Review on phase change materials (PCM) for cold thermal energy storage applications

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Abstract

Thermal energy storage (TES) is a technology with a high potential for different thermal applications. It is well known that TES could be the most appropriate way and method to correct the gap between the demand and supply of energy and therefore it has become a very attractive technology. In this paper, a review of TES for cold storage applications using solid-liquid phase change materials has been carried out. The scope of the work was focussed on different aspects: phase change materials (PCM), encapsulation, heat transfer enhancement, and the effect of storage on food quality. Materials used by researchers as potential PCM at low temperatures (less than 20 ºC) are summarized and some of their thermophysical properties are reported. Over 88 materials that can be used as PCM, and about 40 commercially available PCM have been listed. Problems in long term stability of the materials, such as corrosion, phase segregation, stability under extended cycling or subcooling are discussed. Heat transfer is considered both from theoretical and experimental point of view and the different methods of PCM encapsulation are reviewed. Many applications of PCM at low temperature can be found, such as, ice storage, conservation and transport of temperature sensitive materials and in air conditioning, cold stores, and refrigerated trucks.

Keywords: Review, phase change materials (PCM), thermal energy storage (TES), latent heat, cold storage, heat transfer, refrigerated trucks.

1 Introduction

Latent heat storage using phase change materials (PCM) is one of the most efficient methods to store thermal energy. Therefore, PCM have been applied to increase thermal energy storage capacity of different systems [1-2]. The use of PCM provides higher heat storage capacity and more isothermal behaviour during charging and discharging compared to sensible heat storage [3]. Moreover, thermal energy storage (TES) systems for both heat and cold are necessary for good performance of many industrial processes. High energy storage density and high power capacity for charging and discharging are desirable properties of any storage system. These storage systems have been studied for many years addressing different problems of the used materials such as low thermal conductivity and segregation of the PCM [3].

In the application of PCM, the solid-liquid phase change is used to store large quantity of energy. The substances used can be organic such as paraffin and fatty acids, or inorganic such as aqueous salts solutions; both show a single melting temperature when they are pure, and a melting range, when they are mixtures. Literature show extensive publications for different applications of PCM such as domestic hot water tanks [5-6] space heating and cooling of buildings [7], peak load shifting [8], solar energy applications [9]and seasonal storage, including many reviews [1-4 and 9-13]. PCM in TES systems at high temperature has also been reviewed recently in [15-17].

To our knowledge, there is no literature review available on the use of PCM in low temperature applications. The paper presents large number of PCM which melts below 20 ºC and describes problems associated to their use such as encapsulation and heat transfer enhancement. Cold TES systems are also widely used in various industrial applications such as food storage, where large amount of heat gains to the system occurs [18]. Different applications such as ice storage, transport of temperature sensitive materials, air conditioning and other applications are commented in this review.

2 Phase change materials for cold storage applications

2.1 Classification of PCM at low temperatures

2.1.1 Description

It is well known that there are three methods of TES: sensible, latent and chemical methods of heat storage. The energy storage density in sensible heat storage is determined by the specific heat capacity of the storage media and the temperature changes. This temperature change ($\Delta T = T_2 - T_1$) depends on the application and is limited by the heat source and by the storage system. The sensible heat stored in any material can be calculated as follows:

$$Q_{sensible} = \int_{T_1}^{T_2} c_p \cdot dT$$

Where $Q_{sensible}$ is the sensible heat stored, C_p the specific heat of the material, and dT the temperature change.

The energy storage density could be increased using PCM, having a phase change (latent heat) within the temperature range of the storage. Considering the temperature interval $\Delta T = T_2 - T_1$ the stored heat in a PCM can be calculated as follows:

$$Q_{latent} = \int_{T_1}^{T_{PC}} c_s \cdot dT + \Delta H_{ls} + \int_{T_{PC}}^{T_2} c_l \cdot dT$$

Where Q_{latent} is the sensible and latent heat stored and ΔH_{ls} the heat of fusion at the phase change temperature T_{PC}.

Latent heat TES is particularly attractive due to its ability to provide high-energy storage density per unit mass in quasi-isothermal process. This means that in a specific application where the temperature range is important, for instance in transport of sensitive temperature products, the use of PCM becomes very useful since it can store material at constant temperature corresponding to the phase-transition temperature of the PCM.

Furthermore, any materials to be used for phase change TES must have high latent heat and high thermal conductivity. They should have a melting/freezing temperature lying in the practical range of operation, melt/freeze congruently within minimum subcooling and be chemically stable, low in cost, nontoxic and non-corrosive [2].

Many researchers have presented useful classifications of materials which may be used for thermal energy storage [1-3 and 11-12]. According to the literature, the PCM used in the design of TES systems should have desirable thermophysical, kinetic and chemical properties [3], [11]. It can be concluded from the information compiled over different studies [1-4 and 8-11] that the main characteristics required for a good PCM are:

- Thermophysical properties
    - Melting temperature in the desired operating temperature range
    - High latent heat of fusion per unit volume
    - High specific heat to provide additional significant sensible heat storage
    - High thermal conductivity of both solid and liquid phases
    - Small volume change on phase transformation and small vapour pressure at operating temperature
    - Congruent melting of the phase change material for a constant storage capacity of the material with each freezing/melting cycle
    - Reproducible phase change
- Nucleation and crystal growth
    - High nucleation rate to avoid subcooling of the liquid phase during solidification, and to assure that melting and solidification process occurs at the same temperature
    - High rate of crystal growth, so that the system can meet the demand for heat recovery from the storage system
- Chemical properties
    - Complete reversible freeze/melt cycle
    - No degradation after a large number of freeze/melt cycles
    - No corrosiveness to the construction/encapsulation materials
    - Non-toxic, non-flammable and non-explosive
- Economics
    - Abundant
    - Available
    - Cost effective
    - Easy recycling and treatment
    - Good environmental performance based on Live Cycle Assessment (LCA)

Fig. 1 shows the families of phase change heat storage materials; divided as organic and inorganic materials. Organic materials are further classified as paraffin and non-paraffins (fatty acids, eutectics, and mixtures). Experiments (melting and freezing cycles) using these materials showed that they crystallize with little or no subcooling and are usually non-corrosive and very stable.

Inorganic materials are further classified as compounds and eutectics. An eutectic material is a composition of two or more components, which melts and freezes congruently forming a mixture of the component crystals during crystallization. Eutectic nearly always melts and freezes without segregation, leaving little opportunity for the individual components to separate. Eutectic mixture melts almost at constant temperature. Main inorganic materials are salts, salt hydrates, aqueous solutions and water.

The selection of a salt hydrate as a PCM can be eased by a good understanding of its binary phase diagrams, M-H_2O 0. Fig. 2 shows a binary phase diagram compound for sodium chloride (NaCl) and water (H_2O), where E is the eutectic point of this solution. Furthermore, if the melting temperature of the PCM is critical then using these eutectic systems is beneficial. Yatseko and Chudotvortsev [21] developed correlations between the physicochemical properties of salts and their aqueous solutions. Most water-salt systems have eutectic phase diagrams, having hypoeutectic, eutectic, and hypereutectic compositions. With the known approaches of mapping and analyzing such phase diagrams, detailed information can only be obtained for hypereutectic regions, where salt crystals or crystal hydrates are formed on cooling. It was noted that for hypoeutectic compositions the salt concentration in the liquid is first higher than that in the initial solution, and in the course of melting, the salt concentration decreases approaching zero. For hypereutectic compositions, the opposite behaviour was observed. During the melting of the eutectic composition, the salt concentration in the liquid remains virtually constant, this can be used to locate the eutectic point. It was concluded that there are strong correlations between the physicochemical properties of salts, the phase diagrams of the corresponding water-salt systems, and the crystallization and melting behaviours of ice in such systems.

2.1.2 Non commercial PCM with low freezing point

Table 1 shows the different substances, eutectics and mixtures (inorganic, organic, fatty acids, and water salts solutions), that have been studied by different researchers for their potential use as PCM in cold storage applications. Their most important thermophysical properties are included (melting temperature, heat of fusion, thermal conductivity and density).

2.1.3 Commercial PCM with low freezing point

Table 2 presents a list of the commercial PCM available nowadays in the market and their thermophysical properties (melting temperature and heat of fusion).

2.1.4 Properties of PCM having low freezing temperatures

Properties of many different PCM have been extensively studied by many researchers over the years. All of the materials presented in the following sections are included in Table 1 for non-commercial PCM and in Table 2 for commercial PCM. These materials are mainly paraffin, binary aqueous solution, and capric and lauric acid mixtures.

Some paraffin and non-paraffin organics are available for cold storage applications, being an attractive alternative to chilled water for comfort cooling applications and enable cold storage with high energy storage density. Peng et al. [30] studied paraffin waxes and concluded that paraffin has a melting temperature from -12 to 71 ºC with a latent heat of 128-198 kJ/kg. Non-paraffin organics have a melting temperature range between -13 to 187 ºC with a latent heat of 80-280 kJ/kg. The heat capacity of an emulsion containing 30 wt.% paraffin with a melting peak point of 9 ºC was measured by Huang et al. [31]. This emulsion has a low heat of fusion of 43 kJ/kg over the total melting temperature range of 4-11.5 ºC. In addition, Yamagishi et al. [32] used two paraffins, n-Tetradecane and n-Dodecane with a melting point of 5.5 and -13.5 ºC respectively. Both were microencapsulated and were experimentally investigated as slurry for cold energy applications.

Many researchers have studied binary mixtures with different concentrations. The sodium chloride solution (NaCl-H_2O) is one of the most studied salt solution. Han et al. [33] measured the latent heat during phase change of NaCl-H_2O binary mixture using a differential scanning calorimeter (DSC) at various concentrations observing two different endothermic peaks, one due to a eutectic melting near -22 ºC, and the other for ice. Fig. 3 shows the DSC results for different concentrations of NaCl in water, concluding that the eutectic mixture is the best mixture, as expected. Furthermore, Liesebach et al. [34] determined experimentally the apparent latent heat of freezing of aqueous solutions of different concentrations of NaCl (3 and 16% NaCl), and Kamasa et al. [35] used the DSC to investigate the fraction of unfrozen water during phase transitions for 9 wt.% NaCl-H_2O solution.

Other mixtures have also been studied by researchers. Chen and Chen [36] discussed experimentally the solidification of aqueous ammonium chloride solution (26% NH_4Cl). It was found that finger convection (mixing process that occurs when salty mater overlies cold fresh water) occurred in the fluid region just above the mushy layer in all the experiments done. A method was designed to determine the porosity of the mush by computed tomography. Furthermore, properties of HCl, alkali, alkaline-earth chlorides, sulphates and eutectics in salt-H_2O systems were studied by Yatseko and Chudotvortsev [21]. Devireddy et al. [37] measured the magnitude and dynamics of latent heat during freezing of 14 different pre-nucleated solute aqueous systems using DSC. The value of the latent heat measured in the experiments should have been independent of the cooling rate. However, the experimental data showed that the fraction of heat released at higher cooling rates (5 and 20 ºC/min) was lower than at 1 ºC/min for all the studied solutions. Furthermore, Jochem and Körber [38] examined phase transformations occurring in solutions of NaCl-Glycerol-H_2O and NaCl- Hydroxyethylstarch-H_2O under non-equilibrium cooling and heating conditions using DSC.

Ethylene glycol is commonly used in vehicles as a heat transfer fluid (HTF) in the engine cooling system. This is one of the reasons why it is thoroughly studied in the literature. Liesebach et al. [34] analysed experimentally the apparent latent heat of freezing of aqueous solutions of different concentrations of ethylene glycol. Fig. 4 shows the apparent heat of solution of ethylene glycol with initial concentrations ranging between 9 and 30%. Moreover, Bourton et al. [39] investigated different solutions of water-glycerol-ethanol in order to find stable amorphous states for different water concentrations. The maximum stability occurs at low ethanol concentrations, which is of interest since ethanol is more toxic than glycerol. Specific heats capacity of glycerol (25% to 65%) and of propylene glycol (20% to 50%) with water mixtures, were measured by Gucker and Marsh [40]. They found out that the specific heat of a two-phase mixture is a linear function of composition. The graphs and tables that they generated allow a choice of the most efficient mixture for any particular application.

