



Review

An overview of thermal energy storage systems

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ABSTRACT

Due to humanity's huge scale of thermal energy consumption, any improvements in thermal energy management practices can significantly benefit the society. One key function in thermal energy management is thermal energy storage (TES). Following aspects of TES are presented in this review: (1) wide scope of thermal energy storage field is discussed. Role of TES in the contexts of different thermal energy sources and how TES unnecessitates fossil fuel burning are explained. Solar power generation, building thermal comfort and other niche applications of TES are presented. (2) Insight into classes of TES storage materials with details like their physical properties, cost, operational performance and suitability to application requirements is provided. (3) Insight into types of TES systems is presented. TES systems are classified using different types of criteria. Most common TES systems like seasonal TES systems, CSP plant TES systems, TES systems of domestic solar thermal applications, heat and cold storages of building HVAC systems etc are described. Active TES systems like thermocline, packed bed, fluidized bed, moving bed etc are analyzed. Passive TES systems implemented in buildings, textiles, automobiles etc are presented. TES systems operating in cold, low, medium and high temperature ranges are listed. Design parameters, operational issues and cost model of TES systems are discussed.

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1. Introduction

Discovery of fire is regarded as the most important milestone in the evolution of mankind. Simple activity like cooking food is one of the first applications that humans discovered for thermal energy. Thermal energy was readily available in nature even before human

existence. Our bodies require a minimum ambient temperature to be alive. Due to such realities of our life, a strong need for thermal energy exists. Freely available solar thermal energy from sun helps to maintain the favorable ambient thermal condition needed to sustain our lives on earth. However the availability of solar radiation varies across different locations on the planet resulting in

extreme cold ambient conditions in the high latitude regions to extreme hot ambient conditions near the equator. Since humans are expanding their presence across the planet into places with such extreme local conditions, need for thermal energy management arises. Moreover our modern lifestyle has created plenty of new applications for thermal energy which further increase the demand for thermal energy. Today our main energy consumption forms at the user–end are electricity, heat and mechanical work. International Energy Association (IEA) publishes the user–end energy consumption details as ‘Final consumption’. The user–end energy forms like electricity, heat and mechanical work are produced from energy conversion of multiple energy sources which include both natural sources and fuel sources. International Energy Association (IEA) [1] publishes the energy source details as ‘Primary energy supply’. International Energy Association (IEA) in its world energy statistics report for year 2014 estimated that, world’s annual ‘total primary energy supply’ is 573 EJ (13,699 million tonnes of oil equivalent) and the annual ‘total final consumption’ is 394 EJ (9425 million tonnes of oil equivalent). During the conversion process from ‘Primary energy supply’ to ‘Final consumption’ certain amount of energy ($\approx 31\%$) is lost which is huge due to the sheer amount of energy involved. World is now facing challenges in meeting its energy demand through burning fuels. Rapid burning of fossil fuels results in emission of greenhouse gases like CO_2 . Elevated level of CO_2 in the atmosphere is contributing to climate warming. This has serious consequences like rising sea levels due to melting of ice in the polar region. World realized the importance of renewability of energy sources during the energy crisis of the 1970s. Fossil fuel reserves are limited in supply and are non–renewable. Therefore there is an urgent need to conserve energy and move towards clean and renewable energy sources. Thermal energy storage is a key function enabling energy conservation across all major thermal energy sources, although each thermal energy source has its own unique context.

1.1. Heat sources

1.1.1. Solar thermal energy

Nuclear fusion reaction occurring at the core of sun continuously releases tremendous amount of solar radiation towards earth. According to some estimates annual potential of solar energy is approximately between 1575 and 49,837 EJ. This is much higher than the world’s annual ‘total primary energy supply’ for the year 2014 reported by IEA as 573 EJ. Therefore it can be said that solar energy if it is fully harnessed, alone can satisfy the world’s total energy demand. However IEA world energy statistics report for year 2014 also estimated the current annual ‘primary energy supply’ from other sources which include solar, geothermal and wind together at a mere 1.4% (≈ 8 EJ). Clearly solar energy potential is severely underutilized. It is currently estimated that sun will continue to provide solar energy for 4 billion years and therefore it is a sustainable and renewable energy source. During clear sky conditions, solar radiation emitted from sun is available on the

earth’s surface at an approximate intensity of 1000 W m^{-2} . This intensity is sufficient to satisfy the thermal energy needed for low temperature applications like hot water supply. For high temperature applications the solar radiation needs to be concentrated using suitable reflectors. Electricity generation from solar radiation is achieved through photovoltaic (PV) cells or through concentrated solar power plant (CSP). Solar radiation can also be used for applications like space heating, hot water supply, absorption refrigeration etc using appropriate solar thermal appliances. Its intermittent nature and non–availability during peak consumption hours necessitates the need for energy storage systems like TES system or battery based electricity storage system. TES can be compared with battery based electricity storage technology as below.

- (1) When source energy form to be stored is low grade thermal energy, TES has round–trip efficiency in the range 50%–100%. TES is the most suitable storage technology for thermal electricity generation plants such as a concentrating solar power plant (CSP) or a nuclear reactor [2].
- (2) When source energy form to be stored is high grade electrical energy, battery storage has round trip efficiency in the range 80%–100%. TES is not very suitable for on–grid energy storage from sources such as wind or PV [2]. Although TES can also store grid electricity, but the round trip efficiency of this process would be well under 50%.
- (3) Unlike battery technologies, the performance of TES does not typically experience cycling–induced degradation and TES has better cycle life and longer calendar life.
- (4) TES typically uses abundant materials with limited toxicities.

In CSP plants at locations with large amounts of direct normal irradiance, TES system is where solar thermal energy is stored during the day time and is used for electricity production during the night. Table 1 shows the TES integration feasibility for various types of CSP plants operating in the world. About half of the CSP plants (47%) currently operating in the world are integrated with TES system [3]. There is a notable increase in the use of TES systems. For plants under construction it is 72% and for planned future plants it is 77% [3]. Fig. 1 shows various types of TES systems that can be implemented in CSP plants. Similarly TES systems perform the same role in distributed applications like space heating, hot water supply etc. Depending on the specific need, thermal energy can be stored as both hot and cold energy.

1.1.2. Geothermal energy

Planet earth itself is a huge TES system. Earth’s planetary accretion process and radioactive decay generated tremendous heat which is still stored in layers below earth’s thin crust like mantle, outer core and inner core. Compared to the huge amount of thermal energy stored inside the earth, both the current rate of natural heat loss into space and the world’s annual energy consumption are negligible. Hence even if the geothermal energy is

Table 1
CSP plant types and feasibility of TES integration [3].

CSP plant type	Solar concentration ratio	Operating temperature range ($^{\circ}\text{C}$)	TES feasibility	Remarks
Parabolic trough collectors (PTC)	15–45	20–400	Possible	Most used type of plant
Solar power towers (SPT)	150–1500	300–1000	Possible with lowest cost	Most used type of plant with higher Rankine cycle efficiency
Linear fresnel reflectors (LFR)	10–40	5–300	Possible	Very few in operation
Parabolic dish collectors (PDC)	100–1000	120–1500	Difficult	Very few in operation with higher Rankine cycle efficiency

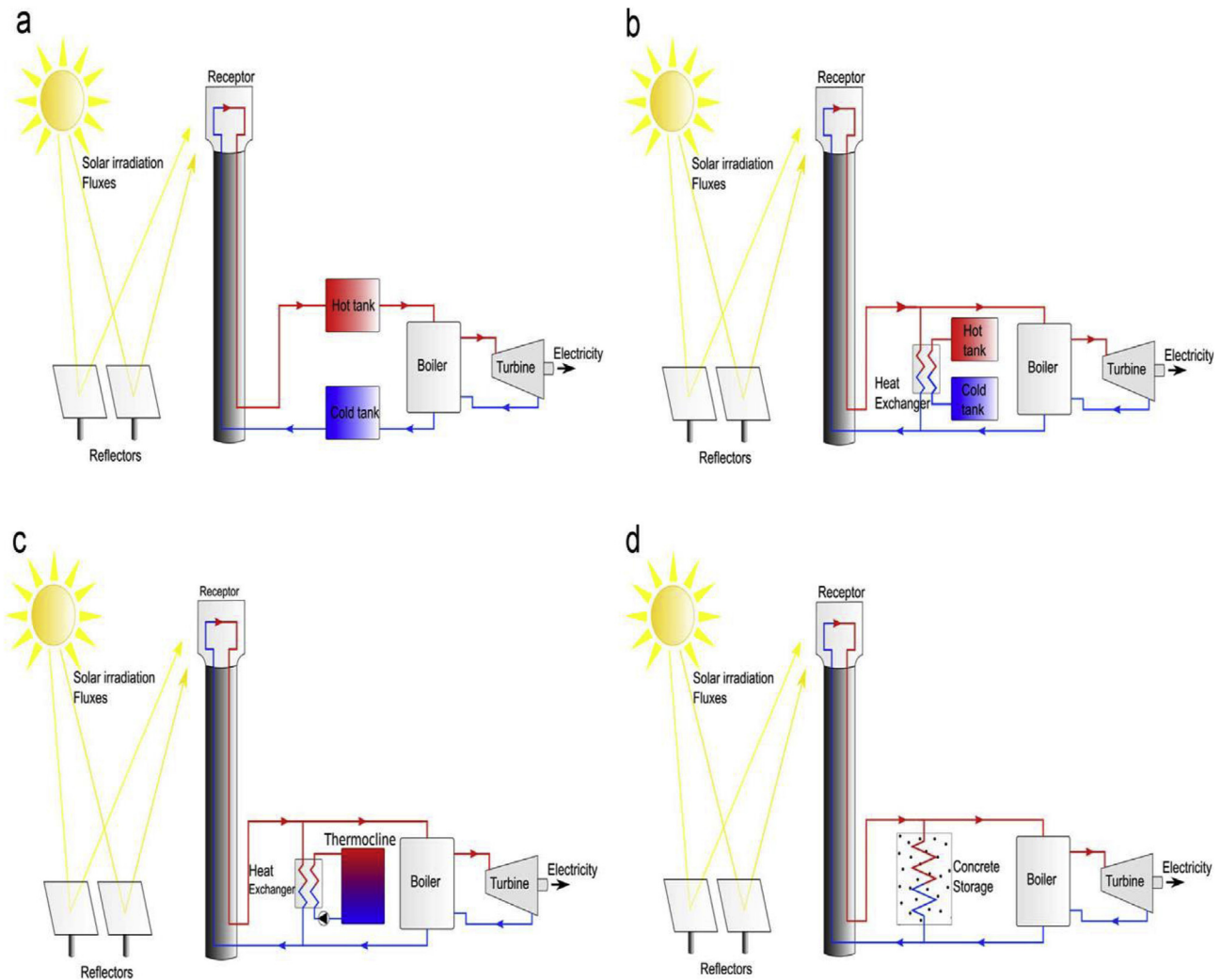


Fig. 1. TES systems in CSP plant (a) Two tank direct, (b) Two tank indirect, (c) Thermocline system and (d) Concrete block system [3].

harvested for satisfying the world's energy demand, this energy source can still sustain and hence is considered as renewable. The heat from the earth's hot mantle heats up the underground water columns inside the earth's crust. These underground hot briny water reservoirs can be used as geothermal fluids. A study of Wairakei geothermal system in New Zealand by O'Sullivan et al. [4] concluded that for every 100 years of electricity generation the geothermal field needs another 400 years for extracted thermal energy to be naturally replenished through deep recharge. Geothermal energy resources are renewable in the long-term because they would fully recover to their pre-exploitation state after an extended shut-down period. Due to the complexity of drilling at high depths, geothermal energy plants can be found mostly near the earth's plate tectonics where geothermal fluid is available at lower depths and with higher temperatures up to 180 °C [5]. Geothermal fluid available at temperatures higher than 150 °C is suitable for electricity generation using steam. Geothermal fluid available at temperatures between 150 °C and 100 °C is suitable for electricity generation using Organic Rankine cycle (ORC) with working fluids like isopentane, isobutane, propane, butane and fluorocarbon family refrigerants [6]. Geothermal fluid at temperature lower than 100 °C is suitable for direct-use purposes like drying of agricultural produce. As geothermal reservoir itself is a TES system, thermal energy is continuously

available 24 h a day. Therefore unlike solar thermal energy, geothermal energy source can be utilized any time of the day on need basis. Still there is scope for manmade TES system when concepts like co-generation, tri-generation or multi-generation are used. In a single generation plant only the electricity is generated from thermal energy. However, overall efficiency of a single generation plant is low due to the loss of thermal energy still available in the working fluid at the turbine outlet which gets wasted at the condenser. In co-generation, tri-generation or multi-generation thermal power plants more functions like district heating, drying, heat storage TES system, absorption chiller and cold storage TES system (example: ice production from the cooling effect produced by absorption chiller) etc are integrated to the plant to improve efficiency. One such example of a cascading tri-generation model was presented by Díaz et al. [7] as shown in Fig. 2.

1.1.3. Fossil-fuel power plants

These power plants generate electricity from the heat generated by burning fossil fuels like coal, natural gas or petroleum products. It is estimated that around 40% of the world's man made CO₂ emissions are caused by burning fuels. The turbines are driven either by steam as the working fluid in a Rankine cycle or by air as the working fluid in a Brayton cycle. Fossil fuel plants such as coal

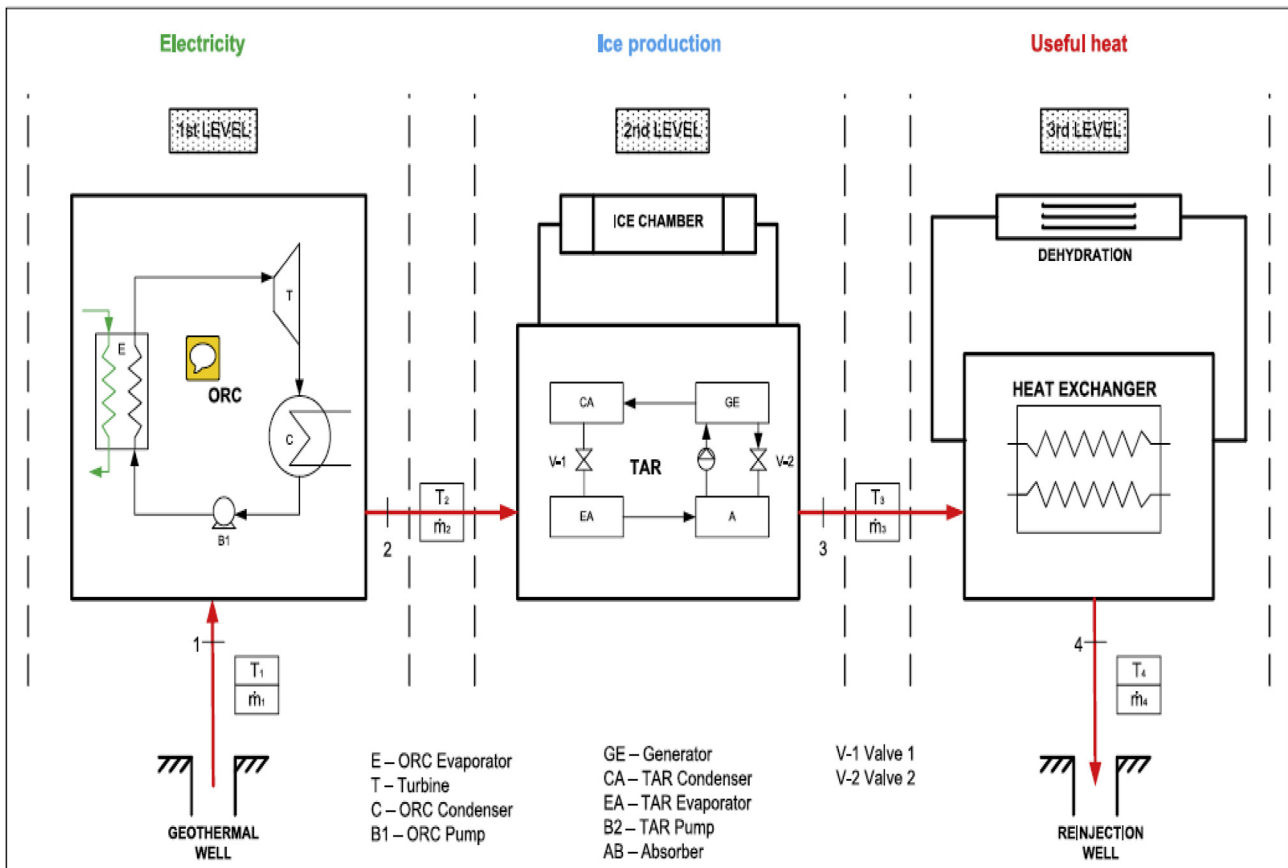


Fig. 2. Cascading multi-generation system [7].

powered plants are load following power plants. They are flexible and can burn more fuel during peak hours and can generate more electricity to satisfy the peak-hour demand for energy. However overall efficiency of such power plants is around 35% which means large proportion of heat is dissipated to the environment. As discussed in the case of geothermal energy above, efficiency of fossil-fuel power plants can be improved by utilizing heat that gets dissipated to environment through co-generation, tri-generation or multi-generation, where TES systems also find a role to play. Similarly fossil fuels can also act as secondary fuels in combined cycle plants like concentrated solar power plant (CSP) or district heating system with solar energy as the primary energy source. B. Rezaie et al. [8] presented a case study of combined cycle district heating system driven by solar-natural gas combined heat sources and with a TES system as shown in Fig. 3.

1.1.4. Nuclear power plants

Nuclear power plants generate electricity from the heat generated by controlled nuclear fission reaction inside a core reactor. The core reactor's heat is transferred to a working fluid like water and steam is generated, which drives the turbines in a Rankine cycle. Nuclear power plants are technically very complex and due to technical constraints associated with the reactor behavior their flexibility in load-following capability during off-peak hours is poor. In older generation of reactor types like boiling water reactor (BWR) and pressurized water reactors (PWR) it is not economical to reduce the plant output below the rated capacity by using control rod mechanism. Therefore they mostly operate as base load power plants which always operate at maximum output. European Utility Requirements (EUR) mandates that future generation III and

III+ nuclear power plant must be capable of minimum load cycling operation from 50% to 100% of rated power capacity with a change rate from 3% to 5% of rated power per minute. Therefore many proposed designs for the future nuclear plants involve TES system, which can play a crucial role of facilitating load following capability at nuclear power plants [2,9]. Concept is to let nuclear plants operate at full capacity. However steam generation rate follows the electricity demand at any point in time. Excess heat at times of low electricity prices or low electricity demand is stored in TES system. Fig. 4 shows a conceptual load following nuclear power plant with TES system.

1.1.5. Industrial waste heat

Excess heat generated by the manufacturing plants during production of various goods usually gets dissipated into environment. Miro et al. [10] reported that in order to reduce CO₂ emissions recently countries have begun an effort to quantify the quality of their industrial waste heat. They gathered industrial waste heat data from 33 countries. In this analysis they presented data that gives us a picture of the potential of industrial waste heat which is presented in Table 2. EU, Canada and USA have very high industrial waste heat potential in terms of amount of heat available to be recovered. These countries have an estimated annual industrial waste heat generation of 2.7, 2.3 and 1.3 EJ respectively. It is noticeable that Canada and Turkey have an estimated 26.4% and 17.4% of their total annual energy consumption as industrial waste heat. This clearly shows how significant is this thermal energy source. Fig. 5 gives the various options to utilize industrial waste heat and in this waste heat recovery scheme TES system is classified as a passive system. Passive system utilizes energy only in thermal form at the end user side

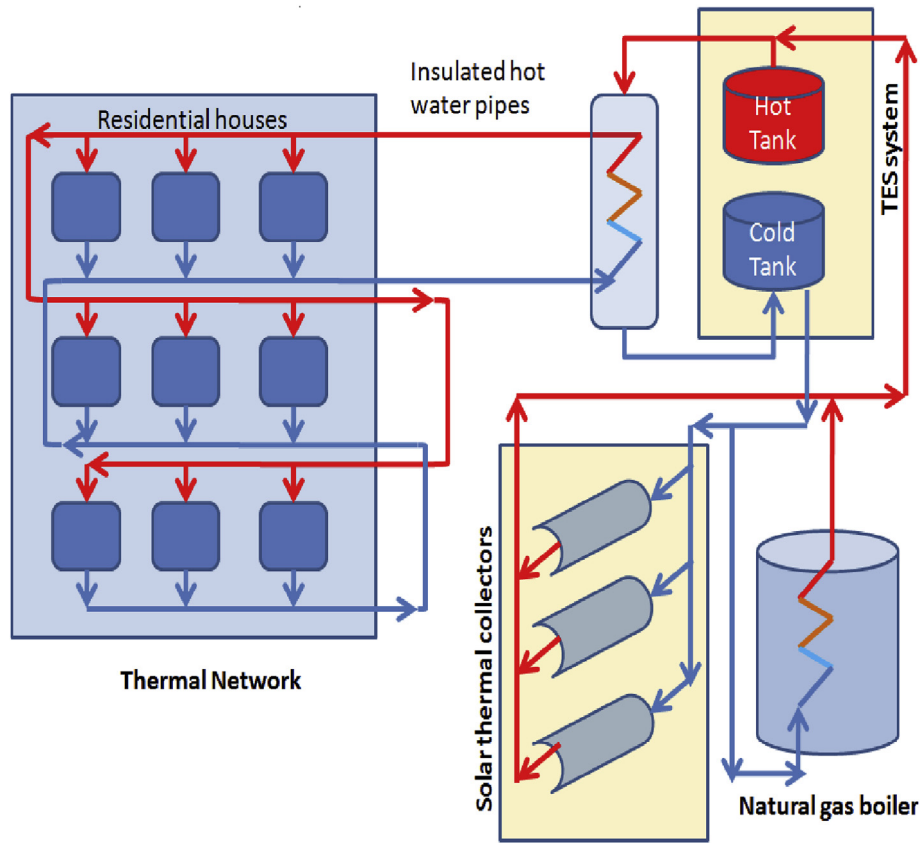


Fig. 3. Hybrid solar–natural gas combined cycle district heating system with TES.

