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# Seasonal Solar Thermal Energy Storage

*Getu Hailu*

## Abstract

Solar intermittency is a major problem, and there is a need and great interest in developing a means of storing solar energy for later use when solar radiation is not available. Thermal energy storage (TES) is a technology that is used to balance the mismatch in demand and supply for heating and/or cooling. Solar thermal energy storage is used in many applications: buildings, concentrating solar power plants and industrial processes. Solar thermal water heaters capable of heating water during the day and storing the heated water for evening use are common. TES improves system performance by smoothing supply and demand and temperature fluctuations. Thermal energy storage has become a fast-growing business. According to a research report, the global thermal energy storage market is expected to reach USD 12.50 billion by 2025. The chapter describes different types of thermal energy storage systems. Brief history, current state of research and the future of thermal storage are presented. Types of thermal storages, classifications, advantages and disadvantages are discussed; important thermal and physical properties are tabulated. Advances in enhancement of thermal properties of materials are briefly discussed. Challenges, opportunities, market outlook, government incentives and policies that support deployment of energy storage systems are outlined.

**Keywords:** thermal energy storage, sensible heat storage, latent heat storage, phase change materials (PCM), energy storage

## 1. Introduction

Solar thermal energy storage is not a new concept. Early humans had realized the abundance of solar energy and devised many methods of capturing that energy. The Greek historian Xenophon wrote of the teachings of Socrates on how to orient a building as to keep it warm in the winter and cool in the summer. Romans would place many windows on a bath houses' south wall to provide heating for their baths and reduce the fuel needed for their hypocaust, or bath fire. Native Americans in the canyons of Arizona used the southern cliff exposure of a canyon to heat their adobe buildings cleverly placed in caves just so that the low winter Sun angle would soak them with sunlight while the summer angle would be higher and therefore missing the buildings [1].

Thermal energy storage dates to the times when humans lived in natural caves. Caves are warm in winter and cold in summer when compared to the outside temperature. Cave dwellers took advantage of deep underground caves (deep underground structures), which have almost negligible temperature variations with

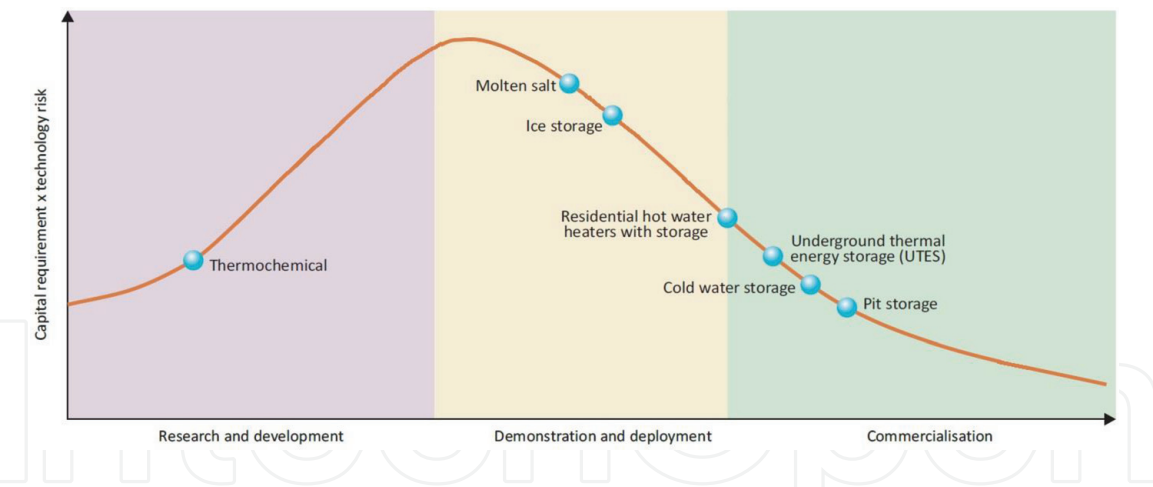
season. Historical records show that the oldest form of thermal energy storage is harvesting ice and snow for food preservation, cold drinks and space cooling [2]. Historical records also show that Romans, Greeks and Chinese explored the use of curved mirrors to concentrate the Sun's rays that could cause flames and explosion. According to a Greek legend, in 212 B.C., Archimedes used mirrors to focus sunlight on ships of an invading Roman fleet at Syracuse and destroyed the fleet [3].

In 1767, a French-Swiss scientist Horace Benedict de Saussure built the first solar heat trapper that could be used for cooking [4]. More than 100 years later, in 1876, Adams invented the first mass-produced solar thermal device, by adding solar energy concentrator to de Saussure's solar heat trapper [5, 6]. Adams' octagonal solar oven equipped with eight solar concentrators (mirrors), reportedly cooked rations for seven soldiers in 2 h. Adams reported, "The rations of seven soldiers, consisting of meat and vegetables, are thoroughly cooked by it in two hours, in January, the coldest month of the year in Bombay, and the men declare the food to be cooked much better than in the ordinary manner." His solar oven was mass produced in India and became quite popular. In the United States, the Adams' solar oven had become a popular product for camping and an educational device for teenage students [3, 6]. Cooking for soldiers using solar oven was also a concept a French mathematician Mouchot investigated. A year after Adams' invention, in 1877, Mouchot devised solar cookers for French soldiers in Algeria, including a shiny metal cone, made from a 105.5° section of a circle. He built a separate cooker to steam vegetables and wrote the first book on Solar Energy and its industrial applications [7]. Wang Xiping, a participant of the First World Conference in Solar Cooking, held in Stockton, California, in 1992, presented the use of solar cooking in China, with Peking duck roasted in Xiao's Duck Shop, Chengdu, China, in 1894 [8].

Clarence Kemp was credited with the first commercially available solar water heater patented in 1891 called "Climax" [9]. The invention of the Climax led to a brief explosion in solar thermal technologies. William Baily in 1909 developed a solar water heater called the "Day and Night," where the heater is separated from an insulated tank to extend the duration of available hot water [9]. The first commercial solar power unit produced steam and was built in Egypt in 1913, with its energy cost being compared to coal at the time [10]. However, these earlier technologies relied on the daily solar cycles and could only be used in climates where ambient temperatures remained above freezing.

Thermal energy storage has now become a fast-growing business. "I expect thermal will be bigger than batteries," said Ice Energy CEO Mike Hopkins, "because thermal loads are the large loads. They are the problematic loads; they are the loads that don't lend themselves to using electrical storage." [11]. Today, most of the thermal energy storage technologies have either been fully developed and commercialized or are in the demonstration and development stage. **Figure 1** shows stages of different thermal storage technologies. In **Figure 1**, some key technologies are displayed with respect to their associated initial capital investment requirements and technology risk versus their current phase of development (i.e., R & D, demonstration and deployment or commercialization phases) [12].

