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Storage of thermal solar energy



Stockage thermique de l'énergie solaire

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ABSTRACT

Solar thermal energy storage is used in many applications, from building to concentrating solar power plants and industry. The temperature levels encountered range from ambient temperature to more than 1000 °C, and operating times range from a few hours to several months. This paper reviews different types of solar thermal energy storage (sensible heat, latent heat, and thermochemical storage) for low- (40–120 °C) and medium-to-high-temperature (120–1000 °C) applications.

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RÉSUMÉ

Le stockage thermique de l'énergie solaire touche de très nombreuses applications, qui vont du bâtiment aux centrales solaires à concentration en passant par l'industrie. Les niveaux de température rencontrés vont de la température ambiante à plus d'un millier de degrés, et les durées d'utilisation de quelques heures à plusieurs mois. Cet article passe en revue les différentes familles de stockage d'énergie solaire thermique (stockage sensible,

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latent et thermochimique), pour des applications à basses (40–120 °C) et moyennes–hautes températures (120–1000 °C).

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1. Introduction

Solar energy is available throughout the world and is sufficient to satisfy all human energy demand. However, it is diluted and intermittent. Therefore, energy storage systems must be associated with solar energy capturing to cover energy needs. Among all the different energy storage systems (pumped storage hydropower, compressed air energy storage, flywheel energy storage, electrochemical energy storage, capacitors, hydrogen storage, power to gas, etc.), thermal energy storage is one of the least expensive systems that can be applied to a broad spectrum of applications such as electricity production (using concentrated thermodynamic solar plants), industrial applications (chemical industry, food industry, etc.) and building applications (district heating, domestic hot water, thermal comfort, etc.). Different techniques are used for thermal energy storage. The most widely used is the sensible heat storage method. Other techniques such as latent energy storage and thermochemical energy storage have appeared in the last two decades, offering great heat storage capacity and reduced heat loss during the storage period. New material involving phase change and chemical reactions (peritectic compounds) appear to be promising given their great heat storage capacity.

Sensible heat storage consists in accumulating thermal energy in a solid or a liquid medium whose temperature then rises. For a given temperature elevation, a material's greater heat capacity will result in a larger amount of energy being stored (Eq. (1)).

$$Q = \int_{T_1}^{T_2} \int_V \rho c dT dV \quad (1)$$

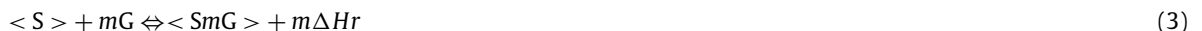
Water has a particularly high heat capacity (about 4180 kJ·m⁻³·K⁻¹), but is limited to applications under 100 °C unless pressure is increased. The heat capacity of most materials used for sensible heat storage varies between 900 and 3000 kJ·m⁻³·K⁻¹. The thermal conductivity of such materials is also limited, ranging from 0.5 to 4 W·m⁻¹·K⁻¹ [1]. Two major applications of sensible heat storage deserve to be discussed further: storage for district heating networks and storage for solar power plants.

Latent heat storage involves the heat absorbed or released when a material changes from one physical state to another (when it is submitted to a phase change) and the sensible heat according to Eq. (2):

$$Q = \int_{T_1}^{T_F} \int_{V_s} \rho_S c_S dT dV + \int_{V_s} \rho_S L_F dV + \int_{T_F}^{T_2} \int_{V_1} \rho_1 c_1 dT \quad (2)$$

Different phase changes can be encountered: solid ↔ solid, solid ↔ liquid, solid ↔ gas, and liquid ↔ gas. Latent heat storage mainly involves solid–liquid transformations of a material called a phase-change material (PCM). Over the last few years, various review papers [2–7] have presented the available latent thermal energy storage technologies and the current research in this field, focusing mainly on the assessment of the thermal properties of the various PCMs used. Moreover, the design of a cost-effective latent heat-storage system requires the development of thermal performance enhancement techniques. For example, this consists in enhancing heat transfers using mostly high-conductive materials, extended heat transfer surface, intermediate heat transfer medium, or multiple PCMs. Other constraints, such as liquid–solid transition, which sometimes exhibits a supercooling phenomenon, and the development of reliable numerical models, remain a challenge from a scientific point of view. The first one, if it exists, can cause system-wide performance downgrade and must also be considered. The second is necessary to optimize and estimate the thermal energy performance of systems.

Thermochemical thermal heat-storage systems can involve various processes: a sorption process, which consists in the fixation or the capture of a reactive gas by a condensed substance (either a solid – the process is called adsorption – or a liquid – the process is called absorption) or a chemical reaction, as described by Eq. (3).



Thermochemical thermal storages are promising given their high-energy densities and the low thermal loss between the storage and recovery steps, because energy is stored as chemical potential. In terms of the whole system, thermochemical storage requires the management of two materials in two different components: the sorbent (solid in a reactor or an adsorber/desorber; liquid in an absorber/desorber) and the active gas (in an evaporator/condenser) rendering the system more complex. The challenge is to take advantage of this complexity: first, it adds degrees of freedom for the management

Nomenclature

<i>Latin</i>		<i>V</i>	volume	m^3
<i>C</i>	heat capacity.....	$\text{J}\cdot\text{kg}^{-1}\cdot\text{K}^{-1}$	<i>Greek symbols</i>	
<i>(G)</i>	reactive gas		ρ	density
<i>L</i>	latent heat	$\text{J}\cdot\text{kg}^{-1}$	ΔH_r	reaction enthalpy
<i>m</i>	stoichiometric coefficient			$\text{J}\cdot\text{mol}^{-1}$ of reactive gas
<i>Q</i>	heat	J	<i>Subscript</i>	
<i>< S ></i>	reactive solid		<i>l</i>	liquid
<i>T</i>	temperature.....	$^{\circ}\text{C}$	<i>s</i>	solid

of its thermal power (by controlling the operating pressure and temperature of both components). Second, in addition to the heat storage function, it allows cold production or heat upgrading by relevantly managing the endothermal and exothermal workings of all the components (reactor or absorber/desorber and evapo/condenser) in both the storage and de-storage steps [8–10]. The absorption heat storage technology involving liquids is still in its early stages of development. Absorption storage technology for long-term solar heat storage was suggested as early as 1981 [11] – 1982 [12] for space heating –, but its actual development and prototype tests have only recently been undertaken in research laboratories [13]. The energy density of the reactive solution typically ranges from 100 to 200 $\text{kWh}\cdot\text{m}^{-3}$. Its main advantage is the storage of the sorbent and the sorbat in specific tanks, and their transport to the reactor using pumps.