A calculation method to estimate the latent heat of fusion of ice in aqueous solutions (ethanol, ethylene glycol, propylene glycol, NaCl and $NaNO_3$) was developed by Kumano et al. [41-42]. They found that effective latent heat of fusion in aqueous solutions could be calculated by considering the effects of the freezing point depression. The effects on the specific enthalpy of the ice when solute is included were also experimentally investigated by Kumano et al. [43]. The measurement and the calculated values agreed well.

Moreover, Asaoka et al. [44] developed a calculation procedure for the effective latent heat of fusion of ice in aqueous solution, in order to clarify the amount of heat generated by the melting of ice in ice slurry through the methodology developed by Kumano et al.

[42]. As a result, it was clarified that the effective latent heat of ice in ethanol solutions is significantly affected by the temperature of the solution, though not so significantly for propylene glycol and ethylene glycol solutions.

In the work done by He et al. [45], the thermal properties of laboratory-grade tetradecane (melting point of 5.8 ºC), hexadecane (melting point of 18.1 ºC), and pentadecane (melting point of 9.9 ºC) were discussed, and the results showed that these materials are attractive PCM candidates for some cold storage applications.

Dimaano and Watanabe [46] investigated the thermal performance of the Capric-Lauric (C-L) acid mixture in the respective composition of 65% and 35 % by mole and its cooling capacity. Pentadecane was used for comparison showing a melting point of 18-19.5 ºC. The calculated stored energy based on the temperature distribution during charge and discharge processes indicates that the C-L acid is a potential PCM. With the same scope, Dimaano and Watanabe [47] proposed a mixture of C-L acid of 90 mol% - 10 mol% respectively, with addition of pentadecane having a melting point of 13.3 ºC and a heat of fusion of 142.2 kJ/kg as PCM for cooling applications. Furthermore, thermodynamic properties of a binary system composed of C-L acids with addition of different additives (the addition of more than 15 wt% of sodium oleate or sodiumlaurate) were investigated by Matsui et al. [48]. The phase transition behaviour on a large scale was constant during 200 heating-cooling cycle tests. Physicochemical degradation of PCM was not observed after repeated tests using Fourier transform-infrared spectrometer.

Several additives are often mixed with the PCM in order to improve its characteristics. Inaba and Morita [49] worked with water as PCM adding tetradecane to improve the flow behaviour of the emulsion as a non-Newtonian fluid. They developed dimensionless correlation for use to calculate pressure loss coefficient, heat transfer coefficient, and cold storage time, derived in terms of modified Dean Number and heat capacity ratio. Lu et al. [50] examined the ability of tween and polyvinil alcohol solutions to prevent recrystallization in ice slurry systems, and compared the ability with that of antifreeze proteins.

2.1.5 Selection of the correct PCM for cold storage applications

In many applications the exact temperature range is not known. The evaluation of the storage density of different PCM are difficult and the standard approaches followed do not provide enough accuracy. Therefore, the phase transition temperature range of the PCM must be known to design the charging and discharging processes properly. Conducting DSC measurements at different scanning rates show different thermal response and thus the resulting information on the phase transition processes varies with scanning rate. Also, the study of phase equilibrium and phase diagram can give the correct phase transition temperature range. If incorrect melting/freezing range is assumed in the design of any TES system, it will result in a lower capacity and economic loss. He et al. [51] studied the liquid-solid phase change diagram of the binary system of tetradecane and hezadecane in order to obtain information of the phase transition processes for cold storage applications. They used DSC to determine the thermophysical properties of the binary system and they concluded that the correct phase transition temperature range cannot be obtained simply from DSC measurements. Therefore, the combination of constructing the phase equilibrium and DSC measurements provide reliable design information on latent heat and freezing/melting rang.

Mehling et al. [52] developed a method to evaluate the heat storage density in a latent heat storage system for arbitrary temperatures ranges. The method allows evaluation of the heat storage density by plotting the enthalpy difference in a two dimensional contour with the upper and lower storage temperatures. From the study it was concluded that the method developed for evaluation and comparison of the heat storage capacity of PCM is extremely helpful when the upper and lower temperatures of the PCM are not known or not fixed at all. In addition, the method can also be helpful in understanding the requirements of heat exchangers and heat transfer enhancement within the PCM.

2.2 Long term stability for PCM at low temperatures

The most important criteria that have limited the use of PCM in different systems are the type of container needed for the PCM and the number of cycles they can withstand without any degradation in their properties. The long term stability of the storage materials is due to the poor stability of the materials properties and/or corrosion between the PCM and its container [11].

2.2.1 Stability of thermal properties under extended cycling

Elsayed [53] investigated the periodic melting of encapsulated ice for cold TES systems. A horizontal rectangular container was used as a storage capsule, using glycol as HTF. The effect of cycling HTF temperature, and convection heat transfer coefficient were studied. The results show that the efficiency of heat transfer and the melting regime are more strongly affected by the HTF temperature than by the convection heat transfer coefficient. It was demonstrated that the temperature in the melt region exhibits oscillation around a mean value similar to that of the adjacent HTF, where the frequency of oscillation decreases as the depth in the melt region increases.

In another study Matsui et al. [48] did standard heating-cooling cycle test of different PCM (C-L acids with different additives). After 200 cycles no physicochemical degradation was observed.

2.2.2 Phase segregation and subcooling problems at low temperatures

Many PCM, for example many salt hydrates, do not solidify immediately upon cooling below the melting temperature, but start crystallization after a temperature well below the melting temperature. This effect is called subcooling. If nucleation does not happen at all, then the latent heat can not be released and the material stores sensible heat only [3]. In an effort to overcome this problem, Kumano et al. [54] experimentally studied the effects of a polymer additive on the subcooling of water. The samples were prepared by dissolving poly-vinyl alcohols (PVA) in water (tap water, pure water and ultra pure water were used as solvents). Subcooling was inhibited by adding PVA to water (from 3 wt. % to 5 wt. %). Furthermore, the study done by Matsui et al. [48] found that the addition of more than 15 wt. % sodium oleate or sodiumlaurate to the L-C acid system was extremely effective for suppressing subcooling and for controlling the phase change temperature between 4 and 7 ºC.

Yilmaz et al. [55] analysed and studied aqueous salt solutions of NaCl and potassium chloride (KCl) as PCM for cooling applications and cold storage systems. Cycling tests were performed in a temperature range of -24 to -10 ºC. All the solutions studied showed subcooling (Table 3).

Crystallization and agglomeration of the materials could be important problems in phase change transitions. Bi et al. [56] studied the crystallization process of the gas hydrate HCFC141b. The influences of using different proportions of calcium hypochlorite or benzenesulfonic acid sodium salt on the crystallization process were measured, concluding that both additives can decrease the degree of subcooling of the gas hydrate formation. Moreover, the use of additives increases the formation rate of gas hydrate and its storage density. Inaba et al. [57] reviewed the technologies used for preventing the agglomeration and the growth of ice particles in water using a small amount of suitable additives. These anti-aglomeration additives are found to disperse ice particles in water at a very low concentration (less than 1 wt. % in water) without a serious depression in the equilibrium freezing temperature. The potential of the ice slurries treated with suitable additives as secondary refrigerants should improve the success of cold storage, handling and heat exchange.

2.2.3 Corrosion of the materials at low temperature

Corrosion tests of three different salt solutions and deionizer water in combination with five commonly used metals were carried for medium melting temperature PCM by Cabeza et al. [24]. Similarly, corrosion tests were performed using 5 different common metals (aluminium, stainless steel, laminated black steel, cooper, and galvanized steel) with aqueous salt solutions of NaCl and KCl during 1 week and 1 month by Yilmaz et al. [55]. Both mixtures are good PCM candidates because of their low cost and melting-freezing point below 0 ºC. Table 4 shows the conclusions and some cautions of using different materials as PCM at low temperature of both studies.

The addition of urea to trimethylolethane and its use as PCM with a melting temperature of 13 ºC (called PCM13) and a heat of fusion of 160 kJ/kg was studied by Kakiuchi et al. [58]. Its thermal properties and thermal durability were analysed using a DSC and liquid chromatography. It was concluded that at low temperatures (less than 25 ºC), the durability of PCM13 was high enough to be used as a PCM.

3 Encapsulation of phase change materials for cold storage applications

In almost all cases, PCM has to be encapsulated otherwise the liquid phase would leak out. PCM containment should have different properties such as the following ones [13]:

- Meet the requirements of strength, flexibility, corrosion resistance and thermal stability.
- Act as barrier to protect the PCM from harmful interaction with the environment.
- Provide sufficient surface for heat transfer.
- Provide structural stability and easy handling.

There are three different types of encapsulation: bulk storage in tank heat exchangers, macroencapsulation and microencapsulation.

The bulk storage system of encapsulation consists of using tank heat exchangers for PCM which are similar in design to the existing tanks used for TES, but with some differences [13]. The problem of PCM bulk systems is the need for an extensive heat transfer area between the PCM and the HTF. This limitation has been extensively addressed by inserting fins or using high conductivity particles, metal structures, or fibers in the PCM side or direct contact heat exchangers.

Microencapsulation system, spherical or rod-shaped particles are made using a thin and high molecular weight polymeric film. The results presented by Roy and Avanic [59] showed that the heat transfer characteristics for PCM emulsions are similar to those of microencapsulated PCM suspensions, thus confirming that the microcapsule walls do not affect the heat transfer process significantly.

If the PCM modules can be so small that could be part of the HTF, then the main part of the heat stored will be transferred out of the storage. In this case, the heat storage and heat transfer medium become one fluid which is always liquid and has a component that stores latent heat. This type of component is known as phase change slurry. Yamagishi et al. [32] and Kumano et al. [41-42] have been working in the enhancement of the slurry systems. Furthermore, Farid and Al-Hallaj patent a microchannel heat exchanger with micro-encapsulated PCM for high flux cooling. The experimental data presented in Alvarado et al. [25] show that microencapsulated PCM slurry can provide considerable heat capacity in heat transfer applications. Other conclusions were:

- Subcooling of the PCM can be suppressed significantly by incorporating the right amount and type of nucleating agent.
- Microcapsules become durable and impact-resistant when they are smaller than 10 µm.
- Heat transfer experiments showed that the heat capacity enhancements are considerable, even at low mass fractions.

Moreover, in Inaba et al. [57], it was concluded that the use of ice slurry systems treated with suitable additives offers attractive opportunities for advanced cold energy storage, transportation and systems with heat exchangers.

Finally, macroencapsulation comprises the inclusion of PCM in some form of package such as tubes, pouches, spheres, panels or other receptacle (Fig. 5). Macroencapsulation, which is encapsulation in containers usually larger than 1 cm in diameter, is the most common form of encapsulation [11]. The major advantages of using macroencapsulated PCM modules are the ease of manufacturing and marketing. There is also the flexibility on the design of the module type storage. The main characteristics of these systems are:

- Medium storage density with high packing factor (more than 70%)
- High power at the initial stage
- Lower power in the later stage

High energy density and high power capacity for charging and discharging are desirable properties of the storage system. Castell et al. [61] investigated experimentally bulk PCM coil-in-tanks in order to maximise its storage density, as well as improving its heat transfer of the system at very low temperature (-27 ºC). It was demonstrated that coil in tank designs are effective at delivering a constant outlet temperature and effective heat transfer with large surface areas, with a high packing factor.

