A Review of the Applications of Phase Change Materials in Cooling, Heating and Power Generation in Different Temperature Ranges

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Abstract

Latent heat thermal energy storage is an attractive technique as it can provide higher energy storage density than conventional heat energy storage systems and has the capability to store heat of fusion at a constant (or a near constant) temperature corresponding to the phase transition temperature of the phase change material (PCM). This paper provides a state-of-the-art review on phase change materials (PCMs) and their applications for heating, cooling and electricity generation according to their working temperature ranges from (-20℃ to +200℃). Four working temperature ranges are considered in this review: 1) the low temperature range from (-20℃ to +5℃) where the PCMs are typically used for domestic and commercial refrigeration; 2) the medium low temperature range from (+5℃ to +40℃) where the PCMs are typically applied for heating and cooling applications in buildings; 3) the medium temperature range for solar based heating, hot water and electronic applications from (+40℃ to +80℃); and 4) the high temperature range from (+80℃ to +200℃) for absorption cooling, waste heat recovery and electricity generation. Different types of phase change materials applied to each temperature range are reviewed and discussed, in terms of the performance, heat transfer enhancement technique, environmental impact and economic analysis. The review shows that, energy saving of up to 12% can be achieved and a reduction of cooling load of up to 80% can be obtained by PCMs in the low to medium-low temperature range. PCM storage for heating applications can improve operation efficiency from 26% to 66%, depending on specific applications. Solar thermal direct steam generation (DSG) is the most common electricity generation application coupled with PCM storage systems in the high temperature range, due to the capability of PCMs to store and deliver energy at a given constant temperature. The recommendations for future research are also presented which provide insights about where the current research is heading and highlights the challenges that remain to be resolved.

Keywords: phase change materials (PCMs); energy storage; latent thermal storage; heating; cooling; power generation

1. Introduction

Nowadays, with the rapid growths in world population and economy, the world energy demand and consumption have increased enormously which led to a wide variety of harsh environmental impacts [1]. Higher usage of conventional fossil fuels is the main underlying cause of global warming and immense damage to environment due to the greenhouse and harmful pollutants emitted during their combustion. According to the data from the International Energy Agency (IEA) [2], the primary energy production has increased by 49% over the past 20 years resulting in an increase of carbon dioxide (CO_2) emissions by 43%. Engineers and scientists all over the world are motivated to solve these challenging issues by developing new technologies to decrease the dependence on fossil fuels and improve the energy use efficiency, and simultaneously avert from environmental hazards, expensive power generation and establishing new power generation plants [3].

As a potential solution for energy conservation storing the excess energy to fill the gap between energy supply and demand, using PCMs has received much attentions. Thermal energy storage with PCM is a promising technology based on the principle of latent heat thermal energy storage (LHTES) [4], where PCM absorbs or releases large amounts of energy at a certain temperature during the phase change transition period (charging and discharging process), with a high heat of fusion around its phase change temperature range [5], as shown in Fig. 1. According to the experimental results of Morrison and Abdel-Khalik [6] and Ghoneim [7], the mass of rock (sensible heat storage) was 7 times larger than paraffin 116 wax (latent heat storage & PCM), 5 times larger than medicinal paraffin (LHS&PCM) and 8 times larger than Sodium Sulfate Decahydrate ($Na_2SO_4 \cdot 10H_2O$, latent heat storage & PCM) to absorb equal amount of thermal energy. Currently, the application of PCM has been widely developed in different fields including, heating and cooling of domestic buildings [8], solar power plants [9], solar drying systems [10], photovoltaic electricity generations [11], refrigerators [12], waste heat recovery [13] and domestic hot water systems [14].

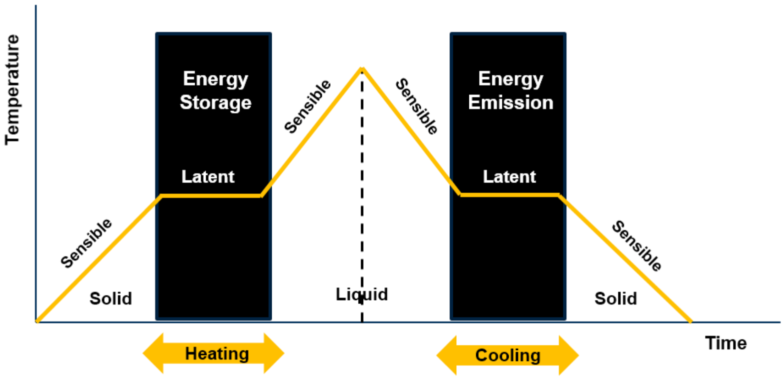


Fig. 1. Schematic diagram of the phase change transition of PCM [15]

Applications of PCMs within specific temperature ranges have been widely reviewed by many researchers [3, 10, 16-25]. Kasaeian et al. [23] reviewed the applications of PCMs and nano-PCMs in buildings for cooling, heating and air-conditioning/ventilation at a relatively low temperature ranging from 10 °C to 40 °C. Agyenim et al. [24] conducted a review of theoretical, experimental and numerical studies of PCMs within three temperature ranges that were classified as 0-65 °C for domestic heating and cooling, 80-120 °C for absorption cooling, and over 150 °C for direct steam electricity generation. Oró et al. [25] completed a review of the applications of PCMs at temperatures lower than 20 °C. Liu et al. [26] reviewed PCM energy storage systems for concentrated solar thermal power plants where PCM has a relatively high melting temperature of up to 300 °C. However, no one has reviewed the application of PCMs covering the temperature ranges from the freezing temperature range to the high temperature range, summarised the classifications of PCMs and applications in these different temperature ranges and discussed the performance improvement, environmental impact and cost of PCM applications.

This paper reviews and discusses the application of phase change materials for heating, cooling and electricity generation within the four working temperature ranges, shown in Fig. 2. The low temperature range from -20°C to 5°C is for the applications of domestic refrigerators and commercial refrigerated products (Section 2), the medium-low temperature range from 5°C to 40°C is for the applications of free cooling, building passive heating and cooling, solar absorption chiller, evaporative and radiative cooling, and air conditioning systems (Section 3), the medium temperature range from 40°C to 80°C is for the applications of solar air heaters, solar stills, solar domestic hot water systems, and electric devices (Section 4), and the high temperature range from 80°C to 200°C is for the applications of solar absorption cooling, on-site waste heat recovery, off-site waste heat recovery, and solar thermal electricity generation (Section 5). The thermal properties of phase change materials and various thermal performance enhancement techniques employed on phase change thermal storage systems for each of the four temperature ranges are reported and summarised. Moreover, an analysis of the environmental impact and economics of the PCM applications is also carried out. Finally, a summary of the findings and the potential future research needs are presented in Section 6.

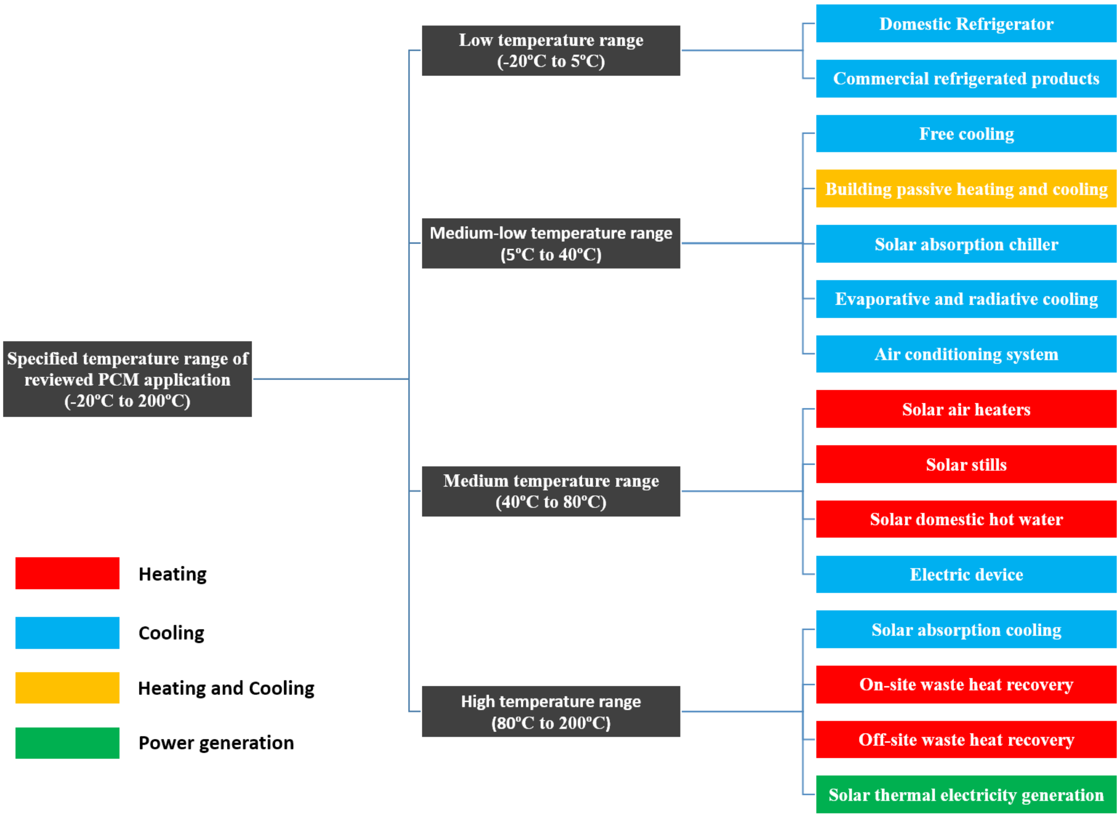


Fig 2. Classification of the reviewed applications of PCMs in defined temperature ranges

2. Applications of PCMs in the low temperature range from -20°C to 5°C

This section reviews the applications of phase change materials in the low temperature range from -20°C to 5°C, including PCMs integrated into domestic refrigerators for operation performance improvement and integrated into refrigerated products for enhanced thermal protection. Freezers integrated with PCM storage were reported to provide energy saving up to 12% and COP improvement up to 19% [27, 28]. Although the cost of a PCM cold storage tank was higher than traditional storage options, the potentials of PCM cold storage were significant in energy savings, CO_2 mitigation, and economical savings [29].

2.1 Domestic refrigerators

PCMs are incorporated into a domestic refrigeration system on the condenser side as heat storage, and on the evaporator side or compartment as cold storage to improve the operation performance. Fig. 3 shows a schematic diagram of PCMs integrated into domestic refrigerators, where PCMs are placed on the evaporator, the freezer internal wall surface and the condenser heat dissipation tubes.

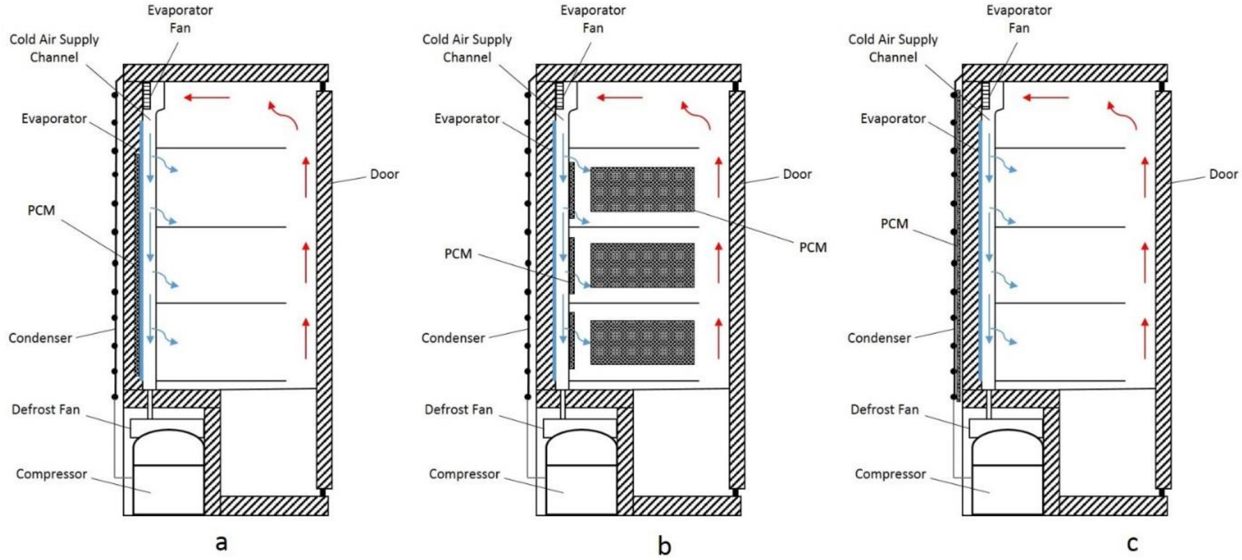


Fig. 3. Three typical solutions of PCMs incorporated in domestic refrigerators: a) at evaporator side; b) at container enclosure; c) at condenser side [30-32]

A condenser in a domestic refrigerator is a heat exchanger which is utilised to reject heat of compression to the ambient air and the more heat removed from the condenser, the better refrigeration cycle achieved. Incorporation of PCM into the condenser enhances the heat transfer by the extending of the heat rejection process to the compressor off time, resulting in a lower temperature in the condenser. The shape-stabilized phase change materials (such as PCMs containing with Linear Low Density Polyethylene (LLDPE) [33], epoxy [34], Poly-Hexadecyl Acrylate (PHDA) [35], etc.) are developed to solve the problem of leakage and deformation, where PCMs are contained in thermoplastic elastomer poly to keep the shape in a solid state. The shape stabilized paraffin exhibits the same performance of pure paraffin and up to 80% of its latent heat, but the heat storage performance is still limited by low thermal conductivities [28].

Cheng et al. [27] experimentally studied the performance of Shape Stabilized Phase Change Materials (SSPCMs) with a peak phase change temperature of 30.5°C mounted around the condenser tubes of a refrigerator as shown in Fig. 4. It was found that the condenser midpoint temperature and outlet temperature were decreased by 2.3℃ and 6.5℃, respectively and an energy saving of 12% was achieved as compared to a standard refrigerator. Further on, Cheng et al. [28] numerically investigated the performance of the SSPCM in a cold storage evaporator (CSE). It was concluded that the increase in ambient temperature and the reduction of freezer temperature could improve the coefficient of performance (COP) by 19%.

A series of experiments to investigate the COP enhancement of a refrigeration system incorporating PCMs were conducted by Wang et al. [36], where the PCM materials were separately placed between the compressor and condenser (PCMA), between the condenser and expansion valve (PCMB), and between the evaporator and compressor (PCMC) as shown in Fig. 5. The melting temperatures of eutectic PCMs are 21°C for PCMA and PCMB and 8°C for PCMC. It was found that PCM integrated in PCMA configuration could be seen as an extra condenser, and the COP was improved by 6% due to a lower temperature and pressure in the condenser. For the PCMB configuration, the COP was increased by 8% due to higher sub-cooling effect caused by a lower phase change temperature.

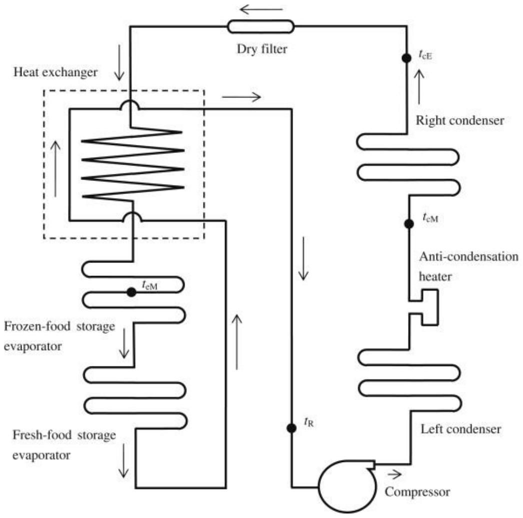


Fig. 4. Schematic diagram of refrigerator with PCM incorporated to the condenser [27]

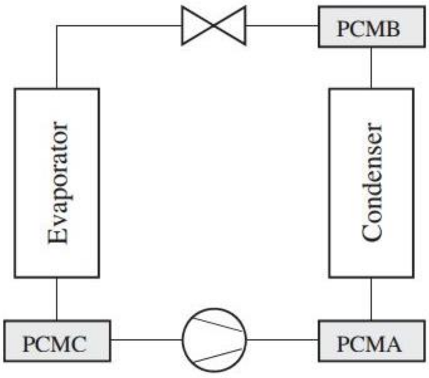


Fig. 5. Considered PCM locations in the refrigeration system [36]

The evaporator in a domestic refrigerator works based on either free or forced convection, with problems on low heat transfer rate and higher energy consumption on forcing internal air circulation [37]. PCMs incorporated into the evaporators can enhance the conduction heat transfer rate from the evaporator to the PCMs in addition to the natural convective heat transfer rate to the ambient air. Azzouz et al. [38] numerically investigated the performance of a refrigerator coupled with a latent thermal storage system. When PCM with a melting temperature between -9°C and 0°C was integrated into the evaporator of a domestic refrigerator, it was predicted that the COP could be increased by up to 15% and the compressor work frequency was reduced therefore increasing the lifespan of the refrigerator. In their later investigation [30], a 5-9 hours continuous operation period without external electrical supply was achieved, when coupling PCMs within the refrigerator (Fig. 6a). It was found that the continuous operation period of water cold storage based refrigerator was longer than eutectic PCM based refrigerator with the increase of ambient air temperature, shown in Fig. 6b.

The energy saving effect of PCMs integrated in the evaporator was investigated by Yusufoglu et al. [31], by testing three alternative PCMs with melting points of -2.5°C, -3.6°C, and -4.4°C, respectively, on two types of conventional refrigerators. It was found that the best energy saving effects were 8.8% and 9.4%, respectively. Moreover, it was concluded that increasing the heat transfer area of the evaporator by 20% could result in a better performance.

