Review

A critical review on thermal energy storage materials and systems for solar applications

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Abstract: Due to advances in its effectiveness and efficiency, solar thermal energy is becoming increasingly attractive as a renewal energy source. Efficient energy storage, however, is a key limiting factor on its further development and adoption. Storage is essential to smooth out energy fluctuations throughout the day and has a major influence on the cost-effectiveness of solar energy systems. This review paper will present the most recent advances in these storage systems. The manuscript aims to review and discuss the various types of storage that have been developed, specifically thermochemical storage (TCS), latent heat storage (LHS), and sensible heat storage (SHS). Among these storage types, SHS is the most developed and commercialized, whereas TCS is still in development stages. The merits and demerits of each storage types are discussed in this review. Some of the important organic and inorganic phase change materials focused in recent years have been summarized. The key contributions of this review article include summarizing the inherent benefits and weaknesses, properties, and design criteria of materials used for storing solar thermal energy, as well as discussion of recent investigations into the dynamic performance of solar energy storage systems.

Keywords: latent storage; sensible storage; thermal energy storage; solar energy; thermochemical storage

1. Introduction

The efficient use of energy has been central to the advancement of human civilization. Electricity, among other sources of energy, is vital to the success of any modern society and has catalyzed many of the great steps forward of the last century. As shown by a statistical review by British Petroleum, there is continuous growth in global energy needs, with the vast majority of the energy, 87%, coming from fossil fuels [1]. In light of increasing awareness of the role of CO_2-emissions in global warming and the dire consequences this may have on human society, the renewable energy sources including wind, tidal, solar, biomass, wave and geothermal are receiving ever-greater attention. These energy sources have the benefits that they have a low environmental impact, are widely available, and produce no or little contamination. However, their widespread adoption is also constrained by geographical location, atmospheric conditions, and both economic and safety considerations [2]. It is increasingly thought that the usage of renewable energy sources, and solar in particular, will be the key factor for continued sustainable human development [3]. The sun produces enormous amounts of radiation energy, with 174 PW (1 PW = 1015 W) reaching the Earth's upper atmosphere [4]. This energy is attenuated twice before reaching the surface, by both the atmosphere, where 6% is lost by reflection and 16% by absorption, and by the clouds, which reflect 20% and absorb 3% [4]. Ultimately, the land and oceans receive 51% (89 PW) of the inward radiation [5]. Hence, the quantity of available solar energy for our use is still very high. Nevertheless to use this intermittent, low-density energy source, an efficient storage is essential [6].

The components through which energy is collected and stored are vital subsystems in any solar thermal applications. The function of solar collectors is to transform solar irradiation either directly into energy using PV (photovoltaic) methods or into thermal energy of a fluid [7,8]. Conversely, an ideal thermal storage necessitate long-term stability, low construction costs, high storage density, the ability to transfer heat efficiently through rapid absorption and release [9,10]. Solar collection is achieved using three main types of collector: solar thermal, PV, and PV/T (photo-voltaic/thermal) [11]. Solar thermal collectors contain working fluids including ethylene glycol (EG) and water and are operated by transferring solar energy into these fluids [12]. The solar thermal systems are relatively matured technology and have been employed in the residential sector for over forty years [13]. Conversely, PV experienced huge interest in the last decade and several installations were done around the world for both domestic and remote production [14]. In a PV collector, solar radiation is directly converted into electricity using semiconductors including SiO_2, Si, CuS, or GaAs. On the other hand, PV/T collector, a hybrid between a PV and thermal collector, uses materials such as Al, Cu, and polyethylene naphthalate to convert absorbed energy into both electricity and thermal energy. This review will summarize the current state of knowledge regarding these solar energy systems and the materials used within them.

2. Solar thermal energy storage

The performance of solar thermal energy systems is primarily controlled by the components that collect and store the energy [1]. A solar collector is a type of energy exchanger that converts irradiation energy from the sun into thermal energy in a working fluid. The most important parameter in solar collector design and fabrication is good optical performance, to ensure that as much as possible of the incoming solar radiation is captured and directed to the receiver. As solar energy

input is not constant, efficient thermal energy storage (TES) materials must then be employed to store any excess energy that is collected throughout the day for use at night [15,16]. Different applications require different output temperatures, such as electrical power generation requiring a high-temperature (>175 ℃) TES system, whereas domestic space heating requiring a low-temperature (<50 ℃) system [17]. The properties of the storage materials generally pose a major effect on the TES performance. Many factors must be considered when designing a solar TES system, most of which fall under the subjects of cost-effectiveness, environmental impact and technical properties. Table 1 shows the thermophysical properties of different TES materials based on the requirements of specific applications.

Table 1. The properties of solar thermal energy storage materials [69].