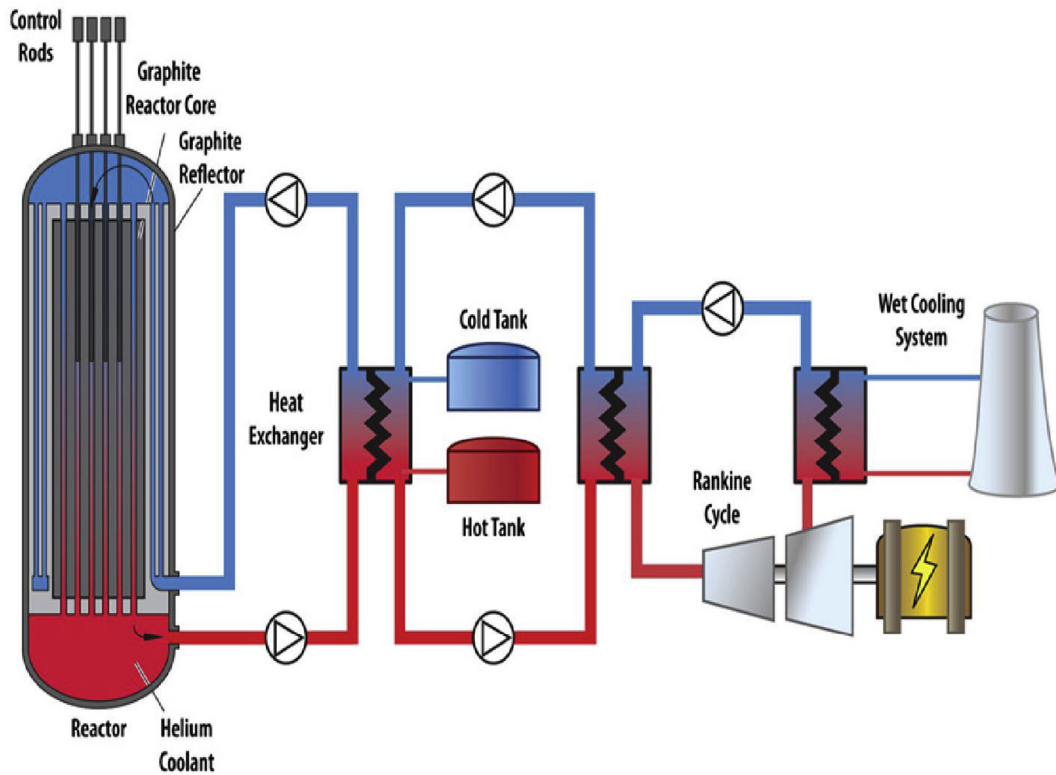


Fig. 4. Conceptual load following nuclear power plant with TES system [2].

Table 2
Industrial waste heat potential for major industrialized countries [10].

Country	Industrial waste heat potential (EJ)	Total Industrial Energy Consumption (EJ)	Industrial waste heat per energy consumed by the industry (%)	Total country energy consumption (EJ)	Industrial waste heat per energy consumed by the country (%)
EU	2.7	12.2	22.2	48.2	5.6
Canada	2.3	3.2	71	8.7	26.4
USA	1.5	37.9	4	102.6	1.4
Turkey	0.857	1.8	46.9	4.9	17.4
Korea	0.384	5.3	8	8.1	4.7
Japan	0.59	5.7	1	13.3	0.4

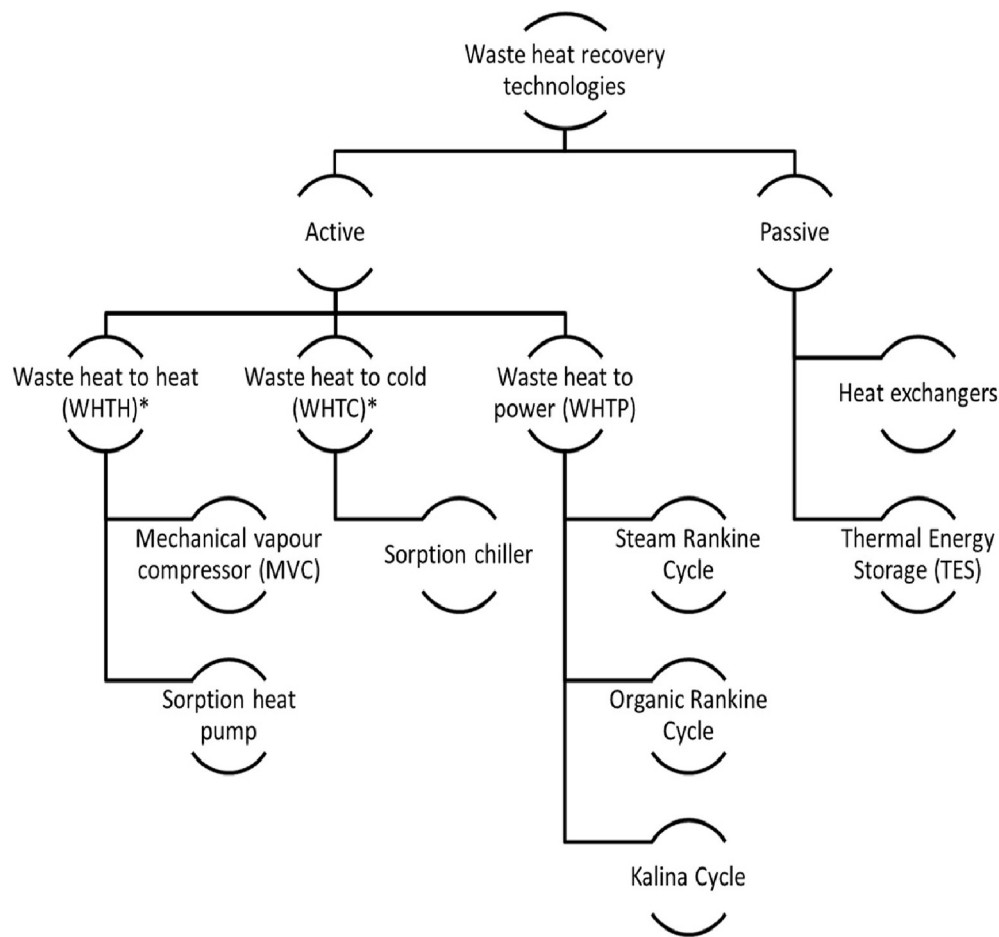


Fig. 5. Waste heat recovery methods classification [11].

with temperature being either same or less than the industrial waste heat source. In this classification, active system means either an energy conversion to other forms like electricity is involved or there is an increase in temperature at the end user side. Quality of waste heat is decided by the temperature at which it is available and based on that, appropriate recovery mechanism from the options available in Fig. 5 can be chosen. Typical industrial waste heat recovery sources are exhaust gases from iron and steel plant furnaces (≈ 1550 °C), glass melting furnaces (≈ 1540 °C), aluminum furnaces (≈ 1200 °C), copper refining furnaces (≈ 820 °C), cement kilns (≈ 620 °C), gas turbines (≈ 540 °C), steam boilers (≈ 480 °C). Typical industrial processes where recovered waste heat can find application are processes like drying (≈ 70 °C– 120 °C), steaming (≈ 130 °C), boiling (≈ 105 °C), sterilizing (≈ 130 °C), cooking (≈ 115 °C) in industries like food and beverages, textile, chemicals, paper industry and wood industry etc [11].

1.1.6. Biomass

Although biomass fuels cause emission of CO_2 gas but they are a renewable source of energy. This renewability is what distinguishes biomass from fossil fuels as both of them cause emission of CO_2 gas. Biomass examples are wood wastes, municipal solid wastes, biogas from animal waste, bio-fuels like ethanol from corn etc. Biomass fuel plants are load following power plants. They have good flexibility in load-following capability during peak hours. However biomass can also act as a secondary fuel in combined cycle plants like concentrated solar power plant (CSP) or district heating system with solar energy as the primary energy source. In these combined cycle plants TES systems also find a role to play. Fig. 6 describes a solar-biomass hybrid power plant concept [12]. This model uses a two-tank direct TES system with molten salt as the heat transfer fluid and thermal storage media. TES system collects heat from a parabolic solar thermal collector unit.

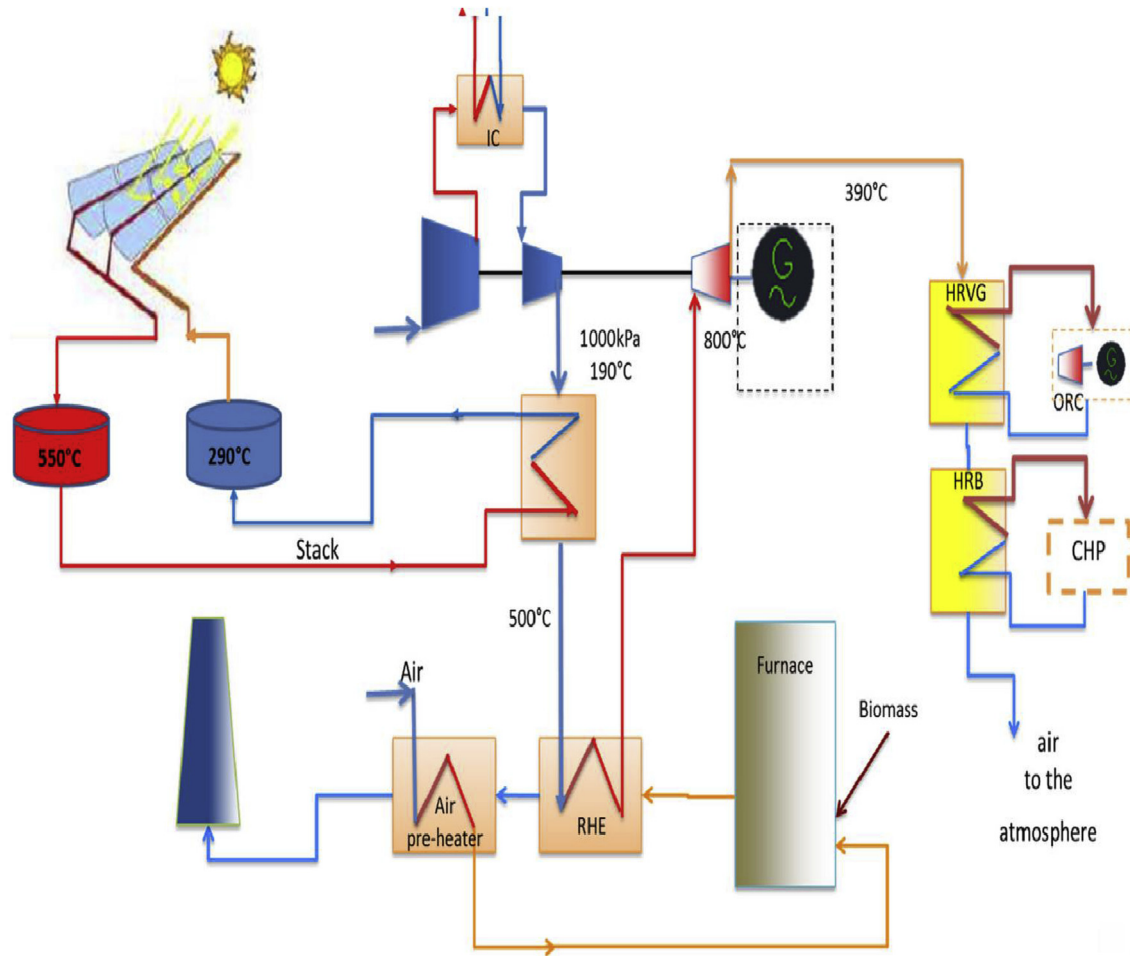


Fig. 6. Hybrid solar–biomass combined cycle power plant [12].

1.2. Role of TES systems

All the details covered so far present us with a picture where on the one side there is a very strong demand for huge amount of thermal energy and on the other side there is plenty of thermal energy available. However there are gaps between the demand and thermal energy supply as listed below.

- Time difference between thermal energy generation and consumption.
- Difference in cost of thermal energy between peak and off-peak hours of the day.
- Distance between source of thermal energy and place of consumption.

Thermal energy if not consumed, simply dissipates into the environment resulting in wastage. By burning fuels, there is a convenience of thermal energy generation on need basis. Therefore demand–supply gaps result in burning of fuels to satisfy the demand. This has following implications.

- Increased environmental pollution due to burning of fuel. This results in increased emission of harmful gases like CO_2 into the atmosphere causing greenhouse effect and also release of unutilized heat into environment. Both these factors lead to global warming.

- Increased cost due to increased fossil fuel consumption. There is a loss of opportunity to harvest freely available thermal energy from a renewable source like solar radiation.

Thermal energy storage (TES) systems provide both environmental and economical benefits by reducing the need for burning fuels. Thermal energy storage (TES) systems have one simple purpose. That is preventing the loss of thermal energy by storing excess heat until it is consumed. Almost in every human activity, heat is produced. Our activities in kitchen, automobile etc when seen at a macro scale, collectively generate huge amount of heat which gets wasted all the time. There may be some scope for innovative ways of utilizing such waste heat economically. But in general, considering the cost of materials and effort required for collecting, storing and utilizing waste heat from such large number of small heat sources distributed over large distances, it is not practical to implement TES system at every heat source. However as discussed above, for large heat sources like solar thermal energy, geothermal energy, fossil–fuel power plants, nuclear power plant, industrial waste heat etc there is scope to implement TES system in an economical way. Table 3 presents a list of operational plants around the globe and the TES systems in operation in those plants.

Besides their use at large thermal energy sources covered in above sections, TES systems have even larger scope in the overall efficient energy management scheme. By classifying based on

Table 3
Large scale operational TES systems.

Location	Energy source		TES system			Remarks
	Primary	Secondary	Type	Storage medium	Annual capacity (MWh)	
Friedrichshafen, Germany	Solar	Natural gas	Underground, Seasonal	Water	4106	District heating network [8,13]
Marstal, Denmark	Solar	Biomass	Underground, Seasonal	Water, Pit storage	19,000	District heating network [13]
Kungälv, Sweden	Industry waste heat	Waste incineration	Underground, Seasonal	Water	90,000	District heating network [13]
Chemnitz, Germany	Solar	Natural gas, fuel oil	Underground, Seasonal	Gravel/water	573	District heating network [13]
Neckarsulm, Germany	Solar		Underground, Seasonal	Borehole/duct	3960	District heating network [13]
Rostock, Germany	Solar		Underground, Seasonal	Aquifer	497	District heating network [13]
Kutch, India	Solar		Diurnal	Solar pond	1357	Industrial process heat supply [14]
Solar two, Nevada, USA	Solar		Diurnal two tank system	Solar salt	105	Electrical power generation. Hot tank (565 °C, 875 m ³) [15]
THEMIS, Pyrenees, France	Solar		Diurnal two tank system	Hitect salt	40	Electrical power generation. Hot tank (450 °C, 310 m ³) [15]
Andasol Andalusia, Spain	Solar parabolic trough		Diurnal, Two-tank, Indirect	Molten salt	1010	Electrical power generation Hot tank (384 °C) [16]
Extresol Torre de Miguel Sesmero, Spain	Solar parabolic trough		Diurnal, Two-tank, Indirect	Molten salt	1010	Electrical power generation Hot tank (384 °C) [16]
Arcosol 50 San José del Valle, Spain	Solar parabolic trough		Diurnal, Two-tank, Indirect	Molten salt	1010	Electrical power generation Hot tank (384 °C) [16]
La Florida Badajoz, Spain	Solar parabolic trough		Diurnal, Two-tank, Indirect	Molten salt	1010	Electrical power generation Hot tank (384 °C) [16]
La Dehesa La Garrovilla, Spain	Solar parabolic trough		Diurnal, Two-tank, Indirect	Molten salt	1010	Electrical power generation Hot tank (384 °C) [16]
Gemasolar (Solar Tres) Fuentes de Andalucía, Spain	Solar power tower		Diurnal, Two-tank, Direct	Molten salt	600	Electrical power generation Hot tank (565 °C) [16]

different criteria, a better picture on the various forms of TES systems can be obtained.

2. Heat storage material type based TES systems

A wide variety of materials are being used for thermal energy storage. TES materials must possess suitable thermo-physical properties like favorable melting point for the given thermal application, high latent heat, high specific heat and high thermal conductivity etc. Other desired properties of thermal energy storage materials are low supercooling, low cost, easy availability, thermal stability, chemical stability, low volume change, non-toxic, low vapor pressure, congruent melting and low flammability etc [17]. TES systems can be broadly classified into three classes based on the type of TES material being selected for heat or cold storage.

2.1. Sensible heat storage systems

Sensible heat thermal energy storage materials store heat energy in their specific heat capacity (C_p). The thermal energy stored by sensible heat can be expressed as

$$Q = m \cdot C_p \cdot \Delta T \quad (1)$$

where m is the mass (kg), C_p is the specific heat capacity ($\text{kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$) and ΔT is the raise in temperature during charging process. During the heat energy absorption process, there is no phase change happening and materials experience a raise in temperature. The amount of heat stored is proportional to the density, volume, specific heat and variation of temperature of the storage material.

2.1.1. Sensible heat storage materials

2.1.1.1. Water. Water can be circulated easily and hence can be used in active systems as both heat transfer fluid (HTF) and thermal energy storage (TES) material. Its advantages are high specific heat ($4.184 \text{ kJ} \cdot \text{kg}^{-1} \cdot \text{K}^{-1}$), non-toxicity, cheap cost and easy availability. Water can be used as ice, liquid and steam. Ice is used in cold storage. Liquid phase is used for low temperature heat energy storage below $100 \text{ }^\circ\text{C}$. Because it is easily available and it is a non-toxic, non-flammable material, it is completely harmless to people. Therefore water is the best suited thermal energy storage material for home space heating, cold storage of food products and hot water supply type of applications. Steam phase is used for high temperature heat energy storage. In CSP plants using direct steam generation (DSG) technique, steam accumulators are used as TES system where saturated steam is stored in high pressure insulated steel tanks [15]. Water in liquid form can form thermocline heat storage. Due to density difference caused by heating of liquid, the buoyancy helps in creating a thermal gradient across the storage which is desirable [18]. In cold storage water is used in chilled water form or in ice form. But water has few drawbacks like high vapor pressure and corrosiveness.

2.1.1.2. Thermal oils. Thermal oils are organic fluids with good heat transfer capability. Table 4 lists thermal oil products currently popular in different CSP plants in operation. Non-edible vegetable oils have also been tested for functioning as thermal oils [19]. Thermal oils are usually colorless clear liquids. Advantage of thermal oils over water is that they remain in liquid phase at higher temperatures than water up to $250 \text{ }^\circ\text{C}$ under atmospheric pressure. Thermal oils have an operating temperature range between $12 \text{ }^\circ\text{C}$ and $400 \text{ }^\circ\text{C}$ which means higher ΔT (in Eq. (1)) and more heat storage. When compared with water, thermal oils have low vapor pressure. When temperature is at $374 \text{ }^\circ\text{C}$ DOWTHERM thermal oil

Table 4
Thermal oil properties [19].

Property	Therminol® VP–1	Xceltherm 600	Syltherm XLT	Dowtherm® A	Vegetable oil
Manufacturer	Eastman chemical company	Radco industries	Dow chemical company	Dow chemical company	[19]
Composition	Diphenyl oxide/biphenyl	Paraffinic mineral oil	Dimethyl polysiloxane	Diphenyl oxide/biphenyl	Triglycerides/free fatty acids
Max bulk temperature (°C)	400	316	260	400	–
Melting point (°C)	12	–	–111	12	–
Atmospheric boiling point (°C)	257	301	200	257	295
Kinematic viscosity at 40 °C (mm ² s ^{–1})	2.48	15.5	1.1	2.56	30
Density at 40 °C (kg m ^{–3})	1068	841	834	1043	926
Density at 210 °C (kg m ^{–3})	904	736	660	897	802
Thermal conductivity at 210 °C (W m ^{–1} K ^{–1})	0.11	0.12	0.06	0.1083	0.11
Specific heat capacity at 210 °C (kJ kg ^{–1} °C ^{–1})	2.075	2.643	2.171	1.63	2.509
Thermal storage capacity at 210 °C (kJ m ^{–3} °C ^{–1})	1876	1945	1433	1462	2012
Cost (€·t ^{–1})	25,000	–	29,400	–	835
Energy storage cost for ΔT = 100 °C (€·kWh ^{–1})	464	–	573	–	12

has a vapor pressure of 7.6 bar, where as water has a vapor pressure of 221 bar. This means low pressure on the container and pipe walls. This leads to lower thickness, and lower container and pipe costs. Thermal oil has low viscosity and good flow properties. It can be circulated easily with lower pumping costs. It is used in active systems as both heat transfer fluid (HTF) and thermal energy storage (TES) material. Thermal oils have mediocre heat transfer characteristics. Therminol–VP has a low thermal conductivity (≈ 0.1 W/m.K) and has an estimated heat transfer coefficient which ranges between 1000 W m^{–2}.K^{–1} and 3500 W m^{–2}.K^{–1} [20]. Thermal oils can form thermocline in liquid state. Thermocline TES system normally has a packed bed of fillers like rocks, sand, encapsulated PCM etc and thermal oil acting as HTF. Thermal oils have an advantage over molten salts in that they do not freeze in pipes because their melting point is very low (below 12 °C) and they do not require anti–freeze mechanism. Disadvantage of thermal oils over water is that they have lower specific heat (≈ 2 kJ kg^{–1}.K^{–1}) and they are expensive as can be seen from Table 4. Thermal oils which may contain aromatic organic compounds have low order toxicity and may bio–concentrate in living organisms. At elevated temperatures above their operating range thermal oils degrade due to reactions like oxidation by air which may produce acids like carboxylic acid, peroxide compounds etc [19] which may accelerate corrosion of containers and pipes. Thermal oil undergoes a slow degradation with aging after long hours of high temperature exposure and repetitive thermal cycles. Thermal oil vapor is a fire hazard risk when mixed with atmospheric air. During system operation, care should be taken to prevent any thermal oil leakage as it is expensive and also due to environmental concerns. The heat transfer properties of thermal oils can be further enhanced with nano–additives like graphene, graphite and metal oxides etc [21].

2.1.1.3. Molten salts. When the temperature of the system exceeds thermal oil temperature limit (≈ 400 °C), molten salts are the

preferred heat transfer fluid and heat storage medium. As seen in Table 1 solar power tower (SPT) and parabolic dish collector (PDC) type of CSP plants the temperature will be higher than thermal oil limits. Molten salts are already most popular thermal energy storage (TES) medium in CSP plants. Due to their favorable thermo–physical properties, they are also becoming popular choice in future generation III and III+ nuclear reactors. They have high volumetric heat capacity, high boiling point and very high thermal stability. Their vapor pressure is near zero and negligible. Molten salts act as both heat transfer fluid and heat storage medium. The current level of the highest operating limit for molten salts is around 565 °C [22]. Higher boiling point and thermal stability at high temperature means they can sustain very high operating temperature which improves the thermodynamic efficiency of Rankine cycle of steam. It also means higher ΔT (in Eq. (1)) and more heat storage. They are cheap, easily available, non–toxic and non–flammable. However there are few difficulties faced with molten salts. Salts have high melting point usually above 200 °C which results in their freezing in pipelines when there is no heat source like solar energy in the night. It is desirable to have a melting point close to the ambient temperature and a very high boiling point so that the HTF can operate at maximum range. Generally speaking, pure salts or salt eutectics with melting point below 250 °C are considered for sensible heat storage in the molten salt form. Eutectic mixtures of two or more salts help to bring down the melting point while still maintaining a very high boiling point. Table 5 lists few commonly encountered salts and their eutectic mixtures. HITEC ternary salt mixture (53% KNO₃, 7% NaNO₃ and 40% NaNO₂) with a melting point near 142 °C is currently very popular [18]. Pure KNO₃ has a melting point of 334 °C and pure NaNO₃ has a melting point of 307 °C. Their binary salt mixture called “Solar salt” (60% NaNO₃ and 40% KNO₃) has a melting point of 220 °C. They have a high viscosity compared to thermal oils and water. Therefore they have poor flow properties which increase the pumping costs. Molten salts have mediocre heat transfer characteristics. Their

Table 5
Molten salts and liquid salt eutectic mixtures [15,17].