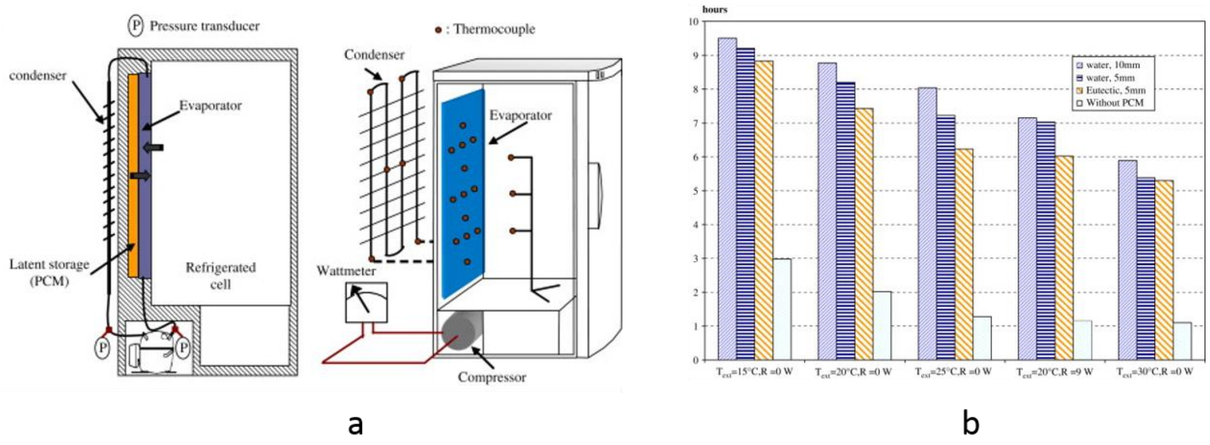


Fig. 6. a) Household refrigerator equipped with PCM slabs on evaporator; b) Cool storage capacity of the system for different thermal loads [30]

PCMs mounted on freezer enclosures can absorb the heat from door openings and maintain a homogeneous temperature distribution, and consequently reduce the on-time of the compressor and its energy consumption. Gin et al. [32] investigated the performance of a refrigerator, when PCM panels (melting point of -15.4°C) were placed against the internal wall of the refrigerator as shown in Fig. 7a. It was found that the peak air and product temperatures was 2.9℃ and 1℃ lower than those of a standard freezer, respectively, with a defrost cycle of 30 min. Moreover, the energy consumption was decreased by 8% during a defrost cycle and by 7% during door openings. The temperature change rate of the product with or without PCM had been compared (Fig. 7b) and it was found that the change rate of the temperature in the product was initially similar but the change rate of the product without PCMs was faster after 1 hour, showing a temperature variation buffer effect with PCMs. A similar experiment was conducted by Gin and Farid [39] and it was found that a much lower peak temperature of -11°C was achieved, as compared to -3°C for a freezer without PCMs during a 3 h power loss test. Fioretti et al. [40] investigated the energy performance of the insulation envelope of a freezer incorporating paraffin wax (melting temperature of 35°C) inserted in polyethylene panels. In contrast to a conventional refrigerator, it was found that the internal surface temperature was reduced by 1-2°C during an indoor test and the heat transfer rate was reduced by up to 8.57% during an outdoor test. Copertaro et al. [41] numerically investigated the operational performance of a refrigerator container envelope using different PCM panels with phase change temperatures from 27.5°C to 46.5°C. It can be concluded that PCM panels filled with paraffin (melting point of 35°C) could effectively reduce the peak heat load in a range between 20.1% and 20.87% and decreased the daily energy rate from 4.55% to 4.74%.

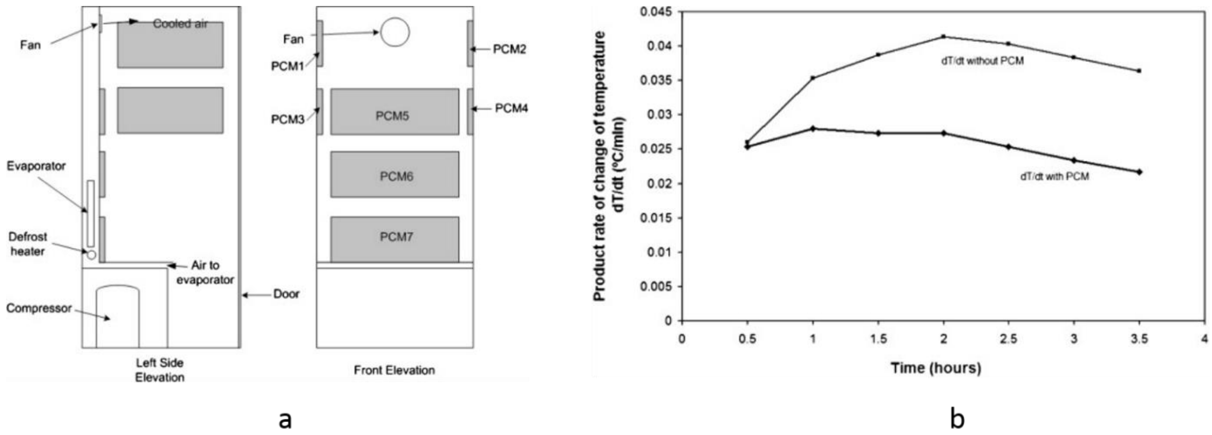


Fig. 7. a) Schematic diagram of the placement of PCM panels against the internal wall of a freezer; b) Product rate of change of temperature with and without PCM during the first 4 h of power loss [32]

2.2 Commercial refrigerated applications

Transport and storage of temperature sensitive products are the main focus of research and commercial applications of PCMs in the temperature range between -20°C and 5°C. PCMs can be integrated in refrigerated trucks, food packaging and medical product, for better thermal buffering capacity to enhance the thermal protection of perishable products.

Liu et al. [42] developed a novel design of refrigerated trucks consisting of an off-vehicle refrigeration unit with an on-vehicle PCM storage unit (melting point of -26.7°C) as shown in Fig. 8. It was found that the energy consumption was reduced by up to 86.4% when compared to conventional systems without PCMs. Ahmed et al. [43] presented a novel method of heat transfer reduction for refrigerated truck trailers equipped with insulating walls using paraffin-based PCMs. An average reduction in peak heat transfer by 29.1% was achieved by adding PCM to the insulation foam of all walls and the daily heat flow into the refrigerated compartment was reduced by 16.3% on average.

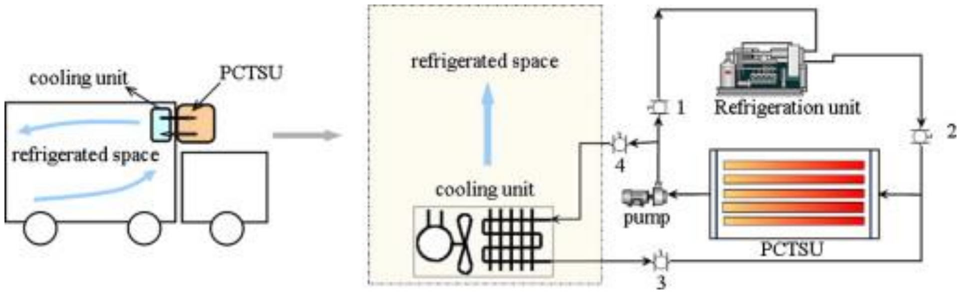


Fig. 8. Configuration of the refrigeration system [42]

An experimental investigation of the cold storage with liquid/solid phase change on Liquefied Natural Gas (LNG) refrigerated vehicles was conducted by Tan et al. [44]. The working process and structure of this novel system is presented in Fig. 9a. LNG was controlled by a valve box and transported into the centre storage unit (CSU). PCMs filled in the CSU were chilled and solidified by the cryogenic natural gas. After vaporized and heated, the natural gas was superheated in the heat exchanger and transported into the vehicle engine for combustion. It was found that the main thermal resistance existed in the gaseous heat transfer fluid inside the tube of CSU and was decreased by adding wave-like internal fins, where the ice later thermal resistances of internal finned tubes were up to 77% on the overall thermal resistance, much higher than that for the cases of smooth tubes (about 65%). Besides, the ice thickness for the internally finned tubes increased more rapidly than that for smooth tubes (Fig. 9b).

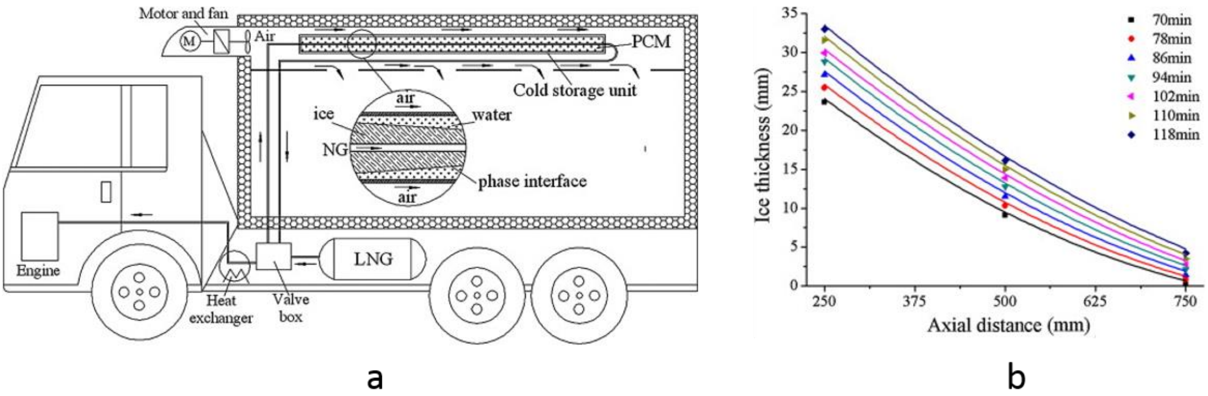


Fig. 9. a) Schematic diagram of the LNG refrigerated vehicle and the CSU; b) The time-wise variation of the ice layer distribution in the axial direction [44]

PCM packaging can be efficient in catering applications to avoid breaking of cold chains during the transportation for quick frozen food, milk, ice-creams and other products. Masiá et al. [45] developed a smart food packaging material that encapsulates dodecane (a paraffin wax with a transition temperature at -10°C) in the zein (a maize protein). It was found that a storage quantity of 25 J/g was achieved by using coaxial electrospinning configuration to obtain encapsulation structures based on zein and dodecane. Both transition temperatures of the developed PCMs were unmodified after 20 heating and cooling cycles, and the melting enthalpy was slightly changed from 34.482 kJ/kg to 30.667 kJ/kg.

The heat transfer of paraffin wax encapsulated in poly-caprolactone with a melting temperature of 5°C for food packaging was investigated by Hoang et al. [46]. As shown in Fig. 10, the PCM plate temperatures were merely increased to 7.5 °C and 5.65 °C for the first two and the third air temperature peaks, respectively, while the temperatures of the plate with commercial material (cardboard) were over 20°C. Moreover, the remaining shelf life of cooked ham in PCM package was 380 h, longer than the one with cardboard packaging (356 h). Hence, it can be concluded that this PCM packaging materials were effective to achieve better thermal buffering capacity and thermal protection for perishable products, compared to cardboard packaging materials.

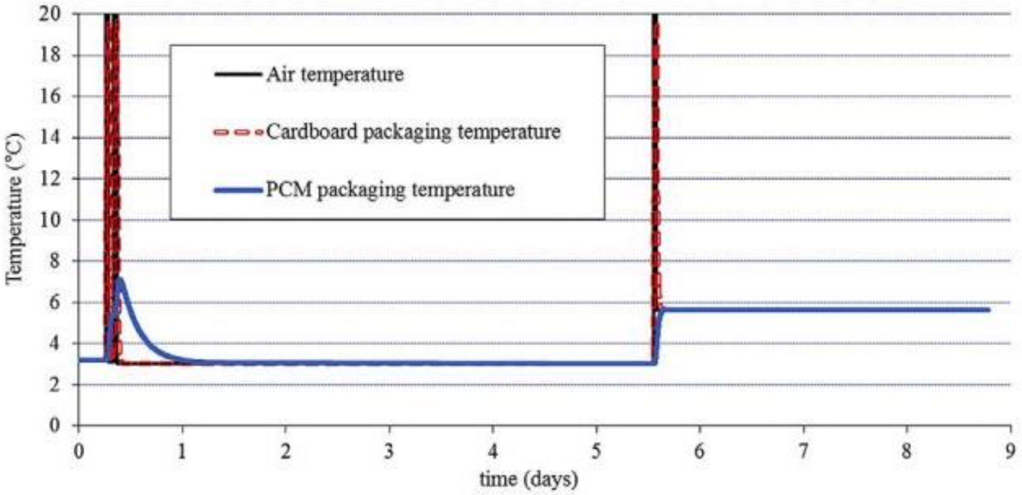


Fig. 10. Packaging temperature evolution along a cold chain - comparison between cardboard and PCM packaging [46]

PCMs can be used in the medical sector for the transportation of blood and organs with strict temperature limitations for biological activities. Mondieig et al. [47] experimentally investigated the thermal protection effect of Molecular Alloys Phase Change Material (MAPCM) with a melting point of 4.8°C on biomedical products during the process of transport and storage as shown in Fig. 11. The MAPCM could release the same quantity of energy stored during melting process in the form of sensible and latent heat, where the quantity of thermal energy was stored by the alloy in a sensible heat form first and then in a latent heat form after the beginning of PCM melting process. It was concluded that when the outside temperature was 22°C, the box package with MAPCMs was able to maintain the temperature of a blood bag lower than 10°C for over 6 hours, 8 times longer than the original container without MAPCMs. Ohkawara et al. [48] developed a Medi Cube container with PCMs for overnight transportation of skin grafts. The temperatures inside the container with PCMs were found to be maintained between 3°C and 6°C even with an outside temperature below 0°C in winter, while the inside temperature can be decreased to -3°C for a Medi Cube container without PCMs.

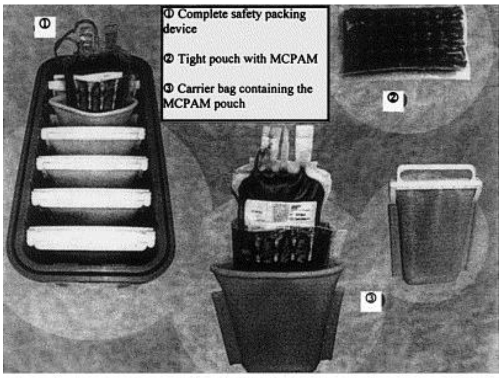


Fig. 11. Packaging for blood thermal protections [47]

2.3 Analysis of PCMs used in the low temperature range

Paraffin (organic) and salt hydrates (inorganic) are found to be the most commonly applied PCMs for reviewed researches in the low temperature range, as shown in Table 1. Several studies on the phase changing process of salts hydrates were carried out. Cabeza et al. [49] studied the thermal performance of sodium sulphite trihydrates mixed with cellulose, bentonite and starch, and reported an thickening improvement of the mixed PCM thickness. Farid et al. found that PCM directly contacting with the heat transfer methodology could completely eliminate the need for extra heat transfer surface. Taylor et al. [50] found that the sub-cooling of calcium hexahydrate was increased with a decrease in cooling rate and nucleation rate similarly. Various salt hydrates have differing levels of toxicity which are generally non-toxic in nature but can cause skin or eye irritation and respiratory problems [51].

The phase change temperature of PCM used in this temperature range must fall in the operation temperature range of refrigeration systems [21]. PCMs with higher phase change temperatures can increase the COP of the refrigeration systems due to lower power consumptions during phase change period but with poor quality of freezing food storage. On the contrary, PCMs with lower phase change temperatures can maintain the relatively low temperature inside the cabinet, while the fresh food storage quality is significantly affected in terms of taste and flavour [38]. Therefore, a suitable PCM should have a phase change temperature that meets both temperature requirements when integrated into refrigeration systems. Moreover, the super-cooling effect should be avoided in the selection of PCM, to prevent the reduction of the efficiency of refrigeration system [25, 52]. A supercooling temperature from 5°C to 10°C completely prevents the proper heat extraction of the energy stored [53]. It is also demonstrated that a refrigeration system with eutectic PCM achieves better COP than water, due to a low melting temperature (-5°C) [54] and approximately 40% increase in the amount of PCM can lead to almost 6% increase in the COP of the system [55]. An increase in the PCM thickness can reduce the on-off time ratio and result in longer compressor-off time[38]. However, due to high costs of materials and energy consumptions during the phase change period, PCM thickness should be determined based on the specific load [21]. The main limitations for PCM integrated into refrigeration systems are the material of the PCM container, the number of cycles without any degradation, cycling stability and corrosion [20].

Table 1. Thermo-physical properties of key PCMs used for the applications within the low temperature range (-20°C to 5°C)

Material	**Type**	**Synthesized by researcher**	**Commercial product**	**Melting temperature (°C)**	**Heat of Fusion (kJ/kg)**	**Thermal conductivity (W/m·K)**	**Specific heat (kJ/kg·K)**	**Application**	**Ref.**
18% NaCl/5% SAP/0.03% diatomite/H_2O	Inorganic (salt hydrate)	✓		-18.98	120.6	0.48	-	Freezer	[34]
Climsel C-18 ($NaNO_3/H_2O$)	Inorganic (salt hydrate)		✓	-18	306	0.5-0.7	3.6	Freezer	[56]
19.5% NH_4Cl/H_2O	Inorganic (salt hydrate)	✓		-15.4	-	-	-	Freezer	[32, 39]
Zein:dodecane (70:30)	Organic	✓		-10	34.5	-	-	Packaging	[45]
90% $NaCl/H_2O$	Inorganic (salt hydrate)	✓		-5	289	-	-	Freezer	[54]
H_2O	Inorganic			0	333	0.58	4.187	Cold storage	[57]
A4 PlusICE	Organic		✓	4	200	0.21	2.18	Freezer	[33]
Paraffin RT3	Organic		✓	2-5	198	0.2	2	Food storage	[35]
Paraffin RT4	Organic		✓	2-4	281	0.2	2	Food storage	[35]
Paraffin RT5	Organic		✓	1-6	198	0.2	2	Food Packaging	[46]

PCMs used for Cold Thermal Energy Storage (CTES) in the low temperature range (-20 to 5ºC) can help to reduce energy consumption of applications therefore providing financial savings and reducing pollutant emissions (CO_2, SO_2, NO_X and Chloro-Fluoro-Carbons (CFC) etc.) when compared with traditional systems without PCM. Table 2 presents the primary features of Cold Water Storage (CWS), Ice Thermal Storage (ITS) and PCM storage (eutectic salt hydrates) investigated by previous research studies [57-59]. Compared to traditional CWS, the space requirement of PCM storage is significantly reduced due to the higher thermal storage capacity. However, the cost of PCM storage tank is relatively higher than CWS and ITS, and this prevents its wide application. Cold thermal energy storage can potentially provide significant contribution to energy savings, CO_2 mitigation and economical savings mainly in domestic and industrial sector in Europe [29], as shown in Table 3.

