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## Thermal Energy Storage Systems for Concentrated Solar Power Plants

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### Abstract

Solar thermal energy, especially concentrated solar power (CSP), represents an increasingly attractive renewable energy source. However, one of the key factors that determine the development of this technology is the integration of efficient and cost effective thermal energy storage (TES) systems, so as to overcome CSP's intermittent character and to be more economically competitive. This paper presents a review on thermal energy storage systems installed in CSP plants. Various aspects are discussed including the state-of-the-art on CSP plants all over the world and the trend of development, different technologies of TES systems for high temperature applications (200 °C – 1000 °C) with a focus on thermochemical heat storage, and storage concepts for their integration in CSP plants.

TES systems are necessary options for more than 70% of new CSP plants. Sensible heat storage technology is the most used in CSP plants in operation, for their reliability, low cost, easy to implement and large experimental feedback available. Latent and thermochemical storage technologies have much higher energy density thus may have a bright foreground. New concepts for TES integration are also proposed, especially coupled technology for higher operating temperature and cascade TES of modularized storage units for intelligent temperature control.

The key contributions of this review paper consist of a comprehensive survey of CSP plants, their TES systems, the ways to enhance the heat and/or mass transfers and different new concepts for the integration of TES systems.

**Keywords:** Concentrated solar power (CSP), Thermal energy storage (TES), Integration, Thermochemical, Energy density

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**Abbreviations:**

CLFR	Compact Linear Fresnel collector
CRS	Central Receiver System
CSP	Concentrated Solar Power
CST	Concentrated Solar Thermoelectric
DNI	Direct Normal Irradiance
DSG	Direct Steam Generation
HCE	Heat Collector Element
HFC	Heliostat Field Collector
HTF	Heat Transfer Fluid
IEA	International Energy Agency
LFR	Linear Fresnel reflector
PDC	Parabolic Dish Collector
PTC	Parabolic Trough Collector
M&O	Maintenance and Operation
n.a.	not applicable
R&D	Research and Development
SPT	Solar Power Tower
STC	Solar Tower Collector
TES	Thermal Energy Storage

## 1. Introduction

The use of renewable energy is essential today to decrease both the consumption of fossil resources and the production of carbon dioxide partly responsible for the greenhouse gas effect [1][2]. Among every renewable resources (e.g., wind, ocean, geothermal and solar), solar energy is showing encouraging promises due to the great quantities of solar irradiation flux arriving on earth.

Among various solar energy technologies, concentrated solar power (CSP) is particularly attractive due to its advantages in terms of high efficiency, low operating cost and good scale-up potential [3,4]. Solar energy is converted into electricity by means of a CSP plant composed of four main elements: a concentrator, a high temperature solar receiver, a fluid transport system and a power generation bloc (e.g., Rankine cycle, Stirling cycle). It is estimated by IEA that the CSP will contribute up to 11% of the global electricity production in year 2050 [5].

### 1.1. CSP technologies

A wide range of concentrating technologies exist; the most developed are parabolic trough collectors (PTC), linear Fresnel reflectors (LFR), solar power towers (SPT) and parabolic dish collectors (PDC), as summarized in Table 1. PTC plants use parabolic reflectors to focus sunlights on an absorber tube located on the focal line of the parabola. Reflectors and the absorber tube can move together to follow the sun from sunrise to sunset [5][6]. LFRs consist of curved reflectors on each side of an absorber tube. A recent design called compact linear Fresnel reflector (CLFR) uses two parallel reflectors for each mirror's row, needing less area than a PTC to reach a given power output [8]. SPTs use heliostat field collectors (HFCs) to reflect and focus sunlights onto a central solar receiver located on the top of the tower. It is a relatively flexible technology because a variety of heliostat fields, solar receiver designs and heat transfer fluids (HTFs) could be used. PDCs concentrate sunlights on a focus point above a parabolic reflector. The reflector and receptor, tracks the sun. Besides these conventional types, CSP technology can also be combined with thermoelectric systems (i.e., concentrated solar thermoelectric) for direct electricity production without using a power cycle [8].

**Table 1. Comparison between different CSP technologies [3,9,10]**

### 1.2. Thermal energy storage

A major drawback of solar energy is its temporal intermittency. To overcome this problem, one solution is to use a backup system (energy hybridization) that burns fossil fuel or biomass. A second solution is to use a thermal energy storage (TES) system to store heat during sunshine periods and release it during the periods of weak or no solar irradiation (Figure 1).

**Figure 1. CSP plant with a TES system**

The development of an efficient and cost-effective TES system is crucial for the future of CSP technologies [14]. Economically, TES allows an increase in the duration of electricity production. Moreover, integrating a TES system in specific CSP configurations permits optimization of electricity resale and the CSP electricity production [15]. Indeed, as shown in Figure 2 [16], electricity prices vary during a day depending on demand. The solar intensity's largest periods do not correspond to the electricity's most expensive

periods. Adding a TES allows heat storage during high solar intensity periods and provides productions during high electricity cost periods.

**Figure 2. Example of peak energy production and cost of energy for a CSP plant [16]**

There are currently three kinds of TES systems available: sensible heat storage, latent heat storage and thermo-chemical heat storage [17,18]. Sensible heat storage systems are most mature. They are widely used in industrial plants, most notably in Spain within the “PS10” and “PS20” projects (2007 and 2009), the “Andasol 1” and “Andasol 2” plants (2008) and also in the USA (e.g., within “Solar One”, 1982) [18]. Latent heat storage allows large amounts of energy to be stored in relatively small volumes (high energy density) and is cost competitive. Among these techniques, thermochemical heat storage receives increasing attention. Two recent reviews were published, focusing on low to medium temperature (0 – 300 °C) thermochemical reactions pertaining to long-term sorption solar energy storage [19] and to chemical heat pump technologies [20]. Cot-Gores et al. [21] and Prieto et al. [22] also presented reviews on sorption and chemical reaction processes for TES application. Reaction candidates for medium or high temperature applications (250 – 800 °C) were listed by Felderhoff et al. [23].

### *1.3 Objectives of this paper*

Based on the existing literature, we observe CSP plants worldwide and their characteristics (e.g., power, presence of a TES system, storage capacity) are partially (e.g., in [24]) presented, but a full description would be beneficial. In parallel, TES materials for CSP application need to be updated, especially those for thermochemical heat storage. Moreover, the issue of appropriate and new concepts for TES integration in CSP plants which is very important, is discussed here in more detail.

The present paper has therefore the following objectives:

- The most complete survey on CSP plants in operation, under construction and in project all over the world and on the trends of development in order to highlight the economic necessity of the integration of TES systems in CSP plants to compete with current energy production technologies.
- A review on different technologies of TES systems and potential materials for CSP application, with a special focus on thermochemical heat storage.
- A summary of storage concepts and integration configurations proposed in the literature

These contributions are important because the literature survey clearly shows the important role of TES systems in current and in future CSP plants. Moreover, if the selection of an adapted TES technology is the first step, its proper integration in a CSP plant is the next important step. Reviewing different storage concepts allows an overview on conventional TES integration configurations as well as innovative concepts recently proposed.

## 2. TES systems in CSP plants: the state-of-the-art

This section presents a literature survey on almost all CSP plants worldwide, including those already in operation, under construction or planned project. First, a large part of the data have been collected from the websites “cspworld.org” and “globalenergyobservatory.org”. Then a detailed research has also been made for each identified CSP plant on its proper website or related documents so as to find additional information. A statistical analysis of these data will show the general trends of CSP technologies such as the increasing plants’ average power or the necessity of TES systems for economic competitiveness.

To better illustrate the historical development, the surveyed CSP plants are divided into five groups: (i) 19 plants in operation with production began before year 2000 (named “before 2000” hereafter); (ii) 24 plants in operation with production started between year 2000 and 2010 (named “2000 to 2010”); (iii) 85 plants in operation with production began after 2010 (named “after 2010”); (iv) 35 plants now under construction and (v) 74 planned plants. The total number of samples thus reaches 237 CSP plants. Detailed data for every plant are provided in Table 1, 2 and 3 of the Data-in-Brief article [25].

Statistical analyses are provided about the purpose of plant, the average power and the storage/hybridization (Figure 3-5). It should be noted that despite all the efforts made by the authors, not all values are available for every CSP plant. In the current study, if a plant’s value was not available (n.a.) for a certain item, then that plant was eliminated from the analysis of that item. Table 2 counts the number of plants with known values used for each item of analysis compared to the total number of plants of each group.

**Table 2. Number of samples for each item of analysis**

### 2.1. Purpose of plants

Figure 3 shows different purposes of CSP plants (commercial, demonstration or Research & Development) and their respective percentage for each group of plants. CSP plants with a commercial purpose always represent the vast majority. Research and development (R&D) used to be the second biggest purpose for plants in operation. However, their installation decreases gradually in recent years. No plant is planned in the future specially for R&D purpose, indicating that CSP technologies have become relatively mature and readily available for commercialization. Meanwhile, the proportion of plants built for a demonstration purpose remains almost constant since 2010.