One of the most studied types of encapsulation over the years is the spherical capsules using water as PCM. Adref and Eames [62] and Eames and Adref [63] studied the dynamic behaviour of single spherical thermal storage elements (capsule of a diameter of 7 cm). This study revealed that 90% of cold energy could be extracted from the ice storage spherical element within 70% of the time required to discharge it completely. The HTF temperature and spherical capsules size have been found to influence the melting process. Fig. 6 shows the melting process that occurs in a spherical capsule.

Bédécarrats et al. [64-65] measured the thermal performance of an encapsulated PCM (water with a nucleation agent) in spherical capsules. Fig. 7 shows the scheme of the tank and the spherical capsules of PCM used. They developed a test plant that permitted to study the behaviour of the tank during the charge mode taking into account the subcooling and the discharge mode. A simplified mathematical model, taking the nodules as heat exchangers, confirmed the experimental results and permitted the detailed analysis of the charge and the discharge mode. Furthermore, in more recent studies, they concluded that there was a significant influence of the subcooling phenomenon during the charging process.

Following the same idea, a numerical and experimental study was conducted by Ismail and Henriquez [66-68] using spherical capsules filled with water as PCM. The capsules were placed inside a cylindrical tank fitted with a working fluid circulation system. The differential equations describing the system were solved by the finite difference method and a moving grid inside the spherical capsules. This model was used then to predict the effect of the dimensions of the spherical capsules and their shell thickness, shell material, initial PCM temperature and the external wall temperature on the solidified mass fraction and time for complete solidification. Some other researchers have done similar studies than those mentioned before [69-71] concluding that the solidification phase front propagates uniformly inwards towards the centre of the sphere and determining some correlation coefficients for the solidification process. Furthermore, MacPhee and Dincer [72] modelled, through heat transfer and thermodynamic analysis, the charging process of an encapsulated ice TES device. With the flow exergy analysis technique, it was possible to optimize a charging process such as the one developed by them once the energy stored is known and viable charging times have been established.

Even though many researchers have dealt with numerical analysis to solve PCM systems, it involves high time consuming. Therefore, Tay et al. [73] and Amin et al. [74] studied the applicability of the effectiveness-NTU method for characterising a cylindrical and spherical PCM encapsulation TES system, respectively. Here the average heat exchange effectiveness of the storage tank was determined and a characteristic design curve was developed as a function of the measured average NTU.

On the other hand, Chen et al. [75] analysed the thermal response of a thermal storage tank during the charging process containing cylindrical capsules. The main conclusions from the work was that cold energy can be fully stored in the form of latent heat, and that the heat transfer coefficient increases as the coolant flow rate increases.

Some researchers have been focusing only in numerical simulation. Kousksou and Bédécarrats [76] modelled the storage of an encapsulated ice tank. They modelled and validated a vertical tank and used the model to predict the behaviour in a horizontal tank. The optimum behaviour was with the vertical tank, where natural convective motions are in the same direction as forced convection. Furthermore, Simard and Lacroix [77] developed a numerical study to examine the thermal performance of a latent heat cold storage unit based on a parallel plate, operating under frosting conditions using a mixture of aqueous-glycol (50%) as PCM. Once the model was validated it was used to optimize the system and to calculate the dimensions of the system for its use in a typical refrigeration truck.

A completely different concept using direct contact between the PCM and the HTF was developed by Martin et al. [78]. A cold storage unit using commercial paraffin, which melts at 7 ºC, as a PCM and water as HTF was studied experimentally. This concept was done in order to enable high power for charging and discharging while providing a high storage capacity.

Some companies (Calmac [79], Cristopia [80], Axima [81], Evapco [82], Ice Energy [83] and Environmental Process Systems Ltd. [84]) are either selling or working with cold storage using phase change, but their work is not published and classified as confidential. Some of them provide commercial ice storages and tank designs that may be suitable for cold applications. A more common technology already used commercially is the ice storage tanks, where the concept of indirect heat exchanger is used. Ice is built directly on the heat exchanger coils of the chiller. Systems that grow ice at the surface of the coils are known as ice-on-coil storages. Since ice is fixed within the storage, they are also called static storages [3]. Some commercial models are:

- CALMAC storage is made of polyethylene, well insulated and contains a spiral-wound polyethylene-tube heat exchanger submerged in water. Fig. 8 shows the storage tank.
- Cristopia storage consists of a spherical macroencapsulation made from a polymer and filled with PCM. Fig. 9 illustrates the storage system.
- EVAPCO storage is also based on the ice-on-coil system as shown in Fig. 10.

A compilation of ice storage processes can be found in the ASHRAE Handbook HVAC. The applications where the different geometries used are described are: spheres, ice on coils containing water with glycol, or over an evaporator. These geometries are used by various manufacturers and commercial brands.

4 Heat transfer enhancement methods for cold storage applications

An important phenomenon occurs during the solidification of the PCM, when during the extraction of the stored energy, the liquid freezes close to the heat transfer surface and a moving boundary layer of solid material continuously grows as it releases its heat of fusion. The low thermal conductivity of the solid layer limits the rate of heat transfer (Fig. 11).

As said before, heat transfer rate in PCM storage systems can be enhanced by using fins, metal honeycombs, metal matrices (wire mesh), rings, high conductivity particles, metal fibers or graphite, etc. Some of the studies done before 1999 were summarized in [85]; and Fan and Khodadadi [86] who reviewed the experimental and computational studies that were conducted over many decades to enhance the thermal conductivity of PCM. Cooper, aluminium, nickel, stainless steel and carbon fiber in various forms (fins, honeycomb, wool, brush, etc.) were used as the thermal conductivity promoters.

On the other hand, the melting process experience higher heat transfer rates due to the influence of free convection. Fukasako and Yamada [85] reviewed the melting heat transfer inside ducts and over external bodies, emphasising on the fundamental, physical transport phenomena during melting process of the PCM. The important role played by buoyancy-driven fluid flow was particularly discussed in that work.

4.1 Mathematical models for heat transfer enhancement

Heat transfer during the melting process of the PCM in a confined space has a relevant importance for determining the feasibility of TES in specific applications. Mathematical modelling of latent heat TES has been investigated over the years. The important characteristics of the different models and their assumptions, based on first and second law of thermodynamics, are presented in the review done by Verma et al. [14]. They concluded that most researchers have used first law of thermodynamics to verify their experimental results. They found out that little work has been done using the second law of thermodynamics and there is a requirement of some experimental work by which the acceptability of second law analysis can be substantiated.

The flow pattern and heat transfer characteristics of a vertical ice sheet at 0ºC melting by free convection under steady-state conditions were studied numerically by Wilson and Lee [87]. Moreover, Ho and Chu [88] studied numerically the melting process of ice from a vertical wall of rectangular enclosure dominated by the free-convection. The effect of the ice-water density difference on the thermal charge or discharge processes is an important factor in the heat transfer, therefore Zhu and Zhang [89] developed an eccentric model for the discharge process in a tank with horizontal tubes. The model is simple and is suitable for system simulation, and experimental validation proved its reliability. It successfully explains the discharge process principle, and reflects the temperature and discharge rate variation during the discharge. However, the discharge model is only applicable for processes that start when the ice cylinders slightly overlap and there is still unfrozen water causing the ice to float. Therefore, work is needed to study the discharge process starting after partial charging without ice overlap. Ismail and Gonçalves [90] analysed numerically a latent heat cold storage unit by an energy balance and in [91] by the enthalpy form, and energy balance. The numerical solution is based upon the average control volume technique and the alternating direction implicit finite difference representation. Results indicate that the solidification mass fraction and effectiveness decrease with R* (ratio of symmetry circle radius to radius of inner tube), while the NTU increases until R* is 4, after which NTU drops very fast. The Biot number has a dominant effect for values below 10. After this value, the Biot number has practically no influence. The increase in the working fluid inlet temperature reduces the solidification mass fraction and the effectiveness and increases the NTU value.

Inaba et al. [92] studied the critical conditions for ice blockage during the continuous freezing of a water-propylene glycol solution in a tube. Their results showed that non-dimensional correlation equations for the critical condition derived as a function of thermo-hydraulic parameters in the laminar and the turbulent flow regions. Furthermore, the equations can be used to predict whether an ice making system is operating in a continuous ice making condition or in the ice blocking phase. In order to predict the temperature distribution in both phases of a PCM (melting temperature range between 12-17 ºC), the two-dimensional, unsteady heat conduction was solved numerically by Farid et al. [93]. The effect of the latent heat of melting was included by using an effective heat capacity. The agreement between the model prediction and the experimentally measured temperatures was good, and the experimental results indicate that the time of discharge was twice that need for charging.

Cheralahan et al. [94] analysed the effect of porosity on the performance of cold TES systems. The studied system was a cylindrical storage tank filled with water as PCM encapsulated in a spherical container. A numerical model was developed and experimentally validated, concluding that for lower porosity, the average charging time, the internal heat transfer coefficient and the heat capacity of a storage system are higher, as the time required for freezing the PCM increases. On the other hand, for high porous systems, the energy storage capacity and the charging time decreases significantly, because increasing the porosity would also increase HTF passage and reduce the mass of PCM capsules in the entire storage tank.

Some other studies have analyzed numerically the enhancement of the heat transfer in different TES systems. The heat transfer efficiency of a cold TES system with ice formation and ice melting during off-peak and on-peak periods was developed by Ho and Tu [95]. The effects of the volumetric air flow rate and recycling ratio on the heat transfer efficiency enhancement and power consumption increment were also discussed and provided an improved heat transfer efficiency design for a cool-thermal discharge system. The mathematical treatment presented in the study can be applied to any heat convection-conduction problem with moving boundaries. In addition, Fukai et al. [96] solved a two-dimensional heat transfer model describing anisotropic heat flow in the composite and a simple model is also developed to predict the heat exchange rate between the composite and the HTF. Fig. 12 shows the scheme of the TES unit studied. They concluded that the transient thermal responses in the composite improve as the diameter of the brush increases until the diameter of the brush is larger than the distance between the tubes, then it shows no increase. They found out that the effective thermal conductivity, including the effect of the thermal resistance of the composite is about three times as large as that of PCM when the volume ratio of brush fibers to the diameter of the tube pitch is 0.012.

Sasaguchik et al. [97] developed a numerical model to analyse solid-liquid phase change heat transfer with and without porous media. The model can also treat conventional (without phase change) transient natural convection with or without porous media filling the cavity. However, this study only addressed a specific enclosure (with a specific height and width) as well as a specific position of cylinders.

Hirata and Matsui [98] studied ice formation and melting phenomena with water flow around isothermally cooled cylinders arranged in staggered and aligned manners, respectively. It was found that melting time was twice as much as the time needed for freezing for both the staggered and aligned arrangements. Experimental correlations for ice storage efficiency as well as for the ice filling-up rate were proposed. Furthermore, it was shown that the ice filling-up rate is strongly affected by the Reynolds number, cooling temperature, and cylinder pitch perpendicular to water flow.

4.2 Experimental heat transfer enhancement

The melting process in a horizontal cylindrical enclosure has been well studied over the years. During this process two different representative melting phenomena take place, if the solid is unfixed and presenting higher density than the liquid phase, the solid sinks to the bottom of the enclosure. On the other hand, in the case where the solid is fixed for some reason and does not sink, then the energy needed for melting must be transported from the enclosure to the solid through the melted part, under conductive or convective dominated mode [85]. The difference in the melting phenomenon in a horizontal tube between ice-water and paraffin systems is schematically showed in Fig. 13. With a similar idea, Hirata el al. [99] carried out an experiment for the melting of ice in isothermally heated rectangular capsules with three aspect ratios (capsule height divided by capsule width). During the melting process, the solid was fixed around the centre axis of the capsules and their melting was dominated by free convective heat transfer. They concluded that the analytical method developed could predict the melted mass fraction in a rectangular capsule of the aspect ratios between 1/3 and 3 within ±10% error band.