Salt/eutectic	Melting point (°C)	Highest operating temperature (°C)	Specific heat (kJ·kg ^{–1} °C ^{–1})	Density (kg·m ^{–3}) (liquid)	Thermal conductivity (W·m ^{–1} K ^{–1})	Sensible heat storage capacity (MJ·m ^{–3} °C ^{–1})	Cost (\$·kg ^{–1})
HITEC, NaNO ₃ –KNO ₃ –NaNO ₂ (7–53–40)	142	535	1.561	1640	0.60	2.56	–
HITEC XL, NaNO ₃ –KNO ₃ –Ca(NO ₃) ₂ (7–45–48)	120	500	1.447	1992	0.519	2.9	1.19
Solar Salt, NaNO ₃ –KNO ₃ (50–50)	220	600	1.5	1899	0.55	2.8	–
LiNO ₃	250	600	–	2380	–	–	–

thermal conductivity is low ($\approx 0.5 \text{ W/m.K}$) and an estimated heat transfer coefficient which ranges between $3600 \text{ W m}^{-2}.\text{K}^{-1}$ and $6700 \text{ W m}^{-2}.\text{K}^{-1}$ [20] for “Solar salt” and ranges between $1500 \text{ W m}^{-2}.\text{K}^{-1}$ and $4000 \text{ W m}^{-2}.\text{K}^{-1}$ [20] for ‘HITEC’. Temperature gradient in heat exchange tubes will be high causing temperature hot spots on the tube walls. Sanchez et al. [23] in their study of solar tower receivers found the maximum temperature at outer tube wall ranging between $580 \text{ }^\circ\text{C}$ and $675 \text{ }^\circ\text{C}$ while the temperature of molten salt flowing increased from $290 \text{ }^\circ\text{C}$ at the inlet to $565 \text{ }^\circ\text{C}$ at the outlet. The temperature gradients on receiver tube walls cause plastic strains which are cumulative and the tubes will eventually fail due to low cycle fatigue [23]. Further enhancement of thermal properties like specific heat and thermal conductivity of molten salt HTFs is being tested with different nano-additives [24]. They are also corrosive and this is exacerbated at higher temperatures. ARCHIMEDE project in Sicily, Italy [25] molten salt is used as a HTF in parabolic troughs. Here auto-regulation of local pipe temperature is done using electric trace heating to prevent freezing during cloudy weather and night. A drain-back system which can drain molten salt in all pipes if sufficient sunlight is not available for long periods is also installed. This large-scale demonstration plant showed that direct molten salt storage is feasible for CSP plants.

2.1.1.4. Liquid metals. Some metals and their alloys possess unique characteristics like low melting points close to or below ambient temperature and yet have a very high boiling point. Such metals are best suited for use as HTF in high temperature TES systems as they do not have the freezing problem and they have almost zero vapor pressure even at high temperatures. High operation temperature leads to high thermodynamic cycle efficiency up to 50% [20]. Wide gap between their melting and boiling points give a broad operational temperature range ΔT (in Eq. (1)) and a large sensible heat storage capacity. Due to their favorable thermo-physical properties, liquid metals have also been in use as coolants for nuclear reactors in Russia. Liquid metals possess outstanding heat transfer characteristics. For example sodium (Na) has a thermal conductivity of ($\approx 64.9 \text{ W m}^{-1}.\text{K}^{-1}$) and an estimated heat transfer coefficient which ranges between $18,000 \text{ W m}^{-2}.\text{K}^{-1}$ and $28,500 \text{ W m}^{-2}.\text{K}^{-1}$ [20]. Similarly lead-bismuth eutectic (LBE) has a thermal conductivity of ($\approx 14.9 \text{ W m}^{-1}.\text{K}^{-1}$) and an estimated heat transfer coefficient which ranges between $10,600 \text{ W m}^{-2}.\text{K}^{-1}$ and $11,900 \text{ W m}^{-2}.\text{K}^{-1}$ [20]. Pacio et al. [26] reported even higher heat transfer coefficient for Na and LBE at $47,000 \text{ W m}^{-2}.\text{K}^{-1}$ and $24,000 \text{ W m}^{-2}.\text{K}^{-1}$ respectively. Solar receiver tube wall temperature will be low and temperature gradient in tubes will be very low. Lower tube wall temperatures also result in lower heat losses to the environment. Therefore liquid metals improve the receiver efficiency. However liquid metals are very expensive and are prone to corrosion. In addition sodium (Na) is a fire risk because of its pyrophoricity and LBE is toxic. Table 6 lists the liquid metals and alloys. Fig. 7 shows conceptual CSP plant operation based on liquid metal.

2.1.1.5. Earth materials. Naturally available earth materials like rocks, sands, gravel etc can be used for sensible heat storage. They are suitable for use as fillers in single tank thermocline thermal

energy storage systems where they are arranged in a packed bed structure inside a container. Heat transfer fluid (HTF) flows through the packed bed and exchanges heat through direct contact. Earth materials are cheap, easily available, non-toxic, non-flammable and act as both heat transfer surface and storage medium. Direct contact not only reduces the need for costly heat exchangers but also increases the contact surface area between HTF and thermal storage medium. Thermal oil is the most used HTF for direct heat exchange with filler materials like rocks and sands in large CSP plants. However other HTFs like air are also being used in smaller space heating solar thermal systems at residential homes. Choosing sand or natural rocks as filler material may reduce the quantity of the HTF required for charging and discharging thermal energy up to 80% in the tank [28]. Local availability, low cost, density, heat capacity and thermal conductivity are decisive criteria for choosing the best rocks and sands etc for use as packed bed filler materials. Other desirable properties like high surface hardness to resist abrasion, low porosity to prevent oil infiltration, high mechanical strength etc are also looked into. Chemical composition and mineralogy of rocks and sands are also studied as it influences their degradation due to thermal oil flow over a long period. Grirate et al. [29] studied various rock samples for TES suitability. They carried out TGA analysis where granite and marble lost weight of about 3.3% and 2.9% respectively at a high temperature of about $350 \text{ }^\circ\text{C}$. Granite is composed of minerals containing hydroxyl bonds which break at high temperature, leading to a weight loss. Marble is composed predominantly of CaCO_3 and its weight loss was caused by the escape of CO_2 during heating. Other rock types quartzite, basalt and hornfels were thermally stable up to $400 \text{ }^\circ\text{C}$ with no weight loss. Table 7 provides details of few common rock types encountered in nature. They concluded that all rock types have almost similar thermo-physical characteristics and are suitable for use as filler materials for operating temperatures up to $350 \text{ }^\circ\text{C}$. Past research data suggested quartzite to be best among the rock types with a high thermal conductivity of $7 \text{ W m}^{-1}.\text{K}^{-1}$ and a higher thermal storage capacity of $3822 \text{ kJ m}^{-3}.\text{K}^{-1}$. Rocks of varying sizes like stones, pebbles, small gravels are used for packed bed fillers while sand with smaller granule size in $0.074\text{--}4.5 \text{ mm}$ range can be used in fluidized bed. Sand is mainly made up of quartz mineral with a high silica (SiO_2) content exceeding 90%. Fine sand and other micron sized particles like ceramics (alumina, silicon carbide), dry cement powder, coal etc are used in air suspensions to directly collect heat from concentrated solar radiation [30]. The suspension particle size is controlled with the help of cyclone separator set up to an appropriate grain size cut point. These solid particles are thermally stable even at very high temperature ranges of solar power tower (SPT) type of CSP plant and direct absorption of solar radiation improves efficiency. Hence they are best suited for use as suspended solids in a gas-solid thermal energy capture/storage system [31]. Similarly Calvet et al. [28] explored the use of a very cheap industrial waste ceramic material called Cofalit. Cofalit was directly in contact with binary eutectic “Solar salt” and ternary eutectic HITEC XL salt at $500 \text{ }^\circ\text{C}$ for 500 h. In the outcome of the test, the Cofalit was found to be compatible with binary eutectic “Solar salt”. However with ternary eutectic HITEC XL salt it reacted and

Table 6
Liquid metals suitable for TES-HTF role [26].

Metal/Alloy	Melting point ($^\circ\text{C}$)	Boiling point ($^\circ\text{C}$)	Specific heat $\text{kJ}\cdot\text{kg}^{-1}\cdot\text{ }^\circ\text{C}^{-1}$	Density $\text{kg}\cdot\text{m}^{-3}$	Thermal conductivity $(\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1})$	Sensible heat storage capacity $(\text{MJ}\cdot\text{m}^{-3}\cdot\text{ }^\circ\text{C}^{-1})$	Cost ($\text{\$}\cdot\text{kg}^{-1}$)
Sodium (Na)	98	883	1.3	1042	64.9	1.354	2
Sodium(22.2%)–potassium (77.8%) eutectic (NaK)	–12.6	785	0.89	780	26.3	0.694	2
Lead(44.5%)–bismuth(55.5%) eutectic (LBE)	125	1533	0.14	10300	14.9	1.44	13

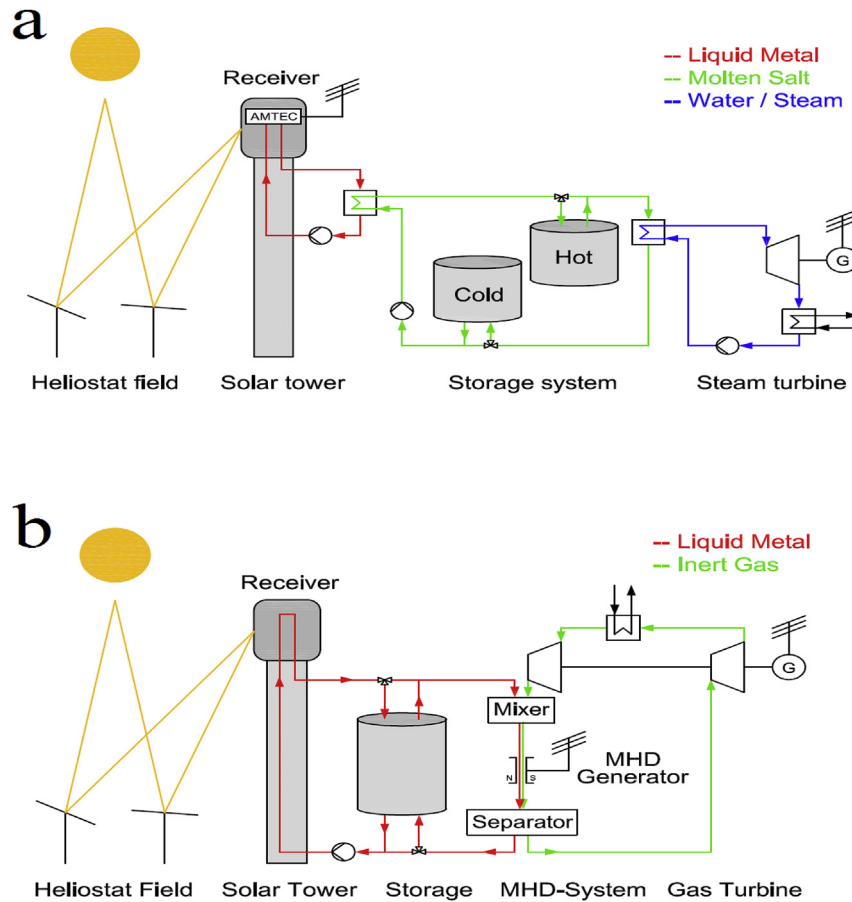


Fig. 7. Conceptual CSP plant using liquid metal (a) Liquid metal as receiver with salt TES and (b) Direct TES system using liquid metal [27].

Table 7
Common rock types [29].

Rock	Type	Porosity (%)	Density ($\text{kg}\cdot\text{m}^{-3}$)	Uniaxial compressive strength (MPa)	Specific heat ($\text{kJ}\cdot\text{kg}^{-1}\cdot\text{C}^{-1}$) @20 °C	Thermal conductivity ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)	Sensible heat storage capacity ($\text{kJ}\cdot\text{m}^{-3}\cdot\text{C}^{-1}$)	Hardness	Major components
Granite	Igneous	1.02–2.87	2530–2620	100–300	0.6–1.2	2.8	1440–2880	High	SiO_2 (69%) Al_2O_3 (14%)
Quartzite	Metamorphic	0.22–22.1	2210–2770	100–350	0.8–0.9	2	1750–2500	Very high	SiO_2 (94%)
Marble	Metamorphic	0.40–0.65	2510–2860	150–300	0.7–1	7.7	3822	Low–medium	CaO (54%)
Basalt	Igneous	0.65–0.81	2610–2670	50–200	1.47	3.2	1680–2520	Medium–high	SiO_2 (47%) Al_2O_3 (17%) Fe_2O_3 (10%) CaO (13%)
Hornfels	Metamorphic	0.8–2.3	2400–2800	100–200	0.7–0.9	1.5	2560–2880	Medium	SiO_2 (63%) Al_2O_3 (21%)

produced a calcium silicate layer. Hence Cofalit was found to be incompatible with ternary eutectic HITEC XL salt.

2.1.1.6. Concrete blocks. Fig. 1d shows an example of concrete blocks used for sensible heat storage. Concrete has benefits like low cost, easy construction, good mechanical properties, non-toxic, non-flammable. As concrete has good mechanical strength it does not require a container to hold which further reduces the cost. Concrete is a mixture of cement, gravel and sand. Gravels have the mineral composition of the type of rock. Sand is mostly quartz mineral which is 90% silica (SiO_2). Cement acts as the binder. Portland cement's main constituents before use in concrete mix are CaO ($\approx 63\%$), SiO_2 ($\approx 19\%$), Al_2O_3 ($\approx 6\%$) etc. During the curing process cement undergoes hydration and forms cement phases like calcium silicate hydrate (C–S–H), calcium alumina silicate hydrate (C–A–S–H), Portlandite ($\text{Ca}(\text{OH})_2$) etc. During the heat absorption

process as temperature raises many changes like dehydration ($105\text{ }^\circ\text{C}$ – $440\text{ }^\circ\text{C}$, C–S–H phase), dehydroxylation ($440\text{ }^\circ\text{C}$ – $580\text{ }^\circ\text{C}$, Portlandite phase), decarbonation ($560\text{ }^\circ\text{C}$ – $1000\text{ }^\circ\text{C}$), phase changes (eg: Quartz, α – β , $571\text{ }^\circ\text{C}$) etc happen within the concrete block [32,33]. These changes result in formation of CaO residue which can be easily rehydrated again during the cooling process by absorbing moisture from the atmosphere with the consequent swelling of the hardened paste which induce cracks due to slight changes in volume and repeated thermal cycles. Concrete has a specific heat close to $0.7\text{ kJ kg}^{-1}\cdot\text{K}^{-1}$ and thermal conductivity close to $0.5\text{ W m}^{-1}\cdot\text{K}^{-1}$. Xu et al. [34] used admixture like silane coated silica fume which increased specific heat to $1.05\text{ kJ kg}^{-1}\cdot\text{K}^{-1}$ and thermal conductivity close to $0.719\text{ W m}^{-1}\cdot\text{K}^{-1}$. Concrete blocks of ordinary Portland cement (OPC) have been tested for medium temperature TES with maximum operating temperature around $400\text{ }^\circ\text{C}$. Alonso et al. [33] tested concrete based on blended calcium alumina cement (CAC)

with an admixture like blast furnace slag (BFS) for 75 thermal cycles within the temperature range 290 °C–550 °C and found it suitable for TES up to 550 °C.

2.1.2. Pros and cons of sensible heat storage

Sensible heat storage materials are thermally stable at high temperatures and hence are the most used TES materials for high temperature applications. Sensible heat storage materials are usually low cost materials with the exception of liquid metals and thermal oils. The main drawback of sensible heat storage materials is in temperature stability during the discharge process. As the thermal discharge continues the outlet temperature of the HTF gradually starts decreasing with the time. Compared to latent heat, specific heat of materials is 50–100 times smaller and therefore the thermal energy storage density is smaller. However sensible heat storage materials can still possess large thermal energy storage density with their large operating temperature range and high density.

2.2. Latent heat storage systems

These storage materials store heat in their latent heat during a constant temperature process like phase change. Usually solid–liquid phase change is used. Solid–solid phase changes are also used. Although for solid–solid phase change specific latent heat is less but it has advantages like no leakage and no need for encapsulation etc. Liquid–gas phase change has the highest latent heat of phase change [35]. However, the enormous change in the volume of the storage materials is a problem and hence is not used in general. The thermal energy stored by latent heat can be expressed as

$$Q = m \cdot L \quad (2)$$

where m is the mass (kg), L is the specific latent heat ($\text{kJ}\cdot\text{kg}^{-1}$).

2.2.1. Thermal energy storage materials for latent heat storage

2.2.1.1. Organic. Many Organic materials possess unique quality of having their solid–liquid phase change temperature within or close to human thermal comfort range between 18 °C and 30 °C. Besides organic materials are chemically stable, non-toxic, non-corrosive, and are easily available in nature. Hence organic materials are the most used TES materials for thermal comfort in buildings, textiles etc. However they decompose at higher temperatures and their thermally conductivity is very poor. Below are the different classes of organic materials for TES.

2.2.1.1.1. Paraffin. Paraffin is the most used organic TES material in commercial applications. Paraffin is saturated n -alkane aliphatic hydrocarbons. They are represented by a general formula $(\text{CH}_3-(\text{CH}_2)_{(n-2)}-\text{CH}_3)$ where n is the number of carbon atoms. Their melting point increases with the number of carbon atoms in the backbone chain. For TES applications usually paraffin from n -pentadecane ($n = 15$, melting point 10 °C) to n -triacontane ($n = 30$, melting point 65 °C) are considered. Under ambient conditions, n -alkanes below $n = 16$ normally exist in liquid phase and n above 16 exist as wax like solid phase. n -Octadecane ($n = 18$) are the most used paraffin in research work. Its melting point at 28 °C is the most comfortable temperature for humans. However pure paraffin needs high refinement and is expensive. Instead a cheaper technical grade paraffin wax, which is a by-product of oil refining, is used as PCM in practical latent heat storage applications. Technical grade paraffin waxes are basically mixtures of paraffin, having different carbon atom numbers. They are available in melting temperatures range between -5 °C and 100 °C. For example Rubitherm RT5 is a commercial paraffin product by Schumann Sasol GmbH in Hamburg, Germany, based on a cut resulting from

refinery production. It consists of paraffin waxes with a carbon distribution as C14(33.4 wt%), C15(47.3 wt%), C16(16.3 wt%), C17(2.6 wt%) and C18(0.4 wt%). Technical grade paraffin melts over a range of temperatures, rather than at a single temperature. The freezing point of the RT5 is 7 °C, and the melting range of the material is between 4 °C and 6 °C [36]. Paraffin is non-polar and hence forms O/W emulsions with water helping the microencapsulation process. Paraffin has advantages like low supercooling, being odorless, compatibility with metal containers, chemical stability and not undergoing phase segregation etc [37]. However they have few drawbacks like large volume change ($\approx 10\%$) during phase change, low density, low thermal conductivity etc [37].

2.2.1.1.2. Non-paraffin. Non-paraffin materials further extend the phase change temperature range available for TES purpose. There are multiple subclasses as listed below.

2.2.1.1.2.1. Fatty acids

Fatty acids contain a carboxylic (COOH) functional group on the aliphatic chain. They have a general formula $\text{R}-\text{COOH}$ where R represents an alkyl group. Fatty acids can be obtained from natural oils. They have low cost, supercooling, chemical stability and not undergoing phase segregation etc. They can be cheaper alternative to costly pure paraffin with sharp melting point. Fatty acids like lauric acid are naturally occurring in agricultural produce like coconut oil and hence can be extracted from such renewal sources at a lower cost. However they have few drawbacks like odor, low density, low thermal conductivity, large volume change ($\approx 10\%$) during phase change etc. Fatty acids have sharp melting points. Fatty acid melting point increases with the number of carbon atoms in the backbone chain. Fatty acids are weak acids and their acidity decreases with the number of carbon atoms. Saturated fatty acids have a general formula $(\text{CH}_3-(\text{CH}_2)_{(n-2)}-\text{COOH})$. Saturated fatty acids between 8 and 18 carbon atoms have the suitable phase change temperature within the low temperature thermal application range. Usually saturated fatty acids from caprylic acid ($n = 8$, melting point 16 °C) to stearic acid ($n = 18$, melting point 69 °C) are considered for TES applications [38]. Unsaturated fatty acids normally have low phase change temperature though a few like oleic acid $(\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH})$ have suitable phase change temperature at 14 °C. Further extended range of phase change temperature can be obtained through fatty acid eutectics. An example of estimating fatty acid eutectic point and preparation is discussed in below reference [39].

2.2.1.1.2.2. Esters

Usually fatty acid esters are considered for TES. They have a general formula $\text{R}-\text{COO}-\text{R}^1$ where R and R^1 represent alkyl groups. They are synthesized from carboxylic acids and alcohols with a balanced, catalytic reaction called esterification [39]. Catalysts like sulphuric acid are used. Esterification is a reversible reaction and hence to force the direction of reaction towards that of esters, methods like removal of water or using excess alcohol are used. Below is a generic equation for esterification.

Along with eutectic mixtures technique, esterification is another tool available to us to modify thermo-physical properties of fatty acids according to our need. For example fatty acids like stearic acid (≈ 69 °C) and palmitic acid (≈ 62 °C) have high phase change temperature where as their esters methyl stearate (≈ 39 °C) and methyl palmitate (≈ 29 °C) have lower phase change temperature near the human thermal comfort zone. Esters have low supercooling, chemical stability and not undergoing phase segregation etc. However they have few drawbacks like being expensive, odor, low density, low thermal conductivity etc.

2.2.1.1.2.3. Alcohols

Among organic PCMs, sugar alcohols have the highest melting points and the highest latent heat. Their phase change temperatures make them suitable heat storage media for medium

temperature (90 °C–250 °C) applications like solar heaters or waste heat recovery [40]. Alcohols are non-toxic, low cost PCM. Alcohols show polymorphism and they can exist in two or more crystalline states. Due to polymorphism, application of alcohols in TES is significantly impacted. Different forms polymorphs can have significant differences in physiochemical properties [40]. Gil et al. [41] studied D-mannitol in a pilot plant storage tank and observed that applying different cooling conditions leads to polymorphic changes in D-mannitol. Kumareshan et al. [42] reported that at different heating rates D-mannitol has different phase change enthalpies. Similarly Solé et al. [40] observed in myo-inositol (C₆H₁₂O₆) that operational temperature range is an influencing parameter. They observed polymorphic changes in myo-inositol when the operational temperature range was 50 °C–260 °C but no polymorphic changes observed when the temperature range was 150 °C–260 °C. D-Mannitol (C₆H₁₄O₆) also showed similar behavior. During thermal charging polymorphic changes can reduce the effective latent heat by releasing heat unexpectedly. In addition galactitol (C₆H₁₄O₆) and D-Mannitol showed poor cycling stability due to oxidation by oxygen from the atmosphere which resulted in changes to phase change temperature and non-stable material with a lower storage capacity [40]. Care should be taken during container design to avoid exposure of sugar alcohol PCM to atmospheric oxygen. Therefore if sugar alcohols are to be used as PCM, cycling and chemical stabilities are the major factors to be tested.