**Figure 3. Purposes of CSP plants and their respective percentage**

### 2.2. Types of CSP technology

Figure 4 shows the historical evolution of used CSP technologies. PTC and SPT are the most used technologies for plants in operation. Meanwhile, trends also show that there will be a higher ratio of SPT for CSP plants in project. LFR represents the third most frequently used CSP technology. PDC is a relatively young technology with no plants in activity. Nevertheless, it represents 7-9% of plants under construction and planned, making it a non-negligible technology in the future.

**Figure 4. Types of technology and their respective percentage**

### 2.3. Average power of CSP plants

Figure 5.a shows the historical evolution of CSP plant's average power. The average power has increased by a factor of 6 from about 21 MW<sub>elect</sub> for power plants in operation before 2000 to more than 120 MW<sub>elect</sub> for planned power plants. One reason for this increasing average power is the change of the purpose of the plants since more than a quarter of plants in operation is related to a demonstration or a R&D purpose (Figure 3). These plants were not built for electricity sale thus produced generally a few megawatts. Plants under construction and planned are more commercial plants of higher power output, including the 2000 MW<sub>elect</sub> facility for the planned "TuNur" plant in Tunisia.

**Figure 5.a. Evolution of average power of CSP plants**

**Figure 5.b. Percentage of hybridization for CSP plants**

**Figure 5.c. Presence of TES system in CSP plants**

**Figure 5.d. Evolution of storage capacity for TES systems in CSP plants**

### 2.4. Hybridization

Sometimes CSP plants are hybridized with a backup system that provides supplementary energy source when solar intensity is not adequate and when a quick response is needed [26]. Fossil fuels (i.e., coal, natural gas or diesel) are the most commonly used backup energy sources while biomass (e.g., "Borges solar", Spain, in operation) or solar photovoltaic (e.g., "Ashalim csp plant", Israel, planned) are occasionally used. Natural gas remains as the preferential fuel for hybridization [27]. With the hybridization of the backup system, the continuous electricity production of the CSP plant can generally be guaranteed which increases the plant global efficiency [26].

The percentage of hybridization for each group of CSP plants is shown in Figure 5.b. The use of hybridization systems is globally decreasing. This is mainly due to the increasing price of fossil fuels. Another possible reason is the increasing use of TES systems that will be discussed later. In fact, very few plants operate only with solar energy. A TES system and/or a hybridization system are always necessary to be added into a CSP plant to overcome the temporal variability of solar energy. However, care must be taken with these results, particularly for plants under construction and planned because of missing data.

### 2.5. Thermal storage

Figure 5.c indicates the percentage of plants implementing a TES system. About half of the plants (47%) currently in operation integrate a TES system. There is a notable increase in the use of TES systems for plants under construction (72%) and planned (77%). This increase can be partially explained by the technological progress and advancements achieved in storage systems and the necessity to install such systems to be economically competitive.

Sensible storage is the dominant TES technology used in CSP plants. It is the most developed technology that has been studied, tested and installed. Ruths tank (also called steam accumulator) is the only alternative for limited storage capacity installed in a CSP plant (e.g., "Augustin Fresnel", France, in operation, 0.25 hour of storage; "Alba Nova", France, under construction, 1 hour of storage). In the meantime, it is advisable to put in perspective these data and particularly those relating to plants under construction and planned, because in a certain number of cases the planned storage mode is not known.

Figure 5.d shows the evolution of the average storage capacity, represented by the time during which the plant is able to work with the energy provided by the TES system. The average storage capacity has steadily increased, from 3 hours to more than 7 hours for plants currently in project. As it will be possible to see in next parts, research on TES have developed more efficient and less expensive technologies. Today, plant stakeholders would benefit to install a TES to increase the profitability of their facilities. Many plants under construction or planned intend to do mass production of electricity and require a TES system large enough for continuous production during periods of low solar intensity. In addition, a number of plants built before 2010 have low storage capacity TES systems because their goal is to investigate the heat and mass transfer characteristics and validate their analytical/numerical models but not to produce electricity at a lower cost.

### *2.6. Short summary*

Table 3 summarizes the state of the art of CSP plants in operation and future trends (plants under construction and planned). CSP plants have a great future, indicated by the increases in the number, the average power output per plant and proportion of commercial plants. To allow plants to operate and to be economically competitive, a hybridization system and/or a TES system is necessary. Hybridization systems used to be a standard option to increase the dispatchability of CSP plants. However, they usually consume fossil fuels with increasing costs and high CO<sub>2</sub> emissions. In the meantime, TES technologies have no such problems and could become an alternative or even a replacement. A quick geographical analysis of the planned CSP plants shows that USA, Italy and Chile are the leading countries for CSP installation. These countries are not traditional oil producers and tend to use TES systems instead of fossil source backups.

Another trend is that even if several storage technologies are available, sensible storage is almost the only choice. However, we will see in the next section that other types of storage have great advantages and deserve to be studied.

**Table 3. Summary for TES systems in CSP plants**

## **3. TES technologies for CSP application**

As we saw in the above section, the integration of a TES system is necessary, which allows a plant to operate more stably and to meet the demands of the power grid. Therefore, selecting appropriate TES technologies and designing highly efficient TES systems are becoming the research focus. In a recent review [28], Tian and Zhao summarized main criteria to be considered in the design of a solar TES system. Aspects were proposed, including technical properties, economic costs and environmental impacts. Among influencing factors, the most expected features of a TES system are a high energy density to reduce the necessary amount of materials and the occupancy space, reliable mechanical and chemical stability and enhanced heat transfer during charges or discharges. Meanwhile, the cost of TES system (including storage materials, reservoirs, heat exchangers) is also an important criterion which directly determines the payback period of the investment. Finally, storage materials should be environmental friendly, low corrosive, complete reversible and non- or low-flammable.

As previously mentioned, TES technologies available for CSP application are classified into sensible, latent and thermochemical categories. Sensible heat storage is currently the most commonly used



technology (Table 3), with a large number of low-cost materials available [29–31]. However, the lowest energy density of this technology results in large size of TES systems. Latent heat storage technology has a higher energy density, but a poor heat transfer performance due to very low thermal conductivity of the materials. Thermochemical storage has the highest storage energy density, thus seems to be the most promising technology for the future. Nevertheless, problems such as more complex design of reactors, low chemical stability, poor heat and mass transfers and degraded performance over charge/discharge cycles hinder its real application in CSP plants [22].

Different technologies to store thermal energy for CSP application (between 200°C and 1000°C) are described below. Emphasis is put on recent advances in thermochemical heat storage technology, which is under-developed but has a great potential.

### 3.1. Sensible heat storage

In sensible heat storage, thermal energy is stored/released by raising/decreasing the temperature of a storage material. It is a pure physical process without any phase change during charge or discharge. Therefore, the amount of heat stored depends on the product of the mass, specific heat, and temperature variation of the storage material. In addition to the density and the specific heat of the storage material, other properties are also important for sensible heat storage: operating temperature, thermal conductivity and diffusivity, chemical and thermo-chemical stability of the materials and the cost [17]. The major drawback of sensible heat storages is their limited energy density (between 60 kWh<sub>t</sub>.m<sup>-3</sup> for sand (200-300°C), rock, mineral oil and 150 kWh<sub>t</sub>.m<sup>-3</sup> for cast iron (200-400°C) [32]) which makes storage units particularly large. Moreover, the storage units should be designed in a proper manner for heat discharge at relatively constant temperatures.

Sensible heat storage materials in solid and liquid form are the most studied materials and are at an advanced stage of development. Solid materials generally have a wide range for possible temperature variation (200 – 1200 °C), with high thermal conductivity (from 1 to 40 W.m<sup>-1</sup>.K<sup>-1</sup>) and relatively low cost (0.05 – 5 \$.kg<sup>-1</sup>). Concrete and castable ceramics are intensively studied which have good characteristics (0.05 \$.kg<sup>-1</sup> and good thermal conductivity: 1.5 W.m<sup>-1</sup>.K<sup>-1</sup> [32]) to be used as a solid heat storage materials [33]. In order to improve the stability of concrete at high temperature, a new concrete with polypropylene fibers was specially developed [29][30]. Other solid materials such as graphite (e.g., “Lake Cargelligo” in Australia) and pebble stone (e.g., “Airlight Energy Baha Plant” in Morocco) are also occasionally used, as listed in Table 1 of [25]. A comprehensive list of solid sensible heat storage materials for CSP applications and their main characteristics are provided by Gil et al. [17].