Current research and development of thermal energy storage is mainly focused on reducing the costs of high-density storage, including thermochemical process and phase-change material (PCM) development [12]. Thermal storage systems have found applications worldwide. For example, cold-water storage tanks have been installed around the world to supply cooling capacity in commercial and industrial settings. In Canada, Germany, the Netherlands and Sweden, borehole and aquifer thermal energy storages provide both heating and cooling. In the United States, an estimated 1 GW of ice storage has been deployed to reduce peak energy consumption in areas with high numbers of cooling-degree days [13]. Borehole and aquifer



**Figure 1.**  
*Maturity of thermal energy storage technologies [12].*

systems have been successfully deployed on a commercial scale to provide heating capacity in the Netherlands, Norway and Canada. The Drake Landing Solar Community in Okotoks, Canada is the first major implementation of borehole seasonal thermal energy storage in district heating in North America. It is also the first system of this type designed to supply more than 90% space heating with solar energy and the first operating in such a cold climate [14].

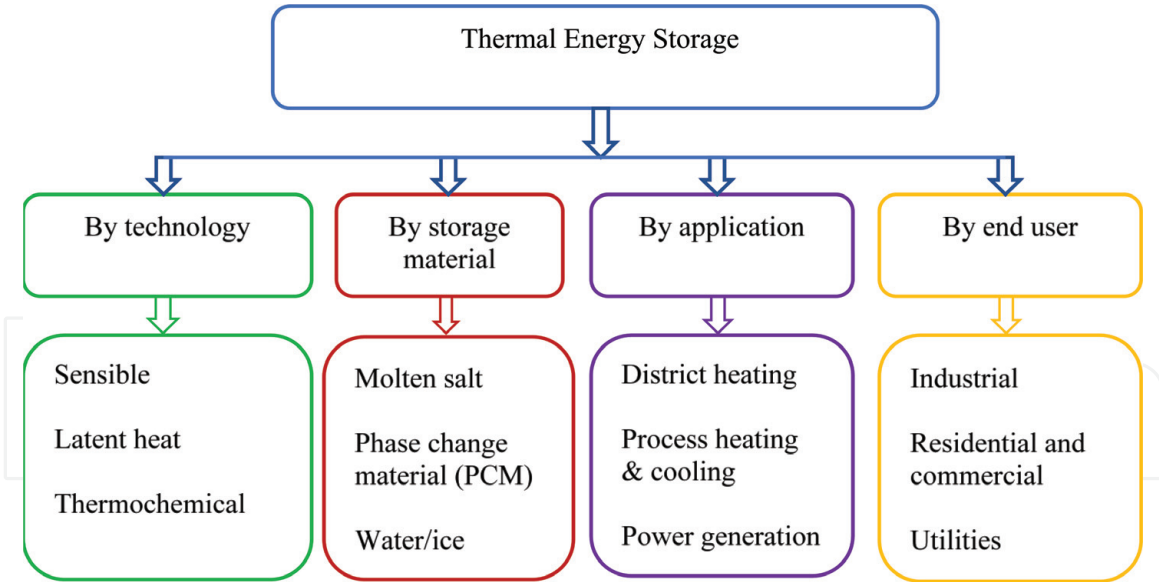
Thermochemical storage, in which reversible chemical reactions are used to store cooling capacity in the form of chemical compounds, is currently a focus in thermal storage R&D projects due to its ability to achieve energy storage densities of 5–20 times greater than sensible storage [12].

The focus of the following section will be on sensible and latent heat thermal storage technologies (i.e., technologies that have been fully developed and commercialized or are in the demonstration and deployment stage).

## 2. Types of thermal energy storage technology

Thermal energy storage is a technology that allows the transfer of heat and storage in a suitable medium. It is a technology that allows storage of thermal energy by heating or cooling a storage medium for a later use for either heating or cooling applications and power generation. Seasonal storage is defined as the ability to store energy for days, weeks or months to compensate for a longer term supply disruption or seasonal variability on the supply and demand sides of the energy system (e.g., storing heat in the summer for use in the winter via underground thermal energy storage systems) [12]. Advantages of using thermal energy storages include: increased overall efficiency, better reliability, better economics and less pollution of the environment (lower carbon dioxide - CO<sub>2</sub>) emissions [15]. The selection of thermal energy storage depends on the required storage duration, that is, diurnal or seasonal, economic viability, the type of energy source and operating conditions. Thermal energy storages can be classified based on the type of application, type of end user, type of technology and by the type of storage material used. **Figure 2** shows the classification in detail.

The major characteristics of a thermal energy storage system are (a) its capacity per unit volume; (b) the temperature range over which it operates, that is, the temperature at which heat is added to and removed from the system; (c) the means of addition or removal of heat and the temperature differences associated therewith; (d) temperature stratification in the storage unit; (e) the power requirements



**Figure 2.**  
Classification of thermal energy storage systems.

for addition or removal of heat; (f) the containers, tanks or other structural elements associated with the storage system; (g) the means of controlling thermal losses from the storage system and (h) its cost [16].

## 2.1 Sensible heat storage system

The most common type of thermal energy storage is sensible heat storage which utilizes both solid and liquid types of storage medium such as rock, sand, clay, earth, water and oil. In sensible heat storage change in temperature of the medium occurs, that is, the temperature is either increased or decreased. Heat is removed from the storage whenever required to satisfy a load, such as space heating or for domestic hot water. The removal of heat from the storage lowers its temperature. Although there are many possibilities of variations, sensible heat storage medium always consists of: an insulated container, heat storage medium and means for adding and removing heat.

In sensible hot heat storage systems, heat is added (i.e., the temperature is increased) to the storing medium, whereas in sensible cold storage systems, heat is removed thus lowering the temperature. In SHS system, the amount of energy stored is proportional to the difference between the storage medium's input and output temperatures, the mass of the storage medium and the medium's heat capacity [17]. The fundamental equation for calculating the amount of heat stored for sensible heat storage systems (SHS) is

$$Q = mC_p\Delta T = \rho VC_p\Delta T \quad (1)$$

where  $Q$  is the amount of heat stored [J],  $m$  is mass of the storage material [kg],  $C_p$  is specific heat of the storage material [J/kg K],  $\Delta T$  is the temperature change [°C],  $\rho$  is the density of the storage material [kg/m<sup>3</sup>] and  $V$  is the volume of the storage material [m<sup>3</sup>].

Heat loss from a sensible thermal storage is directly proportional to the temperature difference between the storage and the environment. An important consideration in sensible thermal storage systems is the rate at which heat can be released and extracted, which is a function of thermal diffusivity. Thermal conductivity,



which is material property of the thermal storage, affects charging and discharging rates of the storage. This relationship is expressed by the following equation [18].

$$\lambda = \rho C_p \alpha \tag{2}$$

where  $\lambda$  is the thermal conductivity [W/m K],  $\rho$  is the density [kg/m<sup>3</sup>],  $C_p$  is the specific heat [J/kg K] and  $\alpha$  is the thermal diffusivity [m<sup>2</sup>/s].