Thermochemical processes based on solid/gas reactions can reach energy densities from 200 to 500 $\text{kWh}\cdot\text{m}^{-3}$ of porous reactive solid and operate in a wide range of temperatures (80–1000 $^{\circ}\text{C}$ according to the reactive pair). Such thermochemical systems are being investigated for storage purposes in a large set of applications and temperatures, from space heating [14] to concentrated solar plants [15,16]. A great deal of research has examined the characterization and control of heat and mass transfer in porous reactive material [17–19]. Pilot plants up to a significant scale have been experimented [16,14]. Regarding commercial products, some of them have existed for approximately 15 years for the transportation of temperature-sensitive products in the health and food domains.

This paper presents an overview of low-, and medium-to-high-temperature heat-storage systems devoted to solar applications that are under development to address the challenges of energy transition. Considering the main techniques used, medium- and high-temperature systems are presented separately from low-temperature systems. The performance of the different systems as well as the scientific challenge associated with their development are based on the results obtained by nine different laboratories belonging to the French CNRS federation on solar energy (FedEsol federation) using specific prototypes and setups.

2. Low-temperature thermal heat storage

2.1. Main applications

In Europe, 26% of the final energy consumption is related to household energy systems [20] and 80% of this energy is needed for heating purposes [21]. In this context, thermal energy storage is a solution to rationalize the use of energy by increasing the solar fraction in buildings [22,23]. Space heating and cooling as well as domestic hot water production are key applications in this sector. In the general context of energy transition, buildings will have to consume less and less energy for economic and environmental reasons and must evolve into positive-energy buildings: they will become energy producers, but consume low levels of energy. The solar energy received by buildings over one year covers their annual energy needs. However, although the peak of solar irradiation occurs during the summer when the cooling demand is high, the heating demand occurs during the winter when solar irradiation is low and sometimes nearly inexistent for several days. Thermal storage systems are therefore needed to match supply with demand. The most widely used techniques for thermal energy storage involve hot water tanks and the thermal inertia of buildings. These techniques make it possible to use the heat produced during sunny days to cover the heating needs during the night and peak demands related to domestic hot water use. Such systems are efficient during spring and autumn, but are not able to cover the energy needs during winter at the individual scale. Other heat-storage systems must be included to increase the storing capacities of single-family houses. Large-scale heat storage is another great problem. For a given temperature condition, the reduction of the external surface/volume ratio with the increase of heat-storage systems as well as the reduction of the storing capacities with the increase in the number of users is favorable to the development of large-scale heat-storage systems associated with district heating. Low-temperature heat-storage systems are not very widespread in industry. Some solar cooling systems, involving water tank PCMs or thermochemical cold storage have appeared for telecommunications, food, and medical applications.

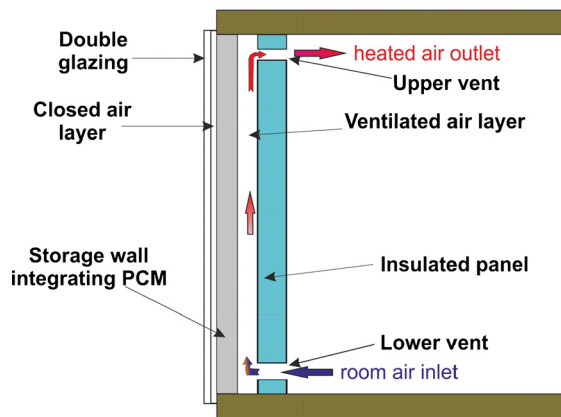


Fig. 1. Diagram of composite solar wall.

2.2. Sensible heat storage

Low-temperature sensible heat storage mainly concerns solar water heaters for domestic hot water applications at the individual scale, and district heating at the large scale. Solar thermal systems are relatively complex, involving major drawbacks such as cost, storage tank location requirements and technical maintenance. The development of passive solar systems is clearly a very interesting strategy. In this context, the new concept of integral collector storage with heat pipes (thermal diode) and a fully insulated storage cavity is a very promising research field. One of the objectives is to improve architectural integration by reducing the system's weight and storage thickness. Both water storage [24] and PCMs [25] have been considered. Similar energy performance can be obtained with simpler systems.

Two million apartments and houses are currently connected to a district heating network in France. The corresponding energy is as high as 20 TWh per year. Storing heat locally, quite close to each building, would allow a smaller time response from the heat management controlling system as well as increased comfort for the consumer. A sensible storage strategy already exists, involving huge water towers (1000 m³ in Brest and up to 200,000 m³ in Vojens, Denmark, in a huge water pit, heated by solar energy during the summer season). The latter examples can be considered as interseasonal heat storage. Geothermal heat-storage systems (GHSSs) have good prospects for the massive storage of low-temperature solar thermal energy [26]. Depending on the underground conditions (native rock, clay, gravel) and the depth of the water table, the GHSS can consist of a cluster of boreholes (a few tens of meters to approximately 100 m in height), or an insulated volume a few meters in height. A GHSS may or may not include heat pumps depending on the storage temperature [27].

2.3. Latent heat storage

PCMs in building construction have been developed for about 10 years to increase the thermal inertia of walls or to increase the compactness of solar domestic hot water storage systems. This is particularly advantageous when, for space reasons, traditional solutions employing sensible heat cannot be used, such as in composite solar walls equipped with heat storage (Fig. 1). Solar walls allow buildings to be provided with free and renewable energy. They ensure a minimum of comfort, maintain sufficient ambient temperatures, and thus avoid condensation problems, which is a source of molds, compromising the health of the occupants and the durability of the building. Standard storage walls are made of concrete blocks; the stored energy is in this case only sensible [28].

