

## Solar Energy Thermal Storage System and Materials

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**Abstract:** Usage of renewable and clean solar energy is expanding at a rapid pace. Applications of thermal energy storage (TES) facility within the solar power field enables dispatch ability within the generation of electricity and residential space heating requirements. It helps mitigate the intermittence issue with an energy source like solar power. TES also helps in smoothing out fluctuations in energy demand during different time periods of the day. During this paper, a summary of varied solar thermal energy storage materials and thermal energy storage systems that are currently in use is presented. The properties of solar thermal energy storage materials are discussed and analysed. The dynamic performances of solar thermal energy storage systems in recent investigations are presented and summarized. Storage methods can be classified into categories according to capacity and discharge time. New developments in solar energy storage require advances in chemical engineering and materials science. Life cycle assessment (LCA) is an important tool to evaluate energy consumption and environmental impact of renewable energy processes. LCAs of some of the storage methods are reviewed. It is important to note that, while using renewable energy sources such as solar power, storage methods based on non-recyclable materials or methods that consume significant amounts of energy may undermine the effort to reduce energy consumption.

**Keywords:** Solar energy, Thermal energy storage, Phase change materials (PCM), Thermal performance, Life cycle assessment.

## **Introduction:**

Solar power applications are found in many aspects of our way of life, like space heating of homes, quandary supply and cooking. One major drawback of alternative energy is intermittence [1]. To mitigate this issue, the necessity for energy storage systems arises in most of the areas where solar power is used. There are different varieties of energy storage solutions [2]. One in all the foremost important fields for solar power application is wattage generation. Here the best-suited energy storage system depends on the kind of technology adopted for electricity generation. For generating power from alternative energy, there's a choice between Photovoltaic (PV) and Concentrated solar energy (CSP) options [3,4]. PV technology usually stores voltage as energy in batteries [5], while CSP utilizes TES to store solar power in thermal energy form. Many comparisons are done between different energy storage technologies [2]. On an outsized scale, high-temperature TES is found to be more suitable than battery technology with its higher load capacity and longer storage duration. Therefore CSP encompasses a better dispatch ability on an oversized scale. But thanks to falling prices of the PV cells, there's an increased competition faced by CSP technology from PV technology [3]. There's a desire for CSP to extend performance altogether aspects like cost, efficiency, reliability, etc. Although the general efficiency of the CSP depends on the performance of all components like collectors, receivers, thermal energy storage systems, heat exchangers, turbines and generators, etc., the performance of the TES system is that the most vital factor [6]. Therefore, progress within the efficiency of the TES technologies and reduction within the cost of electricity generation is that the need of the hour.

Currently, there's a good range of technologies used for the TES. The CSP plants operate TES systems at higher temperatures because it improves the efficiency of the Rankine cycle of the plant. In other application areas, like space heating in buildings, solar predicament supply, and warmth sinks of electronic systems like laptops, etc, the lower temperature TES systems are involved [7]. This review summarizes the present affairs of different technologies within the application fields and their performances. For solar power, electricity generation is unsteady. Generation of electricity fluctuates used for several different reasons. Seasonal conditions, climatic conditions, and locations cause the energy generation process to vary round the year, day, or perhaps within the hour.

In 2007, solar power plants produced 0.22% of the electricity for the state of California, as shown in Figure 2. For solar energy, 99% are generated within the state of California. By 2020, the state of California expects to have 33% of its utilities generated from various renewable energy sources [8]. Without proper electricity storage; this goal will be difficult to reach. Storage methods can be classified in different ways. It is important to review all the different methods and consider their methods from construction to operation and to decommissioning will be needed to perform the LCA study. In this review, the main methods of storing solar energy are reviewed [9]. An assessment of the most recent developments for different storage methods is given. Many key parameters for each method are also presented in order to make specific comparisons between the methods of storage. LCA is discussed as a tool to see the value and environmental impacts [10].

## **The Properties of Solar Thermal Energy Storage Materials**

Applications like house space heating require low-temperature TES below 50 °C, while applications like power generation require high-temperature TES systems above 175 °C [2]. The performances of the TES systems depend upon the properties of the thermal energy storage materials chosen. The thermophysical properties of thermal energy storage materials should be presented within the following aspects in step with the given requirements of the applying fields.