Instead of using new manufactured materials, industrial waste or by-product materials (i.e., asbestos containing wastes, bischofites, slags, etc.) [36,37] and low cost materials (i.e., sand, rocks) are also available [38,39]. Their adapted thermal properties, low cost and strong environmental and societal benefits (reduced landfilled waste amounts and the greenhouse emissions) make them good candidates for TES systems at high temperature [36].

Liquid materials are also widely used in CSP plants. Molten salts are considered as one of the best materials for CSP application [17,29–31] owing to their features including excellent thermal stability at high temperatures, low vapor pressure, low viscosity, high thermal conductivity, non-flammability and non-toxicity. The two leading candidates are “solar salt” (60% NaNO<sub>3</sub> and 40% KNO<sub>3</sub>) used in “Archimede”, Italia, in activity and “MSEE/CatB”, USA, in activity, and “HitecXL” (48% Na(NO<sub>3</sub>)<sub>2</sub>, 7% NaNO<sub>3</sub> and 45% KNO<sub>3</sub> [40]). HitecXL was tested in “PSA plant”, Spain and “Themis plant”, France. It was developed as a second option for

Hitec (40% NaNO<sub>2</sub>, 7% NaNO<sub>3</sub> and 53% KNO<sub>3</sub>, melting point at 142 °C) [29][40]. A new series of ternary salts mixtures was proposed with ultra-low melting temperatures at 76 °C, 78 °C or 80 °C, preventing the solidification of salt and making the TES system much easier to manage [30,41]. Mixtures of salts consisting of KNO<sub>3</sub>, LiNO<sub>3</sub> and Ca(NO<sub>3</sub>)<sub>2</sub> showed reduced viscosity by a factor of 5 compared to that of commercial synthetic oils or molten salts. Such eutectic salts whose melting temperatures points are also below 100 °C have also been reported by Wang et al. [42].

Effective solutions to increase the energy density of sensible heat storage materials like molten salts consist in adding encapsulated PCMs [43–45] or nanoparticles [46–49]. Encapsulation means the coating of PCM particles with a protecting shell to improve the chemical stability and to prevent individual particles from coalescing with one another during melt/freezing cycles. Adding encapsulated PCMs in sensible materials can be considered as a new coupled technology, as will be detailed in the later section of this paper. Adding nano-particles in sensible storage materials will increase its specific heat. Andreu-Cabedo et al. [47] showed that the specific heat of a solar salt can be increased by 25.03% by adding 1 wt.% of silica nanoparticles (SiO<sub>2</sub>).

Other liquid materials are also used in CSP plants. For example, oils have been used in “Dahan Power Plant” in China. Liquid sodium having a very high thermal conductivity (71 W.m<sup>-1</sup>.K<sup>-1</sup>) is used in “PSA SSPS-CRS plant” in Spain. However, additional safety measures are necessary due to their unstable nature caused by their high vapor pressure [30] which may cause serious security problems. Liquid sensible heat storage materials for CSP applications and their main characteristics are described by Gil et al. [17].

Gaseous materials have been used in CSP plants in operation such as compressed air or steam as storage media (e.g., “Exresol-1” “Planta Solar 20” and “Planta Solar 10” in Spain), as shown in Table 1 of [25]. Their main physical properties are shown in Table 4. The advantages of using gaseous materials are their availability, low cost, non-toxicity and wide range of operating temperature. The disadvantages of using gaseous materials are their low thermal conductivity and very low energy density. Even if the gas is stored compressed, the large volume of the reservoirs makes this storage option very challenging for CSP plants with high power output.

**Table 4: Gaseous materials for sensible heat storage**

### 3.2. Latent heat storage

In latent heat storage, thermal energy is stored/released by a material while changing its phase at a constant temperature. It is also a pure physical process without any chemical reaction during charge or discharge. The amount of heat stored is generally the latent heat of phase change (latent heat of fusion for a solid-liquid transition and latent heat of vaporization for a liquid-vapor transition).

Phase change materials (PCM) for latent heat storage have the advantage to charge or discharge in a narrow temperature range, close to their phase change temperature. They also have higher energy densities owing to their high phase change latent heat (between 27 kJ.kg<sup>-1</sup> for TRIS ((NH<sub>2</sub>)C(CH<sub>2</sub>OH)<sub>3</sub>) and 790 kJ.kg<sup>-1</sup> for the eutectic salt (80.5%LiF-19.5%CaF<sub>2</sub>) compared to sensible heat storages. The phase change concerning thermal storage could be either solid-liquid or solid-solid, because volume and pressure are roughly constant.

The main drawback of PCMs is their low thermal conductivity (usually 0.2 – 0.8 W.m<sup>-1</sup>.K<sup>-1</sup> [20,50]), resulting in very slow charge and discharge processes [51]. Several approaches may be considered to enhance their heat transfer, including using transportable PCMs [52] (detailed in section 4.2 of this paper), adding thermal conductivity promoters into pure PCMs and using high conductivity PCMs made of metal alloys [53–

55]. One of the common additives for PCMs is the graphite. The thermal conductivity of PCM/graphite composites could reach 5 to 10  $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$  depending on the amount of graphite added [56]. Other thermal conductivity promoters are also investigated, such as insertion of a metal matrix or foam [57–60], fins [61], dispersion of high conductivity particles [62], micro-encapsulation of the PCMs [63–67] or special designs of TES system with embedded heat pipes [68] or finned heat pipes [69]. Recent advances on the geometrical configurations of TES systems using PCMs are reviewed by Mao [70] and the shell materials used in the encapsulation of PCMs could be found in the review of Jacob and Bruno [71]. PCMs made of metal alloys (i.e., Mg-Zn-Al) have the advantages such as high thermal conductivity (around two orders of magnitude higher than that of molten salts) and good thermo-chemical stability. However, their high price (2-3 \$/kg) is an obstacle to be used in large scale TES [54].

Inorganic and organic substances with potential use as thermal storage material at high temperature and their physical-thermal properties are listed by Gil et al. [15] and Sharma et al. [65]. Melting temperature of these PCMs generally varies between 100 and 900 °C. Materials whose phase change temperatures are the lowest (100 – 300 °C) can be used as TES systems for PTC, LFR and PDC. Materials with higher phase change temperatures (> 400 °C) are suitable to be used in SPT or PDC whose operating temperature goes up to 600 °C or 1500 °C, respectively [3][8].

### 3.3. Thermochemical heat storage

Different from sensible or latent heat storages, thermochemical TES technology is based on reversible chemical reactions, which are characterized by a change in the molecular configuration of the reactants (combination or decomposition). Solar heat is used to drive an endothermic chemical reaction, and then stored in the form of chemical potential. During the discharge, the stored heat can be recovered by the reversed exothermic reaction, sometimes by adding a catalyst. The advantages of thermochemical storage relies on their high energy density (up to 10 times greater than latent storage [14]) and the indefinitely long storage duration at ambient temperature. As a result, it is a very attractive option and fairly economic competitive [29].

Metallic hydrides, carbonates system, hydroxides system, redox system, ammonia system and organic system can be used for thermochemical heat storage at medium or high temperatures (300 – 1000 °C) [14]. Table 5 groups these reactions with their main characteristics, advantages/disadvantages and experimental feedback with corresponding references. Some reactions (e.g.,  $\text{PbCO}_3/\text{PbO}$ ;  $\text{CaCO}_3/\text{CaO}$ ;  $(\text{CH}_4+\text{CO}_2)/(\text{CO}+\text{H}_2)$ ;  $\text{C}_6\text{H}_{12}/\text{C}_6\text{H}_6$ ;  $\text{NH}_3/\text{N}_2$ ;  $\text{BaO}_2/\text{BaO}$ ;  $(\text{CH}_4+\text{H}_2\text{O})/(\text{CO}+\text{H}_2)$ ) suffer from the problem of incomplete reversibility, which is a key drawback because their storage capability gradually decreases after cycles of operation.

**Table 5. Main reactions used in high temperature thermochemical heat storage [14], [17], [33], [84–88]**

Candidate reactions possessing good reversibility include  $\text{Co}_3\text{O}_4/\text{CoO}$ ,  $\text{SO}_3/\text{SO}_2$  and particularly  $\text{TiH}_2/\text{Ti}$ . They have good potential for CSP application but more experimental feedback is needed [72].  $\text{Mg}/\text{MgH}_2$  and  $\text{NH}_4\text{HSO}_4/(\text{NH}_3+\text{SO}_3)$  have shown to have good reversibility by intensive experimental tests but how to store the reaction products remains as a technical barrier. Indeed, these products in gaseous form ( $\text{H}_2$ ,  $\text{SO}_3$  and  $\text{NH}_3$ ) need to be compressed and stored in large tanks, implying higher installation and operation costs. Some alternative solutions were proposed and tested, such as the storage of  $\text{H}_2$  with metals hydrides at low temperatures [73] or by adsorption [74] but additional costs seem inevitable. Hydration/dehydration

of CaO/Ca(OH)<sub>2</sub> is another promising candidate with numerous expected features (e.g., good reversibility, low operating pressure, low price and no-toxicity of the product and large experimental feedback). Meanwhile, technical problems such as low thermal conductivity, agglomeration and sintering still remain to be solved.

