

Thermal Energy Storage

4.1 GENERALITIES

One of the main aspects of solar systems is storage. Thermal energy storage (TES) is a technology that stocks thermal energy by heating or cooling a storage medium so that the stored energy can be used at a later time for heating and cooling applications and power generation. TES systems are used particularly in buildings and industrial processes. In these applications, approximately half of the energy consumed is in the form of thermal energy, the demand for which may vary during any given day and from one day to next. Therefore, TES systems can help balance energy demand and supply on a daily, weekly, and even seasonal basis. Advantages of using TES in an energy system are the increase of the overall efficiency and better reliability, but it can also lead to better economics, reducing investment and running costs, and less pollution of the environment and less carbon dioxide (CO₂) emissions [1]. TES is becoming particularly important for electricity storage in combination with concentrated solar power (CSP) plants where solar heat can be stored for electricity production when sunlight is not available.

In Europe, it has been estimated that around 1.4 million GWh/year could be saved and 400 million tons of CO₂ emissions avoided, in the building and industrial sectors by more extensive use of heat and cold storage [2].

Storage density, in terms of the amount of energy per unit of volume or mass, is an important issue for applications in order to optimize a solar ratio (how much of the solar radiation is useful for the heating/cooling purposes), efficiency of the appliances (solar thermal collectors and absorption chillers), and room consumption. For these reasons, it is worth to investigate the possibility of using phase-change materials (PCMs) in solar system applications. The potential of PCMs is to increase the energy density of small-sized water storage tanks, reducing solar storage volume for a given solar fraction or increasing the solar fraction for a given available volume [3].

It is possible to think of thermal storage in the hot and/or in the cold side of the plant. The former allows the storage of hot water from the collectors (and from the auxiliary heater) to be supplied to the generator of the absorption chiller (in cooling mode) or directly to the users (in heating mode). The latter allows the storage of cold water produced by the absorption chiller to be

supplied to the cooling terminals inside the building. It is usual to identify the three situations just described as, respectively, “hot”, “warm”, and “cold” storage because of the different temperature ranges. Typically, a hot tank may work at 80–90°C, a warm tank at 40–50°C, and a cold tank at 7–15°C.

While heat storages in the hot side of solar plants are always present because of the heating and/or domestic hot water (DHW) production, cold storages are justified in bigger size plants. Cold storages are used not only to get economic advantages from the electricity tariffs (in case of electric compression chiller) depending on the time-of-the-day but also to lower the cooling power installed and to allow more continuous operation of the chiller [4].

Support for research and development (R&D) of new storage materials, as well as policy measures and investment incentives for TES integration in buildings, industrial applications, and variable renewable power generation, is essential to foster its deployment.

This chapter is focused on the analysis of TES technologies that provide a way of valorizing solar heat and reducing the energy demand of buildings. The principles of several energy storage methods and calculation of storage capacities are described. Sensible heat storage technologies including the use of water, underground, and packed-bed are briefly reviewed. Latent-heat storage (LHS) systems associated with PCMs for use in solar heating and cooling of buildings, solar water-heating and heat-pump systems, and thermochemical heat storage are also presented. Additionally, a three-dimensional heat-transfer simulation model of latent-heat TES is developed to investigate the quasi-steady state and transient heat transfer of PCMs. The numerical simulation results using paraffin RT20 are compared with available experimental data for cooling and heating of buildings. Finally, outstanding information on the performance and costs of TES systems are included.

4.2 CLASSIFICATION AND CHARACTERISTICS OF STORAGE SYSTEMS

The main types of TES of solar energy are presented in Fig. 4.1. An energy storage system can be described in terms of the following characteristics:

- *Capacity* defines the energy stored in the system and depends on the storage process, the medium and the size of the system;
- *Power* defines how fast the energy stored in the system can be discharged (and charged);
- *Efficiency* is the ratio of the energy provided to the user to the energy needed to charge the storage system. It accounts for the energy loss during the storage period and the charging/discharging cycle;
- *Storage period* defines how long the energy is stored and lasts hours to months (i.e., hours, days, weeks, and months for seasonal storage);

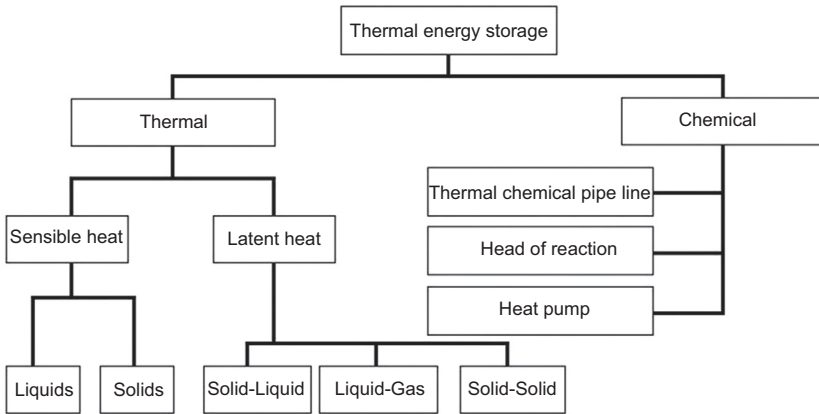


FIGURE 4.1 Types of thermal energy storage of solar energy.

- *Charge and discharge times* defines how much time is needed to charge/discharge the system; and
- *Cost* refers to either capacity (€/kWh) or power (€/kW) of the storage system and depends on the capital and operation costs of the storage equipment and its lifetime (i.e., the number of cycles).

Capacity, power, and discharge time are interdependent variables, and in some storage systems, capacity and power can also depend on each other. Typical parameters for TES systems are shown in Table 4.1 [5], including capacity, power, efficiency, storage period, and cost. High-energy storage density and high power capacity for charging and discharging are desirable properties of any storage system. It is well known that there are three methods for TES at temperatures from -40°C to more than 400°C : sensible heat, latent heat associated with PCMs, and thermochemical storage (TCS) associated with chemical reactions (Fig. 4.2) [6].

The choice of storage medium depends on the nature of the process. For water heating, energy storage as sensible heat of stored water is logical. If air-heating collectors are used, storage in sensible or latent-heat effects in particulate storage units is indicated, such as sensible heat in a pebble-bed heat exchanger. In passive heating, storage is provided as a sensible heat in building the elements. If photovoltaic or photochemical processes are used, storage is logically in the form of chemical energy.

4.3 SENSIBLE HEAT STORAGE

Sensible heat storage (SHS) (Fig. 4.2A) is the simplest method based on storing thermal energy by heating or cooling a liquid or solid storage medium (e.g., water, sand, molten salts, or rocks), with water being the cheapest option.

TABLE 4.1 Typical Parameters of TES Systems

TES System	Capacity (kWh/t)	Power (MW)	Efficiency (%)	Storage Period	Cost (€/kWh)
Sensible (hot water)	10–50	0.001–10	50–90	days/ months	0.1–10
PCM	50–150	0.001–1	75–90	hours/ months	10–50
Chemical reactions	120–250	0.01–1	75–100	hours/ days	8–100

The most popular and commercial heat storage medium is water, which has a number of residential and industrial applications. Underground storage of sensible heat in both liquid and solid media is also used for typically large-scale applications. SHS has two main advantages: it is cheap and without the risks derived from the use of toxic materials.

SHS system utilizes the heat capacity and the change in temperature of the storage medium during the process of charging and discharging. The amount of heat stored depends on the specific heat of the medium, the temperature change, and the amount of storage material [7].

$$Q_s = \int_{t_i}^{t_f} mc_p dt = mc_p(t_f - t_i) \tag{4.1}$$

where Q_s is the quantity of heat stored, in J; m is the mass of heat storage medium, in kg; c_p is the specific heat, in $J/(kg \cdot K)$; t_i is the initial temperature, in $^{\circ}C$; and t_f is the final temperature, in $^{\circ}C$.

The SHS capacities of some selected solid–liquid materials are shown in Table 4.2. Water appears to be the best SHS liquid available because it is inexpensive and has a high specific heat. However, above $100^{\circ}C$, oils, molten

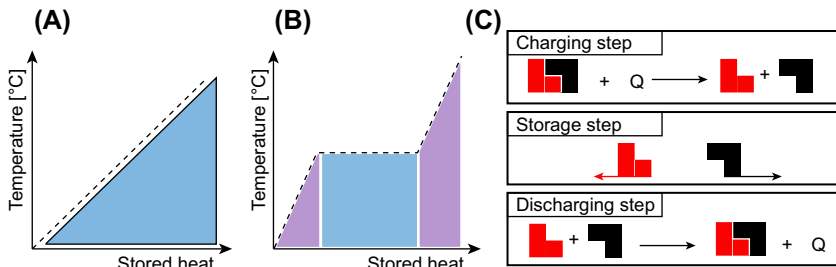


FIGURE 4.2 Methods of thermal energy storage (A) sensible heat; (B) latent heat; (C) thermochemical reactions.

TABLE 4.2 List of Selected Solid–Liquid Materials for Sensible Heat Storage

Medium	Fluid Type	Temperature Range (°C)	Density (kg/m ³)	Specific Heat (J/(kg·K))
Rock	–	20	2560	879
Brick	–	20	1600	840
Concrete	–	20	1900–2300	880
Water	–	0–100	1000	4190
Calorie HT43	Oil	12–260	867	2200
Engine oil	Oil	≤160	888	1880
Ethanol	Organic liquid	≤78	790	2400
Propane	Organic liquid	≤97	800	2500
Butane	Organic liquid	≤118	809	2400
Isotunaol	Organic liquid	≤100	808	3000
Isopentanol	Organic liquid	≤148	831	2200
Octane	Organic liquid	≤126	704	2400

salts, liquid metals, etc. are used. For air-heating applications, rock bed-type storage materials are used.

4.3.1 Water Tank Storage

The use of hot-water tanks is a well-known technology for TES. Hot-water tanks serve the purpose of energy saving in water heating systems based on solar energy and in cogeneration (i.e., heat and power) energy supply systems. State-of-the-art projects [8] have shown that water tank storage is a cost-effective storage option and that its efficiency can be further improved by ensuring optimal water stratification in the tank and highly effective thermal insulation. Today's R&D activities focus, for example, on evacuated super-insulation with a thermal conductivity of 0.01 W/(mK) at 90°C and 0.1 mbar and on optimized system integration. A typical system in which a water tank is used is shown in Fig. 4.3.