Table 2. Primary features of different type of CTES

CTES type	**Latent heat of fusion (kJ/kg)**	**Required tank volume (m^3/kW•h)**	**COP [60]**	**Cost**	
				Chiller ($/t)	**Storage tank ($/t h)**
CWS	-	0.129	5.0 – 6.0	200 - 300	30-100
ITS	334	0.021	2.7 – 4.0	200 - 500	50-70
PCM	80-250	0.048	5.0 – 6.0	200 - 300	100-150

Table 3. Estimation of energy savings, environmental impacts and economic savings of CTES for different sectors in Europe [29]

Sector	**Energy Savings (GWh per year)**		**CO_2 mitigation (1000 tCO_2 per year)**		**Economical savings (millions € per year)**	
	Low-S	**High-S**	**Low-S**	**High-S**	**Low-S**	**High-S**
Domestic sector	5941	25460	3434	14716	1082	4638
Commercial sector	1324	2283	765	1319	230	397
Cold in road transport	959	12788	293	3900	951	12675
Cold in industry	19182	95910	11087	55436	2167	10837
Total	27405	136440	15578	75371	4430	28547

*Low-S: Low scenario, lowest impact factors from case studies
*High-S: High scenario, highest impact factors from case studies

3. Applications of PCMs in the medium-low temperature range from 5°C to 40°C

This section reviews the applications of phase change materials in the medium-low temperature range from 5°C to 40°C. PCMs have been integrated into free cooling, building passive heating and cooling, and evaporative and radiative cooling systems to improve the indoor thermal comfort and reduce energy consumption. Moreover, it has been used for solar absorption chillers to improve the operation efficiency, and for air conditioning systems to shift the daytime electricity load to night-time. Energy saving up to 42% could be achieved by incorporating PCMs in latent thermal storage systems for heating and cooling applications in this temperature range [61]. Cost saving on energy consumptions up to 50% could be achieved for PCM-integrated systems in comparison to the traditional options and the fastest payback period can be as short as about 6 years [62].

3.1 Free cooling

The working principle of a free cooling system with PCM is based on two operation modes as shown in Fig. 12. One is direct cooling for indoor air, where the PCM is melted by absorbing the heat from indoor air during day-time in order to reduce the room air temperature, when it is above the comfort range. The other one is when the outdoor temperature is lower than indoor temperature during night-time, the stored heat in the PCM is released to the warm the incoming outdoor air. The effectiveness of a PCM-based free cooling application depends on the diurnal temperature range (between 12°C and 15°C) [17], and the melting temperature of PCM (between 19°C and 24°C) [63].

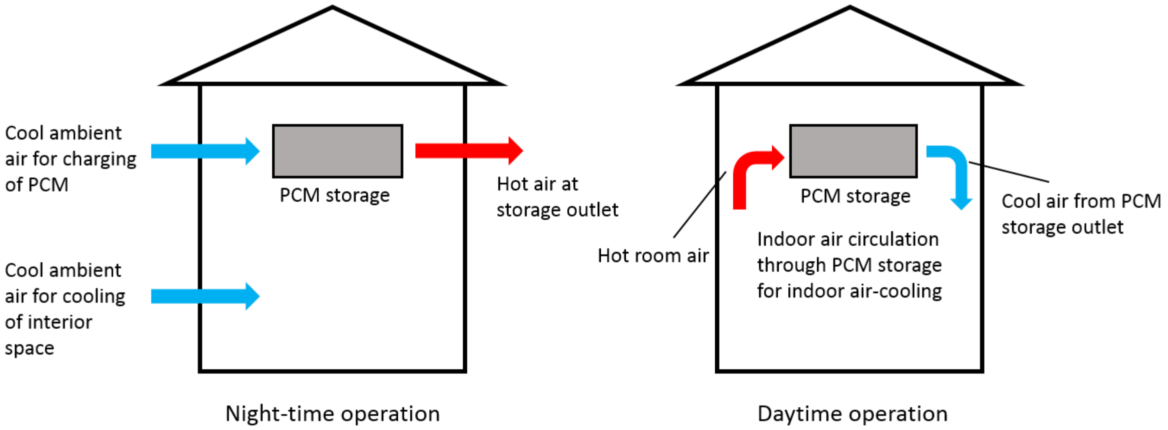


Fig. 12. Two operation modes of a free cooling system with PCMs [64]

Weinläder et al. [65] experimentally investigated the performance of two types of cooling ceiling with PCM (salt hydrate with a melting temperature ranging between 22 °C and 24 °C) installed in two office rooms “R112” and “R113” in Germany, with an 45% area ratio of PCM ceiling and floor. PCM in room R112 was installed on the top of the ceiling graphite layer and PCM in room R113 was placed at the bottom of the ceiling graphite layer. It was found that the measured passive cooling power could reach from 8 to 17W per PCM cooling ceiling area for globe temperatures in the range of 24 °C to 27 °C, significantly lower than that of the active cooling ceilings (80-100W/m^2 at 26 °C). Even with this low passive cooling power and high internal heat gains of almost 50W/m^2, it still took about 7-9 h for the highly insulated test rooms to reach globe temperature of 27 °C as a result of PCM integrated into cooling ceiling systems.

Sun et al. [66] evaluated the cooling energy reduction of a free air cooling system based on organic PCM (melting temperature from 18 to 20 °C) integrated into Telecommunications Base Stations (TBS) as shown in Fig. 13a. The established indoor air temperature was between 18 and 28 °C. The annual Energy Saving Ratio (ESR) was predicted using synthesized hour by hour temperature for five selected cities with different climates, where the ESR was defined as the ratio of energy savings attained by using PCM storage unit when compared to energy consumption of convectional air conditioners. It was found that the largest annual ESR achieved was 67% and the average value across the five cities was close to 50% as illustrated in Fig. 13b.

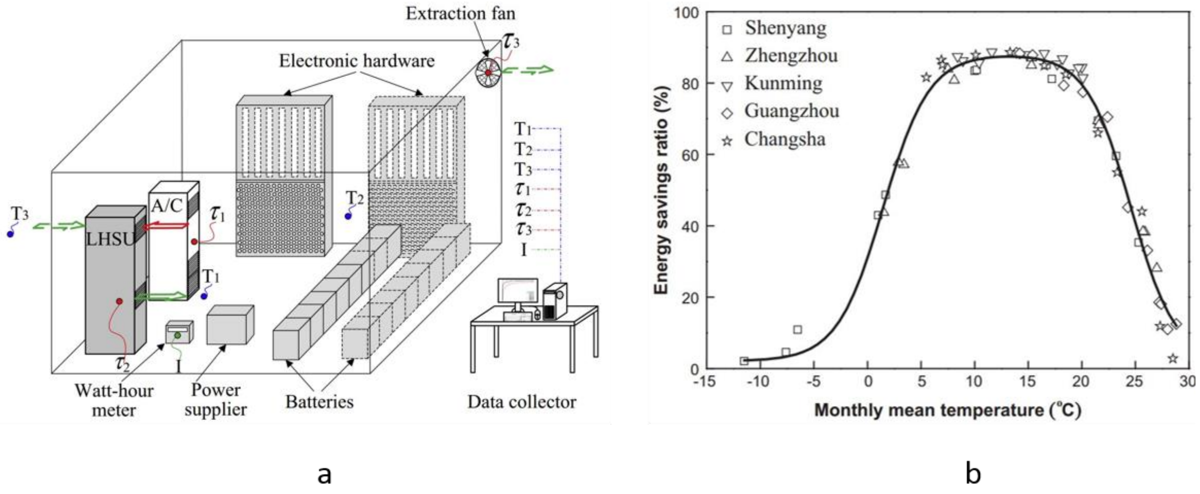


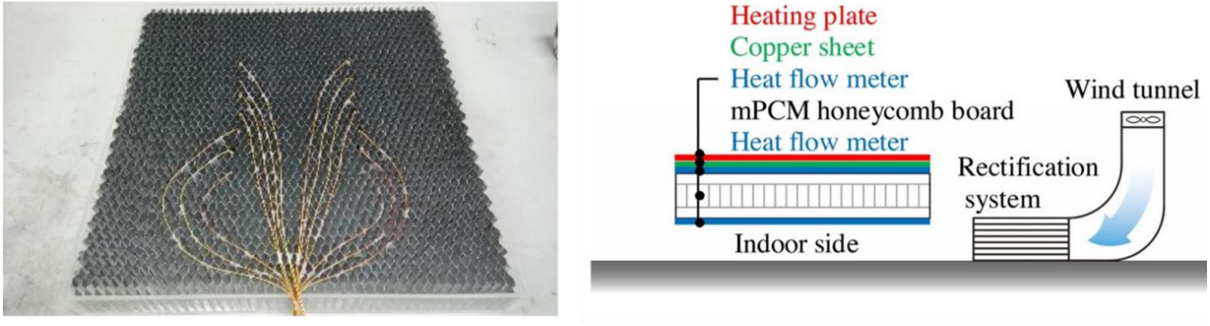
Fig. 13. a) Schematic diagram of the TBSs; b) Variation of ESR for five locations as a function of monthly mean temperature. [66]

Alam et al. [67] numerically investigated the free and passive cooling effectiveness of PCM used in a residential building in Melbourne, where a salt hydrate with a melting temperature of 22 ºC was selected as the PCM. In the free cooling application, a PCM storage unit was utilised to cool the outdoor air and in the passive applications, PCM was installed in the ceilings of the building in this research. Based on the simulation under a typical summer weather condition of Melbourne, it was found that the air temperature of the PCM based free cooling application was reduced by up to 1.8 ºC and the air temperature of the PCM based passive cooling application was reduced by up to 0.5 ºC.

3.2 Passive heating and cooling by building elements

Phase change materials can be integrated into building envelopes i.e. walls, floors, roofs, transparent elements and concretes as part of the building structure or as a building component, to buffer the indoor temperature variation and enhance the thermal comfort.

PCM wallboard placed on the inner side of the building envelope is the most common application of PCM in buildings, as a passive heating or cooling strategy. Wang et al. [68] experimentally investigated the daily thermal behaviour of a microencapsulated Phase Change Material (mPCM) incorporated into aluminium honeycomb board, using paraffin wax with a melting temperature of 37ºC encapsulated by polymer shell as shown in Fig. 14a and Fig. 14b, respectively. It was found that the mPCM wallboard could effectively release the stored heat when the indoor environment was subjected to either forced or natural convection. For indoor conditions of 24 h forced convection and 24 h natural convection, the effective thermal protection periods were 4 h and 4.7 h, respectively, and the heat releasing periods were 2.8 h and 3.8 h, respectively. Research investigations on shape-stabilized PCM with aluminium honeycomb board were also conducted by Lai and Hokoi [69] and Xie et al. [70], reporting an enhanced thermal conductivity of 2.08 W/m.K and stress tolerance limit promoted by 25.2%.



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b

Fig. 14. a) aluminium honeycomb board; b) schematic diagram of the experimental setup [68]

Devaux and Farid [61] numerically investigated the performance of testing hut containing PCM in its walls, ceiling and underfloor heating system. The interior wall was lined with PCM Dupont Sheets with a melting temperature ranging between 27 and 29 ºC. It was found that using PCM with lower melting temperature in walls was effective in building comfort enhancement and a cost saving of 42% with a corresponding energy saving of 32% was obtained.

Evola et al. [71] numerically investigated the effect of PCM wallboard on summer thermal comfort in buildings. The installation of the PCM wallboards on the inner surface of the partition walls could reduce the peak operative temperature by 1ºC. Furthermore, a significant attenuation in the daily surface temperature swing of the partitions was observed, as shown in Fig. 15, where the peak surface temperature of the east wall was decreased from 29.7 ºC to 28 ºC during the second day, and the daily temperature swing was reduced from 5.7 ºC to only 2.9 ºC.

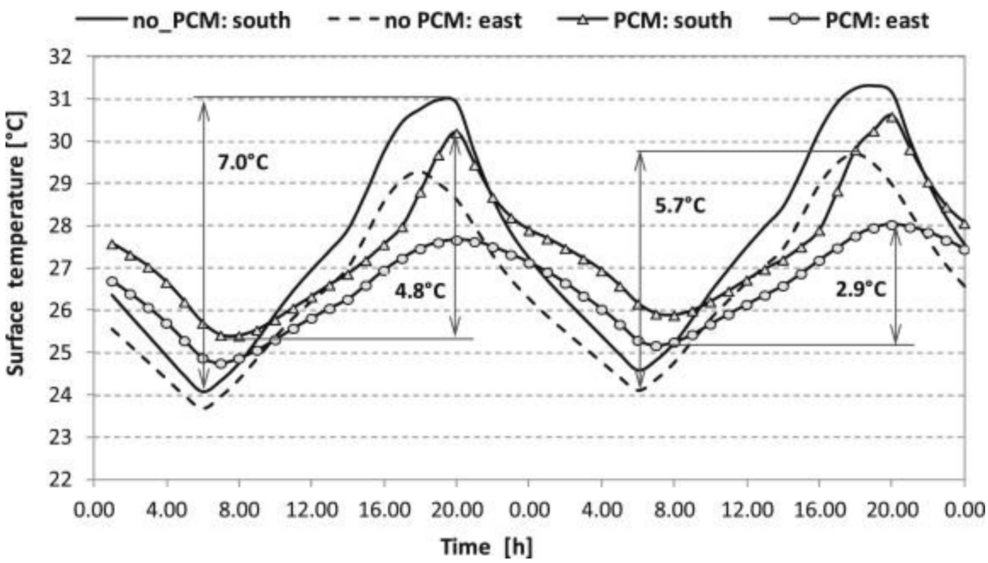


Fig.15. Effect of the PCM on the surface temperature for South and East wall [71]

Yao et al. [72] studied the performance of a novel SSPCM wallboard (a mixture of expanded perlite and paraffin with a melting temperature range of 25-29 ºC) used in a typical office building with an area of 4000 m^2. It was found that an average temperature reduction of 9.22 ºC was achieved in the building operation time from 7:00 to 18:00 and all the incremental cost can be recovered in 5.84 years.

Kong et al. [73] investigated the performance of a SSPCM wallboard for passive cooling in building as shown in Fig. 16a. It was found that the peak temperature of the inside wall surface was reduced by 7.03 ºC and the air temperature of room with PCM wallboard was reduced by 2.35 ºC on average as shown in Fig. 16b.

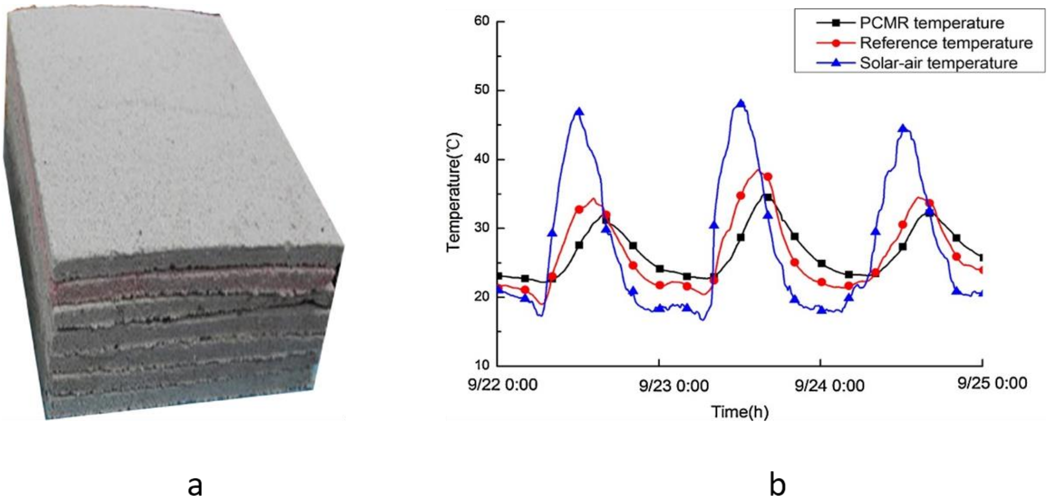
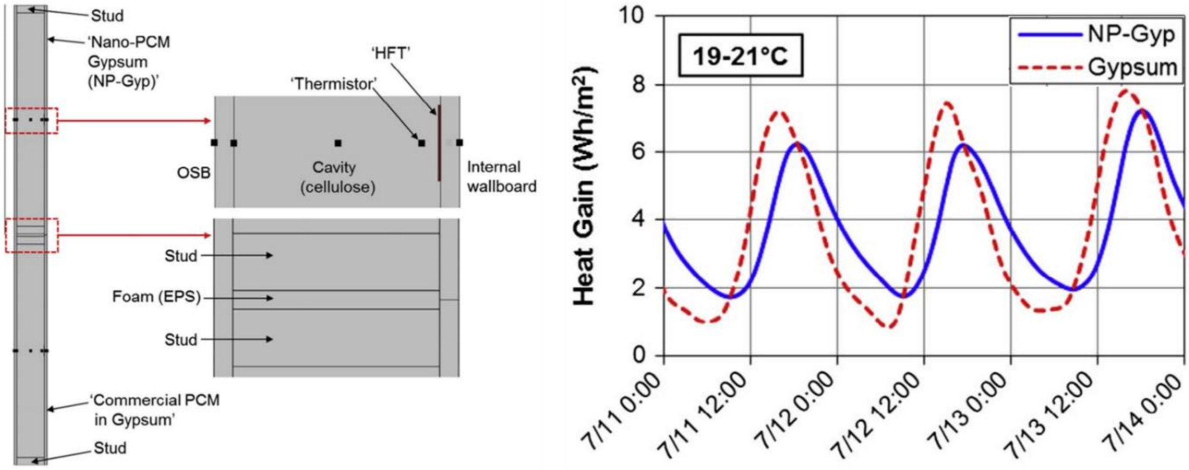


Fig. 16. a) Samples of prepared composite phase change material wallboard; b) Indoor temperature variation in closed building experiment [73]

Lee et al. [74] investigated the thermal performance of PCM-enhanced walls on houses with a typical residential frame wall construction, where PCM with a melting temperature of 28 ºC was mixed with cellulose insulation and incorporated in the walls. It was found that the peak heat flux was time delayed by 1.5 h on average and the daily average peak heat flux reduction for the individual walls was 25.4%.

