International Journal of Low-Carbon Technologies Advance Access published May 30, 2012

A review of PCM technology for thermal energy storage in the built environment: Part I

T.R. Whiffen* **and S.B. Riffat**
Department of Architecture and Built Environment, Engineering Faculty, University of Nottingham, University Park, Nottingham NG7 2RD, UK

Abstract

Pressure to slash CO_2 emissions continues to mount with growing levels of legislation and incentives to preserve our environment. To meet these targets, considerable research into renewable energy sources and energy efficiency is underway. Thermal energy storage (TES) systems offer attractive properties, enabling economical energy utilization within the built environment. Phase change material (PCM) has become a forerunner in the TES field due to its high-energy storage densities (~10 times that of concrete). An extensive review of PCM technology has been undertaken, with specific attention to TES applications within the built environment, assessing the capability of PCM.

Keywords: phase change material (PCM); thermal energy storage (TES); energy efficiency; built environment; technical review

*Corresponding author:
laxtw7@nottingham.ac.uk

Received 10 January 2012; revised 30 January 2012; accepted 2 February 2012

1 INTRODUCTION

The Kyoto Protocol set targets for green house gas (GHG) emissions by 2012. In the 15 years since the growth of energy-efficient technology in the UK has sky rocketed, propelled by a growing amount of legislation, to meet Kyoto targets and reduce CO_2 emissions in all spheres of life.

The built environment has been reported at attributing 30–40% of the total carbon emissions in the UK. Much of the carbon emissions attributed to the built environment in the developing world are due to the energy generation required to maintain inhabitant's quality of life. Sustainable technology offers a solution for ever tightening environmental building legislation, propelled by the charge to alleviate climate change and the desire for increased quality of life.

Most of the available renewable energy sources are incapable of providing constant power. To overcome this, solutions have been proposed by combining batteries, energy storage technology, with renewable energy generation. Thermal energy storage (TES) offers thermal energy efficiency enhancement for intermittent heat sources (e.g. solar heating). By 2050, it is predicted that over 70% of the world population will live in urban environments; thus the need for effective sustainable TES in buildings is ever increasing.

To date, there has been a great deal of research into TES and waste heat recovery to increase heating system efficiency and in turn reduce overall energy consumption within the built environment. This research work is therefore focused on reviewing the state of TES technology, with detailed assessment of a phase change material (PCM), for application within the built environment.

1.1 Thermal energy storage

TES technology acts as a heat battery and thermal buffer, protecting internal spaces from daily temperature fluctuations. The technology primarily operates in either sensible heat storage (SHS) or latent heat storage (LHS) modes [1]. SHS utilizes large bulk materials such as concrete and brick to absorb vast quantities of energy as the bulk temperature gradually rises. LHS makes use of the latent heat absorbed or expelled during phase change of a material to increase thermal capacity.

Built environment codes of practice cite an ideal comfort temperature between 21°C and 25°C [2]. During sunny seasons and without shading, internal building temperatures can regularly exceed guide temperatures, placing demand on effective cooling technology. Increased global demand for cooling has given TES a platform offering an efficient alternative to traditional compression cycle air-conditioning units. Whether utilizing SHS in bulk or novel LHS technologies, TES systems can effectively store sufficient quantities of heat energy to meet the cooling demands of the built environment.

doi:10.1093/ijlct/cts021

To determine the effectiveness of a TES system exergy (available energy) analysis plays an important role [1]. Other key measures of a material's TES capacity are heat density (kJ/m^3) and specific energy (kJ/kg). Depending on the application of the TES system, high or low heat transfer rate (heat flux W/m^2) is desirable, with thermal conductivity (W/m K) being a key factor in solid-based systems [1].

2 SENSIBLE HEAT STORAGE

2.1 Thermal mass

Following a similar mechanism as storage heaters, the thermal mass of a building can be utilized to provide residual heating or cooling. During summer months, the thermal mass absorbs heat generated in the room and creates a buffer from solar gain. The application is limited during consistent hot days, where the external temperature exceeds the desired internal temperature. In this situation, the available TES limit is reached. The heat stored will then be released into the internal space, causing the temperature to rise to uncomfortable levels—an effect called overheating.