The energy storage capacity of a water (or other liquid) storage unit at uniform temperature (i.e., fully mixed, or no stratified) operating over a finite temperature difference is given by Eq. (4.1) redefined as

$$Q_s = mc_p \Delta t_s \quad (4.2)$$

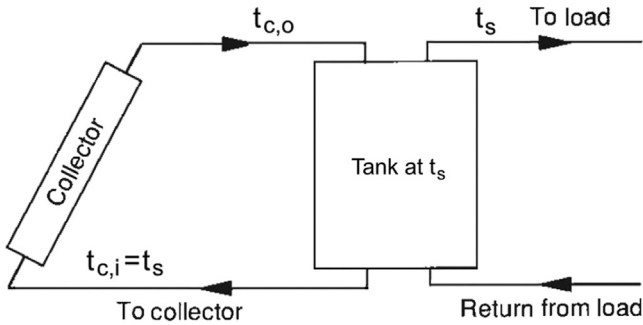


FIGURE 4.3 A typical system using water tank storage.

where Q_s is the total heat capacity for a cycle operating through the temperature range Δt_s and m , c_p are the mass and the specific heat, respectively of water in the unit. The temperature range over which such a unit can operate is limited at the lower extreme for most applications by the requirements of the process. The upper limit may be determined by the process, the vapor pressure of the liquid, or the collector heat loss.

An energy balance on the no stratified tank is

$$mc_p \frac{dt_s}{d\tau} = Q_u - Q_L - U_s A_s (t_s - t_a) \quad (4.3)$$

where Q_u and Q_L are rates of addition or removal of energy from the collector and to the load; U_s is the heat loss coefficient of storage tank; A_s is the storage tank surface area; t_a is the ambient temperature for the tank; τ is the time.

Eq. (4.3) is to be integrated over time to determine the long-term performance of the storage unit and the solar process. Useful long-term analytical solutions are not possible due to the complex time dependence of some of the terms. There are many possible numerical integration methods. Using simple Euler integration is usually satisfactory (i.e., rewriting the temperature derivative as $(t_s - t_i)/\Delta\tau$ and solving for the tank temperature at the end of a time increment):

$$t_s = t_i + \frac{\Delta\tau}{mc_p} [Q_u - Q_L - U_s A_s (t_i - t_a)] \quad (4.4)$$

Eq. (4.4) can be used to predict the water storage temperature as a function of time. Once the tank temperature is known, other temperature-dependent quantities can be estimated.

Hot-water storage systems used as buffer storage for DHW supply are usually in the range of 500 L to several cubic meters (m^3). This technology is also used in solar thermal installations for DHW combined with building heating systems (combisystems). Large hot-water tanks are used for seasonal storage of solar thermal heat in combination with small district heating

systems. These systems can have a volume up to several thousand cubic meters. Charging temperatures are in the range of 80–90°C. The usable temperature difference can be enhanced by the use of heat pumps for discharging (down to temperatures around 10°C).

4.3.2 Underground Storage

Underground thermal energy storage (UTES) is also a widely used storage technology, which makes use of the ground (e.g., the soil, sand, rocks, and clay) as a storage medium for both heat and cold storages.

Means must be provided to add energy to and remove it from the medium. This is done by pumping heat transfer fluids (HTFs) through pipe arrays in the ground. The pipes may be vertical U-tubes inserted in wells (*boreholes*) that are spaced at appropriate intervals in the storage field or they may be horizontal pipes buried in trenches (see Chapter 9). The rates of charging and discharging are limited by the area of the pipe arrays and the rates of heat transfer through the ground surrounding the pipes. If the storage medium is porous, energy transport may occur by evaporation and condensation and by movement of water through the medium, and a complete analysis of such a store must include consideration of both heat and mass transfers. These storage systems are usually not insulated, although insulation may be provided at the ground surface.

Boreholes (ground heat exchangers) are also frequently used in combination with heat pumps where the ground heat exchanger extracts low-temperature heat from the soil.

Aquifer storage is closely related to ground storage, except that the primary storage medium is water, which flows at low rates through the ground. Water is pumped out of and into the ground to heat it and extract energy from it. Water flow also provides a mechanism for heat exchange with the ground itself. As a practical matter, aquifers cannot be insulated. Only aquifers that have low natural flow rates through the storage field can be used. A further limitation may be in chemical reactions of heated water with the ground materials. Aquifers, as with ground storage, operate over smaller temperature ranges than water stores. Most applications deal with the storage of winter cold to be used for the cooling of large office buildings and industrial processes in the summer.

Cavern storage and pit storage are based on large underground water reservoirs created in the subsoil to serve as TES systems. Caverns are the same in their principles of operation as the tanks discussed in the previous section. Energy is added to or removed from the store by pumping water into or out of the storage unit. The major difference will be in the mechanisms for heat loss and possible thermal coupling with the ground. These storage options are technically feasible, but applications are limited because of the high investment costs.

For high-temperature (i.e., above 100°C) SHS, the technology of choice is based on the use of liquids (e.g., oil or molten salts, the latter for temperatures up to 550°C). For very high temperatures, solid materials (e.g., ceramics, concrete) are also taken into consideration. However, most of such high-temperature-sensible TES options are still under development or demonstration.

4.3.3 Pebble-Bed Storage

A pebble-bed (packed-bed) storage unit uses the heat capacity of a bed of loosely packed particulate material to store energy. A fluid, usually air, is circulated through the bed to add or remove energy. A variety of solids may be used, rock and pebble being the most widely used materials.

A pebble-bed storage unit is shown in Fig. 4.4. In operation, flow is maintained through the bed in one direction during addition of heat (usually downward) and in the opposite direction during removal of heat. Note that heat cannot be added and removed at the same time; this is in contrast to water storage systems, where simultaneous addition to and removal from storage is possible.

A major advantage of a packed-bed storage unit is its high degree of stratification. The pebbles near the entrance are heated, but the temperature of the pebbles near the exit remains unchanged and the exit-air temperature remains very close to the initial bed temperature. As time progresses, a temperature front passes through the bed. When the bed is fully charged, its temperature is uniform.

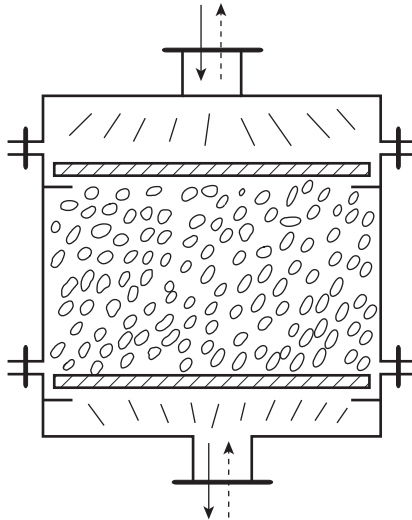


FIGURE 4.4 Pebble-bed storage system.

A packed bed in a solar heating system does not normally operate with constant inlet temperature. During the day, the variable solar radiation, ambient temperature, collector inlet temperature, load requirements, and other time-dependent conditions result in a variable collector outlet temperature.

Many studies are available on the heating and cooling of packed beds. The first analytical study was by Schumann [9] and the basic assumptions leading to this model are one-dimensional plug flow, no axial conduction or dispersion, constant properties, no mass transfer, no heat loss to the environment, and no temperature gradients within the solid particles. The differential equations for the fluid and bed temperatures (t_f , t_b) are:

$$\rho_f c_{p,f} \varepsilon \frac{\partial t_f}{\partial \tau} = -\frac{m_f c_{p,f}}{A} \frac{\partial t_f}{\partial x} + k_v (t_b - t_f) \quad (4.5)$$

$$\rho_b c_{p,b} (1 - \varepsilon) \frac{\partial t_b}{\partial \tau} = k_v (t_f - t_b) \quad (4.6)$$

where ρ_f is the fluid density; $c_{p,f}$ is the specific heat of fluid; ε is the bed void fraction; m_f is the fluid mass; A is the bed cross-sectional area; k_v is the volumetric (per unit bed volume) heat transfer coefficient between the bed and the fluid; and τ is the time.

For an air-based system, the first term on the left-hand side of Eq. (4.5) can be neglected and the equations can be written as [10]:

$$\frac{\partial t_f}{\partial (x/L)} = NTU (t_b - t_f) \quad (4.7)$$

$$\frac{\partial t_b}{\partial \Theta} = NTU (t_f - t_b) \quad (4.8)$$

$$NTU = \frac{k_v AL}{m_f c_{p,f}} \quad (4.9)$$

and the dimensionless time is

$$\Theta = \frac{\tau m_f c_{p,f}}{\rho_b c_{p,b} (1 - \varepsilon) AL} \quad (4.10)$$

where A is the bed cross-sectional area; L is the bed length; and NTU is the effectiveness.

Analytical solutions to these equations exist for a step change in inlet conditions and for a cyclic operation. For the long-term study of solar energy systems, these analytical solutions are not useful and numerical techniques as finite-difference method must be employed.

4.4 LATENT-HEAT STORAGE

The energy storage density increases and hence the volume is reduced, in the case of LHS (Fig. 4.2B). The heat is mainly stored in the phase-change process (at a quite constant temperature) and it is directly connected to the latent heat of the substance. The use of a LHS system using PCMs is an effective way of storing thermal energy and has the advantages of high-energy storage density and the isothermal nature of the storage process.