Common drawbacks of materials used for thermochemical storage are low thermal conductivity which slows the heat transfer and low permeability which reduces the mass transfer. Many studies are devoted to the material properties and reactor designs so as to enhance the mass transfer during combination and also to enhance the heat transfer during decomposition [75,76]. The latest advancements and proposed methods are reviewed by Aydin et al. [77]. The available solutions are the construction of matrix [78] in the reactant part or the melting of the reactant with additives (e.g., expanded graphite matrix [79,80], aluminum foam [81], cobalt/cobaltous oxide based honeycombs [82]). Roßkopf et al. [83] also reported that power bed properties and thermal stability of thermochemical materials can be improved by adding nanoparticles (i.e., SiO<sub>2</sub>).

### 3.4. Short summary

Table 6 summarizes main characteristics of different TES technologies and key features.

**Table 6. Summary for different TES technologies**

## 4. Concepts for TES integration

Beyond choosing the suitable TES technology for CSP application, the TES system must be coupled in a proper way with the power generating cycle (e.g., Rankine cycle). Pertinent concepts that integrate TES system and the power generating cycle remain as one of the key issues for the actual application of TES technology. This section will review the commonly proposed concepts for TES integration and compare their advantages and disadvantages. Special attention is given to new trends of integration concepts, especially when more than one TES technologies are envisaged.

### 4.1. Classification

Based on the motion state of storage materials during charge or discharge, the concepts for TES integration can be broadly classified into two concepts: active concept and passive concept. In active storage systems, the storage medium itself flows to absorb (charge) or release (discharge) heat by forced convection. Contrarily in passive storage systems, the storage medium (often solids) is kept motionless and heated or cooled by the circulation of another heat transfer fluid (HTF).

Active systems can be subdivided into direct and indirect systems. In an active direct system, the storage medium itself also serves as the HTF used for the solar field (Figure 6a). During charge phase, the HTF is directly stored in a hot tank located at the exit of the solar field. During discharge phase, the hot HTF in the hot tank is pumped through the power cycle and then stored in a cold tank at the entrance of the solar field for the next charge/discharge cycle [145]. This concept needs no heat exchanger between HTF and storage materials. But suitable storage materials (molten salts or steam) are required because they should meet the requirements to be a good HTF and a good storage material at the same time.

In active indirect systems, the HTF and the storage medium are different. A typical active indirect concept is shown in Figure 6b, with two separate tanks for the storage. During the charge phase, the storage material in the cold tank is pumped through a heat exchanger where it is heated by the HTF, and then stored in the hot tank. During the discharge phase, the flow direction of storage material is reversed to release the heat to the HTF. In this manner, hot and cold materials are separately stored. An alternative to two tanks concept is using a single tank (Figure 6c) where hot materials are stored on the top while the cold materials on the bottom. They are separated because of the temperature stratification. The zone between the hot and cold fluids is called the thermocline. Usually a filler material (e.g., quartzite rock, sand, concrete, industrial waste) is added in the tank to enhance the thermocline effect and to reduce the needed quantity of storage materials. Therefore, it is about 35% cheaper than two tanks systems [17]. Some studies showed that filled thermocline with encapsulated PCM was also appropriate [45]. One of the key factors for highly efficient thermocline storage is maintaining the temperature stratification by a controlled procedure of charge and discharge and by appropriate methods or devices to avoid mixing. The filling configuration of filler materials in the storage tank is certainly a key point to be considered. Wu et al. [146] studied the thermocline behaviors of four typical concrete structures during the discharging process, including the channel-embedded structure, the parallel-plate structure, the rod-buddle structure and the packed-bed structure. They found that the packed-bed structure seemed to have better thermal performance [146].

In a passive storage system, HTF circulates through the TES system to heat up or cool down the storage materials kept still inside. In the case of sensible storage using concrete, the TES system usually contains a tubular heat exchanger (Figure 6d) integrated into storage materials, forming a compact heat storage-exchanging unit. The high thermal conductivity of materials and the good contact between the concrete and the tubes enable high heat transfer rates. However, the discharge temperature may vary when concrete is cooled down. This problem may be overcome by using PCMs and thermochemical materials, but with lower heat transfer rates.

Table 7 summarizes the concepts for TES integration in CSP plants, principles, storage materials, examples of system integration, as well as their advantages and disadvantages.

**Figure 6.a. Active direct concept for TES integration**

**Figure 6.b. Active indirect concept for TES integration, two tanks**

**Figure 6.c. Active indirect concept for TES integration, single tank**

**Figure 6.d. Passive concept for TES integration**

**Table 7. Different concepts for TES integration, their advantages and disadvantages**

#### 4.2. New trends for TES integration

Based on recent literature, several new trends for TES integration may be observed: (i) coupled TES technologies for possible higher operating temperature; (ii) cascade concept with modularized units; and (iii) mechanical circulation of granular particles.

Coupled systems using two types of storage technologies (e.g., sensible-latent, sensible-thermochemical, sensible-sensible) allow increased storage capacity, reduced delay between charge and discharge and increased power bloc working temperature (till 1400°C [147]). High operating temperature for CSP will increase the CSP's efficiency for cheaper electricity production. However, the TES design, operation and control become more complex with higher associated costs.

A good example is the coupled chemical-thermal solar power system [147], as shown in Figure 7. The CSP system couples a thermal and a chemical energy pathway. The thermal pathway utilizes a HTF to collect concentrated sunlights as thermal energy at medium or high temperature (<700°C) and to transfer this energy to a thermal-to-electric power cycle. In parallel, the chemical pathway uses a redox material (e.g.,  $\text{Co}_3\text{O}_4/\text{Co}_3\text{O}$ ,  $\text{BaO}_2/\text{BaO}$  (Table 5)) which undergoes direct reduction in the receiver to store the solar energy as chemical potential. This redox material is then oxidized at very high temperatures (1400°C) in the power cycle in series with the thermal pathway heat exchanger. This thermal-chemical coupling allows the power cycle to perform at very high temperature, increasing its global solar-to-electric conversion efficiency. However, the receiver design seems complex as it also serves as a reactor for chemical reaction.

**Figure 7. Example of coupled chemical-thermal solar power system [147]**

Another example of a coupled TES system is the three-part thermal energy storage system for direct steam generation (Figure 8) [148]. The storage system is composed of three blocks, two are filled with sensible materials (concrete) for preheating and superheating and an intermediate one with implementing a PCM material ( $\text{NaNO}_3$ ) to evaporate/condensate the HTF. The compact design is particularly adapted for direct steam generation.

**Figure 8. Example of coupled sensible-latent three-part thermal energy storage system for direct steam generation [148]**

Azanganeh et al. [149] proposed a coupled latent-sensible thermocline TES system, as shown in Figure 9. It combines rocks in the main body and encapsulated PCMs placed on the top of the tank, with the purpose of maintaining constant outflow temperature. Their investigation indicated that only a small amount of PCM (1.33% of the total volume) was sufficient to achieve outflow temperature stabilization around the PCM's melting point [149].

Adding encapsulated PCMs in sensible materials as a new trend is intensively investigated [43–45]. Cingarapu et al. [43] showed that adding 10 vol% of coated Zn particles over the base of chloride salt eutectic augments from 15% to 34% the volumetric storage capacity depending on the cycling temperature range ( $\Delta T = 50^\circ\text{C} - 100^\circ\text{C}$ ).

**Figure 9. Scheme of the combined sensible and latent heat concept for thermal energy storage [149]**

The second trend of TES integration is the cascade of modularized TES units. Conventional TES systems used to be made in one block. Novel TES systems now consist of several blocks to reduce thermal inertia of the systems and easy control of the HTF's temperature passing through. The main disadvantages of the cascade concept are their more complicated design than a single unit and their higher costs due to the use of several heat exchangers, tanks and regulation systems.

One example of this trend is the cascade latent heat storage system [150], using different phase change materials with different temperatures of phase change (306 – 380 °C) (Figure 10). Therefore, it is possible to store energy within a wide temperature range or to discharge at a constant temperature. However, the final design is complicated and the low thermal conductivity of PCMs needs to be improved.

**Figure 10. Example of a cascade latent heat storage system [150]**

Another example of cascade TES system for Direct Steam Generation (DSG) is shown in Figure 11 [151]. The storage unit is composed of several blocks of sensible material (e.g., concrete, molten salt, sand). The steam can pass through one or several blocks depending of its temperature. The main advantage of this system is the reduced thermal inertia of the TES system by dividing one storage block into three. However, the costs for construction and for the associated control system are inevitably higher than those for a single block TES system.