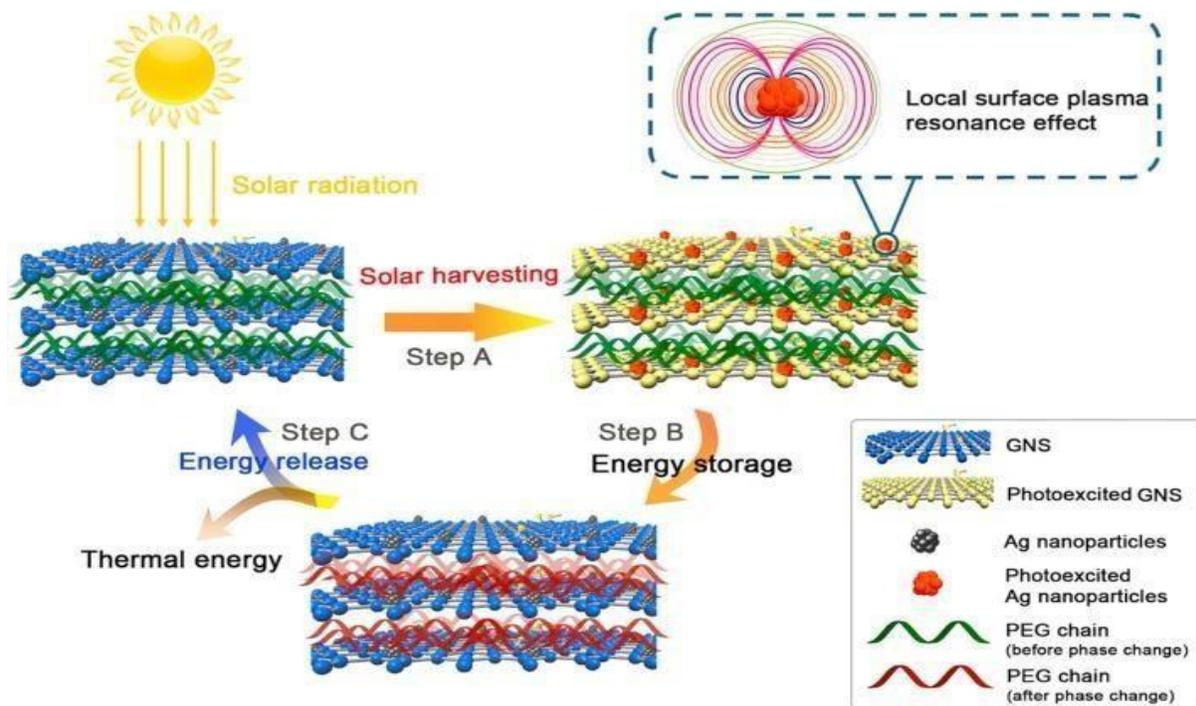


Figure 1: Solar Thermal Energy Storage System

The first one is that the temperature where the phase transition materials should have a freezing point near the specified operating temperature range of the TES system. Secondly, the density of the storage system is a vital property of solar thermal energy storage materials. High density improves energy storage density which reduces the amount of the TES system [11]. The heat of transformation of fusion is another important part where the state change materials should have an awfully high heat of fusion. The high heat energy of fusion improves the energy storage density of the system [12]. Specific heat ( $C_p$ ) of the storage plant is maintaining a crucial part. Sensible heat storage materials should have high specific heat. High specific heat improves the energy storage density of the system. The high thermal conductivity increases the thermal charging and discharging rate which is desired. Super cooling is for physical change materials, during the freezing process, super cooling should be minimal [13]. Storage material should freeze completely at as close as possible to its freezing temperature. Cost and availability are a number of the important concerns. The cheaper price of storage material reduces capital and operational costs. They must be abundantly available. Thermal stability shouldn't decompose at high temperatures [14]. This provides a wider operating temperature range and better energy storage capacity for the fabric. Material properties should be stable even after extended thermal cycles of heating and cooling. Chemical stability is that the high chemical stability of storage materials that increases the lifetime of the energy storage plant [15]. Volume change for action materials, change in volume during the state change process should be minimal. The fabric also should have an occasional coefficient of thermal expansion. Big changes in volume increase the specified size of the container an oversized density difference between two phases also causes a phase segregation issue. Non-toxic shouldn't be harmful to the health of operators and therefore the environment. Non-corrosive is corrosive thermal energy storage materials bring down the energy storage flowers drastically because of the corrosion of containers. Flammability should be non-flammable and non-explosive [16]. Congruent melting is very important within the case of salt hydrates, incongruent melting affects the reverse process because the salt settles down and also the salt is unavailable during the recombination process. The pressure level should have low pressure level within the operational temperature range. High force per unit area requires pressure withstanding containment at high temperatures. It also requires costly insulation.

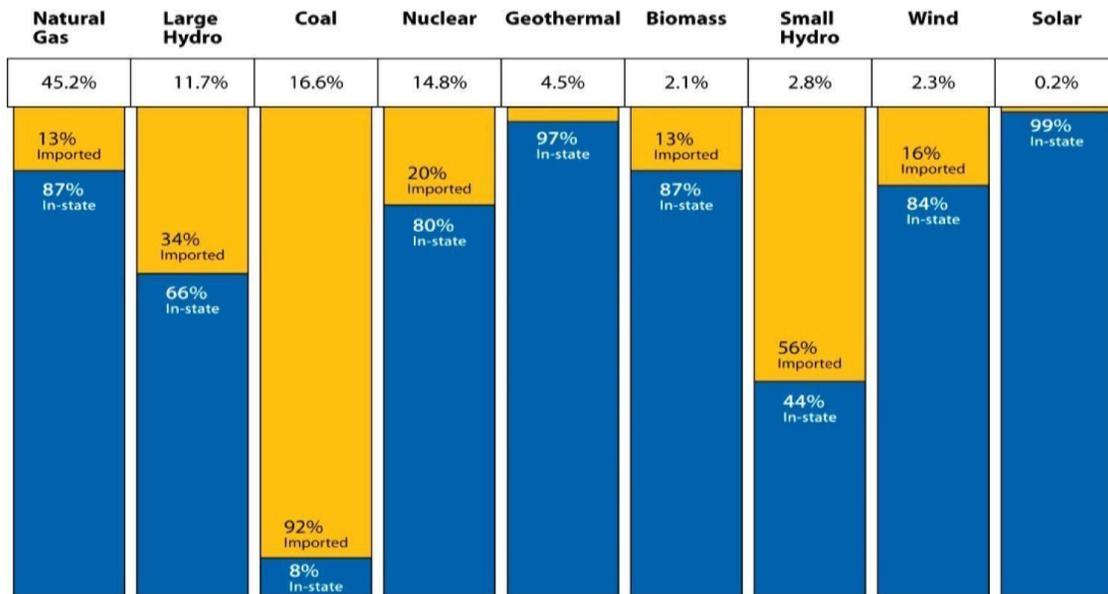


Figure 2: California's electricity mix in 2007

### Classification of Storage Methods

There are many different ways to classify various storage methods. Energy harvested from solar energy consists of two forms: electrical energy from photovoltaic (PV) panels and thermal energy from concentrated solar power. Therefore, in this paper, only the storage methods of electrical energy and thermal energy are reviewed. Since electricity supply is of primary concern, the focus of this review is mainly on electricity storage.