LHS is based on the heat absorption or release when a storage material undergoes a phase change from solid to liquid or liquid to gas or vice versa. The storage capacity Q_s , in J, of the LHS system with a PCM medium [7] is given by

$$Q_s = \int_{t_i}^{t_m} mc_p dt + mf\Delta q + \int_{t_m}^{t_f} mc_p dt \quad (4.11)$$

$$Q_s = m[c_{ps}(t_m - t_i) + f\Delta q + c_{pl}(t_f - t_m)] \quad (4.12)$$

where t_m is the melting temperature, in $^{\circ}\text{C}$; m is the mass of PCM medium, in kg; c_{ps} is the average specific heat of the solid phase between t_i and t_m , in $\text{kJ}/(\text{kg}\cdot\text{K})$; c_{pl} is the average specific heat of the liquid phase between t_m and t_f , in $\text{J}/(\text{kg}\cdot\text{K})$; f is the melt fraction; and Δq is the latent heat of fusion, in J/kg . For example, Glauber's salt ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$) has $c_{ps} \approx 1950 \text{ J}/(\text{kg}\cdot^{\circ}\text{C})$, $c_{pl} \approx 3550 \text{ J}/(\text{kg}\cdot^{\circ}\text{C})$, and $\Delta q = 2.43 \times 10^5 \text{ J}/\text{kg}$ at 34°C .

The measurement techniques presently used for latent heat of fusion and melting temperature of PCMs are: (1) differential thermal analysis (DTA), and (2) differential scanning calorimeter (DSC) [11]. In DSC and DTA techniques, sample and reference materials are heated at constant rates. The temperature difference between them is proportional to the difference in heat flow between the two materials and the record is the DSC curve. The recommended reference material is alumina (Al_2O_3). Latent heat of fusion is calculated using the area under the peak and melting temperature is estimated by the tangent at the point of greatest slope on the face portion of the peak.

Morrison and Abdel-Khalik [12] developed a model applicable to PCMs in small containers, where the length in flow direction is L , the cross-sectional area of the material is A , and the wetted perimeter is P . The HTF passes through the storage unit in the x direction at the mass flow rate m and with inlet temperature t_{fi} .

The model can be based on three assumptions: (1) during flow, axial conduction in the fluid is negligible; (2) the Biot number is low enough that temperature gradients normal to the flow can be neglected; and (3) heat losses from the bed are negligible.

An energy balance on the material gives:

$$\frac{\partial u}{\partial \tau} = \frac{\lambda_s}{\rho_s} \frac{\partial^2 t_s}{\partial x^2} + \frac{UP}{\rho_s A} (t_f - t_s) \quad (4.13)$$

where u , t_s , λ_s , and ρ_s are the specific internal energy, temperature, thermal conductivity, and density of the PCM; t_f , U are the circulating fluid

temperature and overall heat-transfer coefficient between the fluid and PCM; and τ is the time.

An energy balance on the fluid is:

$$\frac{\partial t_f}{\partial \tau} + \frac{m}{\rho_f A_f} \frac{\partial t_f}{\partial x} = \frac{UP}{\rho_f A_f c_{p,f}} (t_s - t_f) \quad (4.14)$$

where ρ_f , A_f , and $c_{p,f}$ are the density, flow area, and specific heat of the fluid.

The equation and boundary conditions for PCM storage can be simplified for particular cases. It has been shown that axial conduction during flow is negligible, and if the fluid capacitance is small, Eqs. (4.13) and (4.14) become [10]:

$$\frac{\partial u}{\partial \Theta} = NTU(t_s - t_f) \quad (4.15)$$

$$\frac{\partial t_f}{\partial (x/L)} = NTU(t_f - t_s) \quad (4.16)$$

where ratio $\Theta = \tau m c_{p,f} / \rho_s AL$ and effectiveness $NTU = UPL / (m c_{p,f})$.

As depicted in Fig. 4.1, the phase-change process takes place in different modes: solid–solid, liquid–gas, and solid–liquid. In the first case, heat is stored by transition between different kinds of crystallization forms. For liquid–gas systems, latent heat is very high, but there are some problems in the storage control due to the high volume variations during a phase change. The most widespread are the solid–liquid PCMs that have a limited volume variation during exchange (generally less than 10%) and a fairly high melting latent heat. Melting processes involve energy densities of 100 kWh/m³ (e.g., ice) compared to a typical 25 kWh/m³ for SHS options. PCMs can be used for both short-term (daily) and long-term (seasonal) energy storages, using a variety of techniques and materials. Possible applications of PCMs are:

- implementation in gypsum board, plaster, concrete, or other wall-covering material being part of the building structure to enhance the TES capacity, with main utilization in peak-load shifting (and saving) and solar energy [13]. In this application typical operating temperature is 22–25°C but it can vary as a function of climate and heating/cooling loads;
- cold storage for cooling plants (operating temperature 5–18°C) [14];
- warm storage for heating plants (45–60°C) [15];
- hot storage for solar cooling and heating (>80°C) [16].

Any latent-heat energy storage system, therefore, possesses the following three components at least:

1. a suitable PCM with its melting point in the desired temperature range,
2. a suitable heat exchange surface, and
3. a suitable container compatible with the PCM.

4.4.1 Characteristics of PCMs

The main properties of PCMs are:

- thermophysical (latent heat of transition and thermal conductivity should be high, density and volume variation during a phase transition should be respectively high and low in order to minimize the storage volume);
- kinetic and chemical (supercooling should be limited to a few degrees, materials should have long-term chemical stability, compatibility with materials of construction, no toxicity, no fire hazard); and
- economics (low-cost and large-scale availability of the PCMs are also very important).

A large number of PCMs (organic, inorganic, and eutectic) are available in any required temperature range. PCMs are classified as different groups depending on the material nature (paraffin, fatty acids, salt hydrates, etc.) (Fig. 4.5).

Considering real applications in thermal energy store, the most widespread materials are paraffin’s (organics), hydrated salts (inorganic), and fatty acids (organics). In cold storage, ice water is quite used as well. Table 4.3 shows some of the most relevant PCMs in different temperature ranges with their melting temperature, enthalpy, and density.

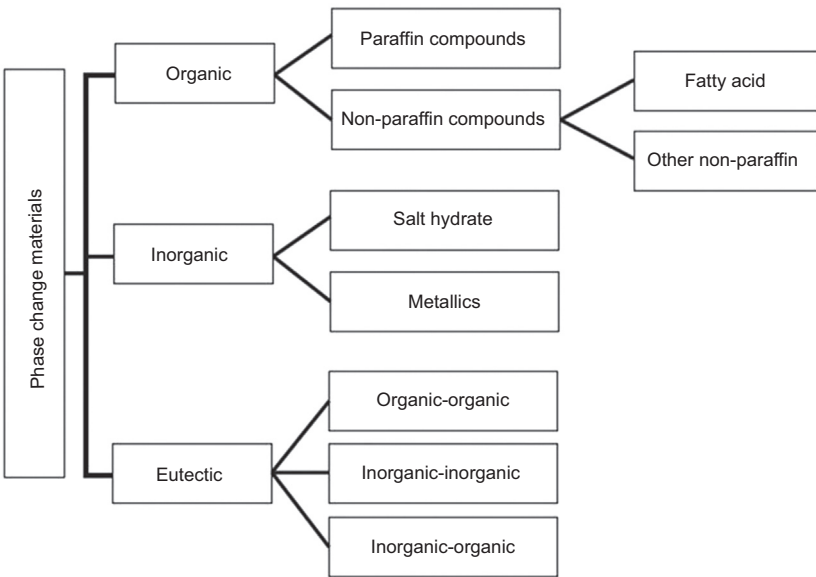


FIGURE 4.5 Classification of PCMs.

TABLE 4.3 Phase-Change Material Properties

PCM	Melting Temperature (°C)	Melting Enthalpy (kJ/kg)	Density (g/cm ³)
Ice	0	333	0.92
Na-acetate trihydrate	58	250	1.30
Paraffin	−5–120	150–240	0.77
Erythritol	118	340	1.30

4.4.1.1 Organic PCMs

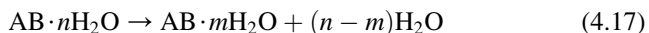
They can melt and solidify a lot of times without phase segregation and consequent degradation of their latent melting heat they crystallize with little or no supercooling and usually noncorrosiveness. The two main groups are:

- paraffin waxes: they consists of a mixture of mostly straight chain *n*-alkenes $\text{CH}_3\text{-(CH}_2\text{)-CH}_3$. The crystallization of the (CH_2) -chain releases a large amount of latent heat. Both the melting point and latent heat of fusion increase with the chain length. Due to cost consideration, however, only technical grade paraffins may be used as PCMs in LHS systems. Paraffin is safe, reliable, predictable, less expensive, noncorrosive, and available in a large temperature range (5–80°C) [17,18];
- non-paraffin organic: they are the most numerous of the PCMs with highly varied properties. A number of esters, fatty acids, alcohols, and glycols suitable for energy storage have been identified [19]. Some of the main features of these organic materials are high heat of fusion, inflammability, low thermal conductivity, low flash points, and instability at high temperatures.

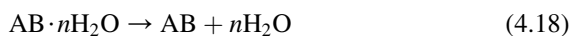
4.4.1.2 Inorganic PCMs

These PCMs do not supercool appreciably and their melting enthalpies do not degrade with cycling. The two main types are:

- salt hydrate. They are alloys of inorganic salts (AB) and *n* kmol of water forming a typical crystalline solid of general formula $\text{AB} \cdot n\text{H}_2\text{O}$ whose solid–liquid transition is actually a dehydration and hydration of the salt. A salt hydrates usually melts to either to a salt hydrate with fewer moles of water, that is,



or to its anhydrous form:



At the melting point the hydrate crystals breakup into anhydrous salt and water, or into a lower hydrate and water. One problem with most salt hydrates is that of incongruent melting caused by the fact that the released water of crystallization is not sufficient to dissolve all the solid-phase present. Due to density difference, the lower hydrate (or anhydrous salt) settles down at the bottom of the container.

Salt hydrates have been extensively studied in heat-storage applications because of their positive characteristics: high latent heat of fusion per unit volume, relatively high thermal conductivity (almost double of that of the paraffin's), and they are not very corrosive and compatible with plastics. As an example, main characteristics of some salt hydrates of the Phase Change Material Product Limited (UK) are depicted in [Table 4.4 \[20\]](#). Some relevant disadvantages are incongruent melting and supercooling, which can be tackled in different ways (adding thickening agents, by mechanical stirring, by encapsulating the PCM to reduce separation, etc.). Other problem faced with salt hydrates is the spontaneous of salt hydrates with lower number of water moles during the discharge process. Adding chemicals can prevent the nucleation of lower salt hydrates, which preferentially increases the solubility of lower salt hydrates over the original salt hydrates with higher number of water moles.