For a thermal energy storage system to be effective, certain requirements must be fulfilled. Requirements for the common sensible heat storage materials are high energy density (high density and specific heat) and good thermal conductivity (for residential applications usually above 0.3 W/m K). The ability of storing heat in a given container depends on the value of the quantity  $\rho C_p$ , the thermal capacity [19]. Thermal capacities of different storage materials are given in **Tables 1** and **2**. Most common sensible storage media include rocks, sand, pebbles packed in an insulated container. These materials have several advantages including non-toxicity, non-flammability and lower price. Thermal storage materials must be cheap and have good thermal capacity. **Table 3** lists low cost thermal storage materials, the cost ranging from 0.05 to 5.00 \$/kg. The only drawback of these materials is their low heat capacities, ranging from 0.56 to 1.3 kJ/(kg °C), which can make the storage unit unrealistically large [20]. For example, one of the drawbacks of rock, sand and

Material	Temperature [°C]	Density [kg m <sup>-3</sup> ]	Specific heat [J kg <sup>-1</sup> K <sup>-1</sup> ]
Clay	20	1458	879
Brick	20	1800	837
Sandstone	20	2200	712
Wood	20	700	2390
Concrete	20	2000	880
Glass	20	2710	837
Aluminum	20	2710	896
Iron	20	7900	452
Steel	20	7840	465
Gravelly earth	20	2050	1840
Magnetite	20	5177	752
Sand	20	1555	800
Rock	20	2560	879

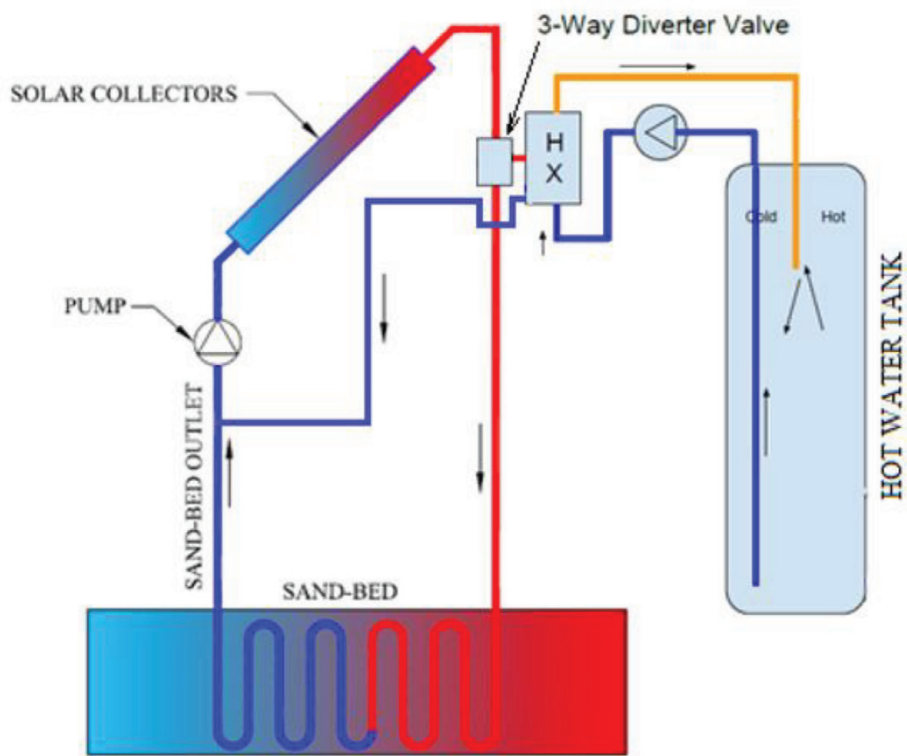
**Table 1.**  
*Thermal capacities of selected solid storage materials [19, 20].*

Material	Temperature [°C]	Fluid type	Density [kg m <sup>-3</sup> ]	Specific heat [J kg <sup>-1</sup> K <sup>-1</sup> ]
Calorie HT43	12-260	Oil	867	2200
Engine oil	≤ 160	Oil	888	1880
Ethanol	≤ 78	Organic liquid	790	2400
Propane	≤ 97	Organic liquid	800	2500
Butane	≤ 118	Organic liquid	809	2400
Isotunaol	≤ 100	Organic liquid	808	3000
Isopentanol	≤ 148	Organic liquid	831	2200
Octane	≤ 126	Organic liquid	704	2400

**Table 2.**  
*Thermal capacities of selected liquid storage materials [20].*

Material	Working temperature [°C]	Density [kg m <sup>-3</sup> ]	Specific heat [J/ kg °C]
Sand-rock minerals	200-300	1700	1.30
Reinforced concrete	200-400	2200	0.85
Cast iron	200-400	7200	0.56
NaCl	200-500	2160	0.85
Cast steel	200-700	7800	0.60
Silica fire bricks	200-700	1820	1.00
Magnesia fire bricks	200-1200	3000	1.15

**Table 3.**  
*Solid-state low-cost sensible thermal storage materials [20].*



**Figure 3.**  
*Schematic of the evacuated tube solar collectors and the thermal storage.*

pebbles is that larger amount is needed because of their lower heat storing capacity. The cost of the storage media per unit energy stored is, however, still acceptable for rocks [18].

### 2.1.1 Sensible solid heat storage system

Sensible solid heat storage media have advantages over liquids because of their higher temperature change. That is, solid thermal storages have the advantage of allowing higher temperature changes as compared to liquids. It should be noted that in sensible thermal storage, there is no phase change of the storing medium be it liquid or solid. Sensible solid storage media do not melt, therefore do not flow, hence no leakage is expected from the storage container. **Figure 3** illustrates the use of solid sensible thermal storage. The schematic shows a sand-bed thermal storage underneath a garage floor. Underneath the garage slab is the solar thermal storage which contains fine sand and pit run gravel as a thermal storage medium. The sand bed was bordered underneath with 20 cm (8") of polystyrene foam resulting in a

thermal resistivity of RSI-5.64 (US R-32) insulation barrier between the sand-bed and ground. The four sides of the sand-bed were insulated with 0.2 m (8") of polystyrene foam board on both sides of a 0.2 m (8") poured concrete foundation wall for a total of 0.4 m (16") of insulating foam. Solar collectors heat a water-glycol solution that, during normal operation, passes through a heat exchanger to heat domestic hot water tank. When the domestic hot water tank is not calling for heat, the excess heat is sent to the sand bed (thermal storage) under the garage floor for heating [21]. The system has dual purpose: heating the garage by radiation and convection and heating domestic water.

An approximate rule of thumb for sizing is to use 300–500 kg of rock per square meter of collector area for space heating applications [18]. Rock or pebble-bed storages can also be used for much higher temperatures up to 1000°C [18].