PCMs can be integrated into the wall to store more energy in the same storage volume: a 2.5-cm-hydrated salt PCMs can store as much energy as a 15-cm concrete wall [29]. However, certain constraints are encountered using salt PCMs, such as segregation phenomena. PCMs must be protected from excessively high temperatures to avoid their thermal degradation. Hence, safety roller shutters must be installed to prevent overheating. Energy management can take advantage of this component using closed shutters during the night to limit thermal losses to the outside or stop heat contributions during the summer periods [30]. An alternative solution proposed is the use of a composite material composed of a microencapsulated PCM integrated into a building material (cement mortar) rather than using a polyolefin container filled with a PCM.

The phase change phenomena are complex and make modeling dynamic thermal transfers difficult. To carry out numerical simulations that are faithful to the thermal behavior of the composite material (mortar cement + microencapsulated PCM), it is essential to characterize the thermophysical properties of the composite material and to develop an adapted numerical model. The numerical model implemented is based on the derivative of the intrinsic enthalpy curve of the composite material. The thermophysical properties of the composite material are estimated from experimental data obtained from an original device [31,32] coupled with identification methods [33], [34]. Modeling shows that in the thermal operating ranges of the solar wall, mortar containing 20% PCM stores 41% more energy than a conventional mortar [32–34].

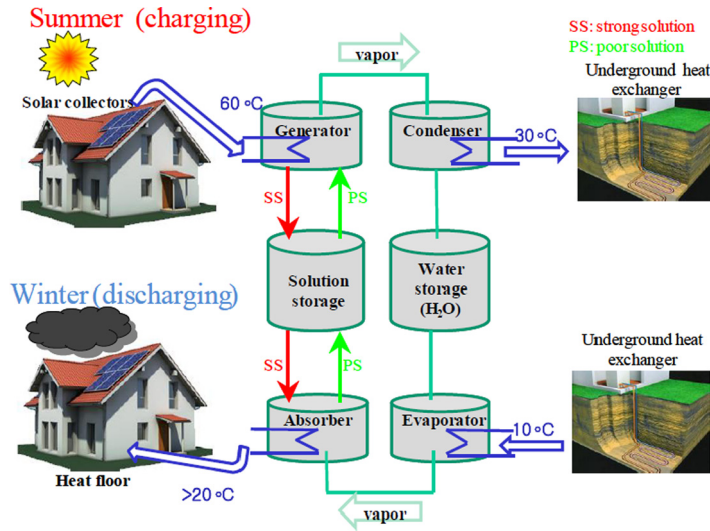


Fig. 2. Functioning principle of the interseasonal absorption heat storage process, with water as the sorbate.

2.4. Absorption heat storage

Absorption technology is an interesting possibility to store space heating in solar buildings, because it allows storing excess heat available during the summer until the following winter. Its operating conditions are compatible with the use of conventional solar heat collectors. The absorption heat-storage system includes the same components as the well-known absorption chiller, to which two or three storage tanks must be added (Fig. 2) [35].

During the charging phase (desorption), the poor solution (with a low mass fraction of sorbent) in the solution storage is pumped to the generator/desorber, where it is heated by a solar flat plate collector. The absorbate in the solution can be endothermically desorbed and transferred to the condenser, where its latent heat is released to the surroundings. The condensed absorbate flows to its tank, where it can be stored. The rich solution (with a high mass fraction of sorbent), which is produced in the generator, flows back to the solution tank. During the inert storage period, the liquid solution and absorbate are kept in their respective tanks. The different connection valves are closed, so no mass transfer occurs during this phase. The chemical potential of the system is thus preserved during this phase. During the discharging phase (absorption), the absorbate is circulated from the absorbate storage to the evaporator, where it is vaporized by low-temperature heat from the surroundings. The absorbate is then absorbed by the rich solution, which is circulated into the absorber. Heat is released and this production meets the needs for building heating. The poor solution flows back to the solution tank.

The current development of the absorption technology for long-term low-temperature heat storage purposes is still at the research stage. The main advantages of this technology are the high heat storage capacity and the possibility of storing heat over long periods [36]. At the research and development level, theoretical, modeling and experimental research has been conducted by different teams. Three different prototypes using LiBr/H₂O and CaCl₂/H₂O as the absorption couples have been designed and tested at the LOCIE. The latter uses the LiBr/H₂O absorption couple and flat plate exchangers. The desorption heat is provided by solar collectors (at about 90 °C). Water vapor absorption during the winter allows low-temperature household heating at up to 35 °C. The theoretical energy density of the solution is 330 kWh·m⁻³. The useful material energy density is 120 kWh·m⁻³ in interseasonal operating mode. The released specific energy density is 66 kWh·m⁻³ of the small size prototype (not optimized) in interseasonal operating mode. The results obtained are encouraging, but the technology must still solve the significant scientific, technical, and financial challenges, at both the micro- and macro-scale levels, before it can be marketed.

A major issue in the development of this technology is the definition and choice of the ideal absorption couple. Research continues in an attempt to find unhazardous and low-cost sorbent materials with long-term stability under the system's operating conditions, while presenting a sufficiently high heat storage capacity to make the system profitable. Moreover, heat and mass exchanger design problems persist, for example wetting and distribution issues, which must be overcome to reach acceptable system efficiency. In most cases, components must be designed to operate in vacuum conditions, which changes the usual dimensioning rules used for engineering purposes. These rules remain to be developed at the research level and then integrated by the engineering community. Various prototypes have been developed to study the performance of absorption systems at the macro-scale level. Most of them achieved temperatures suitable for space heating and some even reached temperatures high enough for domestic hot water production.

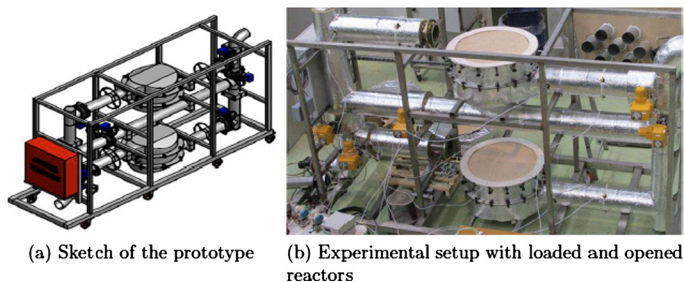


Fig. 3. Experimental adsorption setup using the zeolite 13X as storage media.