- **Metallic's:** This category includes the low melting metals and metal eutectics. They are scarcely used in heat storage applications because of their low melting enthalpy per unit weight, even if they have high melting enthalpy per unit volume and high thermal conductivity. Some of the features of these materials are as follows: (1) low heat of fusion per unit weight (2) high heat of fusion per unit volume, (3) high thermal conductivity, (4) low specific heat, and (5) relatively low vapor pressure. A list of some selected metallic's is given in [Table 4.5](#).

4.4.1.3 Eutectics

Eutectics are a minimum-melting composition of two or more components, each of which melts and freeze congruently forming a mixture of the component crystals during crystallization; eutectics nearly always melt and freeze without segregation. For this reason, they are a promising type of PCM for the future, even if actually they are less diffused than the other groups.

4.4.1.4 PCM's Containment

Containment of PCM is worth in order to contain the material in liquid and solid phases, to prevent its possible variation in chemical composition by interaction with environment, to increase its compatibility with other materials of the storage, to increase its handiness, and to provide suitable surface for heat transfer. Types of containment studied are bulk storage in tank heat exchangers, macroencapsulation, and microencapsulation. The main characteristic of PCM bulk systems is the need for a more extensive heat transfer than that found in

TABLE 4.4 Main Thermophysical Characteristics of Some Salt Hydrates

PCM Type	Phase Change Temperature (°C)	Density (kg/m ³)	Latent Heat Capacity (kJ/kg)	Volumetric Heat Capacity (MJ/m ³)	Specific Heat Capacity (kJ/(kg·K))	Thermal Conductivity (W/(m·K))
S89	89	1550	151	234	2.480	0.670
S44	44	1584	100	158	1.610	0.430
S7	7	1700	150	255	1.850	0.400

TABLE 4.5 Melting Point and Latent Heat of Fusion for Metallic's

No.	Material	Melting Point (°C)	Latent Heat (kJ/kg)
1	Gallium–gallium antimony eutectic	29.8	–
2	Gallium	30.0	80.3
3	Cerro-low eutectic	58.0	90.9
4	Bi–Cd–In eutectic	61.0	25.0
5	Cerro-bend eutectic	70.0	32.6
6	Bi–Pb–In eutectic	70.0	29.0
7	Bi–In eutectic	72.0	25.0
8	Bi–Pb eutectic	125.0	–

non-PCM tanks because the heat storage density of the PCM is higher compared to other storage media. The different approaches extensively used are inserting fins or using high conductivity particles, metal structures, fibbers in the PCM side, direct contact heat exchangers, or rolling cylinder method [21].

The two other possibilities are macro- and microencapsulating [22]. Macroencapsulating consists of including the PCM in some tube, sphere, panel, cylinder, or other, and is the most widespread. The choice of the material (plastic or metallic-aluminum or steel) and the geometry affect the thermal performance of the heat storage. Microencapsulating consists of microsphere (diameter less than 1 mm) of PCM encapsulated in a very thin and high molecular weight polymer. The spheres are then incorporated in some compatible material.

4.4.2 PCMs Used for Thermal Storage in Buildings

Storage concepts applied to the building sector have been classified as active or passive systems [23]. Passive thermal energy systems can enhance effectively the naturally available heat energy sources in order to maintain the comfort conditions in buildings and minimize the use of mechanically assisted heating or cooling systems [24].

The use of active thermal energy systems provides a high degree of control of the indoor conditions and improves the way of storing the heat energy. These systems are usually integrated in buildings to provide free cooling or to shift the thermal load from on-peak to off-peak conditions in several applications, such as DHW applications [25] or heating, ventilation, and air-conditioning (HVAC) systems [26].

4.4.2.1 Passive Technologies

The use of TES as a passive technology has the objective to provide thermal comfort with the minimum use of HVAC energy. When high thermal-mass materials are used in buildings, passive sensible storage is the technology that allows the storage of high quantity of energy, giving thermal stability inside the building. Materials typically used are rammed earth, alveolar bricks, concrete, or stone.

Standard solar walls, also known as Trombe walls, and solar water walls also use sensible storage to achieve energy savings in buildings [27]. Trombe wall (Fig. 4.6) (from the name of the French researcher that first proposed it in 1979) is a wall with high thermal capacity, shielded by a glass pane. A greenhouse effect is created, reducing thermal losses from the wall, heating the air between wall and glass that can be introduced into the room with a natural draught due to the chimney effect of the heated air.

The temperature of the wall increases as energy is absorbed, and time-dependent temperature gradients are established in the wall. Energy is lost through the glazing and is transferred from the room side of the wall to the room by radiation and convection. This storage wall can be considered as a set of N nodes connected together by a thermal network, each with a temperature and capacitance [28]. Heat is transferred by radiation across the gap and by

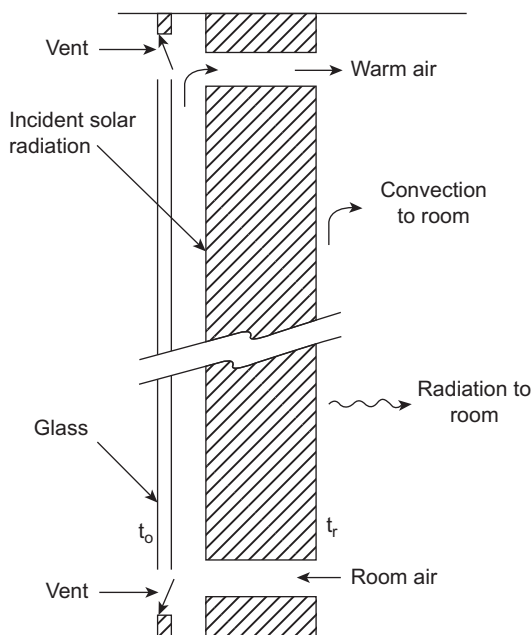


FIGURE 4.6 Schematics of a storage Trombe wall.

convection between air flowing in the gap and the absorbing surface and the inner glazing.

Energy balances are written for each node of thickness Δx , resulting in a set of ordinary differential equations with terms that represent its time-dependent temperature and energy flows to all adjacent nodes. The general energy balance for any node i in the wall is

$$\frac{dt_i}{d\tau} = \frac{\lambda}{\rho c_p \Delta x^2} (t_{i-1} + t_{i+1} - 2t_i), \quad i = 2, \dots, N - 1 \quad (4.19)$$

where λ is the thermal conductivity of wall; ρ is the wall density; c_p is the specific heat of wall; and τ is the time.

Equations for nodes one and N must take into account the node half-thickness and the convection and radiation heat transfer. The set of N equations are simultaneously solved for the time-dependent temperatures at each of the nodes, and from this the energy stored in the wall (relative to a base temperature t_{room}) can be calculated.

If there is airflow through vents and to the room, the energy added to the room by this mechanism will be $m_a c_{p,a} (t_o - t_r)$, where t_o is the outer glazing temperature and t_r is the room temperature.

PCM can be incorporated in construction materials using different methods, such as direct incorporation, immersion, encapsulation, microencapsulation, and shape-stabilization. In direct incorporation and immersion, the potential leakage has to be assessed. When the PCM is encapsulated or added in a shape-stabilized new material, a new layer appears in the construction system of the wall.

Traditionally, wallboards have been studied as one of the best options to incorporate PCM to building walls. A new approach in PCM-wallboards is the addition of an aluminum honeycomb in containing a microencapsulated PCM wallboard (Fig. 4.7) [29]. Similarly, PCM can also be impregnated or mixed with concrete or mortar [30]. One of the objectives pursued here is to maintain the concrete mechanical properties, while increasing its specific heat capacity. Another approach to incorporate PCM in building walls is to mix it with insulation materials. In masonry wall, the PCM incorporation can be, for example, within clay bricks (Fig. 4.8) [31]. In the PCM shutter concept, shutter-containing PCM is placed outside of the window areas. During day-time, when they are opened to the outside, the exterior side is exposed to solar radiation, heat is absorbed, and PCM melts. At night, we close the shutter, slide the windows and heat from the PCM radiates into the rooms.

4.4.2.2 Active Technologies

The use of TES in building active systems is an attractive and versatile solution for several applications for new or retrofitted buildings, such as the implementation of RES in the HVAC for space heating/cooling, the

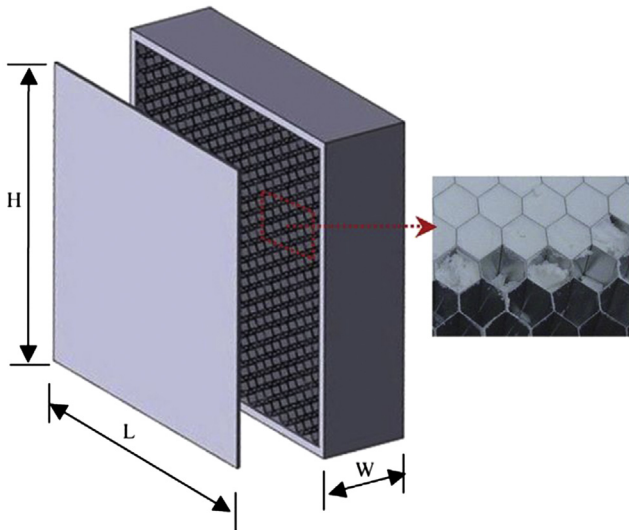


FIGURE 4.7 Microencapsulated PCM honeycomb wallboard.



FIGURE 4.8 Clay bricks including PCM macrocapsules.

improvement in the performance of the current installations or the possible application of peak load-shifting strategies [32].

The integration of the TES in the building can be done using the core of the building (core, floor, and walls), in external solar facades, in suspended ceilings, ventilation system, PV systems, and water tanks. One of the main applications of TES in active building systems is the use of free cooling, when the storage is charged with low night-outdoor temperatures and this stored cold is discharged when required by the cooling demand [33].

Furthermore, TES have been used in building the solar systems in order to convert an intermittent energy source and meet the heating and DHW demand. The most popular solar TES building systems is extended to integrate solar air collectors in building walls [34] or use PCM in ventilated facades (Fig. 4.9) [35].