Similarly, the thermal building mass offers protection from the cold until all heat from the thermal mass has been lost to the external environment. The thermal mass will then absorb internal heat, cooling the room. Insulation materials, typically materials with a low thermal conductivity, reduces the effects of external thermal fluctuations on internal temperatures and can increase the effectiveness of thermal mass applications.

2.2 Thermal active building systems

Many TES systems exhibit good performance as alternative insulators. The heat generated is stored and released as required, offering internal temperature control. The benefits of TES are often more apparent during cooling requirements when insulated spaces are liable to overheating. Active TES systems remove excess heat from the building, maintaining thermal comfort.

Thermal mass efficiency in temperature control is limited by heat exchange area—traditionally, external surfaces of the mass. Due to typically low thermal conductivities of building materials, discharge of heat stored is slow, especially with the typically small temperature differences. Integrating an active system through channels in the thermal mass increases heat exchange area and heating efficiency. Various thermal fluids are used to enhance performance.

2.2.1 *Water-driven systems*

Water-driven systems embed a matrix of pipes in the thermal mass. These pipes connect to a closed-loop water heating system. Water passes through the mass, removing or radiating heat. The heat transfer rate to the thermal mass is increased with the pipe contact area; however, heat transfer to the room remains limited by the active thermal mass external surface.

Room heating rates can be increased by operating higher temperature difference between the room and mass. Thermal mass acts as a diffuser of heat, protecting the room from temperature spikes.

Thermal capacity is enhanced by water, removing excess heat from the slab during extended hot seasons. This type of cooled ceiling technology [3] enables dynamic utilization of the residual thermal mass.

2.2.2 *Air-driven systems*

The Termodeck [4] system utilizes ventilation air as the thermal fluid. Concrete hollow core absorbs heat from the room, while pre-conditioned ventilation air passes through before being released into the room.

The ventilation air serves to maintain hollow core and room temperature. Air passing through the hollow core *en route* to the room increases the heat exchange area while also enabling room temperature control through recycled heat. Heat transfer from the bulk to room is no longer limited by the ceiling surface area, since pre-treated ventilation air conditions the room also.

During hot spells, night ventilation flushes the residual heat from the hollow core thermal mass. This extends the operation envelope and ensures that room temperatures never exceed the national standard office temperature hours [5]. Night heat flush operation limits the applicability to daytime use buildings.

2.3 Underground thermal energy storage systems

Another form of thermal energy SHS utilizes the vast heat density available in the Earth's groundwater systems. Aquifer TES (ATES) systems are operated as open-loop systems pumping ground water through the system. In summer, the water acts as the coolant and the groundwater temperature in the aquifer gradually increases, typically from 9–12 to 15–20°C in Dutch systems. In winter, this warm water acts as low-grade heating, and the temperature in the aquifer drops to between 5 and 10°C [6].

Alternatively, borehole TES systems operate in a closed-loop function. Heat transfer fluid extracts heat from the ground water and is pumped back to the buildings above. No groundwater is transported, allowing systems to operate at more extreme temperatures than the ATES systems [6].

Further systems have been designed in collaboration with solar water heaters. These systems endeavour to store the heat generated in the hot summer months for use in the cold winter months [7].

3 LATENT HEAT STORAGE: PCM

LHS has attracted interest due to its high thermal densities. Using data taken from [1], Figure 1 compares the performance of PCM technology versus traditional energy storage, such as lead batteries. PCM offers high energy storage density,