Calvet [100] studied the enhancement of commercial PCM spherical balls by two different methods. The first one was to disperse synthetic graphite directly into the PCM and the other method was to impregnate an isotropic matrix of expended natural graphite with PCM, which was the best option in terms of conductivity and for that reason was selected as the final solution. This study is under review for patenting with the cooperation of CRISTOPIA ENERGY SYSTEMS.

A supported PCM made of paraffin impregnated by capillary forces in a compressed expanded natural graphite matrix was developed by Py et al. [101]. For that purpose, two commercial paraffins, one of them with a melting temperature of -9 ºC and a commercial hexadecane with a melting temperature of 18.1 ºC were tested. The composite thermal conductivities were found to be equivalent to those of sole graphite matrix: from 4 to 70 W/m·K instead of the 0.24 W/m·K of pure paraffin.

Most studies available in the literature use water as PCM for thermal storage in air-conditioning. Vargas et al. [102] reported a melting process when an ice sleeve rides on a heated horizontal cylinder. It was found that the melting process consists of two distinct regimes; first, an early regime when the cylinder is surrounded by ice and second, a late regime when the cylinder cuts through the top of the ice sleeve. The falling speed of the ice in the second regime was found much greater than in the first regime. Furthermore, White et al. [103], Torikoshi et al. [104], and Sasaguchi et al. [105] reported excellent experimental studies of the melting of ice around a heated horizontal cylinder, around a bundle of horizontal and around vertical tubes immersed within an ice layer, respectively. Moreover, the solidification process of PCM around a vertical cylindrical surface was studied by Mohamed [106] in order to investigate the performance of ice storage system and stored thermal energy. In his study, air bubbles were generated in the PCM at various air flow rates as a gas fold up to enhance the heat transfer rate and accelerate the ice layer growth at the solid-liquid interface. As a result, he found out that the solidification front velocity near the cold surface of test tube increased by 20-45% and the stored thermal energy in the form of ice was also increased as a result of the imposed turbulence generated by the air bubbles.

Some other researchers used different materials as PCM, such as Roy et al. [59] who studied experimentally the laminar forced convection heat transfer in a circular duct with a PCM emulsion. All experiments were done using water as the suspending fluid and using n-octadecane ($C_{18}H_{42}$) as the PCM. Additionally, Lee et al. [107] evaluated experimentally the heat transfer characteristics of an ice slurry made from 6.5% ethylene glycol-water solution flowing through a 1500 mm long horizontal copper tube (13.84 mm internal diameter). The measured heat transfer rates increased with the mass flow rate and ice fraction, however the effect of ice fraction appears not to be significant at high mass flow rates. At the region of low mass flow rates, a sharp increase in the heat transfer coefficient was observer when the ice fraction was more than 10%.

4.3 Direct contact PCM storage

In direct contact melting, it is well known that one of the factors that affect heat transfer is the size of the heat transfer surface. In Saito et al. [108], it was investigated how the heat transfer can be promoted by machining slots on the disk-type heat transfer surface and dividing it into several sector-shaped sections, through theoretical and experiments measurements which were performed varying the number of splits and the width of slots under different surface temperatures and pressures. It was concluded that the enhancement of heat transfer can apparently be achieved according to the number of splits. However, no specific values were given.

Furthermore, in order to enhance heat transfer in any TES system it is important to enhance the heat transfer between the HTF and the storage material (PCM). Erek et al. [109] carried out an experimental and numerical investigation of TES with a finned tube using water as the storage material (Fig. 14), concluding that the total stored energy evaluated by the numerical method agrees with the experimental data. The rate of energy storage increases with increasing fin radius and decreasing fin space. In addition, the stored energy increases with increasing Reynolds number and Stefan number. After a certain value of Reynolds number (5000), the total amount of stored energy does not change significantly.

Other studies focussed in mixing the storage material with high thermal conductivity materials such as cooper, aluminium, etc. Hirasawa et al. [110] proposed an interesting heterogeneous composite material, which consist of both ice and conductive solids as a PCM to control the heat transfer during phase change. Transport characteristics during the melting of heterogeneous material were investigated experimentally, and it was concluded that the melting rate increases markedly with increasing the volume ratio of the high conductive solids. Hirasawa and Takegoshi [111] also determined the melting heat transfer characteristics of the heterogeneous materials, in which the conductive solids are copper lattice metal and porous aluminium. Further, Tong et al. [112] increased the heat transfer rate during melting and freezing of a PCM by inserting a high porosity metal matrix into the PCM. The heat transfer rates for enhanced cases showed an order of magnitude of increment over the base case. Besides, three different heat transfer enhancement methods (addition of stainless steel pieces, copper pieces, and a graphite matrix impregnated with PCM) in a small TES device were experimentally performed by Cabeza et al. [4]. The PCM used was water. In conclusion, the fin effect is only effective if the material used is conductive such as the graphite matrix. Several studies have examined heat transfer enhancement inside or outside the cooling surface [18]. On the other hand, it is not always possible to insert or to mix some materials in the storage medium as many researchers have proposed due to aspects related to safety, space or compatibility. Moreover, the inclusion of these non-phase-change materials will decrease the energy storage density.

Some other researchers proposed to add conductive solids [113-115], or installing fins on the cooling surface of brine-side [116] in order to increase the enhancement of the heat exchange between the HTF and the storage material.

Kazmierczak and Nirmalanandhan [117] worked in the improvement of the heat transfer for the external ice-on-tube using porous cooper mesh in order to increase the volumetric ice production (Fig. 15). The developed Heat Conducting Enhancement Device (HCED) improves the thermal performance and the competitiveness of the external ice-on-tube TES systems. A simple mathematical model showed that the rate of freezing can be increased by enhancing the effective thermal conductivity of the ice layer. Experiments showed that 50-90% enhancement can be achieved by using an inexpensive HCED made from rolled cooper screen mesh.

5 Applications of PCM in cold storage

5.1 Potential use of PCM in cold storage

In this part of the review, the use of PCM in different applications is presented, differentiating those ones that are already in the market from those ones that have been studied by researchers.

PCM offer the possibility of thermal protection due to its high thermal inertia. This protection could be used against heat and cold, during transport or storage. Protection of solid food, beverages, pharmaceutical products, blood derivatives, electronic circuits, cooked food, biomedical products, and many others is possible. Some of the different applications for cold storage found in the literature are the following ones:

- Cooling: use of off-peak rates and reduction of installed power, ice bank
- Thermal protection of food: transport, hotel trade, ice-cream, etc.
- Medical applications: transport of blood, operating tables, cold therapies
- Industrial cooling systems: regasification terminal

One of the most important topics related to the applications of different TES systems is the economic aspects. He and Setterwall [118] discussed the capital cost investment of paraffin waxes as PCM for cold storage. It was concluded that the cooling capacity of existing systems can often be increased by installing cold storage at less cost than adding conventional non-storage equipment. A proper cold storage system can reduce operating costs, often reduce initial costs, reduce the size of chilling equipment, increase operating flexibility, and extend the capacity of an existing system. Moreover, Dincer and Rosen [119] studied the environmental and economic aspects of TES systems for cooling applications. Five types of TES systems were studied, as Table 5 shows. It was concluded that TES can play a significant role in meeting society's preferences for more efficient and environmentally friendly energy uses in various sectors, and appears to be an appropriate technology for addressing the mismatch that often occurs between the energy supply and demand periods. Substantial energy savings up to 50% can be obtained using TES systems. When appropriate demand side management strategies are implemented, the emissions of greenhouses gases, for instance CO_2, SO_2, and NO_x, can be reduced by about 40% [119].

Arce et al. [120] did an interesting overview of TES potential energy saving and climate change mitigation in Spain and Europe. Their work incorporates the associated environmental benefits derived from TES systems. Load reductions, energy savings, and CO_2 emissions reductions were achieved in the buildings and industrial sector. Related to cold storage applications, TES systems could be applied in a re-gasification terminal, where liquefied natural gas at -160 ºC is converted into natural gas. During this process the gas is transported to the vaporization systems, where the temperature is risen by using sea water, thus turning liquid into gas. They concluded that yearly the potential savings at the EU account for 7.5% as a result of TES applications.

5.2 Commercial applications

5.2.1 General containers for temperature sensitive food

One of the most known applications of PCM is that of transport of temperature sensitive food in containers. These containers must be kept in the refrigerator-freezer before use in order to solidify the PCM in it. An example of such a device is the container commercialized by SOFRIGAM [121] with PCM melting points of 0 ºC, -15 ºC, and -20 ºC (Fig. 16). These containers could be rigid or soft. Some companies only commercialize PCM pads for use in any container, such as TCP RELIABLE, Inc. [122], PCM Thermal Solutions [123] or PCM products [124].

Moreover, Melone et al. [125] developed PCM composites with different latent heats in the 4-10 ºC range for cold storage packaging. They also reported an easy technique for PCM incorporation in paperboard and a numerical model, which are useful when a detailed design and engineering of PCM/cellulose packaging system is required for the logistic of perishable products.

5.2.2 Beverages

One application that has been commercialized is the so-called “isothermal water bottle”, specially developed for cycling. It is a double wall bottle, with a PCM as active part. This concept could be used for many other products, such as isothermal maintenance of fresh drinks like wine, champagne, soft drink, etc (Fig. 17).

5.2.3 Catering products

In many catering applications, cooked meals or frozen products are produced in one point and have to be transported (Fig. 18). PCM containers (Fig. 19) could also be used to avoid breaking the cold chain during transportation of precooked meals, smoked salmon, milk derivates, ice-creams, and many others. The main companies that commercialize these products are Rubitherm [29], Climator [26], and Teap PCM [26].

5.2.4 Medical applications

In the medical sector, one of the main applications is the transport of blood (Fig. 20) and organs. Containers used for these purposes work similar to those explained in General containers. Other medical applications can be hot or cold pads to treat local pain in the body.

5.3 Peak load shifting

Cold storage technology is an effective mean of shifting peak electrical loads as part of the strategy for energy management in buildings. Such systems can help the electrical utilities reducing peak loads and increasing the load during off peak periods which could improve the utilization of base load generating equipment, and thereby reducing the reliance on peaking units which have higher operating costs [126].

An example of cold TES system is the storage of coolness generated electrically during off peak hours to be used during subsequent peak hours. Hasnain [126] reviewed the commercially available TES technologies of off-peak air conditioning applications. There are mainly three types of cold storage systems being considered:

- Chilled water storage systems. A tank is charged with water at 4-6 ºC, and in ideal conditions, the water is stored inside the tank in stratified layers for later uses in meeting cooling needs. Therefore, water as the storage material is not used as a PCM.
- Ice storage systems. Water is used as phase change storage medium to take advantage of its high latent heat of fusion removed during the charging cycle which results to ice formation. This type of storage system is further classified as either static or dynamic. In static types, the produced ice bonds to the cooling surface and forms an ice layer on it. While in dynamic types, the produced ice is continuously removed from a cooling surface [18]. It can also be classified either as direct (ice is formed directly on the evaporator) or indirect types (ice is formed by circulation of a brine solution cooled by a refrigerator).
- Eutectic salt storage system. Eutectic salts are another commonly used medium to store cooling energy. Eutectic salts are mixtures of inorganic salts, water and nucleating and stabilizing agents. Similarly as in ice storage, the cooling capacity of a eutectic salt system depends on the latent heat of fusion of the salt and the amount frozen.

A comparison of chilled water, ice and eutectic salt storage systems is given in Table 6. This table reveals the advantages of the ice storage system over the other two cold storage systems. The most obvious benefit of ice as a storage medium is the reasonable reduction in storage volume needed. However, it has to be mentioned that this benefit could change if the required operating temperature is low. Both the reviews of Hasnain [126] and Saito et al. [18] describe successfully the cold thermal energy systems studied over the years.