**Figure 11. Example of a solar energy system [151]**

Other new concepts proposed involve mechanical displacement of solid PCM or chemicals reactants [152][153]. A good example of this type of systems is a CSP system using fluidized-bed technology for thermal energy conversion and solid particles for thermal energy storage [154,155], as shown in Figure 12. This system uses granular particles as both HTF and storage materials. Solid granular particles are moved from the cold tank to the solid-particle receiver by a bucket lifter system. After absorbing the solar heat and reaching a very high temperature (> 1000°C), they then fall into the hot silo used as TES system by gravity. The stored heat could be discharged to the working fluid of the power generation cycle by circulating the granular particles through the fixed bed heat exchanger. The main advantages of this system are the high stability of particles at high temperature and their low cost. However, its application in large-scale is still challenging and needs to be further tested.

**Figure 12. Example of a pressurized fluidized bed for an air-Brayton gas-turbine combined CSP system [154]**

Besides all these new concepts, researchers [156] also proposed to use an intermediate HTF to reduce the HTF pressure in the heat exchanger. But the number of heat exchangers will increase, leading to increased costs. Table 8 summarizes these new concepts proposed in the literature for TES integration with their advantages and disadvantages.

**Table 8. New concepts for TES integration in CSP plants**

## 5. Conclusion

This work provides an extensive review on the thermal energy storage systems (TES) in CSP plants worldwide. The state-of-the-art for CSP plants, different TES technologies and the concepts for their integration in CSP plants are discussed. The major conclusions may be summarized as follows.

- CSP technology is already mature and readily available for commercialization, indicated by the increasing number of commercial CSP plants that are currently under construction or planned and by their increasing average power output.
- TES systems seem indispensable for the future more powerful CSP plants, for the latter to be more economically competitive and more dispatchable. Progress in TES technologies permit the increased storage capacity of their TES systems.
- A vast majority of CSP plants in operation use sensible heat storage, for their reliability, low cost and large experimental results obtained. The low energy density makes them more suitable for small or moderate power plants but less competitive for large-scale powerful CSP plants.
- Technologies of latent storage and thermochemical storage have much higher energy density, thus will have a bright foreground.

Some technological barriers remain to be overcome for latent and thermochemical storage, which are also the key issues of current research and development:

- To enhance the thermal conductivity of PCMs and thermochemical materials;
- To remove solid deposits that form at the exchange surfaces between PCM and the HTF;
- To enhance the heat and mass transfers during thermochemical reactions;
- To reduce the transition time during the switch from charge to discharge (and vice versa);
- To propose suitable and adaptive concepts for TES integration in CSP plants; and
- To design modularized TES units and their appropriate assembling and management.

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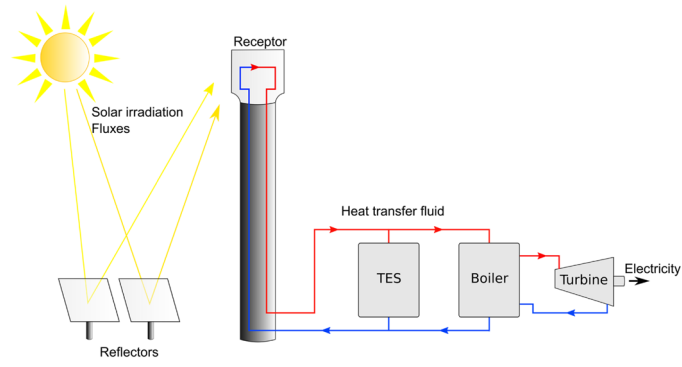


Figure 6. CSP plant with a TES system

Figure 7. Example of peak energy production and cost of energy for a CSP plant

Figure 8. Purposes of CSP plants and their respective percentage

Figure 9. Types of technology and their respective percentage

Figure 10.a. Evolution of average power of CSP plants

Figure 5.b. Percentage of hybridization for CSP plants

Figure 5.c. Presence of TES system in CSP plants

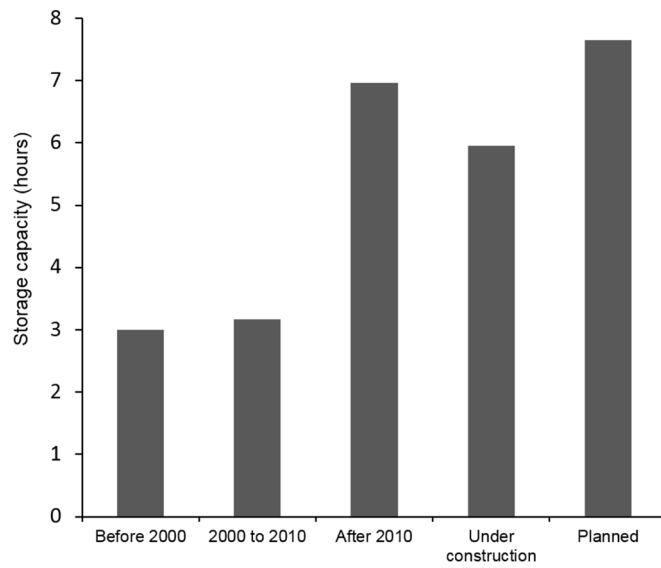


Figure 5.d. Evolution of storage capacity for TES systems in CSP plants

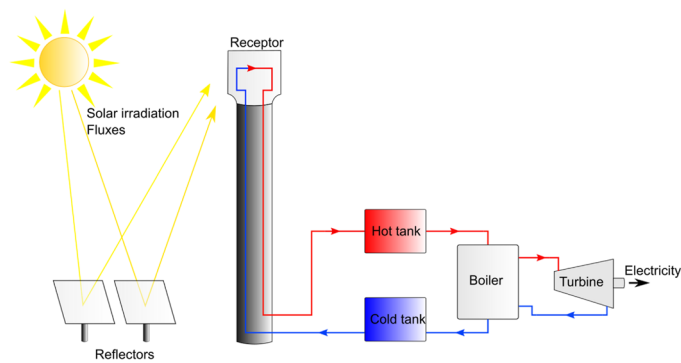


Figure 6.a. Active direct concept for TES integration

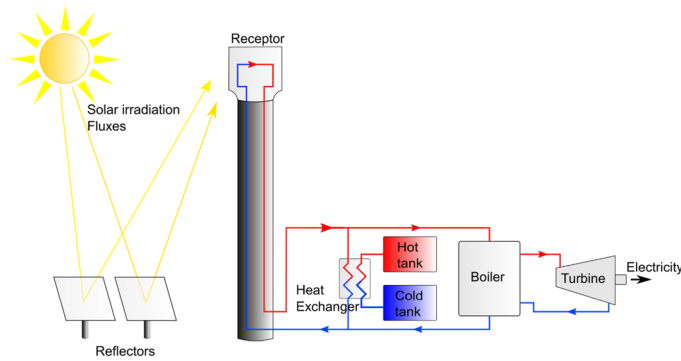


Figure 6.b. Active indirect concept for TES integration, two tanks

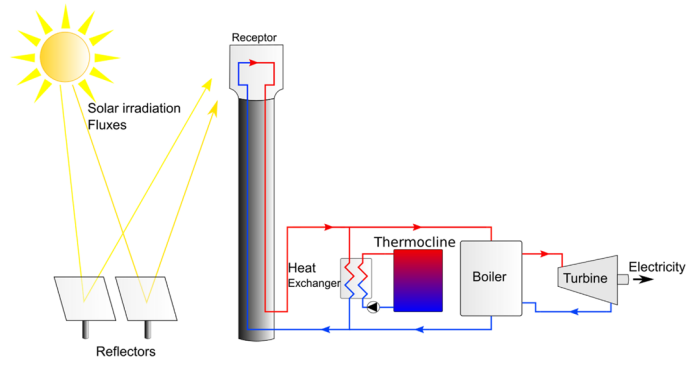


Figure 6.c. Active indirect concept for TES integration, single tank

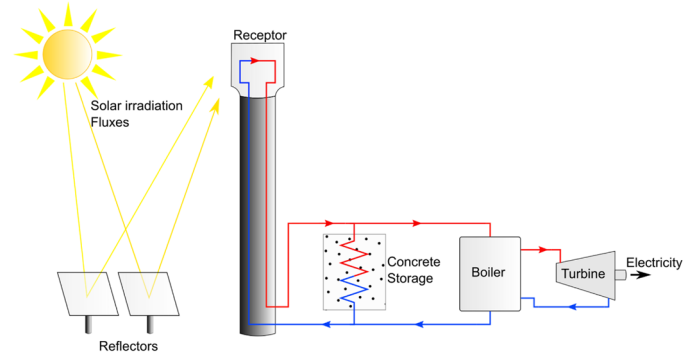


Figure 6.d. Passive concept for TES integration

Figure 7. Example of coupled chemical-thermal solar power system

Figure 8. Example of coupled sensible-latent three-part thermal energy storage system for direct steam generation

Figure 9. Scheme of the combined sensible and latent heat concept for thermal energy storage

Figure 10. Example of a cascade latent heat storage system

Figure 11. Example of a solar energy system

Figure 12. Example of a pressurized fluidized bed for an air-Brayton gas-turbine combined CSP system

Table 9. Comparison between different CSP technologies

CSP technology	Operating temperature (°C)	Solar concentration ratio	Storage integration possibility	Advantages	Disadvantages
PTC	20-400	15-45	Possible	- Relatively low installation cost [11]. - Large experimental feedback.	- Relatively large area occupied. - Low thermodynamic efficiency due to low operating temperature.
LFR	50-300	10-40	Possible	- Relatively low installation cost.	- Low thermodynamic efficiency due to low operating temperature.
SPT	300-1000	150-1500	Highly possible with low storage cost [12,13]	- High thermodynamic efficiency due to high operating temperature.	- Large space area occupied. - Relatively high installation cost. - High heat losses.
PDC	120-1500	100-1000	Difficult	- Relatively small area occupied. - High thermodynamic efficiency due to high operating temperature.	- Relatively high installation cost. - Little experimental feedback.



