Chapter 9
Thermal Energy Storage for Solar Energy

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9.1 Introduction

The increase in global energy consumption and the depletion of conventional energy resources have triggered efforts to explore sustainable renewable energy resources. The adverse effect of conventional fuel-based energy systems on the environment, such as pollution and CO_2 emission, can be mitigated by integrating them with suitable renewable energy resources along with energy storage. Solar energy technology has risen as the prominent renewable energy resource for various energy applications due to its abundant availability. The intermittent nature of solar energy is one of the major challenges in the utilization of this form of energy in various applications. The integration of appropriate storage technology can overcome this challenge. One of the potential energy storage technologies to store energy from solar energy is thermal energy storage (TES). The thermal energy storage is one of the critical parts of any solar energy system. Energy is stored in the form of heat/cold in the working medium of thermal energy storage, which can further be utilized for various applications. The entire working cycle of the TES comprises three different processes, such as the charging, heat retaining, and discharging process. The energy collected from the solar collectors is supplied to the storage medium in the charging process. In contrast, the stored heat has been retrieved from the storage medium during the discharging process (Fig. 9.1). In the heat retaining process, the stored energy is retained in the medium for a specific period. The energy stored in TES solely depends on the inherent characteristics of the storage medium and the temperature difference between the source of energy and the storage medium.

The varying demand for energy requires proper energy redistribution between source and end user. Solar energy system integrated with TES can fulfill the peak

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S. N. Singh et al. (eds.), *Fundamentals and Innovations in Solar Energy*,
Energy Systems in Electrical Engineering,
https://doi.org/10.1007/978-981-33-6456-1_9

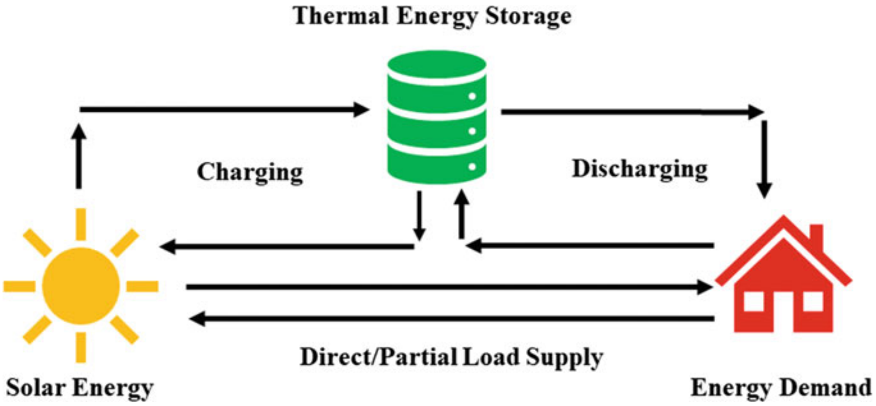


Fig. 9.1 Operation of thermal energy storage. *Source* Author

and fluctuating energy demands and provides high energy security. TES provides operational flexibility and better capacity utilization (extent up to which system uses its overall rated capacity) in the system. The improved performance of solar energy systems incorporated with TES results in economical operation as compared to the solar energy systems without TES. The overall efficiency of the energy systems is interrelated with energy conservation. Hence, any improvement in the energy conservation approach in the system can lead to increased efficiency. The TES can be characterized based on the following performance parameters:

- Power Density: It is the energy transfer rate per unit mass or volume of the storage medium.
- Energy Density: It is the amount of energy accumulated in a given mass or volume of the storage medium.
- Storage Period: It defines the duration of energy storage. It can vary from hours to months.
- Response Time: It is the rate of storing/releasing energy in/from the storage to balance the load demand. It can vary from seconds to minutes.
- Charging/Discharging Time: It is the time required to charge/discharge the storage system.
- Discharge Rate: It is the measure of the rate at which accumulated energy in the storage is discharged.
- Self-Discharge: It is the energy dissipation during idle time.
- Cycle Life: It represents the maximum number of charging/discharging cycles that can be operated into the entire life span of the storage.
- Round-Trip Efficiency: It is the ratio of the energy retrieved to the energy stored in the storage.
- Cost: It comprises capital as well as the operational cost of the energy storage.

The aforementioned performance parameters play an important role in the selection of appropriate storage technology for specific energy applications. The high

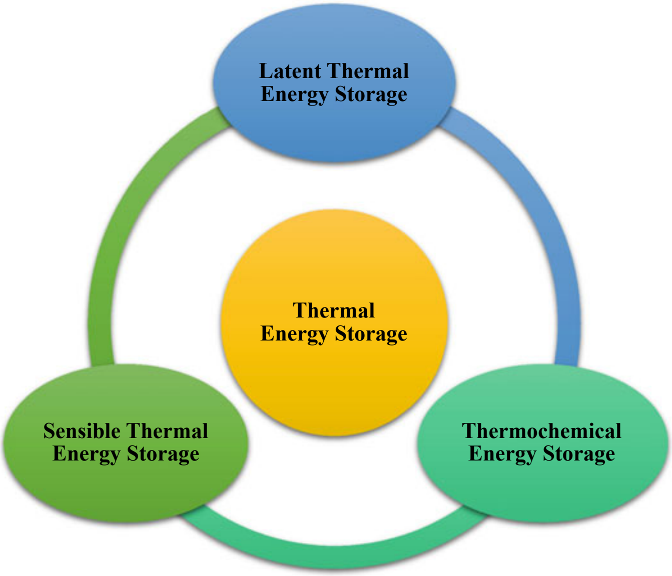


Fig. 9.2 Classification of TES. *Source* Author

energy and power density directly represent the storage capability of the TES. The round-trip efficiency indicates how efficiently the storage technology can be utilized by minimizing energy losses. Efforts are being made by the researchers to develop cost-effective TES technology having a better cycle life. Based on the process of storing energy, thermal energy storage technologies may be classified into three categories, such as sensible thermal energy storage (STES), latent thermal energy storage (LTES), and thermochemical energy storage (TCES) (Fig. 9.2). In a sensible thermal energy storage system, the heat is stored/released by increasing/decreasing the temperature of the storage medium, while LTES stores/releases energy by undergoing the phase change process. The TCES stores/releases energy in the form of the enthalpy of the corresponding chemical reaction. Every type of TES has its own merits and demerits, which should be considered during the selection of the appropriate storage technology according to the specific application (Table 9.1). The detailed description of these technologies is provided in the subsequent sections.

9.2 Sensible Thermal Energy Storage

The roots of the STES technology can be found in our old historical building structures where rocks and stone are used to keep the inner space cool during summer

Table 9.1 Comparison between STES, LTES, and TCES [1]

	STES	LTES	TCES
Capacity (kWh/t)	10–50	50–150	120–250
Power (MW)	0.001–10.0	0.001–1.0	0.01–1.0
Efficiency (%)	50–90	75–90	75–100
Storage period	Days/seasonal	Hours/seasonal	Hours/days
Advantages	• Reliable and inexpensive • Simple system and easy operation • Low cost and eco-friendly • High thermal conductivity	• Moderate energy density (better than STES) • Isothermal operation • Available in wide range of melting temperatures	• Highest energy density • Compact system • Operates at atmospheric temperature • Negligible heat losses
Disadvantages	• Low energy density • Huge volume required for storage • High heat losses and self-discharge • High construction cost and geological constraints	• Low thermal stability • Corrosion • Low thermal conductivity • High cost • Supercooling	• Expensive • Design and operational complexities
Present status	• Matured technology and large-scale deployment have been done	• Technology is in pilot-scale testing phase, and several laboratory-scale prototypes have been developed	• Unmatured technology and laboratory-scale testing have been done

and hot during winter. Nowadays, this technology has emerged as a promising technology for diverse energy applications due to the development of advanced materials. The STES stores energy by altering the temperature of the working medium without undergoing any phase change process (Fig. 9.3). The working cycle of STES comprises two processes, such as sensible heating (charging process) and sensible cooling (discharging process). The energy stored per unit mass in STES is directly proportional to the specific heat and the difference between the initial and final temperatures of the storage media. The materials having high specific heats and high operating temperatures are preferred in STES because they can store more thermal energy. However, the higher temperature of the storage medium leads to higher heat losses to the surrounding. So, insulation plays an essential role in STES. The sensible heat stored in kJ (Q) during charging of STES can be expressed in terms of specific heat in kJ/kg K (c_p), mass in kg (m), and temperature difference in °C (ΔT) as follows:

$$Q = mc_p \Delta T = mc_p (T_{\text{final}} - T_{\text{initial}}) \tag{9.1}$$

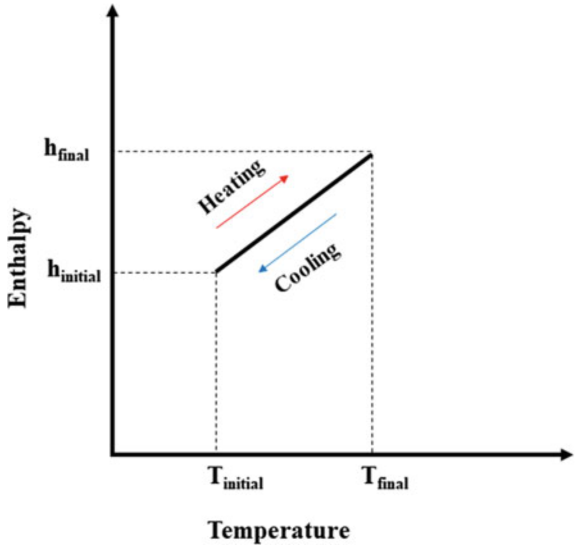


Fig. 9.3 Sensible heating/cooling. *Source* Author

$$\Rightarrow Q = V.\left(\rho.c_p\right).(T_{\text{final}} - T_{\text{initial}}) \quad (9.2)$$

Here, $\rho.c_p$ is the volumetric heat capacity of the STES (in kJ/m^3 K).

The energy stored during charging can be retrieved during the discharging process. The efficiency of STES depends on the inherent characteristics of the medium of storage. The materials having high energy density and thermal conductivity are preferred for storing high energy in a compact space. The thermal and chemical stability of the material and non-reactivity with the container material is necessary for developing STES, having a long cycle life. The structural stability of the storage is judged based on the compressive strength and fracture toughness of the material. The use of non-toxic and non-explosive materials is necessary to develop eco-friendly STES technologies. Generally, sensible storage mediums provide a low-cost storage option for many energy applications, which makes it widely adopted thermal storage technology. The sensible thermal storage materials can be classified into two distinct categories, such as solid and liquid sensible heat storage materials (Fig. 9.4). Gaseous materials are usually not preferred as a sensible heat storage media due to their high specific volume. Rocks, pebbles, refractory bricks, and metals such as steel and cast iron are used as the solid sensible heat storage media, and oil, water, inorganic salts, etc., are used as the liquid sensible heat storage media in STES (Table 9.2). The flowability of liquid sensible materials provides some operational flexibility to the storage. The low-cost storage can be made by using solid materials.

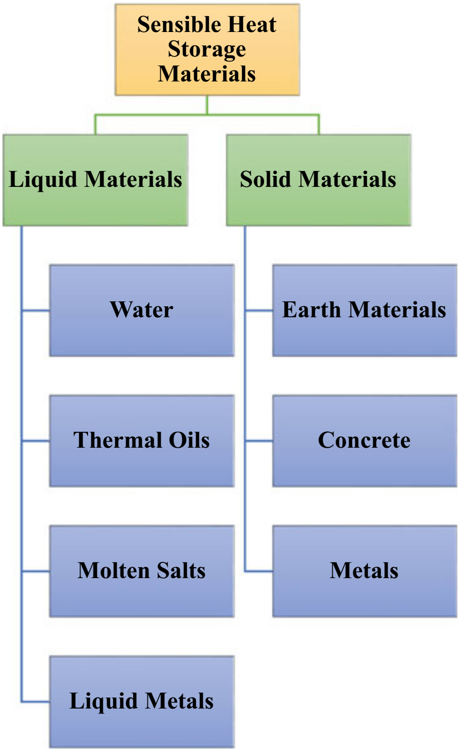


Fig. 9.4 Classification of sensible heat storage materials. *Source* Author

9.2.1 Solid Sensible Heat Storage Materials

Solid sensible heat storage materials are one of the economical media to store thermal energy. These materials have been used in various solar energy applications for the past many years. The solid materials used in sensible thermal energy storage are as follows.