Properties	Requirements	Description
Density	High	High density improves energy storage density which reduces the volume of the thermal energy storage system.
Latent heat of fusion	High	Phase change materials should have very high latent heat of fusion. High latent heat of fusion improves energy storage density of the system.
Specific heat	High	High specific heat improves energy storage density of the system.
Melting point	Relative	Phase change materials should have a melting point near the required operational temperature range of the thermal energy storage system.
Super cooling	Minimal	For phase change materials, during the freezing process, super cooling should be minimal. Storage material should freeze completely at as close as possible to its freezing temperature.
Thermal conductivity	High	High thermal conductivity increases the thermal charging and discharging rate.
Vapor pressure	Low	Low vapor pressure decreases the need of pressure withstanding containment at high temperatures. It also decreases the cost of insulation.
Thermal stability	High	The materials should not decompose at high temperatures. This gives wider operating temperature range and higher energy storage capacity for the material. Material properties should be stable even after extended thermal cycles of heating and cooling.
Chemical stability	High	High chemical stability of storage materials increases life of energy storage plant.

Properties	Requirements	Description
Volume change	Minimal	For phase change materials, change in volume during phase change process should be minimal. Big changes in volume increase the required size of the container. Large density difference between two phases also causes phase segregation issue.
Availability	Abundant and easily available	Abundantly and easily available materials decreases the process cost.
Toxicity	Non-toxic	The materials should not be harmful to health of operators and environment.
Corrosiveness	Non-corrosive	Corrosive thermal energy storage materials bring down the energy storage plant life drastically due to corrosion of containers.
Flammability	Non-flammable	The materials should be non-flammable and non-explosive.
Cost	Cheap	Cheaper price of storage material reduces capital and process cost.

Solar TES materials can be categorized into three main types depending on the storage mechanism: thermochemical (TCS), latent heat (LHS) and sensible heat (SHS) storage. As SHS is the most developed of the technologies, it has the benefit that numerous low-cost materials are available [18], but it also has the least storage capacity, thereby enhancing the dimensions of the system. Compared to other energy storage modes, SHS is commercialized largely, whereas LHS and TCS are still in the development phase [19]. In addition, the durability of SHS system is around twenty years; whereas those of LHS (one-fourth of SHS) and TCS (one-tenth of SHS) were relatively low [20]. Conversely, the capacity of LHS is much higher; but this is usually paired with poor heat transfer unless it is modified with heat transfer enhancement. Table 2 compares the performance of SHS using water and rock with LHS using inorganic and organic phase change materials [21]. This comparison shows that the storage mass and density of LHS is superior to that of SHS. TCS has the highest storage density compared to LHS and SHS, but issues of chemical stability, lack of long-term durability and need for complicated reactors to achieve the required chemical reactions, limits its applicability.

Table 2. Comparison of sensible and latent heat storage [21].

Property	Sensible Storage		Latent Storage	
	Water	Rock	Inorganic phase change materials	Organic phase change materials
Specific heat (kJ/kg)	4.2	1	2	2
Latent heat (kJ/kg)	-	-	190	230
Density (kg/m^3)	1000	2240	1600	800
Storage mass for 10^6 J, kg	16000	67000	4350	5300
Relative storage mass	4	15	1	1.25

2.1. Sensible heat thermal energy storage materials

The materials used in SHS are able to store thermal energy without undergoing a phase change. Energy is stored through varying the temperature of solid or liquid materials during peak energy input periods. The degree of storage depends on the thermophysical properties of the material, as shown by the following relationship:

$$Q = \int_{T_1}^{T_2} mc_p dT \qquad (1)$$

where Q is thermal energy stored as sensible heat; m is the total mass in kg of the storage material; C_p is its specific heat capacity in kJ/kg·K; and T_2 and T_1 are the final and initial temperatures in K. The stored quantity of heat is thus proportional to the volume, specific heat capacity, density, and temperature differences of the storage material. Hence, practical SHS materials require a high specific heat capacity, high density, and good long-term stability when thermally cycled as well as being low-cost, non-toxic, and resilient to contamination [22].

2.1.1. Liquid storage medium

Liquid storage media have the advantage that they can transport heat easily through circulation. A system featuring circulation of storage material is termed an active system. The buoyancy created by the density difference between cool and warm liquid has the added benefit of creating a thermal gradient across the storage system [23]. Cold fluid falls, whereas hot fluid raises thereby leads to separation. Some of the main liquids used for SHS are discussed below.