2.5. Adsorption and solid/gas reaction heat storages

Solid/gas physisorption and chemisorption provide valuable perspectives for long-term low-temperature building heat storage. One of their advantages compared to absorption processes is their ability to be used in an open heat-storage system. The thermal energy storage system is then integrated into the building's ventilation system. During desorption, the air coming from the building or from the outside is heated using a heat source such as solar air collector panels [37] or electrical heaters, provided that the dehydration temperature is reached. During sorption, moist air is extracted from the building and passes through the reactor. The hot airflow leaving the reactor is used to heat cool air.

A real-scale open heat-storage system based on zeolite 13X made of two separate reactors that can be connected in a serial or parallel configuration to test the advantages and limitations of each configuration, has been designed and tested at CETHIL. Each reactor is a 72-cm-diameter cylinder, with a 20-cm bed thickness. Moist air flows vertically inside the reactor. A sketch of the prototype and a picture of the experimental setup are presented in Fig. 3. The reactors are filled with Faujasite zeolite 86 Na – X (Alfa Aesar, 13X, beads 1.6–2.5 mm).

The plan of experiments has been developed to address, with a minimum of tests, the influence of the desorption temperature (120 °C vs. 180 °C), the air flow rate (180 m³·h⁻¹ vs. 90 m³·h⁻¹ vs. 60 m³·h⁻¹), relative humidity in discharging mode (50% vs. 70%), bed thickness (20 cm vs. 10 cm) and the serial/parallel configurations. The main results are the following: the released heating power is 27.5 W·kg⁻¹ or 4.5 kW·m⁻³ for the prototype. The released specific energy density is 0.2 kWh·kg⁻³ or 33 kWh·m⁻³ for the prototype. It is worth mentioning that the material energy density is 180 kWh·m⁻³. More information on how the temperature evolves during the tests can be found in Johannes et al. [38].

A second type of seasonal thermochemical storage process has been built and experimented at PROMES [14]: it is based on a solid–gas reaction involving an environmentally friendly water-based reactive pair, i.e. SrBr₂/H₂O. For the sake of compactness and cost, this system has been designed as an open system, i.e. it operates with moist air, as described for the previous zeolite storage system. The hydration reaction enthalpy allows heating the air flow up to 35 °C. The thermal power during the de-storage step is highly dependent on the gap between the operating and the thermodynamic equilibrium temperatures of the reactive pair. This interseasonal application involves large amounts of stored energy, but it only requires very low specific power (W/kg) because the reaction time is basically very long (up to a whole season). The prototype was designed for approximately one-tenth of the heating demand of a typical house, and a reaction time of 12 days, with 400 kg of reactive salt. The energy density of the reactive salt bed is 390 kWh·m⁻³, and 190 kWh·m⁻³ when related to the whole volume of the reactor (non-optimized). This system could be considered as a part of a modular full interseasonal storage or a storage system dedicated to peak demand periods. This experiment demonstrated the feasibility and performance of such storage and outlined the need for deep optimization of the reactor, including heat and mass diffuser networks [39], to enhance the overall energy density.

2.6. Comparison

To compare the different heat storage technologies, common key performance indicators (efficiency, compactness, economic criteria, life-cycle assessment, etc.) as well as classes of operating conditions must be defined. The problem is complex and there is currently no consensus on this subject. Nevertheless, a rough comparison based on the results obtained with five different heat storage prototypes (sensible (SEN), PCMs, absorption (ABS), physical adsorption (PAD) and chemical reaction (CR) heat-storage systems) is proposed. The systems are used for interseasonal heat storage applications for buildings. The following hypotheses are considered: the energy needs of the low-consumption single-family home covered by the heat-storage system are 2000 kWh. The thermal loading of the systems occurs from May to mid-September. Then, solar energy is used for domestic hot water production. The heat-storage system provides heat from mid-October to mid-March to the family home following a sinus law. The temperature needed by the heating system is 30 °C. The sensible and PCM tanks are insulated with a 30-cm-thick polystyrene wall. The tanks used in the sorption heat-storage systems are not insulated (the sensible part of the energy is lost). Fig. 4 compares the energy density of the active material (sensible material, PCM, absorption solution, solid adsorbents, solid reactant) and the useful energy density of the heat-storage systems (ratio of the energy used to heat the single-family home over the volume of the system).

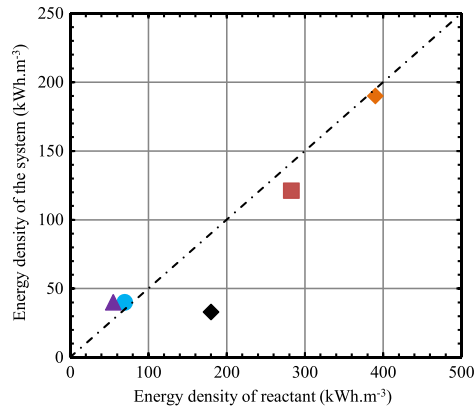


Fig. 4. Energy density of the systems compared with energy density of the reactants. ●: SEN ($\Delta T = 60^\circ\text{C}$); ▲: PCM ($\Delta T = 20^\circ\text{C}$); ◆: PAD; ◆: CR; ■: ABS.

The volumes of the sensible hot water and the PCM tank are comparable (50 m^3). Heat losses generated by the sensible heat-storage system are very high and correspond to about 43% of the total energy stored. The heat loss generated by the PCM tank are twice as low as that obtained with sensible heat and corresponds to about one-third of the energy stored during the summer. The first results obtained with the physical adsorption system leads to a system volume of about 60 m^3 , which is too large for a single-family home. System volumes for absorption and chemical reaction are equal to 16 and 10 m^3 , respectively, which begins to be feasible for a single-family home. As the figure shows, the energy density included in the active material is about twice as high as the useful energy density of the heat-storage systems. This difference can be reduced by optimizing the design of the system and limiting heat loss, which also affects the sorption systems. Finally, the necessary one-third gain in compactness should be obtained by working on these aspects. When prototypes have been developed at a nearly commercial scale, additional economic considerations related to the system's lifetime and operation as well as maintenance costs should be included, with the aim of defining and evaluating a business case.