2.2.1.1.2.4. Glycols

Among glycols, polyethylene glycol (PEG) has potential for TES. PEG is a linear polymer with a generic formula H-(O-CH₂-CH₂)_n-H. PEG is available in a wide range of molecular weights from PEG400 to PEG1000000 where the number in the name represents the average molecular weight. PEG phase change temperature is close to the room temperature and increases with the polymer molecular weight. PEG is unique from other organic PCM in that it dissolves in water while others are hydrophobic in nature. One major problem with PEG is that it has the highest supercooling among all organic PCM. The difference between melting point and freezing point can be as high as 30 °C–40 °C which is not desirable.

2.2.1.2. Inorganic. Appropriate inorganic materials are chosen for a given operating temperature of the system based on their phase change temperature. Inorganic TES materials usually operate in high temperatures where organic materials would have thermally decomposed.

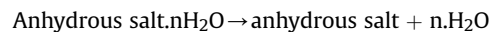
2.2.1.2.1. Salts. Salts have high melting points hence are suitable for high temperature thermal energy storage. In the molten salts section above, salts and salt eutectics of lower melting points were discussed which use their sensible heat capacity in liquid phase to store thermal energy. However choosing an appropriate salt with a melting point within the operational temperature range of TES can greatly enhance the volumetric thermal energy storage capacity. For example in an operating range between 300 °C and 500 °C, by choosing LiNO₃ (melting point: 250 °C) only the sensible heat can be used for thermal energy storage and it will give a volumetric storage capacity of around 440 MJ m⁻³. But by choosing KNO₃ (melting point: 335 °C) both sensible heat and latent heat can be used for thermal energy storage and it will give a volumetric storage capacity of around 935 MJ m⁻³. Therefore when the salt is required to fulfill thermal storage purpose, utilizing latent heat is a good option. Generally speaking, pure salts and salt eutectics with melting point above 250 °C are considered for latent heat storage and used as a PCM. However using latent heat would necessarily involve heating the solid-phase material up to and through the process of melting. In solid phase heat flow through PCM happens only by conduction where as in liquid phase heat flow through PCM

can happen by both conduction and convection. Inorganic salts have poor thermal conductivity within the range between 0.5 W m⁻¹.K⁻¹ and 1 W m⁻¹.K⁻¹. Therefore for use of salts as latent heat storage medium, improving the thermal conductivity is very important [43]. Thermal conductivity enhancement is discussed in section 8.1 below. Salts are of different types like nitrates, hydroxides, chlorides, carbonates, sulfates and fluorides. Among these nitrates have the lowest melting temperatures and are currently the most used salts and salt eutectics in CSP plants. Hydroxides have medium melting point range between 250 °C and 600 °C. Chlorides, carbonates, sulfates and fluorides etc have high melting points above 600 °C. Table 8 provides a detailed list of salts and salt eutectics.

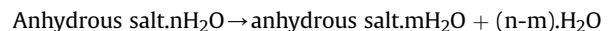
2.2.1.2.2. Salt eutectics. Pure salts have predetermined thermo-physical properties. Eutectics give us an option to modify thermo-physical properties of pure salts as per the system requirement. An example of this is bringing down the melting point of pure salts to mitigate the molten salt HTF freezing issue. Eutectics have sharp melting points. Since there is a large number of pure salt species available, there is even larger number of possible eutectic combinations. Eutectic mixtures have expanded the phase change temperature range of PCMs. R. Raud et al. [44] reviewed few theoretical equations and geometric techniques to predict properties of eutectic mixtures of salt species like eutectic composition, melting point, latent heat, density, and thermal conductivity etc of molten eutectic salts. They concluded that while it is possible to predict properties like eutectic composition and density with reasonable accuracy, properties like latent heat and thermal conductivity are very difficult to accurately predict. Software tools like FactSage provide users with a database of phase diagrams of hundreds of alloys, salts, oxides etc from where required information related to the eutectic mixtures can be retrieved.

2.2.1.2.3. Salt hydrates. Salt hydrates are the most used inorganic TES material in commercial applications. Salt hydrates are the only inorganic PCMs that operate in the low temperature human thermal comfort applications. Salt hydrates are represented by a generic formula “anhydrous salt.nH₂O”. Calcium chloride hexahydrate (CaCl₂·6H₂O) is the most used salt hydrate in practical use. Its melting point at 28 °C–30 °C is the most comfortable temperature for humans and it has a large specific latent heat of 190.8 kJ kg⁻¹. They have the same pros and cons as any salt PCM. Besides one of the main issue faced in this type of PCM is incongruent melting and phase segregation. During the thermal charging the salt hydrates will absorb heat and undergo either partial or full dehydration as below.

- Dehydration:



- Partial dehydration:



After a full dehydration, if the anhydrous salt is completely soluble in water of crystallization then it's a congruent melting. If the anhydrous salt is partially soluble in water of crystallization then it's an incongruent melting. In a partial dehydration scenario the salt hydrate decomposes to a lower salt hydrate which remains in solid phase. This scenario is called semi-congruent melting. It is desirable to have congruent melting otherwise the difference in density between the water and the salt components of the salt hydrate results in segregation and salt hydrate PCM will gradually lose its latent heat with increasing thermal cycles [45]. Schmit et al. [45] in their study of the melting process of CaCl₂·6H₂O found that the maximum latent heat is obtained when the concentration of

Table 8
Phase change materials [17].

Type	Class	Thermal storage material	Phase change temperature (°C)	Latent heat (kJ·kg ⁻¹)	Density (kg·m ⁻³)	Thermal conductivity (W·m ⁻¹ K ⁻¹)	Latent heat storage capacity (MJ·m ⁻³)	Technical grade cost (\$·kg ⁻¹)	Remarks
Organic	Paraffin	n-Dodecane (Carbon atoms-12)	-10	216				10	
		n-Tridecane (Carbon atoms-13)	-5	160			200 (RG)		
		n-Tetradecane (Carbon atoms-14)	6	229	760 (L)	0.21(S)	10	[48]	
		n-Pentadecane (Carbon atoms-15)	10	206	770(L)		330 (RG)		
		n-Hexadecane (Carbon atoms-16)	20	236	773(L)	0.21(S)	182.4	414 (RG)	[48]
		n-Heptadecane (Carbon atoms-17)	22.6	214	778(L)		166.5	770 (RG)	
		n-Octadecane (Carbon atoms-18)	28.4	244	776(L) 814(S)	0.148(L) 0.358(S)	189.3	380 (RG)	[48]
		n-Nonadecane (Carbon atoms-19)	32	222	785 (L)		174.3	1150 (RG)	
		n-Eicozane (Carbon atoms-20)	36.6	247	788 (L)		194.6		
		n-Heneicozane (Carbon atoms-21)	40.2	213	791 (L)		168.5		
		n-Docozane (Carbon atoms-22)	44	249	794 (L)		197.7		
		n-Trikozane (Carbon atoms-23)	47.5	234	796 (L)		186.3		
		n-Tetracozane (Carbon atoms-24)	50.6	255	799 (L)		203.7		
		n-Pentacozane (Carbon atoms-25)	53.5	238	801 (L)		190.6		
		Rubitherm RT-5	5	180	880 (S, -15 °C) 770 (L, 15 °C)		158.4	7	
		Rubitherm RT-25	25	148				6.24	
		Rubitherm RT-50	50	168				7	
		Rubitherm RT-82	82	178				7	
		PRS [®] paraffin wax	40-45	202				1.8	
		Fatty acids		Caprylic acid (Carbon atoms-8)	16	148.6	981 (S, 13 °C) 901 (L, 30 °C)	0.149(L, 38.6 °C)	145.8
Capric acid (Carbon atoms-10)	32			152.7	1004 (S, 24 °C) 878 (L, 45 °C)	0.153(L, 38.5 °C)	153.3		
Lauric acid (Carbon atoms-12)	42			171	870 (L)	0.149	148.8	75 (RG)	
Myristic acid (Carbon atoms-14)	54			190	860 (L)		163.4		
Palmitic acid (Carbon atoms-16)	64			185.4	989 (S, 24 °C), 850 (L, 65 °C)	0.162(L,68.4 °C)	183.4	28	
Stearic acid (Carbon atoms-18)	69			209	940 (L)		196.5	41	
Esters		Methyl palmitate	27	163.2				220(RG)	
		Allyl palmitate	23	173					
		Propyl palmitate	20	190					
		Methyl stearate	39	160.7				63(RG)	
		Isopropyl palmitate	11	100				16	
		Isopropyl stearate	14	142					
		Butyl stearate	23	200				116	
		Ethylene glycol distearate	63.2	215.8				453(RG)	
		Dimethyl sebacate	21	135				63(RG)	
		Methyl-12hydroxystearate	43	126					
Vinyl stearate	27	122				1170(RG)			
Alcohols		Xylitol	93	280	1520		425.6	133(RG)	
		D-Sorbitol	97	110	1490		163.9	179(RG)	
		meso-Erythritol	117	344	1450		498.8	430(RG)	
		D-Mannitol	165	341				90(RG)	
		1-Dodecanol	23.3	184				190(RG)	[49]
		1-Tetradecanol	39.3	221				180(RG)	[49]

(continued on next page)

Table 8 (continued)

Type	Class	Thermal storage material	Phase change temperature (°C)	Latent heat (kJ·kg ⁻¹)	Density (kg·m ⁻³)	Thermal conductivity (W·m ⁻¹ K ⁻¹)	Latent heat storage capacity (MJ·m ⁻³)	Technical grade cost (\$·kg ⁻¹)	Remarks		
	Glycols	PEG400	42	117.6	1128		132.7	12			
		PEG600	42.5	129.1							
		PEG1000	40	168.6							
		PEG3400	63.4	166.8							
		PEG10000	65.9	171.6							
		PEG20000	67.7	160.2							
		PEG35000	68.7	166.9							
		PEG100000	67	175.8							
		PEG1000000	70	174							
	Organic eutectics	Lauric acid-capric acid (45/55)	21	143							
		Capric acid-palmitic acid (76.5/23.5)	21.8	171.2							
		Lauric acid-myristic acid (66.0/34.0)	34.2	166.8							
		Lauric acid-palmitic acid (69.0/31.0)	35.2	166.3							
		Lauric acid-stearic acid (75.5/24.5)	37	182.7							
		Myristic acid-palmitic acid (58.0/42.0)	42.6	169.7							
		Myristic acid-stearic acid (64.0/36.0)	44.1	182.4							
		Myristic acid-stearic acid (65.7/34.3)	52	162							
		Palmitic acid-stearic acid (64.2/35.8)	52.3	181.7							
Inorganic Salt hydrates		CaCl ₂ ·6H ₂ O	29.6	190.8	1562		298	21	Semi-congruent melting [45] Congruent melting [45] Phase segregation problem [46]		
		CaBr ₂ ·6H ₂ O	34	115.5	1956		225.9				
		NaCH ₃ COO·3H ₂ O	58	240				5			
		MgCl ₂ ·6H ₂ O	117	168.6	1569 (S, 20 °C) 1450 (L, 120 °C)	0.694 (S, 90 °C) 0.570 (L, 120 °C)	264.5	6			
		Mg(NO ₃) ₂ ·6H ₂ O	89	162.8	1636 (S, 25 °C) 1550 (L, 94 °C)	0.611 (S, 37 °C) 0.490 (L, 95 °C)	266.3	11			
		Ba(OH) ₂ ·8H ₂ O	78	265.7	2070 (S, 24 °C) 1937 (L, 84 °C)	0.653 (L, 85.7 °C) 1.225 (S, 23 °C)	550	6			
		Na ₂ S ₂ O ₃ ·5H ₂ O	48	200	1750(S)		350	5			
		Na ₂ HPO ₄ ·12H ₂ O	36	280	1520(S)	0.514(S), 0.476(L)	425.6	5			
		Na ₂ CO ₃ ·10H ₂ O	36	247				15			
		Na ₂ SO ₄ ·10H ₂ O	32	251				6			
		CaCl ₂ ·6H ₂ O	29	190.8	1802 (S, 24 °C) 1562 (L, 32 °C)	0.540 (L, 38.7 °C) 1.088 (S, 23 °C)	343.8	6			
		Nitrate salts		NaNO ₃	306	172	2261 (S)			388.9	6
				KNO ₃	335	266	2109(S)	0.5		561	7
Ca(NO ₃) ₂	560			145	2113(S)		306.4				
Mg(NO ₃) ₂	426							226(RG)			
Carbonate salts		Na ₂ CO ₃	854	276	2533(S) 1972(L)		699.1	3			
		K ₂ CO ₃	897	236	2290(S)		540.4	7			
		CaCO ₃	1330	142	2930(S)		416.1	8			
		Li ₂ CO ₃	732	509	2110(S)		1074	111			
Chloride salts		ZnCl ₂	280	75	2907(S)	0.5	218	14			
		AlCl ₃	192	280							

	NaCl	802	430	2980(S)		808.9	2.6	
		MgCl ₂	714	452	2320(S)		1048.6	55
	LiCl	610	441	2070(S)	1680(L)	912.9	55	
	CaCl ₂	772	253	2150(S)		544	5.3	
				2085(L)				
Sulfate salts	Na ₂ SO ₄	884	165	2680(S)		442.2	3.4	
	Li ₂ SO ₄	858	84	2220(S)		186.5	180(RG)	
				2003(L)				
	K ₂ SO ₄	1069	212	2660(S)		563.9	8.25	
	MgSO ₄	1130	122	2660(S)		324.5	13.7	
	CaSO ₄	1460	203	2320(S)		471	27	
Fluoride salts	LiF	850	1044	2640(S)		2756.2	220(RG)	
				1810(L)				
	NaF	996	794	2558(S)		2031.1	7.6	
				1948(L)				
	KF	858	468	2370(S)		1109.2	203(RG)	
				1910(L)				
	CaF ₂	1418	391	3180(S)		1243.4	11.4	
				1910(L)				
Hydroxides	NaOH	318	165	2100(S)		346.5	4.1	
	KOH	380	150	2040(S)		306	5	
	LiOH	462	873	1460(S)		1274.6	165(RG)	
Metals	Copper	1084	208	8960(S)	401	1863.7	84	[50]
				8020(L)				
	Zinc	419	113	7140(S)	116	806.8	10	[51]
	Aluminum	660	397	2707(S)	204	1074.7	25	
				2375(L)				
Alloys	Zn/Mg (53.7/46.3)	340	185	4600(S)		851		
	Zn/Mg (52/48)	340	180					
	Zn/Al (96/4)	381	138	6630(S)		914.9		
	Al/Mg/Zn (59/33/6)	443	310	2380(S)		737.8		
	Al/Mg/Zn (60/34/6)	450.3	329.1					
	Mg/Cu/Zn (60/25/15)	452	254	2800(S)		711.2		
	Mg/Cu/Ca (52/25/23)	453	184	2000(S)		368		
	Al/Mg (65.35/34.65)	497	285	2155(S)		614.2		
	Al/Cu/Mg (60.8/33.2/6)	506	365	3050(S)		1113.3		
	Al/Cu/Si/Mg (64.6/28/5.2/2.2)	507	374	4400(S)		1645.6		
	Al/Cu/Mg/Zn (54/22/18/6)	520	305	3140(S)		957.7		
	Al/Cu/Si (68.5/26.5/5)	525	364	2938(S)		1069.4		
	Al/Cu/Sb (64.3/34/1.7)	545	331	4000(S)		1324		
	Al/Cu (66.92/33.08)	548	372	3600(S)		1339.2		
	Al/Si/Mg (83.14/11.7/5.16)	555	485	2500(S)		1212.5		
	Al/Si (87.76/12.24)	557	498	2540(S)		1264.9		
	Cu/Al/Si (49.1/46.3/4.6)	571	406	5560(S)		2257.4		
	Al/Cu/Si (65/30/5)	571	422	2730(S)		1152.1		
	Al/Si/Sb (86.4/9.6/4.2)	575	471	2700(S)		1271.7		
	Si/Al (86/12)	576	560	2700(S)		1512		
	Si/Al (80/20)	585	460					
	Zn/Cu/Mg (49/45/6)	703	176	8670(S)		1525.9		
	Cu/P (91/9)	715	134	5600(S)		750.4		
	Cu/Zn/P (69/17/14)	720	368	7000(S)		2576		

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Table 8 (continued)

Type	Class	Thermal storage material	Phase change temperature (°C)	Latent heat (kJ·kg ⁻¹)	Density (kg·m ⁻³)	Thermal conductivity (W·m ⁻¹ K ⁻¹)	Latent heat storage capacity (MJ·m ⁻³)	Technical grade cost (\$·kg ⁻¹)	Remarks
		Cu/Zn/Si (74/19/7)	765	125	7170(S)		896.3		
		Cu/Si/Mg (56/27/17)C	770	420	4150(S)		1743		
		Mg/Ca (84/16)	790	272	1380(S)		375.4		
		Mg/Si/Zn (47/38/15)	800	314					
		Cu/Si (80/20)	803	197	6600(S)		1300.2		
		Cu/P/Si (83/10/7)	840	92	6880(S)		633		
		Si/Mg/Ca (49/30/21)	865	305	6880(S)		2098.4		
		Si/Mg (56/44)	946	757	1900(S)		1438.3		
	Salt eutectics	Na ₂ SO ₄ /H ₂ O/NaCl/NH ₄ Cl (32.5/41.4/6.66/6.16)	13	146					
		CaCl ₂ ·6H ₂ O/CaBr ₂ ·6H ₂ O (45/55)	14.7	140					
		Na ₂ SO ₄ ·10H ₂ O/NaCl (50/50)	18						
		CaCl ₂ ·6H ₂ O/MgCl ₂ ·6H ₂ O (66.6/33.3)	25	127					
		CaCl ₂ /MgCl ₂ ·6H ₂ O (50/50)	25	95					
		CaCl ₂ /NaCl/KCl/H ₂ O (48/4.3/0.4/47.3)	27	188					
		Ca (NO ₃) ₂ ·4H ₂ O/Mg (NO ₃) ₂ ·6H ₂ O (47/53)	30	136					
		CH ₃ COONa·3H ₂ O/NH ₂ CONH ₂ (40/60)	30	200.5					
		Mg (NO ₃) ₂ ·6H ₂ O/NH ₄ NO ₃ (61.5/38.5)	51	131.3					
		Mg (NO ₃) ₂ ·6H ₂ O/MgCl ₂ ·6H ₂ O (58.3/41.7)	58	106					
		LiOH/KOH (40/60)	314	341					
		KNO ₃ /KCl (95.5/4.5)	320	74	2100(S)	0.5(S)	155.4		
		KNO ₃ /KCl (96/4)	320	150					
		KNO ₃ /KBr/KCl (80/10/10)	342	140					
		NaCl/KCl/LiCl (33/24/43)	346	281					
		NaOH/NaCl (80/20)	370	370					
		MgCl ₂ /KCl/NaCl (60/20.4/19.6)	380	400	1800(S)		720		
		Li ₂ CO ₃ /K ₂ CO ₃ /Na ₂ CO ₃ (32.1/34.5/33.4)	397	276					
		MgCl ₂ /KCl (39/61)	435	351	2110(S)	0.81(L)	740.6		
		MgCl ₂ /NaCl (52/48)	450	430	2230(S)	0.95(L)	958.9		
		MgCl ₂ /KCl (64/36)	470	388	2190(S)	0.83(L)	849.7		
		MgCl ₂ /KCl/CaCl ₂ (48/25/27)	487	342	2530(S)	0.88(L)	865.3		
		CaCl ₂ /NaCl (67/33)	500	281	2160(S)	1.02(L)	607		
		NaCl/KCl/CaCl ₂ (29/5/66)	504	279	2150(S)	1(L)	599.9		
		BaCl ₂ /KCl/NaCl (53/28/19)	542	221	3020(S)	0.86(L)	667.4		
		BaCl ₂ /KCl/CaCl ₂ (47/24/29)	551	219	2930(S)	0.95(L)	641.7		
		LiF/MgF ₂ /KF (64/30/6)	710	782					mol%
		LiF/CaF ₂ (80.5/19.5)	767	790					mol%

CaCl₂ is at the peritectic point of H₂O–CaCl₂ phase diagram. However they noticed the inconsistency of latent heat value over multiple cycles when the CaCl₂ concentration is above the hypo–peritectic end point and the consistency of latent heat value over multiple cycles when CaCl₂ concentration was below the hypo–peritectic end point. CaCl₂ concentration below the hypo–peritectic end point is the extra water scenario. Since anhydrous CaCl₂ is completely soluble in water, by suppressing the formation of lower salt hydrate under extra water scenario a consistent congruent melting over multiple cycles was achieved, though it results in a slight loss of latent heat. Therefore concentration of water in the mixture is an influencing factor on the specific latent heat. They also found that adding a nucleating agent (1 wt% of Sr(OH)₂·8H₂O) prevented the formation of lower salt hydrate and it resulted in congruent melting. Cabeza et al. [46] tried the approach of using thickening agents to increase the viscosity so that the solid phase lower salt hydrate or insoluble anhydrous salts and nucleating agents remain suspended in the liquid preventing phase segregation. They also noted an alternate approach of using gelling technique such as addition of cross–linked polymer materials, to form a three dimensional network in the solution and keep the solid phase lower salt hydrate or insoluble anhydrous salts and nucleating agents suspended in network and preventing phase segregation.

2.2.1.2.4. Metals and alloys. The advantages of metals and their alloys as PCM are their highest per unit volume heat storage capacity and the highest thermal conductivity. Metals and alloys are expensive but when volume is the criterion they are the best choice for TES. Metals and alloys have a low per unit weight heat energy storage capacity. Therefore they have the problem of excess weight [47]. Sodium (Na) is a good sensible heat storage material as liquid metal, but its latent heat is very low ($\approx 113 \text{ kJ kg}^{-1}$) and melting temperature ($\approx 97 \text{ }^\circ\text{C}$) is also very low. Therefore sodium (Na) is not an ideal PCM although it is considered as a good HTF and sensible heat storage medium. Although metals and alloys have great potential as high temperature PCM TES materials, but there are many issues that need to be taken into consideration. Metals and alloys after repeated thermal cycles can undergo change in their microstructure due to precipitation, oxidation, segregation etc. This can change their properties including phase change temperatures and latent heat. They require an inert atmosphere to prevent oxidation, but these inert gases themselves may be absorbed by metals during the melting and solidification cycles and these retained gases can affect the thermo–physical properties of metals and alloys. Metal and alloy PCM can be contained either inside a metal or a ceramic container. Differences in thermal expansion coefficient can cause strains and ruptures in containers. To solve this problem technique like macro–encapsulation with metal containers or oxide coatings can be used [47]. Supercooling is also an issue in pure metals which can be as high as 100 °C for homogeneous nucleation in Mg and Al metals. Therefore metal and alloys based TES systems are complex in their operations and a thorough understanding of metallurgy is needed.