5.4 Transport of temperature sensitive materials

In the past decade the application of PCM in transport containers became one of the first fully commercial PCM applications [3]. Therefore many researchers put effort in order to study the incorporation of PCM in different systems for that purpose.

Onyejekwe [127] incorporated PCM into a freezer and achieved experimentally the optimal performance of the container inside the freezer, by placing the PCM, close to the evaporator wall and at the lower part of the freezer. It was concluded that it is possible to use an available and very cheap PCM ($NaCl$ + H_2O) for thermal energy storage. However, such type of PCM suffers sever corrosion and subcooling.

Moreover, Azzouz et al. [128-129] placed the PCM in the back side of the evaporator inside a household refrigerator in order to improve its efficiency and to provide a storage capacity allowing several hours of refrigeration without power supply. In this work, two PCM were compared (water and water with a eutectic mixture with a freezing point at -3 ºC). The experimental results and the later simulations indicated that the response of the refrigerator to the addition of PCM and its efficiency were strongly dependent on the thermal load. The integration of PCM allowed 5-9 hours of continuous operation without electrical supply instead of the 1-3 hours without PCM, and an increase in the coefficient of performance (COP) of the system by 10-30%. Furthermore, Subramaniam et al. [130] designed a method of a novel dual evaporator based on a domestic refrigerator with PCM which provided thermal storage in order to improve food quality and extend compressor off time. In addition, there would be scope to optimize capillary and gas quantity of refrigerant for the new PCM based system, which also would help to maximize energy savings.

Cheralathan et al. [131] carried out an experimental investigation on the performance of an industrial refrigeration system integrated with encapsulated PCM based on cold TES system. In the experimental set-up, a vertical storage tank was integrated with the evaporator of the refrigeration system. The effects of inlet HTF temperature on system performance were reported and it was concluded that the thermal performance of the storage system may be improved by charging the system at lower condensing and optimal evaporator temperatures.

The effect of door opening, defrost cycle, and loss of electrical power on a freezer with PCM (aqueous ammonium chloride solution) was studied by Gin et al. [132], during repeated power loss every 24 hours over a 2 week period. They demonstrated that the use of PCM in the freezers reduces the temperature fluctuations of the air and the products. Moreover, the inclusion of PCM into the freezer decreased the energy consumption during defrost cycle by 8% and by 7% during door openings. Furthermore, Gin and Farid [133] observed that the introduction of PCM improved the quality of the frozen food during the storage.

Some other researchers studied the enhancement of PCM in some parts of refrigerator systems. Wang et al. [134-135] dealt with the improvement of a refrigeration system prototype that incorporated PCM (Fig. 21). They located a PCM heat exchanger in different places of the refrigeration system, such as after the compressor (PCM A), after the condenser (PCM B), and after the evaporator (PCM C). The experimental results showed that the integration of PCM heat exchanger into the refrigeration system could improve the COP of the system by 6-8%. Furthermore, Wang et al. [136] developed and experimentally validated a dynamic model of a novel system which can be used to design and optimize the performance of the system.

Moreover, Riffat et al. [137] designed and tested a thermoelectric refrigeration system. It was found that the replacement of the conventional heat sink system with an encapsulated PCM (ClimSel C7) gave an improvement in the performance of the thermoelectric refrigeration system, as well as in the cooling storage capability. Furthermore, Omer et al. [138] analyzed experimentally a 150 W thermoelectric refrigeration system. The system was first tested using a conventional heat sink system (bonded fin heat sink system) and later, using an encapsulated PCM as cold sink. Results of the tests showed that it is feasible to use thermosyphons between the PCM and the cold side of thermoelectric cells in order to prevent heat leakage of the PCM in the event of the power being turned off.

Transport of temperature sensitive products is an important task in the food industry. Therefore, some researchers have been dealing with the improvement of these systems. Experimental investigation of a cold storage system with water as a PCM on cold energy recovery of Liquefied Natural Gas (LNG) refrigerated vehicles (Fig. 22) was done by Tan et al. [139]. The PCM (range temperature from -30 to 10 ºC) was solidified outside the heat transfer tubes that were internally cooled by cryogenic nitrogen gas substituting cryogenic natural gas. It was concluded that the internally finned tube can effectively improve the gas-side heat transfer and the solidification performance. The ice layer increased in radial direction with time and the ice thickness is distributed along the tube length in parabolic shape. The ice increasing rates and axial slope of ice layer on the internally finned tube surface were so remarkable that it should be carefully taken into account in the design and optimization of the CSU (Cold Storage Unit).

Ahmed et al. [140] modified the conventional method of insulation of a refrigerated truck trailer by adding PCM. The inclusion of paraffin-based PCM in the standard trailer walls as a heat transfer reduction technology was investigated. The results showed lower peak heat transfer rates and total heat flows into the refrigerated trailer, thus potentially saving energy and reducing pollution from diesel-driven refrigeration equipment. An average reduction of 29.1% in peak heat transfer and of 16.3% in total heat transfer was achieved by adding PCM to the insulation foam of the trailers walls. It was concluded that the PCM could lower the temperature fluctuations within the refrigerated trailer simulators. The indoor temperature of the trailer would experience fewer oscillations, which could lead to more stable operation and control, longer operating life of the refrigeration equipment, reduction in equipment size, energy conservation, and a decrement in pollution from diesel-driven refrigeration units. Moreover, Liu et al. [141] developed an innovative refrigeration system for refrigerated trucks incorporating PCM. They constructed a prototype and the results proved that the proposed refrigeration system is feasible for mobile transport consuming less than half of the energy cost.

5.5 Air conditioning applications

Air conditioning applications is one of the most studied areas in recent years. Vakilaltojjar and Saman [142] modelled and analysed an energy storage system for air conditioning applications consisting of sections of different PCM implemented in flat containers. The models can be used to predict the behaviour of a thermal storage system with multiple PCM modules in series. The PCM used were calcium chloride hexahydrate and potassium fluoride tetrahydrate. Furthermore, Shuku and Yamaha [143] introduced a PCM unit in an air distribution system for space cooling. The PCM used was an organic hydrate, called PCM-19 with a melting temperature of 13 ºC. On the other hand, a new pumpable thermal storage medium in order to reduce the energy consumption in air-conditioning systems and utilize the exhaust heat from industries was developed by Hayashi et al. [144]. The PCM had a freezing point between 0-12 ºC, variable with the ammonium salt concentration in the aqueous solution.

The use of spherical capsules to encapsulate the PCM in air conditioning applications has been studied by different researchers. Fang et al. [145] studied experimentally the operation characteristics of cold storage air-conditioning systems with spherical capsules packed bed. The spherical capsules with outside diameter of 100 mm and wall thickness of 1 mm were filled with water. The experimental results indicated that the cold storage air-conditioning systems with spherical capsules had a better performance and could work during the charging and discharging period; varying the COP of the system from 4.1 to 2.1 during the ice latent heat storage period. Additionally, Wang et al. [146] introduced a storage tank in a residential central air-conditioning system, based on theoretical calculation and experimental results of the heat transfer between the ice balls as PCM (Fig. 23) and the glycol solution as HTF. It was concluded that throughout the charging process, latent heat storage was mainly used, and it accounted for 81% of the entire storage capacity of the system. In addition Wu et al. [147] presented a mathematical model for a TES system using packed bed containing spherical capsules filled with n-tetradecane to predict the thermal behaviour of this concept in a refrigeration system.

The experimental research done by Bi et al. [148] helped to popularize and utilize the gas-hydrate cold storage technology in air conditioning systems. In this work the influences of different proportions of calcium hypochloride or benzenesulfonic acid sodium salt on the dissolution process were studied. In the analyzed systems, the inner-heat exchange/outer-crystallization technology and the integrated condenser/evaporator structure design were adopted. The results showed that the instantaneous dissolution rate was almost twice as the corresponding instantaneous formation rate of gas-hydrate, and the cold energy storage rate was obviously higher than the corresponding cold energy storage rate at different conditions. Therefore optimization of the crystallisation process was very important to improve the whole operating performance of the cold storage system.

5.6 Other applications

Other applications of the TES systems with PCM have been discussed in the available literature. For example, Erek and Ezan [149] developed a numerical model for predicting the effects of the flow rate and inlet temperature of the coolant on the cold storage inside the TES system, which consisted of an ice-on-coil storage tank integrated in a refrigerator. According to this study, to design an ice-on-coil type TES, geometrical parameters are important to obtain the required energy storage, and in addition, thermal and flow parameters of the coolant are also key factors for optimization of the system. Finally, the developed numerical model could be used to design a TES unit which includes optimizing the geometrical, flow and thermal conditions. Moreover, Rodriguez et al. [150] studied numerically the optimization and design of PCM-water hybrid storage tanks. From the analysis of the results of several detailed numerical simulations, correlations for the Nusselt number at the lateral, top, and bottom walls were obtained. They also validated the mathematical model assumed.

Another application is cryogenic temperature controllers used in electronic and biotechnology industries. Here, systems employing the thermoelectric Peltier effect are mostly used. They are generally less efficient than vapour compression systems but do represent the most direct way of utilizing electricity to pump heat. Riffat et al. [148] designed and tested a thermoelectric refrigeration system with the addition of encapsulated PCM in place of the conventional heat sink on the cold side of the thermoelectric coolers. This gave an improvement in the performance of the thermoelectric refrigeration system as well as the cooling storage capability, which would be particularly useful for handling the peak loads, and overcoming losses during door openings and electrical power failure. Moreover, Omer et al. [151] carried out an investigation of the potential application of PCM integrated with thermosyphons in a thermoelectric refrigeration system.

6 Conclusions

This review paper is focused on the available thermal energy storage (TES) technology with phase change materials (PCM) for cold applications. Only the applications working with PCM with melting temperature lower than 20 ºC have been considered. Therefore, the paper presents the current research in this specific field, focusing on the available PCM either in the market or under research, their thermophysical properties, the encapsulation possibilities, the heat transfer enhancement, and the different applications of PCM at low temperatures.

The most thoroughly studied PCM at low temperature is water for obvious reasons; water is cheap, has the best thermal properties, and also presents good long term stability. It has been used in many applications, mainly in air conditioning systems for peak load shifting. This technology is mature and commercially available. However, for other applications at lower working temperature, such as conservation and transport of frozen products or advanced medical transport, for instance tissues, the melting temperature of water is not suitable.

Most of the PCM analysed by the researchers and commercial companies with a melting temperature below 0 ºC are eutectic water salt solution, and above 0 ºC are organic PCM. Eutectic salt solutions are good in terms of thermophysical properties, such as enthalpy of phase change (since water is the main component) and they are cheap; however due to the incorporation of the mixture with salts they could be chemically unstable and may be corrosive. On the other hand, most organic PCM are non-corrosive and chemically stable, however they have lower thermal conductivity, lower latent heat, larger volume change between solid and liquid phase and they are relatively expensive.

A PCM with an easily adjustable melting temperature would be necessary as the melting point is the most important criteria for the selection of the PCM for any application. Therefore, it is important to keep searching for additive that can be used to adjust PCM melting/freezing temperature.

The use of PCM in many applications, and especially at low temperatures, requires the use of nucleating and thickening agents to minimize subcooling and phase segregation. Hence when a PCM is used in a new application, it is important to study its long term stability, phase segregation, corrosion, and subcooling effects. The enhancement of the heat transfer of many PCM has been thoroughly analysed by the researchers and some of them showed a good performance, but specific to the case studied.

Looking at the commercial applications, such as the use of PCM for catering and medical purposes, significant improvements to existing catering system can be done. Transportation of temperature sensitive materials is another area in which PCM can play an important role and more work is needed.

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Table captures

Table 1. Thermophysical properties of materials for cold storage (melting temperature up to 20 ºC).