Table 2. Number of samples for each item of analysis

Group Item of analysis	In operation, before 2000					In operation, 2000 to 2010					In operation, after 2010				
	<b>Purpose of plants</b>	Commercial	Demonstration		R&D	n.a.	Commercial	Demonstration		R&D	n.a.	Commercial	Demonstration		R&D
	9	0		4	6	13	6		3	2	63	8		13	1
<b>Type of technology</b>	PTC	SPT	LFR	PDC	n.a.	PTC	SPT	LFR	PDC	n.a.	PTC	SPT	LFR	PDC	n.a.
	9	4	0	0	6	12	8	3	0	1	63	14	8	0	0
<b>Average power of CSP</b>	Available Value		n.a.			Available Value		n.a.			Available Value		n.a.		
	19		0			22		2			83		2		
<b>Hybridization</b>	Yes		No		n.a.	Yes		No		n.a.	Yes		No		n.a.
	8		2		9	11		6		7	47		11		27
<b>Storage</b>	Yes		No		n.a.	Yes		No		n.a.	Yes		No		n.a.
	9		7		3	10		10		4	30		38		17
<b>Distribution of TES technology</b>	Sensible	Latent	Thermochemical	other	n.a.	Sensible	Latent	Thermochemical	other	n.a.	Sensible	Latent	Thermochemical	other	n.a.
	6	0	0	0	7	10	0	0	0	5	27	0	0	1	21
<b>Storage capacity</b>	Available Value		n.a.			Available Value		n.a.			Available Value		n.a.		
	1		18			9		15			27		58		
<b>Total number of plants</b>	19					24					85				

Group Item of analysis	Under construction					Planned				
	<b>Purpose of plants</b>	Commercial	Demonstration		R&D	n.a.	Commercial	Demonstration		R&D
	29	4		1	1	66	8		0	0
<b>Type of technology</b>	PTC	SPT	LFR	PDC	n.a.	PTC	SPT	LFR	PDC	n.a.
	21	5	6	3	0	26	29	6	5	8
<b>Average power of CSP</b>	Available Value		n.a.			Available Value		n.a.		
	31		4			74		0		
<b>Hybridization</b>	Yes		No		n.a.	Yes		No		n.a.
	7		11		17	13		10		51
<b>Storage</b>	Yes		No		n.a.	Yes		No		n.a.
	16		6		13	24		7		43
<b>Distribution of TES technology</b>	Sensible	Latent	Thermochemical	other	n.a.	Sensible	Latent	Thermochemical	other	n.a.
	14	0	0	1	1	19	0	0	0	5
<b>Storage capacity</b>	Available Value		n.a.			Available Value		n.a.		
	13		22			13		61		
<b>Total number of plants</b>	35					74				

Table 3. Summary for TES systems in CSP plants

	Current situation	Future trends
<b>Purpose of plants</b>	- 69 % for commercial production - 13 % for demonstration - 18 % for R&D	- Increased proportion of commercial plants; - Almost stable proportion of demonstrative plants; - No plant specifically for R&D
<b>CSP technology</b>	- SPT and particularly PTC are the most used technologies - PDC is hardly used	- SPT is going to be the most used technology - Increased proportion of PDC
<b>Average power output</b>	- 33 MW <sub>elect</sub>	- Increased average power, 126 MW <sub>elect</sub> for plants in project
<b>Hybridization</b>	- Significant presence of hybridization system (77%)	- Reduced use of hybridization systems
<b>Storage</b>	- 47% of plants have a TES system	- Increased presence (>70%) of TES system
<b>Average storage capacity</b>	- 3 h for the plants built before 2010 - 7 h for the plants built after 2010	- Increased storage capacity till 7.65 hours for planned plants
<b>Type of TES</b>	- Vast majority of sensible storage	- Vast majority of sensible storage

Table 4: Gaseous materials for sensible heat storage

Materials	Operating temperature (°C)	Density (kg.m <sup>-3</sup> )	Thermal conductivity (W.m <sup>-1</sup> .K <sup>-1</sup> )	Energy density (kJ.kg <sup>-1</sup> .K <sup>-1</sup> )	Cost of material
Steam	100-700	0.28 (500°C)	0.067 (500°C)	2.13 (500°C)	low
Air	100-1000	0.441 (500°C)	0.0578 (500°C)	1.098 (500°C)	low

Table 5. Main reactions used in high temperature thermochemical heat storage

Reaction & Phase	Charge/discharge temperature & pressure	Reaction enthalpy & Energy density	Advantages	Disadvantages	Experimental feedback
<b>Hydride system</b> $\text{MgH}_{2(s)} + \Delta\text{H} \leftrightarrow \text{Mg}_{(s)} + \text{H}_{2(g)}$ [89,90] Solid-Gas	926/776 °C  1-100 bar	75 kJ.mol <sup>-1</sup>  580 kWh.m <sup>-3</sup>	<ul style="list-style-type: none"> <li>- Good reversibility</li> <li>- No by-product</li> <li>- Large experimental feedback</li> </ul>	<ul style="list-style-type: none"> <li>- Slow reaction kinetics</li> <li>- High operating pressure (equilibrium at 60 bar and 450°C)</li> <li>- Low heat transfer solid/wall</li> <li>- Sintering</li> <li>- Catalyst needed (Ni or Fe)</li> <li>- H<sub>2</sub> storage</li> </ul>	<ul style="list-style-type: none"> <li>- 3 prototypes of 4 kW at maximal pressure and temperature of 50 bar and 723 K designed and built in Max Plant Institute [90]</li> <li>- More than 1000 cycles achieved with Mg-Ni mixed powder, but a sintering phenomenon occurred [90];</li> <li>- More than 600 cycles without sintering with Mg<sub>2</sub>FeH<sub>6</sub> powder [90]</li> <li>- 20 cycles achieved at 420°C without loss of H<sub>2</sub> and reversibility by adding a particle refinement additive (TiB<sub>2</sub>) along with a thermally conductive additive (ENG) [91]</li> <li>- 60 cycles achieved without any capacity drop with a dual-bed metal hydride system (&gt;1.5 kW) [73]</li> <li>- Economic and exergetic analysis compared to ideal metal hydrides materials [92]</li> </ul>
$\text{TiH}_{2(s)} + \Delta\text{H} \leftrightarrow \text{Ti}_{(s)} + \text{H}_{2(g)}$ [73] Solid-Gas	923-973 °C  1-3 bar	150 kJ.mol <sup>-1</sup>  813 kWh.m <sup>-3</sup> (experimental) 3331 kWh.m <sup>-3</sup> (theoretical)	<ul style="list-style-type: none"> <li>- Good reversibility</li> <li>- High energy density</li> <li>- No catalyst needed</li> <li>- No by-product</li> <li>- Low cost</li> </ul>	<ul style="list-style-type: none"> <li>- H<sub>2</sub> storage</li> <li>- Little experimental feedback</li> </ul>	

Reaction & Phase	Charge/discharge temperature & pressure	Reaction enthalpy & Energy density	Advantages	Disadvantages	Experimental feedback
<b>Carbonate system</b>					
$\text{PbCO}_{3(s)} + \Delta H \leftrightarrow \text{PbO}_{(s)} + \text{CO}_{2(g)}$ [93–95]	996/846 °C 0-10 bar	88 kJ.mol <sup>-1</sup> 303 kWh.m <sup>-3</sup>	- No catalyst needed - No by-product	- Low reversibility - Little experimental feedback - CO <sub>2</sub> storage - Toxicity	- Studied for chemical heat pump applications [93–95] - 7 cycles achieved without capacity drop [51] - A packed bed reactor working at 1143 K and 1 bar built [52]
Solid-Gas					