2.2.2. Pros and cons of latent heat storage

Latent heat is 50–100 times larger than sensible heat. Therefore energy storage density of latent heat storage materials near the phase change temperature is very high. Use of PCM results in compact TES systems. In latent heat storage (LHS) TES systems, the outlet temperature of the HTF is steady during discharge. However the main drawback of latent heat storage materials is poor thermal conductivity. Salt PCMs generally have a thermal conductivity range between $0.5 \text{ W m}^{-1}\text{K}^{-1}$ and $1 \text{ W m}^{-1}\text{K}^{-1}$. Organic PCMs have thermal conductivity range between $0.1 \text{ W.m}^{-1}\text{K}^{-1}$ and $0.3 \text{ W.m}^{-1}\text{K}^{-1}$. All PCM in general are non–toxic. However organic

PCM are flammable. As plastics are highly lipophilic, organic PCM like paraffin, long chained fatty acids and esters cannot be stored and transported in plastic containers [37]. Similarly inorganic PCM are corrosive to metal containers. Other drawbacks specific to a particular class of latent heat materials are covered in the respective sections.

2.3. Chemical heat storage systems

2.3.1. Thermal energy storage materials for chemical heat storage

Chemical heat storage systems use reversible reactions which involve absorption and release of heat for the purpose of thermal energy storage. They have a middle range operating temperature between 200 °C and 400 °C. Below equation represents a generic chemical equation for TES function [52].

The direction of the reaction depends on the pressure and temperature. Theoretically the transition temperature for the given standard pressure can be derived with Gibb's free energy concept [52]. Using the thermodynamic equilibrium condition for change in Gibb's free energy as zero, below equation for transition temperature T^* is obtained.

$$\Delta G(T^*) = 0 \quad (3)$$

$$\Delta G(T^*) = \Delta H(T^*) - \Delta S(T^*) \cdot T^* \quad (4)$$

$$T^* = \frac{\Delta H(T^*)}{\Delta S(T^*)} \quad (5)$$

When $T > T^*$ decomposition dominates and thermal charging occurs. When $T < T^*$ synthesis dominates and thermal discharging occurs. For example, at 0.024 bar pressure, Ca(OH)₂ system has a transition temperature T^* at 362 °C [52]. However for Ca(OH)₂ to dehydrate at an acceptable thermal charging rate it needs a temperature $T > 390 \text{ }^\circ\text{C}$, which is an excess temperature of $\Delta T > 28 \text{ }^\circ\text{C}$ over the reaction transition temperature. Similarly rehydration to happen at an acceptable thermal discharging rate it needs a temperature $T < 290 \text{ }^\circ\text{C}$, which is a $\Delta T > 70 \text{ }^\circ\text{C}$ lower than the reaction transition temperature. Fig. 8 shows a sample chemical thermal energy storage test apparatus [53]. The figure shows the test set–up for chemical thermal energy storage. It has mainly a reactor where the chemical storage material is contained and a steam generator. As pressure in the reactor decreases, transition

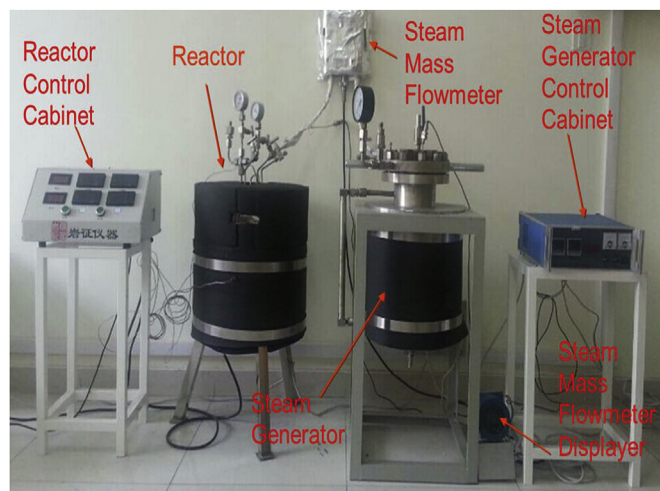


Fig. 8. Chemical thermal energy storage test apparatus [53].

temperature (T^*) of the chemical reaction also decreases. Reactor pressure is maintained using a vacuum pump. Therefore by regulating gas phase pressure through vacuum pump, the charging and discharging temperatures can be controlled. Steam generator temperature is controlled to maintain water in vapor form. During the charging the chemical heat storage material decomposes and water vapor escapes. Another important feature of chemical thermal storage is after the charging process the decomposed products are stored separately for infinitely long time and come in contact with each other when thermal discharge is needed. This is very significant as it results in an infinitely long storage period with no heat loss. Chemical thermal energy storage provides the highest thermal energy storage density of all technologies. Table 9 provides a list of chemical reactions suitable for chemical energy storage.

2.3.2. Pros and cons of chemical heat storage

Chemical thermal energy storage has benefits like the highest thermal energy storage density (both per-unit mass and per-unit volume), long duration of thermal energy storage with low heat losses etc. However there are few technical challenges faced in chemical thermal energy storage. During charging when decomposition occurs, the storage material like $Mg(OH)_2$ may undergo sintering and grain growth resulting in lower porosity. During discharging, this hinders the rehydration process. Another challenge is the rate of dehydration reaction is slow. Different approaches to increase the charging rate like graphite nanoplatelets composites [57], doping with lithium [53], doping with nitrate salts [52] etc are attempted and improvements were observed. However chemical thermal energy storage is still in the laboratory stage and commercial applications requires further refining of the technology through research experience.

3. Storage cycle frequency based TES systems

3.1. Diurnal TES systems

Solar thermal energy based systems charged diurnally and discharged during the night. Few such TES systems are listed below.

3.1.1. Solar thermal power plants (CSP)

Electricity generation during the night requires stored heat in large scale high temperature TES system. CSP plant TES systems mostly use molten salt as thermal energy storage medium. Usage of thermal oils is also popular in CSP plant TES systems. The details of molten salts and thermal oils are already discussed in section 2.1. Fig. 1 shows the different types of TES used in CSP plants. The storage tank type may be two-tank indirect, two-tank direct or

single tank thermocline. These specific types are discussed in detail in section 5.2 below.

3.1.2. Domestic solar hot water supply

This is a user end system that saves individual house electricity consumption and when residential communities install such small systems in large numbers it can significantly reduce load on power grid. These systems operate in the low temperature range between 20 °C and 100 °C and usually do not require concentrated solar radiation. Usually these systems will be mounted on roof tops of houses or commercial buildings. Basic design of a solar water heater has two components, a solar thermal collector and a TES tank. TES tank usually is a small scale thermocline water tank without filler. The capacity of typical commercial solar water heaters varies between 100 L per day to 1000 L per day. Heat storage is achieved through sensible heat of water in the insulated tank. Heat transfer mechanism between the collector and TES tank happens using thermosyphon mechanism. This is a passive system using natural circulation of water due to buoyancy caused by density difference of hot and cold waters. Passive systems work well in hot or moderate climates. In cold climates there may be need for active systems with pumps and anti-freeze measures. There are two kinds of collectors as below.

- Flat plate

Flat plate is more common which has a selective black spray coated copper absorber plate attached to parallel riser tubes. It's a stationary collector usually installed south facing with a fixed tilt. The whole collector is housed inside an insulated body frame with sun facing side having a glass top.

- Evacuated tube

Instead of a flat plate individual stationary copper tube absorbers are housed inside separate evacuated glass tubes usually installed south facing with a fixed tilt. There can be both direct and indirect evacuated glass collectors. Direct type use water as HTF where as indirect type is basically a heat pipe mechanism with a low boiling point organic HTF inside the copper tube absorber. Top end of the copper tube absorber is in contact with water inside TES tank and the evaporated organic HTF condenses there and transfers the absorbed heat to water. In this type of collector temperature can be higher up to 200 °C [58].

The main influencing factors that affect the performance of a solar water heater are optical transmittance of glass cover, absorber plate efficiency with selective coating to reduce radiation loss,

Table 9
Chemical storage materials.

Material	Compound formula	Solid reactants	Working fluid	Onset temperature @1 bar (°C)	Energy storage density (GJ.m ⁻³)	Reference
Magnesium sulfate	$MgSO_4 \cdot 7H_2O$	$MgSO_4$	H_2O	122	3.3	[54]
Magnesium hydroxide	$Mg(OH)_2$	MgO	H_2O	332	2.8	[55]
Iron carbonate	$FeCO_3$	FeO	CO_2	180	2.6	[56]
Iron hydroxide	$Fe(OH)_2$	FeO	H_2O	150	2.2	[56]
Calcium hydroxide	$Ca(OH)_2$	CaO	H_2O	512	2.9	[55]
Calcium chloride	$CaCl_2 \cdot 2H_2O$	$CaCl_2$	H_2O	95	1.1	[54]
Aluminium sulfate	$Al_2(SO_4)_3 \cdot 6H_2O$	$Al_2(SO_4)_3$	H_2O	150	1.9	[54]
Calcium sulfate	$CaSO_4 \cdot 2H_2O$	$CaSO_4$	H_2O	89	1.4	[54]
Magnesium chloride	$MgCl_2 \cdot 6H_2O$	$MgCl_2$	H_2O	150	2.5	[54]
Sodium sulfide	$Na_2S \cdot 5H_2O$	Na_2S	H_2O	80	3.56	[54]
Strontium bromide	$SrBr_2 \cdot 6H_2O$	$SrBr_2$	H_2O		2.3	[54]
Lithium sulfate	$Li_2SO_4 \cdot H_2O$	Li_2SO_4	H_2O	103	0.92	[54]
Copper sulfate	$CuSO_4 \cdot 5H_2O$	$CuSO_4$	H_2O	92	2.07	[54]

thermal conductivity of the absorber plate, contact between absorber plate and riser tube, collector orientation, tilt angle, height between collector and storage tank and material of fabrication etc [59]. Environmental factors like climatic conditions and dust accumulation also impact the performance. Using heat pipe design various indirect heat transfer fluids compatible with copper like methanol, acetone, ethanol [60], refrigerants R134A, R407C and R410A [61] etc have been tested in the past. It is important to minimize the heat losses from storage tank by proper insulation. Instead of the sensible heat thermocline water tank TES system, other TES design options are also possible. Past works have attempted application of latent heat storage technique to domestic solar water heater system by placing PCM directly on backside of flat collector, evacuated tube collector and compound parabolic concentrating collector etc [62]. Similarly packed bed TES system with a fixed bed of macro encapsulated PCM can also be integrated to solar thermal collectors [62].

3.1.3. PV/PCM/T systems

In photovoltaic technology, the temperature of a solar cell may reach up to 80 °C–90 °C which impacts its electrical efficiency. A hybrid photovoltaic–thermal (PV/T) system is a concept where the electrical efficiency of photovoltaic cell is improved by cooling the photovoltaic cell and using this waste heat for other useful purpose. HTF like air and water are used to cool the solar PV cells and the heat carried away has potential applications like as solar heating, water desalination, solar greenhouse, solar still, photovoltaic–thermal solar heat pump/air–conditioning system, building integrated photovoltaic/thermal (BIPVT) and solar power co–generation etc [58]. The idea of using PCM in this type of system is now being explored to enhance the performance of PV/T systems. There are two types possible here as listed below.

- PV/PCM

Unlike PV/T system, in a PV/PCM system there is no heat recovery but it helps to improve electrical efficiency of PV module by bringing down the operating temperature. Huang et al. [63] studied the thermal regulation of photovoltaic cell using PCM (melting point 32 °C) both by numerical simulations and by experiment. When an aluminum front plate was tested under an insolation of 750 W m⁻², they observed maximum temperatures of 63 °C for without PCM scenario and 37 °C for with PCM scenario respectively. It took approximately 1 h time to reach these temperatures. After that for the next 1.5 h, in both without PCM scenario and with PCM scenario, temperatures remained the same. After 2.5 h while for without PCM scenario temperature remains steady at 63 °C, for with PCM scenario it starts increasing from 37 °C indicating a complete melting of PCM. When fins were also used along with PCM the temperature reached 32 °C at 1 h and continued to increase at very slow rate for the next 1.5 h to 33 °C and after 2.5 h it starts increasing from 33 °C indicating a complete melting of PCM. It means the PV cell is almost at 30 °C lower operating temperature for 2.5 h and further it takes few more hours to reach the maximum temperature of 63 °C. When a higher insolation of 1000 W m⁻² was used the complete melting took a shorter time of 2 h. PCM and fins have the effect of delaying temperature increment and maintaining the operational temperature of the PV cell at a much lower level for extended hours. This perfectly suits the solar radiation pattern which lasts only for 6–7 h during the day and is a very convenient method, as it is much simpler than having a HTF flow. Ho et al. [64] studied a water–saturated microencapsulated phase change material (MEPCM) layer which was attached to the back of a photovoltaic (PV) panel to form a MEPCM–PV module. They observed improvement in power

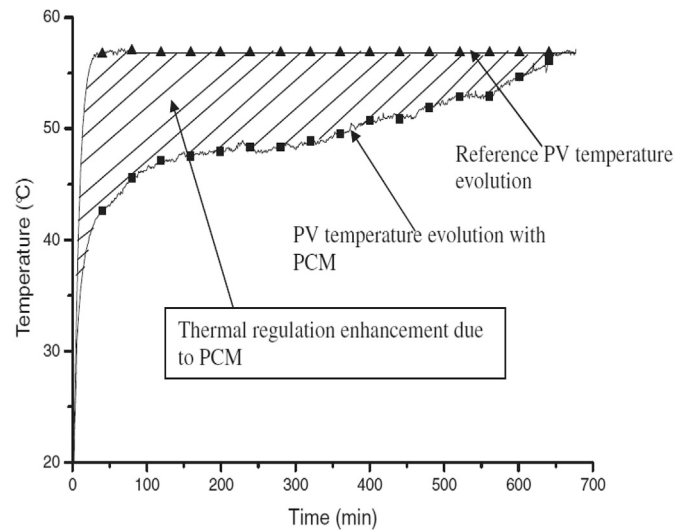


Fig. 9. PV temperature evolution with and without PCM [65].

generation efficiency of PV module when a 5 cm water–saturated MEPCM with a melting point of 30 °C was attached to the back of the PV panel. Fig. 9 shows the temperature evolution of PV cell without and with PCM [65].

- PV/PCM/T

Introducing a PCM layer in the photovoltaic thermal (PV/T) system can improve the efficiency of PV/T system. A numerical simulation by Su et al. [66] found that by attaching a PCM layer to backside of the solar PV cell at top of PV/T HTF channel resulted in an improvement of overall efficiency of the PV/T collector module which was 10.7% higher than that in no PCM mode.

3.2. Seasonal and long duration TES systems

At high latitude areas on earth, summer days are much longer and the winters are harsh with extremely cold weather. This creates huge demand for space heating, hot water supply etc in those areas. These places are best suited for storing excess heat in summer for later use in low temperature domestic applications during winter. The most prominent challenge in this type of seasonal thermal energy storage is the very long duration of storage and the sheer amount of thermal energy that needs to be stored. Marstal district heating system in Marstal, Denmark which supports space heating of 1420 houses has an annual energy consumption of 19 GWh [67]. Such a large size requires huge quantity of thermal storage materials which should be economical, environment friendly and reliable. Similarly long storage duration spanning several months leads to large thermal losses and therefore must be addressed. Another important element in seasonal thermal energy storage is the need for a reliable discharge process with stable temperatures and high recovery efficiency. Seasonal thermal energy is stored at low temperature (27 °C–80 °C) and therefore direct usage in heating distribution network may be difficult. Therefore auxiliary heating system is needed [68]. Seasonal thermal energy storage also helps in increasing the productivity of green houses by extending the plant growing season to even during the winter [69]. Seasonal TES systems, once constructed, can last for 20–30 years.

3.2.1. Underground TES systems

The huge volume requirement of seasonal thermal energy systems makes it more suitable to have underground storage. The

operating temperatures can be up to a high of 95 °C. Table 10 provides a comparison between these TES types.

3.2.1.1. Water tank. Water's TES characteristics are already discussed in section 2.1.1.1. Water tanks are manmade of stainless steel or reinforced concrete and surrounded by thick insulation. They can be either above ground or underground. Water tanks operate as thermocline TES storage with stratified hot and cold layers due to density difference. Additional stratification by physically partitioning the water tank storage space can further improve the performance of TES system [67]. To minimize thermal losses insulation layers up to 1 m thickness are built around the reinforced concrete or stainless steel tanks [70]. Glass wool and polyurethane are widely used as insulation materials [67]. Other insulation materials typically used are XPS (extruded polystyrene), EPS (expanded polystyrene), foam glass etc [70]. Similarly inside the tank liners of steel, polymers like HDPE, geomembranes, clay, bentonite etc are used for water proofing and water vapor proofing the walls [67]. Central solar heating plant with seasonal storage (CSHPSS) plants at places like Friedrichshafen, Hamburg and Hanover etc in Germany, implemented water tank seasonal thermal energy storage systems [13]. Fig. 10 shows an example of water tank type seasonal thermal energy storage system.

3.2.1.2. Pit TES. An underground pit is lined with plastics like HDPE and filled with gravel and water. No load bearing frame like reinforced concrete is needed as the gravels themselves take the load and transfer it to the side walls ground and the bottom bed thus reducing the cost. Pit TES has the lowest specific cost along with aquifer TES type. Heat insulation layers on the sides, top and bed will be provided to reduce heat losses. The charging is either by direct contact of heated water with gravel or by the hot water flowing through plastic pipes installed at different layers of gravel. Gravels have lower specific heat capacity and hence the volume of pit TES will be greater than water tank. Central solar heating plant with seasonal storage (CSHPSS) plants in Germany's Steinfurt and Chemnitz implemented pit TES systems [70]. Fig. 11 shows an example of pit type seasonal thermal energy storage system.

3.2.1.3. Aquifer TES. Aquifers are naturally existing underground geological systems of porous rock structures or soil mixtures of sand, gravel etc containing ground water. In this porous soil layer containing water, pressure head of water is higher than atmospheric pressure and therefore water can be extracted from aquifers by drilling water wells. However aquifer TES system requires specific geological conditions like existence of natural aquifers that can satisfy the criteria below.

Table 10
Underground seasonal TES systems [67].

	Hot water	Gravel–water	Duct	Aquifer
Storage medium	Water	Gravel–water	Ground materials (Soil/rock)	Ground materials (Sand/gravel/water)
Heat capacity (kWh.m ⁻³)	60–80	30–50	15–30	30–40
Relative storage volume (m ³ water equivalent)	1	1.3–2	3–5	2–3
Geological requirements	<ul style="list-style-type: none"> • Can be built at all locations. • High specific cost of construction. • Needs stable ground conditions. • Preferably no ground water. • 5–15 m deep. 	<ul style="list-style-type: none"> • Can be built at all locations. • Low specific cost of construction. • Needs stable ground conditions. • Preferably no ground water. • 5–15 m deep. 	<ul style="list-style-type: none"> • Drillable ground. • Ground water favorable. • Natural ground water flow slower than 1 m/s. • Suitable for places with low hydraulic conductivity ($k_f < 1.10$ m/s). • High heat capacity. • High thermal conductivity. • 30–100 m deep. • High specific cost of construction. 	<ul style="list-style-type: none"> • Requires natural aquifer layer of at least 20–50 m thickness at any depth with high hydraulic conductivity ($k_f > 1.10$ m/s). • Requires confining rock layers on top and below the aquifer layer. • No or low natural ground flow. • Suitable water chemistry at high temperatures. • Low specific cost of construction.

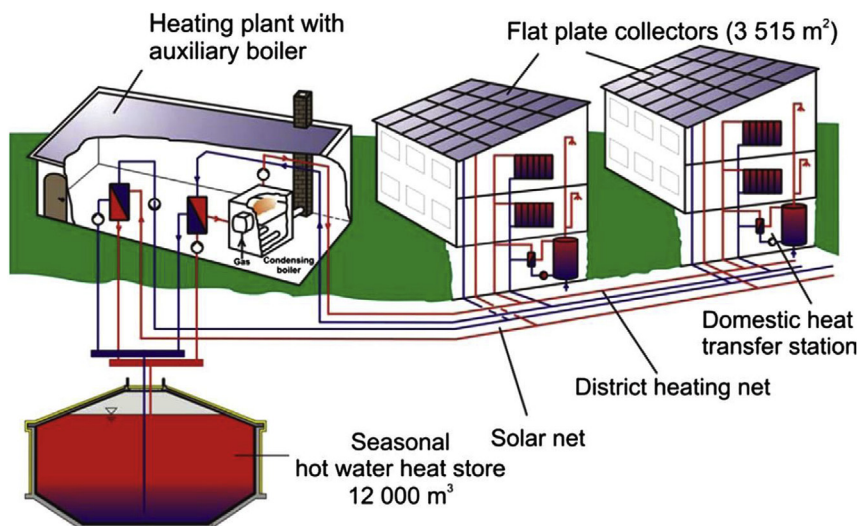


Fig. 10. Water tank type underground seasonal TES system [67].

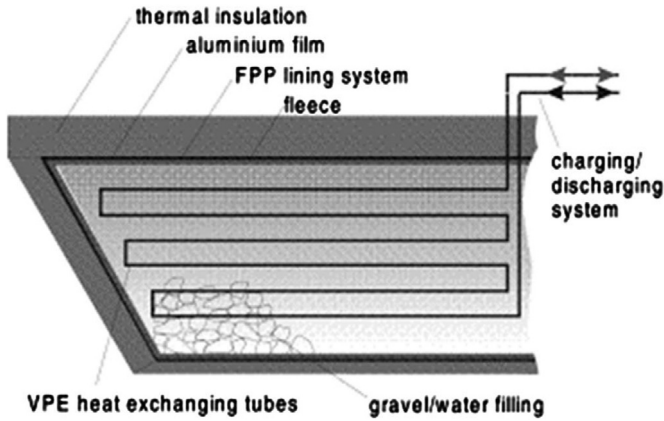


Fig. 11. Pit type underground seasonal TES system [67].

- Presence of two confining rocky beds with extremely low hydraulic conductivity on top and bottom sides. These impermeable rocky layers act as the container walls.
- The thickness of porous aquifer layer between the two rocky beds must be greater than the minimum required. The porous soil media acts as the filler in a packed bed system.
- Availability ground water with very low natural ground flow. Ground water acts as HTF.

This type of TES system does not require any manmade construction and the only cost involved is the drilling of ground water wells. Therefore aquifer TES systems are the cheapest TES systems along with Pit TES systems. Aquifer TES system requires at least two reservoirs one hot and the other cold. During charging the ground water is pumped from cold well to solar collectors and the heated water from solar collectors is pumped and stored in hot well. During discharge the hot water from hot well is used and pumped back to cold well. Central solar heating plant with seasonal storage (CSHPSS) plants in Germany's Rostock implemented aquifer TES systems. Fig. 12 shows an example of aquifer type seasonal thermal energy storage system.

