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### Cool Thermal Energy Storage: Water and Ice to Alternative Phase Change Materials

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# **SOLID-LIQUID THERMAL ENERGY STORAGE** MODELING AND APPLICATIONS

Edited by Moghtada Mobedi Kamel Hooman Wen-Quan Tao



## Solid–Liquid Thermal Energy Storage Modeling and Applications

Edited by Moghtada Mobedi, Kamel Hooman, and Wen-Quan Tao



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### 11 Cool Thermal Energy Storage Water and Ice to Alternative Phase Change Materials

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#### 11.1 INTRODUCTION

Cold thermal energy storage (TES) dates back to ancient times when Hebrews, Greeks, and Romans gathered snow from mountains for various cooling applications. Storing "cold energy" is actually the reverse of adding heat to a material to store energy, since one removes heat from a material in order to "store" the cold. The advent of modern TES began in the mid-nineteenth century when large blocks of ice were cut from frozen lakes in colder climates and transported in insulated railroad cars to other areas. In fact, "a ton of air conditioning" gets its name from one-ton (by weight) blocks of ice measuring 4 ft×4 ft×2 ft. These blocks of ice would provide 12,000 Btu/h of cooling for 24 hours. In the early twentieth century, movie theaters were one of the first businesses to implement an early form of air conditioning by blowing a fan over a one-ton block of ice.

By the mid-twentieth century the implementation of cooling commercial buildings was ubiquitous. Electric utilities saw peak daytime demand and increased revenue due to the energy-intensive air conditioning; however, they also sought ways to increase the off-peak demand load by offering lower rates per kWh at night. This



FIGURE 11.1 Diagram illustrating peak shaving and load shifting.

practice is called peak shaving and load shifting (Figure 11.1). Although, due to regulatory policies, the peak-shifting programs had to be revenue neutral, that is, businesses were required to consume twice as much energy during off-peak times if the discounted rate was half of the peak rate. At this time, many pilot cool TES systems were borne; however, due to revenue-neutral requirements, ice-harvesting type storage systems were used [1]. Ice-harvesting systems produce ice on vertical heat transfer surfaces that operate in a cyclical manner with alternating cold and warm fluid to make ice and remove ice, respectively [2]. Many operational and maintenance issues with these dynamic systems caused the static-type ice storage systems to be the prevailing system used moving forward [1].

Like ice, eutectic salts have a long history of being used as a phase change material (PCM). One of the earliest applications of eutectic salts is not for cooling, but for heating. In the late 1800s railroad cars in Britain used this type of PCM for warming seats. Furthermore, so-called eutectic plates were used to store cold for rail and trucking transportation.

Commercial TES systems utilizing ice began to be installed by a small number of manufacturers in the early 1980s. The business grew in the late 1980s and early 1990s with dozens more manufacturers coming on board to take advantge of new demand-side management rebate incentives [3]. Cool TES systems utilizing ice and water are still growing and taking advantage of new market opportunities such as building very large district cooling (DC) systems with a cool TES system servicing multiple buildings, small-scale rooftop TES systems, and emergency backup cooling for mission-critical facilities [1]. However, the push to move ice TES systems into the residential market (or light commercial) has not been as successful with several companies recently going out of buisness [4].

Water/ice has many advantages when used as a PCM. It has an unusually high latent heat of fusion (334 kJ/kg); in fact, it has the highest latent heat among common PCMs. Furthermore, water is free. However, water is limited to a phase-change temperature of is 0°C. Although commercial heating, ventilating, and air-conditioning

(HVAC) chillers can be retrofitted to make ice, residential HVAC systems are not capable of making ice in an efficient manner, and a PCM with a higher phase-change temperature is needed. Even though ice storage works in commercial buildings, there is the potential for energy and cost savings by implementing alternative PCM (such as paraffin wax or salt hydrates) TES systems that melt and freeze at higher temperatures, saving energy and eliminating the need for a sub-zero chiller.

The goal of this chapter is to present different popular types of TES systems based on water and ice and provide an overview of alternative PCMs. Emerging alternative PCM TES systems, their implementation, challenges, and outlook will be presented.