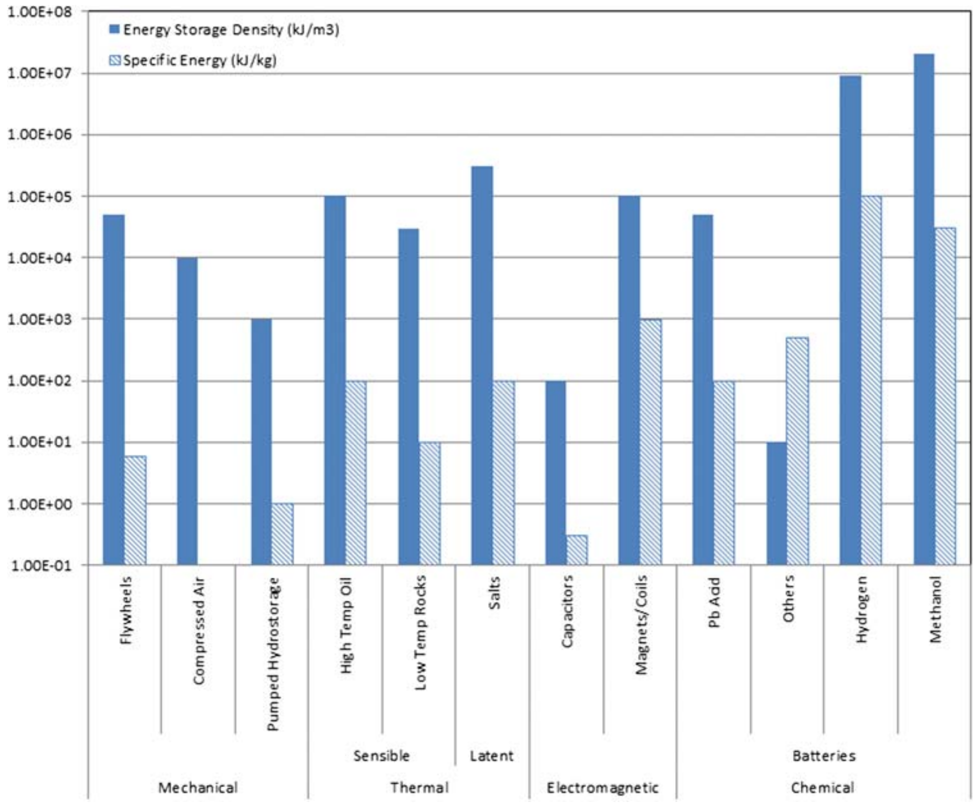

Figure 1. *Comparison of energy storage technologies [1]. Reprinted from I Dincer, MA Rosen. 'Comparison of Energy storage Technologies' Chart in Thermal Energy Storage Systems and Applications, 2nd edn., Copyright Wiley & Sons 2011, reprinted by permission of the publisher*

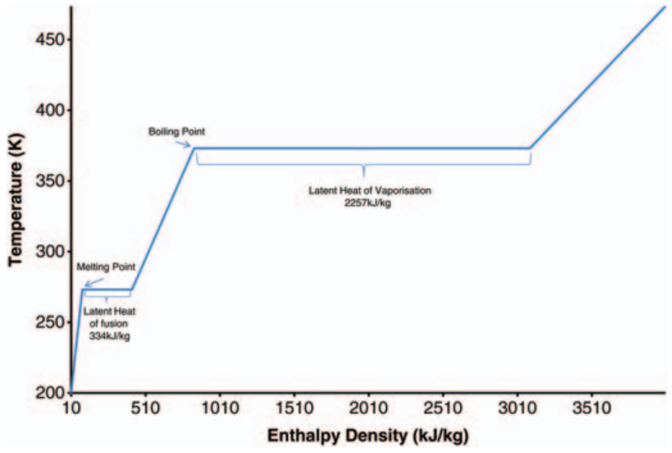

Figure 2. *Water phase transition curve.*

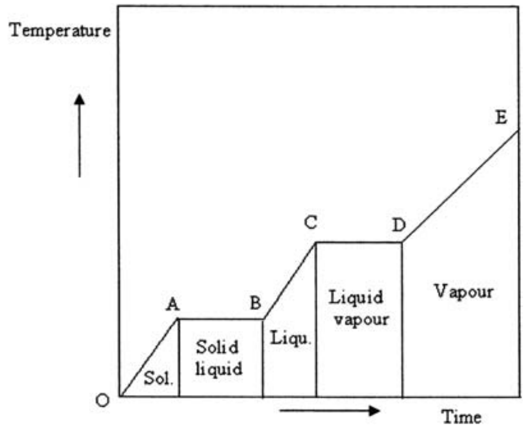

Figure 3. *Phase transition curve [7]. Thermal Energy Storage and Phase Change Materials: An Overview, M Fatih Demirbas, Energy Sources, Part B: Economics, Planning, and Policy, 2006, Copyright Taylor & Francis 2006, reprinted by permission of the publisher.*

surpassed only by chemical storage in hydrogen and methanol, demonstrating its high suitability as a main contributor towards energy efficiency.