9.2.1.1 Earth Materials

The commonly used earth materials are gravels, sand, and rocks. The better thermal conductivity, significant storage capacity, nonflammability, non-toxicity, and the lowest cost make these materials suitable for storing thermal energy in diverse solar applications such as solar power generation, solar cooking, desalination, and solar drying. The packed bed configuration of storage is the most suited configuration for storing thermal energy in earth materials in a large quantity [8]. In space heating applications, earth materials have been utilized in the packed bed storage as the filler materials and air have been utilized as the heat transfer fluid (HTF). The heat

Table 9.2 Sensible heat storage materials [2–7]

Materials	Density (kg/m^3)	Specific heat at 20 °C (kJ/kg K)	Thermal conductivity at 20 °C (W/m K)	Thermal capacity (MJ/m^3 K)
Concrete	2200–2700	0.75–1.13	0.9–2.0	1.68–3.0
High alumina concrete	2400	0.98	0.2	2.35
Reinforced concrete	2200	0.85	1.5	1.87
Cement mortar	1900–2000	0.64	0.6–0.7	1.19–1.30
Castable ceramic	3500	0.86	1.4	3.03
Alumina ceramic	3800–4000	0.75–0.88	18.0–33.0	2.83–3.48
Silicon carbide ceramic	3200	0.75	120	2.40
Brick	1700–1800	0.84	0.5–0.7	1.419–1.51
Brick magnesia	3000	1.13–1.15	5.0–5.1	3.39–3.45
Silica fire brick	1800	1.00	1.5	1.82
Soil (clay)	1500	0.88	1.3	1.27
Soil with gravel	2000	1.84	0.5	3.68
Silica-based refractory	2300	0.86	1.8	2.01
Copper	8300–9000	0.38–0.41	372.0–385.0	3.17–3.72
Iron–cast iron	7200–7900	0.46–0.83	29.3–73.0	3.34–6.61
Aluminum	2700	0.89–0.94	204.0–238.4	2.41–2.55
Lead	11300	0.13	35.3	1.48
Steel–cast steel	7800	0.57–0.60	40.0–50.0	4.45–4.68
Steel slag	3000	0.99	2.0–3.5	2.96
Cofalit	3100	0.80–1.03	1.4–2.7	2.49–3.22
Graphite	2200–2300	0.40–0.61	122.0–155.0	0.88–1.37
Sodium chloride	2200	0.85–0.86	6.5–7.0	1.83–1.86
Molten salts	500–2600	1.50	0.2–2.0	1.35–3.90
Mineral oil	800	2.6	0.1	2.0
Synthetic oil	900	2.10–2.30	0.1	1.89–2.07
Liquid sodium	900	1.30	71	1.10
Water	1000	4.18	0.6	4.17

capacity, thermal conductivity, density, porosity, cost, and availability are the parameters that need to be considered for selecting appropriate earth material for the given applications.

9.2.1.2 Concrete Block

Concretes are a mixture of gravel, sand, and cement, where cement acts as a binder. Concrete blocks are the low-cost and eco-friendly sensible heat storage materials having significant thermophysical properties. Due to the excellent mechanical properties, concrete does not require any storage container, which reduces the cost of the storage. When concrete-based sensible heat storages are operated for many high-temperature thermal cycles, then it can lead to the swelling of the concrete structure, which further can generate the cracks in the structure.

9.2.1.3 Metals

Metals are also used as sensible heat storage in many applications. Metals can store/release heat at a faster rate as compared to the other storage materials due to their high thermal conductivity and diffusivity. Therefore, the heat transfer area required for the metallic storage medium is less than the other mediums. Aluminum, steel, cast iron, zinc, and copper are some of the preferred metals which are used in STES. The solid industrial waste such as metal slag and metal chips can also be used as the storage medium. Metals are preferred for high-temperature (200–700 °C) storage applications [4]. It is to be noted that the cost of the metal-based STES is much higher as compared to other STES materials.

9.2.2 Liquid Sensible Heat Storage Materials

Storing thermal energy in the liquid sensible heat storage medium is a widely adopted storage technology in solar energy applications. The liquid materials used in sensible thermal energy storage are as follows.

9.2.2.1 Water

It is one of the widely used sensible heat storage materials due to its easy availability, low cost, significant specific heat, nonflammable and non-toxic nature. It is also used as the heat transfer fluid in various applications. It is used in the form of ice, water, and steam in cold storage, medium temperature storage (below 100 °C), and steam accumulator, respectively. The high vapor pressure of water increases the material cost of the container.

Table 9.3 Thermophysical properties of thermal oils used in concentrating solar power plants [9]

Properties	Therminol VP-1	Xceltherm 600	Syltherm XLT	Dowtherm A
Composition	Diphenyl oxide/biphenyl	Paraffinic mineral oil	Dimethyl polysiloxane	Diphenyl oxide/biphenyl
Max bulk temperature (°C)	400	316	260	400
Melting point (°C)	12	–	−111	12
Atmospheric boiling point (°C)	257	301	200	257
Kinematic viscosity (mm^2/s)	2.48	15.5	1.1	2.56
Density (kg/m^3)	904	736	660	897
Thermal conductivity (W/m K)	0.11	0.12	0.06	0.1083
Specific heat capacity (kJ/kg °C)	2.075	2.643	2.171	1.63
Thermal storage capacity (MJ/m^3 °C)	1.876	1.945	1.433	1.462

9.2.2.2 Thermal Oils

The organic fluids having excellent heat transfer characteristics are used as the HTF as well as the storage fluid in various solar energy applications. Table 9.3 shows various thermal oils used in solar power plants. These oils remain in the liquid phase at the higher temperature (up to 250 °C at atmospheric pressure) as compared to water, so it can be used for high-temperature heat transfer as well as heat storage applications. Owing to low vapor pressure than water, thermal oils require a low thickness of material for containers and pipes. Thermal oils do not freeze in pipes as molten salts during direct storage, where they have used as the HTF as well as the storage fluid because thermal oils have a low melting point ($\leq$12 °C). The specific heats of thermal oils (~2 kJ/kg K) are lower than water, and their cost is also high; nevertheless, they are one of the reliable materials for energy storage in various applications.

9.2.2.3 Molten Salts

The stability issues of thermal oils at high temperature ($\geq$400 °C) limit its applications in many energy systems. In those systems, molten salts are preferred for heat transfer fluid as well as storage media. Table 9.4 shows the thermophysical properties of various molten salts used in solar energy applications. The high volumetric storage

Table 9.4 Thermophysical properties of molten salts used in the solar energy applications [10–13]

Properties	Solar salt	Hitec	Hitec XL	Na-K-Li nitrates
Composition	$NaNO_3$ (60%)-KNO_3 (40%)	$NaNO_3$ (7%)-KNO_3 (53%)-$NaNO_2$ (40%)	$NaNO_3$ (7%)-KNO_3 (45%)-$Ca(NO_3)_2$ (48%)	$NaNO_3$ (28%)-KNO_3 (52%)-$LiNO_3$ (20%)
Melting point (°C)	220	142	120	130
Stability limit (°C)	600	535	500	600
Viscosity (Pa s)	0.00326	0.00316	0.00637	0.03
Density (kg/m^3)	1899	1860	1992	–
Thermal conductivity (W/m K)	0.55	0.2	0.52	–
Heat capacity (kJ/kg K)	1.1	1.56	1.45	1.091

capacity, stability at the high temperature, high boiling point, and low vapor pressure make the molten salts one of the preferred materials in concentrating solar power plants. The major drawback of molten salts is its very high melting point due to which it solidifies in the pipes when there is no heat source (during off-sunshine hours). Although the melting point of the pure salts can be reduced by making a eutectic mixture of two or more salts, they still have a high melting point. The high viscosity of molten salts increases the pumping power requirements of the storage systems, such as direct two-tank sensible storage of solar power plants. The selection of container material requires special attention because molten salts are corrosive in nature.

9.2.2.4 Liquid Metals

Liquid metals possess excellent heat transfer characteristics. Generally, the liquid metals having a low melting point are preferred in this category to store thermal energy (Table 9.5). The high thermal conductivity, negligible vapor pressure, and significant heat capacity make them a potential candidate as HTF and heat storage media. The large difference between the melting and boiling points of liquid metals provides them a wide operational temperature range as compared to the other materials. The very high cost and susceptibility to corrosion are the major obstacles in the wide utilization of liquid metals in various energy-related applications.

Table 9.5 Thermophysical properties of liquid metals used in concentrating solar applications [11]

Properties	Na	Na (22.2%)-K (77.8%)	Pb (44.5%)-Bi (55.5%)
Melting point (°C)	98	−12	125
Stability limit (°C)	883	785	1533
Viscosity (Pa s)	0.00021 (at 600 °C)	0.00018 (at 600 °C)	0.00108 (at 600 °C)
Density (kg/m^3)	1042	780	10300
Thermal conductivity (W/m K)	46.0 46 (at 600 °C)	26.2 (at 600 °C)	12.8 (at 600 °C)
Heat capacity (kJ/kg K)	1.25 (at 600 °C)	0.87 (at 600 °C)	0.15 (at 600 °C)

9.2.3 Sensible Thermal Energy Storage Systems

There are various TES systems in which sensible heat storage materials are used to store thermal energy collected from solar collectors. One such popular sensible thermal energy storage system is water heat storage. Solar water heating storage system stores thermal energy collected by either flat plate solar collector or evacuated tube solar collector in the form of the enhanced sensible heat of the water. The efficient utilization of sensible heat storage materials in diverse solar energy applications depends upon the proper design of the TES. The operating parameters also play a critical role in the designing of the storage system. The sensible storage materials can directly be used in the solar energy systems itself, or a separate storage system can be integrated with the solar energy system. A separate storage system can be operated in either a direct or indirect mode of operation. In the direct mode of operation, the fluid which receives energy from the source and the fluid which is utilized as the medium of storage will be the same. In contrast, both the fluids will be different in the case of an indirect mode of operation. The existing STES technologies which have been utilized in various solar energy applications for the past many years are discussed in the following sections.

9.2.3.1 Single-Tank Thermocline Storage

Single-tank sensible heat storage filled with liquid HTF provides an economical option to store thermal energy. In CSP plants, the single-tank thermocline storage is being used from the past many years. The same HTF, which collects energy from the solar field, also acts as the storage medium in the insulated single-tank thermocline storage. The hot HTF stored in the tank can be utilized in the power cycle at the time of need. During charging, the hot fluid was fed at the top, and cold fluid is drawn from the bottom. The flow is reversed during the discharging operation (Fig. 9.5). The hot fluid (at the top half of the tank) remains separated from the cold fluid (at the bottom half of the tank) due to the thermal stratification (buoyancy difference).

In another configuration, the low-cost filler material can be used as the primary storage medium in the tank, and liquid HTF is used as the secondary medium of storage as well as to maintain the thermocline. It decreases the overall cost of the system by reducing the required quantity of costly liquid HTF [14, 15].

9.2.3.2 Two-Tank Storage

Two-tank sensible heat storage is one of the most widely used thermal energy storages in concentrating solar plants. Two-tank thermal storage can be classified into direct and indirect two-tank thermal storage. In the direct two-tank TES (Fig. 9.6), the same fluid is used as the HTF in the solar field as well as the storage media in the storage tanks.

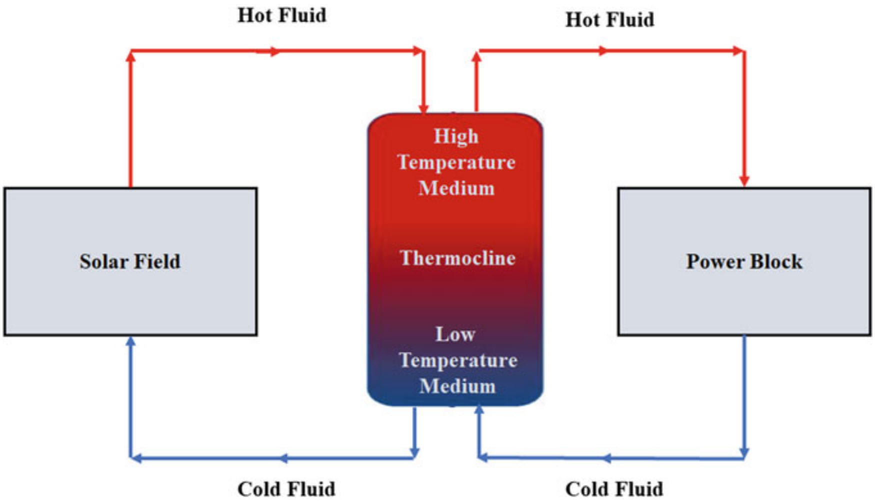


Fig. 9.5 Single-tank thermocline storage for concentrated solar thermal power plant. *Source* Author