Biswas et al. [75] numerically investigated the energy saving potential of a prototype PCM wallboard, consisting of a nano-PCM (n-heptadecane $C_{17}H_{36}$ with a melting temperature of 21.1 ºC) supported by expanded graphite nano-sheets for enhancements of thermal storage and energy distribution. A 2D wall section model was created with gypsum wallboards and nano-PCM gypsum wallboards for an annual simulation with three room temperature set points of 19-21ºC, 20-22 ºC and 20-23.3 ºC, as shown in Fig. 17a. It was found that the annual heat gain of the wall equipped with nano-PCM wallboards was reduced up to 24.65% in the room temperature set points within 20-22 ºC, and the best energy saving effect (21.12%) was achieved within 19-21 ºC. Moreover, the summer peak heat gains at 19-21 ºC set points were reduced by using nano-PCM wallboards, as shown in Fig. 17b.



a b

Fig. 17. a) Cross section of the numerical model of Nano-PCM gypsum (top) and commercial PCM in Gypsum (bottom) wallboards; b) Calculated heat gains through the South wall during summer days with cooling set points of 19-21 [75]

PCMs incorporated into floors and roofs, can also be suitable solutions for room thermal energy storage. Xu et al [76] investigated the thermal performance of a PCM floor system in a passive solar building and developed a dynamic model to analyse the thermal performance of a SSPCM which was verified by experimental results. By using the model, it was found that the suitable melting temperature of PCM was roughly equal to the average indoor air temperature of sunny winter days. Additionally, it was concluded that the thickness of PCM should not be larger than 20mm, and the heat of fusion and thermal conductivity of PCM should be greater than 120 kJ/kg and 0.5W/mK, respectively. Barzin et al. [77] investigated the application of PCM floor heating in combination with PCM wallboards for energy saving as shown in Fig. 18, where a paraffin based PCM was used with a melting temperature of 28 ºC. Experimental results showed that the total energy saving and electrical cost saving over a period of 5 days were 18.8% and 28.7%, respectively, and the highest energy saving was 35% with a corresponding cost saving of 44.4% during the experimental period.

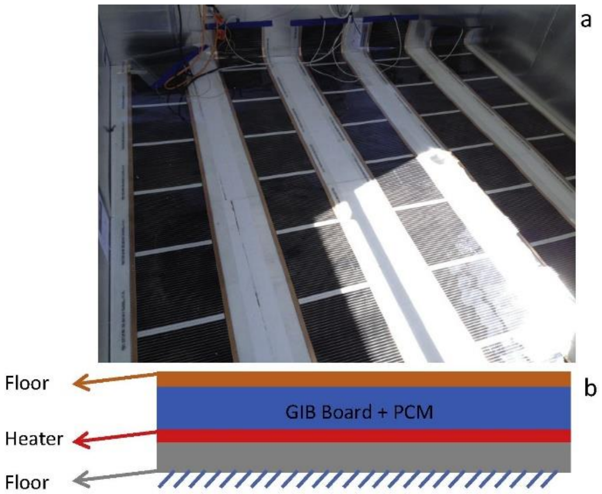


Fig. 18. The underfloor heating system used in the prototype. (a) Devi foil heaters, (b) underfloor heating system layout [77]

The performance of a double layer of PCM incorporated into a roof was investigated by Pasupathy and Velraj [78], using inorganic eutectic of hydrated salts with a melting temperature from 26°C to 28°C. It was found that the PCM-roof could be efficient for all seasons in Chennai, India, when the upper PCM layer had a melting temperature 6-7°C greater than the ambient temperature in summer and the lower PCM layer with a melting temperature close to the indoor temperature. Alawdhi and Alqallaf [79] studied the performance of a concrete roof with cone frustum holes filled with PCM (melting temperature of 37 ºC) in a hot climate. The results showed that the heat gain was significantly reduced with PCM incorporated into the roof and the heat flux at the indoor space could be reduced by up to 39%. Kośny et al. [80] developed a naturally ventilated roof/attic system with PV-PCM to reduce annual heating and cooling energy consumption (Fig. 19a). By incorporating a paraffin-based granulate form organic PCM with a melting temperature of 32°C, the heating load and cooling load (Fig. 19b) of the reference room were reduced by 30% and 55%, respectively.

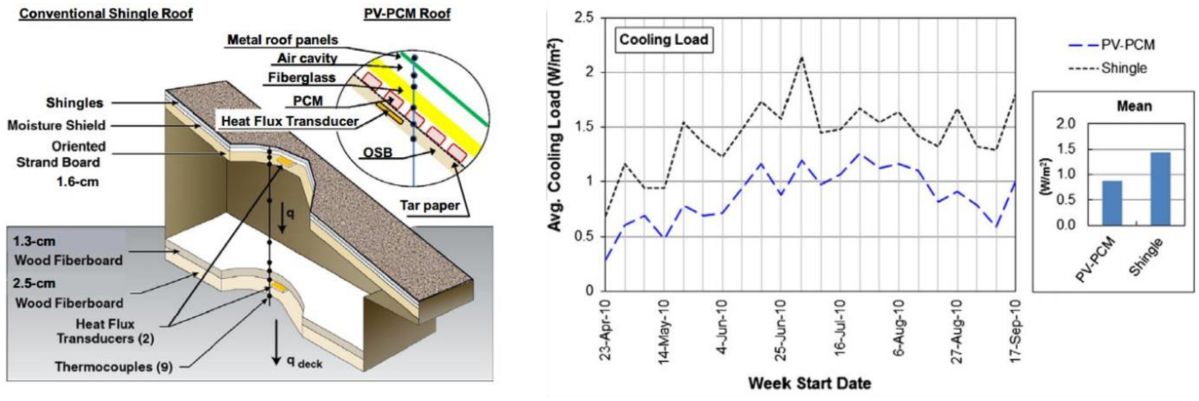


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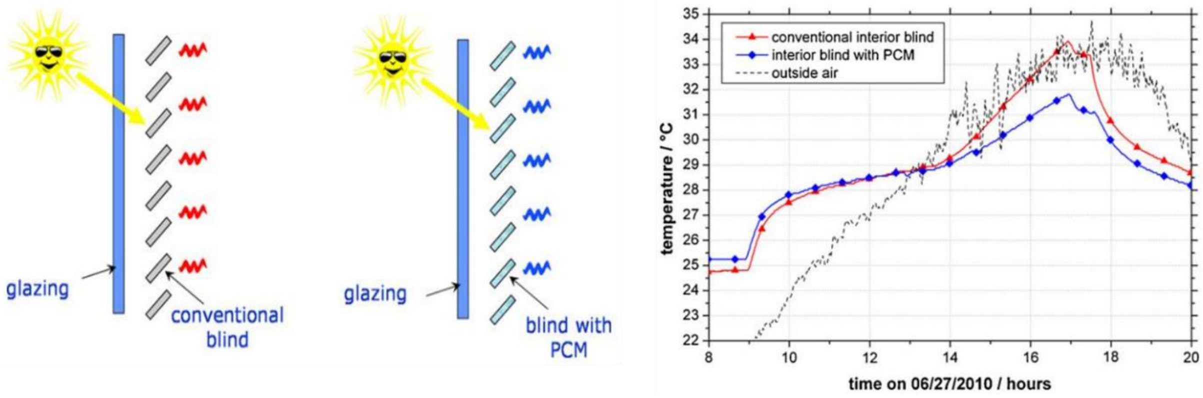
Fig. 19. a) Construction details of the tested roof; b) Average weekly attic cooling loads measured during the spring–summer–fall time period [80]

PCMs applied in transparent building elements can be effective solutions for reducing the heating load in cold climates or reducing the cooling load by absorbing solar heat gain from glazing in hot climates. Ismail et al. [81] numerically investigated the thermal performance of two glass windows, one was filled with absorbing gases and the other with PCM exposed to solar radiation in a hot climate, respectively. It was found that the window filled with an absorbing gas had an F factor (the coefficient of total heat gain) in the range of 0.55-0.65, indicating that the double glazing filled with absorbing gas had better performance than that of double glass window filled with PCM (F factor in the range of 0.65-0.80).

Silva et al. [82] investigated the performance of a window shutter incorporated with PCM (melting temperature of 28 ºC) during a summer period, compared to a traditional window shutter without PCM. It was found that the maximum temperature peak in the PCM compartment was reduced by up to 4 ºC and the minimum temperature was up to higher 3 ºC.

Gola et al. [83] investigated the performance of PCM incorporated into glazing in three different seasons, using a simple glazing prototype with a commercial paraffin wax (melting temperature of around 34°C). In contrast to a conventional double glazed unit, the thermal comfort condition in the glazing prototype with PCM integration was significantly improved during all periods of the year except for cloudy days.

Weinlaeder et al. [84] evaluated a solar shading system for an office room consisting of vertical slats filled with a commercial PCM based on a salt hydrate with a melting range between 26°C and 30°C shown in Fig. 20a. It was found that the maximum air temperature in the room with PCM blinds was reduced by up to 2°C, in comparison to a reference room with conventional blinds (Fig. 20b).



a

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Fig. 20. a) Schematic sketches of a conventional sun protection system and a sun protection system with PCM; b) Measured operative temperatures in comparable test rooms with conventional interior blind and interior blind with PCM [84]

Gracia et al. [85] numerically studied the thermal performance of an opaque ventilated facade with macro-encapsulated PCM (salt hydrates with a melting temperature of 21.5 ºC) in its air cavity for cooling purposes. It was found that the ventilated facade could provide a net energy supply of 2.49 MJ per day and the use of a wooden structure would increase the duration of cooling supply to 5h with a maximum increase of net energy supply by 61.6% compared to the one with a metallic structure.

Liu and Li [86] numerically studied the thermal performance of a PCM based solar chimney as shown in Fig. 21, which incorporates paraffin with a melting temperature ranging from of 38 ºC to 43 ºC. It was found that with the increase of latent heat from 70 to 170 kJ/kg, the melting time of the PCM was increased by 103% and freezing time was prolonged by 60%. Moreover, if the heat flux was increased by 33%, the melting time could be reduced by 36.4%.

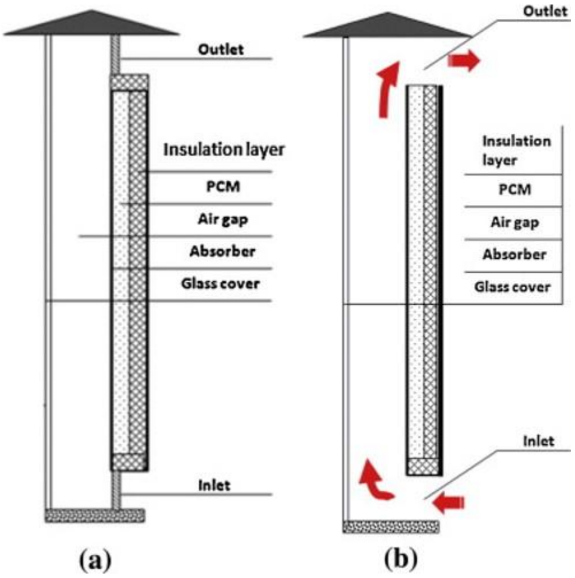


Fig. 21. Schematic diagram of the solar chimney combined with PCM: (a) closed mode; (b) open mode [86]

The benefit of incorporating PCMs into building construction materials or concrete is to increase the heat storage leading to a lower indoor temperature in warm climates. Entrop et al. [87] experimentally investigated the performance of a concrete floor with PCM (micro-encapsulated mixture of paraffin with a melting temperature of 23 °C) incorporated into two rooms. It was found that after incorporating PCM into concrete floors, the temperature difference in using light or heavy weight insulation was reduced from 2.8 - 4.2 ºC without PCM compared to 0.1 – 1.5 ºC with PCM. Cabeza et al. [88] studied the thermal and energy saving performance of an innovative concrete with microencapsulated PCM (melting point of 26°C). It was found that a reduction in temperature fluctuation was achieved in the room with PCM-concrete floor as compared to a conventional concrete without PCM as shown in Fig. 22.

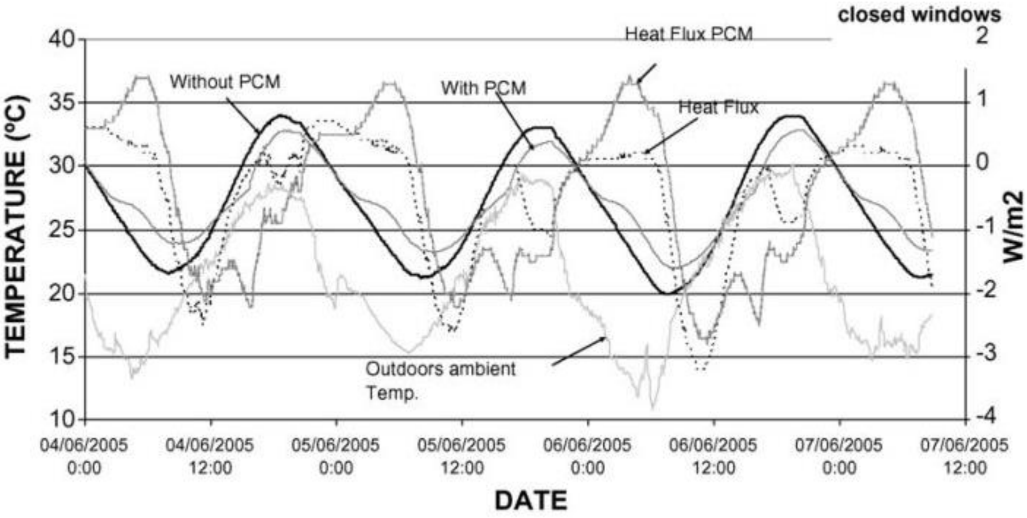


Fig. 22. Comparison between south wall temperature in both cubicles, outdoors ambient temperature, and heat flux. [88]

3.3 Solar absorption chillers

Wet cooling towers are normally applied in solar absorption cooling systems to provide the heat rejection and fulfil the low returning temperature requirements, but simultaneously brings space and maintenance limitations particularly for domestic applications as shown in Fig. 23. PCM is presented as an alternative choice used in the thermal energy storage system to replace the conventional wet cooling tower in the heat rejection loop of the chiller, for supplying a stable re-cooling temperature during peak load period and storing latent thermal energy to be discharged in the evening hours with lower space and maintenance limitations compared to a traditional wet cooling tower [5].

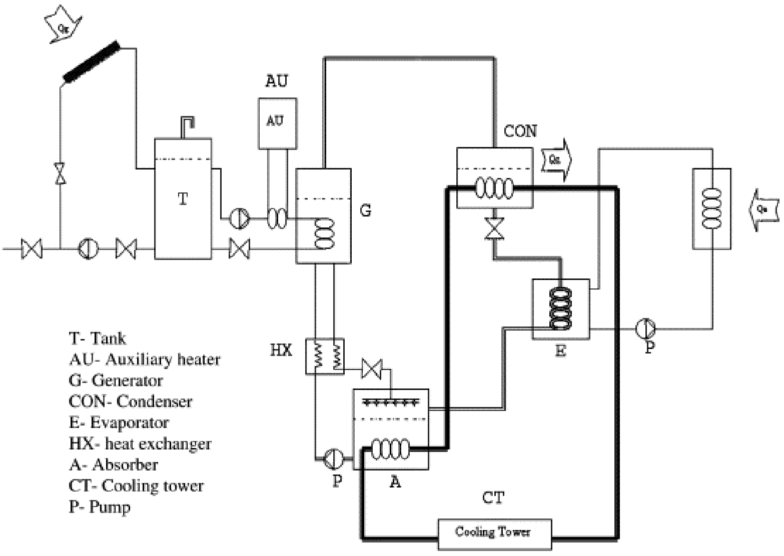


Fig. 23. Schematic diagram of a solar absorption system [89]

Helm et al. [90] investigated the performance of a solar driven absorption cooling system based on a dry air cooler combined with PCM as shown in Fig. 24, using Calcium Chloride Hexahydrate ($CaCl_2 \cdot H_2O$) with a phase change temperature of 29°C. It was found that with ambient temperature above 30°C, up to 50% of the daily reject heat load was absorbed by the PCM and the latent heat storage could fully support the dry air cooler and ensure a 32°C constant cooling water temperature to the chiller. In a similar research [91], it was predicted that the daily Energy Efficiency Ratio of the solar cooling system was increased significantly to 11.4 as compared with a traditional wet cooling tower and nearly 22% of the waste heat produced by the absorption chiller could be dissipated to the ambient air at night.

Belmonte et al. [92] compared the performance of a conventional wet cooling tower and an alternative PCM thermal storage coupled with a dry air cooler for an absorption solar cooling system. Both the conventional and alternative configurations were simulated and compared under 52 provinces' climate conditions in Spain within 3 months. Greater system efficiency in terms of cooling energy produced and chiller COP was achieved for the conventional configuration at all locations. When the influence of the mean relative humidity and temperature was included in the analysis, it was observed that the alternative configuration was able to reach or surpass the energy performance of the conventional configuration but only in few locations with a temperate and humid summer season.

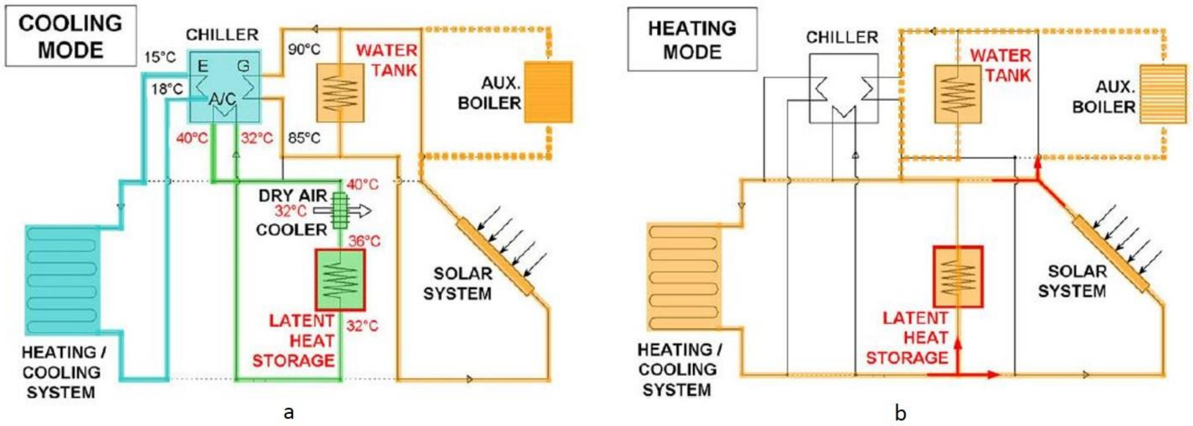


Fig.24. Solar absorption chiller coupled with PCM: a) under cooling mode; b) under heating mode [90]

3.4 Evaporative and radiative cooling systems

By using PCM as a storage media, a much higher working temperature can be achieved by the heat transfer media in radiators, making it possible for summer cooling.

Zhang and Niu [93] developed and evaluated the performance of a novel hybrid cooling system consisting of a microencapsulated PCM slurry storage tank and a nocturnal sky radiator as shown in Fig. 25a and Fig. 25b. The numerical analysis was carried out based on an hour by hour calculations in five typical cities with different climates in China. The micro-encapsulated PCM slurry was based on hexadecane ($C_{16}H_{34}$) with a phase change temperature of 18°C. It was found that for Chinese climates, the energy saving potential in Lanzhou and Urumqi were up to 77% and 62% for low rise buildings, respectively.