Within this context, the utilization of heat pumps with TES systems are presented as a promising technology to shift electrical loads from high-peak to off-peak periods, thus serving as a powerful tool in demand-side management.

TES has a very big potential as a key technology to reduce the energy demand of buildings and/or to improve the energy efficiency of their energy systems.

4.4.3 Advantages and Disadvantages of PCMs

The main advantages and drawbacks of PCM versus water SHSs are [36]:

- the possibility to reduce the tank volume for a given amount of energy stored, that is, true only if the storage is operated in a very narrow temperature range of around the phase-transition temperature;

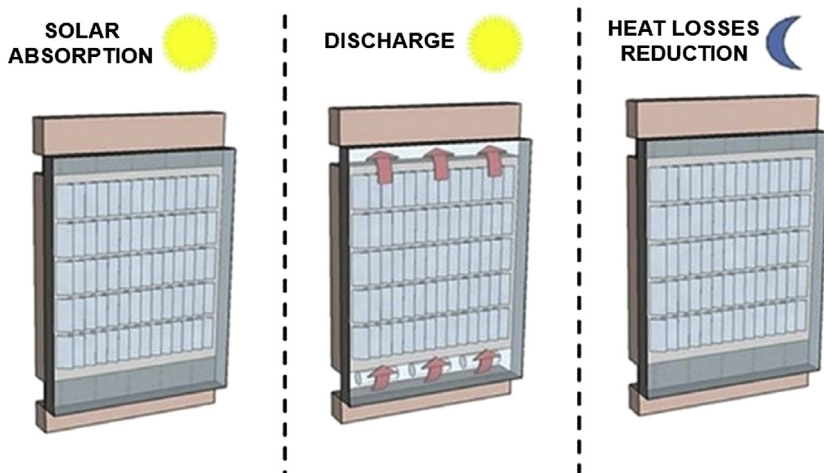


FIGURE 4.9 Operational mode of the ventilated facade with PCM.

- less on–off cycles of auxiliary heaters (for plants with storage in the hot side) and chillers (for plants with storage in the cold side);
- higher investment costs; and
- higher risks due to leak of stability and erosion of material encapsulating PCMs.

These materials make use of the latent heat between the solid- and liquid-phase changes, and must be encapsulated or stabilized for a technical use in any building system, either active or passive. This can be achieved using a direct inclusion in the wall [37], by impregnation in a porous material as gypsum [38], by using microencapsulation techniques [39], by using a shape-stabilization or slurries of PCM suspended on a thermal fluid [40]. The encapsulation is a key issue for the implementation of these technologies in the buildings and must be designed to avoid leakage and corrosion.

4.4.4 Heat Transfer in LHS Systems and Materials

The study of heat transfer characteristics of melting and solidification process is also one of the most attractive areas in the contemporary heat transfer research.

4.4.4.1 Enthalpy Formulation

By introducing an enthalpy method, the phase change problem becomes much simpler and has the following advantages: (1) the governing equation is similar to the single-phase equation; (2) there is no condition to be satisfied at the solid–liquid interface as it automatically obeys the interface condition, and (3) the enthalpy formulation allows a mushy zone between the two phases. Phase-change problems are usually solved with finite difference or finite element methods in accordance with the numerical approach. The enthalpy formulation is one of the most popular fixed-domain methods for solving the Stefan problem [17]. The major advantage is that the method does not require explicit treatment of the moving boundary.

For a phase-change process involving either melting or freezing, energy conservation can be expressed in terms of total volumetric enthalpy and temperature for constant thermophysical properties, as follows:

$$\frac{\partial H}{\partial \tau} = \nabla(\lambda_k(\nabla t)) \quad (4.20)$$

where H is the total volumetric enthalpy, in J/m^3 ; τ is the time, in s; λ_K is the thermal conductivity of phase k in PCM, in $W/(m \cdot ^\circ C)$; and t is the temperature. Total volumetric enthalpy is the sum of sensible and latent heat of the PCM, that is,

$$H(t) = h(t) + \rho_l f(t)L \quad (4.21)$$

where h is the sensible volumetric enthalpy, in J/m^3 ; ρ_l is the density of liquid PCM, in kg/m^3 ; f is the melt fraction; and L is the latent heat of fusion, in J/kg .

The sensible volumetric enthalpy has the expression

$$h = \int_{t_m}^t \rho_k c_k dt \quad (4.22)$$

where ρ_k is the density of phase k in PCM, in kg/m^3 ; c_k is the specific heat of phase k in PCM, in $\text{J}/(\text{kg} \cdot ^\circ\text{C})$; t is the temperature, in $^\circ\text{C}$; and t_m is the melting temperature, in $^\circ\text{C}$.

In the case of isothermal phase change, the liquid fraction of melt is given by

$$f = \begin{cases} 0, & \text{if } t < t_m \text{ (solid)} \\ 0 - 1, & \text{if } t = t_m \text{ (mushy)}. \\ 1, & \text{if } t > t_m \text{ (liquid)} \end{cases} \quad (4.23)$$

Following Eqs. (4.21) and (4.22), the enthalpy of PCM is

$$H = \int_{t_m}^t \rho_s c_s dt, \quad t < t_m \text{ (solid)} \quad (4.24)$$

$$H = \rho_l f L, \quad t = t_m \text{ (melting)} \quad (4.25)$$

$$H = \int_{t_m}^t \rho_l c_l dt + \rho_l L, \quad t > t_m \text{ (liquid)}. \quad (4.26)$$

Solving Eqs. (4.24)–(4.26) for the PCM temperature, one gets

$$t = \frac{t_m + H}{\rho_s c_s}, \quad H < 0 \text{ (solid)} \quad (4.27)$$

$$t = t_m, \quad 0 \leq H \leq \rho_l L \text{ (interface)} \quad (4.28)$$

$$t = \frac{t_m + (H - \rho_l L)}{\rho_l c_l}, \quad H > \rho_l L \text{ (liquid)} \quad (4.29)$$

Using Eqs. (4.21) and (4.22), an alternative form of Eq. (4.20) for a two-dimensional heat transfer in the PCM can be obtained as

$$\frac{\partial h}{\partial \tau} = \frac{\partial}{\partial x} \left(\alpha \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left(\alpha \frac{\partial h}{\partial y} \right) - \rho_l L \frac{\partial f}{\partial \tau} \quad (4.30)$$

and for the heat-exchanger container material it is

$$\frac{\partial h_f}{\partial \tau} = \frac{\partial}{\partial x} \left(\alpha_f \frac{\partial h_f}{\partial x} \right) + \frac{\partial}{\partial y} \left(\alpha_f \frac{\partial h_f}{\partial y} \right) \quad (4.31)$$

where τ is the time, in s; x and y are the space coordinates, in m; α is the diffusivity of PCM, in m^2/s ; α_f is the thermal diffusivity of container material, in m^2/s ; and h_f is the sensible volumetric enthalpy of container material, in J/m^3 .

4.4.4.2 Numerical Solution

In order to obtain the algebraic equations using the control volume technique developed by Voller [41], it was necessary to divide the domain into elementary control volumes and then integrate the equation in these control volumes. Eq. (4.30) is solved using a fully implicit finite difference method. The finite difference equation for the PCM is obtained on integrating Eq. (4.30) over each control volume. The discretization of Eq. (4.30) for $\Delta x = \Delta y$ leads to the following scheme (Fig. 4.10):

$$h_P = h_P^o + \alpha R(h_E - 4h_P + h_W + h_N + h_S) + \rho_1 L(f_P^o - f_P^k) \quad (4.32)$$

$$a_E h_E + a_W h_W + a_P h_P + a_N h_N + a_S h_S = Q \quad (4.33)$$

in which

$$a_E = a_W = a_N = a_S = -\alpha R \quad (4.34)$$

$$a_P = 1 - a_E - a_W - a_N - a_S$$

and

$$Q = h_P^o + \rho_1 L(f_P^o - f_P^k), \quad R = \frac{dt}{(dx)^2} \quad (4.35)$$

where W, E, P, N, S are the west, east, center, north and south nodes.

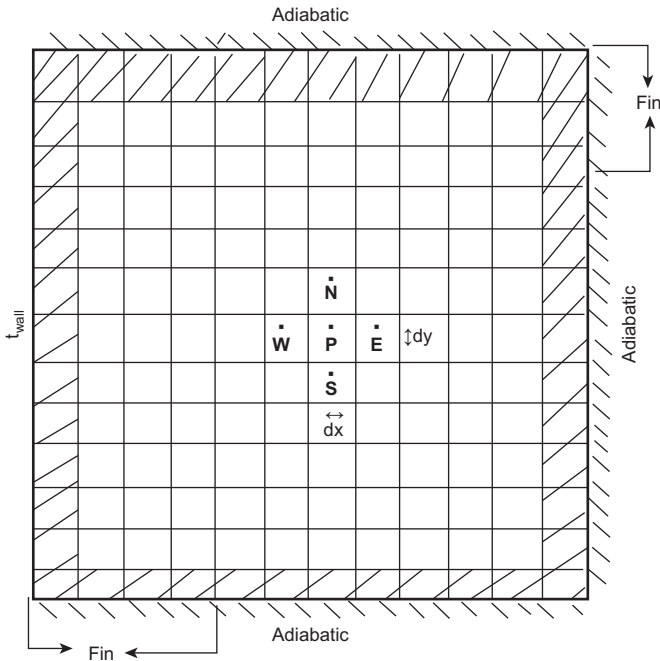


FIGURE 4.10 Two-dimensional domain.