### Thermal Energy Storage

Thermal energy is typically stored in a thermal reservoir for later usage. Thermal energy storage can also be classified according to usage. Thermal energy harvested from a solar source can be stored via thermal physical reaction (i.e., using the temperature difference of materials (or phase changes) to store energy). It can also be stored via chemical reaction (i.e., creating new chemical species (solar fuels)). These methods are shown in Figure 3 and are described as follows:

### Chemical Energy Storage

Heat generated from concentrated solar power is used to carry out endothermic chemical transformation and produce storable and transportable fuel. Examples are solar hydrogen, solar metal, and the solar chemical heat pipe.

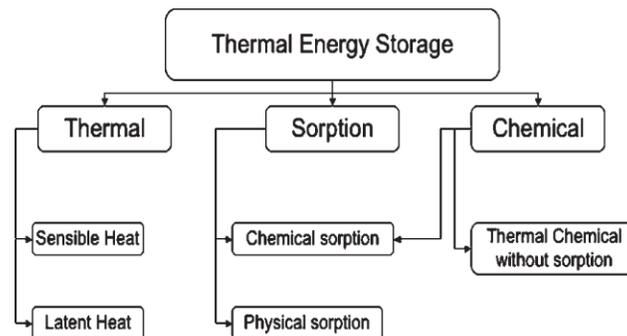


Figure 3: Conceptual Diagram of Thermal Energy Storage.

Table 1: Classification of Energy Storage systems

Classification According to Storage	
Electrical Energy Storage	Direct electricity storage in devices such as capacitors or superconducting magnetic devices; those storage methods have the advantage of quickly discharging the energy stored
Mechanical Energy Storage	Storage of electrical energy in the form of kinetic energy such as flywheel or potential energy such as pumped hydroelectric storage (PHS) or compressed air energy storage (CAES)
Chemical Energy Storage	Storage in chemical energy form as in batteries, fuel cells, and flow batteries; chemical energy storage usually has small losses during storage
Classification According to Usage	
Bulk Energy Storage	Bulk energy storage has discharge power range of 10—1000 MW, discharge times are 1—8 h, and the stored energy range of 10—8000 MWh; the applications of such storage are in load levelling and spinning reserve
Distributed Generation	Distributed generation storage has discharge power range of 100—2000 kW, discharge time range of 0.5—4 h, and the stored energy range is 50—8000 kWh; the application of such storage is in peak shaving and transmission
Power Quality	Power quality storage has discharge time range of 0.1—2 MW, the discharge time is 1—30 s, and the stored energy range is 0.028—16.67 kWh. The applications are end-use power quality and reliability

### Thermal Energy Storage Methods

Thermal energy can be stored directly. In sensible heat storage, such as steam or hot water, by changing the temperature of materials (liquid or solid) during peak-hour energy, the energy is stored by temperature difference of the material. In latent heat storage, such as phase change materials, by changing the phase of materials (liquid or solid) during peak hour energy, the energy is stored in the form of latent heat.

### Sorption Storage

In sorption storage, two chemicals, which are bonded together under standard conditions, are separated using peak-hour energy. Energy is released when the two chemicals are mixed and exposed to standard conditions. The choice of materials has great impact on the performance of the storage system.

### Sensible Heat Storage

Changing the temperature of materials (liquid or solid) by using solar energy generated at its peak hour, energy is stored by the temperature difference of the material with the original temperature. Some examples include solar water and air heaters, graphite, and concrete storage. The concept of solar water and air heaters is simple: using the solar radiation to store thermal energy in air and water. This storage method is becoming popular, because of its relative low cost and simple manufacturing process, but the density of thermal storage is low. For concrete storage, 20 m<sup>3</sup> of concrete storage material can store up to 400 kWh of energy.