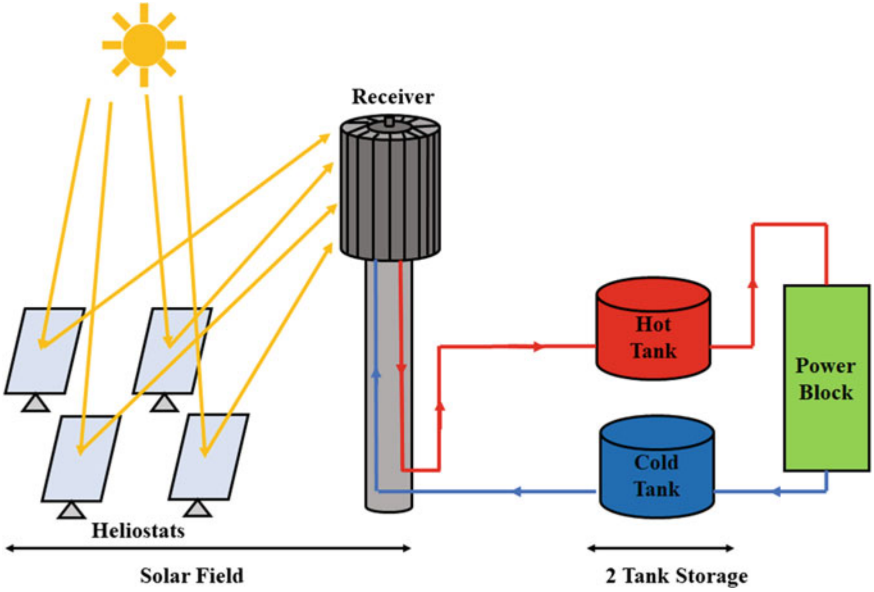


Fig. 9.6 Direct two-tank sensible heat storage in central receiver-based concentrating solar thermal power plant. *Source* Author

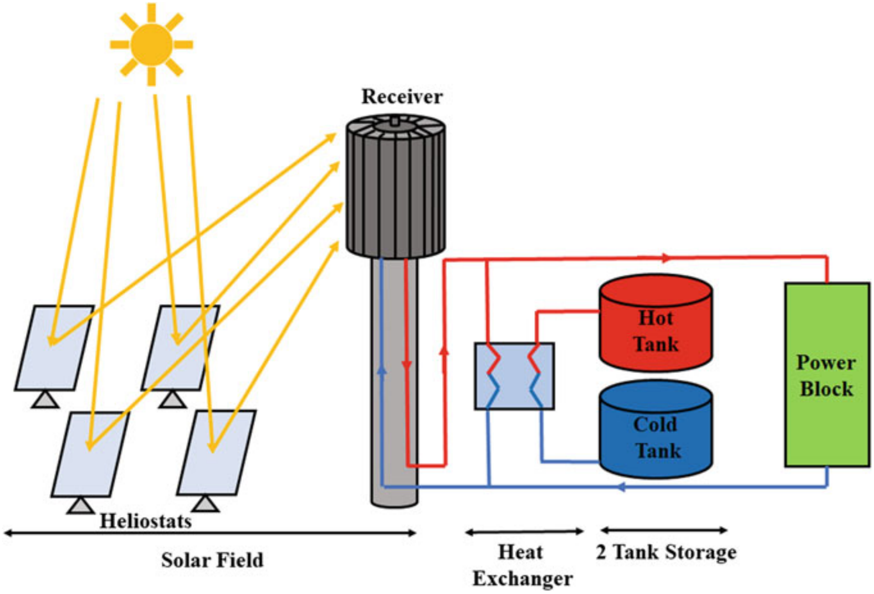


Fig. 9.7 Indirect two-tank sensible heat storage in central receiver-based concentrating solar thermal power plant. *Source* Author

During the charging cycle, the HTF is pumped from the cold tank and collects energy from the solar field, and it is stored in the hot tank. During the discharging cycle, the stored energy in the hot tank can be utilized for generating steam in the power cycle. In contrast, in the indirect configuration of two-tank storage (Fig. 9.7), separate fluids are used in the solar field and storage tanks. A heat exchanger is provided to facilitate the heat transfer between the HTF of the solar field and storage fluid. During sunshine hours, the energy collected by the HTF which is passing through the solar collectors can be fed directly to the power block to generate electricity. The excess energy can be supplied to the storage medium with the help of an intermediate heat exchanger. The storage fluid can store the thermal energy in the hot tank, which can further be utilized for generating the steam during off-sunshine hours and cloudy weather conditions. Both the modes of operations have its own advantages and disadvantages, which need to be considered during the selection of the appropriate two-tank storage. Generally, thermal oils are used as the HTF in the parabolic trough solar collector field, and salts are used as the storage fluid in indirect two-tank storage. Due to the low operating temperature range of thermal oils and low boiling points ($\leq$400 °C), the vapor pressure rises quickly at the temperature higher than the boiling point of the respective oil. It can lead to the leakage of costly thermal oils. In that case, low-cost salts can be used as the HTF in the solar field as well as the storage fluid (direct two-tank storage). It will eliminate the need for a costly heat exchanger between the solar field and two-tank storage. On the other hand, the high melting point of molten salts can lead to the freezing of HTF in the

Fig. 9.8 Two-tank molten salt storage of Andasol solar power station located in Spain [16]

solar field during the unavailability of the heat source. The requirement of trace heating/auxiliary heaters, anti-freezing, and the draining mechanism will add the extra cost to the system. In early concentrating solar plants, direct two-tank storages were used, but nowadays, indirect two-tank storages are being preferred. Figure 9.8 shows the two-tank molten salt storage of the Andasol solar power station located in Spain.

9.2.3.3 Steam Accumulator

The low volumetric energy density restricts the direct use of saturated as well as superheated steam in the storage. Instead, pressurized water having a high temperature can be used for storing thermal energy in steam accumulators. It is a promising technology which has been widely utilized in CSP plants as well as conventional power plants as a buffer storage system. In the direct steam generation (DSG)-based solar thermal plants, the steam can directly be stored as the high-temperature pressurized water in the steam accumulators. This eliminates the need for auxiliary components such as heat exchanger and additional pumps, which are being utilized in molten salt-based storages. The steam accumulators also eliminate the limitation of the maximum allowable temperature of common oil-based storages and eliminate the cost of intermediate heat exchangers. Water has significant heat capacity and can be used for high-temperature heat transfer as well as storage fluid. The high-temperature steam from the solar field can be fed into the steam accumulator based on the Ruth accumulator system (Fig. 9.9), where it starts condensing in the water, which is already

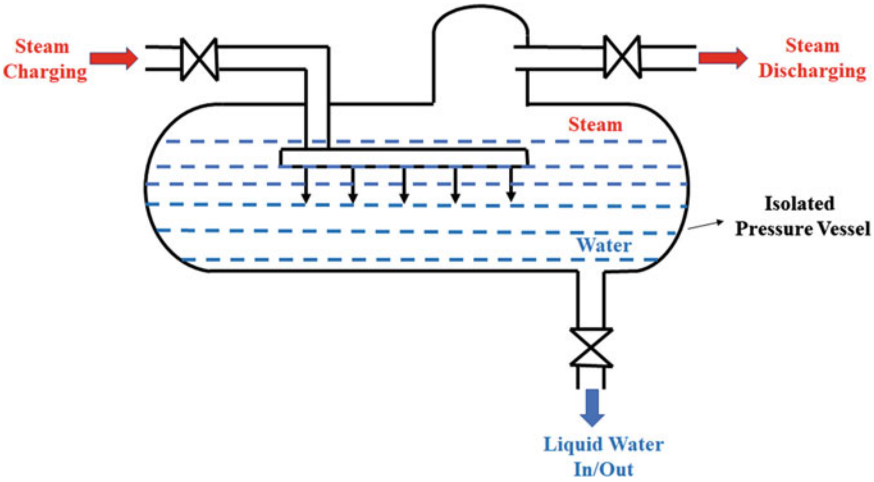


Fig. 9.9 Schematic of a steam accumulator [17]

filled in the accumulator (covering 50–90% of the total volume of the accumulator). Due to the condensation of the high-temperature pressurized steam, the temperature and pressure of the filled water increase. However, most of the energy received from steam is stored in the form of the sensible heat of the water, but some part is also stored directly as the steam over the water. The water at high temperature and highly pressurized state can be converted into saturated steam by flash evaporation, while it is exposed to the low-pressure atmosphere. Generally, steam accumulators are manufactured in cylindrical shapes, and carbon steel is used as the material of fabrication, which can withstand high temperature and pressure.

For the appropriate designing of the steam accumulators, it is necessary to focus on the thermomechanical stability of the system for multiple charging/discharging cycles. It directly affects the life span of the storage. Steam accumulators can be vertical and horizontal in orientation, but horizontal steam accumulators are preferred because it provides a large surface area of water to condense the steam. The size of the accumulator depends on the required storage capacity. Generally, multiple units are preferred for storing a large amount of energy due to its easy transportation and maintenance. The major drawback of steam accumulators is its short storage period. Steam accumulators are used to overcome the effect of inappropriate weather conditions on the operation of the CSP plants for a short period of time. It cannot be utilized for extending the operation of the plant after sunset and during the long duration of cloudy conditions. The steam accumulator-based storage system having a storage capacity of 20,000 kWh, which is utilized in commercial power tower plant PS10 located in Spain (Fig. 9.10), can provide 50 min of operational capacity at 50% turbine load [18].

Fig. 9.10 Steam accumulators of PS10 power tower plant, Spain [16]

9.2.3.4 Underground Thermal Energy Storage

The ground (clay, rock, soil, sand) can be a potential storage medium for storing thermal energy at low temperatures (≤80 °C). Due to the low operating temperature, underground thermal storages are more suited to the water and space heating/cooling applications at the domestic and district level [19]. The thermal energy collected from the solar collectors can be stored in the underground storage during the charging process, and later it can be retrieved from the storage. Underground spaces can also be used for storing cold fluid. Generally, underground storages are referred as seasonal storage, i.e., in cold areas, they store excess thermal energy in summer and utilize that energy in winter. There are different configurations available in which underground space can be utilized for storing thermal energy, which are aquifer storage, borehole storage, pit storage. Aquifer storage stores energy in the natural underground water reservoir and its surrounding porous matrix.

There are two different underground wells of warm and cold water that are used to store energy. The water from the cold well can be passed through the solar collectors to gain thermal energy, and then it can be stored in the warm well. Later this warm water can be utilized for the space heating and water heating applications (Fig. 9.11). Aquifers are location specific and depend upon the geological and hydrogeological conditions of the site. Borehole storage is the closed-loop underground thermal energy storage where a vertical heat exchanger surrounded by the grouting materials such as Portland cement, silica sand, and bentonite is inserted into the drilled boreholes to transfer the thermal energy to the underground rocks. After receiving the energy from the source, the heat transfer fluid can transfer that energy to the

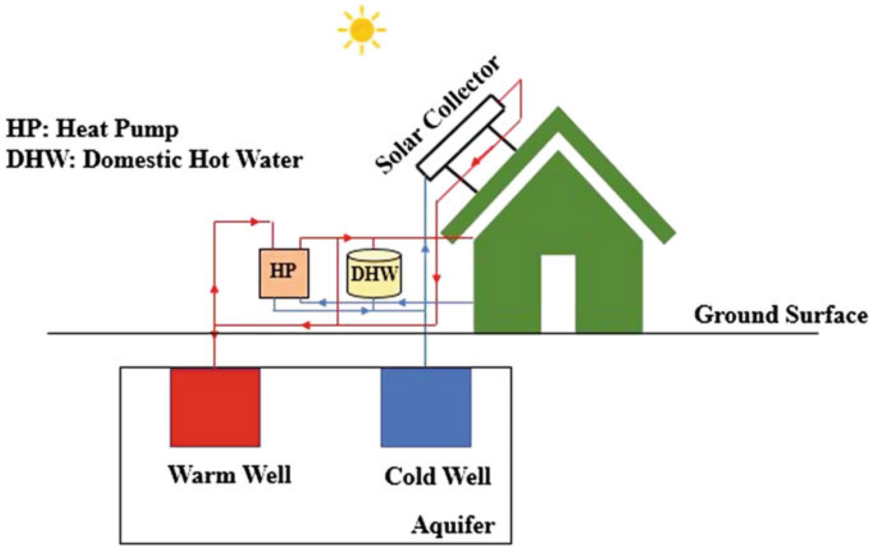


Fig. 9.11 Aquifer storage [20]

underground rocks (Fig. 9.12). However, the presence of a heat exchanger in the borehole provides flexibility to use any HTF as per the operating temperature of the respective applications; it also increases the overall cost of the system. Underground oil wells and mining sites can be used as the pit thermal energy storage where the