Reaction & Phase	Charge/discharge temperature & pressure	Reaction enthalpy & Energy density	Advantages	Disadvantages	Experimental feedback
CaCO <sub>3(s)</sub> + ΔH ↔ CaO <sub>(s)</sub> + CO <sub>2(g)</sub> [96–105]  Solid-Gas	1406/1429 °C  0-1 bar	178 kJ.mol <sup>-1</sup>  692 kWh.m <sup>-3</sup>	- High energy density - Availability and low cost of materials - No catalyst needed - No by-product	- Low reversibility - Agglomeration & sintering - Important volume change - CO <sub>2</sub> storage	- Reversibility improved by the use of submicron particles [55] - A fluidized bed in a batch mode, 1.4 kW and a temperature between 873-1573 K. A total conversion of the CaCO <sub>3</sub> reached with a thermal efficiency between 20 and 40% [100] - A continuous rotary kiln, 1.4 kW and a temperature between 873-1573 K. A maximal conversion of 60% reached [100] - An annular continuous fluidized bed reactor developed and demonstrated by Foro [103] - 10 cycles achieved with CaTiO <sub>3</sub> at 1023 K without capacity drop [105] - A solar rotary kiln reactor of 10 kW developed by Meri et al. [59], with a conversion rate of 90-98% and a thermal efficiency of 20%

Reaction & Phase	Charge/discharge temperature & pressure	Reaction enthalpy & Energy density	Advantages	Disadvantages	Experimental feedback
<b>Hydroxide system</b>					
Ca(OH) <sub>2(s)</sub>	996/571-946 °C	104 kJ.mol <sup>-1</sup>	- Good reversibility	- Agglomeration & sintering	- 290 cycles achieved [1]
+ ΔH ↔	0-2 bar	437 kWh.m <sup>-3</sup>	- Low operating pressure (1 bar)	- Important volume change	- with a conversion rate of 95%
CaO <sub>(s)</sub> + H <sub>2</sub> O <sub>(g)</sub>			- Availability and low cost of the product	- Low thermal conductivity	- 50 cycles achieved in a fluidized bed with 70%Al <sub>2</sub> O <sub>3</sub> -B/30%Ca(OH) <sub>2</sub> [123],
[1,106-122]			- Non-toxicity		Dehydration at 480°C and hydration at 350°C
Solid-Gas			- Large experimental feedback		- 20 cycles achieved [71]; better reversibility when air atmosphere was not in contact with the reactant
			- No by-product		- Economic feasibility demonstrated [72-75]
<b>Ammonia system</b>					
NH <sub>4</sub> HSO <sub>4(l)</sub>	1473/973 °C	336 kJ.mol <sup>-1</sup>	- High energy density	- Corrosive product	- Only preliminary studies [124]
+ ΔH ↔	1-2 bar	860 kWh.m <sup>-3</sup>	- High reaction enthalpy	- Toxicity	
NH <sub>3(g)</sub> + H <sub>2</sub> O <sub>(g)</sub> + SO <sub>3(g)</sub>			- No catalyst needed	- No experimental feedback	
[106,124]					
Liquid-Gas					

Reaction & Phase	Charge/discharge temperature & pressure	Reaction enthalpy & Energy density	Advantages	Disadvantages	Experimental feedback
$2\text{NH}_3(\text{g}) + \Delta\text{H} \leftrightarrow \text{N}_2(\text{g}) + 3\text{H}_2(\text{g})$ [106], [125-130] Gas-Gas	996 °C 10-300 bar	$66,9 \text{ kJ.mol}^{-1}$ (charge) $53 \text{ kJ.mol}^{-1}$ (discharge) $745 \text{ kWh.m}^{-3}$	<ul style="list-style-type: none"> <li>- High energy density</li> <li>- low cost of the product</li> <li>- Large experimental feedback</li> <li>- No side reaction</li> </ul>	<ul style="list-style-type: none"> <li>- High operating pressure (80-200 bars)</li> <li>- Low reversibility</li> <li>- Catalyst needed (Fe/Co)</li> <li>- H<sub>2</sub> and N<sub>2</sub> storage</li> </ul>	<ul style="list-style-type: none"> <li>- First solar driven high pressure ammonia reactor of 1 kW tested in a closed loop system [82]</li> <li>- Scale-up of the first solar driven ammonia reactor in order to receive 15 kW from a dish system [125]</li> <li>- A closed loop system composed of a solar reactor of 15 kW for the dissociation and a 10 kW reactor for the synthesis built for continuously operation during 24h [129]</li> </ul>
<b>REDOX system</b> $2\text{Co}_3\text{O}_4(\text{s}) + \Delta\text{H} \leftrightarrow 6\text{CoO}(\text{s}) + \text{O}_2(\text{g})$ [131,132] Solid-gas	1416-1446 °C 0-1 bar	$205 \text{ kJ.mol}^{-1}$ $295 \text{ kWh.m}^{-3}$	<ul style="list-style-type: none"> <li>- Good reversibility</li> <li>- High reaction enthalpy</li> <li>- No catalyst needed</li> <li>- No by-product</li> </ul>	<ul style="list-style-type: none"> <li>- Cost of CH<sub>4</sub></li> <li>- Toxicity</li> <li>- O<sub>2</sub> storage</li> <li>- Little experimental feedback</li> </ul>	<ul style="list-style-type: none"> <li>- 500 cycles achieved in a packed bed reactor with a progressive magnification of the particles during the cycles [14]</li> <li>- 30 cycles achieved with a solar power of 22 kW in a rotary kiln [133]</li> <li>- Several cycles achieved in a ceramic honeycomb structure with 100% reversibility [134]</li> </ul>

Reaction & Phase	Charge/discharge temperature & pressure	Reaction enthalpy & Energy density	Advantages	Disadvantages	Experimental feedback
2BaO <sub>2(s)</sub> + ΔH ↔	1236-1326 °C	77 kJ.mol <sup>-1</sup>	- Low operating pressure (0-10 bars)	- Low reversibility - Little experimental feedback	- Only equilibrium or kinetic study [122,135]
2BaO <sub>(s)</sub> + O <sub>2(g)</sub> [122,135]	0-10 bar	328 kWh.m <sup>-3</sup>	- No catalyst needed - No side reactions	- O <sub>2</sub> storage	
<b>Solid-gas</b>					
<b>Organic system</b>					
CH <sub>4(g)</sub> + H <sub>2</sub> O <sub>(g)</sub> + ΔH ↔ 3H <sub>2(g)</sub> + CO <sub>(g)</sub> [136-139]	1496/1076 °C 20-150 bar	250 kJ.mol <sup>-1</sup> 7.8 kWh.m <sup>-3</sup>	- High reaction enthalpy - Large experimental and industrial feedback (for the transport of thermal energy)	- Side reaction - Low reversibility - Cost of CH <sub>4</sub> - Catalyst needed - H <sub>2</sub> storage	- Studies for the transport of thermal energy [93-94]
<b>Gas-Gas</b>					
CH <sub>4(g)</sub> + CO <sub>2(g)</sub> + ΔH ↔ 2H <sub>2(g)</sub> + 2CO <sub>(g)</sub> [136,138,140-142]	1496/1076 °C 3.5 bar	247 kJ.mol <sup>-1</sup> 7.7 kWh.m <sup>-3</sup>	- High reaction enthalpy - Large experimental and industrial feedback	- Side reaction - Low reversibility - Cost of CH <sub>4</sub> - Catalyst needed (Ni-based or Ru-based) - H <sub>2</sub> storage	- Technical-economic survey realized for the production of 100 MWe [141] - A solar reactor of 300 kW developed by DLR; problems of catalyst deactivation observed [142]
<b>Gas-Gas</b>					
C <sub>6</sub> H <sub>12(l)</sub> + ΔH ↔ C <sub>6</sub> H <sub>6(g)</sub> + 3H <sub>2(g)</sub> [106,139,143]	863/943 °C 1-70 bar	206 kJ.mol <sup>-1</sup> 530 kWh.m <sup>-3</sup>	- High reaction enthalpy	- Low reversibility - Side reaction - Catalyst needed - Toxicity - H <sub>2</sub> storage	- Only simulation work [96-98]
<b>Liquid-Gas</b>					
SO <sub>3(l)</sub> + ΔH ↔ SO <sub>2(g)</sub> + ½.O <sub>2(g)</sub> [106,144]	1346-1546/1046-1146 °C 1-5 bar	98 kJ.mol <sup>-1</sup> 646 kWh.m <sup>-3</sup>	- High energy density - Industrial feedback	- Corrosive product - Toxicity - Catalyst needed - O <sub>2</sub> storage	- Only simulation work [144]
<b>Liquid-Gas</b>					

Table 6. Summary for different TES technologies

Technology	Cost	Energy density	Occupied area	Temperature for material storage	Technology feedback	Flexibility charge/dischARGE	Heat transfer	Advantages	Disadvantages
Sensible	Low cost materials	Low	High	High	- Large experimental feedback - Majority of CSP plants in operation	Switch within a short time	Quite good	- Large experimental and commercial feedback - Easy implementation	- Heat losses during storage - Low energy density