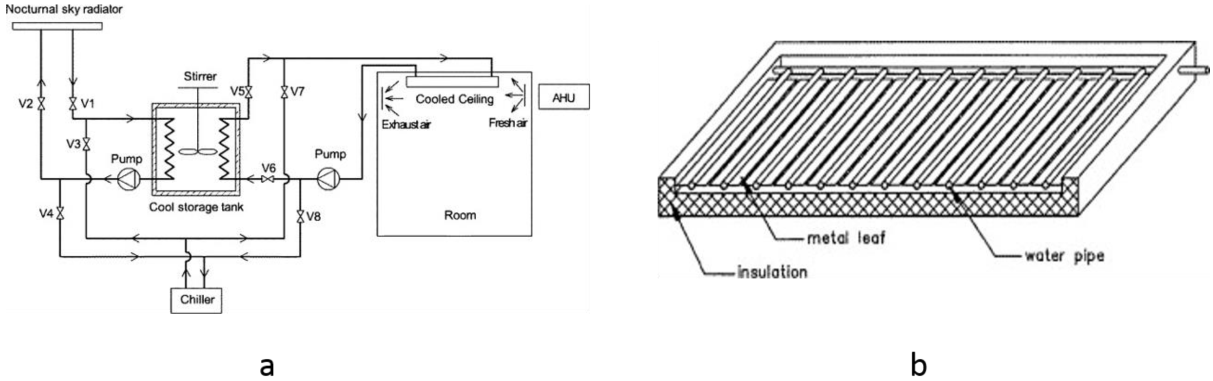


Fig. 25. a) schematic diagram of the hybrid system; b) Construction of the nocturnal sky radiator [93]

Ansuini et al. [94] developed a lightweight piped radiant floor prototype with PCM (paraffin based in granulate form) aimed to buffer internal gains at a constant temperature during summer seasons without affecting its warming capacity in winter seasons. The internal structure of the radiant floor was optimized by inserting a special steel matrix. The numerical simulation results showed that the usage of cooling water was reduced approximately by 25% in summer seasons and the floor peak temperature was reduced by 3.5°C. Wang et al. [95] investigated the performance of a hybrid cooling system, which is a combination of cooled ceiling, microencapsulated PCM slurry storage (hexadecane as core PCM with a melting point of 18.1°C) and evaporative cooling technologies under five different Chinese climatic conditions as shown in Fig. 26. It was indicated an energy saving for North-Western and South-Eastern Chinese climate was up to 80% and 10%, respectively.

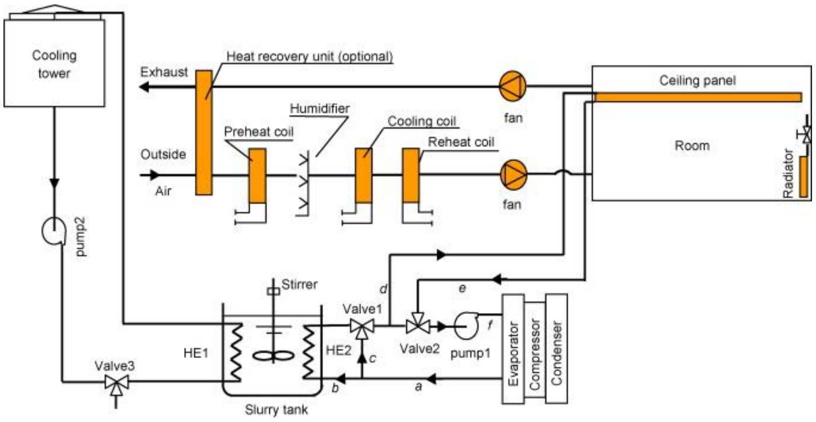


Fig. 26. Schematic diagram of the hybrid system [95]

3.5 Air conditioning (AC) systems

Integrating PCM into an air-conditioning system as a cool storage, is an effective approach of shifting daytime peak electrical loads to night-time with a low cooling load, on which daytime cooling can be supported by the cooling medium storing cool energy at night, resulting in a reduction of building cooling energy consumption and size of the air conditioning system.

Fang et al. [96] carried out an experimental investigation of the performance of an air conditioning (AC) system incorporated with spherical capsules packed bed which used a 25% ethylene glycol solution as PCM as shown in Fig. 27. They investigated the evaporation pressure and the condensation pressure of the refrigeration system, the refrigeration capacity and the coefficient of performance (COP) of the system, and other performance parameters. It was found that the operation performance of the AC system with the spherical capsules packed bed was improved during the charging and discharging period of PCM capsules, where the outlet air temperature stabilized between 20.7 °C and 24.4 °C and the inlet air temperature was stable between 27.5 °C and 28.8 °C during the discharging period.

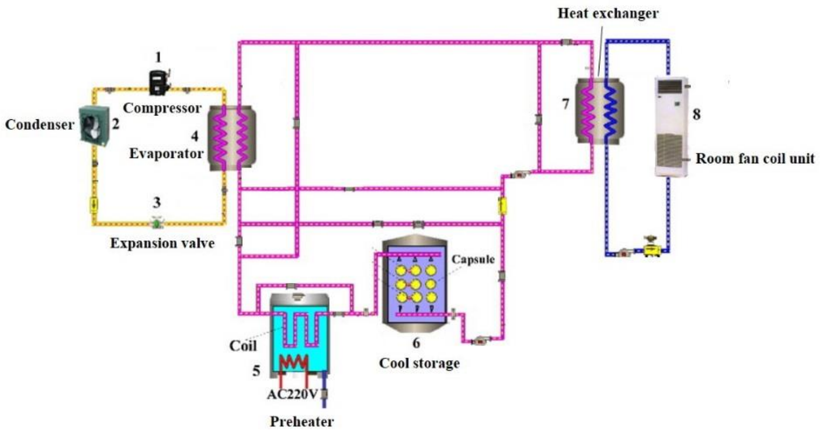


Fig. 27. Schematic diagram of the experimental AC system with PCM capsules [96]

Cheng et al. [97] developed a packed bed cold storage installation with a composite PCM (melting temperature of 12.6°C) for an air conditioning system as shown in Fig. 28, composed of carpic and lauric acid eutectic mixtures with 6% mole fraction of oleic. It was found that the inlet heat transfer fluid (HTF) temperature had more influence on the charging rate and maximal charging capacity and less effect on the exergetic efficiency, while the average charging rate, maximal charging capacity and exergetic efficiency declined by 73.9%, 44.7% and 10.4% respectively, when the inlet HTF temperature was elevated from 7 °C to 12 °C. Chaiyat [98] presented a concept of PCM bed placed in the return duct of an AC system for improving its cooling efficiency by reducing the air temperature entering the evaporating coil. A paraffin wax with a melting point of 22°C was selected as PCM and the thermal performance of the system was evaluated under Thailand climate. It was found the electrical power of the modified system could be saved around 9% or 3.94 kW h/d compared to the normal system by 39.36 kW h/d.

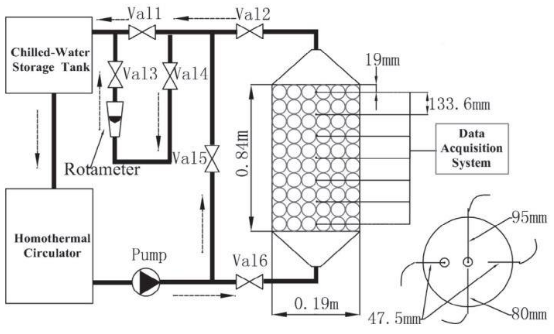


Fig. 28. Schematic of the experimental setup of [97]

3.6 Analysis of PCMs used in the medium-low temperature range

Based on the reviewed literature, typical PCMs such as paraffin, fatty acids and salt hydrate compounds are typically used in the medium low temperature range as presented in Table 4. Paraffin wax is the most typical commercial organic PCM. It is non-corrosive to most materials, which doesn't suffer from sub-cooling with over 1500 stable cycles [99, 100]. Commercial paraffin waxes are found to be hazardous with long term exposure to their vapours due to the benzene and toluene components [101]. Fatty acids are found to be corrosive [102], inflammable and releasing undesirable odor [103].

Although these PCMs have a high latent heat of fusion and good nucleation, paraffin waxes and fatty acids are not suitable for direct use in practical application due to their low thermal conductivity typically less than 0.2 W/m^2/K [104], high volume variation and liquid seepage during state changes [105], compared to inorganic materials. However, chemical instability is the main limitation of salt hydrates for application, as they begin to degrade and lose water content during every heating cycle. Chemically aggressive, low heat conductivity and relatively high degree of super-cooling are both considerable issues when using salt hydrates as PCMs [106].

Table 4 Thermo-physical properties of key PCMs used for the applications within the medium-low temperature range (5°C – 40°C)

Materials	**Type**	**Synthesized by researcher**	**Commercial product**	**Melting temperature (°C)**	**Heat of Fusion (kJ/kg)**	**Thermal conductivity (W/m·K)**	**Specific heat (kJ/kg·K)**	**Application**	**Ref.**
Capric Acid/Lauric Acid (65:35)	Organic	✓		19.1	35.2	0.21	-	Wallboard	[107]
n-heptadecane/graphite (92:8)	Organic	✓		21.1	26.9	-	-	wallboard	[75]
SP-22	Inorganic (salt hydrate)		✓	21.5	154.7	0.6	3.5	Transparent elements	[85]
RT-23	Organic		✓	22-24	128	0.2	2.1	Free/passive cooling	[65]
GR-25	Organic		✓	23.2	45.3	1.2	-	Free cooling	[108]
48%CaCl$_2$+4.3%NaCl+0.4%KCl+47.3%H$_2$O	Inorganic (salt hydrate)	✓		26-28	188	1.09	1.44	Floor heating	[78]

Delta®-Cool 28	Inorganic (salt hydrate)		✓	26-30	188	-	-	Transparent elements	[84]
Paraffin 28	Organic		✓	28	120	0.2	2	Wallboard	[61]
PCMD-32SP	Organic	✓		32	140-160	-	1.6	Electronic device cooling	[109]
MPCM-37D	Organic		✓	37	166.5	0.13	3.21	Wallboard	[68]

When comparing PCMs with the same latent heat storage, paraffin is better than fatty acid both in volume and mass and glycerine has the largest heat storage capacity in same volume as shown in Table 5. Compared to organic PCMs, salt hydrates are more attractive in thermal energy storage due to high volumetric storage density (350 MJ/m^3), relatively higher thermal conductivity (0.5 W/m^2/K) and moderate costs [110]. To overcome the disadvantages of PCMs applied in this temperature range, encapsulation of PCM is widely used in practical applications to enhance the heat transfer process and minimize the volume change and quality loss for better performance, as reported by [93, 95-98, 111-113].

Table 5. Evaluation of the quantity of different types of PCM with the same heat storage capacity and volume [114]

PCMs	**Fatty Acid**	**Paraffin**	**Glycerine**
Latent heat storage (kJ)	**200**	**200**	**200**
Volume (dm^3)	1.47	1.06	0.79
Mass (kg)	1.34	0.82	1.00
Latent heat storage (kJ)	136	189	253
Volume (dm^3)	**1.00**	**1.00**	**1.00**
Mass (kg)	0.91	0.78	1.26

Life Cycle Assessment (LCA) is an effective approach for conducting environmental impact analysis of any product or system's total environmental performance during its life cycle, while the energy and the materials consumed for the extraction of raw materials, transportation, maintenance and disposal life-cycle stages are main indicative key factors for evaluation [115]. The Eco-Indicator 99 (EI99) methodology was employed by many studies about PCMs [108].

It is a LCA weighting method that aggregated LCA results into clear and easily understanding units as the Eco indicators [116]. It can convert the inventory emission data into intuitive aggregated potential environmental impacts, where the environment impact is defined with three types of damage: Human health, Ecosystem quality, and Resources. The Eco indicator values are dimensionless figures, and higher value means greater environmental impact.

Several works on the LCA of PCMs in the medium to low temperature ranges were carried out. De Gracia et al. [62] reported the use of PCM in ventilated facades with steel frames could reduce the overall environmental impact by 7.5% with an environmental payback of 31 years, considering a building lifetime of 50 years and a further study indicated that the environment payback of the system with a wooden frame could be reduced to 6 years. Moreover, the addition of PCMs did not produce a significant variation of the global impact results and the manufacturing impact of salts hydrates was 75% lower than that of paraffin [117]. Table 6 presents the synoptic LCA studies on PCMs used in building applications.

Table 6. Synoptic LCA on PCMs used in building applications

Research	**System boundaries**	**Investigated constructions**	**Impact categories (Eco-indicator points)**			**Total**
			Ecosystem quality	**Human health**	**Resources**	
De Gracia et al. [117]	M&O	REF$_{brick}$	220.77	2169.4	1459.93	3850.09
		PU	138.08	1356.48	936.46	2431.11
		PU+PCM$_{paraffin}$	137.44	1347.93	950.41	2435.77
Castell et al. [118]	M&D	ALVbrick	141.14	1382.41	946.64	2470.01
		ALV$_{brick}$+PCM$_{salt\ hydrate}$	140.23	1369.32	941.82	2451.34
Menoufi et al. [119]	M&D	REF$_{brick}$	5.46	47.55	63.55	116.58
		PU	6.02	55.17	80.01	141.22
		PU+PCM$_{paraffin}$	6.61	57.1	102	167.35
		PU+PCM$_{salt\ hydrate}$	6.98	58.88	86.25	152.14
		PU+PCM$_{ester}$	6.39	57.17	86.18	149.79
Rincón et al. [120]	M&D&O	REF$_{brick}$	117	8198	28	8343
		PU	141	5028	26	5195
		PU+PCM	152	4981	27	5160

	ALV$_{\text{brick}}$	130	5137	27	5294
	ALV$_{\text{brick}}$+PCM$_{\text{salt hydrate}}$	141	5072	27	5240

Abbreviations: ALV$_{\text{brick}}$ – Alveolar brick; PU – Polyurethane; REFbrick – Reference conventional brick; M – Manufacture; O – Operation; D – Disposal

Cost savings by using PCM were investigated and reported by many researchers. Cunha et al. [121] reported that the heating and cooling energy consumption of mortars with PCM and different blinders used in buildings was approximately 0.3 € /m^3 during spring, and 0.7 € /m^3 for autumn season. Moreover, the energy consumption showed a decrease of 11% by incorporating PCM into mortars used in buildings during summer seasons. Saffari et al. [122] reported short payback periods for residential buildings and official building with less than 3 years and 6 years to recover the investment of PCM storage, based on the numerical analysis of incorporating PCM into buildings equipped with HVAC system. Mi et al. [123] numerically investigated the Static Payback Period (SPP) and Dynamic Payback Period (DPP) with a discount ratio (r) considering the time value of money for PCM applied in five cities in China. It was found that PCMs applied in cities with cold winter (Shenyang, Zhengzhou, and Changsha) were sufficient to recover the investment within 9 years, as shown in Table 7.

Table 7. Economic analysis for PCM integrated into building in China [123]

Payback period (year)	**Locations**				
	Shenyang	**Zhengzhou**	**Changsha**	**Kunming**	**Hong Kong**
SPP (r=0)	5.91	5.99	7.07	19.91	30.09
DPP (r=5%)	7.18	7.29	8.94	NA	NA
DPP (r=7%)	7.88	8.01	10.08	NA	NA
DPP (r=9%)	8.82	8.98	11.74	NA	NA

NA: payback period exceeds the lifespan of target building (35 years)

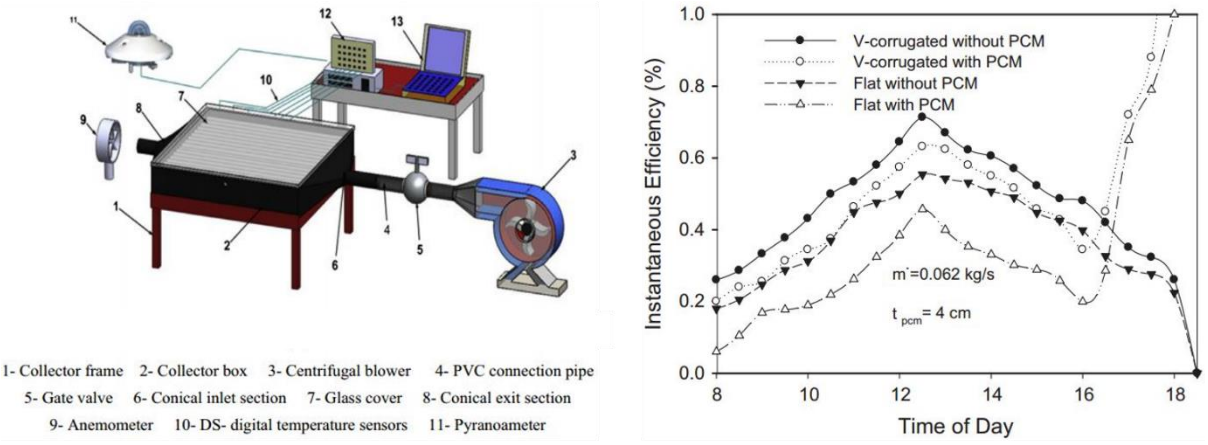
4. Applications of PCMs in the medium temperature range from 40°C to 80°C

This section reviews the applications of phase change materials in the medium range temperature from 40°C to 80°C, where PCMs are used in solar air heaters, solar stills, and solar domestic hot water systems for heating purpose and in electronic devices for cooling and operational performance improvements. PCMs integrated into such solar based systems could improve the operation efficiency by up to 26%, while electronic devices with a PCM heat sink could extend the lifetime by up to 300% [124, 125]. The total lifespan cost of the PCM applications could be reduced by using PCMs with higher melting temperatures in this temperature range.

4.1 Solar air heaters

PCMs used in solar air heaters have the ability to store the excess thermal energy during the daytime and recover it after sunset, effectively enhancing their thermal performances.

Kabeel et al. [126] experimentally investigated the performance of the flat and the v-corrugated plate solar air heaters with built-in PCM (paraffin wax with a melting temperature of 54°C) as shown in Fig. 29a. It was found that when the air mass flow rate was 0.062 kg/s with a PCM storage unit, the outlet temperature of the v-corrugated plate solar air heater was higher than the ambient temperature by 1.5-7.2°C in a period of 3.5 h after sunset, while the outlet temperature of the flat plate solar air heater was 1-5.5 °C higher than the ambient air in a period of 2.5 h after sunset. Moreover, it was concluded that the daily efficiencies of the v-corrugated and flat plate solar air heaters with PCM were both higher than the corresponding ones without PCM as shown in Fig. 29b.



a b

Fig. 29 a) Schematic diagram of the experimental setup; b) a comparison of instantaneous thermal efficiency between v-corrugated and flat plate solar air heater with and without PCM when mass flow rate = 0.062 kg/s. [126]

Khadraoui et al. [127] developed an indirect forced convective solar dryer consisting of a solar air panel for direct heating of the drying agent, a solar air collector with PCM (melting temperature range of 56-60°C) and a drying chamber. It was found that the temperature of the drying chamber was higher than the ambient temperature by 4-16°C. Additionally, the relative humidity in the drying chamber was 17-34.5% lower than the ambient relative humidity. A similar indirect solar dryer using PCM (paraffin wax with a melting temperature of 49°C) was experimentally investigated by Shalaby and Bek [128] and it was found that the temperature of the drying air was higher than ambient temperature by 2.5-7.5°C in a period of 5 hours after sunset.