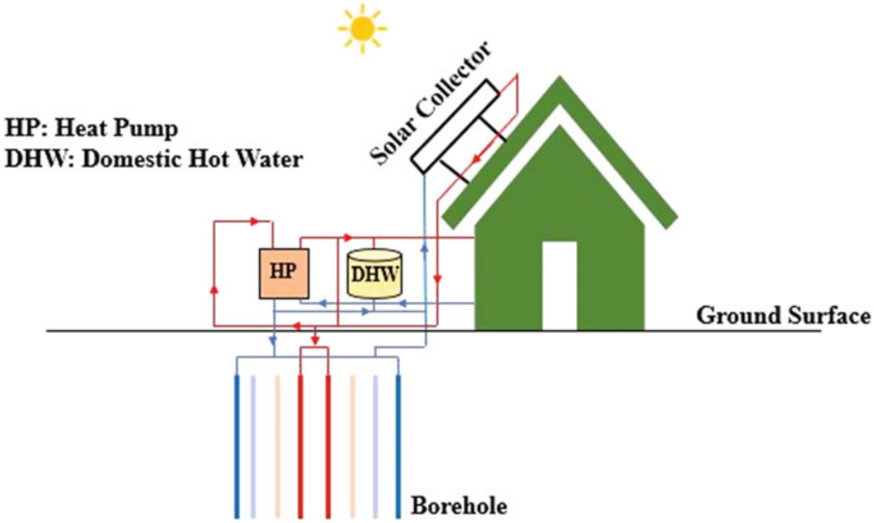


Fig. 9.12 Schematic of borehole storage [20]

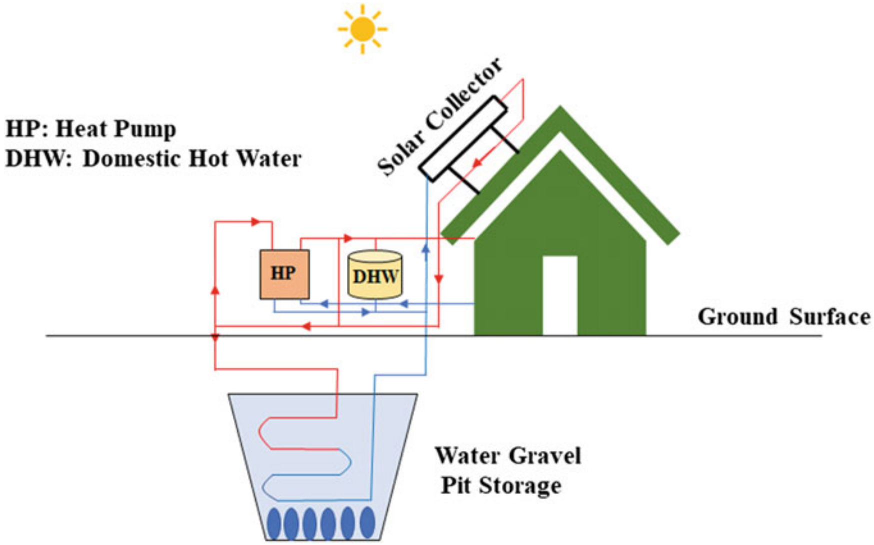


Fig. 9.13 Pit storage [20]

thermal energy of the warm/cold water can be stored. These underground storages are lined with plastic (HDPE) and filled with water or gravel. Top of the pit storage is insulated to reduce thermal losses. The thermal energy of the warm water can be transmitted to the different layers of the pit storage either by direct contact or through the heat exchanger tubes installed at different layers (Fig. 9.13). From an economic perspective, aquifer and pit storages are the favorable storage technologies due to their low cost.

9.2.3.5 Solar Pond

In lakes and ponds, the sun rays heat the water, which decreases the density of the water. The less-dense water moves to the surface and loses its energy to the atmosphere. The repetition of this process keeps the temperature of the lake and ponds nearly equal to the atmospheric temperature. In the solar pond, the natural convection of the heated water is restricted by creating the salt gradient. The bottom region of the solar pond is made densest by dissolving salt in it. Due to the high density of the bottom region, the water cannot lift to the upper region even after it gets heated. According to the presence of salt, the solar pond can be divided into three different zones, such as upper convective zone (surface zone), intermediate non-convective zone (gradient zone), and lower convective zone (storage zone) (Fig. 9.14). The highly dense lower convective zone (LCZ) stores energy, while the intermediate non-convective zone (NCZ) insulates it due to the salt gradient developed in it.

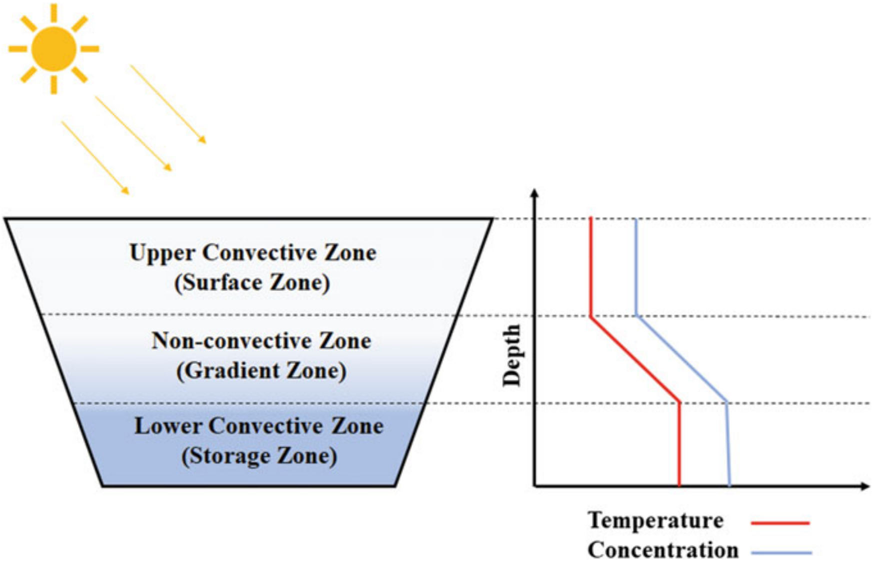


Fig. 9.14 Various zones of the salt gradient in the solar pond [21]

The upper convective zone (UCZ) has low salinity water or freshwater generally at atmospheric temperature.

The sun rays reach the black painted absorber surface at the bottom and sides of the pond due to the significant transparency of water to the visible radiation and heat the absorber surface. Further, the heat is transferred to the salty water in the storage zone. The gradient zone traps this energy in the storage zone itself. The stored thermal energy can be utilized for many low-temperature applications. The conduction losses from the storage zone can be minimized by using proper insulation on the bottom and side surfaces of the pond. Owing to the substantially low thermal conductivity of water, if the appropriate thickness of the intermediate non-convective zone is maintained then the heat losses from the top region, i.e., UCZ, can be reduced. In this way, the solar pond acts as the solar collector as well as a sensible thermal storage system. At the location where large land area, significant solar radiation, and water are available, this technology can be utilized to store solar thermal energy. In Bhuj (India), a 6000 m^2 solar pond supplies energy to the dairy industry [22].

Owing to the low cost, the solar pond has been utilized for many solar energy applications for the past many years, such as solar desalination [23] and electricity generation using thermal energy generator [24]. Researchers have fabricated the mini solar pond having a salt gradient in it and a shallow solar pond without having a salt gradient inside it for small size storage applications. Initially, the energy is absorbed either by the black painted inner surface of the pond or by a black rubber kept at the bottom of the pond. To retain the thermal energy in the system for a longer duration, two glass covers were used. These solar ponds were utilized in integration with solar stills, and it was found that these storage systems are capable of improving the daily performance of the solar stills [25, 26].

9.3 Latent Thermal Energy Storage

The latent heat storage materials store energy in the form of phase transition enthalpy by undergoing a phase change process at nearly a constant temperature. These materials are commonly known as phase change materials (PCMs). Although the solid–liquid, liquid–gas, solid–gas, and solid–solid phase transformations can store energy, owing to a better enthalpy of phase transition and acceptable volume change, solid–liquid phase transitions are preferred for storing energy in LTES. During the melting cycle (charging cycle) of PCM, it absorbs heat, which increases the vibrational energy of its atoms or molecules. The atomic bonds loosen due to the absorbed energy, and material changes its phase from solid to liquid (Fig. 9.15).

A reverse process occurs during the solidification cycle (discharging cycle) of the PCM, and it releases the stored energy. The heat absorbed/released during the charging/discharging cycle is termed as latent heat. It is important to note here that the latent heat represents the energy of phase transition only. It does not contain the heat stored/released during the process in which the temperature of medium changes significantly, which is often termed as sensible heat. It can be understood from the example of the melting of ice. If heat is supplied to the ice, it absorbs heat at a

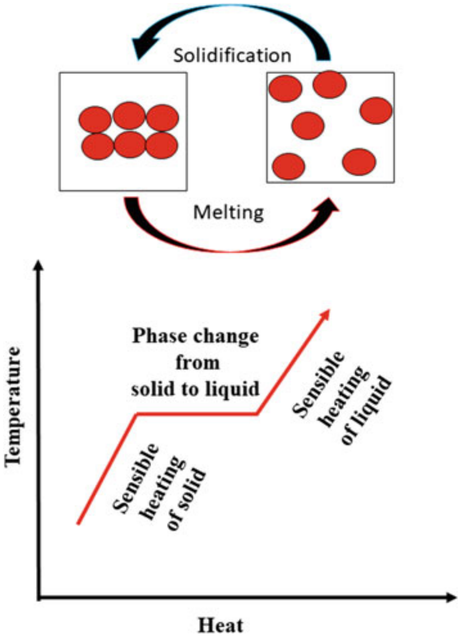


Fig. 9.15 Melting/solidification process and melting curve [27]

nearly constant temperature in the form of latent heat until it completely melts. If further heat is supplied to the liquid water, then it starts absorbing heat in the form of sensible energy, and its temperature starts rising. However, the LTES stores energy in the form of sensible and latent heat both, but the energy stored during phase change remains much higher than its counterpart. The latent heat stored during solid–liquid and liquid–gas transformation is known as latent heat of fusion and latent heat of vaporization, respectively. The heat stored/released during the solid–liquid phase transition of the PCMs can be expressed as:

$$Q = \int_{T_i}^{T_m} mc_{ps}\mathrm{d}T + m\beta L + \int_{T_m}^{T_f} mc_{pl}\mathrm{d}T \tag{9.3}$$

$$\Rightarrow Q = m\left[c_{ps}(T_m - T_i) + \beta L + c_{pl}\left(T_f - T_m\right)\right] \tag{9.4}$$

where c_{ps}, c_{pl} are the specific heats of PCM in the solid state and liquid state, respectively. β and L are the fraction of PCM melted and latent heat of fusion, respectively. T_i, T_m, and T_f represent the initial temperature, melting temperature, and final temperature of the PCM, respectively. The efficient design and development of the PCM-based storage depend on the appropriate selection of the PCM. The desirable properties of the PCMs are as follows:

- Thermophysical Properties: The selection of the melting point of the PCM should be made according to the applications. The PCM should be capable of storing large energy per unit volume; i.e., it should have high latent heat. The high specific heat of the PCM permits additional heat storage as its sensible energy. The heat transfer rate in LTES depends on the thermal conductivity of the PCM; higher the thermal conductivity, better will be the heat transfer rate. For the structural point of view, the volume changes of PCM during phase transition and the vapor pressure should be low.
- Chemical Properties: The better chemical and thermal stability of the PCM makes the LTES durable for the multiple operational cycles. The PCM should be non-toxic, nonflammable, and eco-friendly.
- Kinetic Properties: The PCMs having a good nucleation rate are preferred in LTES. The congruent melting of PCM improves the performance of the storage. The solidification/melting cycles of the PCM should be reversible, and there should be no or less supercooling.
- Economic Properties: For the development of economically viable LTES, the cost of the PCM should be low, and it should be readily available. The recyclable PCMs are preferred over non-recyclable PCMs.