									- High freezing point for liquid materials - Variable discharging temperature
Latent	Low cost materials	Medium	Medium	High	- More R&D work needed	Switch within a short time	Slow Low thermal conductivity	- Constant charge/discharge temperature - Medium energy density	- Low thermal conductivity - Solid deposits on the PCM/heat exchanger area
Thermochemical	Low cost materials High design and installation costs for the reactor	High	Low	Low (ambient temperature)	- No feedback	Switch within a medium time	Slow Low thermal conductivity	- Possibility to store energy during a long period without heat losses - High energy density	- Incomplete reversibility - Storage of gaseous products - Necessity of heat & mass transfer enhancement

Table 7. Different concepts for TES integration, their advantages and disadvantages

Concept	Principle	Storage materials	Example of integration	Advantages	Disadvantages
<b>Active direct</b>	HTF used in the solar field is also used as storage material	- Molten salts - Steam	Two tanks system (Figure 6a): the HTF is directly stored in a hot tank at the exit of the solar receiver or in a cold tank at the entrance of solar receiver	- No need of heat exchanger between the HTF and the storage material - Separate storage of hot and cold materials	- Possible freezing of molten salts (120-220°C) - High cost of molten salts - Low energy density of steam
<b>Active indirect</b>	Heat transfer between HTF and storage materials via a heat exchanger	- Molten salts - Steam - Solids	- Two tanks (Figure 6b) for separate storage of hot and cold materials  - Single tank (Figure 6c) to store hot and cold fluids, separated by temperature stratification.	- Separate storage of hot and cold materials  - Relatively low cost due to the use of only one tank and low cost filler materials (e.g. quartzite rock and sand)	- Possible freezing of molten salts (120-220°C) - High cost of molten salts  - Difficulty in maintaining the thermal stratification - Complex design and control of the thermocline

<b>Passive</b>	HTF circulates through the TES to heat up or cool down the storage materials while the latter do not move	- Concrete - rocks - Sands - PCMs - Thermochemical materials	- Shell-and-tube type heat exchanger for the TES system (Figure 6d)	- Low cost of the materials - Simple and compact storage unit - Possible high heat transfer rates	- Cold and hot materials not separated - Possible varying discharge temperature
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Table 8. New concepts for TES integration in CSP plants

Project	Type of storage & concept	Temperature & Pressure	Description	Advantages	Disadvantages
Distor [156]	Latent	230-330 °C	- Intermediate HTF between the principle HTF and the TES (KNO <sub>3</sub> -NaNO <sub>3</sub> )	- Reduced HTF pressure in the heat exchanger	- Intermediate HTF and an extra heat exchanger needed - Increase the inertia of the system
	Passive	30-100 bar			
Cascade latent heat storage system (CLHS) [150]	Latent	290-390 °C	. Cascade of multiple phase change materials with different temperature of phase change (Figure 10)	- Higher utilization of the possible phase change - A more uniform outlet temperature over time	- Complicated final design - Low thermal conductivity of PCMs
	Passive	n.a.			
Three-part storage system for direct steam generation (DSG) [148]	Latent-sensible	295-400 °C	- 2 sensible storage modules (concrete) used for preheating and superheating, a PCM storage module used for evaporate/condensate the HTF (Figure 8)	- Compact storage system adapted for DSG	- 3 storage modules used
	Passive	80-127 bar			
Reflux heat transfer storage (RHTS) [157]	Latent	350-400 °C	- TES system composed of a HTF, a block of PCM with crossing channels, one heat exchanger at the bottom (charge) and one heat exchanger at the top (discharge)	- Good heat transfer due to the two-phase HTF and the proper design of the storage system - Good stability and reversibility with alloy-Zn70Sn30 as PCM	- Complicated design for storage unit - High cost of the PCM
	Passive	n.a.			
Hybrid storage system integrating a packed bed thermocline tank and a two tank storage system [158]	Sensible	290-500°C	- TES composed of 2 systems: one big thermocline tank and tow small tanks	- Cost reduction compared with classic two tanks storage - Continuous steady power generation of the plant - Avoiding degradations of the thermocline system due to frequent charge/discharge	- Regulation of complex charge and discharge phases
	Passive – Active-Indirect	n.a			
Heat transfer and latent heat storage in inorganic molten salts for concentrating solar power plants [159]	Latent-sensible	550 °C	- Biphasic thermocline concept where the molten salt used to store heat is also a HTF between the solar receiver and the power cycle	- Constant temperature in the power block boiler - Use of latent and sensible energy to increase thermal capacity of the TES	- Solidification of the salt on heat exchanger surfaces - Intelligent control needed to avoid complete solidification of the PCMs
	Active-Indirect	n.a.			

Project	Type of storage & concept	Temperature & Pressure	Description	Advantages	Disadvantages
Combined sensible-latent heat for thermal energy storage at 575°C and above [149,160]	Latent-sensible	575°C  n.a.	- Thermocline composed of encapsulated PCM on the top and sedimentary rocks on the bottom	- Higher and more steady temperature of the HTF outgoing from the TES tank	- complicated design for the storage unit
A Solar Energy System [151] (Figure 11)	Sensible (molten salt, concrete, rock)	200-600 °C (Depending on materials)	- DSG for SPT or PTC - Storage unit composed of several blocks - Steam can pass through one or several blocs depending of its temperature	- Reduce the inertia of the TES system - No evaporator for the power bloc	- Presence of two phase water in the cycle - Design of the solar receptor for evaporation of the HTF (not only to heat it)
	Passive	n.a.			- Possible solidification of HTF - Mechanical process to bring the solid HTF to the solar receiver - Complex design of the solar receiver
Concentrating Solar Power Methods and Systems with Liquid-Solid Phase Change Material for Heat Transfer [152]	Latent (salts, organic and inorganic polymers, metals)	200-600 °C (Depending on materials)  n.a.	- Use of a solid-liquid PCM as HTF and storage medium - PCM is melt in the solar receiver and a part is store in a tank - The solid PCM at the boiler exit need to be brought to the solar receiver by a mechanical process to be liquefied	- High heat transfer rate in the evaporator	- Possible solidification of HTF - Mechanical process to bring the solid HTF to the solar receiver - Complex design of the solar receiver
	Active-Indirect				
Thermochemical storage system with improved storage efficiency [161]	Thermochemical	200-600 °C (Depending on materials)	- TES system composed of 2 reactors in series with 2 different reactants (different range of reaction temperature) - The HTF passes successively through either the first or second reactor and subsequently through the other reactor	- Heat storage within a wide range of temperature	- Realization of at least two thermochemical reactors with two tanks for the storage of the reactions products
	Passive	n.a.			
Fluidized-bed technology for thermal energy conversion and solid particles for TES [154][155]	Sensible	> 600 °C	- HTF and storage media replaced by solid particles moved by a bucket lifter system.	- No risk of fluid freezing - Low cost equipments, HTF and energy storage media - Good stability at high temperature (>1000°C)	- Development of a particles receiver -Development of a heat exchanger for particles - Few experimental feedback
	Active direct				
Chemical looping fluidized-bed concentrating solar power system and method [153]	Thermochemical	500-1500 °C (in the solar receiver)	- Reduction reaction in the solar receiver - A first storage container store solid state particles produced by the reduction reaction - Boiler configured to combine solid state particles and gas through an oxidation reaction - Mechanical process to bring oxidized material to the solar receiver	- High storage energy density - HTF serves as the storage material	- Complex design of the solar receiver/reactor - Storage of the gaseous products - Mechanical process to bring the chemical materials to the solar receiver
	Active direct	n.a.			
Solar thermochemical processing system and method [162]	Thermochemical	800 °C in the first unit; 250 °C in the second unit	- First thermochemical reaction in the solar receiver; Second thermochemical reaction in a second reactor - A part of the second reaction products are stored and the second part serves as HTF	- HTF serves as the storage material	- 4 tanks for the storage of reactants and products - Control of chemical reactions to avoid side reactions
	Active direct	50-100 bar			

<b>Project</b>	<b>Type of storage &amp; concept</b>	<b>Temperature &amp; Pressure</b>	<b>Description</b>	<b>Advantages</b>	<b>Disadvantages</b>
Coupled chemical-thermal solar power system and method [147]	Sensible-thermochemical Active direct	1400 °C (in the power bloc) n.a.	- Two pathway (thermal and thermochemical) to transfer energy from the receiver to the power cycle (boiler)(Figure 7)	- Very high temperature in the power cycle, higher than with classical HTF (e.g., oil, molten salt, steam)	- Complex design with a solar receiver which is at the same time a thermochemical reactor and a heater for the thermal pathway HTF - 4 tanks needed to store Hot HTF, cold HTF, reduced reactants and oxidized reactions