#### 11.2 TYPES OF ICE-BASED THERMAL ENERGY STORAGE SYSTEMS

Ice-based TES systems are classified as either static, where ice is formed directly onto a surface, or dynamic, where ice is produced on the cooling surface and then removed. The majority of ice-based TES systems are of the static type. A typical ice-based TES system for peak shaving and load shifting is shown in Figure 11.2. The following sections outline static and dynamic ice-based systems.

#### **11.2.1 STATIC SYSTEMS**

Static types of ice-based TES systems involve producing an ice layer that bonds to a heat exchanger cooling surface (typically coils) in the storage tank itself. Once ice has been formed on the surface, it is available until chilled water is needed for cooling. Warm return water is cooled by the melting ice before it is returned to the building. Other static systems use an alternative fluid, like a refrigerant, that is pumped through tubes. These systems are manufactured as packaged units that are implemented into a building chilled-water system. The ice is either formed inside or



FIGURE 11.2 Ice storage tanks for off-peak load shifting.

outside of the coil. One of the downsides of static systems is that as the layer of ice on the surface increases, the thermal resistance also increases, causing the efficiency of the system to decrease.

#### 11.2.2 DYNAMIC SYSTEMS

Dynamic systems (also referred to as ice shucking or ice harvesting) make crushed ice or slurries and deliver it to a storage tank. These systems typically remove the ice layer via buoyancy [6,7] or fluid flow [8,9]. In theory, dynamic systems offer better efficiency than static systems since the ice layer does not build up, decreasing the thermal performance. Ice slurries are also advantageous because they can cool chilled water to temperatures as low as 1.1°C [5]. However, most TES systems of this type use water solutions, such as ethylene glycol/water and oil/water mixtures, to aid in the ice removal. The efficiency of the system is decreased due to the addition of other fluids into the water which lower both the freezing point and latent heat of fusion.

#### 11.2.3 STATIC VERSUS DYNAMIC SYSTEMS

Although dynamic systems offer better efficiency since the ice is cyclically removed, the cost-per-ton of removing the ice is high. Because of this, dynamic ice harvesters were typically configured on a weekly cycle where ice was made on the weekend and then was melted during the rest of the week. The systems were also very complex, which led to many operation and maintenance issues. This caused the static ice storage systems to be the prevailing TES system on the market.

#### 11.3 PHASE CHANGE MATERIALS

Generally, PCMs can be categorized as organic, inorganic, or eutectic (Figure 11.3). Organic PCMs include paraffin waxes (e.g.,  $C_nH_{2n+2}$  [10]), plant-based materials (e.g., plant fats [11]), or fatty acids (e.g., lauric acid [12]). Organic PCMs are widely used in a number of applications, including emerging TES storage systems for commercial buildings, which will be discussed later. Inorganic PCMs encompass salt hydrates (e.g., AB·*n*H<sub>2</sub>O [13]) and metals (e.g., gallium [14]). Finally, eutectics are mixtures of two or more materials that have a lower phase-change temperature than either of the individual materials (e.g., eutectic solution of polyethylene glycol [15]).



FIGURE 11.3 Classification of different types of PCMs.

Several criteria need to be evaluated before selecting a PCM for a particular application. First, materials with very latent heats of fusion  $(h_{el})$  are advantageous. The latent heat of fusion is the amount of energy absorbed or released by a material during melting or solidification, respectively. Traditionally, the latent heat of fusion is described on a per-mass basis, and water has the highest latent heat on a per-mass basis of any other common substance used as a PCM at moderate temperatures. Recently, it has become popular to describe PCMs on a per-volume basis for building applications, since space, rather than weight, is more of an issue in HVAC-related applications [16]. By describing PCMs in terms of energy storage density, often described in units kWh/m<sup>3</sup>, instead of kJ/kg as for the per-mass basis, other PCMs become more attractive when space-based issues are relevant. Water has an energy storage density of ~92 kWh/m<sup>3</sup>; however, some inorganic PCMs such as salt hydrates have energy storage densities well above 100 kWh/m<sup>3</sup>. Salt-hydrate PCMs have also been gaining popularity due to new demand for reducing the footprint of TES systems in buildings. Furthermore, although nothing can surpass pure water in terms of cost, salt hydrates are relatively inexpensive.