PCMs can be categorized broadly in three distinct categories, such as inorganic PCMs, organic PCMs, and eutectic PCMs (Fig. 9.16). Every type of PCMs has certain advantages and disadvantages associated with them. The selection of the appropriate PCM based on requirements of the particular application is necessary for the fruitful utilization of these materials in storage technology. PCMs are available in a diverse

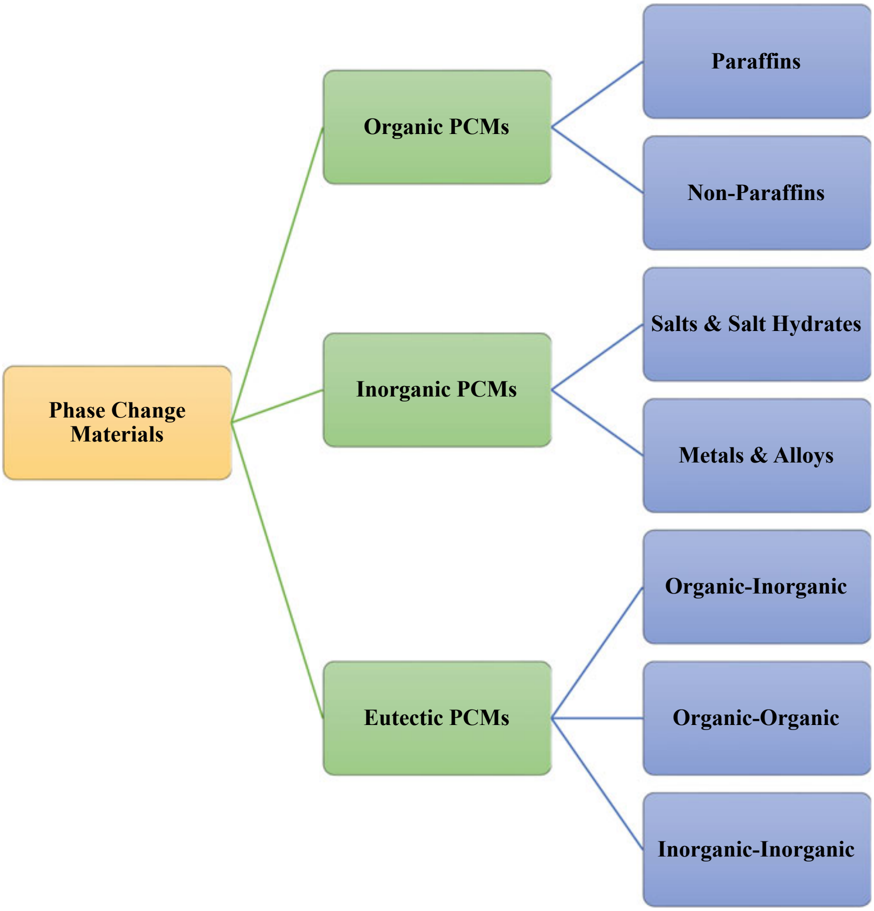


Fig. 9.16 Classification of phase change materials. *Source* Author

range of thermal properties, which can be efficiently utilized for storage applications in various solar energy systems.

9.3.1 Organic PCMs

Organic PCMs are readily available in a wide range of temperatures. The melting without phase segregation and low or no supercooling makes them a prominent material for storing latent energy. Organic PCMs are usually non-corrosive due to which it is compatible with many container materials. These PCMs can further be classified into the groups of paraffins and non-paraffins.

9.3.1.1 Paraffins

The paraffin having straight-chain alkanes is used as the latent heat storage materials where the length of the chain directly indicates the melting temperature of the paraffins (Table 9.6). Longer the chain, higher will be the melting point. Their chemical formula is $CH_3-(CH_2)_{(n-2)}-CH_3$; here, "n" represents the no. of "C" atoms.

Table 9.6 Thermophysical properties of paraffins used in the LTES and their properties [28–31]

Materials	Melting temperature (°C)	Latent heat (kJ/kg)	Density (kg/m^3)	Thermal conductivity (W/m K)	Storage capacity (MJ/m^3)
Decane (carbon atoms-10)	−29.65	202	726 (liquid)	–	147
Pentadecane (carbon atoms-15)	10	205–210	765–768 (liquid)	–	157–161
Eicosane (carbon atoms-20)	36.7	247	785 (solid), 778 (liquid)	0.15	192
Triacontane (carbon atoms-30)	65.4	252	806	–	203
Tetracontane (carbon atoms-40)	81.5	272	817	–	222
Pentacontane (carbon atoms-50)	92	276	825	–	228
Hexacontane (carbon atoms-60)	99	279	831	–	232
Heptacontane (carbon atoms-70)	105.5	281	836	–	235
Hectane (carbon atoms-100)	115.25	285	846	–	241
Rubitherm RT-5	5	180	880 (solid), 770 (liquid)	–	158.4
Paraffin wax	32–32.1	251	830	0.514 (solid), 0.224 (liquid)	208
Medicinal paraffin	40–44	146	830	0.5 (solid)	121
Commercial paraffin wax	52.1	243.5	809.5 (solid), 771 (liquid)	0.15 (solid)	197.1
Bees wax	61.8	177	950	–	168

Pure paraffins are costly because it requires high refinement. So, the low-cost technical grade paraffins are preferred for LTES, which are actually the by-product of oil refining. Generally, paraffins are incompatible with the plastic containers and can be stored in metal-based containers. The sufficient availability of paraffins for a wide range of melting temperatures, moderate latent heat, congruent melting, low cost, low vapor pressure, low volume change, and negligible supercooling increases its adaptability in various energy applications. The thermal conductivity of paraffins is low, and they are moderately flammable. These drawbacks can be overcome by proper designing of the storage systems.

9.3.1.2 Non-paraffins

Easters, fatty acids, alcohols, and glycols come under this category, which have good heat storage capability in terms of significant latent heat. Fatty acids ($\mathrm{R{-}COOH}$) obtained from natural oils can be an appropriate substitute material for pure paraffins. The fatty acids have low thermal conductivity, and their high-volume change during phase transition and instability at the high temperature, which limits its applications. Fatty acid easters having chemical formula $\mathrm{R{-}COO{-}R'}$, where R and $\mathrm{R'}$ are alkyl groups, can also be utilized as the PCMs. Easters have low supercooling and are chemically stable, but these PCMs also have the drawbacks of low thermal conductivity and unpleasant odor like fatty acids. For medium temperature storage applications such as waste heat recovery and solar heating, alcohols are preferred. They possess the highest melting temperature and latent energy of fusion among other non-paraffin PCMs. Polyethylene glycols (PEGs) are one of the most used glycols in LTES. PEGs have the highest supercooling among all other paraffin and non-paraffin PCMs. The non-paraffins have diverse properties where every type of material possesses unique advantages and disadvantages. The low thermal conductivity, instability at high temperatures, is the major shortcoming of non-paraffins. Table 9.7 shows various non-paraffin PCMs used in solar energy applications.

9.3.2 Inorganic PCMs

The inorganic PCMs have high energy densities and high melting temperatures as compared to most of the organic PCMs. In high-temperature solar applications, inorganic PCMs are preferred over organic PCMs because their enthalpies do not degrade with the operating cycles. These materials can be classified in the salts, slat hydrates, and metallic.

Table 9.7 Thermophysical properties of non-paraffins used in LTES [28–31]

Materials	Formula	Melting temperature (°C)	Latent heat (kJ/kg)	Density (kg/m^3)	Thermal conductivity (W/m K)	Storage capacity (MJ/m^3)
Fatty acids						
Caprylic acid	$CH_3(CH_2)_6.COOH$	16	148.6	981 (solid), 901 (liquid)	0.149 (liquid)	145.8
Lauric acid	$CH_3(CH_2)_{10}.COOH$	42	171	870 (liquid)	0.149	148.8
Myristic acid	$CH_3(CH_2)_{12}.COOH$	54	190	860 (liquid)	–	163.4
Palmitic acid	$CH_3(CH_2)_{14}.COOH$	64	185.4	989 (solid), 850 (liquid)	0.162 (liquid)	183.4
Stearic acid	$CH_3(CH_2)_{16}.COOH$	69	209	940 (liquid)	0.097	196.5
Easters						
Isopropyl palmitate	$C_{19}H_{38}O_2$	11	100	–	–	–
Butyl stearate	$C_{22}H_{44}O_2$	18	123	–	0.21 (solid)	–
Methyl palmitate	$C_{17}H_{34}O_2$	27	163.2	–	–	–
Vinyl stearate	$C_{20}H_{38}O_2$	27	122	–	–	–
Alcohols						
Xylitol	$C_5H_{12}0_5$	92.7–94.5	232–263.3	1520	–	353–400
D-sorbitol	$C_6H_{14}0_6$	97	110	1490	–	163.9
Erythritol	$C_4H_{10}0_4$	117–118	315–344	1480 (solid), 1300 (liquid)	0.733 (solid), 0.326 (liquid)	466–509
D-mannitol	$C_6H_{14}0_6$	165–168	294–341	1489–1520	0.19 (solid), 0.11 (liquid)	438–518

(continued)

Table 9.7 (continued)

Materials	Formula	Melting temperature (°C)	Latent heat (kJ/kg)	Density (kg/m^3)	Thermal conductivity (W/m K)	Storage capacity (MJ/m^3)
Glycols						
Diethylene glycol	$(HOCH_2CH_2)_2O$	−10	247	1200 (liquid)	–	296
Triethylene glycol	$C_6H_{14}O_4$	−7	247	1200 (liquid)	–	296

9.3.2.1 Salts and Salt Hydrates

Salts are utilized for high-temperature storage applications. They have high energy density but low thermal conductivity. Salts can be utilized in LTES, either in pure form or in the form of hydrates (Table 9.8). Salt eutectic mixtures are also used in many storage systems. The alloys of inorganic salts and water having chemical formula $AB.H_2O$ are referred to as the salt hydrates. The dehydration of salt hydrates results either in its anhydrous form or in the dehydration of salts in the form having fewer moles of H_2O.

$$AB.nH_2O \leftrightarrow AB.mH_2O + (n - m)H_2O \tag{9.5}$$

or

$$AB.nH_2O \leftrightarrow AB + nH_2O \tag{9.6}$$

When salt hydrate melts, the solid crystal releases the water. The anhydrous salts cannot be dissolved in the stoichiometric volume of water present in the hydrated salt. The less hydrated salt settles down in the storage and creates phase segregation. This irreversible melting of the salt hydrates is called the incongruent melting. The poor nucleation properties and its consequence due to the incongruent melting are the major shortcomings of salt hydrates. Although the salt hydrates have some other demerits, such as significant supercooling and irreversible phase transition, its high storage capacity and thermal conductivity make it one of the feasible choices for latent heat storage applications.

9.3.2.2 Metals and Alloys

Metallic PCMs offer excellent thermal conductivities and volumetric energy density (Table 9.9). However, the cost of these PCMs remains high as compared to the other, but for low volume storages, these PCMs are the most preferred PCMs. These PCMs have not been considered as the general-purpose LTES mediums due to its low latent heat per unit weight, which creates the problem of excess weight. These PCMs can be stored in metal and ceramic containers. During multiple thermal cycles, their microstructures can be changed due to segregation, oxidation, and precipitation. To avoid this, inert gas atmosphere is needed, which further can lead to the absorption of inert gas in the metal during phase transition cycles. It can change the thermophysical properties of the metal. The operational complexities have reduced its adaptability in energy storage applications.

Table 9.8 Thermophysical properties of PCMs based on salt and salt hydrate [28, 29, 31]

Materials	Formula	Melting temperature (°C)	Latent heat (kJ/kg)	Density (kg/m^3)	Thermal conductivity (W/m K)	Storage capacity (MJ/m^3)
Salt hydrates						
Calcium chloride hexahydrate	$CaCl_2.6H_2O$	29	190.8	1802 (solid), 1562 (liquid)	1.088 (solid), 0.540 (liquid)	343.8
Sodium phosphate dibasic dodecahydrate	$Na_2HPO_4.12H_2O$	36	280	1520 (solid)	0.514 (solid), 0.476 (liquid)	425.6
Barium hydroxide octahydrate	$Ba(OH)_2.8H_2O$	78	265.7	2070 (solid), 1937 (liquid)	1.225 (solid), 0.653 (liquid)	550
Magnesium chloride hexahydrate	$MgCl_2.6H_2O$	117	168.6	1569 (solid), 1440 (liquid)	0.694 (solid), 0.570 (liquid)	264.5
Nitrate salts						
Sodium nitrate	$NaNO_3$	306	172	2261 (solid)	0.5	388.9
Potassium nitrate	KNO_3	335	266	2109 (solid)	0.5	561
Carbonate salts						
Sodium carbonate	Na_2CO_3	854	276	2533 (solid), 1972 (liquid)	–	699.1
Potassium carbonate	K_2CO_3	897	236	2290 (solid)	–	540.4
Chloride salts						
Zinc chloride	$ZnCl_2$	280	75	2907 (solid)	0.5	218
Sodium chloride	$NaCl$	802	420	2160 (solid)	–	907.2
Sulfate salts						
Sodium sulfate	Na_2SO_4	884	165	2680 (solid)	–	442.2
Lithium sulfate	$LiSO_4$	858	84	2220 (solid). 2003 (liquid)	–	186.5

(continued)

Table 9.8 (continued)

Materials	Formula	Melting temperature (°C)	Latent heat (kJ/kg)	Density (kg/m^3)	Thermal conductivity (W/m K)	Storage capacity (MJ/m^3)
Fluoride salts						
Lithium fluoride	LiF	850	1044	2640 (solid). 1810 (liquid)	–	2756.2
Sodium fluoride	NaF	996	794	2558 (solid). 1948 (liquid)	–	2031.1
Hydroxide salts						
Sodium hydroxide	NaOH	318	165	2100 (solid)	–	346.5
Potassium hydroxide	KOH	380	150	2040 (solid)	–	306