### 2.1.2 Sensible liquid heat storage system

For liquid heat storage systems, the temperature range that can be reached is limited by their boiling points. The type of liquid used as a storage medium is determined by the desired storage temperature. Water, with its high specific heat, is the most common storage medium below 100°C temperature. Cost-effective, large-scale thermal storage is possible by using naturally occurring confined underground water such as aquifers. Hot water is pumped to be stored into such aquifers, thereby displacing the existing cold ground water. This would lower the cost of the thermal storage as the only investment required is the cost of drilling openings for injecting and withdrawing water.

If water is used for higher temperature applications, (temperatures above 100°C), it must be pressurized, adding to the cost; for such a case the limitation of water is the critical point, that is, 374°C [17]. Organic liquids and high molecular weight oils are also effective at higher temperature. Although there are oils in the market, such as Terminol, which can be used without pressurization in the range of –10 to 320°C, they have the disadvantage of being of low specific heat (2.3 kJ/kg K vs. 4.19 kJ/kg K for water). In addition, oils are liable to high-temperature cracking, polymerization and formation of volatile products. The advantages and disadvantages of water as a storage medium are listed below [18].

#### Advantages:

- i. Relatively inexpensive, easily available, nontoxic and noncombustible,
- ii. Water has a comparatively high specific heat and high density,
- iii. Heat exchangers may be avoided if water is used as the heat carrier in the collector,
- iv. Simultaneous charging and discharging of the storage tank are possible and
- v. Adjustment and control of a water system are variable and flexible.

#### Disadvantages:

- i. Freezing or boiling,
- ii. Corrosive properties and
- iii. Working temperatures are limited to less than 100°C.



Eq. (3) can be used to predict water storage temperature as a function of time [20].

$$t_s = t_i + \frac{\Delta\tau}{mC_p} (Q_u - Q_L - U_s A_s (t_f - t_a)) \quad (3)$$

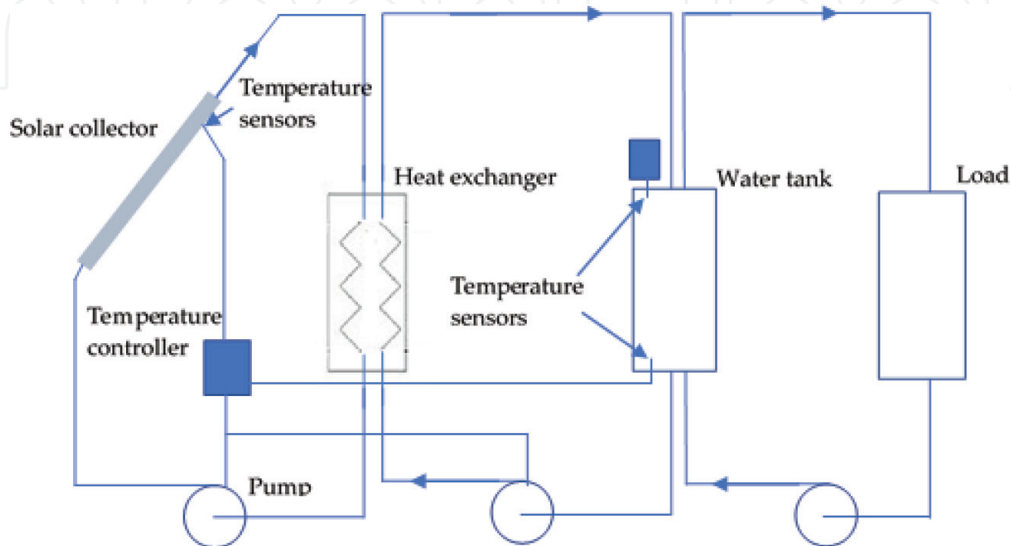
where  $Q_u$  is rate of energy addition to the thermal collector,  $Q_L$  are rate of removal of energy from the collector,  $U_s$  is the heat loss coefficient of storage tank,  $A_s$  is the storage tank surface area,  $t_f$  is the final temperature,  $t_a$  is the ambient temperature for the tank and  $\tau$  is the time.

**Figure 4** shows schematic of a typical water tank thermal storage system. In this system, a solar thermal collector supplies the input heat and a load is served by circulating hot water through the heat exchanger. In the schematic shown, the system can also be applied for domestic hot water systems since the heat exchanger prevents contamination of potable water in domestic hot water systems.

Hot water storage systems used as buffer storage for domestic hot water supply are usually in the range of 500 L to several cubic meters. This technology is also used in solar thermal installations for domestic hot water combined with building heating systems [20].

### 2.1.3 Sensible cold storage system

In sensible cold storage systems, heat is removed from the storage medium. This has the effect of lowering the temperature of the storage medium. Cold storage has the potential to save operating costs. This is possible using cheaper electricity rate during off peak hours. A cold storage may consist of cold rocks or chilled water. An air-conditioning system can benefit from heat sinks that can be used as cold storage to which heat is dumped. Coupling chillers to cold storages is a more efficient way of using them, although the initial investment cost is higher as compared to conventional air conditioning systems without cold storage. If water is used as cold storage medium, a large quantity is needed as its useful temperature is somewhat limited as compared to when it is used as sensible hot storage.



**Figure 4.**  
Schematic of a typical water thermal storage tank.

## 2.2 Latent heat storage system

Latent heat storage (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. Latent heat thermal storage system involves the storage of energy in phase change materials (PCMs). For example, when solid material melts and turns to liquid, it absorbs heat without changing its temperature. Thermal energy is stored and released with changes in the material's phase. Latent heat storage has the advantage of being compact, that is, for a given amount of heat storage, the volume of PCM is significantly less than the volume of sensible heat storage. This leads to use of less insulation material and applicability in places where space availability is a concern. Another advantage of phase change materials is that they can be applied where there is strict working temperature as the storage can work under isothermal conditions. Latent heat storage systems also have the advantage of having high storage density. Furthermore, small temperature changes in LHS result in storing large amount of heat.

A comparison of the LHS and SHS system shows that with LHS systems, about 5–10 times higher storage densities can be obtained [18]. The volume of PCM storage is two times lesser than that of water. LHS systems can also be used over a wide temperature range [18]. Phase change can be from solid to solid, from solid to liquid, from solid to gas, from liquid to gas and vice versa. When a phase change is from solid to solid, heat is stored as the material transitions from one crystalline arrangement to another. Solid-to-solid transitions have low latent heat. Solid-to-gas and liquid-to-gas transformations are associated with higher latent heat release and higher volume change; however, the large change in volume is an issue as a huge container is required making the system more complex and impractical. As a result, the most advantageous phase change is the transition from solid to liquid (small change in volume), although solid to liquid transitions have low latent heat as compared to liquid to gas. Solid-to-liquid phase change materials are cost-effective as thermal energy storage media.

Since PCMs themselves cannot be used as heat transfer media, a separate heat transfer media must be used with heat exchanger in between to transfer energy from the source to the PCM and from PCM to the load. The heat exchanger to be used must be designed specially, in view of the low thermal diffusivity of PCMs in general. Generally, it is required that the PCM container must be compatible with the PCM and be able to handle volume changes.