Composition	Type	Melting temperature (ºC)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m·K)	Density (kg/m^3)	Reference
24.8 wt. % HCl	Eutectic water-salt solution	-86	-73.77 (kJ/mol)	-	-	[22]
24 wt. % LiCl	Eutectic water-salt solution	-67	-36.26 (kJ/mol)	-	-	[22]
30.5 wt. % CaCl2	Eutectic water-salt solution	-49.5	-76.81 (kJ/mol)	-	-	[22]
21.01wt. % $MgCl_2$	Eutectic water-salt solution	-33.5	-36.30 (kJ/mol)	-	-	[22]
$Al(NO_3)_3$ (30.5 wt. %) + H_2O	Eutectic water-salt solution	-30.6	131	-	1283 (l) 1251 (s)	[4]
27.9wt% Li_2SO_4	Eutectic water-salt solution	-23	-26.10 (kJ/mol)	-	-	[22]
NaCl (22.4 wt. %) + H_2O	Eutectic water-salt solution	-21.2	222	-	1165 (l) 1108 (s)	[4]
23.3 wt. % NaCl	Eutectic water-salt solution	-21.2	233 (5.0) (kJ/mol)	-	-	[22]
0.8 wt. % NaCl	Eutectic water-salt solution	-	235	-	-	[22]
4.3 wt. % NaCl	Eutectic water-salt solution	-	231	-	-	[22]
8.4 wt. % NaCl	Eutectic water-salt solution	-	233	-	-	[22]
26.3 wt. % NaCl	Eutectic water-salt solution	-	234	-	-	[22]
19.7 wt. % KCl	Eutectic water-salt solution	-10.6	18.43 (kJ/mol)	-	-	[22]
Diethylene glycol	Eutectic	-10	247	-	1200 (l)	[4]
6 wt. % KCl + H_2O	Inorganic	-10	-	-	-	[24]
Dodecane	Organic	-9.6	216	2.21 (l)	-	[17]
22.1 wt. % $BaCl_2$	Eutectic water-salt solution	-7.7	-10.2 (kJ/mol)	-	-	[22]
Triethylene glycol	Organic	-7	247	-	1200 (l)	[4]

16.5 wt. % $KHCO_3$ + H_2O	Inorganic	-6	-	-	-	[24]
18.63 wt. % $MgSO_4$	Eutectic water-salt solution	-4.8	-84.96 (kJ/mol)	-	-	[22]
tetradecane + octadecane	Eutectic Organic	-4.02	227.52	-	-	[17]
20.5 wt. % $NaCO_3$ + H_2O	Inorganic	-3	-	-	-	[24]
6.49 wt. % $KsSO_4$	Eutectic water-salt solution	-1.55	26.88 (kJ/mol)	-	-	[22]
4.03 wt. % Na2SO$_4$	Eutectic water-salt solution	-1.2	-1.07 (kJ/mol)	-	-	[22]
H_2O		0	333	0.6 (l)	998 (l)	[4]
		0	333	2.2 (s)	917 (s)	[4]
		0	333	0.612 0.61	998 (l)	[11]
		0	334	0.612 0.61	917 (s)	[11]
		0	334	0.61	996 (s)	[13]
H_2O + polyacrylamida	Compound	0	295	0.486	1047 (l)	[4]
91.67% tetradecane + 8.33% hexadecane	Eutectic Organic	1.7	156.2	-	-	[17]
tetradecane + docosane	Eutectic Organic	1.5 - 5.6	234.33	-	-	[17]
tetradecane + geneicosane	Eutectic Organic	3.54 - 5.56	200.28	-	-	[17]
$K_2HPO_4 \cdot 6H_2O$	Salt hydrates	4	109	-	-	[12]
Na_2SO_4 (31 wt. %) NaCl (13 wt. %) KCL (16 wt. %) H_2O (40 wt. %)	Inorganic Eutectic compounds	4	234	-	-	[3]
KF $4H_2O$	Paraffin	4.5	165	-	-	[3]
Tetrahidrofurano (THF)	Eutectic Organic	5	280	-	970 (s)	[4]
Microencapsulated 94% tetradecane + 6% tetradecanol	Organic	5.1	202.1	-	-	[25]
Microencapsulated 100% tetradecane	Organic	5.2	215	-	-	[25]
Microencapsulated 96% tetradecane + 4% tetradecanol	Organic	5.2	206.4	-	-	[25]
Bulk 100% tetradecane	Organic	5.5	215	-	-	[25]
Bulk 96% tetradecane + 4%	Organic	5.5	206.4	-	-	[25]

tetradecanol						
Bulk 94% tetradecane + 6% tetradecanol	Organic	5.5	202.1	-	-	[25]
Paraffin C_{14}	Organic	5.5	228	-	-	[18]
		4	153	-	-	[11]
		4.5	165	-	-	[13]
No. of carbon atoms: 14	Paraffin	5.5	228	-	-	[12]
n-tetradecane	Organic	6	230	-	-	[13]
		5.8-5.9	258-227	0.210 (s)	-	[17]
pentadecane + heneicosane	Eutectic Organic	6.23 - 7.21	128.25	-	-	[17]
Formic acid	Fatty acid	7.8	247	-	-	[17], [12]
$LiClO_3 \cdot 3 H_2O$	Inorganic	8	253	-	1720 (s)	[11], [13]
	(hydrated salt)	8	155	-	1530 (l) 1720 (s)	[4], [16]
	Inorganic compounds	8	255	-	-	[3]
Polygycol E400	Organic	8	99.6	0.187 (l)	1125 (l)	[1], [13]
		8	100	0.19	1228 (s)	[4]
Paraffin C_{15}-C_{16}	Organic	8	153	-	-	[11], [13]
$KF\ 4H_2O$	Paraffin	8	153			[3]
$LiClO_3 \cdot 3H_2O$	Inorganic	8.1	253	-	-	[1]
pentadecane + octadecane	Eutectic Organic	8.5 - 9.0	271.93	-	-	[17]
pentadecane + docosane	Eutectic Organic	7.6 - 8.99	214.83	-	-	[17]
n-pentadecane	Organic	10	-	-	770 (l)	[13]
		9.9	193.9	-	-	[17]
No. of carbon atoms: 15	Paraffin	10	205	-	-	[12]
$ZnCl_2 \cdot 3 H_2O$	Inorganic (hydrated salt)	10	-	-	-	[13]
Paraffin C_{15}	Organic	10	205			[18]
$ZnClO_2 \cdot 3H_2O$	Inorganic	10	-	-	-	[1]
Tetrabutyl ammoniumbromide (type A - type B)	Organic	10-12	193 - 199	-	-	[4]
Isopropyl Palmitate	Organic	11	95-100	-	-	[13]
$K_2HPO_4 \cdot 6 H_2O$	Inorganic	13	-	-	-	[1], [13]
	(hydrated salt)	14	109	-	-	[18]
90% Capric acid +10% Lauric acid	Organic	13.3	142.2	-	-	[13]
38.5% Triethylolethane + 31.5% H_2O +	Organic eutectic	13.4	160	-	-	[13], [18]

30% urea						
Isopropyl Stearate	Organic	14 - 18	140 - 142	-	-	[13]
38.5% Trimethyloletane +31.5% H_2O + 30% urea	Organic mixture	14.4	160	0.66	1170 (l)	[17]
55% $CaCl_2 \cdot 6\ H_2O$ +55%$CaBr_2$ 6 H_2O	Inorganic eutectic	14.7	140	-	-	[18]
$CaCl_2 \cdot 6H_2O$ (45 wt. %) + $CaBr_2 \cdot 6H_2O$ (55 wt. %)	Eutectics	14.7	140	-	-	[12]
$NaOH \cdot 3/2H_2O$	Inorganic	15	-	-	-	[1]
$NaOH \cdot (3/2)\ H_2O$	Inorganic	15	-	-	-	[13]
	(hydrated salt)	15.4	-	-	-	[13]
$Mn(NO_3) \cdot 6\ H_2O$ + $MgCl_2\ \cdot 6\ H_2O$	Inorganic	15-25	125.9	-	1738 (l)	[17]
NaOH 3l /2H_2O	Inorganic compounds	16	200	-	-	[3]
Propyl Palmitate	Organic	16 - 19	186	-	-	[4], [15]
		10	186	-	-	[3], [13]
Caprylic acid	Fatty acid	16	148.5	0.149	901 (l)	[1], [4], [11], [13]
		16.3	149	-	981 (s)	[4], [11], [13], [18]
		16.5	150			[1]
Dimethyl Sulfoxide (DMSO)	Organic	16.5	85.7	-	1009 (l)	[4], [13]
Paraffin C_{16}	Organic	16.7	237.1	-	-	[12], [18]
Acetic acid	Fatty acid	16.7	184	-	-	[13]
45% Capric acid + 55% Lauric acid	Organic	17 - 21	143	-	-	[17]
		21	143	-	-	[4], [13]
48% Butyl Palmite + 48% butyl stearate + 3% other	Organic mixture	17	140	--	--	[17]
45-52% $LiNO_3 \cdot 3H_2O$ + 48-55% $Zn(NO_3)_2 \cdot 6H_2O$	Inorganic mixture	17.2	220	-	-	[4]
Glycerin	Organic	17.9	198.7	0.143	-	[12], [18]
$Na_2CrO_4 \cdot 10H_2O$	Inorganic	18	-	-	-	[1]
Capric acid + Lauric acid	Fatty acid mixture	18	120	0.143	-	[17]
n-hexadecane	Organic	18	210	-	760 (l)	[13]
			238	0.21		
		18.1	236	-	-	[17]
			211.5	-	-	
$Na_2CrO_4 \cdot 10\ H_2O$	Inorganic (hydrated	18	-	-	-	[1], [4], [13]

	salt)					
65% mol Capric acid + 35% mol Lauric acid	Fatty acid mixture	18-19.5	140.8	0.143	-	[4], [17]
		18	143-148	-	-	[13]
KF · 4 H_2O	Inorganic (hydrated salt)	18.5	231	-	1447 (l)	[1], [3], [4], [13], [15-16]
n-heptadecane	Organic	19	240	-	760 (l)	[13]
			-	0.21	-	
		20.8-21.7	171-172	-	-	[17]
61.5% mol Capric acid + 38.5% mol Lauric acid	Fatty acid mixture	19.1	132	-	-	[17]
Butyl stearate	Organic	19	140	-	760 (l)	[4], [11], [13], [16]
		18-23	123-200	0.21	-	[4], [11], [15]
Paraffin C_{16}-C_{18}	Organic	20-22	152	-	-	[4], [11], [13], [16]

(l) liquid
(s) solid

Table 2. Thermophysical properties of commercial products for cold storage (melting temperature up to 20 ºC) [11].