3. Medium- and high-temperature thermal heat storage

3.1. Main application

At high temperatures, the applications for thermal energy storage from solar energy mainly involve electricity generation by thermodynamic cycles concentrating solar power (CSP). The objectives are:

- for short-term storage (30 min), to maintain electricity production for partly cloudy periods, so that the storage plays the role of regulating the incoming energy to the turbine by providing a thermal buffer and then preventing nonstationary solar production due to weather conditions;
- for medium-term storage (a few hours), to extend the production to the nighttime when the home electricity demand peaks, or to maximize the financial income to produce only during peak hours.

Depending on the solar collector technology, different operating temperatures can be obtained: from 200 to 500°C with solar Fresnel and for parabolic collectors and above 600°C with heliostat field collector technology [40]. Energy conversion is then operated using a steam turbine or the Organic Rankine Cycle (ORC) system. Industrial applications for high-temperature thermal storage account for less than 1% of the application from solar energy [41]. Sensible, latent, or chemical systems are the three types of heat storage in decreasing order of technological readiness and increasing energy density. Eighty percent of thermal storage in CSP is designed with two tanks able to contain cold or hot molten salt. Research has been conducted on one thermocline tank as well as the use of PCMs to stabilize the outflow temperature (in packed bed thermal storage) [42].

3.2. Sensible heat storage

Two types of Thermal Energy Storage (TES) should be considered: active and passive systems Py and Olives [43]. In the active system, the storage system is often composed of two tanks, one for the coldest fractions of the storage media and the other for the warmest fraction. The storage media is a fluid within the range of temperature considered, and is also used as a heat transfer fluid (HTF). It can flow through heat exchangers to transfer heat during the charging and discharging steps. Fig. 5 presents the principle of the two-tank storage system.

The essential current industrial technology is based on the two-tank molten-salt systems used in the chemistry and metallurgy industries and in concentrated solar power plants (CSPs) such as Themis in the 1980s and Andasol and Gemasolar

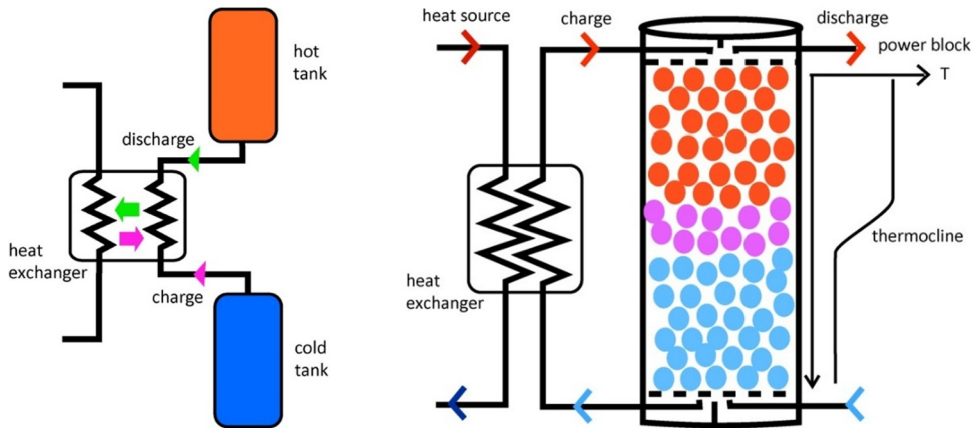


Fig. 5. Sensible heat-storage system principle: a) two-tank storage system; b) single-tank thermocline-based TES integrated into a CSP plant.

today [44,45]. For example, in the Andasol CSP, the TES absorbs a part of the heat produced during the day to restore it at night or during cloudy periods. The TES is composed of two circular tanks 36 m in diameter and 14 m in height, which contain 28,000 tons of molten nitrate salts between 293 and 393 °C. The quantity of storage media corresponds to 1010 MWh, allowing the equivalent electric power of 50 MW over 7.5 h due to energy conversion. In this case, the energy density is about 35 kWh·m⁻³ for the two-tank volume or 36 Wh·kg⁻¹ of storage material.

The passive system corresponds to a regenerator. In this case, a HTF circulates through a storage media. Practically speaking, the storage media can be solids such as rocks, sand, concrete, ceramics, or recycled materials from wastes [1,46]. When the HTF thermal capacity is significant and consequently contributes to the whole storage capacity, the system is a dual-medium system. This technology is based on the thermocline concept. The storage material remains in place in the storage system and a HTF is used to charge and discharge it. For example, at the PROMES-CNRS laboratory, a thermocline that contains 325 kg of quartzite can store 8.3 kWh between 160 and 210 °C. The TES is a single circular tank measuring 0.4 m in diameter and 1.8 m high. The energy density is about 36 kWh·m⁻³ of single-tank volume or 25.5 Wh·kg⁻¹ of storage material. Nevertheless, due to its small size, this TES has a storage capacity also ensured by HTF and a steel wall. Hoffmann et al. [47] showed that the thermocline tank presents an optimum mass flow corresponding to a maximum discharge efficiency near 75%. This experimental setup can test different types of material filler and HTF couple.

In these technologies, different criteria can be considered: energy performance, availability of storage materials, compatibility between storage materials and HTF, embodied energy, energy pay-back time, capital cost, life cycle cost, levelized cost of the stored energy and environmental impacts such as greenhouse gas emissions [7]. Low-cost and eco-friendly systems are proposed to offer sustainable options in the industry. To satisfy the objectives of IEA about the development of CSP, a huge quantity of storage materials is necessary. In this way, the use of recycled wastes is an interesting alternative to molten salts, which may be unavailable at acceptable cost [48]. The compatibility between storage material and HTF is a key point and can be analyzed on a case-by-case basis [49,50].