The storage capacity of the LHS system with a PCM medium is given by [22]:

$$Q = m(C_{sp}(T_m - T_i) + a_m \Delta h_m + C_{lp}(T_f - T_m)) \quad (4)$$

where  $a_m$  is fraction melted,  $C_{lp}$  is average specific heat between  $T_m$  and  $T_f$  [J/kg K],  $C_{sp}$  is average specific heat between  $T_i$  and  $T_m$  [kJ/kg K],  $\Delta h_m$  is heat of fusion per unit mass [J/kg],  $m$  is mass of heat storage medium [kg],  $Q$  is amount of heat stored [J],  $T_f$  is final temperature [°C],  $T_i$  is initial temperature [°C] and  $T_m$  is melting temperature [°C].

When a phase change material is heated, initially it behaves like sensible heat energy storage and there is a change in temperature. That is, at the beginning, the temperature of the PCM starts to rise (**Figure 5**). Once the phase change transition temperature is reached, the PCM continues to absorb heat without changing its temperature. The PCM starts to melt and transition from solid to liquid phase. The heat absorbed at constant temperature is called the latent heat of the phase transition. **Figure 5** shows the transition process from solid liquid. It is seen from **Figure 5** that the phase transformation process occurs at a constant temperature, and the amount of heat required to carry out the process is known as latent heat. Phase-transition enthalpy of PCMs is usually much higher (100–200 times) than sensible heat,

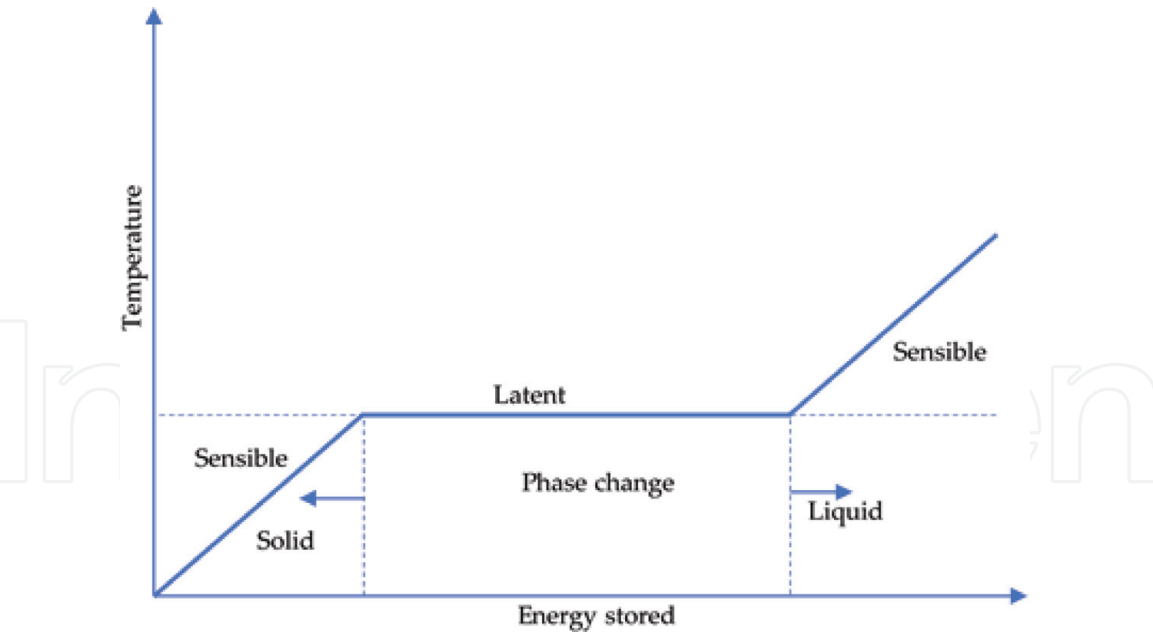


Figure 5.  
Latent energy storage for solid-liquid phase change.

Storage material	Phase change temperature [°C]	Density [kg/m³]	Latent heat [kJ/kg K]	Latent heat [MJ/m³]
RT100 (paraffin)	100	880	124	N/A
RT110 (paraffin)	112	N/A	213	N/A
E117 (inorganic)	117	1450	169	245
A164 (organic)	164	1500	306	459
NaNO <sub>3</sub>	307	2260	172	389
KNO <sub>3</sub>	333	2110	226	477
KOH	380	2044	149.7	306
AlSi <sub>12</sub>	576	2700	560	1512
MgCl <sub>2</sub>	714	2140	452	967
NaCl	800	2160	492	1063
LiF	850	N/A	N/A	1800
Na <sub>2</sub> CO <sub>3</sub>	854	2533	275.7	698
K <sub>2</sub> CO <sub>3</sub>	897	2290	235.8	540
KNO <sub>3</sub> -NaNO <sub>2</sub> -NaNO <sub>3</sub>	141	N/A	275	N/A
LiNO <sub>3</sub> -NaNO <sub>3</sub>	195	N/A	252	N/A

Table 4.  
Properties of some commercial PCM materials: organic, inorganic slats and eutectics [24, 25].

consequently latent heat storages have much higher storage density than sensible heat storages [23].

**Table 4** gives thermophysical properties of available commercial PCMs: organic, inorganic salts and eutectics. No single material can have all the required properties for an ideal thermal storage medium. Therefore, in practice, available material is used, and designers try to make up for the poor physical property by an adequate system design.

2.3 Classification of PCMs

Many phase change materials are available in any required temperature range. PCMs are generally divided into three main categories: organic PCMs, inorganic

PCMs and eutectics of organic and inorganic compounds. A detailed classification of PCMs is shown in **Figure 6**. **Figure 7** shows the typical range of melting enthalpy and melting temperature of common material classes used as PCM.

2.3.1 Organic PCMs

Organic PCMs have several characteristics which make them useful for latent heat storage. They are chemically stable than inorganic PCMs. They have been found to be compatible with and suitable for absorption into various building materials. One of the drawbacks of organic compounds is their initial cost, which is higher than inorganic PCMs [27]. However, the installed cost of organic PCMs is

