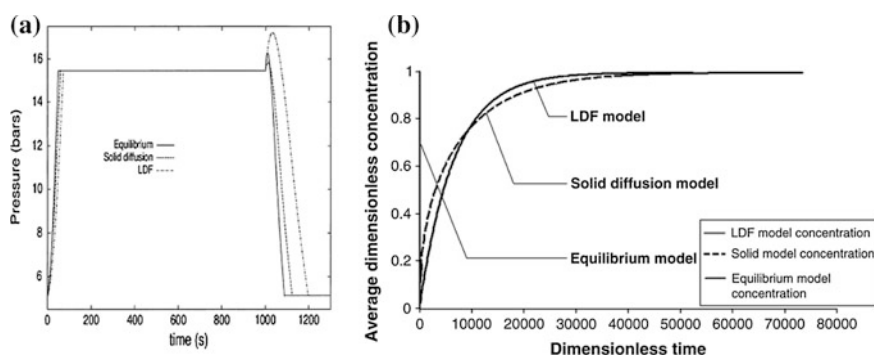


Fig. 2.16 Dynamic comparison of **a** bed pressure (Chahbani et al. 2002) and **b** adsorbate concentration on the process time (Ilis et al. 2010)

measurements performed on a calorimeter combined to the equilibrium model is proposed. The equilibrium model has been chosen among the above reasons for thermochemical and sorption processes due to the low energy source needed such as solar energy (Duquesne 2013) or micro-cogeneration. This model seems sufficient to describe the sorption kinetics. In the following chapter 3, the model is developed.

2.4 Conclusion

This chapter reviews the technology concept around the thermal energy storage systems. It allows drawing up an inventory of different storage systems, highlighting the thermochemical system as the better one. The idea of coupling or integrating thermal energy storage systems with existing power and/or thermal systems is not new and has proved an effective feasibility through different studies. This concerns mainly the latent and sensible energy storage. The first part of the chapter gave some detailed and practical examples. However, the idea of coupling thermochemical energy storage systems due to their high energy storage density with a combined heating and power system is rather new and challenging. How a reactor should be designed has been covered, showing why an integrated and closed (favoured vapour transport into the bed) reactor is preferred, although technical handling may offer more complexity (heat exchanger) and technological constraints (vacuum control).

From a flourished literature on material selection, each of the researchers or institutes/universities have defined what they found as best thermochemical material for their application. It appears that the strontium bromide has particularly drawn attraction due to the fact, it can reach or be closed to the target of the project: high prototype energy density of $80 \text{ kW}\cdot\text{m}^{-3}$ if possible, compatible charging temperature from the micro-CHP heat loss, environmentally safe, discharging temperature of 50°C sufficient for heating and DHW. It can be for the moment, the best material for the low-temperature THSS. However, like most of pure salt, it presents kinetic issues leading to low system power. So composites are developed with larger surface in which chemical reaction can proceed and may overcome this issue. Hence, a high amount of heat release via the combined phenomena of sorption and chemical reaction.

The review also reveals the well-known heat and mass transfer issue into the reactive bed and in the whole system. It is mandatory to understand these coupled phenomena and characterise them, at least the main parameters. Numerical studies are used to bring some responses and solutions to that issue. Pinel et al. found that numerical studies on heat and mass transfer are very basis and do not try to be more real (such as 3D or 2D per example), but instead of that, too many assumptions are drawn to replace the reality of such system (Pinel et al. 2011). An emphasis is placed on heat transport, mass transport and kinetic in order to described the involved phenomena so that it will be modelled in the next chapter. For these transport/transfer phenomena, thermal conductivity, permeability and reaction

advancement describe or represent them completely well. The next chapter will therefore present numerical modelling of the reactive bed under pure water vapour in the close system, after a brief description of the practical system.

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