While salt hydrates have high energy density and low cost, they suffer from a number of disadvantages [17]. These disadvantages include incongruent melting and phase segregation, which is caused by insufficient water needed to dissolve the solid-state material. This causes less-hydrated salts to sink to the bottom, causing the phase transition to become irreversible over long periods of time. Supercooling is also a major issue in which the solidification of the material begins at a much lower temperature than its phasechange temperature. Since PCMs need to be packaged into heat exchangers, another issue that prevents wide-spread implementation is the corrosivity of salt hydrates. Furthermore, salt hydrates have limited phase-changetemperature availability, and environmental control is necessary for maintaining proper hydration of the salts if not in a sealed environment.

Although PCMs have high latent heats of fusion, they are known to have very low thermal conductivity. Materials with low thermal conductivity cannot efficiently distribute the heat. Current research focuses, perhaps too heavily, on trying to increase the thermal conductivity of PCMs through additives such as carbon fibers [18], metal and metal oxide nanoparticles [10,19], and expanded graphite [19]. Implementing additives to increase thermal conductivity can be challenging due to the inability to obtain a homogeneous mixture and the fragility of some fillers such as carbon nanotubes. Furthermore, thermal-conductivity-enhancing additives occupy space, effectively reducing the energy storage density of the composite material. The trade-off of adding particles is that there is less effective latent heat capacity.

There have been a number of attempts to quantify the trade-offs between thermal conductivity and latent heat by developing simplified figures of merit (FOM), such as the one defined by Shamberger [20], shown here.

$$FOM = \sqrt{kL_{sl}} \tag{11.1}$$

In this equation, k is the thermal conductivity h, and  $L_{sl}$  is the volumetric latent heat of fusion  $(\rho h_{sl})$ . The FOM suggests that the higher the thermal conductivity and volumetric

latent heat of fusion, the better. Of course, a material with both high thermal conductivity and capacity is desirable, but materials that are useful TES materials and are high in both properties are rare, or likely to occur in materials where the phase-change temperature range is not desirable for the intended application.

The Ragone framework has also emerged as a popular way to quantify energy versus power for TES systems [21–23]. The potential energy capacitance is material specific, as defined by its latent heat fusion, and the power is dependent on both the thermal conductivity of the material and the geometry of the heat exchanger. Many Ragone analyses focus on simplified thermal resistances and do not consider the overall geometrical configuration when assessing power capabilities. The low thermal conductivity of a particular material can be mitigated by the overall thickness of the material in the heat exchanger.

The total thermal resistance through PCM is not only a function of the conductivity of the material, it is also a function of the thickness. The thermal resistances, in W/K, for a plane wall and annulus are

$$R_{\text{wall}} = \begin{cases} \frac{t}{(kA)_w}, & \text{plane wall} \\ \frac{\ln(r_o/r_i)}{2\pi k_w L}, & \text{annulus} \end{cases}$$
(11.2)

In the equation  $k_w$  is the thermal conductivity of the material. For the plane wall, *t* is the thickness, and *A* is the area perpendicular to the heat transfer. For the annulus, *L* is the length of the pipe, and  $r_o$  and  $r_i$  are the outer and inner radii, respectively. As can be seen from Eq. (11.2), there are two ways in which to reduce the total thermal resistance through heat exchanger wall. First, the thermal conductivity can be increased; however, the same effect can be achieved by decreasing the wall thickness as seen in the application of polymer heat exchangers.

Polymer materials have been used for heat exchangers since the 1960s. The first polymer heat exchangers were in the form of flexible tube bundles made of Teflon (polytetrafluoroethylene or PTFE) [24]. In order to overcome the low thermal conductivity of the material, the diameter of the Teflon tubes was made proportional to the wall thickness. These designs took advantage of the high surface area to increase heat transfer. With the advent of additive manufacturing, polymer heat exchanger devices with very thin walls and heat-transfer-enhancing elements can be made [25–27]—making the low thermal conductivity of the material irrelevant. As shown in Figure 11.4, the total thermal resistance of a heat exchanger is dependent on the convective resistances of the fluids, the fouling, and the wall thickness. Another advantage of polymer heat exchangers is that unlike metals, they are resistant to fouling, eliminating the additional thermal resistances due to fouling on both the cold and hot side.