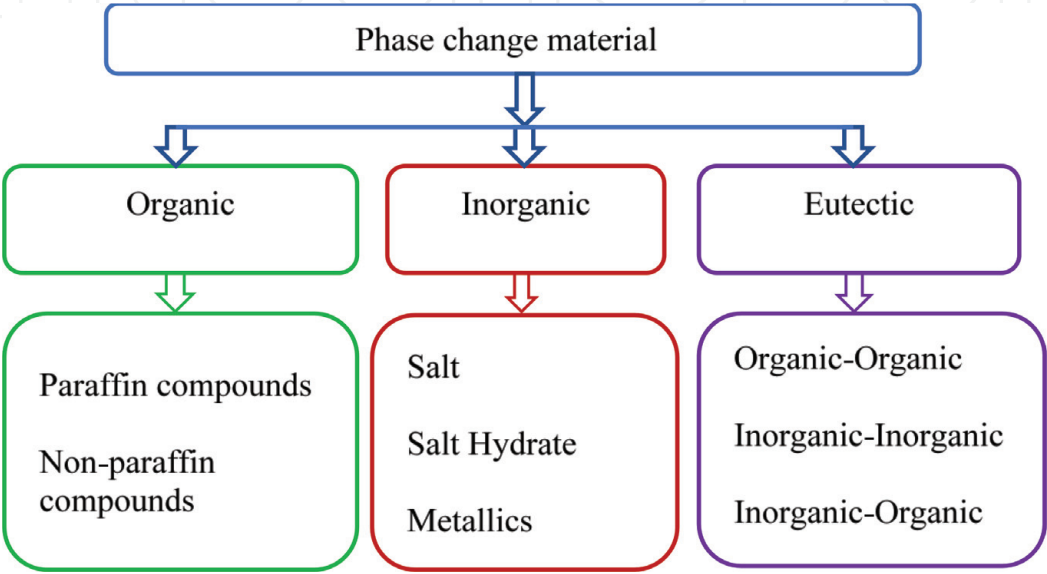


Figure 6.  
Classification of PCMs [22].

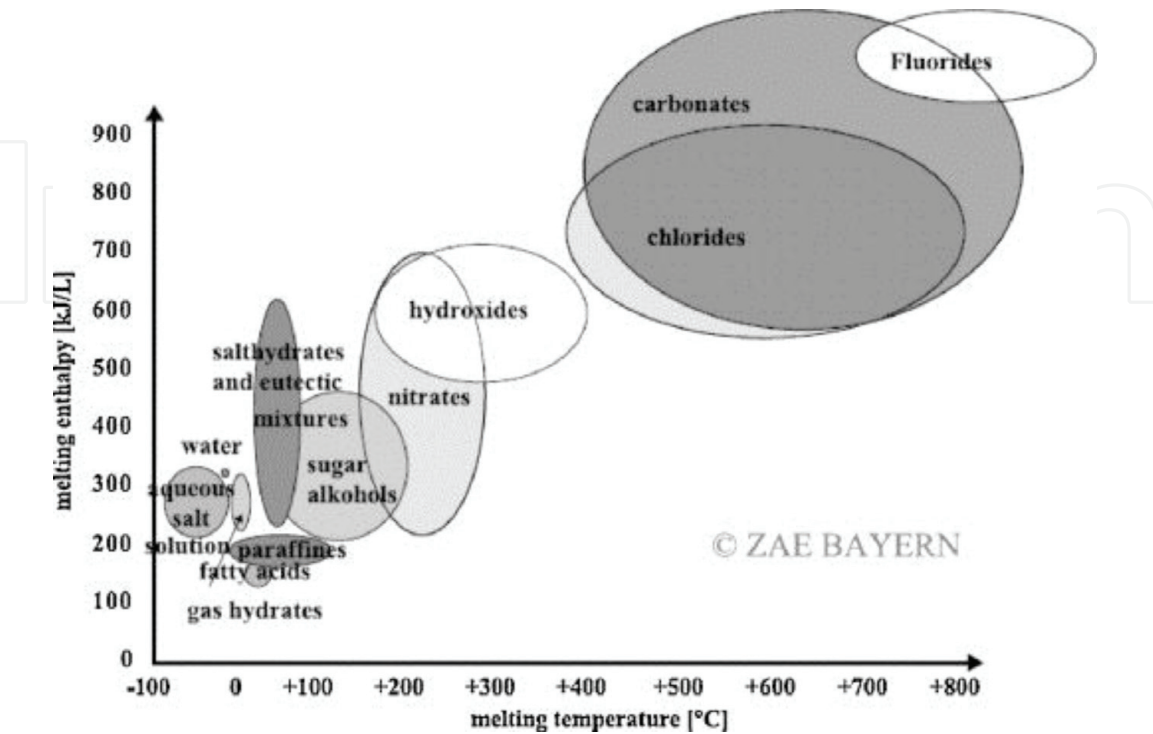


Figure 7.  
Classes of materials that can be used as PCM and their typical range of melting temperature and melting enthalpy [26].



	Organic	Inorganic
Advantages	No corrosion	Greater phase change enthalpy
	Low or non subcooling	
	Chemical and thermal stability	
Disadvantages	Lower phase change enthalpy	Subcooling
	Low thermal conductivity	Corrosion
	Flammability	Phase separation
		Phase segregation
		Lack of thermal stability

**Table 5.**  
*Comparison of organic and inorganic materials for heat storage [26, 28].*

competitive to inorganic PCMs. Organic PCMs are flammable, and they may generate harmful fumes on combustion, which is undesirable. They have also been found to react with the products of hydration in concrete. **Table 5** summarizes the advantages and disadvantages of organic and inorganic PCMs.