3.2.1.4. *Borehole TES.* This system is also called duct heat storage in some literature. Borehole TES systems are suitable for places which have drillable ground with soil mixture content of high specific heat, high thermal conductivity and a very low hydraulic conductivity. Unlike an aquifer, extraction of ground water is difficult in such geological conditions due to low hydraulic conductivity. Therefore for charging and discharging multiple vertical boreholes of 30–100 m depth are drilled to form a cluster and vertical tube heat exchangers which are inserted into the drilled boreholes. Presence of ground water is preferred as water has high specific heat. At the same time to reduce the heat losses, ground water flow should be completely absent or very low. The gap between borehole and heat exchanger tubes is filled with high thermal conductivity grouting. For grouting materials like bentonite, portland

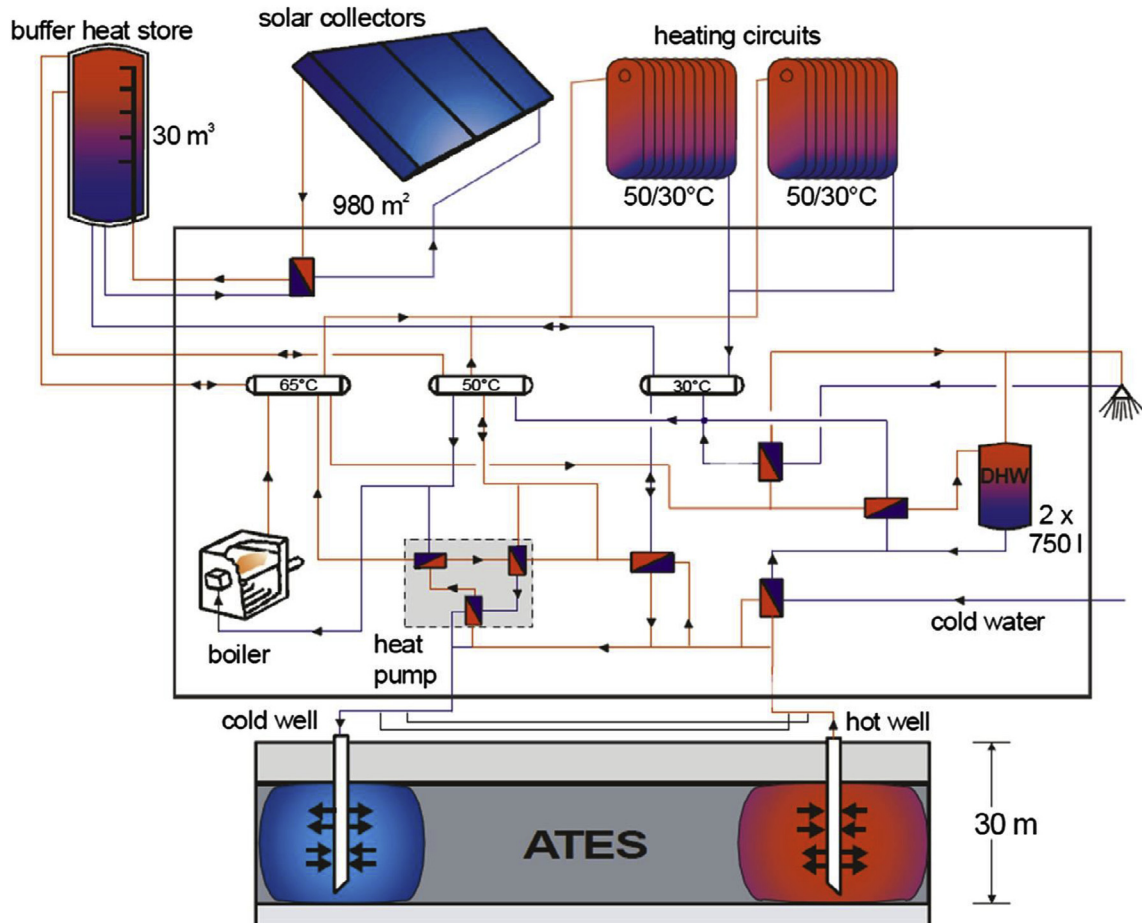


Fig. 12. Aquifer type underground seasonal TES system [67].

cement/blast furnace slag/silica sand/water mixtures etc have been used in the past. A thermal insulation is provided on the top surface to prevent heat loss from surface. The thermal charging of boreholes starts from boreholes at the center and then gradually heat is diverted towards periphery such that boreholes at the center are the hottest and boreholes at the periphery are the coldest regions in the TES system. While discharging the heat extraction starts from the periphery and gradually moves towards the center. Use of heat exchangers gives the flexibility to choose the appropriate HTF based on the operational temperature of the borehole TES. However, it also makes borehole TES as one of the highest specific cost system. Central solar heating plant in Neckarsulm, Germany has a borehole TES of storage volume 63,400 m³ [13]. Fig. 13 shows an example of borehole type seasonal thermal energy storage system.

3.2.2. Solar ponds

Systems like solar ponds can act as both daily and seasonal thermal energy storage [71]. Solar pond at Kutch in India [14] supplies processing heat to a local dairy. Solar pond at El Paso, Texas provided industrial processing heat to Bruce foods, Inc and was used for studying experimental solar pond electricity generation and water desalination plants [72]. Solar ponds are large natural or manmade brine ponds with dissolved salts that act as both a solar collector and TES system. The salt concentration gradient along the depth of the pond creates a barrier for natural convection and traps the water heated by sun at the bottom of the pond. Such systems can supply heat at low temperature between 20 °C and 90 °C depending on the ambient conditions. In summer the temperature at the bottom of the pond can reach 90 °C. In winter even when the top surface of the pond is frozen, the bottom of the pond can remain at 20 °C. The typical operating temperature of the university of Texas solar pond at El Paso ranged from 70 °C in winter to 90 °C in early fall. The highest temperature observed at the El Paso solar pond was 93 °C, and the maximum temperature difference between the LCZ and UCZ was above 70 °C [72]. The salt concentration gradient results in three distinct layers [73].

- Upper convective zone (UCZ)

Top layer of the pond with fresh water, having least salt concentration and least density.

- Non-convective zone (NCZ)

Layer of salt water in which brine density gradually increases with the depth. The NCZ is the key to the working of a solar pond. It allows solar radiation to penetrate into LCZ but prevents long-wave solar radiation from escaping as it is opaque to infrared radiation. It also prevents natural convection during heating of water by sunlight as brine water maintains its higher density even after heating.

- Lower convective zone (LCZ)

This is the heat storage zone. It has the highest salt density and is the hottest region where thermal energy is stored. As this layer has the highest temperature most heat losses happen from pond bed or side walls of the pond. To reduce heat loss, the bottom and the side-walls of the pond can be insulated with layers like flexible polypropylene geo membrane liner and geosynthetic clay liner [72].

Heat is extracted from LCZ layer using two methods. At Kutch in India [14] hot saline water is extracted from the LCZ and passed through an external heat exchanger. At Pyramid Hill, Victoria [72] an in-pond heat exchanger is used for heat extraction from the LCZ.

3.2.3. Deep water source cooling systems

This is a cold thermal energy storage system. In northern high latitude areas like Canada, water close to 3.98 °C temperature having the highest density settles to the bottom of deep water bodies and gets trapped below a certain depth, known as the hypolimnion. During summer, this cold water can be used as a heat sink to produce air cooling in buildings. This saves electricity consumption for running air conditioning of buildings in summer. Air conditioning consumes nearly 18% of electrical output in US [74]. Newman et al. [74] presented case studies of two such systems in Canada.

- Purdy's wharf, Halifax system

It used the cold water from sea to cool three large buildings covering 65,000 m². The cost of seawater cooling system was \$400,000 and had an annual savings of \$177,350 due to reduced

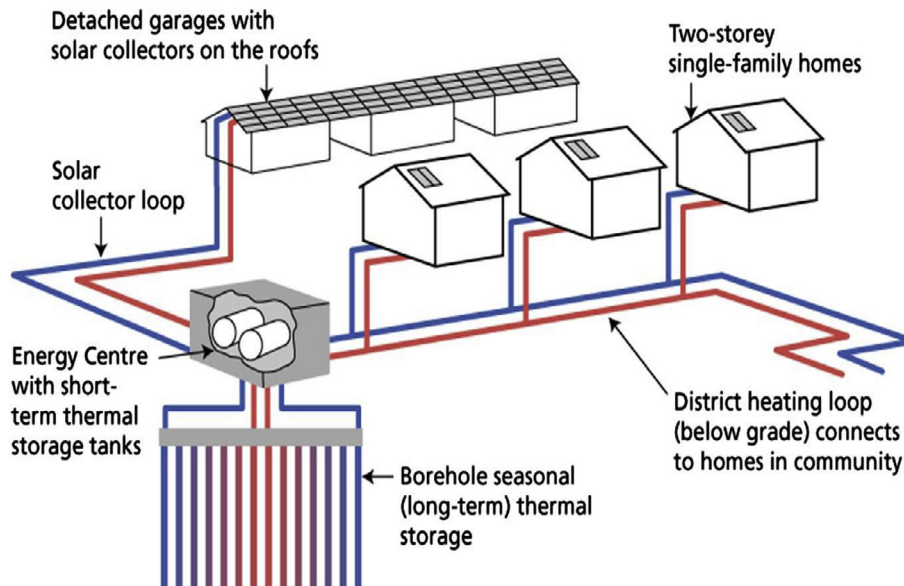


Fig. 13. Borehole type underground seasonal TES system [67].

electricity and maintenance load of a conventional air conditioning system. Payback period was estimated to be 2.3 years. The system cannot function year round due to fluctuating temperatures of deep water cooling systems. However such systems can provide financial benefits, even when they cannot operate year round.

- Enwave, Toronto system

This system cooled a network of downtown Toronto cooling loop which had around 27 city buildings connected in 2006. Water from Ontario lake at a depth of 83 m was pumped to Toronto city for cooling purpose in summer. After cooling the buildings, the water was later used for domestic water supply.

4. Delivery scheme based TES systems

As already listed in the introduction section one of the gaps between energy demand and supply is the distance gap between the energy source location and place of consumption. TES systems play a role in delivering the heat to the place of consumption. Based on the delivery scheme TES systems can be found in below formats.

4.1. Centralized scheme

Centralized schemes using purely solar thermal energy or hybrid energy sources with a secondary fuel are more cost favorable than having separate heater systems in individual houses [13]. Centralized solar heating plants (CSHP) have an array of solar thermal collectors that receive solar thermal energy at a central plant and the heat is stored in a TES and distributed to residential area end user houses through district heating pipe networks. In high latitude areas like Europe such centralized schemes have been integrated with both diurnal (CSHPDS: centralized solar heating plants with diurnal storage) and seasonal thermal energy storage (CSHPSS: centralized solar heating plants with seasonal storage). District heating plants in places like Kungälv and Nykvarn of Sweden CSHPDS scheme has been used with water tank type TES of volumes 1000 m³ and 1500 m³ respectively [13]. Similarly district heating plants in places like Friedrichshafen, Germany CSHPSS scheme has been used with concrete water tank TES of volume 12000 m³ [13].

4.2. Distributed scheme

Keeping in mind the overall efficiency of the energy supply chain, effort is on to study to the impact of TES at both utility end and building end. The effect of TES on utility end is to enable continuous power generation and fulfillment of demand. Building end TES systems decrease the load during peak demand period through load shifting [75]. Building end TES systems are part of distributed applications on the end–use locations like building heating and cooling systems. These systems are owned and operated by building owners themselves. Such systems make use of the difference in electricity unit pricing between peak hours and off–peak hours. The TES system stores the excess cold or heat produced during the off–peak hours which will be discharged during the peak hours to reduce the load on building heating and cooling systems. This results in shifting of energy purchases to periods of low electricity unit price. There are three types of operational strategies for peak shaving [76].

- Full storage

In full storage strategy, the chiller operates only during off–peak hours and during peak hours entire load is on TES.

- Partial storage–load leveling

In partial storage strategies chiller operates at partial capacity during peak hours and the remaining load is shared by TES system. In load leveling strategy, chiller operates at the same load throughout the day. This average load would be estimated based on history data of the building's thermal load and local climate conditions. This helps to bring down the maximum capacity of a chiller.

- Partial storage–demand limiting

In demand limiting strategy chiller operates at lower capacity during peak hours and it operates at full capacity during off peak hours.

An example of distributed TES system is cold TES tank coupled with a building cooling chiller. The thermal storage medium can be chilled water (3.3 °C–5.5 °C), ice (0 °C), ice slurry, plastic container encapsulated ice, eutectic salts (8.3 °C) etc [77].

4.3. Mobile TES

When pipe–line bound connection between heat source and demand site is economically not feasible, heat can be supplied to needy remote locations through mobile TES systems transported on trucks. The preferred TES materials for this purpose are chemical heat storage material like zeolite and PCM. In addition passive TES technology plays a key role in food & drug shipping.

4.3.1. Mobile sorption TES

Mobile sorption system typically uses a physical sorption pair system like zeolite/water system or silica–gel/water system. Bayern and its partner Industrieanlagen Hoffmeier GmbH built a prototype of a mobile storage based on an open sorption system with zeolite as absorbent [78]. Typical heat sources are industrial waste heat and waste incineration plants etc, and typical demand sites are industrial drying plants. The charging process involves blowing ambient air first through a heat exchanger where it gets heated by industrial waste heat and then through a zeolite packed bed to dehydrate the zeolite bed. Cooled air exits the zeolite bed with water vapor. During discharge at the demand site, the humid air flowing out of the drier is redirected and blown through the hot zeolite bed to rehydrate the zeolite bed with water vapor present in the humid air. This process results in release of heat which heats up the air passing through the zeolite bed. At the demand site, temperature of dry air exiting zeolite bed outlet could reach up to 160 °C. The hot dry air again gathers humidity from product being dried in the drier chamber and the cycle continues. Two prototypes of 2.3 MWh capacity each were tested and the experience with prototypes showed a transportation fuel demand of approximately 80 kWh per cycle, CO₂ savings of 616 kg per cycle and a gas savings of 3.5 MWh per cycle [78]. The charging time needed per storage was 15.6 h and discharging time was 19.5 h. Mobile TES truck can even deliver heat to multiple demand sites in one cycle. Fig. 14 shows an example of mobile TES system.

4.3.2. Mobile latent heat storage

Mobile TES can also be achieved using PCM. Deckert et al. [79] tested a pilot mobile latent heat storage prototype. They used a salt hydrate, sodium acetate trihydrate with a phase change temperature of 58 °C as the TES material. They used a thermally insulated container. It discharged heat at a constant temperature and the latent heat capacity of the storage was 1.3 MWh. This storage system could also store an additional 2 MWh of sensible heat. During charging with an inlet heat source at 90 °C it reached a capacity of 2 MWh including sensible heat in 12–14 h time.



Fig. 14. Mobile TES [78].

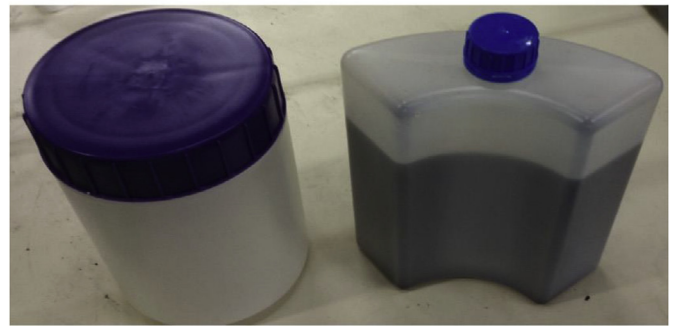
Discharge continued till the lowest temperature of 25 °C was reached. Discharging recovered 1.5 MWh heat in 27 h. Including 1 h of transportation time total cycle time was estimated at 40 h which meant 220 cycles per year.

4.3.3. Food & drug shipping cold storage

Applications like temperature controlled shipping of food and perishables, pharmaceutical distribution containers, blood transport reusable containers etc can use passive thermal energy storage techniques. In food industry, increase in external temperature increases the rate of deterioration of perishable fresh food and affect the shelf life of fresh food. Cold storage (2 °C–8 °C) is needed to prevent or slow down microbial, physiological (ripening, senescence, respiration), organoleptic, physical (moisture loss) and chemical (food browning, lipid oxidation, pigment degradation) changes in food produced by microbial, chemical and/or enzymatic activity [80]. When perishables are taken out of refrigerated stores, in order to sustain the cold as long as possible, conventional insulation is combined with PCM where cold can be stored as latent heat. Polystyrene (PS) is a preferred insulating packing material for making food trays. Sandoval et al. [81,82] tested a heat management PS foam tray containing an ultra-thin polymer/PCM fiber mat coating on PS film substrate with RT5 (phase change temperature 5 °C) as the PCM. The coating was applied using electro-spinning technique. Electro-spinning is a technique for producing ultrafine fibres with diameters in the range of nanometers, by applying a high-voltage electric field to a polymeric solution. Due to the applied electric field, electrically charged polymer solution is accelerated and a jet is being ejected from the tip of a capillary and then accelerated towards a target where it gets deposited. PCM is added into the polymer solution and this mixture forms the electro-spun fiber mat coating on the PS film substrate. Polycaprolactone (PCL) is a popular bio-degradable polymer used in electro-spinning. Two different fiber mat coatings with different polymer/PCM combinations like PS/PCM [82] and PCL/PCM [81] have been attempted. When the coated trays were taken out of cold storage and placed in room temperature, PCM fiber mat coating on the PS tray extended the time needed to increase the temperature above the chilling temperature (>10 °C) of food



a



b



c

Fig. 15. Cold storage packages [83].

products and this time extension was found to be proportional to the thickness of the coating. Hoang et al. [80] directly prepared (without PS film substrate) 0.5 cm–1 cm thickness plates by lightly pressing the PCL/PCM fibre mats using a hot-plate hydraulic press. This material was found to have a better thermal buffering capacity compared to a standard packaging material which can enhance the thermal protection of perishable products. Kozak et al. [83] tested the thermal performance of transported insulated cold storage packages. Inside a cardboard package, they placed PCM containing arched bottles between the product container and polystyrene insulation as shown in Fig. 15. PCM had a melting temperature of –33 °C. Johnston et al. [84] used a novel composite of paraffin wax and nano-structured calcium silicate (NCS) as a thermal buffer for food packaging. NCS has a highly porous structure of self assembled nano-size platelets and it can absorb up to 300 wt% of paraffin. The results showed that the thermal buffer maintained the inner wall temperature below 10 °C for more than 5 h after the food package was kept in an ambient temperature of 28 °C. However, at

present the use of PCM to extend the cold storage duration in refrigerated vehicles is not very popular [85]. Although using PCM is suitable for short distance delivery, but perishable raw foods are usually transported over longer period and longer distance. Besides, use of PCM can overload the compressor of vehicles' refrigerator and cause excessive rise in condenser temperature [85].

5. Heat storage mechanism based TES systems

5.1. Passive systems

Passive systems do not require input like pumping work during charging and discharging process [76]. They make use of phenomena like thermal inertia, natural convection etc to achieve the intended purpose. Passive TES techniques are used in buildings, automobiles, textiles, food & drug shipping etc for temperature control. Fig. 16 shows the working principle of passive TES systems. By using the latent heat of a PCM to increase the thermal inertia, the temperature fluctuations can be smoothened to within the thermal comfort limits thus reducing the overall load on HVAC systems.

5.1.1. Thermal energy storage in buildings

Fig. 17 shows the different types of TES systems used in buildings. In passive TES technology, thermal mass of buildings increased by using novel building composite PCM (BCPCM). Table 11 presents a list of various building composites being explored in the past.

5.1.2. Automobiles

Jamekhorshid et al. [89] estimated the amount of PCM (*n*-nonadecane) needed for the temperature control in the interior compartment of a car exposed to sun light to be 755 g. Their model had a thin layer of PCM inside a pouch placed in the ceiling of the car. On a day in the month of July, without the PCM cabin temperature curve peaked at 13:50 h to 68.5 °C and during the night fell below 30 °C. The passive temperature control system with 755 g of PCM (melting point: 32 °C) was able to maintain the maximum temperature at about 35 °C. In another type of application, Gumus et al. [90] developed an experimental TES system of 2 MJ storage capacity for preheating internal combustion engine

with $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ as the PCM. In an ambient condition of 2 °C, the TES system helped maintain the engine at an average 17.4 °C. During charging (engine run period) the TES system stored 2.27 MJ of heat and during discharge (engine switched off for 12 h and then preheating before cold start), it released heat at 57.5% thermal efficiency. Such a system helps minimize the engine pollution of automobiles in cold climate region. Efficiency of catalytic converter is low during cold start and by preheating the engine with heat stored in passive TES system, emission of toxic gases like CO and HC can be reduced.

5.1.3. Thermal comfort textiles

PCM is incorporated into fabrics to make thermo-regulated textiles which are used for clothing in cold environments. A treated fabric with 22.9% add-on microencapsulated PCM (*n*-eicosane/melamine-formaldehyde) is capable of absorbing approximately 4.44 J/g heat and past results indicated that the heating effect lasts approximately 12.5 min depending on PCM add-on percentage and cold outdoor conditions [91]. Heat released by PCMs decreases the clothed-body heat loss by an average of 40–55 W m⁻² [91]. There are different methods to incorporate PCM into fabric.

- Fiber

After adding microencapsulated PCM into molten polymer solution, fiber is spun using dry spinning, wet spinning, electro-spinning or extrusion of molten polymer solution. Chen et al. [92] prepared ultrafine thermo-regulating fibers of polyethylene glycol (PCM)/cellulose acetate (matrix) via electro-spinning method.

- Coating

A coating composition is prepared with microencapsulated PCM, polymer binder, surfactant, dispersant, antifoam agent and a thickener. This coating is then applied to a textile substrate. Koo et al. [93] used dual coating (both wet and dry coating layers) method to coat microencapsulated PCM on to Nylon fabric.

- Lamination

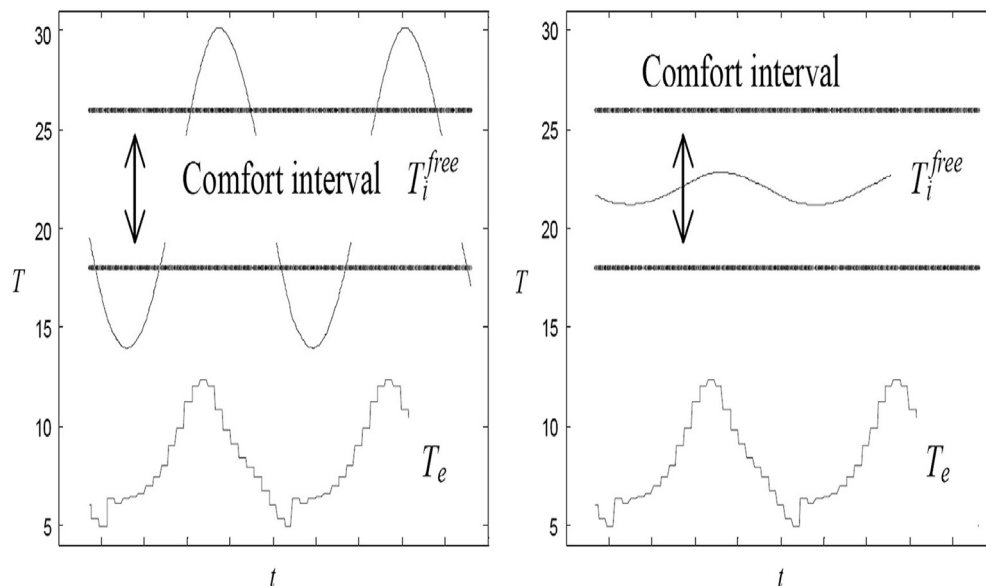


Fig. 16. Curve of building indoor free running temperature (T_i^{free}) with the changing external temperature (T_e) without PCM (left) with PCM (right) [76].