TES systems can also potentially take advantage of geometric design to overcome their inherently low thermal conductivity. If PCM can be 3D printed into compact high surface-area-to-volume heat exchangers, then filling PCMs with thermal



FIGURE 11.4 Schematic diagram of heat exchanger thermal resistances.

conductivity additives may no longer be necessary. Pioneering work by Freeman et al. [28–30] has shown the ability to combine PCM with polymers to additively manufacture compact TES systems.

Whereas TES systems for cooling started out utilizing large blocks of ice cut from lakes, the future of TES relies upon considering both the type of materials used and the arrangement of the materials in a TES system to achieve optimal TES density and power.

#### 11.4 PCM-BASED THERMAL ENERGY STORAGE SYSTEMS

Alternative PCM-based TES systems to replace water- and ice-based systems for cold storage are beginning to be implemented in commercial applications. While ice-based thermal energy systems have been proven to work and are cost effective, there are several disadvantages of such systems when compared to alternative PCM TES systems. First, water melts and freezes at 0°C; this requires a sub-zero ice-making chiller. Often, existing chillers are not configured for making ice. Since a PCM with a higher phase-change temperature can be chosen, a higher set-point can be used and a sub-zero chiller is not necessary, thus saving energy.

Ice TES systems usually require two separate loops. Glycol (typically at a temperature between  $-7^{\circ}$ C and  $-4^{\circ}$ C) is used to freeze the water in the TES system during off-peak hours and transfer heat to the ice during peak hours. A secondary



**FIGURE 11.5** Comparison between (a) ice storage and (b) PCM thermal energy storage systems.

loop is used to transfer heat from the glycol side to the chilled-water side and vice versa. However, PCM-based TES systems can store energy at higher temperatures and work directly with a building chilled-water system, thus eliminating the need for a separate glycol loop (see Figure 11.5).

Another issue encountered with ice-based systems is that as water expands and contracts during the phase change, it causes thermal stresses and potential problems with thermal contact of the ice and water on the heat transfer pipes. Furthermore, very large tanks are often required to handle the expansion of the water as it freezes. Most other PCMs do not expand when they solidify.

Often, upgrading existing HVAC systems to include ice TES is complex and costly. As previously stated, most existing chillers cannot make ice. Furthermore, the addition of a glycol loop with a heat exchanger also complicates matters. On the other hand, alternative PCM-based systems can be integrated more easily into existing equipment without the need to increase the capacity of the chiller or install a separate glycol flow loop.

Since the technology is nascent, only a few papers available in the open literature detail the components and techno-economic analysis of commercial-scale alternative PCM HVAC TES systems [31–34]. For reference, the technical details regarding the PCM used in each system is detailed in Table 11.1.

#### TABLE 11.1 Summary of PCMs Used in Commercial-Scale Non-Ice-Based TES Systems Found in the Literature

	Jokiel [31] (2016)	Alam et al. [32] (2019)	Saeed et al. [33] (2018)	Tan et al. [34] (2020)
Type of Study	Case Study: Bergen, Sweden	Case Study: Melbourne, Australia	Commercial-Scale Laboratory Experiment	Case Study: Gothenburg, Sweden
PCM	PCM Products Ltd. Salt Hydrate	PCM Products Ltd. Salt Hydrate	Hexadecane (C <sub>16</sub> H <sub>34</sub> )	Rubitherm Salt-Hydrate SP11
$T_{pc}$ (°C)	10	15	18.3 (melting) 15.5 (freezing)	11
$h_{sl}$ (kJ/kg)	170	160	238.4 (melting) 234.5 (freezing)	155
$\rho$ (kg/m <sup>3</sup> )	1470	1510	828 (solid) 775 (liquid)	1330 (solid) 1320 (liquid)
$c_p (J/kg \cdot K)$	1900	1900	1925 (solid) 2350 (liquid)	2000
k (W/m·K)	0.43	0.43	0.295 (solid) 0.152 (liquid)	0.6

#### 11.4.1 COMMERCIAL-SCALE PCM TES SYSTEMS

In 2016, the performance of a salt-hydrate-based TES system at the University College of Bergen in Norway was modeled and compared to manufacturer performance data sheets [31]. The TES system at the University College of Bergen, which is the largest system of its kind in Europe, comprises very large tanks filled with containers called FlatICE (PCM Products Ltd., Yaxley, Cambridgeshire, UK) comprising salt-hydrate-based PCM. The projected annual cooling demand for the educational building on campus is 1060 MWh, and the size of the cooling system is reduced through use of the TES system (e.g., the chillers provide 1400kW for the entire day, although the peak cooling-load demand is 3000kW). The PCM storage tanks, with a total volume of 228 m<sup>3</sup> and a total TES capacity of 11,200 kWh, have the potential to reduce the chiller load by up to 50%.