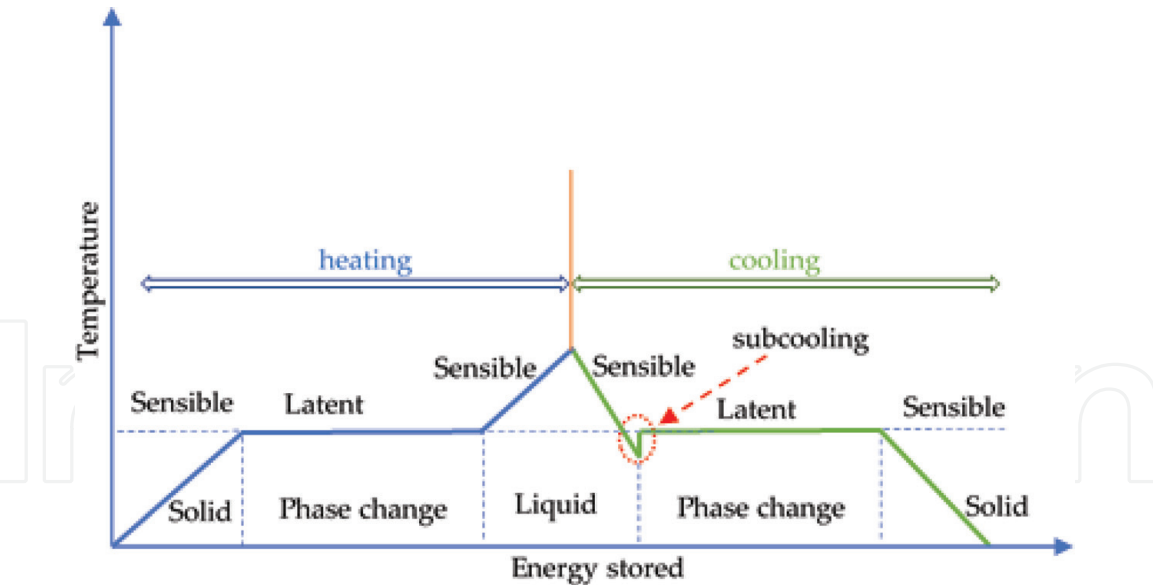
2.3.2 Inorganic PCMs

Inorganic PCMs are further classified as salts, salt hydrates and metallics. In general, inorganic PCMs have double the heat storage capacity per unit volume as compared to organic PCMs. They have a higher thermal conductivity, higher operating temperature and lower cost relative to organic phase change materials [27]. The advantages of these materials are: high latent heat values, inflammable, low-cost and availability. However, inorganic PCMs are corrosive, resulting in a short service life of the system and a higher cost [29]. Salts and salt hydrates can suffer from phase segregation and supercooling, which will reversibly affect the energy storage capacity [30]. The high storage density of salt hydrate materials is difficult to maintain and usually decreases with cycling. On the other hand, metals and metallic alloys do not suffer from phase segregation and supercooling, thus they have the potential for high temperature applications [31]. Supercooling (also called subcooling) is the process of chilling a liquid below its freezing point, without the liquid becoming a solid. This means that a temperature significantly below the melting temperature must be reached until the PCM begins to solidify and release heat. If that temperature is not reached, the PCM will not solidify at all and thus only store sensible heat [26]. **Figure 8** illustrates the process of heating/melting and cooling/solidification including subcooling.

The best-known PCM is water and it has been used for cold storage for more than 2000 years [26]. Currently, cold storage with ice is state-of-the-art. For temperatures below 0°C, usually, water-salt solutions with a eutectic composition are used [26].

2.3.3 Eutectic PCMs

Eutectic compositions are mixtures of two or more components that solidify simultaneously out of the liquid at a minimum freezing point [26]. Therefore, none of the phases can sink down due to a different density. Eutectic compositions do not segregate during melting and freezing process because they freeze to a friendly blend of crystals [32]. Supercooling is observed with many eutectic solutions [33]. Also, some eutectic solutions may be susceptible to microbiological attack; therefore, they



**Figure 8.**  
*Schematic of temperature change during melting and solidification of a PCM with subcooling (supercooling).*

must be protected with biocides [34]. It has been reported that eutectic mixtures of fatty acid-alcohol have suitable phase change temperature, high latent heat, lower price and the potential as thermal storage materials for building energy storage [35].

#### 2.4 Selection of appropriate PCM

The PCM to be used in the design of thermal storage systems should possess desirable thermophysical, kinetics and chemical properties [22]. As far as thermal properties are concerned, when selecting a PCM for a given application, the operating temperature of the heating or cooling should be matched to the transition temperature of the PCM. The latent heat should be as high as possible, especially on a volumetric basis, to minimize the physical size of the heat store. The following thermal properties need to be considered.

- i. Suitable phase-transition temperature,
- ii. High latent heat of transition and
- iii. Good heat transfer.

Phase stability during freezing/melting helps in setting heat storage. High density is desirable to achieve a smaller storage size. Small volume changes during phase transformation and small vapor pressure at operating temperatures help reduce containment issues. For these reasons, the following physical properties need to be considered:

- i. Favorable phase equilibrium,
- ii. High density,
- iii. Small volume change and
- iv. Low vapor pressure.

Supercooling has been an issue with PCM development, particularly for salt hydrates. Supercooling of more than a few degrees will interfere with proper heat extraction from the storage, and 5–10°C supercooling can prevent it entirely. Thus, the following kinetic properties need to be considered in selecting a PCM:

- i. No supercooling and
- ii. Sufficient crystallization rate.

PCMs can degrade, chemically decompose or they can be incompatible with materials of construction. PCMs should be non-toxic, nonflammable and non-explosive for safety. Chemical properties need to be considered are as follows:

- i. Long-term chemical stability,
- ii. Compatibility with materials of construction,
- iii. Non-toxicity and
- iv. No fire hazards.

In terms of economics, for PCM to be cost-effective, in general, large-scale availability of the phase change materials is very important.

### **3. Improvement of PCM thermal properties**

For PCMs to be cost-effective and efficient their thermal properties need to be enhanced. The enhancement of thermal properties such as thermal conductivity, latent heat and specific heat is important for the PCM under consideration to effectively transfer the heat and store more thermal energy during phase transition.

Thermal conductivity can be enhanced by: (1) inserting stationary metallic structure, (2) adding metallic nanoparticle, (3) by adding carbon additives such as graphite, graphene and carbon nanotubes (CNTs) and (4) by encapsulating the PCM [36]. Most of the researchers who studied insertion of stationary metallic structures focused on investigating configurations, shape, size and number of these insertions for optimization of thermal energy storage performance [37–39]. For example, in study conducted by Sheikholeslami et al. [40], fins and nano-enhanced phase change materials (NEPCM) were used as passive techniques to accelerate solidification process. They used finite element method to find the roles of radiation parameter, fin length and shape factor in minimizing solidification time. They used water as PCM and CuO as nanoparticles. They reported that using platelet nanoparticles leads to the greatest performance and that solid fraction of NEPCM radiation parameter has a direct relationship with solid fraction of NEPCM. As length of the fins increases, charging rate accelerates due to improvement in conduction mode [40]. In another study, Sheikholeslami investigated the effects of inner cylinder shape, diameter of nanoparticles and nanofluid volume fraction on solidification process of CuO nanoparticles and water mixture. They reported that adding nanoparticles could promote the PCM solidification with the optimum value of diameter for accelerating solidification being 40 nm [41].

Parameters such as varying volume fractions and percent weight of nanoparticles that enhance thermal performance (heat transfer) of thermal storage have been studied [42–44]. Carbon-based additives, namely graphite, graphene and

carbon nanotube (CNT) have attracted much attention and are one the most promising additives that can enhance the heat transfer of PCM [36]. It has been reported that the thermal conductivity of paraffin wax can be increased by saturating porous graphite matrices in paraffin [45, 46]. The low thermal conductivity of paraffins and fatty acids may also be enhanced by using thin encapsulation, maximizing the heat transfer area [47]. Encapsulation is a method of covering the PCM (that forms the core part of the encapsulated PCM) with an appropriate coating or shell material [36]. The purpose of encapsulation is to hold the liquid and/or solid phase of the PCM and keep it isolated from the surrounding, ensuring the correct composition of the PCM that would have otherwise changed due to the mixing of the PCM with the surrounding fluid [36]. Encapsulation has also the benefit of reducing the reaction of PCM with the surrounding, providing flexibility in frequent phase change processes, increasing mechanical stability of the PCM, improving the compatibility of hazardous PCMs that cannot be directly used or immersed in certain applications such as building cooling/heating systems [36]. Based on size, encapsulated PCMs can be classified as follows [48]:

- macro (above 1 mm),
- micro (0–1000  $\mu\text{m}$ ) and
- nano (0–1000 nm) encapsulated PCM.