2.1.1.1. Water

For low-temperature (25 to 90 ℃) applications, water is the most popular storage liquid. This is owing to its low environmental impact, cost effectiveness, easy availability, and high C_p [24]. Water is able to store 81.7 kWh of energy at 90 ℃ [1]. However, its use in high-temperature applications is complicated by its high vapor pressure, which means that expensive insulation and pressure containment measures are required. Water is thus best-suited to lower-temperature domestic applications such as hot water supply and space heating [25]. During analysis of large-scale solar development in Europe over a decade, Fisch et al. [26] referred to two main large-scale solar heating applications. These include, seasonal (long term) storage systems with potential to supply 50 to 70% of the yearly heating demand and diurnal (short term) storage systems with potential to supply 10 to 20% of the yearly heating demand. These systems are very efficient in minimizing the usage of fossil fuel as well as compatible with CO_2 emission policies. A variety of materials are used for water storage tanks, such as aluminum, steel, reinforced concrete, and fiberglass. These are insulated using polyurethane or glass or mineral wools. Tanks can be as small as a few hundred liters but can range up to thousands of cubic meters. To ensure that tanks in solar heating plants provide good thermal performance over a long lifetime, they need to utilize materials that are watertight and allow limited heat loss by steam diffusion, as well as technologies that optimize stratification within the water column. Another application of water as an energy storage medium is as brine in salt ponds, where it can collect large amounts of solar thermal energy in temperature range of 50–95 ℃. Due to the

retarding effect of dissolved salts such as NaCl and $MgCl_2$ on convection, heat becomes trapped in a thick layer at the bottom of the pond. Water can also be mixed with sand or gravel-filled underground aquifers to provide large-scale seasonal energy storage. This avoids the expense of water tank construction, making it very cost-effective [27,28].

2.1.1.2. Mineral oil

Concentrated solar power plants commonly use mineral oil as the heat transfer fluid (HTF). The oil passes through the receiver, collecting heat, and then transports it to the boiler, where the heat is utilized to produce steam to drive a turbine. With the use of highly insulated tanks, mineral oil can also be used as an overnight storage medium. In a study comparing the thermal efficiency (TE) of oil versus water as the HTF in a flat plate collector (FPC), the TE of oil was found to be 15–19% lower than that of water [29]. However, when the oil was kept flowing through the FPC, this increased by 4–9%, indicating that circulation is the best way to get optimal performance from this medium at temperatures relevant to water. Furthermore, because mineral oil has a lower vapor pressure than water and remains in a liquid form up to 400 ℃, it can operate at much higher temperatures. It also performs well at very low temperatures as, unlike molten salts, it does not freeze in pipes at night, obviating the need for an antifreeze system. One limiting factor for the use of oils is that they are age- and temperature- dependent; so they start to degrade when temperature increases beyond a certain point [30]. They are also high-cost, and for this reason, several molten salt mixtures with lower melting points have recently been investigated as potential replacements for mineral oil for energy storage.

2.1.1.3. Molten salts

The superior thermal stability at high temperature, elevated thermal conductivity, low vapor pressure and viscosity, non-toxicity, and non-flammability of molten salts make them ideal for use in solar power plants [18,31]. Their lower vapor pressure and ability to remain in the liquid form up to 400 ℃ mean that, unlike water, they can be used at high temperatures, improving the efficiency of the Rankine cycle in power plants. One issue that can limit their cost-effectiveness is that they can have high melting points. The most useful molten salts have a melting point near ambient temperature so that they stay in liquid phase throughout operation and do not require antifreeze overnight when there is no solar energy. A common practice is to utilize salt composites to achieve a melting point below 100 ℃ and a boiling point above 500 ℃ [32]. For example, Zhao and Wu [18] documented several ternary salt mixtures with melting temperatures that were all below 100 ℃, the lowest being 76 ℃. These $Ca(NO_3)_2$, $LiNO_3$ and KNO_3 mixtures had viscosities as much as 80% lower than commercial molten salts and synthetic oils and remain chemically stable up to 500 ℃. A quaternary eutectic salt with a melting point of 99 ℃ was also described more recently [33]. Molten salts do have the drawback that they are oxidizing and are very corrosive at high temperatures, making their containment problematic. They also exhibit low thermal conductivity as well as change in volume by approximately 6% during melting.

2.1.1.4. Other strategies

It is desirable to enhance the energy density of SHS materials such as molten salts, and one of the most effective solutions is by amending encapsulated phase change materials (PCMs) [34,35] or nanoparticles [36–38]. PCM particles are encapsulated by coating them in a shell that improves their chemical stability and impedes the coalescence of individual particles during melting and freezing cycles. The addition of encapsulated PCMs to sensible materials is an example of a coupled technology, and will be discussed in a later section. Further, nanoparticles can be added to a sensible storage material to increase its specific heat. Andreu-Cabedo et al. [36] showed that 25.03% enhancement in specific heat of a solar salt can be achieved through amendment of 1 wt% of silica nanoparticles (SiO_2).