Table 9.9 Thermophysical properties of metals and their alloys used as the PCMs [28, 29]

Materials	Melting temperature (°C)	Latent heat (kJ/kg)	Density (kg/m^3)	Thermal conductivity (W/m K)	Storage capacity (MJ/m^3)
Metals					
Zinc (Zn)	419	113	7140 (solid)	116	806.8
Aluminum (Al)	660	397	2707 (solid), 2375 (liquid)	204	1074.7
Copper (Cu)	1084	208	8960 (solid), 8020 (liquid)	401	1863.7
Alloys					
Zn/Mg (53.7%/46.3%)	340	185	4600 (solid)	–	851
Al/Mg/Zn (59%/33%/6%)	443	310	2380 (solid)	–	737.8
Si/Al (86%/12%)	576	560	2700 (solid)	–	1512
Zn/Cu/Mg (49%/45%/6%)	703	176	8670 (solid)	–	1525.9

Table 9.10 Thermophysical properties of eutectic PCMs [5, 29, 32, 33]

Materials	Melting temperature (°C)	Latent heat (kJ/kg)	Density (kg/m^3)	Thermal conductivity (W/m K)	Storage capacity (MJ/m^3)
Organic–organic					
Stearic acid–palmitic acid (36%/64%)	53	182	971	2.34 (solid)	165.6
Urea–acetamide (38/62)	53	224	1216	0.510 (solid)	262.8
Inorganic–inorganic					
KNO_3-KOH (80/20)	214	83	1905	0.88 (solid)	154.8
$NaNO_2$-$NaNO_3$ (55/45)	233	163	2210	0.64 (solid)	349.2
Organic–inorganic					
Urea-$NaNO_3$ (71-29)	83	187	1502	0.75 (solid)	273.6
Urea-KNO_3 (77/23)	109	195	1416	0.810 (solid)	266.4

9.3.3 Eutectics

Eutectics are the PCMs having two or more amalgamated materials having congruent melting points (Table 9.10). They melt and solidify irreversibly without phase segregation. Although they have low heat capacities and latent heat, the desirable properties of the eutectic PCMs can be obtained by varying the weight proportion of amalgamated materials in the mixtures. This quality makes them one of the prominent latent heat storage mediums for the future.

9.3.4 Latent Thermal Energy Storage Systems

The latent heat storage materials are utilized for a wide range of solar energy applications. These materials are utilized in the photovoltaic (PV) and photovoltaic/thermal (PV/T) systems to improve their performance by reducing the operating temperature [34, 35]. These materials have also been tested to improve the nocturnal performance of solar stills [36]. Apart from this, the use of the PCMs to store energy in solar cookers has been studied by various researchers [37]. Many other applications can also be found in the previous literature, such as in space heating and solar drying. LTES technology has a high potential of being utilized for diverse energy applications. Generally, for indirect use, latent heat storage systems are designed in either the shell and tube configuration or macro-encapsulated packed bed configuration. These configurations improve the heat transfer between the HTF and the PCM.

9.3.4.1 Macro-encapsulated Packed Bed Storage

Macro-encapsulated packed bed storage is the widely adopted LTES configuration, which not only improves the performance of the inbuilt PCM; it also maintains an efficient charging/discharging operation. In this configuration, a significant volume of the PCM is enclosed by a shell, and multiple discrete units of such type are put together into a storage tank (Fig. 9.17). The HTF can pass over these units through voids for exchanging heat during the charging/discharging cycles. One of the potential advantages of macro-encapsulation of the PCMs is it provides a self-sustaining structure to the PCM and eliminates the chance of reaction with its surrounding. It also improves the thermal conductivity of the PCM, which is one of the major limitations of most of the PCMs. For the durability of this system, the shell materials should have better thermal and chemical stability, and it should not be reactive to the encapsulated PCM. The typical containers which are used for the macro-encapsulation of PCMs are bottles made of polyethylene and polypropylene, mild steel cans and tin-plated metal cans, etc. The shape of macro-encapsulation can be sphere, rectangular, cylindrical, etc. The tank used in this application is similar to the tanks which are used in other storage systems. The flow passage of the HTF plays a vital role in the overall performance of the packed bed storage. It should be designed in such a way that HTF should maintain a large heat transfer area in contact with

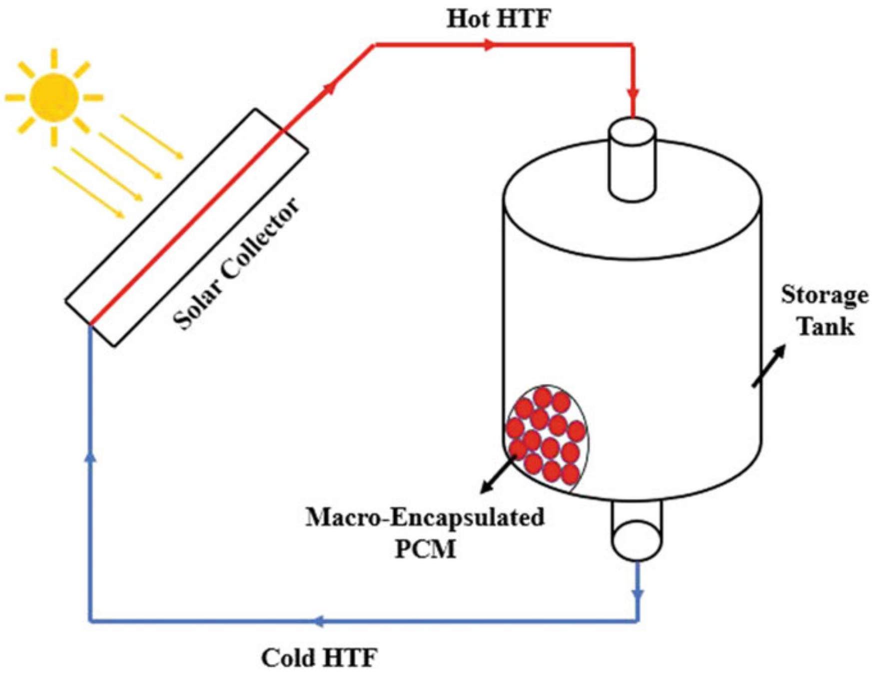


Fig. 9.17 Charging of macro-encapsulated packed bed storage. *Source* Author

the capsules, and there should be less pressure drop in the flow passage. During the charging operation of the storage, the hot HTF from any energy source passes over the capsules, which transfer heat to the encapsulated PCM through the shell. The energy stored in the melted PCM can be retrieved by passing cold HTF over it during discharging operation. The major performance parameters of the packed bed storage are the void fraction, inlet temperature, flow velocity of the HTF, and overall bed size [38]. The high finite temperature difference between the HTF and PCM leads toward better heat transfer. Researchers have utilized this storage configuration for solar air heating purposes, where the air itself is used as the HTF [39]. This technology has been explored for solar cooking applications as well, where energy collected from the solar collectors has been transferred to the packed bed storage, and the stored energy further be utilized for cooking applications [40].

9.3.4.2 Shell and Tube Latent Heat Storage

Another potential configuration for LTES is shell and tube configuration. In this configuration, generally, the PCM is stored at the shell side, and HTF passes through the tube side (Fig. 9.18). There are various parameters such as the diameter and length of the shell as well as the tube, inlet mass/volume flow rate and temperature of the HTF, and the number of tubes, which influence the performance of the shell and tube-based TES. The temperature difference between the shell side PCM and tube side HTF is the major driving force for the melting/solidification process in the storage. Higher the inlet HTF temperature, better will be the heat transfer. The high mass flow rate of HTF can improve the performance of the storage. Hence, the optimization of the mass flow rate is necessary for the efficient operation of the storage. Researchers have tested shell and tube storage for CSP applications and highlight the role of various geometrical parameters [41]. The large length and the

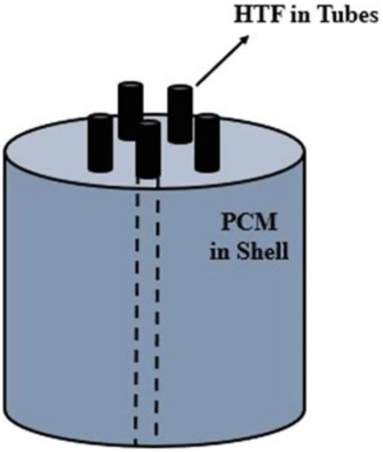


Fig. 9.18 Schematic of shell and tube-based LTES. *Source* Author

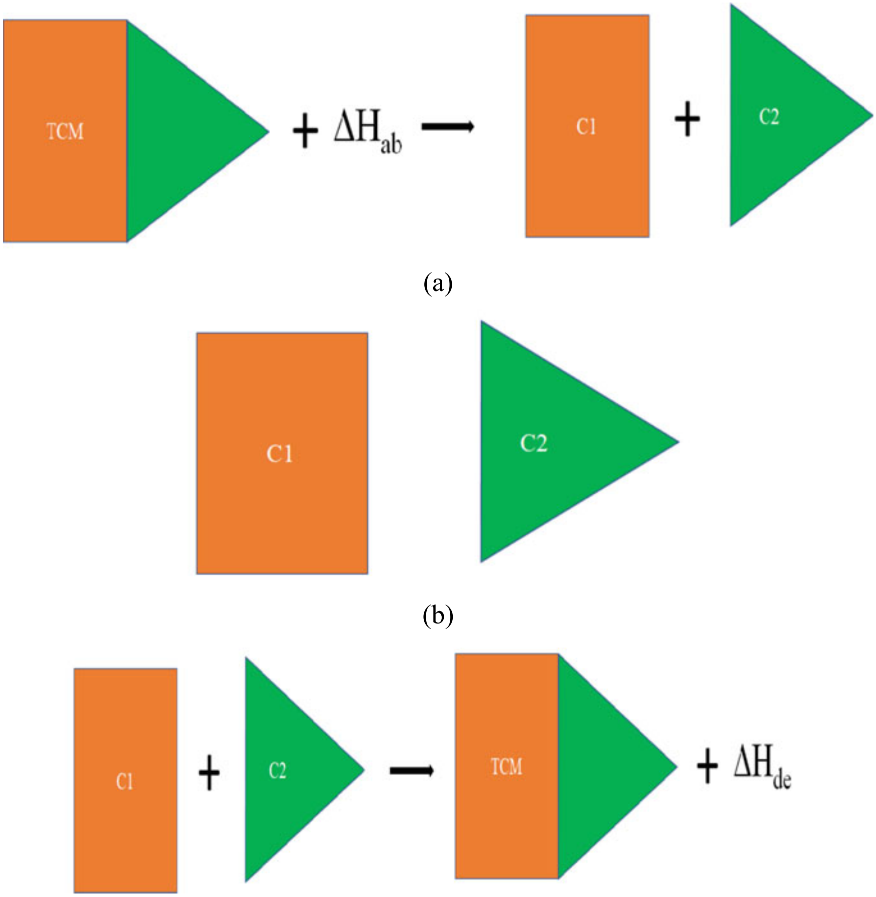
small diameter of the tubes can improve the effectiveness of the storage, but the small diameter can lead to a large pressure drop in the flow passage.

9.4 Thermochemical Energy Storage

In this technique, the thermal energy is stored in the form of a chemical reaction. A chemical reaction which is reversible in nature is preferred to store thermal energy. To understand the phenomenon, let us consider the example of a chemical reaction in analogy with phase change material.

$$\mathrm{TCM} + \Delta\mathrm{H} \leftrightarrow \mathrm{C1} + \mathrm{C2} \tag{9.7}$$

Here in the above reaction, TCM is thermochemical material similar to PCM in the latent heat storage technique. The thermal energy equivalent of enthalpy of absorption of the reaction is stored in the chemical reaction. This supplied energy to the TCM initiates dissociation reaction and dissociates the TCM into two or more compounds, i.e., compounds C1 and C2 in the reaction. When it is required to utilize the stored energy, the reaction is reversed, i.e., compounds C1 and C2 combine, and energy equivalent to the enthalpy of desorption of reaction is released during the reverse chemical reaction. From the above example, it can be clearly understood that the storage of energy is performed by an endothermic chemical reaction where heat equivalent to the enthalpy of absorption is stored, and the discharge of energy is performed by exothermic chemical reaction. The mechanism of thermochemical energy storage can be divided into three different steps, such as charging, storage, and discharging of energy. The charging of energy is an endothermic chemical reaction where the thermal energy from sources like solar collectors can be supplied to TCM. The TCM gets dissociated into two or more compounds like C1 and C2 in Fig. 9.19a. The dissociated compounds C1 can be ammoniate, hydroxide, carbonate, and hydrate, while C2 can be ammonia, water, carbon dioxide, and hydrogen. The storage of energy includes the storage of dissociated compounds separately, as shown in Fig. 9.19b. The dissociated compounds are stored at nearly ambient temperature due to which there is either no heat loss or very minimal heat loss as compared to other storage techniques. Discharging of energy is an exothermic chemical reaction where the thermal energy is supplied to the end-use applications when required. During the discharge, the dissociated compounds react together at definite temperature pressure conditions to release the heat, as shown in Fig. 9.19c. To discuss the thermochemical energy storage in detail, it is necessary to understand terminology turning temperature (T*). Turning temperature is the temperature at which reaction rate constant (k) is unity. Turning temperature is calculated as the ratio of reaction enthalpy to reaction entropy ($T^* = \Delta H/\Delta S$) [42]. It indicates the required temperature to carry an endothermic or exothermic reaction. The thermochemical energy storage can be classified either based on the physical state or based on the chemical composition of the reacting compounds in the chemical reaction (Fig. 9.20).