4.2 Solar stills

Desalination of the saline seawater is an efficient technique for fulfilling the demand for fresh water. Solar stills incorporated with PCMs, are effective systems for improving the yield of fresh water especially in remote areas.

Faegh et al. [129] numerically studied the performance of a solar still equipped with an external heat storage system using PCM (paraffin wax) and solar tubes shown in Fig. 30. During the daytime period, the wasted latent heat from the generated water vapour was absorbed and stored in PCM. During the night-time period, the heat stored in PCM was transferred to saline water by heat pipes to continue the desalination process. It was found that this solar still could continue the desalination process after the sunset without a yield reduction during the daytime and the daily yield was increased by 86% to reach to 6.555 kg/m^2 per day.

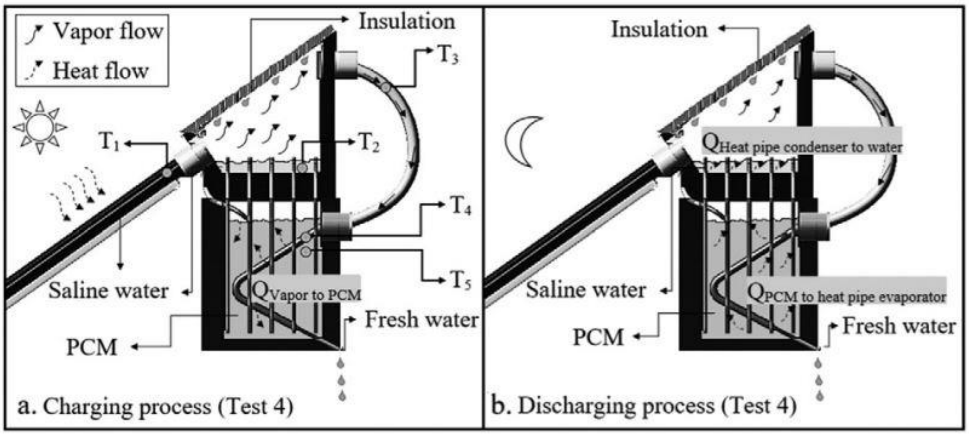


Fig. 30. Schematic diagram of the system processes of solar still with external condenser containing PCM and heat pipes: a) charging process b) discharging process [129]

Arunkumar et al. [130] investigated a modified parabolic concentrator coupled to a single slope solar still with paraffin wax (melting temperature of 58-60°C) loaded with copper balls for heat transfer enhancement placed in the still basin shown in Fig. 31 and evaluated its improvement on the overnight productivity. It was found that adding PCM in the basin of the solar still was more cost effective than increasing the flow rate of cooling water over the top cover. Kabeel et al. [131] experimentally investigated the performance of a cylindrical parabolic concentrator with a focal pipe coupled with a solar still with PCM (paraffin wax with a melting temperature of 56°C) to improve the freshwater productivity. It was found that the freshwater productivity of the solar still with PCM was 140.4% higher than that of a conventional one without PCM on average

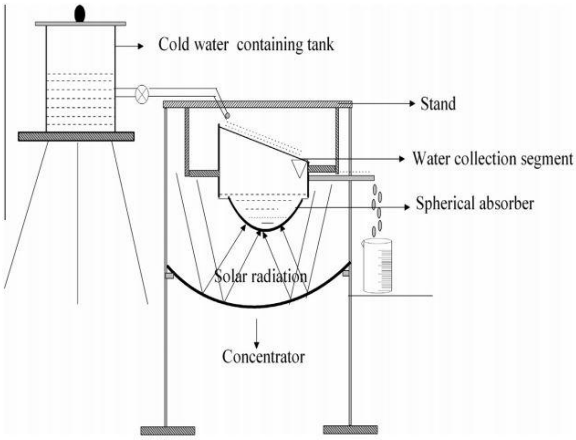
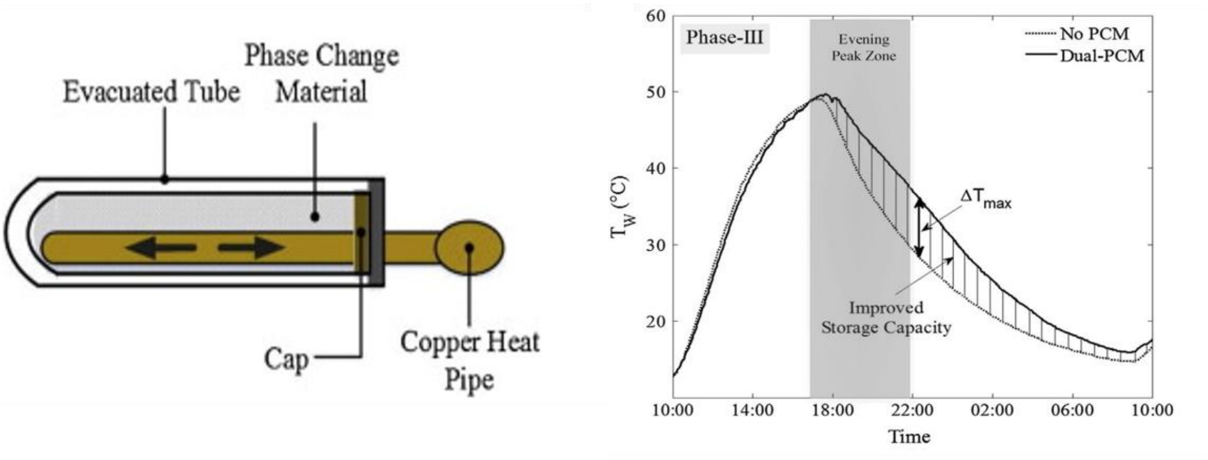


Fig. 31. Schematic diagram of a PCM (spherical absorber) solar still with a top cover cooling unit [130]

4.3 Solar Domestic Hot Water systems (SDHW)

Latent thermal storage with PCM is one of the potential solutions to fill the gap between the energy supply and consumer demand, for the development of efficient solar domestic hot water systems, reduction of the storage tank volume and improvement of the system efficiency. Mahfuz et al. [132] investigated the performance of a solar water heating system with PCM (paraffin wax with a melting point of 56°C) in the shell and tube thermal energy storage system. They found that with water flow rates of 0.033 kg/min and 0.167 kg/min, the energy efficiencies were 63.88% and 77.41%, respectively. And the total life cycle costs were predicted to be $ 654.61 and $ 609.22, respectively, indicating the total life cost decreased with the water flow rate. However, Padovan and Manzan [133] concluded from their numerical investigations that the tank with PCMs was not a viable solution for SDHW systems, due to a large temperature variation inside the tank, which could reduce the sensible heat absorbed and offset the benefits of PCMs.

To achieve latent thermal storage of SDHW systems, the direct integration of PCM into a evacuated tube as a thermal storage medium can be a solution to the simultaneous development of solar thermal and thermal energy storage technologies. Papadimitratos et al. [125] presented a novel method of integrating PCMs (Tritriacontane and Erythritol, with melting temperatures of 72°C and 118°C, respectively) within the evacuated solar tubes of solar water heaters. The heat pipe was immersed inside the PCM as shown in Fig. 32a, where the thermal energy can be effectively accumulated and stored for an extended period due to a good thermal insulation of the evacuated space. It was found that the efficiency was improved by up to 26% for the normal operation and increased by up to 66% for the stagnation mode, compared to a standard solar water heater without PCM as shown in Fig. 32b.



a b

Fig. 32. a) Schematic diagram of a evacuated solar collector filled with PCM; b) water temperature variation of dual-PCMs under the normal operation mode [125]

Similar experiments were conducted by Feliński and Sekret [134, 135]. They investigated a paraffin-containing evacuated thermal collector and storage (ETC/S) system equipped with a compound parabolic concentrator (CPC) to reduce heat loss and increase the amount of useful heat obtained from solar energy as shown in Fig. 33. Technical grade paraffin with an onset melting temperature of 51.24°C was used and it was found that the average gross charging efficiency of the ETC/S with a CPC was 36%, which was 5% higher than that of the ETC/S without a CPC. The maximum charging efficiencies for the ETC/S with a CPC were 66% (aperture) and 49% (gross), whereas for the ETC/S without a CPC they were 63% (aperture) and 40% (gross), respectively.

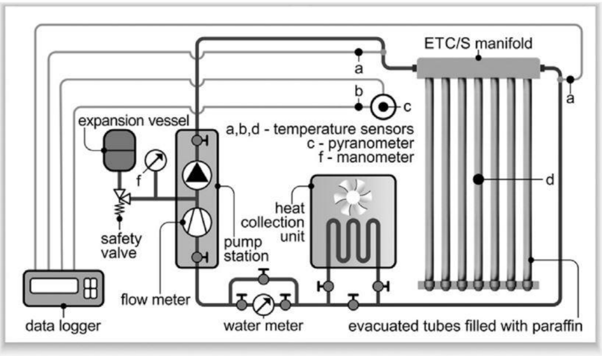


Fig. 33. Schematic diagram of the test setup for paraffin-containing ETC/S system [134, 135]

4.4 Electronic devices

Phase change materials can be solutions for rapid cooling of electronic devices to get higher performances and a long lifespan. To achieve an enhanced lifetime for a micro-electronic device, Muratore et al. [124] developed a microscale PCM based thermal management system to mitigate the transient temperature excursions and thermal loads, consisting of a textured Si matrix filled with micro-reservoirs of a paraffin wax with a melting temperature of 60°C. It was found that this microscale embedded PCM storage system was sufficient to stabilize and control the surface temperature of selected electronic devices and finally increase their lifespans by up to 300%. Tomizawa et al. [109] investigated the application of PCM sheets to mobile phones. Microencapsulated paraffin with a melting temperature of 32°C was composited to copper sheets used as a high thermal conductivity material incorporated into experiments as shown in Fig. 34a and Fig. 34b. It was found that PCMs with thicker thickness pasted on the copper sheets were more effective for the delay of the temperature increase rate as compared to other cooling methods (Fig. 34c).

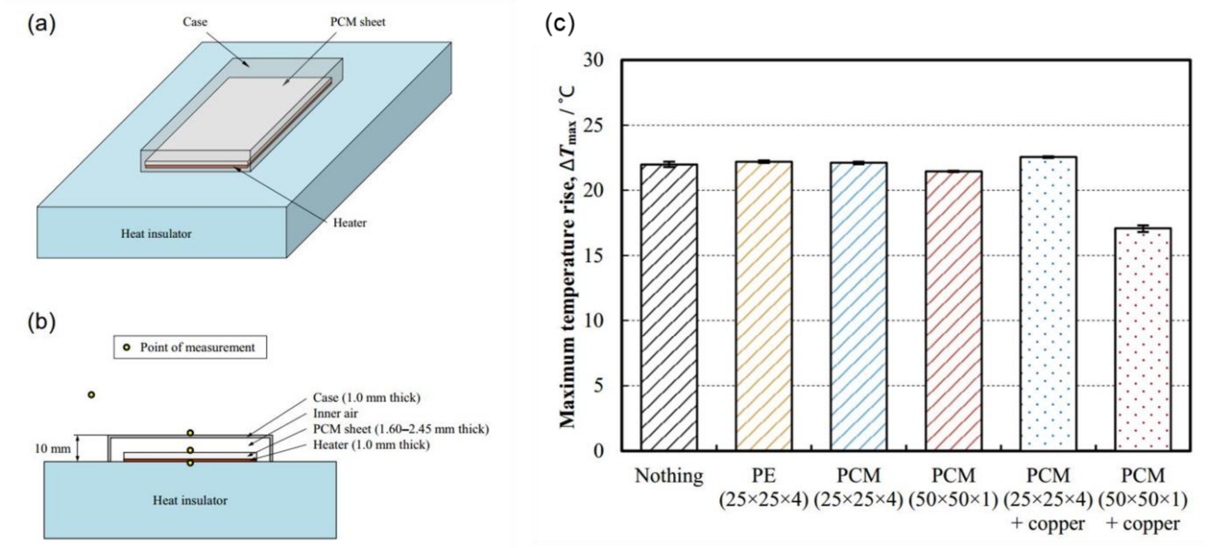


Fig. 34. Experimental setup of thermal performance investigation of PCM sheets for cooling mobile phones: a) General view; b) Cross-sectional view and c) maximum front case temperature rise at different conditions [109]

Tan and Tso [136] carried out an experiment on the thermal performance of a Heat Storage Unit (HSU) filled with n-eicosane (melting temperature of 36°C) as the PCM. It was found that the HSU with PCMs could stabilize the system temperature around allowable working temperature (50°C). An experiment on the same PCM placed inside the heat sink was conducted by Fok et al. [137], investigated the cooling effect of PCM incorporated into portable hand-held electronic devices. It was found that using n-eicosane in a finned heat sink was effective for cooling mobile devices under frequent and heavy usage conditions with power levels ranging from 3 to 5 W, under daily ambient temperature varied from 24 to 34ºC. Kandasamy et al. [138] experimentally investigated the thermal management of a portable electronic device utilising PCM package containing Perspex with a melting temperature of 80°C as shown in Fig. 35. It was found that increased power inputs could increase the melting rate of PCM, while the effect of package orientation to the gravity on thermal performance was negligible.

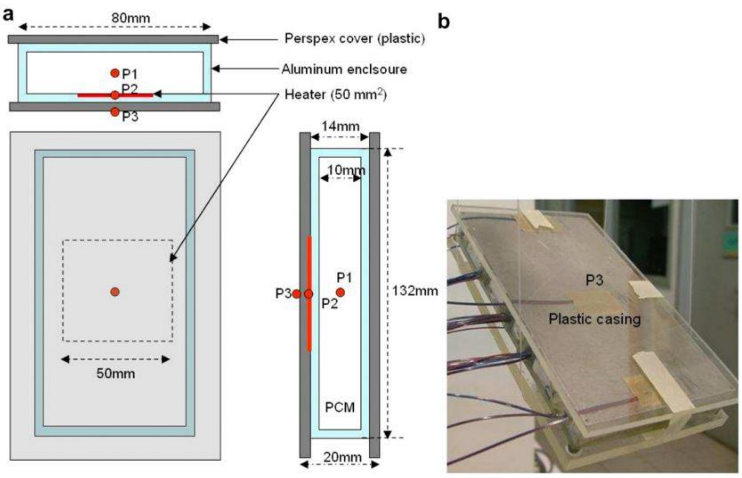


Fig. 35. a) Schematic and b) illustration of the experimental setup [138]

4.5 Analysis of PCMs used in medium temperature range

Organic compounds are typically applied in this temperature range, such as several types of paraffin waxes and fatty acids, due to their suitable melting temperatures and relative long lifetimes with low costs. Thermo-physical properties of key PCMs used for the applications within the medium temperature range are presented in Table 8. To overcome the drawback of low thermal conductivities of organic compounds, several heat transfer enhancement techniques have been conducted in this temperature range, including adding fins [126, 139-146], heat pipes [125, 129, 147], dispersing nanoparticles [148-153], microencapsulated PCM [154-158], carbon fibre brushes [159, 160], graphite composite [161-166].

Table 8. Thermo-physical properties of key PCMs used for the applications within the medium temperature range (40°C -80°C)

Materials	Type	Synthesized by researcher	Commercial product	Melting temperature (°C)	Heat of Fusion (kJ/kg)	Thermal conductivity (W/m·K)	Specific heat (kJ/kg·K)	Application	Ref.
Lauric Acid	Organic		✓	42.5	211.6	1.6	1.76	Solar assisted thermal storage	[167]
Myristic Acid	Organic		✓	53	181	-	-	Solar heating and cooking	[168]
RT54	Organic		✓	54	190	0.21	2.1	Solar air heater	[126]
Stearic Acid	Organic		✓	54.7	159.3	-	-	Solar assisted thermal storage	[169]

Paraffin 130/135	Organic		✓	55.8	232.4	0.09	2.18	Solar domestic hot water	[170]
Paraffin wax 56	Organic		✓	56	226	0.24	2.95	Solar stills	[131]
Palmitic Acid	Organic		✓	61.3	179.9	-	-	Solar assisted thermal storage	[169]
Stearic Acid/Carbonized sunflower straw	Organic	✓		66.4	186.1	0.33	2.18	Solar assisted thermal storage	[15]
Stearic Acid	Organic		✓	67-69	-	0.16	1.03	Solar cookers	[171]

Rezaei et al. [172] and Kabeel et al. [173] carried out economic analysis of PCMs in this temperature range. Spoletini [174] concluded the levelized cost of electricity (LCOE) of a PCM storage tank combined with a condensing micro-CHP over a system lifespan of 15 years. It was found that the LCOE of the PCM storage tank is 0.16 €/kWh, only 5% lower than the LCOE of the water tank. The main benefit of adopting PCM was to reduce the tank size up to 400%. Table 9 presents the economic analysis of different PCMs storage systems under a lifespan of 40 years and it could be found that the total life cycle cost of a PCM storage system could be reduced by using PCMs with higher melting temperatures.

Table 9. Economic analysis of different PCM storage systems for a lifespan of 40 years [172]

PCM type	T_m °C	Heat fusion (kJ/kg)	PCM weight (kg)	PCM price ($)	Total life cycle cost ($)
A32	32	130	336	2186	5573247
A39	39	105	416	2707	4687327
A42	42	105	416	2707	4319699
A53	53	130	336	2186	3030095
A55	55	135	324	2105	2805082
A58	58	132	331	2153	2472916

5. Applications of PCMs in the high temperature range from 80°C to 200°C

This section focuses on the applications of phase change materials in the high temperature range from 80°C to 200°C, where PCMs are integrated into the solar absorption cooling systems to achieve higher COP, and into waste heat recovery systems and solar power plants to improve energy usage efficiencies and reduce environment pollutants.

5.1 Solar absorption cooling

PCM incorporated into a solar absorption refrigeration system stores and releases thermal energy in a relatively narrow temperature range, which can be used as a constant inlet heat source to drive an absorption chiller for a long time operation contributing to the performance improvements.