2.1.2. Solid storage media

Solid materials including metals, concrete, rocks, sand and bricks can be utilized for both high and low temperature energy storage because they will not boil or freeze. They also do not suffer from issues such the high vapor pressure of water or the drawbacks of other liquids. As operating pressures are close to ambient, pressure-containing vessels are not needed, and there are no issues relating to leaks. However, solid storage media do have some limitations. They cannot be circulated easily so they can only be used for passive storage, with a fluid, commonly air, being used to transfer heat in and out of a storage tank loosely packed with the solid sensible medium. Direct contact between the HTF fluid and the solid maximizes heat transfer efficiency during charging and discharging. One major issue is that the temperature of the storage material is reduced by the discharging process, and this generally results in decline of HTF temperature over time. Microbial activity in this warm, moist environment can also introduce difficulties. Solid storage is therefore most commonly used in low-temperature applications including industrial waste heat recovery and space heating. Solid SHS materials also generally have a low energy density. This is not in the case of cast iron, which has an energy density exceeding that of water [39]. However, it is much costlier than brick or stone and therefore takes a longer period to become profitable. Due to their low cost, rock piles and pebble beds are the most commonly used materials.

2.1.2.1. Storage in rocks

Rocks usually take the form of a loosely packed rock pile or pebble bed. During charging, hot air is circulated through the gaps between the rocks; whereas during discharging, cold air is likewise circulated and gets heated. Heat transfer is efficient due to the large surface area over which the air comes into contact with the rocks. Rocks have numerous advantages, such as their easy availability, very low cost, non-flammability, and lack of toxicity. Nevertheless there are limitations such as requirement of increased pressure drops and elevated air mass flow rates [40]. The quantity of energy that can be stored in rocks depends on both the thermophysical properties of the solid media and its packing density, the shape and size of particles, and the heat transfer fluid used. The geometric and thermal properties of packed beds were described by King and Burns [41] on the basis of a number of factors including void fraction, particle size, the cross-sectional area and length of the bed, Reynolds number and superficial air velocity. In terms of size, 300 to 500 kg rock/m^2 can be

considered a reasonable area for solar collection for space heating application. Concrete and rocks will store approximately 36 kJ/kg, for a temperature difference of 50 ℃ [40].

2.1.2.2. Concrete

Concrete is very straightforward to implement as a solid SHS due to its high mechanical strength and there being no need for a container. Heat exchange can be achieved between concrete and an HTF by circulating the HTF through pipes installed within a concrete block. Its tendency to crack under repeated cycles of thermal expansion and contraction can be a disadvantage in high-temperature applications, but work is being carried out to develop the optimal mixing method to enhance chemical-physical properties and durability at higher temperatures [42]. In terms of energy density, 400 kWh of energy can be stored in 20 m^3 of concrete.

2.1.2.3. Sand

Fine-grained materials such as silica sand and gravel have a good capacity for thermal energy storage. This would commonly be achieved in beds of 0.2–0.5 mm diameter sand grains, using air as an HTF. Such beds have been shown to have storage potential up to 550 ℃ [43]. The finer the sand, the greater is the packing density. Gravels have larger grains, c.a. 0.4 mm in diameter. Basalt gravel grains can be directly employed to collect solar thermal energy in a solar receiver. In such a system, they drop under gravity from the top of the receiver tower and absorb heat from concentrated solar rays as they fall. The sand, which reaches temperatures of 700–1000 ℃, is collected at the bottom and used to produce steam to drive a Rankine cycle power plant.

2.1.2.4. Bricks

Bricks making up the walls of a building can be employed to store thermal energy and thereby minimize electricity costs for space heating [39]. They are heated using cheaper off-peak electricity at night, and then the stored heat can be extracted during the day through natural radiation and convection or with an electric fan to force convection [21]. This reduces the cost of heating during the hours when peak electricity prices are in effect.

All sensible heat storage solutions have the advantage of being low cost: 0.05–5.00 US$/kg versus the 4.28–334.00 US$/kg of latent heat storage [5].

2.2. Thermochemical heat storage

Thermochemical heat storage is where heat energy is stored in chemical bonds. It makes use of chemicals that have endothermal and exothermal reactions when certain chemical bonds are broken and formed, absorbing and releasing large amounts of energy [44]. For efficient storage, these reactions should be fully reversible. An example is that of cobalt oxide:

$$2Co_3O_4 + \Delta H \leftrightarrow 6CoO + O_2 \tag{2}$$

The forward, endothermic reaction in (2) is induced by introducing solar heat to the material using a solar concentrator in the on-sun charging process. As long as the reaction is fully reversible,

the energy can be recovered and used to produce electricity in the off-sun discharging phase through the reverse reaction. Thermochemical heat storage has several major advantages: a constant discharge temperature, high energy density (allowing a smaller storage unit volume and so fewer heat losses), and the ability to store heat for as long as the materials remain non-degraded.