3.3. Latent heat storage

To the best of our knowledge, there is no commercial thermal energy storage module using PCM storage at high temperatures, and only research and development modules exist, stemming for the most part from an economic bottleneck. To extend the use of latent heat-storage systems, many scientific and technological obstacles need to be overcome. For a given application, the choice of a PCM results from a compromise between its energy storage properties, heat exchange performance, compatibility with the container (i.e. the structure) and economic constraints (mainly cost). For nominal operation of latent heat-storage systems, many criteria must be considered and some technological barriers persist: PCM at a cost suitable for the application, aging of the material (performance degradation), and return of power. These technological barriers correspond to scientific obstacles: thermophysical characterization and improvement of PCMs. The methodology to select a PCM often combines experimentation and modeling. The properties of a good PCM comprise: adapted melting temperature (high latent heat), high density, low cost, low danger and toxicity, stability over time, reliability of containment materials, and low supercooling (delay at the liquid–solid transition).

Many shortcomings remain in the development of reliable and practical storage systems using PCM, such as incongruent melting, supercooling, low thermal conductivity, and insufficient long-term stability. These shortcomings limit their applications. However, research and development of new materials is overcoming many of the shortcomings. To prevent incongruent melting (phase separation where the liquid phase does not have exactly the same chemical composition as the solid phase), it is possible to add suspension media or thickening agents. Nevertheless, thickening agents displace a part of the PCM in the system. As a result, the volumetric heat storage capacity is lower than the capacity of the pure

substance. Another possibility consists in mixing the PCM when it is in the liquid state. While this method does not reduce the volumetric storage capacity, it does require a means of mixing the PCM, with added energy consumption.

All substances do not crystallize at the melting temperature (liquid–solid equilibrium), but at a lower temperature. This delay, called supercooling, can be reduced by adding nucleation catalysts (whose crystal structure is similar to that of the PCM) or using a nucleating device that is maintained at a cooler temperature than the maximum supercooling temperature or using a surface roughness to create nucleation sites.

PCMs are known to have low thermal conductivity, usually between 0.2 and 0.7 W/m·K. This low thermal conductivity reduces the transfer of energy in and out of the PCM. During crystallization, the phase change starts at the heat transfer surface, causing the PCM solid–liquid interface to move away from the heat transfer surface. The solid layer of PCM between the exchange surface and the interface acts as an insulator reducing the heat transfer, thus increasing thermal resistance. Therefore, even if the same amount of energy is exchanged, the dynamic (i.e. the heat flux) may be small. Generally, due to the convection effect, low conductivity is less disadvantageous during the melting process. To resolve the problem of a low heat transfer rate, several heat transfer enhancement techniques are available. Heat transfer surface areas can be increased, using, for example, metal fins with high thermal conductivity. The thermal characteristics of the PCM can be improved using a high conductivity matrix or graphite particles. Scraped heat exchangers or direct contact latent heat-storage systems can also be used. All the solutions can effectively improve heat transfer, but they increase the final cost.

Appropriate PCMs must undergo many melting and freezing cycles without degrading their properties. The stability of PCMs and sometimes the corrosion between PCMs and containers must be experimentally tested.

Finally, although several problems persist in the use of PCMs, solutions exist and PCM storage technology is one of the most promising technologies. Nevertheless, continuous research and development efforts are needed to reduce costs further and scaling-up this technology.

3.4. Thermochemical heat storage

High-temperature thermochemical storage for CSP is addressed by several types of reactive pairs and reactors. The main ones are: (1) redox cycles using air flow [51,52] and (2) oxide/hydroxide cycles [53,54] in fixed-bed reactors [15] or fluidized reactors [55].

For such systems to be fully developed, the challenge is to define reactors and processes that are simple and secure, with high energy density, acceptable cost, and a design upscalable at a pilot plant level. The CaO/Ca(OH)₂ cycle implemented in fixed-bed reactors and a closed process (operating with pure vapor within the 300–600 °C range) is a promising configuration.

This type of system has been investigated from two perspectives:

- heat and mass transfer in the porous bed: storage systems aim to reach high energy density (kWh·m⁻³), but they also must provide the thermal power required by the power cycle. These two criteria are antagonistic: enhancing the density of the storage bed requires primarily reducing the porosity of the reactive bed, which can result in a limitation of vapor transfer and consequently a decrease of the thermal power released [56]. On the other hand, an inert conductive binder is usually added to improve bed heat transfer (expanded graphite called ENG [57]). Since both transfers impact the thermal power, they must be carefully investigated to determine the best compromise between energy density and thermal power for each application;
- performance of CaO/Ca(OH)₂ fixed-bed reactors: they have been measured on approximately 1-kg reactive beds and for various configuration parameters (energy density, conductive binder) and operating conditions. Fig. 6 displays the released power measured as a function of the stored energy of these beds (both related to the volume of the reactive bed, i.e. kW/m³ vs kWh/m³) and highlights the significant incidence of the operating temperature.

Therefore, within the range investigated, the specific power ranges from 10 to 70 kW/m³ of reactive bed; the reaction time for this de-storage step ranges from 2 to 12 h. Such storage systems are therefore suitable for the operation of a solar power plant for various storage/de-storage scenarios.

Future investigations should focus on developing knowledge and tools to optimize the reactive solids in fixed beds, experiments at a significant pilot scale and more detailed analysis of efficient integrations of such thermochemical processes in a CSP plant.

3.5. Peritectic heat storage

The term “peritectic” refers to reactions in which a liquid phase (*L*) reacts with at least one solid phase (α) to form a new solid phase (β). The reaction is reversible and takes place at constant temperature. The phase (β) formed is a solid solution of one of the components, an allotropic phase of one of the components or a new stoichiometric compound. In these materials, thermal energy is stored by two consecutive processes: a melting/solidification process and a liquid–solid chemical reaction. Under thermodynamic equilibrium conditions, the pro-peritectic phase α (s) starts to nucleate on cooling (discharge process) once the liquid phase crosses the liquidus temperature; then it grows until the peritectic temperature is