After developing a lumped model to analyze the TES, Jokiel [31] determined that while the maximum cooling capacity of 11,200 kWh could be reached when the discharge time was sufficiently long, it was unable to be realized under normal night-time (charging) and daytime (discharging) cycles, and the tanks were oversized for the current mode of operation. Jokiel [31] also pointed out a number of disadvantages of such a system. Since the PCM containers are horizontally aligned, due to natural convection, the heat transfer is higher on the bottom than the top during melting. Furthermore, since a salt hydrate is utilized, subcooling occurs and the long-term efficacy of the PCM is not known.

Alam et al. [32] analyzed the energy savings of an inorganic hydrated-salt PCM TES system designed to minimize the daytime cooling load on the chiller for an 11-story building in Melbourne, Australia. Active and passive chilled beams are used to supply the required cooling and heating load, and the chilled beams are served by a secondary chilled-water system. The insulated PCM tanks are 40m<sup>3</sup> in volume. The TES system also was made of 5120 FlatICE panels, stacked in layers, totaling 15,360kg of PCM (PCM Products Ltd., Yaxley, Cambridgeshire, UK, same supplier as [31]) encapsulated in HDPE. In this system, water is used (as opposed to glycol) as the heat transfer fluid. It utilizes free cold air during the night to reduce the peak demand during the day. More technically, if there is no cooling call from the building, and ambient temperatures are less than 11°C, then charging of the PCM is activated. Similarly, charging is deactivated if the building calls for cooling, the ambient temperature rises above 11°C, or when the temperature exiting the PCM heat exchanger falls below 13°C for 5 minutes. When discharging the tank during daytime hours, the system takes advantage of PCM cooling until the outlet temperature of the fluid flowing through the PCM is 14°C.

They found that only 15% of the theoretical thermal storage capacity was used. One reason for the poor performance was possibly due to supercooling, which is a known issue with salt hydrates. Interestingly enough, the PCM tank was essentially useless during the summer months (when cooling demand is highest) because the nighttime ambient temperature was not cold enough to charge the PCM. Furthermore, the energy consumed by the pumps utilized in the TES charging and discharging was higher than the actual energy stored in the PCM. The authors of [32] highlight the issue of the difference between the design of the TES tank versus the actual performance of the TES tank.

Saeed et al. [33] designed a plate-type heat exchanger TES tank utilizing hexadecane (Sigma-Aldrich, St. Louis, MO, 99% purity) as the PCM. The investigators in [33] emphasize that the single most important factor in designing PCM TES systems is the heat exchanger geometry. In other words, the device must be compact and comprise thin slabs of PCM. Alternative methods of trying to increase thermal response, such as additives decrease performance, as shown by Marín et al. [35] who added PCM to a porous matrix for the purposes of increasing the thermal conductivity, but then observed a 20% reduction in TES density.

The hexadecane TES system had a net latent heat capacity of 114 MJ and had a volume of 1.5 m<sup>3</sup> and a mass of 480 kg. The performance of the commercial-scale TES system was tested in the laboratory. Inlet temperatures between 45°F (7.2°C) and 55°C (12.8°F) were used to "freeze" the PCM, which had a phase-change temperature of 18°C. Inlet temperatures between 75°F (23.9°C) and 95°F (35.0°C), mimicking uncooled-air conditions, were tested in discharging the PCM TES. Heat exchanger fluid circulated. The authors also noted that due to the aluminum material and very close spacing between aluminum sheets, fouling may result. Overall, they concluded that the latent heat system had the potential to deliver cost savings compared to ice storage systems; however, the TES unit was not tested in a real-life building environment.