Although probable thermochemical storage materials were first proposed in the 1970s [45], it has only been recently that high-temperature heat storage using thermochemical reactions has received significant attention. However, it should be emphasized that the development of thermochemical storage systems is still in its early stages and yet to reach commercial stage [19,46]. Several researchers investigated and showed interest on thermochemical energy storage because for several types of materials the thermochemical energy storage can offer an energy density approximately 6 folds more than latent heat storage and 15 folds more than sensible heat storage [20,47]. Table 3 shows the current state of knowledge regarding several materials that have potential in this regard. Some have significant weaknesses: for example, ammonia requires high pressures, and the dissociation of carbonates or hydroxides produce CO_2 and H_2O, respectively, which have to be removed or evaporated away. Of the possible reversible gas-solid reactions, the most promising for large-scale development is where a pair of redox reactions involving multivalent solid oxides is used. Here, air is both the reactant and the HTF, and so can directly contact the storage material, and the two reactions generally produce O_2-rich or O_2-lean air. One of the most promising oxides for this method is cobalt oxide, as its endothermic reduction proceeds in air at around 900 ℃. The new generation of solar tower power plants, which use volumetric receivers at atmospheric pressure, can achieve this temperature. The energy density of cobalt oxide is also among the highest of such oxides, 844 kJ/kg [48]. Numerous other oxides were studied by Xiao et al. [49] for their applicability in solar chemical reactors, including Fe_3O_4/FeO, MgO/Mg. ZnO/Zn, CeO_2/Ce_2O_3, GeO_2/GeO and SnO_2/SnO. Nevertheless, extensive exploration of the potential of thermochemical storage has been discouraged by inherent limitations of the method such as issues with the chemical stability, durability, long-term reaction reversibility of the materials and the need for complicated chemical reactors.

Table 3. Thermochemical energy storage materials reported in literature

Materials	Temperature range (℃)	Enthalpy change during chemical reaction (GJ/m³)	References
Aluminium ore alumina	2100–2300	-	[89]
Calcium carbonate	800–900	4.4 GJ/m³	[90]
Hydroxides	500	3 GJ/m³	[91]
Iron carbonate	180	2.6 GJ/m³	[92]
Metal hydrides	200–300	4 GJ/m³	[91]
Metal oxides (Zn and Fe)	2000–2500	-	[93]
Methane/water	500–1000	-	[91]
Methanolation			[92]
demethanolation	200–250	-	

2.3. Latent heat storage

Thermal energy can be effectively stored as latent heat [17,50]. Latent heat storage (LHS) relies on the absorption and release of heat as the storage material undergoes a solid–solid, solid–liquid or liquid–gas phase change. The energy that the material absorbs on heating to accomplish a phase change is termed as the latent heat of vaporization or of fusion, depending on the phases involved. LHS generally has a high storage density, exhibit low energy losses as well as cost-effective compared to sensible storage systems, and has therefore received significant research attention. Padmaraju et al. [51] showed that, for the identical volume and size of storage tank, LHS systems stored significantly more energy than SHS (0.234 kJ/cc versus 0.144 kJ/cc). Thus, LHS systems offer a substantial space saving over SHS for the same heat storage capacity. The following equation describes the heat storage capacity of LHS system using a PCM:

$$Q = \int_{T_i}^{T_m} mc_p dT + ma_m \Delta h_m + \int_{T_m}^{T_f} mc_p dT \tag{3}$$

where m is the mass in kg of the storage material, C_p is its specific heat capacity in kJ/kg K, a_m is its melted fraction, Δh_m is its latent heat of fusion (enthalpy of fusion) in kJ/kg, and T is temperature in K. The first part equates to the amount of sensible energy stored within the solid-state material, the second is the latent heat that is absorbed/released during the phase change, and the third part of the equation corresponds to the increase in temperature happens in the liquid phase for solid to liquid LHS. Martinopoulos et al. [52] experimentally evaluated 2 sq. meter phase change flat-plate solar collection unit to study the impact of the inclination of the collector and volume ratio of heat carrier to the collector. The authors examined 19 sets and optimized that 50% volume filament at 40° inclination provided very high performance.