Eq. (4.33) can be solved using a three-diagonal matrix algorithm. The central feature of the present fixed grid enthalpy method is the source term Q . Here, h_P^o and f_P^o refer to the enthalpy and the melt fraction, respectively, from the previous time step. The source term Q keeps track of the latent-heat evolution, and its driving element is the melt fraction. Its value is determined iteratively from the solution of the enthalpy equation. Hence, after the $(k + 1)$ th numerical solution of the enthalpy equation of the P th node, Eq. (4.33) may be rearranged as

$$a_P h_P = -a_E h_E - a_W h_W - a_N h_N - a_S h_S + h_P^o + \rho_1 L (f_P^o - f_P^k). \quad (4.36)$$

If a phase change is occurring about the P th node (i.e., $0 \leq f \leq 1$), the $(k + 1)$ th estimate of the melt fraction needs to be updated such that the left side of Eq. (4.36) is zero, that is,

$$0 = -a_E h_E - a_W h_W - a_N h_N - a_S h_S + h_P^o + \rho_1 L (f_P^o - f_P^k). \quad (4.37)$$

Eq. (4.37) may be rearranged as

$$f_P^{k+1} = \frac{-a_E h_E - a_W h_W - a_N h_N - a_S h_S + h_P^o}{\rho_1 L + f_P^o}. \quad (4.38)$$

The melt fraction update Eq. (4.38) is applied at every node after the $(k + 1)$ th solution of Eq. (4.33) for sensible volumetric enthalpy h , along with an under/over correction, that is,

$$f = \begin{cases} 0, & \text{if } (f)^{k+1} \leq 0 \\ 1, & \text{if } (f)^{k+1} \geq 1 \end{cases}. \quad (4.39)$$

Convergence at a given time step is declared when the difference in the total enthalpy fields falls below a given tolerance, that is,

$$\frac{|H^{k+1} - H^k|}{\rho_k c_k} \leq \varepsilon. \quad (4.40)$$

The value of ε can be set to 10^{-4} . The thermophysical properties of various heat exchanger materials [42] are given in Table 4.6.

4.4.4.3 A Three-Dimensional Heat Transfer Simulation Model of LHS

Centralized LHS system offers potential benefits in energy efficiency, in load shifting, and in emergency heating/cooling load systems. This section reports the development of a mathematical model of a centralized finned LHS for analyzing the thermal performance of melting process for both quasi-steady state and transient conjugate heat-transfer problems [43]. The developed model utilizes PCM technology that stores and retrieves energy at almost a constant temperature and is subjected to constant convective boundary

TABLE 4.6 Thermophysical Properties of Various Container Materials

Name of Material	Thermal Conductivity (W/(m·°C))	Density (kg/m ³)	Specific Heat (kJ/(kg·°C))
Glass	0.78	2700	0.840
Stainless steel	7.70	8010	0.500
Tin	64	7304	0.226
Aluminum mixed	137	2659	0.867
Aluminum	204	2707	0.896
Copper	386	8954	0.383

conditions of free air stream based on a specific ventilation air flow rate. The numerical solution is conducted using the commercial software package FLUENT-12 [44]. The numerical simulation results using paraffin RT20 are compared with available experimental data for cooling and heating of buildings.

Numerical technique is employed to simulate PCM heat transfer within a certain range of phase change temperature, which typically uses the enthalpy porosity theory to deal with solid–liquid interface. The porosity effect is found to be similar to the liquid volume fraction of the porous media at mushy region [45]. Based on multiphase flow models such as volume of fluid (VOF) method, mixture and Euler model, only VOF and solidification/melting model can be applied simultaneously.

For simplicity, the following assumptions are considered:

- The axial conduction and viscous dissipation in the fluid are negligible and are ignored.
- PCM and porous matrix material are considered homogenous and isotropic.
- The thermophysical properties of the PCM and transfer fluid are independent of temperature; however, the properties of the PCM could be different in the solid and liquid phases.
- The PCM is considered at a single mean melting temperature t_m .
- The effect of radiation heat transfer is negligible.

Governing equations. Density and dynamic viscosity of the liquid PCM depend on its temperature. The density ρ of PCM, in kg/m³, is approximated by [46]

$$\rho = \frac{\rho_1}{\phi(t - t_1) + 1} \quad (4.41)$$

where ρ_1 is the reference density of PCM at the melting temperature t_1 , and ϕ is the expansion factor. The value of $\phi = 0.001\text{K}^{-1}$ can be selected [46].

The dynamic viscosity μ of the liquid PCM, in $\text{kg}/(\text{m}\cdot\text{s})$, can be calculated using equation

$$\mu = \exp\left(-4.25 + \frac{1790}{t}\right) \quad (4.42)$$

where t is the temperature of PCM, in K.

The energy equation is written in terms of the sensible enthalpy as following:

$$h = \int_{t_{\text{ref}}}^t c_p dt \quad (4.43)$$

Or

$$\frac{\partial \rho h}{\partial x} + \text{div}(\rho \bar{u} h) = \text{div}\left(\frac{\lambda}{c_p} \text{grad } h\right) + Q_h \quad (4.44)$$

where h is the sensible enthalpy, in J/kg ; $\bar{u} = (u, v, w)$ is the velocity, in m/s ; λ is the thermal conductivity, in $\text{W}/(\text{m}\cdot\text{K})$; c_p is the specific heat at constant pressure, in $\text{J}/(\text{kg}\cdot\text{K})$; and Q_h is the latent-heat source term. In order to describe the fluid flow in the full liquid and mushy regions, the conservation equations of momentum and mass are required. In the enthalpy-porosity approach, the energy equation source term Q_h , which is accounting for the latent-heat term, could be written in the following form:

$$Q_h = \frac{\partial(\rho \Delta H)}{\partial t} + \text{div}(\rho \bar{u} \Delta H) \quad (4.45)$$

where $\Delta H = F(t)$, the latent-heat content, in J/kg , is recognized as a function F of temperature t . The value of $F(t)$ can be generalized as follows:

$$F(t) = \begin{cases} L, & t \geq t_{\text{liquid}} \\ L(1 - f_s), & t_{\text{liquid}} \geq t \geq t_{\text{solid}} \\ 0, & t < t_{\text{solid}} \end{cases} \quad (4.46)$$

where L is the latent heat of phase change, in J/kg , and f_s is the local solid fraction. Assuming a Newtonian laminar flow, the continuity and momentum equations are

$$\frac{\partial \rho}{\partial \tau} + \text{div}(\rho \bar{u}) = 0 \quad (4.47)$$

$$\frac{\partial(\rho u)}{\partial \tau} + \text{div}(\rho \bar{u} u) = \text{div}(\mu \text{grad } u) - \frac{\partial p}{\partial x} + Au \quad (4.48)$$

$$\frac{\partial(\rho v)}{\partial \tau} + \text{div}(\rho \bar{u} v) = \text{div}(\mu \text{grad } v) - \frac{\partial p}{\partial y} + Av + Q_b \quad (4.49)$$

$$\frac{\partial(\rho w)}{\partial \tau} + \operatorname{div}(\rho \bar{u} w) = \operatorname{div}(\mu \operatorname{grad} w) - \frac{\partial p}{\partial z} + A w \quad (4.50)$$

where $\bar{u} = (u, v, w)$ is the velocity, p is the effective pressure, and μ is the viscosity.

The parameter A in Eqs. (4.48)–(4.50) represents a sources term for PCM. Based on Darcy's law, Carman-Koseny [47] suggested the following equation for calculating A :

$$A = \frac{C(1 - \varepsilon)^2}{\varepsilon^3 + \omega} \quad (4.51)$$

where ε is the porosity. Value of C is related to the morphological properties of porous medium, and it is an assumed constant of 1.6×10^5 . The constant ω is used to avoid dividing over zero and is set to be 10^{-3} .

The buoyancy source term, Q_b is introduced by [45]

$$Q_b = \frac{\rho_{\text{ref}} \beta_t (h - h_{\text{ref}})}{c_p} \quad (4.52)$$

where β_t is the thermal expansion coefficient, in K^{-1} ; c_p is the specific heat, in $\text{J}/(\text{kg K})$; h_{ref} and ρ_{ref} are reference values of enthalpy, in J/kg , and density, in kg/m^3 , respectively. Darcy's law is used to describe the flow of the fluid through the porous medium as

$$\bar{u} = -\frac{k}{\mu} \operatorname{grad} p \quad (4.53)$$

where k is the permeability, which is considered as a function of the porosity.

The total enthalpy H of the PCM is the sum of sensible heat, $h = c_p t$, and latent heat ΔH as

$$H = h + \Delta H \quad (4.54)$$

The liquid fraction f can be expressed as

$$f = \begin{cases} 0 & t < t_{\text{liquid}} \\ 1 & t > t_{\text{liquid}} \\ \frac{t - t_{\text{solid}}}{t_{\text{liquid}} - t_{\text{solid}}} & t_{\text{solid}} < t < t_{\text{liquid}} \end{cases} \quad (4.55)$$

The latent-heat content of the PCM can be written in the following form

$$\Delta H = fL. \quad (4.56)$$

In the enthalpy-porosity technique, the mushy region is treated as a porous medium. For the purpose of the methodology development, it is worthwhile to

consider the whole cavity as a porous medium. In fully solidified regions, the porosity (ϵ) is set to be equal zero and takes the value $\epsilon = 1$ in fully liquid regions, while in mushy regions ϵ lies between 0 and 1. Accordingly, the flow velocity is linked to the porosity state and is defined as $u = \epsilon u_i$ where u_i is the flow velocity.

Physical model: The schematic diagram of the three-dimensional physical model of the centralized storage unit filled with PCMs is shown in Fig. 4.11. Two different fins, made of aluminum, are used to increase the thermal performance of the storage unit and are connected to the metal box from both sides of lower and upper faces. The fins on the external side of the box are to increase the exposed area for convective heat flux whilst fins inside the box are aimed at boosting the thermal conduction heat flux. The box is filled with paraffin RT20 with a melting point of 22°C, heat storage capacity of 172 kJ/kg within an operating temperature range of 11–26°C, and specific heat capacity of 1.8 and 2.4 kJ/(kg·K) for solid and liquid, respectively [48].