For a single effect absorption cycle, an commercial absorption chiller usually requires an inlet driving temperature of at least 70°C to achieve a good operational efficiency [175]. Agyenim et al [176] experimentally investigated the performance of a LiBr/H_2O solar absorption cooling system as shown in Fig. 36, driven by a thermal storage system using erythritol with a melting point of 117.7°C. It was concluded that using erythritol as a storage media was able to drive a LiBr/H_2O solar absorption cooling system. An outdoor experiment of a solar cooling system with PCM was carried out by Agyenim et al. [177] and concluded that 100 litres of erythritol could store enough thermal energy for approximately 4.4 hours of peak cooling loads, based on a COP of 0.7 for absorption chiller applied in a 82 m^3 office building in Cardiff, during a hot summer day.

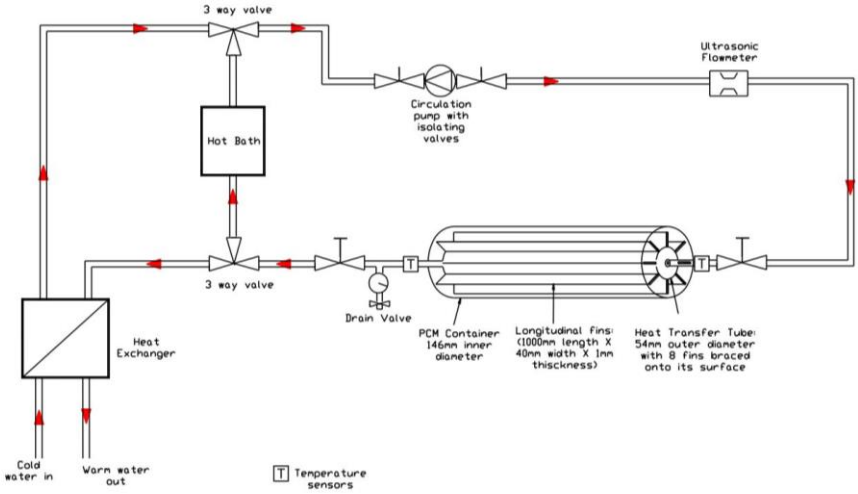


Fig. 36. Schematic diagram of the solar cooling experimental system [176]

Double-effect absorption cycle has a COP value in the range between 1.1 and 1.2, requiring hot water supplied to the low pressure generator with an temperature of 90°C and a primary driving temperature in the range of 140-180°C [178, 179]. Gil et al. [180] experimentally investigated the feasibility of latent thermal storage with PCMs to drive a double effect absorption chiller through a pilot thermal energy storage (TES) rig as shown in Fig. 37. The hydroquinone with a melting temperature range between 166°C and 173°C was selected as the PCM to drive the pilot plant with a working temperature range between 150°C and 200°C. It was found that the hydroquinone was able to drive a double effect absorption pilot installation.

Fan et al. [181] carried out a numerical investigation of a double effect solar absorption system combined with a latent thermal storage (LHTS) system. The numerical model of the LHTS system was coupled with a mathematical model of the absorption system and hydroquinone was selected as the PCM. It was found that with a PCM volume of 12.55 m^3, it was possible to fulfil the considered 100 kW cooling load without an external energy supply.

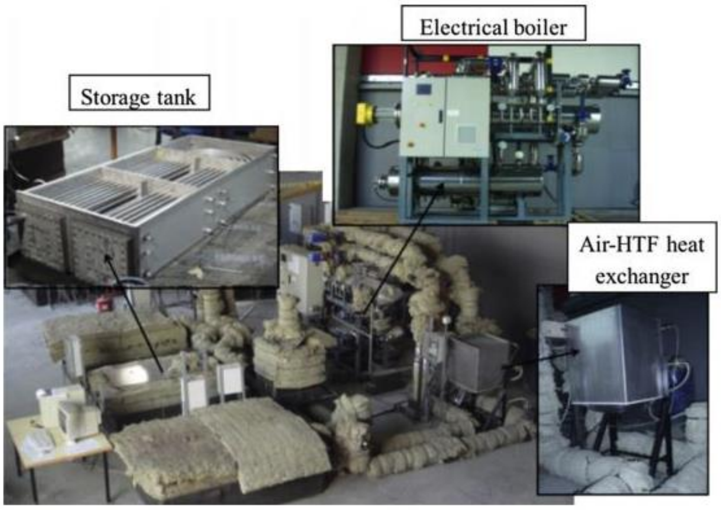


Fig. 37. Schematic diagram of the pilot plant [180]

5.2 On-site waste heat recovery

There is a huge potential in waste heat recovery for the combustion of fossil fuels and industrial activities, and by using latent thermal storage systems with PCMs, the utilization of the waste heat can reduce the energy consumption and CO_2 emissions by recycling it as a heat source for energy reutilization.

De Boer et al. [182] carried out a case study of an industrial PCM heat storage system incorporated into an existing production facility of organic surfactants as shown in Fig. 38. Three different thermal storage systems with operating temperatures from 110°C to 160°C were evaluated. It was found that PCM with a melting temperature of 140°C was efficient both in reduction on steam demand and primary energy demand in batch processes with an energy saving up to 70%. Johansson and Soderstrom [183] evaluated electricity generation of three typical technologies for heat recovery in low temperature, including Thermoelectric Generator (TEG), Organic Rankine cycle (ORC), and PCM engine. It was concluded that the PCM engine system could be profitable at all investigated temperature ranges and its size could be adjusted properly to utilise the heat sources under 55°C.

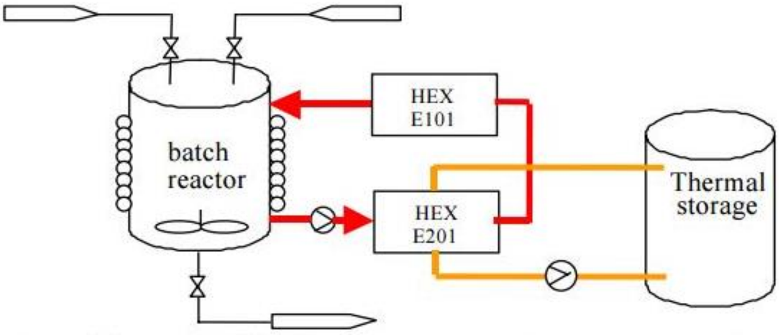


Fig. 38. Schematic diagram of the integration of a thermal storage system with the batch reactor [182]

Preheating is currently a common and the easiest solution to solve the cold-start problems of engines, including inefficient performances, deteriorations and increases of fuel consumption. PCMs can be feasible solutions to store waste heat of engine and use it to preheat the engine. Korin et al. [184] experimentally evaluated the reduction of pollutant emissions during an cold-start process of an internal combustion (IC) engine by means of a catalytic converter embedded with PCM (a eutectic mixture of LiCl/KCl). It was found that under normal engine operating conditions, some of the thermal energy from exhaust gases could be stored in the PCM. Larger amount of PCMs and better insulation materials were recommended for better results. Subramanian et al. [185] developed a heat recovery thermal exchanger integrated with an IC engine and a combined sensible/latent heat storage system with spherical PCM capsules (melting temperature between 50-60°C) as shown in Fig. 39. It was found that about 15% of the fuel power was stored in the combined storage system. Wu et al. [186] numerically studied a PCM storage system to recover and store the engine exhaust heat to preheat straight plant oils

(SPOs) during cold-start process for a tri-generation application. A commercial paraffin wax with a phase change temperature range between 90°C and 112°C was selected to meet the optimal preheating temperature from 70 to 90°C. It was found that the PCM thermal storage could be fully charged by the exhausted heat from engine and preheat the cold SPOs to the target temperature within 10 min.

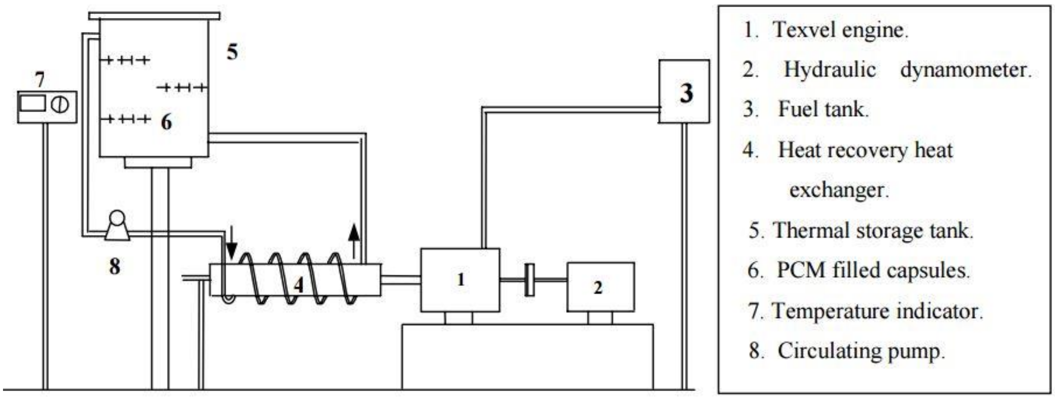


Fig. 39. Schematic diagram of the experimental setup [185]

5.3 Off-site waste heat recovery

As a promising technology for off-site waste heat recovery, mobilized thermal energy storage (M-TES) with PCM storage has been attractive to researchers, which collects heat from various heat sources and flexibly transports to distributed users by carriers, as shown in Fig. 40. The advantages of these systems are flexibility, high efficiency and stable heat supply [187].

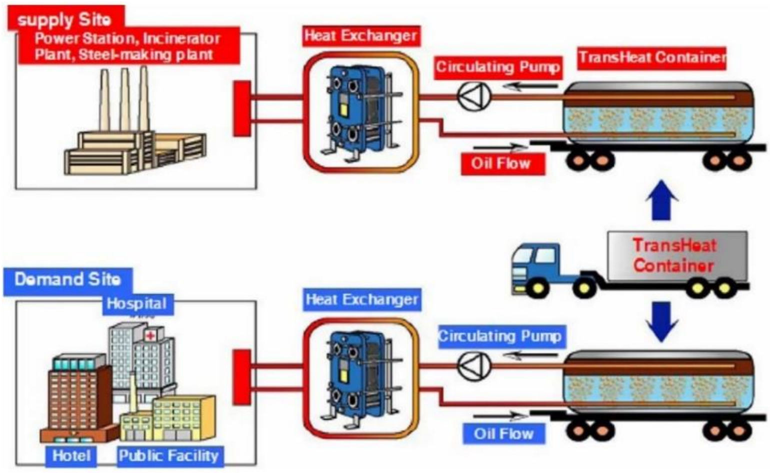


Fig. 40. Schematic diagram of phase change storage and transportation systems for low temperature heat transportation [188]

Kaizawa et al. [189] studied the thermal behaviour in a trans-heat (TH) container by using a two-dimensional model treated as a black box. With erythritol (melting point around 117°C) proposed as the suitable PCM [190] to supply hot water at a temperature of 50°C, it was found that the energy requirement, exergy loss, and CO_2 emissions of the TH system were 7.7%, 8.1%, and 20.2%, respectively, to those of the conventional system with kerosene on site [191].

Nomura et al [192] developed a novel waste heat transportation system using NaOH as the PCM to recover the industrial waste heat and supply it to a distillation tower of Benzene, Toluene, and Xylene (BTX) with a transportation distance up to 35 km. It was found that the largest amount of heat stored for a PCM heat transportation system was 2.76 times greater than the heat stored in a sensible heat transportation system, and the energy requirements, exergy losses and CO_2 emissions of this novel waste heat transportation system were merely 8.6%, 37.9% and 17.5%, respectively, to those of a conventional system using fossil fuels.

Wang et al. [193] experimentally investigated the mechanisms of heat charging and discharging process of mobilized thermal energy storage systems with direct/indirect contact storage containers as shown in Fig. 41, using erythritol (melting temperature of 118 ºC) as the latent storage medium. It was found that the direct-contact storage container was better than the indirect-contact storage container with higher charging and discharging speeds, where the heat transfer fluid (HTF) could enhance the thermal conductivity of the PCMs in a direct-contact storage container.

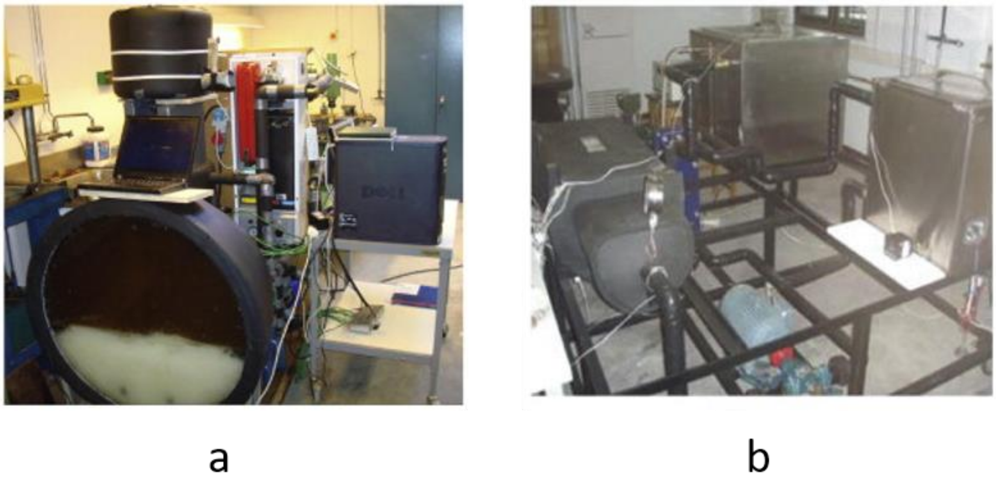


Fig. 41. Lab scale M-TES: a) direct contact storage container; b) indirect contact storage container [193]

Further on, Wang et al. [194] numerically studied the discharging process of a direct contact storage container used in M-TES system. The results showed the discharging time of an M-

TES could be reduced by increasing the flow rate of HTF. When the flow rate of HTF was increased from 0.46 m^3/h to 0.92 m^3/h, the volume proportion of solidified PCM was increased from 25 % to 90 % within 30 min. Moreover, the volume proportion of solidified PCM was increased from 60% to 90%, while the inlet temperature of HTF was reduced from 50 ºC to 30 ºC. Two phases in the melting process of a direct contact mobilized thermal energy storage were reported by Wang et al. [195]. In the liquid PCM region, vortexes generated by force and natural convection were found and the heat transfer was consequently enhanced; while in the solid region near the wall of the storage unit, PCM was melted slowly due to the low heat conduction dominating the heat transfer inside the solid PCM.

Guo et al. [196] numerically studied the charging process of a direct contact mobilized thermal energy storage (DC-TES) and the results showed that the charging time of a M-TES could be reduced by increasing the inlet flow rate of HTF. When the thermal oil flow rate was increased from 9.2 L/min to 21 L/min, the charging time was reduced by 25%. Moreover, Guo et al. [197] investigated the performance improvements of an indirect contact mobilized thermal energy storage (ICM-TES) container by adding the expanded graphite (EG), adjusting the tube diameter and internal structure of the container, or installing fins, as shown in Fig. 42. It was found that the optimal combination of three parameters for the best performance were 10 vol% (volume proportion of EG), 22 mm (tube diameter) and 0.468 m^2 (fin area), where the charging time and discharging time of the ICM-TES container were reduced by 74% and 67%, respectively.

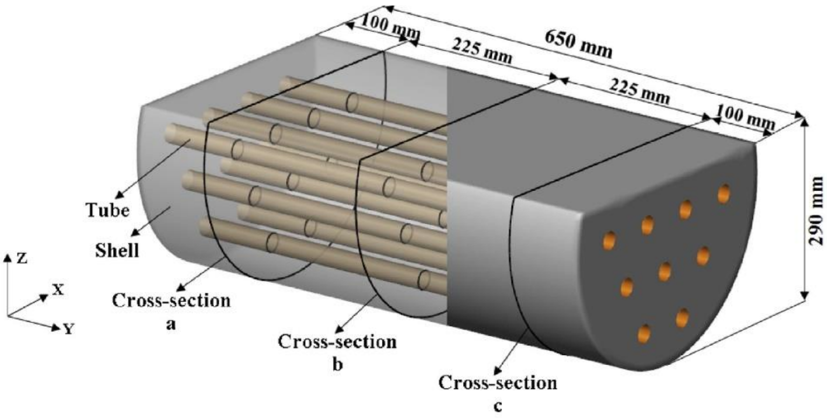


Fig. 42. Schematic diagram of the ICM-TES container [197]

5.4 Solar thermal electricity generation

For electricity generation applications, PCM solutions have been usually related with the direct steam generation (DSG) technology to store and deliver energy at a given constant temperature. Since steam exchanges heat at a constant temperature during the evaporating and condensing process, the temperature difference between the storage media and the steam minimizes the exergy destruction by the heat exchanged between PCMs and the steam. Additionally, the use of PCM offers a higher storage density with a potentially smaller storage size and a higher performance during its melting and solidification process, when compared to sensible heat storage systems used for DSG technologies.

Pirasaci and Goswami [198] presented a thermal model for the optimization of a latent heat storage unit for a direct steam generation using a NaCl-MgCl$_2$ eutectic mixture as the storage medium as shown in Fig. 43. The effectiveness of the storage was considered as an important design criterion and it was found that the length of the storage, HTF flow rate and tube diameter were all significant for the evaluation of effectiveness. Oró et al. [199] studied the environmental impacts of three different thermal energy storage systems for solar power plants and concluded that PCMs integrated into solar power plants were able to balance the energy saving with lower environmental impacts produced during the manufacturing and operation process, in a comparison to sensible storage systems. Tamme et al. [200] developed three design concepts for thermal storage technologies using PCMs in the temperature range of 120-300°C° for a solar thermal power generation. It was concluded the significant increase of efficiency by graphite PCM composites, which could enhance the effective thermal conductivity from below 0.5 to 3-20 W/m.K.