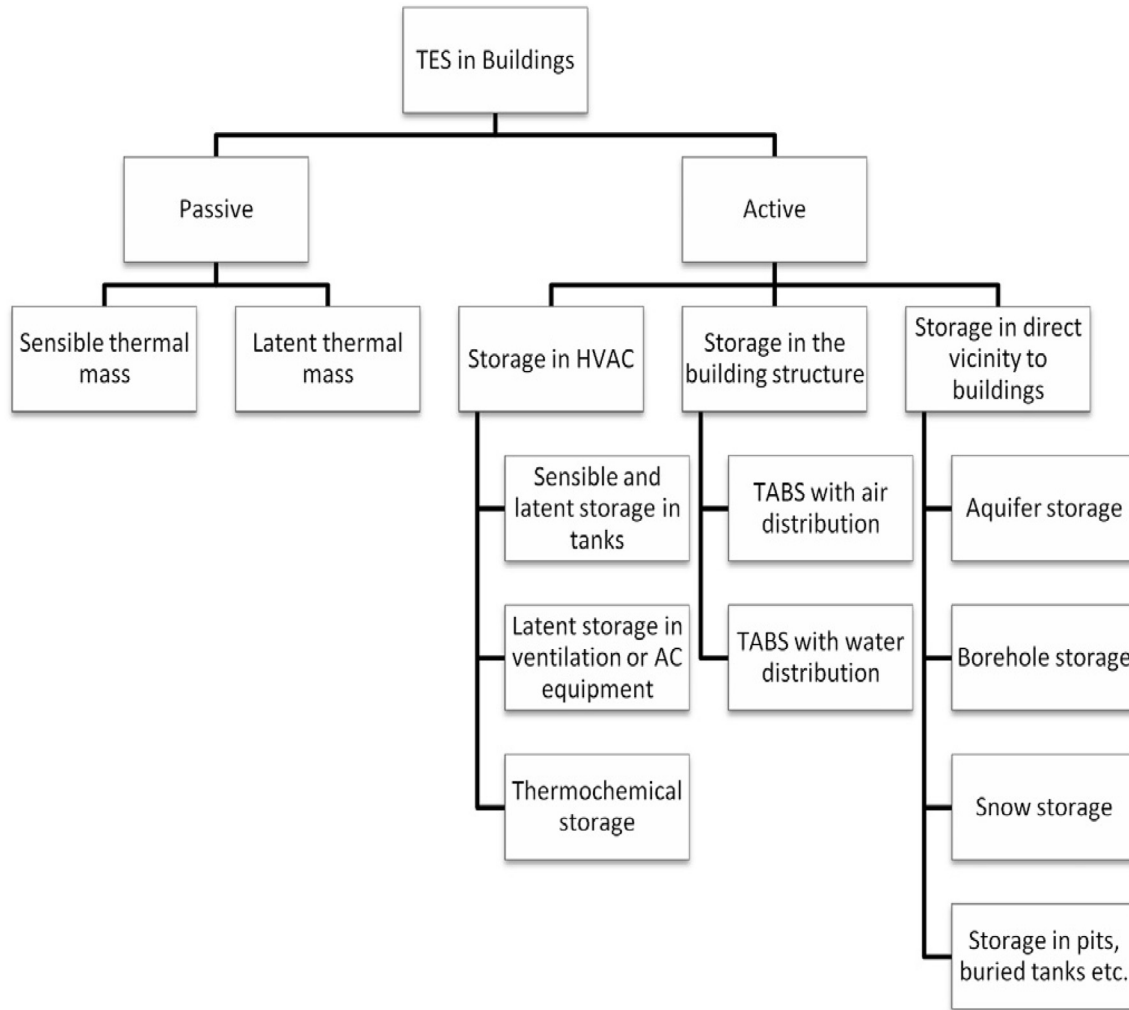


Fig. 17. Thermal energy storage in buildings [76].

Table 11
Building composite PCM.

Building materials	PCM	Maximum absorption rate (%)	Melting temperature (°C)	Latent heat (kJ·kg ⁻¹)	References
Gypsum	Xylitol pentalaurate	20	40.44	31.77	[86]
Gypsum	Xylitol pentamyristate	22	52.58	43.89	[86]
Cement	Xylitol pentalaurate	19	44.07	31.09	[86]
Cement	Xylitol pentamyristate	25	54.59	46.37	[86]
Perlite	Xylitol pentalaurate	71	41.88	120.09	[86]
Perlite	Xylitol pentamyristate	66	52.63	126.08	[86]
Diatomite	Xylitol pentalaurate	52	41.35	91.07	[86]
Diatomite	Xylitol pentamyristate	50	53.10	97.01	[86]
Vermiculite	Xylitol pentalaurate	40	42.62	73.16	[86]
Vermiculite	Xylitol pentamyristate	41	53.30	76.80	[86]
Perlite	Galactitol hexa myristate	67	43.83	121.13	[87]
Diatomite	Galactitol hexa myristate	55	45.86	96.21	[87]
Vermiculite	Galactitol hexa myristate	52	44.90	83.75	[87]
Perlite	Galactitol hexa laurate	70	39.53	119.45	[87]
Diatomite	Galactitol hexa laurate	51	39.03	63.08	[87]
Vermiculite	Galactitol hexa laurate	39	39.48	61.38	[87]
Bentonite clay.	Capric acid	40	29.31	69.30	[88]
Bentonite clay.	PEG600	43	4	51.43	[88]
Bentonite clay.	Dodecanol	32	22.17	59.21	[88]
Bentonite clay.	Heptadecane	18	22.01	35.13	[88]

PCM is incorporated into a thin polymer film and this polymer film is then applied to the inner side of fabric by lamination. Ke et al. [94] prepared a thin porous flexible polyethylene glycol/polyurethane membrane which can keep its solid shape even at

temperatures above the melting point of polyethylene glycol. Such a polymer membrane was found suitable for use as a functional material in textiles for purposes like lamination inside the fabric for thermal control.

5.1.4. Electronics

One of the major causes of electronic device failures is over-heating of critical components like chips. Today's electronic chips can produce up to 50 W cm^{-2} of heat flux. For safe operation, electronic device temperature must be kept within a tolerable limit of $100 \text{ }^\circ\text{C}$. Therefore heat sinks are used for cooling the chips. In the past heat sink design used a flat metal plate with fins which is in thermal contact with the chip. Metal plate transports the heat away from chip through conduction. Heat is then discharged to the surroundings through the fin surfaces, either through natural or forced convection of surrounding air or a liquid coolant. Past designs of such heat sinks used fans to circulate air through fins which were noisy, vibrating and involved moving parts that failed often. However if the usage of electronic devices is intermittent as in the case certain portable devices in use these days, then a passive heat sink system using PCM to absorb heat from the fins is a better option than using fan [95]. Hosseinizadeh et al. [96] studied the various influencing parameters of a PCM based heat sink system like heat flux level, number of fins, fin height, fin thickness etc. They used a test heater surface of $50 \text{ mm} \times 50 \text{ mm}$ dimensions with varying fin heights between 10 mm and 40 mm and RT80 paraffin (melting point: $80 \text{ }^\circ\text{C}$) as PCM. Complete PCM melting in heat sink took 30 min for a heat flux of 25 W cm^{-2} where as it took 16 min for a heat flux of 45 W cm^{-2} . Heat sink without PCM reached $100 \text{ }^\circ\text{C}$ at the sink base in just 5 min . Once melted completely, the PCM will continue to absorb sensible heat but the heat sink's performance will be similar to that of heat sink without PCM. This demonstrates the potential of PCM cooled heat sinks in case of intermittently used electronic devices where there is adequate time for PCM to solidify between usages. Sahoo et al. [95] published a detailed review paper on the extensive research works done on this subject.

5.2. Active systems

Active systems use pumping work to circulate a heat transfer fluid (HTF) during charging and discharging process. In large scale TES systems, lengthy pipe lines and viscous HTF lead to large pressure head drop. High heat flux and high temperature require fast heat transfer rate with higher mass flow through forced convection. These factors necessitate circulation of HTF through pumping.

5.2.1. Tank systems

Tank systems use heat transfer fluid as the primary heat storage medium and store the fluid medium in either one or two insulated tanks.

5.2.1.1. Two tank indirect system. Fig. 1b shows an example of two tank indirect system. Two tank indirect systems require two heat transfer fluids. First HTF collects the solar thermal energy from solar receivers in the solar field and the second HTF acts as the primary storage medium in the TES system. An intermediate heat exchanger facilitates transfers of heat between solar field HTF and TES HTF. During the day time, solar field HTF transfers collected solar thermal energy to steam generating heat exchangers (boilers) at the power block and the excess solar thermal energy collected is transferred to the TES HTF using the intermediate heat exchanger. TES HTF acts as the primary heat storage medium which is maintained in two separate tanks with a temperature difference between them. Heated TES HTF is stored in the hot tank. During the night time, TES HTF is pumped from hot tank to the intermediate heat exchanger where it transfers the stored thermal energy to the solar field HTF which in turn transfers heat to steam generating heat exchangers at the power block. The cooled TES HTF is then stored in the cold tank. An example of this is the oil-salt system

where thermal oil acts as the solar field HTF and salt acts as the TES HTF. In parabolic trough collectors (PTC) type of CSP plants where temperatures are within thermal oil operational range and solar fields may have many kilometers long pipes. In such a scenario due to the freezing issue of molten salts at low temperatures thermal oil with its very low melting point near ($12 \text{ }^\circ\text{C}$) is the most suitable medium as solar field HTF. However thermal oil will be in vapor phase at the higher end of their operational limit (i.e. $> 250 \text{ }^\circ\text{C}$) and above the boiling point vapor pressure increases quickly. DOW-THERM thermal oil reaches 1 bar at the boiling point of $257 \text{ }^\circ\text{C}$ and thereafter it quickly reaches 10.64 bar when the temperature reaches its operational limit at $400 \text{ }^\circ\text{C}$. Given the huge quantity of expensive thermal oil required for storing thermal energy, this vapor pressure may lead to leakage of thermal oil vapor thereby causing loss of expensive HTF. Therefore cheaper salts are a better option for TES HTF as their vapor pressure is almost zero. However in such a scenario to avoid mixing of two different HTFs, only an indirect heat transfer using a heat exchanger is possible between solar field HTF and TES HTF.

5.2.1.2. Two tank direct system. Fig. 1a shows an example of two tank direct system. In two tanks direct system, a single HTF performs both solar field HTF and TES HTF roles. This system does not require the costly intermediate heat exchanger. For example molten salts themselves can act as both solar field HTF and TES HTF. Similar to two tank indirect systems, hot and cold TES HTF are maintained in two separate hot tank and cold tank. However as mentioned in the molten salt section 2.1.1.3, molten salts as solar field HTF require costly anti-freeze and drain-back mechanism during cloudy days or during the night.

5.2.1.3. Single tank thermocline system. Fig. 1c shows an example of single tank thermocline system. In single tank thermocline system, a single HTF performs both solar field HTF and TES HTF roles. This system have a liquid heat transfer fluid which gathers solar thermal energy from solar receivers during the day time and stores that heat with it being the primary heat storage medium inside a single insulated thermocline tank and then transfers that heat to steam generating heat exchangers on need basis. Thermocline storage system relies on thermal buoyancy to maintain thermal stratification and discrete hot and cold thermal regions of the TES system. Sun lab, a partnership between Sandia National Laboratories in Albuquerque, New Mexico and the national renewable energy laboratory in Golden, Colorado evaluated the more traditional two-tank energy storage systems and single-tank thermocline storage systems and found single tank TES system can save up to 35% of investment cost [97].

5.2.1.3.1. Stratified liquid thermocline systems. In this case, single thermocline tank contains only the liquid heat transfer fluid acting as primary thermal storage medium. This type requires heat transfer fluid in more quantity to store heat inside the single thermocline tank.

5.2.1.3.2. Stratified liquid thermocline systems with filler. A low-cost fixed bed of filler material like rock, sand etc is packed inside a single insulated thermocline storage tank. Cheaper filler material acts as the primary thermal storage medium and reduces the required quantity of the costly liquid heat transfer fluid. Due to the potential size of TES systems and tanks for large power plants, properly specifying and qualifying the filler material as a significant component of this system is a major element for both initial-cost and long-term maintenance costs associated with TES systems.

5.2.2. Packed bed system

Packed bed TES systems have an insulated container holding a fixed bed of filler material which acts as the primary heat storage

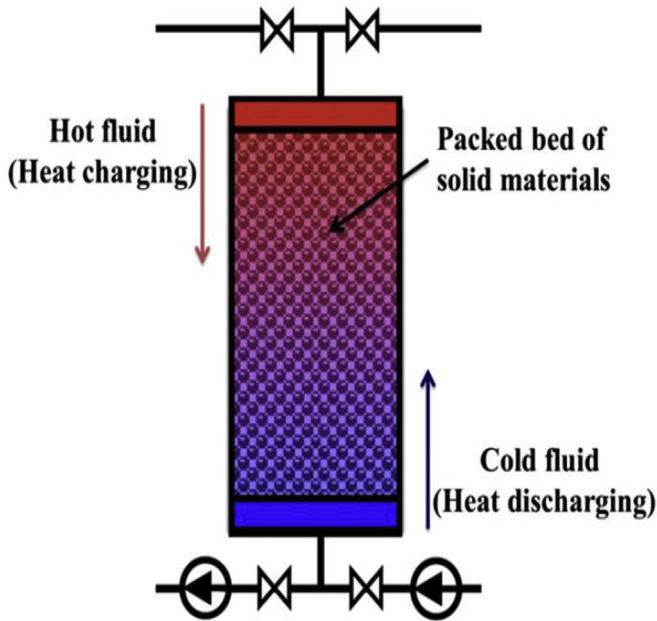


Fig. 18. Packed bed TES system [99].

medium. The HTF fluid is used to charge and discharge a packed bed by heat transfer through direct surface contact without the need for a heat exchanger as shown in Fig. 18. The direct contact provides large contact surface area for heat transfer improving the efficiency. Packed bed system has characteristic temperature stratification effect along the bed. Stratified liquid thermocline system with filler discussed in section 5.2.1.3.2 is a type of packed bed system. Thermocline systems use liquid as HTF with fillers arranged in a packed bed format and liquid also stores a part of the total thermal energy stored. Packed bed systems can also have gaseous HTF like air which act purely as HTF and filler in the packed bed stores the entire thermal energy. Typical working fluids are air, water, thermal oils and gases like supercritical CO₂. Typical bed filler materials are rocks, pebbles, gravel, sand, gypsum, soil, macro-encapsulated PCM containers, metal blocks, small concrete cubes, small concrete spheres, masonry brick, porcelain balls, zirconium oxide pellets, irregular solids particles of iron ore, coke, limestone, coal, blast furnace charge, copper slag, iron slag, aluminum slag etc [98]. The operating temperature range of TES is limited by thermal stability of filler material. Earth materials like rocks, gravels, sand are the most used filler materials and such systems operate in the medium temperature range around 50 °C–300 °C. In packed bed TES systems, normally heat is stored as sensible heat of fillers. However in case of macro-encapsulated PCM container beds, heat is stored as latent heat of PCM. Packed bed TES systems with sensible heat bed materials operate with variable outlet temperature. In case of solar air heaters, on a particular day factors like insolation, ambient temperature, temperature of HTF at the solar collector inlet, load etc result in a variable temperature of HTF at the solar collector outlet. As this hot HTF from solar collector outlet charges the packed bed, temperature to which packed bed is heated also varies depending on these factors. Moreover during discharging, the temperature of the bed falls rapidly. Another operational issue with packed beds is the thermal ratcheting. Repeated thermal cycles result in uneven thermal expansion and contraction between bed materials like rock and container material like steel. This results in slow accumulation of plastic strains especially on the lower container walls. Singh et al. [98] published a review article on the ongoing research works

related to packed bed TES systems. Influencing parameters for a packed bed TES system are HTF mass flow rate, gravel size to container size ratio, HTF pressure drop across the bed, bed porosity, dimensions of the bed etc. Typical application of packed systems is for solar air heaters, underground pit seasonal TES systems, waste heat recovery from exhaust gases used for preheating etc.

5.2.3. Fluidized bed systems

In central tower type CSP plants, the temperatures involved are extremely high. Liquid heat transfer medium like thermal oils and molten salts have limitations in operating under extremely high temperatures. Therefore solid particles like sand granules are the best medium to directly collect heat under highly concentrated radiation and store the absorbed heat. However the problem with solid particles is that they cannot be easily circulated like a fluid and they cannot run turbines. When direct contact between working fluid and solid particles is not possible, discharge of stored heat from solid particles to working fluid is difficult. In indirect type of heat exchangers with fixed bed of heated solid particles, heat transfer rate to working fluid flowing in steel pipes embedded in the fixed bed is poor. Heat transfer rate can be improved by using fluidized bed heat exchangers. Fluidized bed systems have solid particles suspended in a flowing fluid making a fluid like transport of particles through ducts possible. Fluid flow velocity through the bed of solid particles is high enough, so that the drag produced on solid particles overcomes the gravitational force on the solid particles. A fine mesh screen through which uniform fluid flow throughout the chamber happens is mounted at the bottom to prevent the solid particles from entering the plenum chamber below [100]. The cold and hot solid particles are stored in separate storage tanks as shown in Fig. 19. In this proposed concept [101] of a particle receiver solar power plant, fluidized bed heat exchangers (FB-HEX) with sand particles suspended in air acting as fluidized bed and water flowing through the steel tubes acting as working fluid driving the turbines. In a fluidized bed, temperature along the bed is uniform [100]. Similarly fluidized bed has been proposed as a solution to the problem of poor heat and mass transfer in a thermo-chemical reactor to external HTF [102]. Fluidized bed can improve the performance of thermo-chemical TES systems by providing large specific surface area for reaction and short residence time for solid and gas particles. Barrientos et al. studied the fluidized bed of microencapsulated PCM [100] for the direct contact heat exchanger scenario. They found that after an initial stabilization period of 1 h both fixed and fluidized bed has similar charging efficiency. They also found that complete discharge of stored heat was not possible in case of fluidized bed for the direct contact heat exchanger scenario due to the higher than ambient temperature of the working fluid. The higher than ambient temperature is caused by heating of air inside the blower. Due to their low density, microencapsulated PCM can be easily fluidized with a lower fluidizing velocity. With liquids like water, low density microencapsulated PCM is also aided by higher buoyancy factor and therefore easily forms stable slurry with much better heat transfer properties than water.

5.2.4. Moving bed systems

Moving bed systems are similar to fluidized bed in concept except that the particles slowly move downwards with the aid of gravitational force in slanted ducts rather than through a high speed fluid flow [103]. Advantage of moving beds is that they need low parasitic load compared to fluidized beds which require pumping of fluid. In a moving bed heat exchanger (MBHX), hot solid particle granules slowly flow around heat exchanging surfaces of steel tubes through which working fluid like the water flows and absorbs heat. In a continuous medium, mechanical interaction

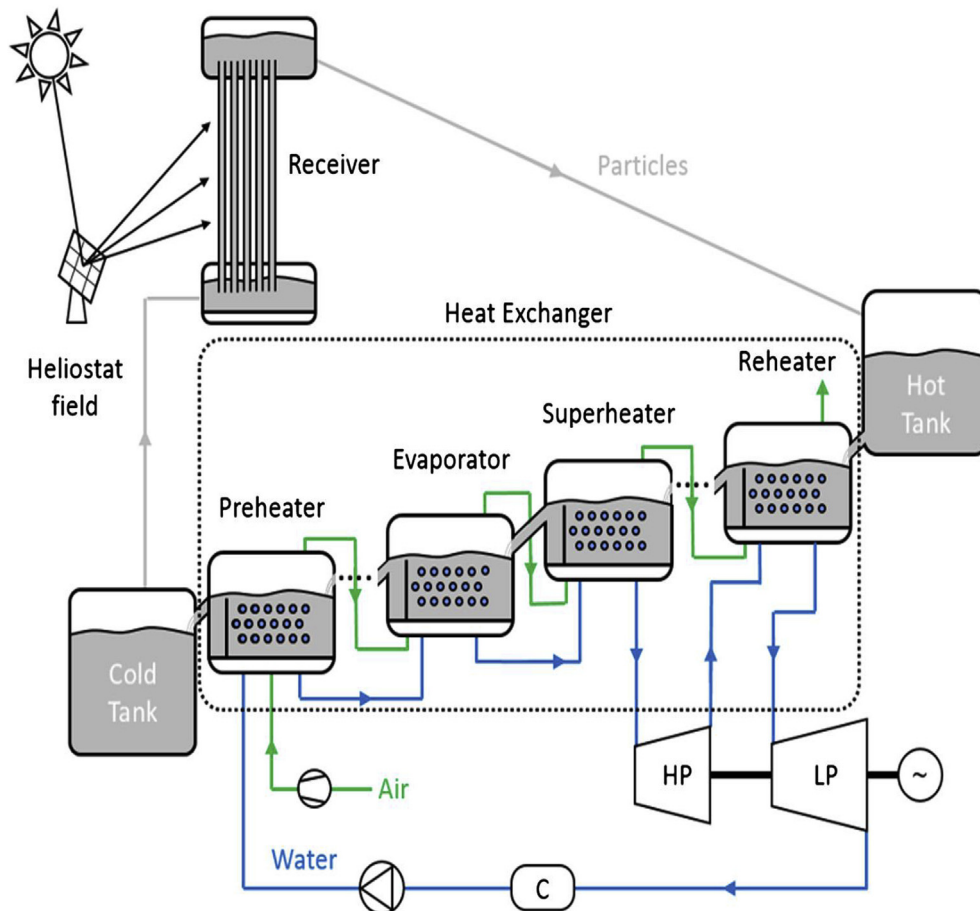


Fig. 19. Fluidized bed TES system [101].

between grains is described as stresses. In a fluidized bed, the solid particle grains move rapidly in diluted concentration (compared to solids) and primarily interact through collisions which can be modeled through kinetic theory of granular gases. In a moving bed, solid particle grains have dense concentration and interact through frictional contact with multiple neighboring grains.

5.2.5. Concrete blocks

Thermal energy storage characteristics of concrete are discussed in section 2.1.1.6. The thermal charging and discharging in concrete blocks needs a HTF flowing in heat exchanger tubes permanently embedded inside the concrete. An insulating cover will prevent the heat losses from outer surfaces of the concrete block. The cyclic volume changes affect the steel pipes causing ruptures and gap between concrete and steel pipe. Upon corrosion, replacement of the embedded old pipes is difficult.

6. Operating temperature range based TES systems

6.1. Cold thermal energy storage systems (CTES)

CTES systems maintain a cooling medium below 10 °C temperature. Producing cold requires compressor work and it is more economical to operate compressors during off-peak hours in the night when the electricity cost is low. The charging of cold storage systems during the night time is more efficient due to lower ambient temperatures. During the day time peak hours, load on building HVAC system compressor can be reduced by cooling through circulation of cooling medium from cold storage [104]. The

cold storage medium are either sensible heat medium like chilled water or latent heat medium like ice, PCM, eutectic salts etc. Ethylene glycol is a typical HTF. CTES have applications in building air conditioning, food and pharmaceutical industries etc.