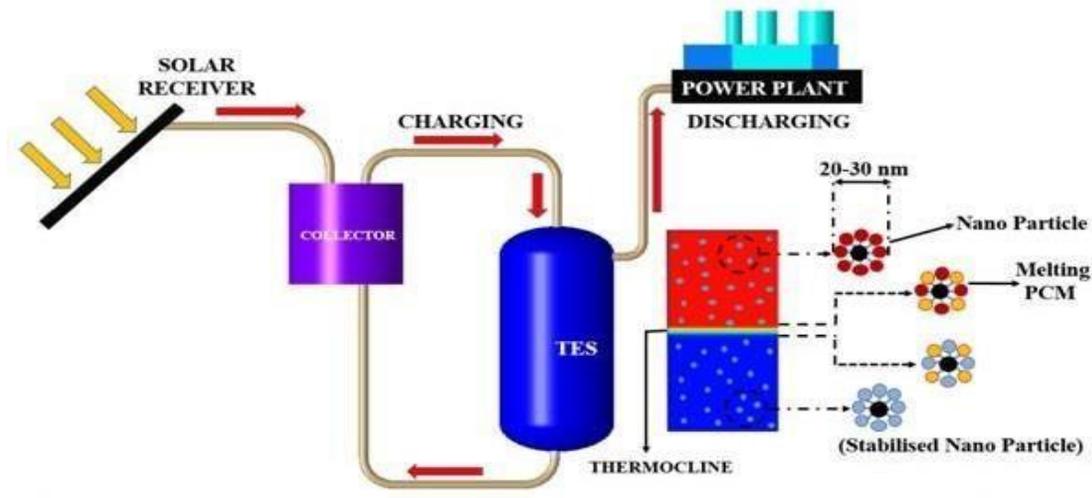


Figure: Sensible heat thermal storage system

### Phase Change Material Storage (PCMS)

Latent heat refers to the energy associated with phase change of a material. When a material undergoes a phase change, heat is absorbed or released. The latent-heat materials store 5 to 14 times more heat per unit volume than do sensible heat storage materials. Phase-change materials (PCMs) are classified into three categories: organic (paraffin, fatty acids), inorganic (hydrates, molten salts, metal), and eutectic (organic organic, organic inorganic, inorganic inorganic compounds) [17]. The latent heat of organic PCM ranges from 10 kJ/kg to 300 kJ/kg. For inorganic PCM, the latent heat ranges from 20kJ/kg to 250kJ/kg. A eutectic is a mixture of two or more components, to minimize the melting temperature of the mixture. The latent heat of the eutectic material is in the range of 100 200 kJ/kg. Recently, many developments in latent heat storage have been observed, mainly because the utilization of solar and industrial heat is a promising method to save energy and reduce CO<sub>2</sub> emission. The advantages of using latent heat storage include a large density of heat storage and constant temperature [18]. In recent years, especially after 2005, the research has focused on integrating the latent heat storage into the solar power generation system. For this purpose, the development of latent heat storage for temperatures relevant for solar thermal power plants is required. A recent review on research and technology directions on developing latent heat storage for high-temperature application can be found elsewhere. A typical design for a PCM-storage system includes a heat exchanger embedded in the storage material [19]. The energy from the sun is collected by melting the PCM impregnated into the thermal storage block, and then using the heat released from the phase change of the material to produce steam and generate electric power.

### Sorption Storage

Sorption is the fixation or capture of a gas or a vapor (sorbet) by a solid or liquid substance (sorbent). The sorption of gas by liquid is called absorption, while the sorption of gas by solid is called adsorption. Adsorption includes two mechanisms: thermo physical reaction by van der Waals forces (physisorption) and thermochemical reaction by valence forces (chemisorption). Chemisorption processes typically store more heat per unit mass than physisorption but may be irreversible. The principle of using sorption (also for thermochemical storage) to store energy is based on a reversible physicochemical reaction. Several pairs of materials have been studied; [20] each pair has drawbacks that prevent its practical use. For NaOH/H<sub>2</sub>O, LiCl/H<sub>2</sub>O, and LiBr/H<sub>2</sub>O, the absorption process can be performed. The NaOH/H<sub>2</sub>O pair is highly corrosive; therefore, its use requires additional care when handled and recycled. The LiCl/H<sub>2</sub>O pair has a high storage

density of 253 kWh/m<sup>3</sup>, but it is not suitable for seasonal storage, because the LiCl salt is expensive, costing 3600 euros/m<sup>3</sup>.<sup>54</sup> The LiBr/H<sub>2</sub>O pair has a storage density of 180–310 kWh/m<sup>3</sup> of a diluted solution.<sup>55</sup> Zeolite/H<sub>2</sub>O and silica gel/H<sub>2</sub>O are two systems that can undergo physisorption. The zeolite/H<sub>2</sub>O pair has a storage density of 124 kWh/m<sup>3</sup> for heating and 100 kWh/m<sup>3</sup> for cooling, when used within a district heating net [21]. Synthetic zeolite is expensive; natural zeolites can be used when the heating temperature is <100 °C. The silica gel/H<sub>2</sub>O pair was reported to have a theoretical storage density of 200–300 kWh/m<sup>3</sup>. However, only 50 kWh/m<sup>3</sup> was obtained experimentally, which has an energy density less than water [22]. Na<sub>2</sub>S/H<sub>2</sub>O and MgSO<sub>4</sub>/H<sub>2</sub>O are two systems that can be used for chemisorption. The Na<sub>2</sub>S/H<sub>2</sub>O pair not only has a high energy storage density (1980 kWh/m<sup>3</sup> for heating and 1300 kWh/m<sup>3</sup> for cooling), but also a high thermal power density. However, this material is very corrosive and must be operated under a vacuum environment. The MgSO<sub>4</sub>/H<sub>2</sub>O pair has a theoretical storage density of 780 kWh/m<sup>3</sup>, but its low power density undermines its practical use.

### **Solar Fuels**

Using optical devices, scattered sunlight can be concentrated and the heat generated from concentrated solar power can be used to carry out endothermic chemical transformation to produce storable and transportable fuels. The engine combusts hydrogen to generate power is called the hydrogen engine [23]. There are three different ways to generate hydrogen with solar power: electrochemical, photochemical, and thermochemical. Electrical energy also can be directly stored as solar fuel. It is not efficient to convert electricity to thermal energy and then produce hydrogen; therefore, this option is not considered. By using the thermochemical route, water and fossil fuel can be used as sources for hydrogen. The solar project UT-3 in Japan has achieved a production capacity of 702 GJ/day. Metals can also be used to store solar energy. Using concentrated solar power as a heat source to dissociate metal oxides, the solar energy can be stored in the metal and energy can be released during the combustion process. Zinc has been shown to be an attractive candidate for this process. During a pilot study, a 300-kW solar chemical plant was built for the production of zinc [24]. Two efficiencies were defined: the thermal efficiency of the solar reactor, which is the fraction of solar power input entering through the reactor's aperture that is absorbed as a sensible and process heat, and the process efficiency, which is the ratio of the heating value of Zn and CO produced to the thermal energy input. Both efficiencies were 30%. The Zn production rate was 50 kg/h, with a purity of 95% [25].

### **Sensible Heat Thermal Energy Storage Materials**

Sensible heat thermal energy storage materials store heat in their specific heat capacity ( $C_p$ ). The thermal energy stored by sensible heat are often expressed as  $Q = m \cdot C_p \cdot \Delta T$ , where  $m$  is that the mass (kg),  $C_p$  is that the specific heat capacity (kJ kg<sup>-1</sup> K<sup>-1</sup>) and  $\Delta T$  is that the rise in temperature during the charging process. During the warmth energy absorption process, there's no physical change happening and materials experience an increase in temperature the number of warmth stored is proportional to the density, volume, specific heat, and variation of temperature of the storage material. A number of the foremost common sensible heat storage materials are listed below.