Tan et al. [34] performed a techno-economic assessment of a multi-story office building on the Chalmers University of Technology Campus Johanneberg in Gothenburg, Sweden. The air-handling unit (AHU) uses water at  $T=12^{\circ}$ C from a

district cooling system to cool down 16°C return-air flow from the AHU. The system includes a commercial salt-hydrate PCM TES system that is connected by two heat exchangers to the district cooling and the AHU. A direct connection of the PCM TES unit to the district cooling and the AHU was not implemented due to the potential contamination if the PCM leaks. Water at 8°C from the district cooling is used to charge the PCM TES system. Water between 14°C and 16°C is used to discharge the system, and dependent on the cooling load, a fraction of the return air flows through the heat exchanger attached to the PCM TES unit. The storage outlet temperature can vary between 8°C and 16°C during a complete discharge or charge cycle.

The actual PCM TES tank consists of a rectangular steel tank of volume 11.2 m<sup>3</sup>. The inside of the tank is filled to a height of 1.6 m with 9380kg of Rubitherm SP11 salt hydrate. Due to phase separation that was discovered in a laboratory-scale test [36], an additional 3%-by-weight of a cross-linked polymer (sodium polyacrylate) thickening agent was added to the PCM to prevent phase separation. Copolymer polypropylene capillary-tube heat exchangers were submerged into the PCM. Interestingly, this heat exchanger configuration is flexible and can also work with ice TES systems. The reason that a submerged heat exchanger in a vat of PCM was chosen over a design where PCM is encapsulated was to reduce the risk of the PCM contaminating the system.

The initial requirement for the TES capacity of the system was specified to be 190 kWh, which would cover approximately 9.5% of the peak cooling demand of the building over 5 hours. However, as a safety measure the system was oversized, and the capacity ended up as 275 kWh.

Overall, Tan et al. [34] found that the manufacturer of the TES system overestimated the performance. This is likely due to the lack of knowledge in designing these types of systems with salt hydrates. The authors recommend more laboratory-scale tests for validation and improvement of the design. Tan et al. [34] also determined that the charging and discharging rates were the limiting factor for using more storage capacity. The authors also conducted a techno-economic analysis regarding the PCM TES system and found that the current existing TES system is not a viable business because of the high cost of investment and the costs due to cycling losses and auxiliary equipment.

#### 11.5 FUTURE OUTLOOK OF IMPLEMENTATION OF PCM TES SYSTEMS

Alternative PCM systems for cool TES for HVAC applications are in their infancy as witnessed by the nascent technologies describe in this chapter. Many professional societies, such as the American Society of Heating, Refrigerating and Air-Conditioning Engineers (ASHRAE) and the Federation of European Heating, Ventilation and Air Conditioning Associations (REHVA), are working hard to develop design guidelines for PCM TES systems.

As seen from the preceding sections on commercial implementation of cool TES systems, effective use of the total latent heat capacity of the PCM has not been achieved, and many issues have resulted. This is due to both utilization of salt hydrates (since they have many disadvantages) and the configuration of the PCM in the TES



FIGURE 11.6 Evolution of TES systems from the 1800s to the future.

heat exchanger. Furthermore, the use of metals in these types of systems led to fouling due to the close spacing. It is interesting to note that most ice-based TES systems use polyethylene to prevent corrosion; however, polyethylene also helps prevent fouling.

In the future, TES system researchers and designers will need to focus on PCM heat exchanger geometry in order to effectively use the full latent heat capacity of the PCM material. Attempting to mitigate the low thermal conductivity of the PCM by adding thermal-conductivity-enhancing particles may not be a viable solution. Cool TES started by cutting large blocks of ice from lakes and has morphed into the large ice tanks with polyethylene tubes that are seen in commercial applications today (see Figure 11.6). In the future, ultra-compact and modular next-generation TES systems need to be developed. In these compact heat exchangers, PCM is arranged in layers so thin that the impact of the thermal conductivity of the material is negligible (see Eq. (11.2)), and the surface area is very high as to promote effective heat transfer and utilization of the total latent heat capacity of the PCM material. With the advent of advanced manufacturing techniques, such as additive manufacturing, geometries not possible with traditional manufacturing are now able to be realized.

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