6.1.1. Chilled water storage systems

Thermocline water storage system with operating temperature range around 4 °C–6 °C is a sensible heat system. In this type of system, water which is the storage medium gets circulated for charging and discharging. During the day chilled water from bottom level of the thermocline tank is pumped to the cooling coil of building HVAC system and the water with absorbed heat from building HVAC system is returned to the top of the tank. During the night, water from top layer is pumped to the cooling chiller for cold charging and chilled water is pumped back to the bottom of the tank. Nelson et al. [105] conducted a parametric study of stratified chilled water storage tank. Degree of thermal stratification is an important performance factor and it improves with aspect ratio of the tank (height to diameter ratio) up to a value of 3 [105] after which appreciable improvement was not seen. The thermoclines degradation happens due to the heat transfer from the ambient, thermal diffusion in the storage tank, axial wall conduction and mixing due to admission of the fluid in the storage tank during charging and discharging [105].

6.1.2. Coil pipe cool storage systems

This type of system uses latent heat of medium of like ice, paraffin etc. The PCM stored in an insulated tank is frozen by a cooling HTF flowing through an indirect heat exchanger type like

coiled–tube or shell–and–tube or tube–in–tank etc [105]. In this type of system, storage medium remains static in the insulated TES tank and only the HTF is circulated inside coils for charging and discharging. During charging process, HTF from evaporator of the cooling chiller is supplied through the coil at a sub–cooling temperature approximately 3 °C below the freezing point of the latent heat storage medium. During discharge, return temperature of HTF from the building HVAC system load is higher than the freezing point of the latent heat storage medium. In case of an internal melt–ice–on–coil tank system, Navarro et al. [106] observed the effect of density inversion of water at 4 °C temperature. They found that an inlet HTF supply temperature of between –2.5 °C and –5.2 °C was needed to charge CTES without using nucleating agents [106]. Jaime et al. [107] studied the effect of HTF mass flow and supply temperature of HTF on a paraffin based coiled storage tank. The storage medium was paraffin and had melting temperature in the range of 5 °C–10 °C. Temperature difference between the HTF supply temperature and the melting temperature of paraffin acts as the main driving force for both charging and discharging. During charging process, faster charging was achieved with higher mass flow rate and lower supply temperature (1 °C–5 °C). During discharging process, faster discharge with a higher discharged energy was achieved with higher mass flow rate and higher supply temperature (10 °C–16 °C). Inside the coil, the HTF transports heat through forced convection where as inside the TES tank main heat transfer mechanism within the liquid state storage medium is natural convection. However as the storage medium solidifies around the coil, conduction gradually becomes more dominant and poor thermal conductivity of the storage medium is a major issue faced during the charging and discharging process.

6.1.3. Packed bed cold storage systems

In a packed bed system, the storage medium is a multilayered fixed bed of spherical or any other shaped capsules containing a PCM, assembled inside an insulated storage container. The storage medium remains static inside the capsules and a HTF transports heat. Typical capsule materials are stainless steel, polyolefin etc. HTF is in direct contact with the outer surface of capsules and therefore large contact surface area is available for heat transfer. During charging process, the cold HTF which is supercooled below the freezing point of PCM absorbs heat from the encapsulated PCM which solidifies inside the capsule. During discharging process, the hot HTF at a temperature above the melting point of encapsulated PCM gets cooled by melting the PCM inside the capsules. Ereik et al. [108] conducted a numerical analysis on encapsulated ice TES system. They identified important influencing parameters on heat transfer coefficient and solidification time during charging process. During charging process, heat transfer coefficient increased with higher mass flow rate, lower inlet temperature of cold HTF and lower capsule layer number along the flow path. Stefan number, Reynolds number, and capsule diameter were inversely proportional to the solidification time. The impact of Stefan number was more dominant on solidification time compared to other parameters. Other influencing parameters which have been studied in past literature are porosity [109], degree of supercooling [110], dimensions of the capsule like diameter for spherical capsules and slab thickness, length, width for slab type capsules [111], capsule material and thickness [112] etc.

6.1.4. Ice slurry cool storage systems

Ice slurry TES is a dynamic cool storage system. In dynamic cool storage system, a slurry with dispersed two–phase (solid–liquid) flow properties acts as both the storage medium and HTF. In a slurry, liquid carrier fluid acts as the continuous phase and solid

PCM acts as the dispersed phase. Slurry with dispersed solid latent heat medium has much better heat transfer coefficient compared to a single phase liquid HTF and this helps in more efficient charging at the chiller and discharging at the building cooling coils. Ice slurry has ice crystals dispersed in water with freezing point depressant solution and it maintains a constant low temperature level during the cooling process and provides a higher heat transfer coefficient than single phase water. The ice slurry cool storage system can achieve increased temperature drop over the conventional chilled water system and makes it an attractive choice for achieving high degree of cooling. Continuous ice slurry formation is a key technical challenge here. Matsumoto et al. used a functional fluid consisting of 10 vol% silicone oil and 90 vol% water with a small amount of silane–coupler additive for continuous ice slurry generation. This method was free from problems like adhesion of ice on the cooling chamber and nearly all the water in the functional mixture could be frozen and kept in dispersed state over a long period [113]. Wijesundera et al. [114] evaluated a system for the production and storage of ice slurry using direct contact heat transfer between water and a liquid coolant spray. Fluorinert (FC–84) with a higher density than water and which is immiscible with water was used as the coolant. The coolant was sprayed into the water through a nozzle. As the coolant drops, it absorbed heat from the water and descended to the bottom of the cylinder owing to its higher density. A pump circulated the coolant collected at the bottom through a cold bath with temperature control maintained at –5 °C.

6.1.5. Gas hydrate cool storage systems

A gas hydrate, also called clathrate, is an ice like crystalline compound that occur when water molecules form a cage like structure around smaller “guest molecules” of gas or easily volatile liquid at certain temperature and pressure [115]. A large variety of gases or volatile liquids can form clathrate hydrates with water under certain conditions of temperature and pressure. Some examples of gases that form hydrates are natural gas, CO₂ and many kinds of refrigerants. Chilled water as a cool storage medium utilizes sensible heat which results in lower storage capacity. Ice and eutectic salts utilize the latent heat of phase change. However phase change temperature of ice is lower than human thermal comfort temperature range and the latent heat of phase change of the eutectic salt is smaller and it also causes serious corrosion. Hydrate crystals formed by the interaction between refrigerants and water under a hydrate formable temperature range (4 °C–30 °C) [116]. The phase change latent heat of the gas hydrate is similar to that of ice and can vary in the range between 270 and 430 kJ/kg [116]. For example ideal critical decomposition temperature and pressure of alternative refrigerant R141b are 8.44 °C and 43.0 kPa, respectively, and the latent heat of phase change is 344 kJ/kg [115]. Gas hydrates just need chilled water as continuous medium and antifreeze is not required. Gas hydrates only require conventional water chillers instead of the expensive ice slurry generators [116]. Xie et al. [116] studied the cold storage characteristics of a novel small scale low pressure gas hydrate cold storage apparatus. The mixture of water (80 kg) and volatile refrigerant HCFC–141b (20 kg) inside the hydrate slurry generation chamber is cooled to produce hydrate crystals. Mechanical blending of refrigerant and water through a mixing pump can accelerate the hydration process.

6.2. Low temperature heat storage

TES systems operating in the temperature range of 20 °C–100 °C can be considered as low temperature heat storage TES systems. Typical end uses in this temperature range are space heating, bathing, laundry, cleaning etc. The type of storage materials involved are

water, salt hydrates, organic latent heat storage materials like paraffin, fatty acids etc. Water exists in liquid form and stores sensible heat. Most paraffin and non-paraffin class organic PCM materials and salt hydrates have their melting points in this range.

- Solar domestic hot water supply

Solar water heating system is a diurnal type TES system operating in the temperature range between 20 °C and 100 °C which is covered in section 3.1.2.

- Seasonal TES system

Seasonal TES system is a long term heat storage system operating in the range of 27 °C–80 °C which is covered in section 3.2.

- Passive heat storage

Passive heat storage in buildings, automobiles etc is covered in section 5.1.

6.3. Medium temperature heat storage

Thermal energy storage at temperatures in the range of 100 °C–250 °C is considered as medium temperature heat storage. At these temperatures, water exists as steam in atmospheric pressure and has vapor pressure. Typical applications in this temperature range are drying, steaming, boiling, sterilizing, cooking etc. The type of storage materials involved are sugar alcohols and chemical sorption storage materials.

- Industrial waste heat recovery

One of the end user applications for recovered industrial waste heat is industrial process heating method like drying. Mobile sorption TES system covered in section 4.3.1 is an example.

6.4. High temperature heat storage

As the temperature crosses 250 °C, melting points of salts and metals can be reached. The type of storage materials involved are salts, earth materials, concrete and metals.

- Thermal power generation

Thermal power plants like CSP plants and nuclear power plants operate in this temperature range.

7. Design and performance parameters for TES systems

7.1. Capacity and size

This is maximum thermal energy in kWh or MJ which can be charged to the TES system. TES container size increases with capacity. It is the product of selected thermal storage material's volumetric heat storage capacity and the volume of the container.

7.2. Power

It is the discharge/charging rate of TES system expressed in kW.

7.3. Operating temperature range

TES systems operate normally in temperature range between –40 °C and 600 °C temperature range. Chosen TES

materials and container materials should be thermally, chemically and mechanically stable in this temperature range. In case of chemical sorption materials, charging and discharging temperatures can be different. Discharge temperature control scenarios are as below.

- With sensible heat storage materials

High temperature TES systems in CSP plants have a large operating temperature range. In small sized TES systems with sensible heat storage materials, discharge temperature is highly fluctuating and rapidly decreases.

- With PCM

Latent heat storage materials operate in a narrow range near the phase change temperature. Heat is discharged in a stable manner, with near constant HTF outlet temperature.

- With multiple PCM

Improved heat transfer rate is achieved by arranging multiple PCM in an ascending order of their melting points along the discharge path [117]. Although HTF temperature raises as it gets heated while flowing along the discharge path, still maximum temperature gap between the HTF and PCM can be maintained.

7.4. Storage period

Short term diurnal TES systems operate at higher temperature, smaller capacity and size. Sensible heat storage materials operating at very high temperatures like molten salts and liquid metals are good choices for short term storage. Latent heat materials are good choice for short term thermal energy storage. Long term seasonal TES systems store heat at low temperatures below 80 °C and require huge amount of storage material and very large capacity. Cheap naturally available sensible heat storage materials like rock, sand and water are used in long term seasonal storage because of the shear amount of storage material requirement, their economical advantage and environmental compatibility. Chemical storage materials are theoretically zero heat loss materials and hence are suitable for long term heat storage. Heat losses should be minimized with adequate insulation to prolong the storage duration.

7.5. Efficiency

It is the ratio of total energy discharged to the end user to the total energy supplied to charge the TES system. The difference between total heat discharged to end user and heat supplied during charging will be the total heat losses during charging, storage duration and discharging.

7.6. Cost

Cost of a TES system includes the initial capital expenses and operational expenses during the service life. Expenses related to initial activities like designing, and construction of storage tank, purchase costs related to equipments, instrumentation, insulation, pipelines, fittings, and labor costs related to installation and commissioning of the TES unit. Operation and maintenance costs include costs of parasitic load like pumping, electric trace heating, replenishment of storage materials, etc. System Advisor Model (SAM) software by national renewable energy laboratory (NREL) is currently available with readymade financial models for residential, commercial and utility scale renewable energy projects [118]. One

of the key cost metric for such projects is Levelized cost of energy (LCE) expressed in \$/kWh. This software model requires inputs like installation cost components, collector and receiver types, solar multiple, power block capacity etc. Among these inputs, one important input that needs to be keyed into the software is the storage capacity. The software then generates a cash flow for revenues, installation costs and operating, maintenance and replacement costs. For cost estimation of a TES system in particular, Nithyanandam and Pitchumani [119] reference model can be followed. They modeled two different types of TES systems. Encapsulated PCM type TES system and heat pipe based PCM TES system. Based on the same model various cost components of a TES system can be generalized into categories as below.

- Container cost

Container design choice strongly influences the capital cost. Designs like shell and tube, packed bed of encapsulated PCM, fluidized bed, two tank systems etc are expensive. Packed bed of rocks and sand, single tank thermocline liquid storage, rigid solid blocks of concrete etc are the cheaper options available. Seasonal thermal storage tanks due to their enormous storage capacity requirement need very high capital investment. Typical container materials are stainless steel and reinforced concrete. Cost of insulation is included in container cost component. Typical insulation material is fiber glass. Smaller size containers cost less, therefore storage medium with poor volumetric energy storage density increases container cost. Higher vapor pressure of storage medium leads to thicker walls and increased cost.

- Storage material cost

Storage materials like water, salts, rock, sand and concrete are cheaper options while thermo–chemical, organic PCM, thermal oil, metals, refrigerants used in gas hydrates etc are costly. Cost per unit mass of thermal energy storage material in \$/kg can be used for estimating the total storage material cost. Storage material cost may also include thermal conductivity enhancement costs like microencapsulation or composite preparation.

- Overhead cost

Typical overhead cost component includes miscellaneous costs such as electrical, instrumentation, piping, valves, fittings etc. To simplify the estimation process, it can be taken as 10% of the total cost [119].

- Design specific cost components

Below are few cost components specific to the particular design selection.

(1) Encapsulation cost

This cost component exists when the TES type is packed bed of encapsulated PCM. It depends on the encapsulation material chosen. Cheap options like plastics are used for low temperature TES systems. For high temperature systems, costly encapsulation materials like metals and alloys may be needed. Microencapsulation is a costly option.

(2) Heat exchanger cost

In latent heat TES systems, heat exchange between PCM stored in the container and HTF happens through a coiled tube or a shell

and tube model. In this type of system, HTF flows through heat exchanger tubes. Therefore these systems have the added cost component of the heat exchanger tubes. Such tubes are made of costly metals like copper and will also require metal fabrication. To enhance the heat transfer, there could be additional components like fins on the tube wall surfaces further increasing this cost component.

(3) Heat pipe cost

Heat pipe is another way to facilitate heat transfer between HTF and latent heat storage material like PCM. Heat pipes are costly but they show very good performance. Heat pipes used in TES systems need to be bidirectional and should have equal effective thermal conductivity during both charging and discharging processes. They need to work in any possible orientations. Such heat pipes require a sealed container, capillary wick and a working fluid. Metals like copper are used as heat pipe container and capillary wick material. The capillary wick can be wired mesh, sintered metal, axial grooves etc. Working fluid is chosen based on operating temperature. Gravity assisted thermosyphon heat pipes can also be used by having two separate channels for charging and discharging process. In such a design, during charging process, hot HTF flows in the bottom channel. During discharging process, cold HTF flows in the top channel [119]. In this type of heat pipes, there is no need for capillary wick and hence are cheaper. In case of domestic solar water heaters with evacuated tube design, heat pipes only perform the function of charging and hence use thermosyphon mechanism with unidirectional heat transfer from bottom towards upward direction.

8. Operational issues management in TES systems

8.1. Poor heat transfer

Poor heat transfer severely affects the charging and discharging rate of a TES system. This in turn leads to a large cycle time. In a shell and tube model using latent heat storage material, during discharge heat is transferred from liquid TES material to HTF flowing in the heat exchanger tubes. In the beginning heat transfer is entirely due to natural convection of TES material. Solidification of TES material starts along the walls of the heat exchanger tubes, and as solidification proceeds, convection gets limited to a smaller and smaller region within the TES material. Solid layers formed on the walls of the heat exchanger tubes create barrier to heat transfer from the inner liquid, limiting heat transfer to the thermal conductivity of the PCM.

8.1.1. Heat transfer surface area extension techniques

Use of extended surfaces like fins within PCM improves natural convection in the systems. This additional heat transfer area compensates for the poor heat transfer coefficient.

- Macro–encapsulation [50]
- Micro–encapsulation [49,120].
- Fins [121].
- Heat–pipes [122].
- Porous matrices like metal foam [123].

8.1.2. Composites with filler dispersion

Dispersing the highly conductive fillers in PCM greatly enhances the thermal conductivity within the TES material. However most works in this area have been mainly focused on thermal conductivity in the solid phase. Though these fillers may improve the

thermal conductivity of the solid phase, but if they significantly increase the viscosity of the liquid PCM, they may hinder natural convection and thereby decrease the overall heat transfer rate. Fillers used for dispersion can be broadly classified as below.

- Carbon based fillers

Carbon nanofiber [124], graphene [124], carbon nanotube [124] and expanded graphite [125].

- Metallic based fillers

Copper nanowires [126], silver nanowires [127] and aluminum nanowires.

- Ceramic filler

Alumina [128], boron nitride [129], silicon carbide and zinc oxide.

8.2. PCM leakage control

PCM leakage problem occurs after the melting of PCM and the liquid PCM starts flowing. Hence a container to hold the TES material is needed. There are several methods to mitigate this issue.

- Macro [50] and micro [120] encapsulation.
- Form stable PCM with polymer matrix blending technique [49,130].
- Form stable PCM chemical grafting technique [131].
- Electrospun fiber [82].

8.3. Heat loss

Rezaie et al. [8] in their study on Friedrichshafen district heating system (seasonal TES) of 3017 MWh annual capacity estimated an annual heat loss of 421 MWh. Heat loss in a TES system is accelerated by below factors.

- High operating temperature of the TES system.

Higher temperature difference between TES and ambient temperature means higher heat losses and shorter storage duration.

- Poor or damaged insulation

For example in underground TES storage tanks insulation material becomes wet due to drainage of ground water resulting in extra heat loss for the TES.

- Connection pipes

Lengthy piping between heating plants and the TES creates noticeable heat loss and a drop in temperature from the TES outlet to the thermal network.

8.4. Phase separation

This issue is mainly faced in salt hydrates and covered in section 2.2.1.2.3.

8.5. Supercooling

In PCM type thermal storage materials, supercooling results in large difference in charging and discharging temperature which is

not desirable. Nucleating agents help mitigate this problem. Some TES materials like poly ethylene glycol (PEG) and metals inherently have a huge supercooling degree.

8.6. Container corrosion

Inorganic TES materials like salts are highly corrosive to the container material.

8.7. Vapor pressure

Water has a very high vapor pressure which leads to thicker container and piping walls. This increases cost and leakage.

8.8. vol changes

Large volume changes require larger containers and increases the container cost.

8.9. Safety

Organic TES materials are combustible and are a fire risk. Thermal oils need to be used within the safe temperature limits. Metals like sodium, potassium etc have a high fire risk.

8.10. Toxicity

TES materials are generally not toxic. However formaldehyde used as a shell material in microencapsulation is a known toxin. Similarly thermal oils also contain aromatic hydrocarbons.

9. Conclusions

- TES is the key to overcoming our dependency on fossil fuel burning. Fossil fuel burning is a consequence of our failure to harvest and store energy from clean renewable sources. If the thermal energy is not stored, it simply dissipates into environment necessitating burning of fossil fuel.
- Economic footprint of TES field spans many areas like thermal power generation, buildings, textiles, automobiles, health care, agriculture, food processing etc. TES is the best suited energy storage technique for thermal electricity generation plants. It plays a key role at both utility end and building end of energy supply chain.
- TES systems most commonly seen today are seasonal TES systems, CSP plant TES systems, distributed TES systems of domestic solar thermal applications, passive TES in buildings, heat and cold storages of building HVAC systems etc. In addition TES also has niche applications in textiles, automobiles, pharmacy, agriculture etc.
- There are three main classes of TES materials. In case of large size and high temperature TES systems, sensible heat storage materials are the main TES materials. In case of low temperature human thermal comfort applications, phase change materials are the main TES materials. Thermo-chemical heat storage materials are in the laboratory stage and currently have very limited practical applications. Most commonly used TES materials are sensible heat storage materials like water, inorganic salts, thermal oils, sand, gravel and organic latent heat storage materials like paraffin. TES materials like water, salts, sand etc are cheap where as organic TES materials are costly.
- Seasonal thermal energy storage systems have very large capacity and need large quantities of cheap TES materials. Such systems operate at low temperatures and their storage duration is long. These systems are common in high latitude areas like

Europe and their main end use is for human thermal comfort purpose. Seasonal TES system can also be implemented in smaller scales at remote houses. Diurnal TES systems have medium to small capacities. Large diurnal TES systems mostly operate in countries like USA and Spain which have areas of high solar insolation and their main end use is to smoothen the intermittency of solar radiation in solar power plants. Small scale diurnal TES systems are used in domestic solar thermal applications.

- TES system is classified as an active system if any input like pumping work to circulate a HTF is needed during operation or as a passive system if no input work is needed during operation. Tank type systems like thermocline, packed bed, fluidized bed, moving bed etc are active TES systems. Passive TES systems are implemented in buildings, textiles, automobiles etc for thermal comfort purpose.
- Based on how the thermal energy is stored and delivered to the end user, TES systems can be classified as centralized TES, building end TES, mobile TES etc. Centralized TES systems are used in applications like district heating plants. Building end TES systems are used in applications like HVAC systems. Mobile TES systems are used in applications like heat delivery to remote locations and food and drug shipping etc.
- A large number of TES materials are available across a wide operating temperature range. Using techniques like eutectic mixture, esterification etc, the operating temperature of pure materials can be further modified. Sensible heat storage systems can store very large amount of heat over a large temperature range but the outlet temperature of the HTF during discharge is not steady like in a latent heat storage system. By choosing a TES material with solid-liquid phase change temperature between minimum and maximum operating temperatures, the storage capacity of the TES system can be increased significantly.
- In phase change materials the main drawback is low thermal conductivity. PCM undergoes solid-liquid phase change during operation. In liquid phase, problem of poor thermal conductivity is not felt seriously due to convective heat transfer. However, during the phase change process poor thermal conductivity of solid layers affects the thermal charging and discharging rates. Thermal conductivity enhancement of PCM is a major research area. Currently for low temperature PCM adequate research data is available but high temperature PCM are insufficiently researched.
- TES systems can operate in a broad range of temperatures (between $-40\text{ }^{\circ}\text{C}$ and $600\text{ }^{\circ}\text{C}$) as per application requirements. Cold TES systems operate below $10\text{ }^{\circ}\text{C}$ temperature. Water and gas hydrates are the main TES materials in this range. Low temperature TES systems operate in the temperature range of $20\text{ }^{\circ}\text{C}$ – $100\text{ }^{\circ}\text{C}$. Paraffin and non-paraffin class organic PCM materials and salt hydrates are the main TES materials in this range. Medium temperature TES systems operate in the temperature range of $100\text{ }^{\circ}\text{C}$ – $250\text{ }^{\circ}\text{C}$. Sugar alcohols and chemical sorption storage materials are the main TES materials in this range. High temperature TES systems operate in the temperature range above $250\text{ }^{\circ}\text{C}$. Salts, earth materials, concrete and metals are the main TES materials in this range.
- High initial capital cost requirement is an impediment to implementation of TES. Continued research effort is needed to reduce cost through the use of alternative cheap TES materials from renewable biosources, naturally occurring earth materials, industrial waste materials etc.
- Usage of TES is not as convenient as the usage of fossil fuel due to limitations in the current level of technology. Higher energy storage densities, faster charging and discharging cycles, easy

delivery mechanisms to end user, lower heat losses, lower parasitic loads etc are desired in future TES systems.

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