### **Liquid Data Storage Medium**

The advantage of a liquid medium is that it may be circulated easily then can transport heat if required. Such a system where the data-storage medium is circulated is termed a vigorous system. Also thanks to density difference caused by heating of liquid, the buoyancy helps in creating a thermal gradient across the storage which is desirable [6]. Hot fluid moves up, and cold fluid moves down separating them. Some sensible heat storage liquids are as follows:

## Water

Water is one in all the most effective storage media for low-temperature applications. Its operating temperature range is between 25–90 °C [26]. Its advantages are high specific heat, non-toxicity, cheap cost, and simple availability. But it's few drawbacks like high vapour pressure and corrosiveness. Water is best used for house space heating and slight supply variety of applications. Salty water in solar ponds is employed for collecting large amounts of solar thermal energy at low temperatures (50–95 °C). Heat gets at the dense layer at the underside of the pond because of dissolved salt which hinders natural convection. Salts like NaCl and MgCl<sub>2</sub> are used here. Water storage tanks are made of a large type of materials, like steel, aluminium, concrete, and fiber glass. The tanks are insulated with dielectric, non-conductor or polyurethane. The sizes of the tanks used vary from some hundred liters to some thousand cubic meters. Large water tanks require the event of technologies capable of guaranteeing water tightness, to reduce heat losses caused by steam diffusion through the walls, and to optimize stratification within the tank, so as to preserve the thermal performance and lifelong of the solar heating system [27]. Water may be used for giant scale seasonal energy storage purposes in underground aquifers where water can be found mixed with sand gravel. Such a system is very cost effective as we are able to avoid expensive cistern construction.

Medium	Fluid type	Temperature range (°C)	Density (kg/m <sup>3</sup> )	Specific heat (J/kg K)
Rock		20	2560	879
Brick		20	1600	840
Concrete		20	1900–2300	880
Water		0–100	1000	4190
Caloria HT43	Oil	12–260	867	2200
Engine oil	Oil	Up to 160	888	1880
Ethanol	Organic liquid	Up to 78	790	2400
Proponal	Organic liquid	Up to 97	800	2500
Butanol	Organic liquid	Up to 118	809	2400
Isotunaol	Organic liquid	Up to 100	808	3000
Isopentanol	Organic liquid	Up to 148	831	2200
Octane	Organic liquid	Up to 126	704	2400

Table: Material for heat storage of solar

## Mineral Oil

Mineral oil is employed as a heat transfer fluid (HTF) in CSP plants. It collects the warmth at the receiver then transports the warmth to the boiler where steam is generated for driving the turbine the identical is also wont to store thermal energy during a highly insulated tank during the night. When the HTF also becomes energy storage material, it is a direct system. It eliminates the requirement for a device reducing the price oil features a lower pressure than water and is capable of operating at high temperatures within the liquid make up to 400 °C. Also unlike molten salts, oil doesn't freeze during the night in pipes which creates the necessity for an antifreeze system [28]. But oil is dear compared to molten salts and recently few molten salt mixtures with low melting points are discovered replacing oil as energy storage material. A recent trend in CSP is to use indirect systems where oil acts as HTF and molten salt mixtures act as sensible heat storage materials.

## Molten Salts

Molten salts are currently the foremost used thermal energy storage materials in CSP plants they're cheap (especially the nitrates). Their density is high compared to a different liquid data-storage medium, giving them high energy storage density. Molten salts have a lower force per unit area than water and are capable of

operating at high temperatures within the liquid make up to 400 °C this enables operation of the plant at high temperatures which improves the efficiency of the Rankine cycle it's desirable to own a lower temperature for molten salts and shut to ambient temperature so they continue to be liquid during operation and therefore the need for antifreeze is minimal during the night when solar power isn't available. But pure molten salts usually have melting points above 200 °C which could be a disadvantage. However, today the practice is to use salt composites (more salt mixtures) which brings down the freezing point below 100 °C and yet incorporates a high maximum temperature above 500 °C [29] they will also act as HTF but it's safer to own an antifreeze system to cope with any freezing risk. Otherwise, oil is going to be used as HTF one among the drawbacks of molten salts is that they're oxidizing agents and extremely corrosive and to contain them at high temperatures is problematic. Also, their thermal conductivity is low and incorporates a volume change of around 6% during the melting process.

### **Liquid Metals and Alloys**

Pure metals and alloys having low melting points but above 300 °C even have potential as sensible heat storage media they need high thermal conductivity and a high maximum operating temperature. Their pressure is minimal. But they need drawbacks like high costs. Also, they will require oxygen and an oxide-free environment so as to scale back corrosion [19].

### **Solid Medium**

Solid storage materials have low cost and simply available everywhere they need no force per unit area issues. Therefore the operating pressure is near ambient pressure and then no need for pressure containing vessels and no leak issues. Since they can't be circulated easily, they will only do passive heat storage and want a fluid, usually air (HTF) for transporting heat into and out of loosely packed solid materials in an exceedingly vessel to extend the warmth transfer efficiency there's direct contact between the flowing air and solid heat medium during the charging and discharging process. one in every of the problems with sensible storage is that in the discharging process the temperature of the medium decreases, therefore the HTF temperature also decreases with time. The low-temperature applications like space heating and industrial waste heat recovery may use a number of the solid sensible heat storage materials [27-29].