Specific heat can be enhanced by improving crystallinity of the PCM [49, 50]. A number of studies have shown that the enhanced crystallinity of PCMs in certain composites can increase specific heat capacity of the PCM [51]. In the study conducted by [49], 26 nm  $\text{SiO}_2$  particles were added at 1% weight into a eutectic of alkali chloride salts ( $\text{BaCl}_2$ ,  $\text{NaCl}$ ,  $\text{CaCl}_2$  and  $\text{LiCl}$ ) with a melting point of  $378^\circ\text{C}$ . Addition of  $\text{SiO}_2$  resulted in an increase of the specific heat capacity of the PCM by an over 14%, as repeatedly shown by differential scanning calorimetry (DSC) measurements. Shin et al. [50] studied further the effect in detail using  $\text{SiO}_2$  particles having 2–20 nm diameter embedded in molten salt eutectic of  $\text{Li}_2\text{CO}_3$ – $\text{K}_2\text{CO}_3$ . DSC measurements showed 38–54% and 118–124% increase in specific heat for the solid and the liquid phase of these composites, respectively.

Energy storage using PCM is directly dependent on the latent heat of the material. Therefore, it is always of great interest to develop materials with higher latent heat capacity. This allows either the storage of more energy within the same material mass or the use of reduced levels for a constant energy storage need [51]. Latent heat can be enhanced by increasing the crystallinity of the PCM. Warzoha and Fleischer studied the increase in latent heat resulting from the addition of multi-wall carbon nanotubes (MWCNT), alumina or  $\text{TiO}_2$  to a base paraffin at levels of 20 vol. % concentration [52]. They found that the thermal energy that can be harnessed is 15–17% lower than the amount that can be extracted from the base paraffin during solidification; however, the thermal energy harnessed in the presence of graphene nanoparticles (15 nm thick, 15  $\mu\text{m}$  diameter at 20 vol. %) is 11% higher than that for the base paraffin.

#### 4. Challenges, opportunities and supporting policies

There are several reasons for increased deployment of energy storage technologies. The need to reduce greenhouse gas emission, the need to increase energy access and security, the need to replace aging energy infrastructure, and the need



Country/Region	Organization and overview	Type of support
Canada	<p><b>Ontario Ministry of Energy</b></p> <p>The Ontario government will include storage technologies in its energy procurement process by the end of 2014. Initially, 50 MW of storage technologies will be installed to assist with the integration of intermittent renewable generation, optimize electric grid operation, and support innovation in energy storage technologies.</p> <p>Former standard offer feed-in-tariff procurement process for renewable generation projects (&gt;500 kW) will be replaced with a competitive procurement model in Ontario. This new process will provide opportunities to consider systems that integrate energy storage with renewable energy generation.</p>	Direct mandate, market evolution
European Union	<p><b>European Commission – Framework Research Program (FP7)</b></p> <p>Co-funding (with the Intelligent Energy Europe Program) of the storE project, with the goal of creating a framework that will allow energy storage infrastructure to be developed in support of higher variable renewable energy resource penetrations. Target countries include Spain, Germany, Denmark, Austria, and Ireland.</p>	International collaboration, policy framework development
Germany	<p><b>Federal government</b></p> <p>Support of R&amp;D in the framework of the energy research program and in the framework of the “funding initiative storage”</p> <p>Financing of a website presenting progress of funded projects.</p>	Support of RD&D documentation, public information
Germany	<p><b>Federal Ministry of the Environment, Nature Conservation, and Nuclear Safety</b></p> <p>Subsidy for small-scale energy storage projects to encourage distributed energy storage deployment to complement high small-scale PV penetration (2013).</p>	Direct subsidy for distributed storage
Japan	<p><b>Ministry of Economy, Trade, and Industry (METI)</b></p> <p>Government support of energy storage projects to demonstrate the ability to time-shift demand by 10% in conjunction with expanded use of renewable generation resources. METI funding up to 75% of storage system cost with a goal of driving down total cost of USD 234/kWh within the next seven years.</p>	Support of demonstration projects, performance documentation
United States	<p><b>California Public Utilities Commission</b></p> <p>Requiring the state’s three largest utilities to invest in over 1.3 GW of new energy storage capacity by 2020.</p> <p><b>FERCs – Orders 755 and 784</b></p> <p>Taking proactive steps to open United States electricity markets to energy storage technologies</p> <p>Permitting companies other than large utilities to sell ancillary services in the electricity market</p> <p>Recognizing value of super-fast response technologies, including energy storage. Requires operators to compensate for frequency regulation based on the actual service provided.</p> <p><b>Department of Energy</b></p> <p>Global Energy Storage Database.</p>	Direct mandate, market evolution, price distortion reduction, international collaboration

**Table 6.**  
Examples of government actions that have positively supported energy storage technology deployment [12].

for decentralized energy production; all these are reasons for increased deployment of thermal energy storages. According to Grand View Research report, the global thermal energy storage market is expected to reach USD 12.50 billion by 2025 [53]. According to the report, increasing demand for access to efficient and cost competitive energy sources is expected to favor market growth. The expansion of thermal energy storage technologies is expected to be significant in Europe and Asia (particularly Japan) and somewhat lower (50%) in the United States. The global potential is estimated at approximately three times the European potential [54].

While there is great potential for thermal energy storages to be widely deployed, there are several obstacles that need to be overcome, of which the main two are cost and performance. Thermal storage market development and penetration varies considerably, depending on the application fields and regions. Penetration in the building sector is comparably slow in Europe where the construction of new buildings is around 1.3% per year and the renovation rate is around 1.5%; of course, the integration of thermal energy storage systems (TES) is easier during construction [54]. The estimate of the European potential is based on an implementation rate of TES systems in buildings of 5% [55]. Penetration could be higher in emerging countries with high rates of new buildings. TES potential for cogeneration and district heating is also 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% [18]. As far as TES for power applications is concerned, a driving sector is concentrating solar power in which almost all new power plants in operation or under construction are equipped with TES systems, mostly based on molten salt [18].

Additional obstacles are related to material properties and stability, in particular for thermochemical systems. Each storage application needs a specific TES design to fit specific boundary conditions and requirements [18]. Most of such R&D efforts on TES technologies deal with materials (i.e., storage media for different temperature ranges), containers and thermal insulation development. For complex systems such as latent heat storage and chemical storages, more R&D is required in understanding system integration and process parameters as well as improving reacting materials.

A key to achieving widespread storage technology deployment is enabling compensation for the multiple services performed across the energy system [12]. Many governments have already acted in support of energy storage project development through efforts such as direct financial support of demonstration projects, comprehensive market transformations and mandates for energy storage projects (see **Table 6**) [12].

## 5. Conclusion

Thermal energy storage (TES) is a technology that works by storing thermal energy for later use. TES can be applied for heating, cooling, power generation and industrial processes. In the building area, TES are applied for use with single family houses, multi-user buildings, large commercial buildings and district heating. Most TES research has focused on materials, such as investigating storage media for different temperature ranges, containers and thermal insulation material development. PCM and thermochemical storage systems require further R&D work, for example, in the area of improving reacting materials, gaining better understanding of system integration and process parameters.

TES technologies face some barriers, cost being the key issue. Additional barriers are associated with material properties and stability, especially the thermochemical storage systems.

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