3.1 Background

The most well known and abundant PCM is ice/water; however, every chemical compound will change phase at a given temperature and pressure. Early research into PCM for TES was carried out by researchers at the University of Delaware in the 1970s. PCM was incorporated with solar collectors to store heat [1]. In these early applications, a wide range of melt temperatures were utilized. In modern built environment applications, the useful melting temperature range has been reduced more narrowly around indoor comfort temperature.

The science behind the high energy density of PCMs is due to the latent heat of fusion. When a substance changes phase, a vast amount of energy is absorbed or released despite no significant change in the measured temperature [1]. This change in energy is due to the difference in intermolecular energies in each phase.

Figure 2 [8] outlines the relationship between temperature and energy as water is heated. Three stages of sensible heating occur when in phase. At the transition temperature (melting and boiling points), latent heating occurs where an extensive amount of energy is released or absorbed with little temperature change. The heat of fusion, utilized in PCM systems, is significant, almost equal to that of the entire liquid heating section.

Figure 3 plots the change in temperature against time, with the same observations. During the sloped sections of Figure 3 (OA, BC, DE), the material undergoes sensible heating; thus the energy change is a function of temperature change, specific heat capacity and the mass. During the flat sections (AB, CD), where temperature is constant, latent heating is occurring. Here the energy change is simply a function of the materials mass and latent heat of transformation. The following equation combines the sensible and latent heat equations to determine the overall change in energy. Dincer and Rosen [1] explain in further detail the theory behind the curve.

$$\Delta Q = m\left[\int_{T_{\mathrm{O}}}^{T_A} C_{\mathrm{ps}}(T)\,\mathrm{d}T + \Delta H_{\mathrm{f}} + \int_{T_{\mathrm{B}}}^{T_{\mathrm{c}}} C_{\mathrm{pl}}(T)\,\mathrm{d}T + \Delta H_{\mathrm{v}} + \int_{T_{\mathrm{D}}}^{T_{\mathrm{E}}} C_{\mathrm{pv}}(T)\mathrm{d}T\right] \tag{1}$$

Any latent heating system will utilize both sensible and latent heating during its operation. Operation at temperatures on either side of the transition temperatures will drive sensible heating even in a PCM. For detailed understanding of PCMs, a good foundation in thermodynamics, crystallization, heat transfer and fluid dynamics is desirable.

3.2 Thermal analysis methods

The thermal properties of any TES system are a clear way of quantifying performance and comparing methods [9]. A variety of analytical methods characterizing the thermal properties of pure PCMs and phase-change-incorporated building materials (PCIBM) have been developed [10–13].

3.2.1 *Differential scanning calorimetry [14]*

Differential scanning calorimetry (DSC) measures the amount of heat required to keep a substance at a given temperature [9]. Tests vary temperature linearly with time [15]. PCM samples are tested against a reference sample (with known thermal properties). The product of a DSC test is a curve displaying the heat flux versus temperature or time. The DSC curve produced reveals crystallization and melting temperatures along with the size of latent heat. The drawbacks of DSC are the accentuated super-cooling effects reported due to small sample sizes and thus poor nucleation effects [16].

3.2.2 *Differential thermal analysis*

Similar to DSC, differential thermal analysis (DTA) keeps the heat flux as constant and monitors the difference in temperature change between the reference and test samples. Thermal properties, including thermal conductivity, are then calculated from the temperature differences [9]. Buddhi *et al.* [16] constructed a simple variation of DTA that tested samples with an accuracy of 5% when compared with DSC results. DTA produces time versus temperature graphs, graphically presenting the heat transfer rate at a variety of temperatures [17]. Small sample sizes used in testing may misrepresent the thermo-physical performance of a given material when operating in bulk units [18]. Further limitations of DSC and DTA are the expense and their inability to measure multiple samples simultaneously [18].