### **Rocks**

They can be employed in a packed bed after crushing to rough sizes of around 5 cm and employing a heat transfer fluid like air or a combination of sand-rock-mineral oil combination. Hot air flows between the gaps of the packed rocks and warmth the rock during the charging process and cold air flows between the gaps of the packed rocks and gets heated during the discharging process there's an oversized contact extent available for warmth transfer between air and rocks which improves heat transfer efficiency. Rocks are poor thermal conductors and there's a little contact area between rock pieces which minimizes heat loss during storage. Rocks have advantages like being non-toxic, non-flammable, very cheap, and simply available. There are few drawbacks prefer it requires large atmosphere flow rates and better pressure drops [29].

### **Concrete**

Concrete is an easily workable medium. Since it possesses good mechanical strength, it doesn't require a container to carry. One design approach for warmth exchanger between concrete and HTF is to own pipes through the concrete block through which the HTF flows. One issue faced at high temperatures is crack formation after repeated cycles of thermal expansion and contraction. Research work [29-30] is on to develop an

appropriate concrete mixing, optimizing chemical–physical and sturdiness performances in an exceedingly higher temperature range.

## **Sand**

Locally available small grained materials like gravel or silica sand may be used for thermal energy storage. Silica sand grains are average 0.2–0.5 mm in size and might be utilized in packed bed heat storage systems using air as HTF. Packing density are going to be high for little grain materials. Gravel materials like basalt gravel are going to be around 0.4 mm in size. They'll be used directly within the solar receivers to gather solar thermal energy as they make up gravity from the highest within the solar receiver tower. After absorbing the warmth of concentrated solar rays during their fall inside the tower, the new sand gets collected in an insulated vessel below. The temperature of hot sand can go up to 700–1000 °C which is able to then be used for producing steam to drive the Rankine cycle powerhouse. Schlipf et al. [30] studied the chance of using sand during a packed bed as a heat data-storage medium for high-temperature thermal energy storage systems. The results presented that the sands have storage potential for temperatures up to 550 °C.

## **Bricks**

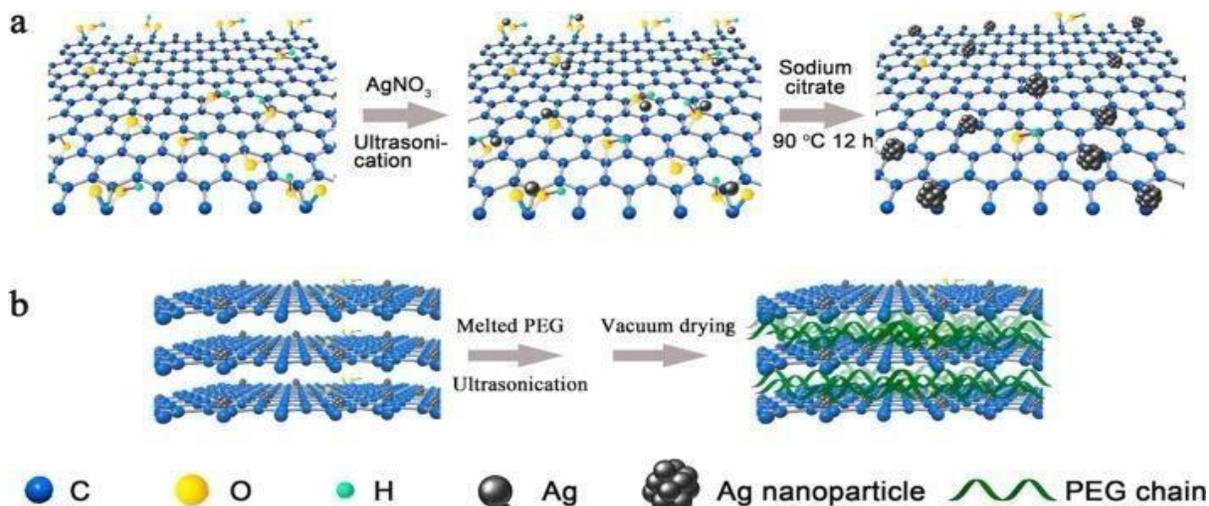
Bricks in building walls can store thermal energy to reduce space heating electricity costs [19] they will be heated during off–peak hours during the night with cheaper electricity and store heat. The stored heat is extracted from the bricks during the day by natural convection and radiation or by forced convection using an electrical fan [21]. This stored heat keeps the building warm during peak hours during the day with no electricity consumption.

## **Latent Heat Thermal Energy Storage Materials**

Latent heat storage materials also called phase change materials (PCM) absorb heat energy as their “latent heat of fusion” during the melting process. During the heat energy absorption process there is a phase change happening and the temperature swing is very small. The thermal energy stored in phase change material can be expressed as  $Q = mL$ , where the mass (kg) is and  $L$  is the latent heat of fusion ( $\text{kJ kg}^{-1}$ ). Usually, it is the solid-liquid phase change process that is used. Transformations from liquid to gas have the highest latent heat of phase change. However, the enormous changes in the volume of the storage materials associated with the evaporation make the storage complex and highly impractical [28]. If solid-solid latent heat storage materials are used, the lack of liquid material eliminates the risk of leakage and there is no need for encapsulation. But their latent heat of transition is about one order of magnitude smaller than that of the solid-liquid latent heat storage material, which is a major drawback [28]. Latent heat storage materials must have a large latent heat and high thermal conductivity [27]. They should have a melting temperature point near the required operating temperature range of the TES system and should melt congruently with minimum sub cooling [28] and should be chemically stable, low in cost, non–toxic, and non–corrosive. During the discharging process, the temperature of the storage medium is constant, so the HTF temperature also remains stable with time, which is an advantage over sensible heat storage materials. For latent heat storage materials, there is a smaller temperature difference between storing and releasing heat [30]. The “latent heat of fusion” of the material will be very large compared to specific heat. For example, sodium nitrate salt has a specific heat of  $1.1 \text{ kJ kg}^{-1} \text{ K}^{-1}$  but its “latent heat of fusion” is around  $172 \text{ kJ kg}^{-1}$ . This kind of large difference gives the latent heat storage materials advantage of high energy storage density. This reduces the volume of the TES vessels, which reduces their outer wall surface area and minimizes heat loss.