As mentioned above, PCMs can undergo solid–solid, solid–liquid, and liquid–gas transformations. On the whole, solid–solid PCMs do not have appropriate transition temperatures and heats of fusion to be employed for thermal storage: as they have a latent heat of transition that is approximately an order of magnitude lesser than that of solid–liquid PCMs used for energy storage [53]. However, if they are used, they present the benefit that the lack of liquid means there is no risk of leakage so they do not require encapsulation. Though liquid–gas PCMs generally have a high heat of transformation, they undergo enormous volume changes during evaporation, and this makes storage complex or impractical [53,54]. Solid–liquid PCMs outperform them in this regard, as there is little volume change. They also have the advantage of storing a high amount of heat over a narrow range of temperature [55]. Liquid–solid PCM LHS systems usually take the form of long thin tubes within a container. For storage, collected solar heat is circulated through the spaces between the tubes, melting the PCM and storing the heat as both the latent heat of fusion and sensible heat. For recovery, low-temperature air is circulated through those spaces, picking up the stored energy and transporting it onwards for use. Thus, this storage method uses both the sensible heat in the liquid and solid phases and the latent heat associated with the melting and freezing phase changes. Thus, a good latent heat storage material requires high thermal conductivity and large latent heat [21]. Its melting temperature should be within the operational range of the TES system, have congruent melting and minimum subcooling [56], and be low-cost, chemically stable, non-corrosive, and non-toxic. In an LHS system, the temperature of the storage medium remains constant during discharge, giving it an advantage over the SHS method. There is also a minor difference in temperature between

storing and discharging heat [21]. The energy from the latent heat of fusion is far superior to the specific heat. For example, the specific heat of sodium nitrate salt is 1.10 kJ/kg K, but it has a latent heat of fusion about 172 kJ/kg. This variation means that LHS materials offer a high density of energy storage, reducing the volume of vessels within TESs, which in turn reduces the surface area of the outer wall and reduces heat loss.

Table 4. Thermo-physical properties of important PCMs [5,23].

Storage materials	Density (kg/m^3)	Phase change temperature (℃)	Latent heat (kJ/kg)	Thermal conductivity (W/m K)	Specific heat (kJ/kg K)
$NaNO_3$	2260	307	172	0.5	n.a
KNO_3	2110	333	226	0.5	n.a
NaCl	2160	800	492	5	n.a
Na_2CO_3	2533	854	275.7	2	n.a
K_2CO_3	2290	897	235.8	2	n.a
$AlSi_{12}$	2700	576	560	1.6	1.04
$MgCl_2$	2140	714	452	n.a.	n.a.
LiF	n.a	850	n.a	n.a	n.a
KNO_3–$NaNO_2$–$NaNO_3$	n.a	141	275	n.a	n.a
$MgCl_2$-KCl-NaCl	2044	380	149.7	0.5	n.a
$LiNO_3$-$NaNO_3$	n.a	195	252	n.a	n.a
E117 (inorganic)	1450	117	169	0.70	2.61
A164 (organic)	1500	164	306	n.a.	n.a.
RT100 (paraffin)	880	100	124	0.20	n.a.
RT110 (paraffin)	n.a.	112	213	n.a.	n.a.

Many materials have been reported to be suitable for LHS applications [57]. They can be categorized as organic or inorganic compounds or eutectics of such compounds. Suitable organic compounds can be classed into paraffin, non-paraffins, and polyalcohols, while salt hydrates, salts, metals, and alloys make up the inorganic alternatives. Some of the most important PCM materials that have been stated in the literature are listed in Table 4.

2.3.1. Organic

Successful testing and implementation of organic LHS materials and their eutectic mixtures have been carried out for both commercial and domestic applications, including building space heating, refrigeration and air-conditioning, electronic devices, fabrics, food, automobiles, and space industries [58]. Organic PCMs have the advantageous property of undergoing congruent melting without separation of phases [58]. However, they also have low thermal conductivity (ranging 0.1 W/m.K to 0.35 W/m.K), meaning that high heat transfer rates require a large surface area [58]. Their low melting points also pose an obstacle to their use in high-temperature applications, e.g., power plants. The specific strengths and weaknesses of different types of organic PCMs are explored below.

Paraffin waxes mainly comprise of straight-chain *n*-alkanes (CH$_3$–(CH$_2$)–CH$_3$) [59]. Commercially produced waxes have a moderate (200 kJ/kg or 150 MJ/m^3) thermal storage density, and are cheap as well as have a narrow melting temperature range (−10–67 ℃) [21,60]. They accomplish heat storage because they melt when they absorb heat and release that heat when they solidify. They can be effective: for example, Al-Hinti et al. [61] placed paraffin wax in aluminum cylinders in an FPC's conventional water tank and witnessed that the water temperature remained above 30 ℃ over 24 h. They have numerous positive aspects as they are chemically stable and inert, have no phase segregation, and undergo little subcooling. Commercial-grade paraffin waxes remain stable and have good thermal reliability even after 1000–2000 cycles. They are also long-lasting, non-corrosive, odorless, environmentally friendly, non-toxic and easily available. This means that they are safe and can be stored in metal containers without risk of corrosion. However, they can sometimes cause infiltrations and softening in few plastic types that are chemically similar to paraffin. For example, polymers like polyolefin [60] should be avoided for containment vessels. Despite the advantages of paraffin PCMs, their low (0.2 W/m.K) thermal conductivity means that heat transfer rates will be low and their applications are limited [60]. Paraffin PCMs are mostly mixtures of different types of saturated hydrocarbons containing various quantities of carbon atoms. The longer the average hydrocarbon chain length, the higher the heat of fusion and melting temperature. This makes it possible to design the optimum PCM by mixing physically different paraffins. In an attempt to enhance thermal conductivity and to address the need to adequately encapsulate the wax and avoid leakage during solid–liquid transitions, Li et al. [62] developed a composite of paraffin@SiO$_2$ and microencapsulated it in inorganic shells using in situ emulsion interfacial hydrolysis and polycondensation. This composite perfectly maintained its phase transition over 30 cycles of melting and freezing, and no leakage occurred after being held for 20 min at 70 ℃. This composite, with its elevated heat storage capacity and thermal stability has outstanding potential for practical thermal energy storage. Further, Chai et al. [63] prepared microencapsulated paraffin PCM with a brookite TiO$_2$ shell. Apart from exhibiting enhanced thermal conductivity and superior latent-heat storage capacity, the authors observed that synthesized microcapsules showed additional photocatalytic efficiency due to crystalline TiO$_2$.