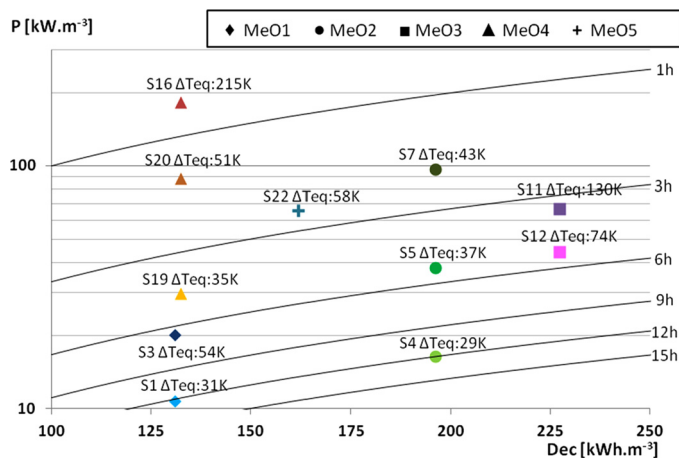


Fig. 6. Specific powers for the de-storage step for various reactive beds. Energy densities and amount of expanded graphite binder (ENG) in the beds: ♦: bed1 (131 kWh/m³, 37 kg ENG/m³); ●: bed2 (196 kWh/m³, 24.3 kg ENG/m³); ■: bed3 (228 kWh/m³, 0 kg ENG/m³); ▲: bed4 (132 kWh/m³, 37 kg ENG/m³); +: bed5 (162 kWh/m³, 46 kg ENG/m³). Temperature: the gap between the operating and equilibrium temperatures (ΔT_{eq}) is labeled near each point. Black lines: points of the iso-reaction time for the de-storage step.

reached. At this point, the liquid phase reacts with $\alpha(s)$ to form $\beta(s)$. On heating (charging process), the solid β decomposes at the peritectic temperature into a liquid phase and the solid α ; then the solid α melts.

The use of peritectic compounds (PCs) for TES at high temperatures (300–600 °C) has recently been proposed by Achchaq et al. [58]. PCs in salt-based and metallic binary systems have been extensively searched using FactSage 6.4[®] software [59]. A significant number of PCs with high theoretical potential for compact TES has been found. Under normal equilibrium cooling, the volumetric energy density provided by the peritectic reaction ranges from 200 kWh/m³ to 400 kWh/m³, which is comparable to the effective energy density provided by the best gas–solid reactions investigated so far. Considering the latent heat delivered during the pro-peritectic formation as well, volumetric energy densities from 400 to 650 kWh/m³ can be achieved.

Li₂K(OH)₃ was chosen for preliminary experimental analysis. This stoichiometric PC appears in the LiOH/KOH system at 58%wt of KOH/(KOH+LiOH). It is formed at 314.8 °C by the liquid+LiOH → Li₂K(OH)₃ reaction, whose theoretical enthalpy is 534 J/g (three times higher than the latent heat of NaNO₃). It has been synthesized by the melting/solidification route and submitted to thermal analysis. The main experimental results obtained are summarized in Fig. 7. As shown in the figure insert, the enthalpy change measured during successive cycles of heating and cooling is very high (480 J/g), although it is less than the theoretical value (534 J/g) due to the incomplete annihilation of the pro-peritectic phase. Indeed, the SEM images of the final material (Fig. 7, top) show a core-segregated structure in which the remaining pro-peritectic phase (LiOH) is encapsulated by a thin layer of Li₂K(OH)₃ and embedded in a background formed by direct precipitation of LiOH and Li₂K(OH)₃ from the melt. It is well known that a PC forms by means of two mechanisms: a peritectic reaction and peritectic thickening. The peritectic reaction, where all three phases (L , α , β) are in contact with each other, proceeds by short-range diffusion through the liquid and is usually very fast. In contrast, the thickening of the peritectic layer formed around the pro-peritectic phase takes place by long-range atom diffusion through the peritectic solid and is a sluggish process. Unless the cooling rate is unrealistically slow, an out-of-equilibrium structure will be obtained at the end of the discharge process. The values of enthalpy measured on cooling are displayed in the enthalpy-temperature graph (points) in Fig. 7 and compared to those calculated assuming both normal equilibrium cooling (blue line) and metastable Scheil–Gulliver cooling (green line). An intermediate behavior between these two cooling situations is observed, again indicating that an out-of-equilibrium microstructure has been obtained.

The efficiency of PCs should be increased by boosting the kinetics of the peritectic formation. One solution consists in providing appropriate sites for the heterogeneous nucleation of the pro-peritectic phase so that the latter has a finer distribution. This requires an increased specific surface area between the reactants, namely the liquid phase and the pro-peritectic phase, and this can be achieved either by infiltrating the storage material within appropriate porous/fibrous structures or by dispersing appropriate particles within the storage material. Different types of carbon structures providing a wide variety of structural and textural characteristics can be produced and investigated as the PC's host medium (within the Pc2TES project). Two types of carbon–salt composites have already been prepared to test the concept. The first one is obtained by dispersion of small particles (micrometric size, 20%wt) of vitreous carbon into the LiOH/KOH melt. The second one consists in a graphitic carbon foam (82% porosity, 0.24 g/cc apparent density) filled with Li₂K(OH)₃. Both composites have been submitted to 100 successive cycles of heating/cooling in the DSC. It was observed that the onset temperature of the composites remains unchanged while the enthalpy change is significantly improved and becomes even higher than the predicted theoretical value.