Name	Type	Melting temperature (ºC)	Heat of fusion (kJ/kg)	Source	References
-	Salt solution	-50	325	TEAP	[26]
SN 33	Salt solution	-33	245	Cristopia	[13]
TH 31	Salt Hydrate	-31	131	TEAP	[13]
MPCM (-30)	Paraffin	-30	140-150	Microtek laboratories, INC	[27]
SN 29	Salt solution	-29	233	Cristopia	[13]
SN 26	Salt solution	-26	168	Cristopia	[13]
-	Salt Hydrate	-23	230	TEAP	[26]
TH 21	Salt Hydrate	-21	222	TEAP	[13]
SN 21	Salt solution	-21	240	Cristopia	[13]
STL 21	Salt solution	-21	240	Mitsubishi Chemical	[13]
ClimSel C-18	Salt solution	-18	306	Climator	[28]
SN 18	Salt solution	-18	268	Cristopia	[13]
TH 16	Salt solution	-16	289	TEAP	[13]
STL 16	Salt solution	-16	---	Mitsubishi Chemical	[13]
AN 15	Salt solution	-15	311	Cristopia	[13]
AN 12	Salt solution	-12	306	Cristopia	[13]
STLN 10	Salt solution	-11	271	Mitsubishi Chemical	[13]
AN 10	Salt solution	-11	310	Cristopia	[13]
TH 10	Salt solution	-10	283	TEAP	[13]
MPCM (-10)	Paraffin	-9.5	150-160	Microtek laboratories, INC	[27]
STL 6	Salt solution	-6	284	Mitsubishi Chemical	[13]
AN 06	Salt solution	-6	284	Cristopia	[13]
RT -4	Paraffin	-4	179	Rubitherm GmbH	[29]
TH 4	Salt solution	-4	386	TEAP	[13]
SLT 3	Salt solution	-3	328	Mitsubishi Chemical	[13]
AN 03	Salt solution	-3	328	Cristopia	[13]
-	Salt solution	0	335	TEAP	[26]
RT 3	Paraffin	4	198	Rubitherm GmbH	[29]
RT 4	Paraffin	4	182	Rubitherm GmbH	[29]
-	Salt solution	4	105	TEAP	[26]

RT 5	Paraffin	5	198	Rubitherm GmbH	[29]
RT 6	Paraffin	6	175	Rubitherm GmbH	[29]
MPCM (6)	Paraffin	6	157-167	Microtek laboratories, INC	[27]
-	Salt solution	7	300	TEAP	[26]
ClimSel C 7	Salt solution	7 7	130 158.3	Climator	[28]
RT 5	Paraffin	9	205	Rubitherm GmbH	[17]
RT 20	Paraffin	8	140	Rubitherm GmbH	[17]
-	Salt solution	10	170	TEAP	[26]
-	Salt solution	15	175	TEAP	[26]
-	Salt solution	18	175	TEAP	[26]

Table 3. Freezing-melting temperature range and subcooling for aqueous NaCl and KCl solutions [41].

Solutions	Subcooling [ºC]	Freezing temperature [ºC]	Melting temperature [ºC]	ΔT (Freezing point depression)
5% NaCl	3.87	-3.87/-4.27	-4.87/-3.18	3.04
10% NaCl	6.28	-7.60/-7.70	-7.80/-6.10	6.56
15% NaCl	5.30	-15.19/-15.29	-10.40/-9.20	10.88
20% NaCl	2.79	-18.22/-17.92	-18.92/-14.62	16.45
21% NaCl	2.20	-18.46/-18.36	-18.86/-18.26	17.77
22% NaCl	1.60	-21.95/-21.85	-20.15/-19.65	19.17
23% NaCl	0.20	-20.89/-21.39	-22.39/-20.89	20.66
24% NaCl	0.30	-20.19/-19.79	-22.08/-19.59	-
5% KCl	1.59	-3.38/-3.58	-3.28/-2.08	2.32
10% KCl	7.48	-6.60/-7.10	-11.79/-6.00	4.80
15% KCl	4.40	-12.80/-13.20	-11.40/-9.60	-
20% KCl	5.59	-12.93/-13.13	-10.23/-9.43	-
21% KCl	4.80	-10.35/-10.65	-10.15/-9.65	-
22% KCl	6.90	-10.45/-11.25	-10.95/-9.15	-
23% KCl	7.48	-12.12/-12.82	-12.32/-9.83	-
24% KCl	5.10	-10.80/-11.10	-11.10/-9.10	-

Table 4. Recommendation related with corrosion using different materials as containers with different PCM (Adapted from [24-25]).

Metal/PCM	20.5 wt. % Na2CO3 + water	16.5 wt. % KHCO3 + water	6 wt. % KCl + water	Deionized water	KCl + water	NaCl + water
Aluminium	Only in short term applications	Only in short term applications	Only in short term applications	Used in short and long term application	Used without problems with exception of 20% KCl solution	Used in short and long term application. However, some combinations tested produced bubbles
Brass	Only in short term applications	Only in short term applications	Only in short term applications	Used in short and long term application	-	-
Steel	Used in short and long term application	Used in short and long term application	Only in short term applications	There were problems	-	-
Stainless steel	Used in short and long term application	Used in short and long term application	Used in short and long term application	Used in short and long term application	For short and long term applications without any problem. Only caution with 5 wt. % in long term because it gave some oxidation	For short term applications without any problem. For long term application, with high concentrations (21%, 22%, 23%, and 24%) presented a little bit of precipitate
Laminated black steel	-	-	-	-	Caution for short and long term due to precipitation	Caution for short and long term due to precipitation
Cooper	Only in short term applications	Only in short term applications	Only in short term applications	Used in short and long term application	-	Avoid it with NaCl for short term applications
Galvanized black steel	-	-	-	-	Should never be used because of the high corrosion	Should never be used because of the high corrosion

Table 5. Major TES cooling system types according to [119].

Chiller	Storage	Distribution
Conventional	Chilled water	Conventional water
Conventional	Eutectic salt/water solution	Conventional water
Ice-making	Ice	Conventional water
Ice-making	Ice	Cold air
Ice-making	Ice	Unitary (Rooftop)

Table 6. Primary features of cold storage systems [126].

	Chilled water	Ice storage	Eutectic salt
Specific heat (kJ/kg·K)	4.19	2.04	-
Latent heat of fusion (kJ/kg)	-	333	80-250
Cooling capability	Low	High	Medium
Tank volume (m^3/kWh)	0.089-0.169	0.019-0.023	0.048
Charging temperature (ºC)	4-6	-6 - -3	4-6
Discharge temperature (ºC)	1-4 above charging	1-3	9-10

Fig. 1. Families of phase change heat storage materials [3,11].

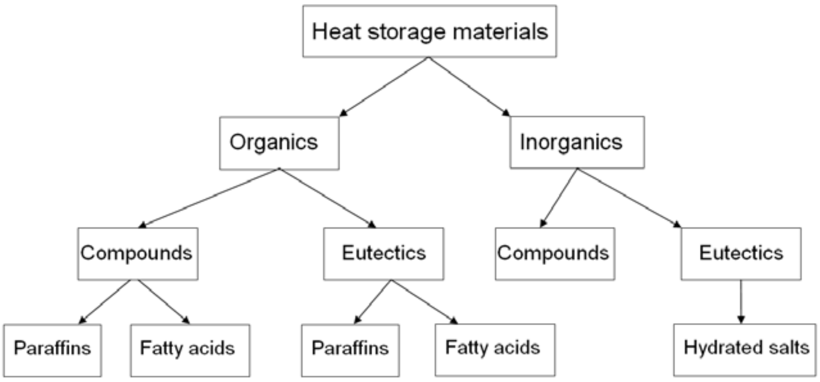


Fig. 2. Binary phase diagram for NaCl-H_2O at 100 kPa [22].

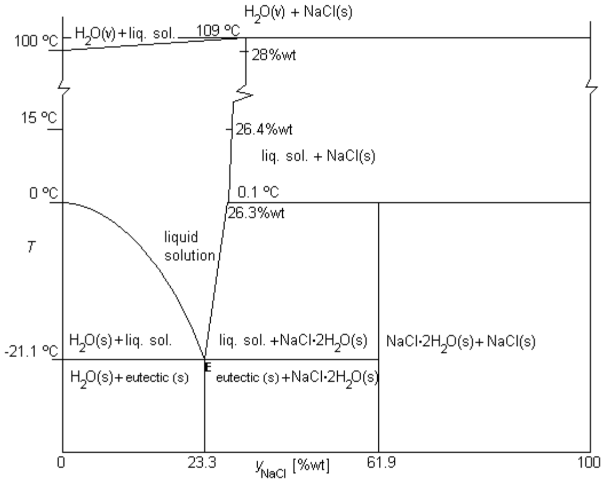


Fig. 3. DSC thermograms for some concentrations of NaCl-H_2O mixture [33].

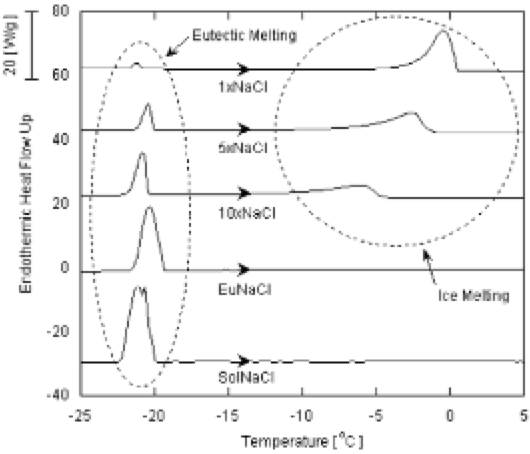


Fig. 4. Apparent heat of ethylene glycol solutions [34].

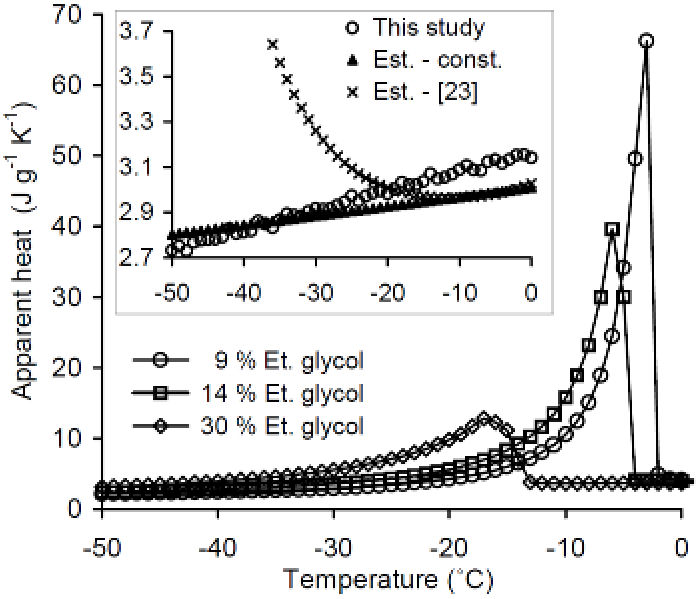


Fig. 5. Macroencapsulated PCM modules (Module type): principle and general performance [3].

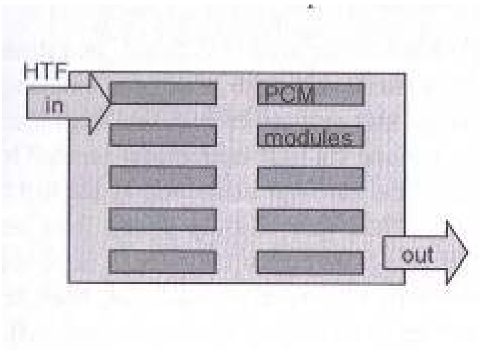


Fig. 6. Typical melting process of a spherical capsule [62].

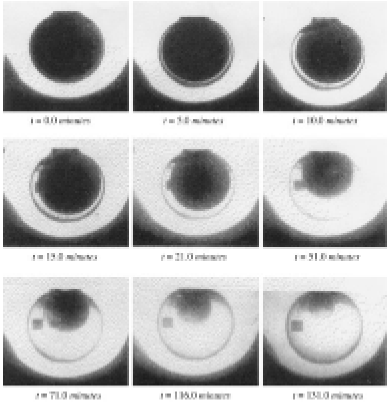


Fig. 7. Scheme of the tank and the spherical capsules [64-65].