Nanomaterials are advanced materials with a very high surface area to volume ratio and are used in a variety of applications, including those that require enhanced thermal properties [64,65]. Paksoy and Sahna [66] investigated whether adding nanoparticles of magnetite (Fe$_2$O$_3$) to paraffin with a melting range of 56–58 ℃ and latent heat of 119 J/kg would improve the thermal properties of the paraffin. The authors found that the addition of 10% nanocomposite enhanced the thermal storage capacity of paraffin by approximately 20%. Additionally, Sari and Karaipekli [67] performed a research to evaluate the influence of different amounts of expanded graphite on the thermal conductivity of *n*-docosane paraffin wax. The results indicated that increasing the concentration of expanded graphite increased the thermal conductivity and decreased melting time. More recently, Liu et al. [68] have used self-assembly to combine neicosane@TiO$_2$ microcapsules with 5 wt% of highly thermally conductive graphene nanosheets. They found that microencapsulated graphene/TiO$_2$/paraffin composite PCMs fabricated in this way had phase-change enthalpies over 160 J/g and thermal conductivity enhanced from 0.64 W/m.K to 0.98 W/m.K.

An alternative to paraffins are fatty acids (general formula: (CH$_3$ (CH$_2$)$_{2n}$-COOH)). These have thermophysical properties that are ideally suitable for a low-temperature LHS material. They have high melting and boiling points relative to paraffins and undergo only minor volume changes on

phase transition. Their melting and freezing behavior is reproducible, and there is very little or no supercooling. They do have some disadvantages: as they are mildly corrosive, have a disagreeable odor, are more costly than technical grade paraffins, and are combustible [59]. In general, as the number of carbon atoms per molecule surges, there is a rise in the heat of melting, degree of crystallization, and melting/freezing points [69].

Polyethylene glycol (PEG), also known as polyethylene oxide (PEO) or polyoxyethylene (POE), comprises dimethyl ether chains with the hydroxyl group at the end ($HO–CH_2–(CH_2–O–CH_2–)_n–CH_2–OH$) [59]. They are soluble in both water and organic compounds. There are various grades of PEG, e.g., PEG400 and PEG600. Numerous experimental and numerical studies have characterized these materials, finding that they are thermally and chemically stable, non-flammable, non-toxic, cost-effective and non-corrosive. However, in common with other organic PCMs, they have low thermal conductivity. An improvement in melting point an latent heat of fusion of PEGs can be achieved with an increase in their molecular weight [70,71].

Sugar alcohols (polyalcohols) perform well as medium temperature (90–200 ℃) PCMs. Though they have been tested as potential PCMs for four decades, thorough research into them is still lacking. Studies of xylitol, erythritol, and mannitol have given promising results, showing a latent heat of fusion (c. 300 kJ/kg), far surpassing other organic PCM materials of this type.

Esters are compounds that are derived from acids where one alkyl (–O) group replaces one hydroxyl (–OH) group. They have several thermophysical properties that make them suitable PCMs for LHS. The solid-liquid transition of fatty acid esters occurs over a narrow range of temperatures, and they form eutectics without significant subcooling. The phase transition temperatures of ester eutectic mixtures are near room temperature and have a high enthalpy of transition [21]. Fatty acid esters are easy to obtain, owing to their abundant usage in the smart clothing, cosmetics and polymer industry.