3.2.3 *T-history method*

A simplified T-history method has been developed with results comparable to DSC and DTA [9]. This method was initially developed by Zhang and Jiang [18], wherein the test samples are placed in test tubes equipped with thermocouples connected to a data logger. The samples are heated and cooled in water baths for a set period of time. From temperature versus time curves, the thermal properties of the sample can be obtained. Zhang and Jiang [18] reported an accuracy of ~10% with literature data for the samples tested. The process has since been refined by Hong *et al.* [19] and Peck *et al.* [20] to correct some assumptions in the initial method and widen the operation envelope. Despite this being a simple method and it is useful for characterizing bulk PCM, giving a more realistic representation of applied performance, many still rely on DSC and DTA to characterize the performance of the heat storage technology.

4 PCM DESIGN

4.1 Methodology

The incorporated PCM (IPCM) design process is inherently iterative. When incorporating PCMs, various specifications are outlined, determining what properties the PCMs should exhibit. The initial requirements of a TES unit design are: (i) the operational temperature envelope for the unit and (ii) the required heat load to maintain the specified temperature (dependent on heat transfer and environmental conditions) [21]. From the specified properties, the iterative design process in Figure 4 is followed to establish the optimum PCM and encapsulation for the application.

Figure 4 flowcharts this multistage iterative design process. At each design stage, there are two inputs: the design specification and available technology. If the availability matches the specification, then the process can move onto the next design stage. If there is incompatibility at any stage, two potential

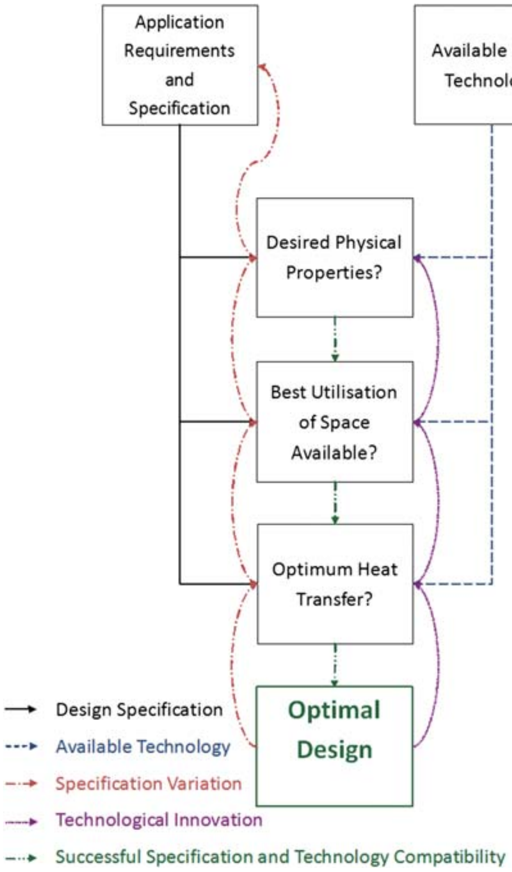

Figure 4. *Iterative PCM design methodology.*

variables can be explored to find a solution: either minor specification variation or the development of technological innovation. Once compatibility is reached, the design process may progress until the optimal design is reached.

Figure 5 flowcharts the design stages required to introduce a new PCM product to market. The flow chart in Figure 5, redrawn from [21], goes into greater detail than that in Figure 4, explaining the steps involved in the iterative design steps represented in Figure 4. Much of the data determined during the stages in Figure 5 would feed into the optimization stages of Figure 4. Both flow sheets involve necessary analysis and optimization stages.

After theoretical modelling of a system, workable experimental tests must always be undertaken to confirm the validity of the numerically optimal design. The final branch in Figure 5 outlines this practical process. Dolado *et al.* [22] recently determined a justifiable variation between theoretical and practical results.

4.2 Desirable properties

Zhou *et al.* [9] highlighted three key properties for any potential PCM: 'suitable melting temperature, desirable heat of fusion and thermal conductivity as specified by the practical application'. The seven important criteria identified by Dincer and Rosen [1] and with further desirable features summarized from [23] are tabulated in Table 1.