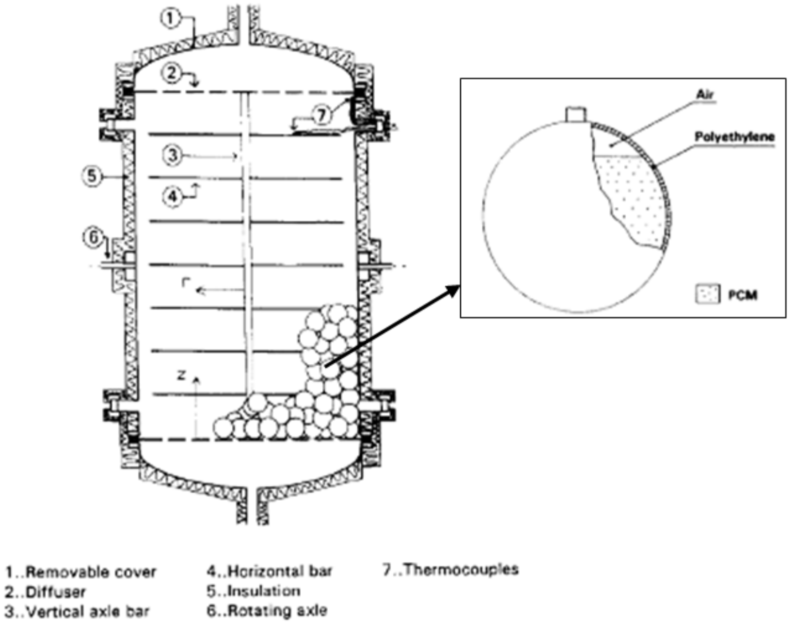


Fig. 8. Cross section of CALMAC's ICEBANK cold storage system [79].

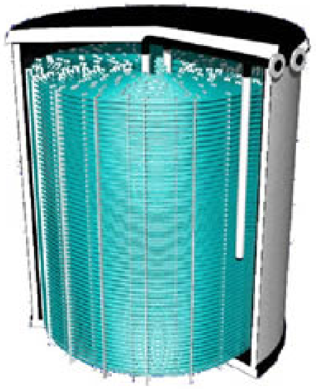


Fig. 9. Cold storage based on a module type design with spherical encapsulation, as developed by Cristopia [3].

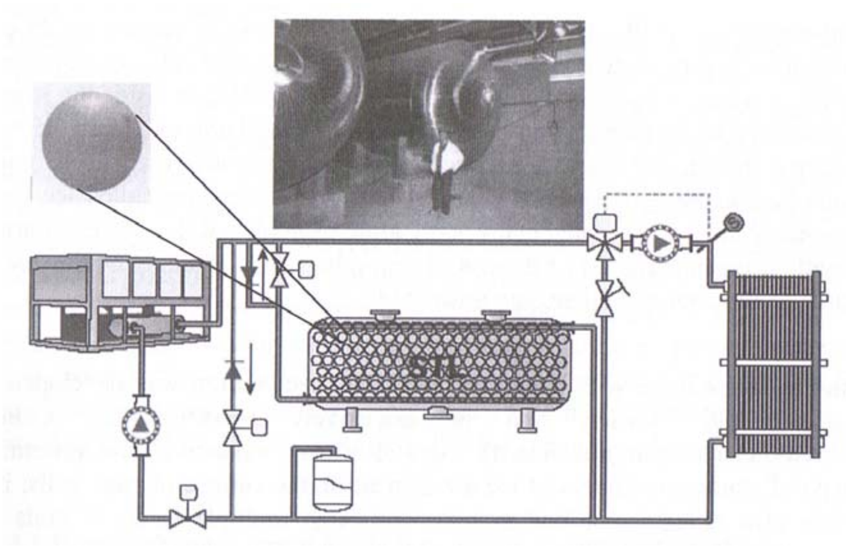


Fig. 10. Sketch of a system layout with EVAPCO ice-on-coil storage [82].

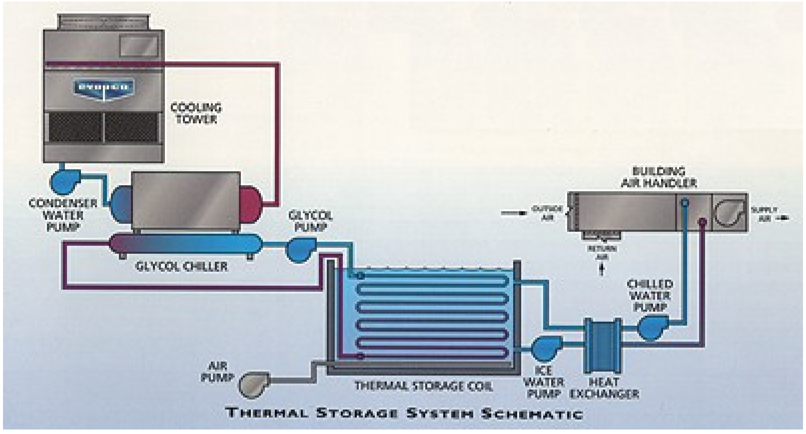


Fig. 11. Melting and solidification processes.

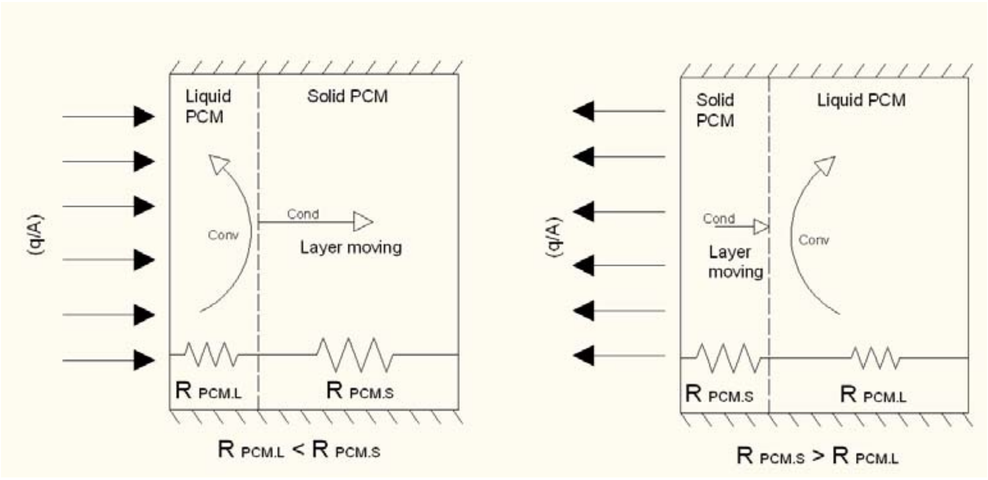


Fig. 12. TES units where brushes made of carbon fibers are inserted [96].

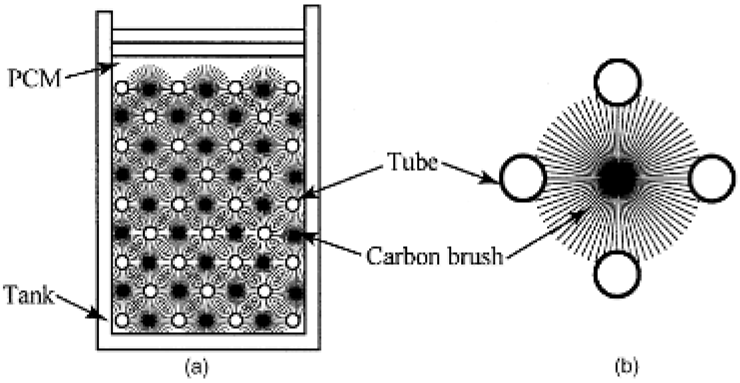


Fig. 13. Schematic representation of flow regime for ice-water and n-heptadecane systems [85].

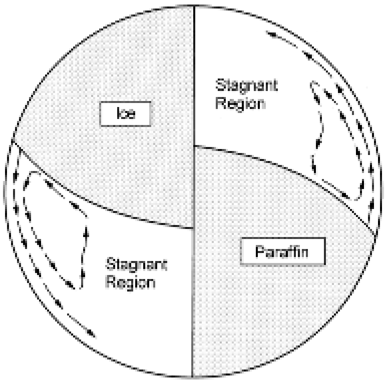


Fig. 14. The solidification of a finned tube after 2 hours for an inlet temperature of HTF of -10 ºC and Reynolds number of 500 [109].

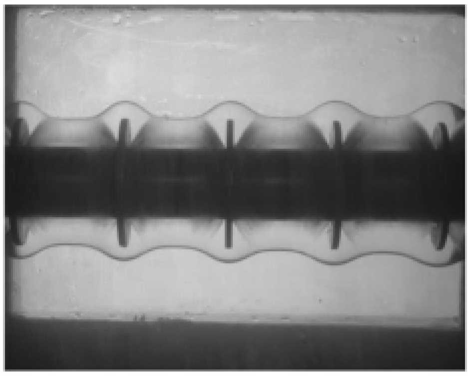


Fig. 15. Photographs of the ice shapes in different moments of the experiment [117].

Fig. 16. Gel packs of SOFRIGAM [121].

Fig. 17. Isothermal water bottle available in the market.

Fig. 18. Concept of catering applications [29].

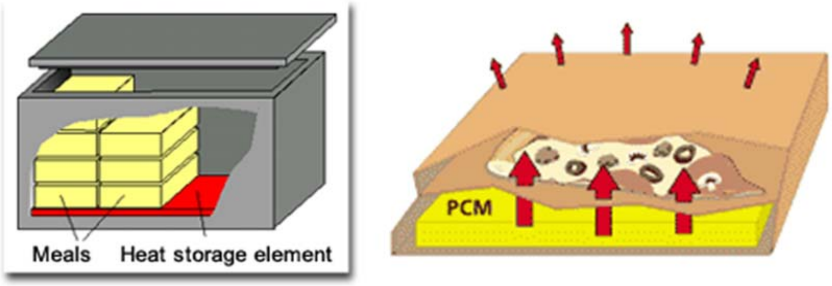
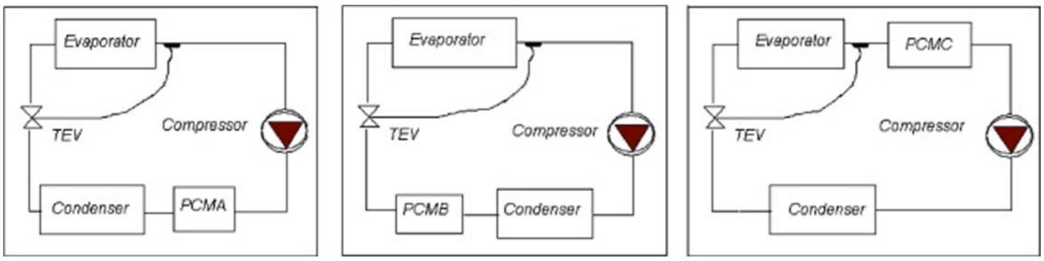


Fig. 19. Different PCM containers [26], [29].

Fig. 20. Containers to transport blood and organs containing PCM [29].

Fig. 21. PCM heat exchanger integrated into refrigeration system [135].



PCM A PCM B PCM C

Fig. 22. Diagram of a LNG refrigerated vehicle and its cold storage unit [139].

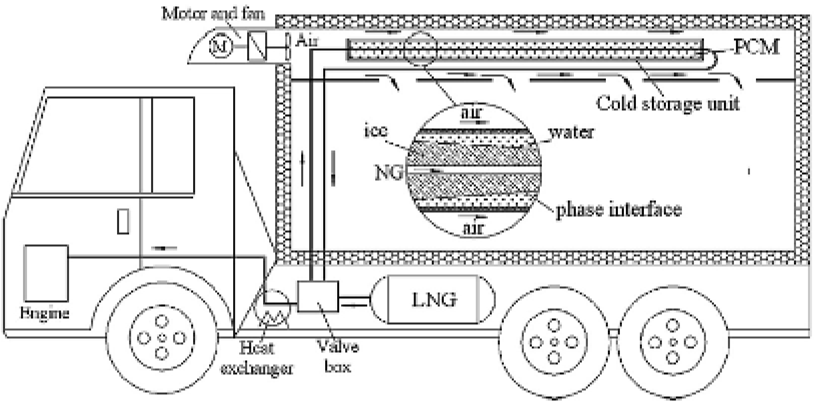


Fig. 23. The appearance of balls before and after crystallization used in the air conditioning system [146].