2.3.2. Inorganic

As shown in Table 4, inorganic PCMs generally have two times the capacity for heat storage compared to organic materials per unit volume. They also outperform organic PCMs in that they have superior thermal conductivity, lower cost and operating temperatures [32]. The downside to these materials is that they are corrosive to metals and so systems containing them have shorter service lives, increasing costs [72]. Salt and salt hydrate inorganic PCMs have the added disadvantages of demonstrating supercooling and phase segregation, which impact their energy storage capacity [73]. Nevertheless, these issues do not arise with metals and metallic alloys; hence these inorganic PCMs have better potential for elevated temperature applications [74]. The inorganic PCMs are broadly categorized into (a) metals and their alloys; and (b) salt hydrates and salts.

Salt hydrates are generally employed in low temperature ranges of 30 to 50 ℃. Their general formula is $A_xB_y•n(H_2O)$, where A_xB_y indicates metal carbonate, sulfate, acetate, phosphate, chloride, or nitrite; and n is the number of water molecules. Their chemical bonding is by ion-dipole (an ion and a polar molecule) or H-H bonds. Molecules of H_2O are loosely bounded to anion or, less commonly, to cation. A variety of inorganic salts are potential PCMs for energy storage, including $NaNO_3$, $LiNO_3$, LiH, $AlCl_3$, $KClO_4$, KOH, $MgCl_2$, and KNO_3. On the other hand, potential salt hydrates include $Ba(OH)_2•8H_2O$, $MgC_{12}•6H_2O$, $(NH_4)Al(SO_4)_2•12H_2O$, $Mg(NO_3)_2•6H_2O$ and $Na_2P_2O_7•10H_2O$ [60,75]. When the salt hydrates, some or all of the water molecules are lost and

latent heat is adsorbed, and this is released on dehydration. This dehydration and hydration can take the form of a solid–liquid phase transformation. Though these materials have some characteristics that make them promising for usage as PCMs, there are several obstacles to their use in practice. A major technical issue is basically their inferior thermal conductivity (1 W/m.K). This limitation can be eliminated through usage of large area for heat transfer or to form a composite with a higher thermal conductivity material such as graphite. A further issue is that they undergo a volume change at phase transition, sometimes exceeding 10% [76,77]. This requires due consideration prior to the adoption of any salt as a PCM. Additionally, salt hydrates have poor nucleating ability and undergo substantial supercooling. In an effort to address this problem, Kazemi and Mortazafi [78] successfully minimized the supercooling of Glauber's salt by using a nucleating agent, sodium tetra borate. Other nucleating agents have also been successfully implemented for this purpose, such as silver nanoparticles [79], aluminum nitride [80], Si_3N_4, ZrB_2 and SiO_2 [81]. Lane [82] have also suggested that certain nucleating materials may prevent the problem of metal container corrosion, which is a common issue with salt hydrates.

Metals and metallic alloys (eutectics) form the other class of inorganic PCMs. Their high thermal conductivity, thermal stability, repeatability, and reliability [60,83,84] make them very suitable materials. In addition, the heat from their phase transition is the highest per unit volume or unit mass of the different types of PCM, giving them an extremely high capacity for energy storage. They undergo little volume change during the phase transition and have low vapor pressure. Despite all these advantages, they are not commonly considered good PCM materials due to their low heat of fusion per unit weight, which means that the requirement of high weight makes them problematic on practical grounds.

A major issue relating to the use of metallic PCMs for solid–liquid energy storage is the potential for interactions with metal containers [85]. Encapsulation of molten PCMs may be a good approach to solving this problem. Zhang et al. [38] performed encapsulation of copper balls in chromium/nickel layers which prevented leakage and interaction with the environment, even over 1000 thermal charge-discharge cycles at 1050 ℃ to 1150 ℃. These coatings can also provide benefits for the handling and thermal stability of the PCMs [86,87]. The former is demonstrated by Ma et al. [88], in which covering of Fe-23Cu alloy with a layer of FeO enhanced its resistance to wear.

3. Conclusions

This work comprehensively reviews recent advances in solar thermal energy storage systems, discussing the various types of state-of-the-art thermal energy storage and the methods by which they are integrated into solar collectors. The major conclusions are as follows:

- The most relevant factors for evaluating types of thermal energy storage are currently storage efficiency and the cost of materials and operations.
- Sensible heat storage, owing to its reliability, low cost, ease of implementation and the number of experimental results, is the most commonly used type of thermal energy storage.
- Latent heat energy storage is most applicable for storage of excess thermal energy during periods of low consumption. However, the proper selection of appropriate phase change materials (PCMs) for a particular application is vital.

- Thermochemical heat energy storage, a method whereby heat energy is stored in chemical bonds, offers the highest energy storage capacity by volume of the storage methods. The thermochemical heat energy storage materials exhibit poor long-term reversibility, chemical stability, durability as well as need for a complicated reactor presents obstacle to its use and thereby limited its practical application.
- We strongly believe that the discussion of and comparisons between these technological advances within this paper will aid in the selection of suitable materials for achieving effective solar thermal energy storage.

Conflict of interest

The authors declare no conflict of interest.

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