For building applications, the optimum melting point varies between 0 and 30°C, depending on application. As recorded in Zhou *et al.* [9], Peippo *et al.* [24] determined that to maximize the benefits of a diurnal PCM cycle, the PCM melting point should be 1–3°C higher than the average room temperature, though various sources [25–27] concluded that the optimum temperature varied slightly from Peippo *et al.* [24]. Equations were developed by Drake [28] to calculate the optimum melting temperature:

$$T_{\mathrm{m,opt}} = \bar{T}_{\mathrm{r}} + \frac{Q}{ht_{\mathrm{stor}}} \tag{2}$$

where Q is the total heat absorbed per room surface area, h the average heat transfer coefficient between wall surface and surroundings and t_{stor} the storage time.

$$\bar{T}_{\mathrm{r}} = \frac{t_{\mathrm{d}}T_{\mathrm{d}} + t_{\mathrm{n}}T_{\mathrm{n}}}{t_{\mathrm{d}} + t_{\mathrm{n}}} \tag{3}$$

where $\bar{T}_{\mathrm{r}}$ is the average room temperature calculated from Equation (2), T temperature, t time and the subscripts d and n refer to day and night.

PCMs with lower melting points have heats of fusion above 200 kJ/kg, though many commercially available PCMs have a heat of fusion between 100 and 200 kJ/kg [9]. After thermal storage at the operating temperature, the most important aspect of PCMs is their long-term stability [11].

4.3 Materials and properties

4.3.1 *Classification*

It has been reported by Regin *et al.* [21] that Lane [29] reviewed ~20 000 chemical materials, with a view to identify those with a melting point in the region between 10 and 90°C. The following classification trees (figure 6 and 7) show the groupings for common PCMs. PCM is classified based on the particular phase change that occurs in the operation temperature envelope. Solid–liquid PCMs have shown the most promise [9], though solid–solid transitions attracted some initial interest.

Figure 7, redrawn from [9], best illustrates the classification stages for solid–liquid PCMs. There is slight discrepancy in the classification of eutectics, hence the differences in classification diagrams. As highlighted in Figure 6, the most commercially promising PCM for building applications is that of organic paraffin.

Figure 8, redrawn from [8], plots the range of available materials with low temperature (−100 to 200°C) melting points against their relative melting enthalpies. It serves as a good initial comparison to understand the different PCMs available and their respective properties.

4.3.1.1 *Ice/water* The most well-known and abundant phase change material is ice/water. Early phase change research explored the application of ice/water systems for effective cooling; however, the relatively low (0°C) melting point limits