(a)

(b)

(c)

Fig. 9.19 Principle of thermochemical energy storage (**a**) charging, (**b**) storage, and (**c**) discharging of heat. *Source* Author

9.4.1 Ammonia System

The TCM materials such as ammonia and ammonium bisulfate get dissociated when heat at high temperature is supplied to it. The feasibility of an ammonia-based thermal energy storage system was studied in 1995 [43]. The reaction of ammonia is an example of a gas–gas phase reaction, while the ammonia bisulfate reaction is an example of a liquid–gas reaction. The two reactions are mentioned and discussed below one by one.

$$2NH_3(g) + \Delta H \leftrightarrow N_2(g) + 3H_2(g) \tag{9.8}$$

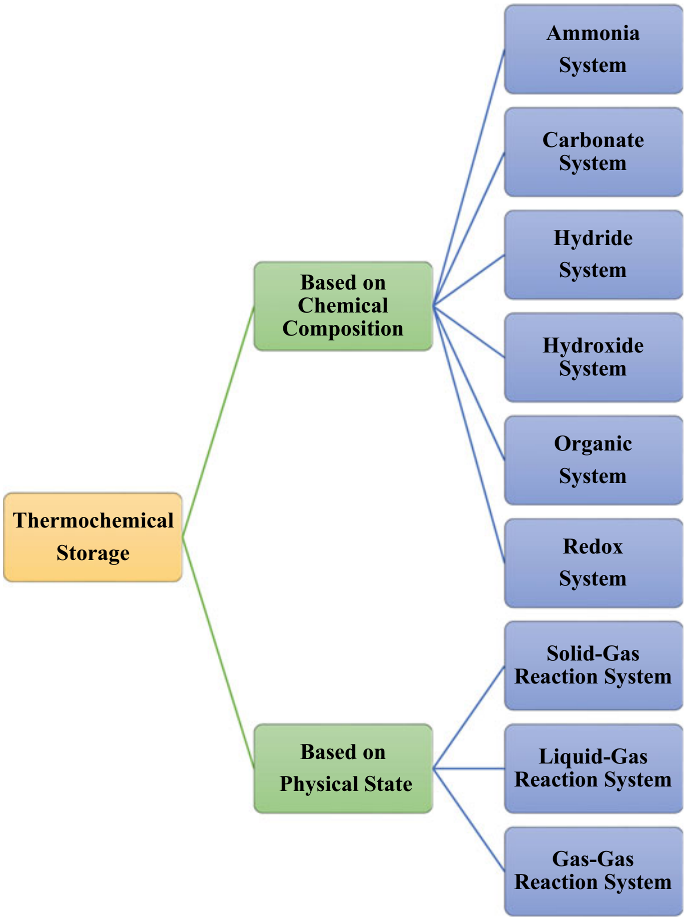


Fig. 9.20 Classification of thermochemical energy storage. *Source* Author

Ammonia has an enthalpy of absorption 66.9 kJ/mol and enthalpy of desorption 53 kJ/mol. Ammonia as gas is dissociated into nitrogen and hydrogen both as a gas; hence, it comes under the category of gas–gas reaction. The reaction takes place at temperature 996 °C at 10–300 bar pressure range with an energy density of 2682 MJ/m^3 [44, 45]. The TCM cost is low with simple reaction, high enthalpy of reaction, and high energy density. There are few disadvantages associated with ammonia, such as low reversibility, high operating pressure, the need for catalyst (Fe/Co), and hydrogen and nitrogen handling difficulty. Let us take another example of an ammonia system-based thermochemical energy storage

$$NH_4HSO_4(l) + \Delta H \leftrightarrow NH_3(g) + H_2O(g) + SO_3(g) \tag{9.9}$$

Liquid ammonium bisulfate absorbs high-temperature heat and dissociates into gaseous compounds, ammonia, sulfur trioxide, and water vapors. This is an example of a liquid–gas reaction. The absorption and desorption reaction temperatures are 1473 and 996 °C, respectively, at 1–2 bar operating pressure range. The reaction enthalpy of ammonium bisulfate is 336 kJ/mol, and the energy storage density is 3096 MJ/m^3 [44, 46]. Similar to the ammonia reaction, this system also has high energy storage density and high enthalpy of reaction. This reaction does not require any catalyst, but the product formed in the chemical reaction is corrosive and toxic in nature.

9.4.2 Carbonate System

The carbonates of metal, such as lead (Pb) and calcium (Ca), can store thermal energy at high temperatures. Metal carbonates are solid in nature and dissociate into oxides of metal, which is also solid, and carbon dioxide as a gas. This system comes under the category of solid–gas reaction. The two TCMs which come under the carbonate category are discussed below.

$$\mathrm{PbCO_3(s) + \Delta H \leftrightarrow PbO(s) + CO_2(g)} \tag{9.10}$$

Lead carbonate has a relatively lesser reaction enthalpy 88 kJ/mol and energy storage density 1090.8 MJ/m^3 [47]. The absorption and desorption temperature of this reaction is 996 and 846 °C at pressure up to 10 bar. No catalyst is required for the reaction, and the by-product handling is relatively easier. The reversibility of the reaction and toxic nature of PbO are the challenges associated with lead carbonate. Another example of the carbonate system is calcium carbonate, which follows the reaction, as shown below.

$$\mathrm{CaCO_3(s) + \Delta H \leftrightarrow CaO(s) + CO_2(g)} \tag{9.11}$$

The dissociation of all the metal carbonates is similar and produces metal oxide and carbon dioxide. Calcium carbonate is also in the category of solid–gas reaction. The absorption and desorption temperature of this TCM is 1406 and 1429 °C. Calcium carbonate has a relatively better reaction enthalpy 178 kJ/mol and energy storage density 2491.2 MJ/m^3 [47, 48]. Calcium carbonate has a lesser cost and good availability, and no catalyst is required for the reaction. Few challenges associated with the calcium carbonate system are its irreversibility, agglomeration at the higher temperature, and volume change during the reaction. Major metal carbonate systems have issues of irreversibility due to which their application at a commercial scale is not possible. Some other metal carbonates are listed in Table 9.11 with their thermochemical properties.

Table 9.11 Thermochemical properties of carbonate materials for thermochemical energy storage [49]

TCM	Turning temperature (°C)	Reaction enthalpy (kJ/mol)	Gravimetric energy storage density (kJ/kg)
$ZnCO_3$	120	68.32	544.9
$CdCO_3$	290	96.57	560.1
$MgCO_3$	300	98.98	1174
$SrCO_3$	1220	202.34	1370.65
$BaCO_3$	1555	165.09	836.6

9.4.3 Hydride System

Several metals react with hydrogen to form metal hydrides and release thermal energy (exothermic reaction). Metal hydrides came in existence for hydrogen storage application initially, but later in the 1970s, the use of metal hydride for thermal energy storage was started. Very few materials were known at that time for the temperature application up to 200 °C. Later with development in research on ionic and complex metal hydrides, the energy storage was possible for temperature up to 1000 °C. Lithium (Li)-based metal hydride was the first metal hydride which was studied and found suitable for high-temperature applications [50]. The high cost of Li makes the thermal energy storage system expensive. Later, magnesium (Mg)-based hydrides attracted the researchers due to its low material cost. The most common metal hydride which can be used for thermal energy storage application is magnesium (Mg)-based metal hydride.

$$\mathrm{MgH_2(s) + \Delta H \leftrightarrow Mg(s) + H_2(g)} \tag{9.12}$$

Magnesium-based metal hydride comes under the category of solid–gas reaction. Magnesium hydrides have a large range of operating temperatures and pressure from 750 to 1000 °C with a pressure up to 100 bar. The reaction enthalpy and energy storage density of magnesium metal hydride are 75 kJ/mol and 2088 MJ/m^3, respectively [51]. Magnesium metal hydride has comparatively good reversibility with low cost and easily available materials. The disadvantages associated with magnesium hydride are slow reaction kinetic, high operating pressure, sintering, and need of a catalyst. Titanium, well known for anticorrosive property and high-temperature resistance, is also explored for thermal energy storage at high temperatures.

$$\mathrm{TiH_2(s) + \Delta H \leftrightarrow Ti(s) + H_2(g)} \tag{9.13}$$

The operating temperature range of titanium hydride is 900–1000 °C, with a pressure range of 1–3 bar. The reaction enthalpy and experimental energy storage density of magnesium metal hydride are 150 kJ/mol and 2926.8 MJ/m^3, respectively [52]. Titanium metal hydride reaction also comes in the category of solid–gas reaction similar to magnesium hydride. Titanium metal hydride possesses good reversibility and high reaction enthalpy, and no need for a catalyst makes it a suitable candidate for thermal energy storage. However, the high specific weight of titanium reduces the gravimetric storage capacity significantly. Metal hydrides are in the advanced research phase for thermal energy storage applications. Several models and prototypes of metal hydride-based thermochemical energy storage have been developed with good storage capacity, good cyclic stability, and ease in operation.

9.4.4 Hydroxide System

The dehydration of metal hydroxide requires energy, and this is used to store the thermal energy in hydroxide systems. The major metal hydroxides have relatively lower operating temperatures except for calcium and barium hydroxide. Magnesium hydroxide has the highest enthalpy of reaction, but calcium hydroxide ($Ca(OH)_2$), being reversible, easily available, and low-cost material, has been studied extensively for high-temperature thermal energy storage. The feasibility of $Mg(OH)_2$ was verified by studying its reaction kinetics for the application of a chemical heat pump [53]. The poor heat transfer performance, cyclic stability, and sintering of Mg particles restricted the use of $Mg(OH)_2$ for thermal energy storage applications.

$$\mathrm{Ca(OH)_2(s) + \Delta H \leftrightarrow CaO(s) + H_2O(g)} \tag{9.14}$$

The operating temperature range of calcium hydroxide is 950–1000 °C, with pressure up to 2 bar. The enthalpy of reaction and energy storage density for calcium hydroxide are 104 kJ/mol and 1573.2 MJ/m^3, respectively. $Ca(OH)_2$ comes under the category of solid–gas reaction. Calcium hydroxide is a reversible, low-cost material and operates at low pressure. The major challenges with calcium hydroxide are agglomeration and sintering of its particles. Some of the famous metal hydroxides have been listed in Table 9.12 with their thermochemical properties.

9.4.5 Organic System

Methane gas (CH_4) is one of the most popular organic compounds and used for the production of synthesis gas ($CO + H_2$), also popular as syngas. The two methods of syngas production are endothermic chemical reaction, and these methods are discussed here for the application of thermal energy storage.

$$\mathrm{CH_4(g) + H_2O(g) + \Delta H \leftrightarrow CO(g) + 3H_2(g)} \tag{9.15}$$

The mentioned reaction is well known as methane steam reforming or steam reforming. The major application of this reaction is hydrogen production. As this is

Table 9.12 Thermochemical properties of hydroxide materials for thermal energy storage [49]

TCM	Turning temperature (°C)	Reaction enthalpy (kJ/mol)	Gravimetric energy storage density (kJ/kg)
$Zn(OH)_2$	55	49.60	498.96
$Ni(OH)_2$	70	47.84	516
$Be(OH)_2$	70	51.27	1191
$Cd(OH)_2$	125	59.95	409.4
$Mn(OH)_2$	190	67.07	754
$Mg(OH)_2$	265	77.74	1333
$Sr(OH)_2$	755	88.58	728.3
$Ba(OH)_2$	1005	93.46	545.47

an endothermic reaction, hence it is also used to store thermal energy. The absorption and desorption temperature of this reaction is 1496 and 1076 °C at a wide pressure range from 20 to 150 bar. The reaction enthalpy and energy storage density of this thermochemical reaction are 250 kJ/mol and 28.08 MJ/m^3, respectively [54]. Another reaction of methane with carbon dioxide, also known as dry reforming, is an endothermic reaction and can be used for thermal energy storage.

$$CH_4(g) + CO_2(g) + \Delta H \leftrightarrow 2CO(g) + 2H_2(g) \tag{9.16}$$

The absorption and desorption temperature of this reaction is the same as the reaction of methane with steam, but the operating pressure is comparatively lower at 3.5 bar. The reaction enthalpy and energy storage density of this thermochemical reaction are 247 kJ/mol and 27.72 MJ/m^3, respectively [54]. Both these reactions come under gas–gas type reaction and have high reaction enthalpy. The challenges associated with these two thermochemical methods are low energy storage density, the need for a catalyst, low reversibility, and high cost of methane.