## Organic

Organic latent heat storage materials and their eutectic mixtures have been successfully tested and implemented in many domestic and commercial applications, such as space heating in buildings, electronic devices, refrigeration and air-conditioning, solar air/water heating, textiles, automobiles, food and space industries [30]. Organic materials possess the capability of congruent melting without phase separation [29]. Organic PCM has an inherent characteristic of low thermal conductivity (0.1–0.35 W/m K), hence, a larger surface area is required to enhance the heat transfer rate [30]. In addition, because of the low melting point of organic PCM, they have not yet been explored for high-temperature applications such as in power plants



## Paraffin

Paraffin waxes consist of the straight n-alkanes chain ( $\text{CH}_3\text{-(CH}_2\text{)-CH}_3$ ) [30]. Pure paraffin waxes are very expensive, and therefore, only technical grade paraffin can be used. Commercial paraffin waxes are cheap with moderate thermal storage density (200kJ/kg or 150 MJ/m<sup>3</sup>) and a narrow range of melting temperatures from  $-10\text{ }^\circ\text{C}$  to  $67\text{ }^\circ\text{C}$ . They undergo a very little sub-cooling and are chemically inert and stable with no phase segregation. They are non-corrosive, odorless, long-lasting, inexpensive, easily available, ecologically harmless, and nontoxic. However, they have low thermal conductivity (0.2 W/m K), which limits their applications [29]. Commercial grade paraffin wax is obtained from the distillation of crude oil. Most paraffin PCM are mixtures of saturated hydrocarbons with different numbers of carbon atoms in the molecules. The melting temperature and heat of fusion of the paraffins increase with the average length of the hydrocarbon chain. This relationship can be employed to design the PCM properties by mixing physically different paraffin. Even after 1000–2000 cycles commercial-grade paraffin waxes and other pure paraffin have stable properties and good thermal reliability. Paraffin waxes are safe. Since they do not promote corrosion, they are compatible with metal containers. However, they interact with some plastic containers which have chemical similarity to paraffin. Polymers like polyolefin experience problems like infiltrations and softening.

## Fatty Acids

They have a general formula of  $\text{CH}_3\text{(CH}_2\text{)}_{2n}\text{-COOH}$  and have ideal thermophysical properties of a low-temperature latent heat storage material. The melting and boiling points of fatty acids are relatively high compared to that of the paraffins, and the saturated fatty acids exhibit low phase transition volume changes. They have reproducible melting and freezing behavior with very little or no super-cooling. They are more expensive

than technical grade paraffins, mildly corrosive, and possess a disagreeable odor. They are combustible in nature [24]. Generally, the melting and freezing points, the heat of melting and the degree of crystallization of fatty acids increase with the number of carbon atoms in their molecules [26].

### **Esters**

Esters are derived from acids in which one hydroxyl (–OH) group is replaced by one alkyl (–O) group. Fatty acid Esters show solid-liquid transition over a narrow temperature range. They can form the eutectics without or little sub-cooling. Eutectic mixtures of Esters have phase transition temperature close to room temperature with a high enthalpy of transition [14]. Fatty acid Esters have good availability, due to their commercial applications in polymer, cosmetics, and smart clothing industries in large quantities.

### **Alcohols**

Sugar alcohol, also known as poly alcohols, are considered as medium temperature (90–200 °C) PCM. They have not received much attention by researchers. Previous studies revealed that alcohols such as xylitol, erythritol and mannitol possess a latent heat of fusion close to 300kJ/kg, which is much higher value than other materials in this family. Alcohols have been tested as potential phase change materials in the last four decades.

### **Glycols**

Polyethylene glycol (PEG) has different names like poly oxyethylene (POE) or polyethylene oxide (PEO). PEG is composed of dimethyl ether chains having the hydroxyl group at the end, with a formula of HO–CH<sub>2</sub>–(CH<sub>2</sub>–O–CH<sub>2</sub>)<sub>n</sub>–CH<sub>2</sub>–OH. They are soluble in water as well as in organic compounds. PEGs come in various grades like PEG400, PEG600 etc [30]. Many numerical and experimental studies are done on these materials in the past. They are chemically and thermally stable, nonflammable, non-toxic, non-corrosive and inexpensive. The melting point and latent heat of fusion of the PEGs increase with increasing molecular weight [19]. Like other organic PCM, the PEG also has low thermal conductivity problem.

### **Inorganic:**

These materials have a high volumetric latent heat density of around 350 MJ/m<sup>3</sup>. They have stable properties even after a large number of thermal cycles and have a relatively higher thermal conductivity of around 0.5 W/m K. However, they melt incongruently [31]. They are prone to phase segregation and sub cooling. Another major issue with them is corrosion of salt on metal container.

### **Salt Hydrates**

Salt hydrates are normally used at low operating temperatures in the range of 30–50 °C. They have a general formula AB·nH<sub>2</sub>O, which are inorganic salts containing water of crystallization. During phase transformation, dehydration of the salt occurs. This can occur in two ways. There could be a salt hydrate that contains fewer water molecules or there could be anhydrous form of the salt.

### **Composite Phase Change Materials**

To address the poor thermal conductivity issue, by dispersing high thermal conductive particles like carbon, graphite or metals into the PCM, the thermal conductivity of the PCM can be improved. Such a mixture is called composite phase change material. Composites can be prepared using both organic and inorganic phase change materials. The added thermal conductive materials should be compatible with the PCM. For example, if the PCM is corrosive in case of few inorganic salts, the added conductive material should be corrosion resistant.