Paraffin RT20 is chemically stable and commercially available compared with the other materials. In addition, the phase change temperature range of paraffin RT20 is suitable to regulate the indoor air temperature within the range of the comfort condition inside the building [49]. The centralized LHTES system is integrated into a mechanical ventilation system with an advanced control unit through suitable air supply ducts for free cooling of a

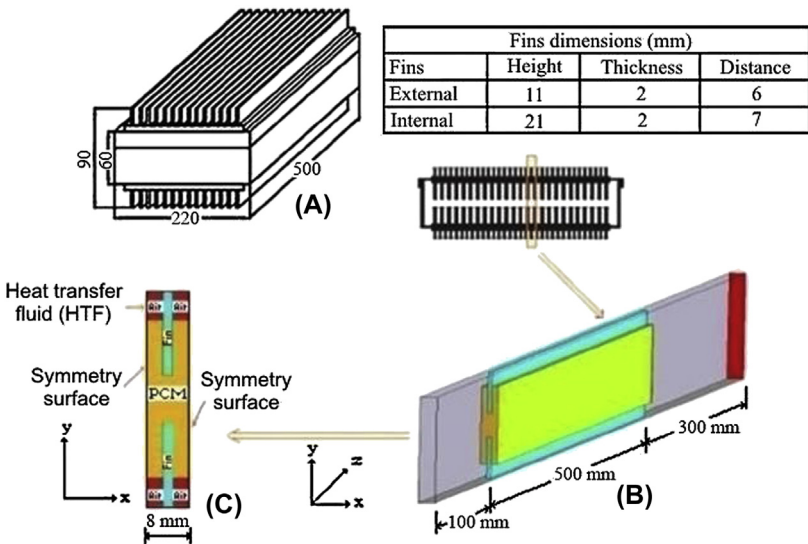


FIGURE 4.11 Geometrical configuration of LHTES. (A) schematic of LHTES system; (B) three-dimensional computational domain; (C) cross-section of computational domain.

low-energy building. Thus, the swing of indoor air temperature is stabilized during the day-time.

Model description: The three-dimensional computational domain storage unit filled with PCMs where the aluminum fins are arranged orthogonal to the axis of the unit. The HTF flows in the vicinity of such unit. The model has three zones: (1) air box with airflow around the fins and system, (2) PCM box (fluid/solid), and (3) fins box (solid).

All boxes are coupled to each other as one geometrical body. Air and PCM are coupled so that the energy transfers from air to fin and then from fin to PCM. Due to a symmetrical structure of the considered unit, the computational domain is simplified to only one symmetry unit cell in which the planes of symmetry are in the middle of the fin and are in middle between the two subsequent fins, as illustrated in Fig. 4.11.

Model validation: To verify the model, we compared the numerical simulation of evolution of fraction of melted phase with Gua and Viskanta experiment [50]. Gua and Viskanta measured the performance of a physical model in a rectangular cavity of a length of 88.9 mm and height of 63.5 mm filled with another PCM (gallium). The melting temperature of gallium is assumed to be 29.8°C. At the initial time, the left wall temperature suddenly rises to 38°C and remains constant while the temperature at the right wall was maintained constant at 28.3°C. Table 4.7 gives properties of paraffin, gallium, air, and aluminum. The model employed a single precision, unsteady solver to solve the implicit scheme of second order, time step was set to 0.2 s. The numerical solution was performed using FLUENT-12. Computational domain of two-dimensional physical model was meshed to 44×32 using GAMBIT software. Fig. 4.12 shows the solid–liquid interface positions for 2, 6, 10, and 17 min of melting process.

The numerical simulation results are in good agreement with the experimental results as presented in Fig. 4.12. The numerical model shows a great potential to predict the fluid-flow and heat transfer performances of a centralized LHS system.

4.5 CHEMICAL ENERGY STORAGE

The TCS uses thermochemical materials (TCMs) that store and release heat by a reversible endothermic/exothermic reaction process (Fig. 4.2C). During the charging process, heat is applied to the material A, resulting in a separation of two parts $B + C$. The resulting reaction products can be easily separated and stored until the discharge process is required. Then, the two parts $B + C$ are mixed at a suitable pressure and temperature conditions and energy is released.

The products B and C can be stored separately, and thermal losses from the storage units are restricted to sensible heat effects, which are usually small compared to heats of reaction.

Thermal decomposition of metal oxides for energy storage has been considered by Simmons [51]. These reactions may have the advantage that the

TABLE 4.7 Properties of Paraffin, Gallium, Air, and Aluminum Used for Calculation

Materials	ρ (kg/m ³)	λ (W/(m·K))	c_p (J/(kg·K))	t_{PCM} (°C)	L (J/kg)	μ (kg/(m·s))
Paraffin	$740/(0.001 \times (t - 293.15) + 1)$	0.15	RT20(DSC)	20–22	172.000	$0.001 \times \exp(-4.25 + 1970/t)$
Gallium	6093	32	381.5	29.78	80.160	1.81×10^{-3}
Air	$1.2 \times 10^{-5} t^2 - 0.01134 t + 3.498$	0.0242	1006.43	–	–	1.7894×10^{-5}
Aluminum	2719	2024	871	–	–	–

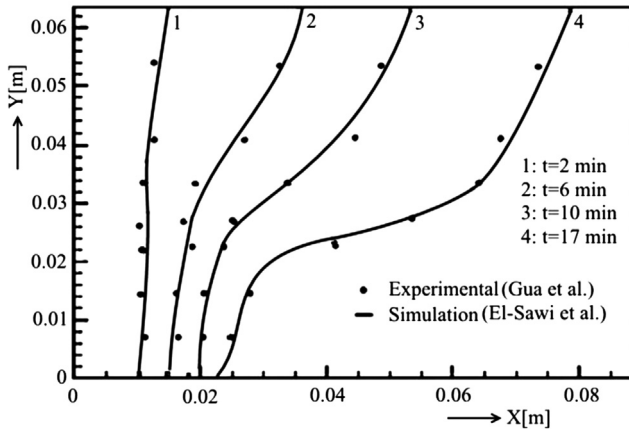
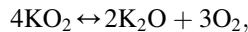
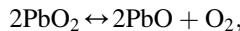


FIGURE 4.12 Comparison between experimental and numerical results.

oxygen evolved can be used for other purposes or discarded and oxygen from the atmosphere used in the reverse reactions. Two examples are the decomposition of potassium oxide



which occurs over a temperature range of 300–800°C with a heat of decomposition of 2.1 MJ/kg, and lead oxide



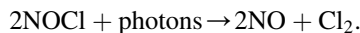
which occurs over a temperature range of 300–350°C with a heat of decomposition of 0.26 MJ/kg. There are many practical problems yet to be faced in the use of these reactions.

Energy storage by thermal decomposition of $\text{Ca}(\text{OH})_2$ has been extensively studied by Fujii et al. [52]. The reaction is $\text{Ca}(\text{OH})_2 \leftrightarrow \text{CaO} + \text{H}_2\text{O}$. The forward reaction will proceed at temperatures above about 450°C; the rates of reaction can be enhanced by the addition of zinc or aluminum. The product CaO is stored in the absence of water. The reverse exothermic reaction proceeds easily.

An example of a photochemical decomposition reaction is the decomposition of nitrosyl chloride, which can be written as



The atomic chlorine produced forms chlorine gas, Cl_2 , with the release of a substantial part of the energy added to the NOCl in decomposition. Thus, the overall reaction is



The reverse reaction can be carried out to recover part of the energy of the photons entering the reaction.

TABLE 4.8 Some Chemical Reactions for Thermal Energy Storage

Reaction		Temperature (°C)	Energy Density (kJ/kg)
Methane steam reforming	$\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2$	480–1195	6053
Ammonia dissociation	$2\text{NH}_3 = \text{N}_2 + 3\text{H}_2$	400–500	3940
Thermal dehydrogenation of metal hydrides	$\text{MgH}_2 = \text{Mg} + \text{H}_2$	200–500	3079 (heat) 9000 (H ₂)
Dehydration of metal hydroxides	$\text{Ca(OH)}_2 = \text{CaO} + \text{H}_2\text{O}$	402–572	1415
Catalytic dissociation	$\text{SO}_3 = \text{SO}_2 + \frac{1}{2} \text{O}_2$	520–960	1235

Processes that produce electrical energy may have storage provided as chemical energy in electrical storage batteries or their equivalent.

Thermochemical reactions, such as adsorption (i.e., adhesion of a substance to the surface of another solid or liquid), can be used to store heat and cold, as well as to control humidity. The high storage capacity of sorption processes also allows thermal energy transportation.

Table 4.8 lists some of the most interesting chemical reactions for TES [53]. While sorption storages can only work up to temperatures of about 350°C, chemical reactions can go much higher.

4.6 COOL THERMAL ENERGY STORAGE

Cool thermal energy storage (CTES) has recently attracted increasing interest in industrial refrigeration applications, such as process cooling, food preservation, and building air-conditioning systems. CTES appears to be one of the most appropriate methods for correcting the mismatch that occurs between the supply and demand of energy. Cool energy storage requires a better insulation tank as the energy available in the cool state is expensive, compared to the heat available in a hot storage tank. Cheralathan et al. [54] investigated the performance of an industrial refrigeration system integrated with CTES. The authors have indicated significant savings in capital and operating cost, in thermal storage-integrated systems. The size of the PCM-based CTES system was also considerably reduced when compared with that of a chilled water system.

The sorption phenomenon can also be applied for TES. In that case, a heat source promotes the dissociation (endothermic process) of a working pair, whose substances can be stored separately. When they come into contact again, heat is released (exothermic process). Therefore, the energy can then be stored with virtually no loss because the heat is not stored in a sensible or latent form but rather as potential energy, as long as the substances are kept separate.

Typical applications involve adsorption of water vapor to silica-gel or zeolites (i.e., microporous crystalline alumina-silicates). Of special importance for use in hot/humid climates or confined spaces with high humidity are open sorption systems based on lithium-chloride to cool water and on zeolites to control humidity.

Adsorption TES is a promising technology that can provide an excellent solution for long-term TES in a more compact and efficient way. Solar thermal energy or waste heat from several processes can be used to regenerate the adsorbent and promote the energy storage [55].

The adsorption cycle has already been used in several research projects to promote TES. In 1990, Kaubek and Maier-Laxhuber [56] patented an adsorption apparatus to be used as an electric-heating storage, working with the zeolite/water pair and reporting a 30% savings in the energy consumption. The system can be used as an air-heating device or combined with a hot-water tank. In the first case, the adsorbent bed is heated by electric heating rods during desorption phase, regenerating the adsorbent and releasing the condensation heat into the space to be heated. In the latter case, the condensation heat is released into a water tank during the desorption phase, while the adsorption heat is transferred to the water tank through a specific closed circuit in the adsorption stage. Hauer [57] presented a seasonal adsorption TES system, working with the silica-gel/water pair (Fig. 4.13). During the summer, while the system is charging, the heat from the solar collectors is conducted to three adsorbent beds, promoting the desorption stage. In the winter, the low temperatures in the solar collector promote the evaporation of the water in the evaporators/condensers, and the heat of adsorption is released to the building heating system.