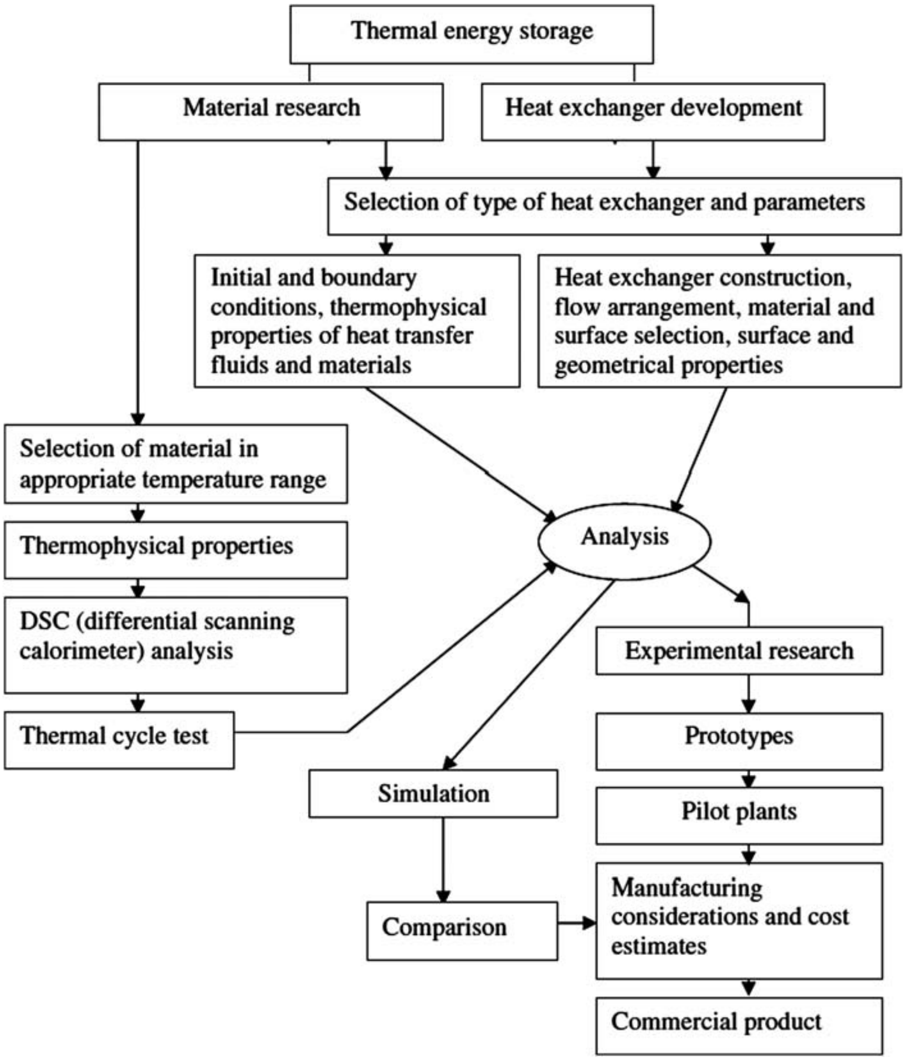

Figure 5. *Design flow sheet redrawn from Regin AF, Solanki SC, Saini JS. Heat transfer characteristics of thermal energy storage system using PCM capsules: a review. Renew Sustain Energy Rev 2008;12:2438–58 [21].*

the applicability of ice/water systems, and the performance has since been surpassed.

4.3.1.2 *Organic* The organic classification largely includes fatty acids and paraffins, with the later attracting increased attention. Paraffins make for attractive PCMs because:

- they have wide and variable melting point range,
- they have relatively high heat of fusion,
- they show no super-cooling,
- they are chemically stable and recyclable,
- they show good compatibility with other materials (for mixtures).

The disadvantages of paraffins versus alternative PCMs are their low thermal conductivity (around 0.2 W/m K), their relatively large volume change and their flammability risk [9]. Methods to alleviate those disadvantages have been presented in the literature, by addition of high thermal conductivity materials and fire-retardant additives [11].

4.3.1.3 *Inorganic materials* Of the inorganic materials, hydrated salts have received the most attention, with researchers exploring their particular application in solar heating systems. Inorganic salts are favourable as PCMs due to their:

- high heat of fusion,
- high thermal conductivity (around 0.5 W/m K),
- low volume change,
- low cost.

The disadvantages of inorganic salts are their poor nucleation rates, causing super-cooling, and their corrosive nature, both of which hamper the stability of the PCM and its supporting system [9]. To avoid super-cooling, nucleating agents are added and arranging PCM in a thin layer increases stability [11].

Table 1. *Desirable PCM properties [1, 9, 23].*

Thermodynamic	Kinetic	Chemical	Economic
Melting temperature in desired range	High nucleation rate	Completely reversible freeze/melt cycle	Low cost
High latent heat of fusion per unit mass	High rate of crystal growth	Chemical stability	Widely available
High thermal conductivity		High freeze/melt stability	
High specific heat and high density		Non-corrosive	
Small volume changes on phase transition		Non-toxic, non-flammable and non-explosive material	
Complete melting			
Small vapour pressure at operating temperatures			

4.3.1.4 *Eutectics* Eutectics are mixtures of chemical compounds, either crossing the organic–inorganic divide or made up solely of either class, that all undergo phase transition at the same temperature [7]. These mixtures are developed to offer specific melting points, thus have an advantage in their sharp melting temperatures [9]. These synthesized materials also boast high volumetric storage densities.

The current stumbling block for eutectic mixtures is the lack of available thermo-physical data. With greater understanding of these properties, the true potential of eutectic mixtures can be ascertained.