## Graphite Composites

Graphite can be used in different forms as below tested the performance of the PCM composites composed by the NaNO<sub>3</sub>/KNO<sub>3</sub> eutectic PCM with thermal conductive graphite by dispersion of graphite within the molten salt, and found an improvement of the thermal conductivity by 14 times up to an effective conductivity of 9 Wm<sup>-1</sup> K<sup>-1</sup>. Sari et al. [31] tested the performance of the PCM composites composed by the n-docosane paraffin with expanded graphite. Thermal conductivities of the composite PCM with mass fraction of 2%, 4%, 7% and 10% expanded graphite indicated that the thermal conductivity of the paraffin (0.22 W/m K) increased as 81.2%, 136.3%, 209.1% and 272.7%, respectively.

## Graphite Fakes or Natural Graphite

They have a well-aligned crystal structure and high thermal conductivity. They have stacked sheets of carbon, where carbon atoms are held together by strong covalent bonds and these stacked sheets are held together by weak van der Waals bonds. Hence they have a dense packing and high density. They require minimum treatment during production and their cost is very low. A sole particle size is around 400 nm.

## Expanded Natural Graphite

This is produced from natural graphite after undergoing two processes, such as chemical treatment and thermal exfoliation. In reactions with various acids, the weak bonds are overcome and molecules of the reactant are incorporated between the layers of the graphite. The graphite structure has to expand to accommodate the reactant molecules, but the sheet structure remains intact. This is called an intercalated compound. After the graphite intercalated compound is washed in water and dried, it is heated to cause rapid expansion of the graphite layers. The heat treatment is done in an air atmosphere at temperatures greater than 500 °C. The water is incorporated between the layers of carbon during the formation of the intercalated compound. The near instantaneous vaporization of the water during the heat treatment process is responsible for the expansion. Each natural graphite particle is modified into the form of worm in which the graphene layers are spread leading to high particle porosity. These worms can be made into a bed and then compressed to form a consolidated graphite matrix of high porosity and thermal conductivity.

## Expanded Graphite Powder

This is prepared by grinding expanded graphite into powder. It has a less compact structure than natural graphite and tends to build networks even at small concentrations. Thus compared to natural graphite, smaller amounts of expanded graphite powder are required to reach a similar thermal conductivity. Nevertheless, due to the corresponding treatments needed for their production, it is more expensive than natural graphite. In the present study, particle sizes vary between 50 and 500 nm.

## Nano Composites

It can also use different nanostructures as thermal enhancement additives in PCM [31] explored following types of nanoparticles as the materials of the thermal conductivity promoters. Nanoparticles have the advantage being extremely small in size. Hence they behave like fluid and avoid being clogged during flow in pipes. Generally, the thermal enhancements achieved with carbon based nanostructures are found better than that with metallic and metal oxide [32]. It performed a review of current experimental studies on variations in thermo-physical properties of PCM due to dispersion of nanoparticles. The types of nanoparticles are as follows:

- (1) Carbon-based nanostructure nanofibers, nanoplatelets, graphene flakes and carbon nanotubes.
- (2) Metallic (Ag, Al, C/Cu and Cu)

- (3) Metal oxide (Al<sub>2</sub>O<sub>3</sub>, CuO, NiO, SiO<sub>2</sub>, ZnO, MgO and TiO<sub>2</sub>)
- (4) Silver nanowires.

### **Form-Stable Composite**

A composite is called form-stable composite PCM if it could keep the same shape in solid state even when the temperature of the composite is over the melting temperature of the PCM. In a form-stable composite, the PCM can be molded to required shapes with higher surface area to volume ratio without the aid of an encapsulation to increase heat transfer rate. Here the main idea is to improve the contact surface area of the PCM with HTF and increase of thermal conductivity is not the priority. Sari [32] explored form-stable paraffin/high density polyethylene composites where paraffin acts as latent heat storage material and high density polyethylene acts as supporting material which gives structural strength to prevent leakage of melted paraffin. An improvement of up to 24% in thermal conductivity was obtained.

### **Conclusions and Future Outlook**

Solar energy storage methods are urgently needed, because of the increased demand and unsteady nature of solar power. The implementation of proper energy storage remains crucial to achieve energy security and to reduce environmental impact. It is difficult to compare different types of storage methods using only one factor. In fact, no single type of storage method can be used universally to store energy. For specific situations, geological locations, and existing facilities, different storage methods are possible and must be considered. Currently, batteries are the most common method in use to store solar energy. In thermal energy storage, currently the main focus areas are cost reduction of storage material, cost reduction of operation and improvement in the efficiency of energy storage. Applications for the TES can be classified as high, medium and low temperature areas. In high temperature side, inorganic materials like nitrate salts are the most used thermal energy storage materials, while on the lower and medium side organic materials like commercial paraffin are most used. Improving thermal conductivity of thermal energy storage materials is a major focus area. Cost effective manufacturing technologies for microencapsulated PCM and composite materials are being explored. Optimizing the thermo physical properties like melting point of thermal energy storage materials to suite a given requirement is also explored with techniques like eutectic mixtures and hydrocarbon chain length etc. For sensible and latent heat storage materials, the technologies are quite mature and are already commercialized, but thermochemical materials are still at lab stage. Thermochemical materials have great potential as thermal energy storage materials in the future due to their highest volumetric energy storage capacity. For more mature technologies such as PHS and CAES, current developments are primarily focused on performance optimization and integration with the power grid. For many other storage methods, such as batteries, capacitors, sorption, and solar fuels, the advancements for those methods depend on the discovery of new materials and the characterization of materials and properties. Less-expensive, high-capacity, and environmentally friendly materials are some of the criteria in choosing the right materials. It should be noted that some materials needed for certain storage methods are scarce, such as ruthenium for capacitors and lithium for batteries. With new materials and hybrid technologies, the demand for storage can be met. Solar power can become a main energy source in the near future.

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