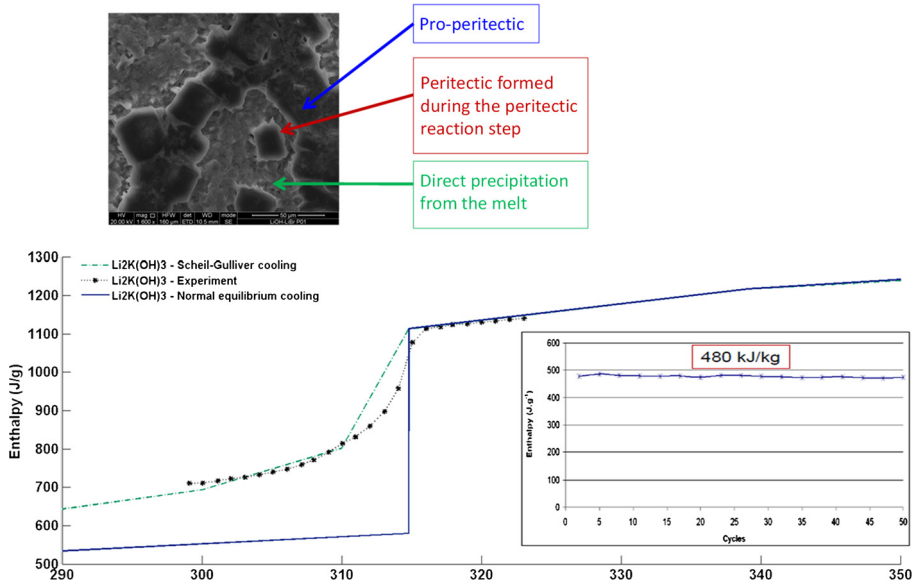


Fig. 7. Summary of the experimental results obtained for $\text{Li}_2\text{K}(\text{OH})_3$. Bottom: enthalpy-temperature curve (symbols: experimental points; continuous lines: theoretical calculations); insert: enthalpy change measured during successive cycles of heating and cooling. Top: SEM image of the final material.

Table 1
Main features of storage material and systems investigated in the set of laboratories.

Material	Material availability	– Development of systems – Key points of the process	Estimated cost €/kWh	Project & references
Sensible heat storage				
Molten salt (nitrate)	0.8 MT/an	– Commercial system – 15 h thermal storage for a solar plant operating 22 h out of 24	20–50 (storage system)	Gemasolar 2-tanks tower solar plant
Molten salt (nitrate)	0.8 MT/an	– Commercial system – 7 h thermal storage	20–50 (storage system)	Andasol 2-tanks parabolic trough
Alumina–oil	90 MT/an	– Demonstration (6.3 t of solid) – Common solid material with useful thermal properties at high T	20 €/kWh (material)	Micro sol plant
Quartzite–vegetable oil	Abundant	– Lab experiment (325 kg solid) – Low environmental impact	1 €/kWh (material)	Dual media thermocline
Cofilin–air	Abundant (wastes recycling)	– Lab experiment (7 kg) – Useful thermal properties, recycled ceramics from asbestos-containing waste	Low cost (waste)	Air–cobalt, Pease case
Latent heat storage				
Confidential	Good	– Lab experiment – Simple system (common tubes and shell heat exchanger), TRL 5	NA	STEEP ANR-13-SEED-0007
Thermochemical heat storage				
$\text{CaO}/\text{Ca}(\text{OH})_2$	Very abundant	– Lab experiment (~1 kg) – Management of thermal power and energy density	0.04 to 0.4 (material)	Instore ANR-12-SEED-0008
Peritectic heat storage				
$\text{Li}_2\text{K}(\text{OH})_3$	NA	– Experimental material characterization – Compactness, technology, simplicity	NA	Pc2TES ANR-16-CE06-0012

The theoretical analysis as well as the preliminary experimental results achieved indicates that using PCs might be an appealing solution for TES at high temperatures. Compared to the state of the art, the main expected advantages of PCs are: (i) compactness, with volumetric energy density comparable to that of the best gas–solid reactions investigated so far; (ii) simple storage technology, with charge/discharge processes at atmospheric pressure and reactants that separate and recombine by themselves, and (iii) acceptable cost due to enhanced compactness and technology simplicity.

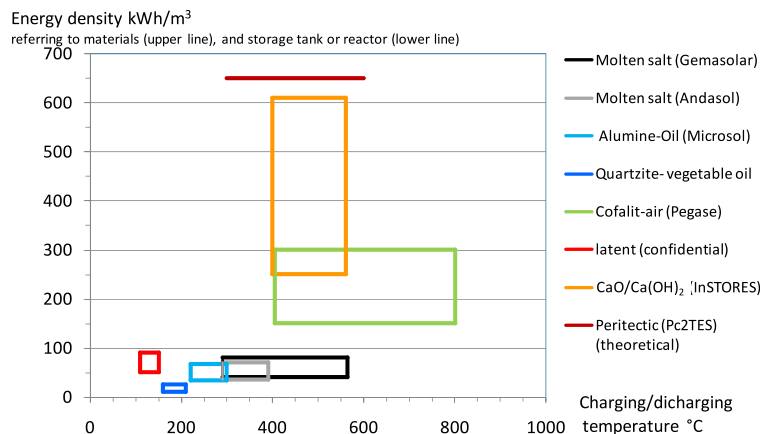


Fig. 8. Energy density of TES systems experimented in Fedele laboratories. Upper lines refer to the material volume. Lower lines refer to the tank or system volumes and are indicative values measured on non-optimized laboratory devices or prototypes. Only black and gray lines correspond to well-known commercial CSP plants.

3.6. Comparison

Research on high-temperature thermal storage carried out in FEDESOL laboratories is summarized in Table 1. They explore all the thermal storage routes, from already commercial systems (sensible heat) to very innovative systems (peritectics), covering a wide range of technology readiness levels (TRL from 8 to 3). The corresponding operating temperatures and energy densities are gathered in Fig. 8. Nevertheless, these studies mainly focused on lab-scale experiments. More detailed investigations on the implementation of storage materials, optimization of transfers and higher-scale experiments must be conducted before reliable conclusions and performance can be obtained. Many criteria can be considered when defining a storage system: energy density, thermal power, but also cost, availability, technical-complexity, etc. (Table 1). They should lead to different compromises depending on the applications.

4. Conclusions

Among the different energy storage systems, thermal energy storage is one of the cheapest ones that can be applied to a broad spectrum of applications. The most widely used is the sensible heat storage method. Other techniques such as latent energy storage and thermochemical energy storage have appeared in the last two decades and offer great heat storage capacity and reduced heat loss during the storage period.

This paper presented an overview of low-, and medium-temperature heat-storage systems devoted to solar applications that are currently under development to address the challenges of energy transition. The paper reviews the results obtained by nine different laboratories belonging to the French CNRS federation on solar energy: the Fedele federation. These laboratories explore all the thermal storage routes, from commercial systems (sensible heat) to very innovative ones (peritectics), covering a wide range of technology readiness (TRL from 8 to 3).

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