Schwamberger et al. [58] performed a simulation study of a new cycle concept for the adsorption heat pumps operating with the zeolite/water pair (Fig. 4.14). This cycle makes use of stratified TES to improve the internal heat recovery between the adsorption and desorption phases of the cycle. During the adsorption phase, the heat of adsorption is carried away by cooler HTF from the adsorber to the storage tank, entering at a height corresponding to its temperature. During the desorption phase, the adsorber is heated by supplying warm fluid from the storage tank, while the cooler fluid returning from the adsorber is stored in the storage tank. An external heat source helps to preserve the stratification effect in the tank. The heat rejected in the condenser and in an external heat sink can be used for space heating.

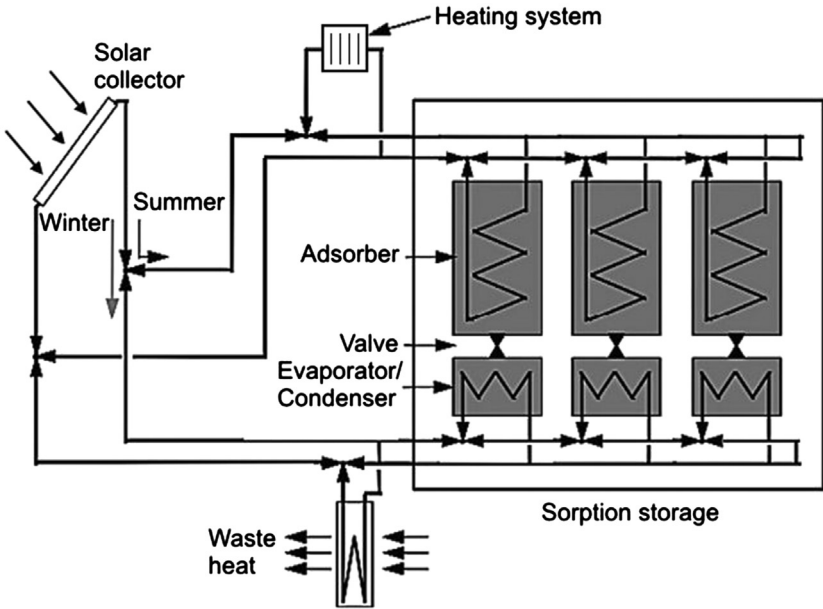


FIGURE 4.13 Seasonal adsorption thermal storage system.

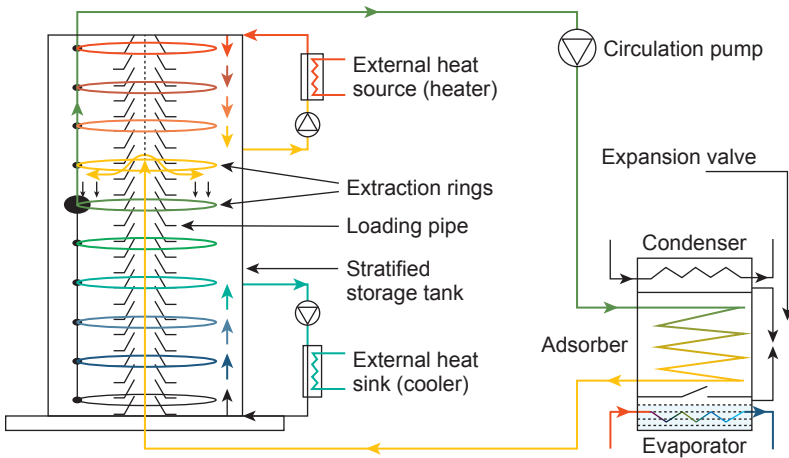


FIGURE 4.14 Schematic of an adsorption heat pump working with the zeolite/water pair.

A cascade storage system offers vast potential for the improvement of a solar cooling-system performance. In a cascaded storage system, PCMs with different melting temperatures are arranged in a series to store heat in different temperatures. In comparison with a conventional single PCM-based storage system, a cascaded multiple PCM-based storage system would improve solar

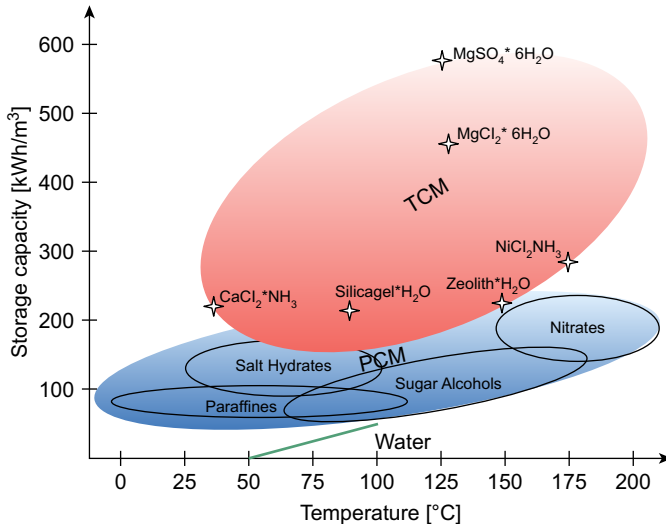


FIGURE 4.15 Storage capacity depending on temperature for TES.

collecting efficiency as the lower temperature at the bottom of the tank is connected to the inlet of the solar collector. The numerical results from the parametric study investigated by Shaikh and Lafdi [59] indicated that the total energy charged rate can be significantly enhanced by using composite PCMs as compared to the single PCM.

Fig. 4.15 shows the different TES technologies: sensible heat (i.e., water as an example); latent heat (i.e., different materials); and thermochemical (i.e., sorption and chemical reactions).

4.7 PERFORMANCE AND COST OF THERMAL ENERGY STORAGE SYSTEMS

TES includes a number of different technologies, each one with its own specific performance, application and cost.

Important fields of application for TES systems are in the building sector (e.g., DHW, space heating, and air-conditioning) and in the industrial sector (e.g., process heat and cold). TES systems can be installed as either centralized plants or distributed devices. Centralized plants are designed to store waste heat from large industrial processes, conventional power plants, combined heat and power plants, and from renewable power plants, such as CSP. Their power capacity ranges typically from hundreds of kW to several MW. Distributed devices are usually buffer storage systems to accumulate solar heat to be used for domestic and commercial buildings (e.g., hot water, heating, and appliances). Distributed systems are mostly in the range of a few to tens of kW.

TES systems based on SHS offer a storage capacity ranging from 10 to 50 kWh/t and storage efficiencies between 50 and 90%, depending on the specific heat of the storage medium and thermal insulation technologies. PCMs can offer higher storage capacity and storage efficiencies from 75 to 90%. In most cases, storage is based on a solid–liquid phase change with energy densities of 100 kWh/m³ (e.g., ice). TCS systems can reach storage capacities of up to 250 kWh/t with operation temperatures of more than 300°C and efficiencies from 75% to nearly 100%. The cost of a complete system for SHS ranges between 0.1 and 10 €/kWh, depending on the size, application, and thermal insulation technology. The costs for PCM and TCS systems are in general higher. In these systems, major costs are associated with the heat (and mass) transfer technology, which has to be installed to achieve a sufficient charging/discharging power. Costs of LHS systems based on PCMs range between 10 and 50 €/kWh while TCS costs are estimated to range between 8 and 100 €/kWh. The economic viability of a TES depends heavily on application and operation needs, including the number and frequency of the storage cycles.

Costs estimated of TES systems include storage materials, technical equipment for charging and discharging, and operation costs.

TES systems for sensible heat are rather inexpensive as they consist basically of a simple tank for the storage medium and the equipment to charge/discharge. Storage medium (e.g., water, soil, rocks, concrete, or molten salts) are usually relatively cheap. However, the container of the storage material requires effective thermal insulation, which may be an important element of the TES cost.

In the case of UTES systems, boreholes and heat exchangers to activate the underground storage are the most important cost elements. Specific costs range from 0.1 to 10 €/kWh [2] and depend heavily on local conditions.

PCM storage and TCS systems are significantly more complex and expensive than the storage systems for sensible heat. In most cases (e.g., thermochemical reactors), they use enhanced heat and mass transfer technologies to achieve the required performance in terms of storage capacity and power, and the cost of the equipment is much higher than the cost for the storage material. The cost of systems using expensive microencapsulated PCMs, which avoid the use of heat exchange surfaces, can be even higher.

The difference between the pure PCM and the complete TES system is even higher for active PCM installations. As an example, the costs of a calcium-chloride storage for the heat rejected from a thermally driven absorption chiller includes the cost of calcium chloride, which is rather inexpensive (0.3 €/kg) and the cost of a container, heat exchanger, and other components that is around 65 €/kWh [2].

Materials for TCS are also expensive as they have to be prepared (e.g., pelletized or layered over supporting structures). Also expensive are the containers and the auxiliary TCS equipment for both heat and mass transfer

during energy charging and discharging. TCS systems can be operated as either open systems (i.e., basically packed beds of pellets at ambient pressure) or closed systems. Open systems are often the cheapest option while closed systems need sophisticated heat exchangers.

The overall economic evaluation of a TES system depends significantly on the specific application and operation needs, including the number and frequency of storage cycles.

TES technologies face some barriers to market entry and cost is a key issue. Other barriers relate to material properties and stability, in particular for TCS. Each storage application needs a specific TES design to fit specific boundary conditions and requirements. R&D activities focus on all TES technologies.

TES market development and penetration varies considerably, depending on the application fields and regions. Thus, TES potential for cogeneration and district heating in Europe is associated with the building stock. The implementation rate of cogeneration is 10.2%, while the implementation of TES in these systems is assumed to be 15%. As far as TES for power applications is concerned, a driving sector is the CSP where almost all new power plants in operation or under construction are equipped with TES systems, mostly based on molten salt. This is perhaps the most important development filed for large, centralized TES installations.

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