9.4.6 Redox System

Oxides of metal undergo a reduction reaction, which is an endothermic reaction. Redox systems are also known as metal oxide systems. Oxides of cobalt (Co), barium (Ba), and manganese (Mn) are the most popular in this category. Let us discuss cobalt oxide with the reduction reaction, as mentioned below:

$$2Co_3O_4(s) + \Delta H \leftrightarrow 6CoO(s) + O_2(g) \tag{9.17}$$

Oxide of cobalt has an operating temperature 1416–1446 °C in a pressure range from 0 to 1 bar. The reaction enthalpy and energy storage density of this thermochemical reaction are 205 kJ/mol and 1062 MJ/m^3, respectively [55]. This reaction

Table 9.13 Thermochemical properties of metal oxides for thermal energy storage [49]

TCM	Turning temperature (°C)	Reaction enthalpy (kJ/mol)	Gravimetric energy storage density (kJ/kg)
Cr_5O_{12}	105	126.17	279.1
Li_2O_2	145	34.22	745.9
MgO_2	205	21.43	380.6
PbO_2	295	55.23	230.9
Sr_2O_5	325	68.06	210.4
PtO_2	420	62.8	276.5
Mn_2O_3	915	90.03	190.1
Fe_2O_3	1360	232.61	485.6
Mn_3O_4	1700	194.63	850.6
V_2O_5	1710	176.59	970.9

comes under the category of solid–gas type reaction. This reaction is reversible with high reaction enthalpy and does not require any catalyst. The toxic nature of CaO and oxygen handling difficulty are the disadvantages associated with this thermochemical reaction.

$$2BaO_2(s) + \Delta H \leftrightarrow 2BaO(s) + O_2(g) \tag{9.18}$$

Barium peroxide has operating temperature 1236–1326 °C in a pressure range from 0 to 10 bar. The reaction enthalpy and energy storage density of this thermochemical reaction are 77 kJ/mol and 1180.8 MJ/m^3, respectively [56, 57]. This reaction comes under the category of solid–gas type reaction. The reaction does not require any catalyst and has low operating pressure. The reversibility of the reaction, sintering, agglomeration, and oxygen handling difficulty are a few challenges associated with barium oxide. Several oxides were studied, and it was reported in the study that oxides of barium, cobalt, manganese, copper, and iron are suitable for high-temperature applications [58]. Cobalt oxide (Co_3O_4) has the best reversibility and energy storage density among the other oxides. Some popular metal oxides with their thermochemical properties have been listed in Table 9.13.

9.4.7 Utilization of Thermochemical Energy Storage in Solar Thermal Applications

Thermal energy is required in various process industries for their operations, power generation, and space heating applications [52]. Thermochemical energy storage can be one of the best possible options for thermal energy storage in solar thermal power plants. Let us consider one such example of thermochemical energy storage using

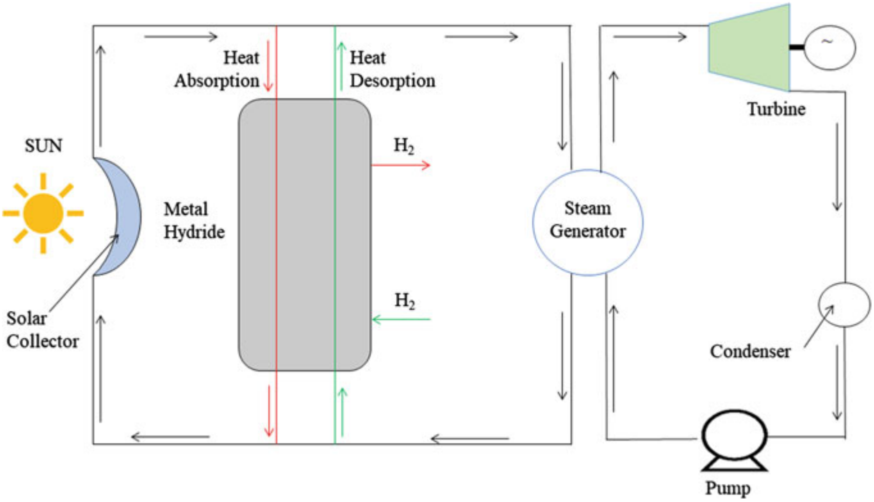


Fig. 9.21 Schematic of solar thermal power plant with thermochemical energy storage system. *Source* Author

metal hydride discussed earlier. Consider a metal hydride-based thermochemical energy storage system integrated with a solar thermal power plant, as shown in Fig. 9.21. The schematic includes the solar field, energy storage, and power cycle. The hydride-based thermochemical energy storage unit consists of a metal hydride system to store thermal energy. Let us discuss the working of a metal hydride-based thermochemical energy storage system in detail. During the daytime, a part of the thermal energy collected in the solar field is supplied to the thermal energy storage unit. The red color line indicates the storage of thermal energy. During the endothermic reaction, metal hydride stores thermal energy equivalent to reaction enthalpy. This endothermic reaction leads to the dissociation of the metal hydride into metal and hydrogen, as shown in Fig. 9.21. The liberated hydrogen from metal hydride can be stored separately, which can further be utilized during the discharging cycle. In this way, the thermal energy supplied from the solar field to the storage system gets stored in the metal hydride. This stored energy, when required by the power plant during non-sunshine hours, can be released by supplying the hydrogen to metal. The green color line indicates the discharging process. The discharged thermal energy is supplied to the heat exchanger to produce superheated steam. Similarly, the stored energy can be used in various process applications in the industries. The selection of TCM is made based on the application parameter, where the heat is to be utilized.

9.5 Economic Aspects of TES

The successful deployment of any technology in various applications depends upon the cost involved in technology development. The cost involved in the TES technologies can be categorized as the capital cost and operational and maintenance costs. The capital cost includes cost related to the design and construction of the TES and cost involved in the development of various components such as instrumentations, pipes, fittings, and insulation. The cost involved in the parasitic load, such as pumping, trace heating, refilling, and other operational costs, is associated with the operational cost. System Advisor Model (SAM) developed by National Renewable Energy Laboratory can be utilized for the financial study of renewable energy projects [59]. There are many financial models that are given for commercial and residential renewable energy systems. SAM may provide the information related to the various costs involved in the renewable energy system integrated with TES based on the input parameters such as design parameters of solar collectors, storage, and operation strategy. To understand the cost matrix of the TES system, Nithyanandam and Pitchumani et al. [60] model can be referred. Based on this model, the cost of the entire TES system can be categorized into different sections, as follows [28]:

- **Container Cost**: The configurations such as packed bed and shell and tube have high cost as compared to the single tank and single concrete block. The preferred and cost-effective materials used for the fabrication of the storage container are mild steel and reinforced concrete. The most used insulation material is fiberglass. The cost matrix of the container is linked to the storage density. Lower the density, larger will be the size of the storage as well as higher the container cost.
- **Storage Material Cost**: Storage cost can be calculated by using cost per unit mass of the material. Water, sand, and gravels are cheap storage mediums, while organic PCM, thermochemical reactors, and thermal oils are costly mediums.
- **Overhead Cost**: It includes the miscellaneous cost such as pipes and fitting cost, and instrumentation cost.
- **Design-Specific Cost**: It includes the heat exchanger cost and cost associated with the implementation of various performance enhancement techniques. The cost associated with the implementation of various performance enhancement techniques should be justified by the superior performance of the TES. For the development of the TES, which can work efficiently at very high temperature, the cost of the used materials increases drastically. So, the selection of the material plays a vital role in the development process.

Most of the STES technologies are economical in terms of materials, design, and operation. Its cost varies from 0.11 to 11.12 \$/kWh [1]. The geometrical simplicity and easy availability make STES an economical technology. LTES and TCES are complicated and also relatively expensive. Although these technologies have a high energy density, the storage material and the system design make it expensive. Due to the low thermal conductivity of the PCMs, LTES requires better heat transfer arrangements, which increases its cost further. The complexities associated with the reactor design, costly storage material, and heat transfer equipment are the major sources of the increased cost of the TCES. The cost of LTES and TCES can be found in the range of 11.12 to 55.6 $/kWh and 9 to 111 $/kWh, respectively [1].

9.6 Current and Future Outlook of TES Technologies

Nowadays, TES technology is being utilized in many energy-related applications [61–63], but there are few demerits of these technologies which restricts its utilization in diverse applications. The STES technology is a cost-effective technology, but its low energy density is one of the major obstacles in its utilization in a wide range of applications. Similarly, the low thermal conductivity is the major problem associated with PCMs, which needs to be overcome for its large-scale deployment because it hampers the heat transfer process in the LTES. The process complexities have to be minimized for utilizing TCES technology. Researchers are developing many new age TES technologies as well as improving the existing TES technologies to get full-scale benefits of these technologies. The hybrid sensible heat and latent heat storage system have been developed by the researchers, which can overcome the problem of the quick temperature drop of the STES during the discharging process, and it improves the energy density of sensible storage systems [64, 65]. There are various heat transfer intensification techniques that have been highlighted in the previous literature which can overcome the problem of the poor heat transfer associated with the PCMs. These techniques are: the use of the extended surfaces, the use of nanofluids, cascading of multiple PCMs in a single unit, in-building of low-density porous materials in the PCM, integration of heat pipes in the LTES, etc. [66–69]. The use of fins is one of the most preferred heat transfer enhancement techniques in PCM-based storage due to its low cost and easy fabrication. The use of cascade PCMs maintains uniformity in the heat transfer process during the melting/solidification of the PCMs. Heat pipes improve the available heat transfer area in the system, which enhances the thermal performance of the LTES. For improving the thermal conductivity of the PCMs, nano-sized metallic particles are being used, which reduces the response time of the system [70, 71]. The low-density metal foams and metal matrices are being used to intensify the thermal performance of the PCMs, which also reduces the response time of the LTES. Various innovative designs of the TES, such as shell and tube design, encapsulated packed bed design, and triplex tube design, have also been explored by researchers, which provides better heat transfer in the system. Thermochemical energy storages are currently under the research phase, and few laboratory-scale models have been developed, as discussed in the earlier sections. The major challenges associated with thermochemical energy storage systems are enhancement of thermal conductivity, cyclic stability, thermal stability, heat exchanger efficiency, energy storage density, and reversibility of thermochemical materials. These properties can be improved by changing the chemical composition, adopting more advanced manufacturing techniques, and improving the design of the thermochemical energy storage systems. There are various parameters that are involved in the design and operation of the TES. To obtain the best thermal performance from the TES system, it is necessary to choose these parameters appropriately. The studies on the optimized design of TES and implementation of the various heat transfer enhancement techniques in the TES are one of the growing fields of research in this area.

9.7 Summary

Thermal energy storage is one of the essential parts of any energy system. It improves the overall efficiency of the system as well as it reduces the operating cost of the system. Apart from this, the integration of TES with the energy systems also reduces the CO_2 emission and manages the mismatch between demand and supply. In solar energy applications, it provides a sustainable solution to the problem of the intermittent nature of solar energy. The thermal energy can be stored in the form of sensible heat, enthalpy of phase transition, and enthalpy of the chemical reaction. The materials used in the diverse storage applications have been discussed in this chapter. The potential merits/demerits of the available thermal energy storage systems have been highlighted. There are certain requirements, which need to be fulfilled for the efficient designing of the TES. These requirements are high energy density and thermal conductivity of the storage medium, better thermal and chemical stability of the TES materials, compatibility of the storage media with the container material, better heat transfer between storage medium and HTF, low thermal losses to the environment, reversible charging/discharging, and better control on the operation. TES systems have been developed in various innovative designs, which improve the charging/discharging performance of the storage. The existing TES technologies and their operating strategies have been discussed. A discussion on the cost associated with the TES technologies has been highlighted here. Various ongoing researches in this area have been discussed. The correction in the mismatch between demand and supply of the energy systems by using TES can improve the dispatchability of the overall system. TES contributes to fulfilling the energy demand of the society in an efficient and eco-friendly manner. It decreases the dependency on conventional fuels, which degrade the atmosphere. Although TES technologies are one of the most sought technologies due to its extreme importance in various applications, there are many problems associated with it, which need to be overcome for its efficient utilization in diverse energy applications. A coordinated effort to develop high performance and cost-effective TES technologies can unlock the doors of the maximum benefits of the TES technologies for various applications.

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