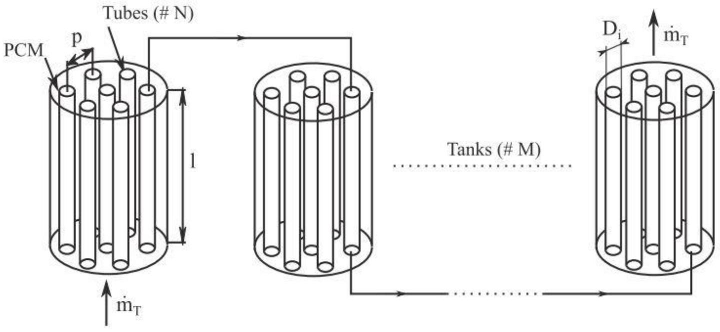


Fig. 43. Schematic of the designed PCM storage [198]

5.5 Analysis of PCMs used in high temperature range

Organic compounds, salts hydrates, and eutectic mixtures are typically applied for latent thermal storage systems in this temperature range. Attractive organic compounds in this temperature range are some of the carboxylic acid [201-204], sugar alcohols [205, 206], alkanes (paraffin) [207] and amides [18]. Binary and ternary mixtures of nitrate salts of alkali and alkaline metals, such as potassium, lithium and sodium are the main compounds used to produce eutectic mixtures working in the temperature range from 120 to 200°C, known as ionic liquids [208]. The toxicity, health hazard and environmental impacts of the eutectic mixtures are governed by the constituents whether they are organic or inorganic materials. Thermo-physical properties of typical PCMs in the high temperature range are presented in Table 10.

Table 10. Thermo-physical properties of key PCMs used for the applications within the high temperature range (80°C - 200°C)

Materials	**Type**	**synthesized by researcher**	**Commercial product**	**Melting temperature (°C)**	**Heat of Fusion (kJ/kg)**	**Thermal conductivity (W/m·K)**	**Specific heat (kJ/kg·K)**	**application**	**Ref.**
$Mg(NO_3)•6H_2O$	Inorganic	✓		89	162	0.611 (solid) 0.49 (liquid)	-	Solar cooker	[171]
RT-100	Organic		✓	99	168	0.2 (solid) 0.2 (solid)	1.8 (solid) 2.4 (liquid)	Solar cooling	[207]
$MgCl_2•6H_2O$	Inorganic	✓		116.7	168.6	0.704 (solid) 0.570 (liquid)	2.25 (solid) 2.61 (liquid)	Thermal energy storage	[209]
Erythritol	Organic		✓	117.7	339.8	0.733 (solid) 0.326 (liquid)	-	Solar cooling	[205]
Adipic acid	Organic		✓	152	275	-	-	Thermal storage	[203]
d-Mannitol	Organic		✓	165	300	-	-	Thermal storage	[206]

Due to the drawback of low thermal conductivity of PCM in this temperature range, heat transfer enhancement techniques were widely investigated and reviewed from previous researches, including finned tubes of different configurations [176, 177, 210-218], metal matrix (foam) [219-226], shell and tube (multi-tubes) [215], graphite composites [227-230], and heat pipes [231-234], employing different experimental settings and materials of containers and PCMs. In terms of performances on heat transfer enhancement techniques and systems used in all reviewed researches, the best enhancement technique for organic compounds was reported by Xiao et al. [235], using copper foam integrated into paraffin with an average effective thermal conductivity of 5 W/m.K, which is 25 times larger than that of pure paraffin (0.2 W/m.K). It must be noted that the achievement of heat transfer enhancement can't be directly compared to other results due to the difference in experimental setups and materials. For inorganic PCMs, the best enhancement achieved was detailed by Acem et al. [227], reported thermal conductivities close to 20W/m.K, obtained from graphite amounts between 15% and 20% wt mixed with eutectic salts, 20 times greater than those of normal eutectic compounds.

Moreover, different researches also used different parameters to evaluate the heat transfer enhancements of PCMs in their investigations as summarised in Table 11. Agyenim et al. [176, 214, 215] used the "overall utilisation efficiency" which is the cumulatively discharged energy divided by the ideal energy capacity of PCMs, to evaluate the heat transfer mechanism improvement in terms of energy charging and discharging process of a finned PCM system and a multi-tube PCM system. Shabgard et al. [231] reported the "heat pipe effectiveness" to quantify the energy storage augmentation due to the addition of heat pipes, defined as the amount of sensible and latent energy stored in or extracted from either module with different number of heat pipes, relative to the energy stored or extracted without heat pipes. Xiao et al. [236] evaluated the enhancement of heat transfer on metal foams with pure paraffin using "effective thermal conductivity" which is the thickness difference of specimens divided to the thermal resistance difference between the thick and thin specimens.

Table 11 Different heat transfer enhancement evaluation parameters from reviewed works

Reference	Heat enhancement technique	Heat Enhancement Evaluation Parameters	Remarks
[176, 214, 215]	Finned single tube and multi-tube	Overall utilisation efficiency: $\eta_{store,overall} = \frac{Energy\ discharged}{Ideal\ energy\ capacity\ of\ PCM}$	-
[231]	Heat pipes	Heat pipes effectiveness:	Q_t is the HTF tube energy storage; N is the number of heat pipes; Q_{HP} is the energy stored in or extracted from a

		$\varepsilon = \frac{N \times Q_{HP} + Q_{t,HP}}{Q_t}$	module. $Q_{t,HP}$ is the energy stored in or extracted from a module when the presence of the heat pipes is accounted for.
[236]	Metal foams	Effective thermal conductivity: $\lambda_e = \frac{h_{tk} - h_{tn}}{A\Delta R_{tk-tn}}$	h_{tk} and h_{tn} are the thicknesses of the specimens respectively; A is the cross sectional area of the fluxmeters/specimen; ΔR_{tk-tn} is the thermal resistance difference between the thick specimen and thin one.

Miró et al. [237] investigated the health hazard of five PCMs used in the temperature range of 150-200 ºC and concluded that benzanilide and D-mannitol were both suitable PCMs. Oró et al. [199] and López-Sabirón et al. [238] have carried out the life cycle assessment (LCA) of PCMs used in this temperature range. Although PCMs entail the highest global impacts per kWh during the manufacturing and operation processes compared to solid media and molten salts, due to the CO_2 emissions from transportation and material production, the global impacts per kWh of PCM can be reduced with the increase of energy storage capability. Table 12 presents the global impact per kWh comparison of the solid media system (sensible heat storage in concrete), molten salts system (sensible heat storage in liquid media) and a PCM system (latent and sensible heat storage).

Table 12. Global impact per kWh comparison of three TES system [199]

		Manufacturing + operation GLOBAL IMPACT/kWh					
		High temperature (ºC)	**Low temperature (ºC)**	**Eco system quality (Impact/kWh)**	**Human health [Impact/kWh]**	**Resources [Impact/kWh]**	**Total**
Normal conditions	Solid media	390	120	0.01	0.10	0.04	0.15
	Molten salts	550	290	0.47	2.55	2.65	5.67
	PCM	235	195	1.12	6.31	6.36	13.79
△T=50ºC	Solid media	390	340	0.04	0.53	0.22	0.80
	Molten salts	550	500	2.43	13.27	13.76	29.47
	PCM	246	196	1.02	5.76	5.80	12.59
△T=250ºC	Solid media	390	140	0.01	0.11	0.04	0.16
	Molten salts	550	300	0.49	2.65	2.75	5.89

	PCM	346	96	0.38	2.14	2.16	4.68

A significant amount of researches on the economic analysis of PCM applications in this temperature ranges have been carried out so far. For example, Zhao et al. [239] numerically investigated the cost of a multi-layered solid-PCM (MLSPCM) thermocline TES used in a concentrating solar power (CSP). It was found that the capital cost of MLSPCM was lower than the traditional sensible TES with an equivalent thermal storage capacity. Table 13 presents a comparison of capital cost among different TES systems of a 250 MWt storage capacity. It can be seen that longer operation hours offer lower capital cost for PCM storages. Li et al. [240] reported the cost of using M-TES to supply 1 kWh heat in a range between 0.03 and 0.06 $, primarily determined by the transport distance and heat demand. Jacob et al. [241] numerically investigated the capital expenditure of three high temperature TES options proposed for CSP including an Encapsulated PCM (EPCM) system (using two chloride PCMs), a coil in tank system (latent heat storage) and a liquid sodium system (two tank sensible heat system) and concluded that the final installation cost of EPCM was 11.15 $/kWh$_t$, which was significantly lower than the coil in tank system (19.22 $/kWh$_t$) and the liquid sodium system (43.34 $/kWh$_t$), as shown in Table 14.

Table 13. Cost comparison of a 250 MWt storage capacity among MLSPCM, Sensible TES and Two-tank TES system [239]

Required cyclic operating time duration, h	Capacity factor, %	Capital cost, $ kW h^{-1}		
		MLSPCM	Sensible TES	Two-tank TES
8	84.27	16.53	21.73	26.16
9	84.48	15.88	20.93	25.44
10	84.52	15.36	20.21	24.85
11	84.48	14.93	19.57	24.35
12	84.48	14.55	19.04	23.93

Table 14. Capital expenditure of investigated TES system [241]

Cost	EPCM (latent storage)	Coil in tank system (latent storage)	Liquid sodium system (sensible storage)

Storage tank ($)	1044950	1063795	3058098
Storage material ($)	556896	895111	8015925
Construction ($)	885350	1526361	3448280
Installation ($/kWh$_t$)	11.15	19.22	43.43

6. Summary and Conclusions

This paper reviews the current PCM research status, material properties, microencapsulation, shape stabilization techniques, commercial applications and environmental issues and also covers areas which have not been given much attentions in previous studies like toxicity, health hazards, and current market scenario.

To the best of our knowledge, the application of PCMs has been comprehensively reviewed for the first time from the sub-zero temperature range as low as -20 ºC to the high temperature as high as 200 ºC. In order to adequately discuss the performance improvements, environmental impacts and capital cost, and the classifications of PCMs and applications in different temperature ranges, previous studies on latent thermal storage with PCMs integrated into applications for cooling, heating and electricity generation in different temperature ranges have been critically reviewed. Different types of applications of phase change materials are presented and discussed, in terms of the applied material properties, thermal performances, heat transfer enhancement technologies, environmental impacts and capital costs. The typical PCMs applied at each temperature ranges and their contribution to the system performances are summarised in Table 15, while the toxicity, health hazards and environmental impacts of these typical PCMs are summarised in Table 16. The main obstacles for PCM’s commercial implementation are from the thermal property (low thermal conductivity around 0.1-0.3 W/mK with corrosion and toxicity for most organic materials) and long payback period of the installation investment (minimum 6 years due to high cost of material), even though PCM storage has been reported with operational performance improvements and similar environmental impacts as compared to conventional storage options. It is suggested that PCM can be further investigated in mobilized-thermal energy storage and other thermal storage applications where consumers are willing to afford the cost for better operational performance, such as the storage of temperature sensitive valuables (food, organ, etc.), cooling of electric devices, domestic thermal storage, etc.

Table 15. Highlighted results of key phase change materials applied to different temperature ranges

Temperature range	Applications	PCM		PCM - application			Drawbacks	Solution
		Melting temperature range (ºC)	Type	Performance improvement	Environmental impact	Economical assessment		
Low (-20 to 5 ºC)	Domestic refrigerator	-15 to 30	Organic/salt hydrates	Energy consumption ↓12% COP ↑19%	CO2 ↓ 14716000 t/year for Europe	Cost ↓4638 million €/year for Europe	PCM leakage; super cooling	PCM-encapsulation
	Commercial refrigerated product	-20 to 5	Organic/salt hydrates	Energy consumption ↓84%	CO2 ↓1319 t/year for Europe	Cost ↓397 million €/year for Europe	Low thermal conductivity	Heat transfer enhancement
Medium-Low (5 to 40ºC)	Free cooling	19 - 24	Organic	T_{air} ↓1.8 ºC energy ↓50%	NA	NA	Low thermal conductivity	PCM-encapsulation
	Building passive heating and cooling	21 - 38	Organic/inorganic	Energy ↓32%	Overall environmental impact ↓7.5%	Cost ↓42% Payback from 6 years	Low thermal conductivity	PCM-encapsulation
	Solar absorption chillers	26-30	Inorganic	Daily energy efficiency ratio ↑11.4	NA	NA	NA	NA
	Evaporative and radiative cooling	Around 18	Organic/inorganic	Energy ↓10% - 80%	NA	NA	Low thermal conductivity	Micro-encapsulation
	Air conditioning	8-18	Organic	Energy ↓3.09 kWh/day	Global warning potential ↓17% Human health ↓18%	Installation 180-200 €/kWh Payback 4.12 years	Low thermal conductivity	PCM-encapsulation
Medium (40 to 80ºC)	Solar air heater	49-60	Organic	T_{air} ↑up to 7.5 ºC	NA	NA	Low thermal conductivity	Heat transfer enhancement
	Solar still	55-60	Organic	Productivity ↑up to 140%	NA	0.0174 $/L water produced	NA	NA
	Solar hot water	56-120	Organic	Efficiency ↑26% to 66%	NA	Lifespan cost 600 – 650 $	NA	NA
	Electric devices	30 - 60	Organic	Lifespan ↑300%	NA	NA	Low thermal conductivity	PCM-encapsulation
High (80 to 200ºC)	Solar absorption cooling	117 - 173	Organic	COP 0.7	NA	NA	Low thermal conductivity	Heat transfer enhancement

On-site waste heat recovery	50-200	Organic/inorganic	Energy consumption ↓70%	NA	11.15 $/kWh	Low thermal conductivity	Heat transfer enhancement
Off-site waste heat recovery	117-200	Organic/inorganic	Energy requirement ↓7.7%	CO_2↓20.2%	0.03-0.06 $/kWh	Low thermal conductivity	Heat transfer enhancement
Solar thermal electricity generation	120-200	Organic/inorganic	Energy savings	Environmental impacts ↓with △T ↑	14.5 -16.5 $/kWh	Low thermal conductivity	Heat transfer enhancement

Table 16. Toxicity, health hazard and the environmental impact of typical PCMs

PCM	Toxicity/health hazards/environmental impacts
Paraffin wax	Carcinogenic compounds in commercial product, flammable, non-biodegradable
Fatty acid	Variable toxicity, undesirable odor, flammable, corrosive
Salt hydrates	Varying grades of toxicity, usually not flammable, skin or eye irritation and respiratory problems
Eutectic	Depends on the constituents, i.e. if it is organic or organic (fatty acids/ paraffinic).

The following conclusions can be drawn from this review:

- Phase change materials used in the low temperature range (-20 °C to 5 °C) for operation performance improvements of domestic refrigerator and commercial applications, are mainly organic compounds, e.g. alkane hydrocarbon with melting temperatures above 0 °C and eutectic salt solutions with melting temperature below 0 °C. It is important to select suitable materials with appropriate melting temperatures and encapsulation techniques to prevent the super-cooling effect and leakage for the cold storage systems. When PCM is used for cold thermal energy storage (CTES) in the low temperature range (-20 to 5ºC), it can significantly reduce the energy consumption of appliances and therefore reduce the environmental pollutions including CO_2, SO_2, NO_X and Chloro-Fluoro-Carbons (CFC) emissions, when compared to conventional storage options.
- Phase change materials in the medium-low temperature range (5 °C to 40 °C) can be integrated into building components for free cooling and passive heating, and it can also be coupled with evaporative and radiative cooling systems to improve indoor thermal comfort and reduce energy consumptions. They can also be integrated into solar absorption chillers to improve their operation efficiency and into air conditioning

systems to shift the daytime electricity load to night-time. Organic compounds and salt hydrate compounds are commonly used in this temperature range.

- For the medium temperature range from 40 °C to 80 °C, organic compounds like paraffin and fatty acids are widely used and integrated into solar air heaters, solar stills, and solar domestic hot water to extend their operation periods with higher yield increased by up to 86% and into electronic devices as heat sinks to improve the operation efficiency by up to 26% and increase their lifetime by up to 300%. The investment of a PCM storage system used in the medium temperature range is slightly lower than that of a conventional storage system, as the tank size can be massively decreased compared to a conventional thermal storage system.
- The phase change materials in the high temperature range from 80°C to 200°C are applied for solar absorption cooling to achieve higher COP, thermal storage of waste heat recovery and solar thermal electricity generation to improve their energy usage efficiencies and reduce environment pollutants. The cost of an off-site PCM storage system is significantly lower than that of an on-site PCM storage system. However, the performance of PCM from life cycle assessments is not attractive in a normal working condition and there are only a few organic PCMs available in this temperature range with acceptable performance improvements, while molten salts would still dominate the thermal energy storage sector for a long time, when considering the cost and lifespan benefits of molten salts.
- The heating applications of PCMs are mainly in the temperature range from 40°C to 200°C with an improvement of operation efficiency from 26% to 66%, achievable depended on specific applications. Cooling applications with PCMs are primarily in the temperature range between -20°C and 40°C with energy saving and cooling load reduction by up to 12% and 80%, respectively. Solar thermal direct steam generation is the typical electricity generation application in the temperature range from 40°C to 200 °C coupled with a PCM storage system.
- Most phase change materials have low thermal conductivities especially organic compounds, requiring heat transfer enhancement techniques to improve the thermal performance during their phase change periods. The most applied heat transfer enhancement methods are using fins, insertion/dispersion of high thermal conductivity materials (metal foam, graphite, metal powder, etc.), multitubes and micro/macro encapsulation. Additionally, the sandwich structure (PCMs segmented by rectangular

fins) is the most common commercial heat transfer enhancement technique in high temperature power generation applications with PCMs, due to the low cost and simple structure of fins.

- Heat transfer enhancement is one of the most important design criteria for PCM storage applications. When PCMs are used as heat sinks or heat sources, the heat transfer rate is directly related to the operation performance improvement. However, for some passive cooling applications with PCMs (PCMs in wallboard, floor, ceiling, etc.), relatively lower thermal conductivity helps to buffer the temperature variation and maintain the designed temperature for a longer operation period. Hence, the heat transfer enhancement of PCM storage system should be carefully considered and designed based on the specific working condition in order to achieve the best performance improvement.
- Although the applications of PCMs in each temperature range show significant performance improvements and huge potential for CO_2 emission reduction, being environmentally friendly and having a short payback period are also important for the public and the end users, particularly the PCMs used for large-scale commercial thermal storage options.

Finally, the following are recommended for future researches and investigations on the development and application of PCMs:

- Due to the high cost of experimental test and model validation with experimental data under real conditions, development and continuous improvement of numerical and analytical methods are needed to accurately and reliably predict the performance of PCMs in different applications especially in the extremely low or high temperature range.
- The application of PCMs as an alternative thermal storage medium has been evaluated through numerous experimental tests and analytical investigations. However, there are much less effort on the study of environmental impacts of PCMs used for commercial applications such as industrial heat recovery and solar power plants.
- Heat conduction and heat convection are two forms of heat transfer methods occurring inside the PCMs during the phase change process. However, most heat transfer enhancement techniques can lead to an increase of heat conduction and suppression of heat convection. Further researches on the heat conduction and heat convection of

PCMs are needed for the optimization of heat transfer enhancement technique and PCM container.

- Most of the literature in the temperature range from 5°C to 80°C has focused on the commercialized organic PCM materials in particular the paraffin. It is recommend to investigate other inorganic PCM materials like hydrate salts and synthesized PCMs, which may be suitable for some specific application requirements.

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