4.3.2 *Thermal properties*

To date, numerous potential PCMs have been identified. In literature, authors have listed extensive thermal properties of these [11] reported thermal properties for all known PCMs with melting points between −10 and +100°C. For the purpose of building applications, however, the most optimum operating temperature range lies between 0 and 35°C. Their thermal

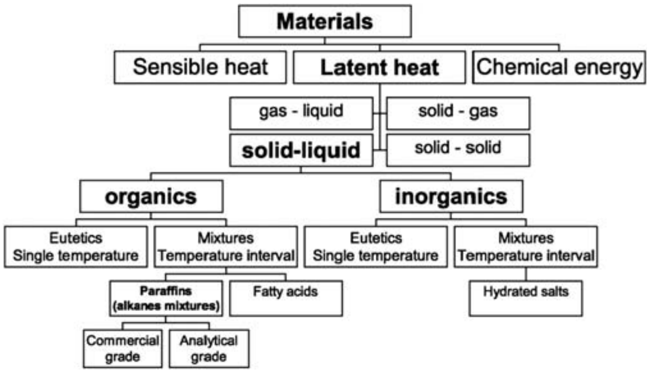

Figure 6. *Classification of TES materials [11, 13]. Reprinted from Renewable and Sustainable Energy Reviews 15(3), LF Cabeza, A Castell, C Barreneche, A de Gracia and AI Fernández, Materials used as PCM in thermal energy storage in buildings: A review, 1675–1695, Copyright 2011, with permission from Elsevier.*

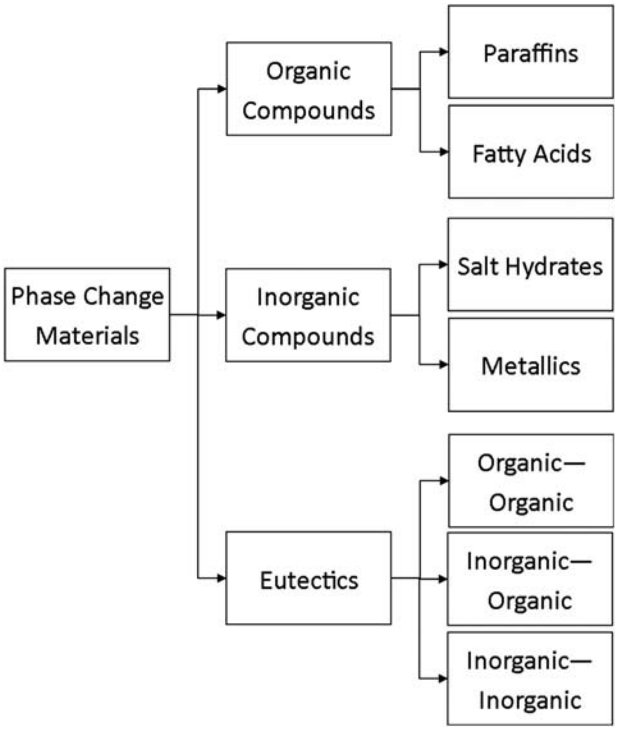

Figure 7. *PCM classification tree [9]. Reprinted from Applied Energy 92, D Zhou, CY Zhao, Y Tian, Review on thermal energy storage with phase change materials (PCMs) in building applications, 593-605, Copyright 2012, with permission from Elsevier.*

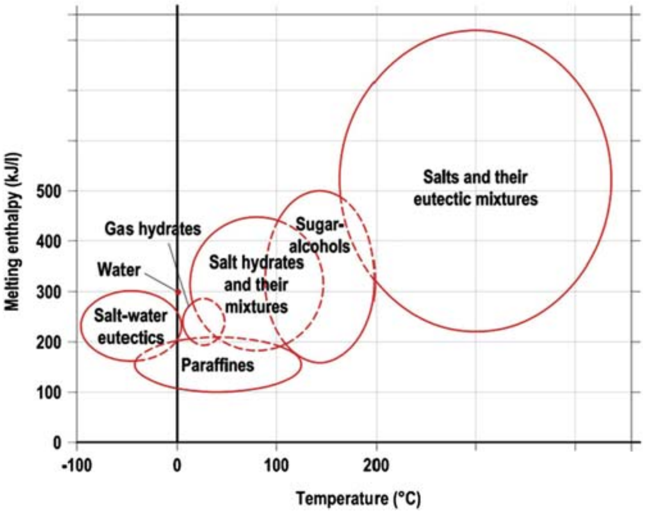

Figure 8. *Melting enthalpy and temperature for a range of PCMs [10] redrawn from Dieckmann [8]. Reprinted from Energy and Buildings 42(9), Ruben Baetens, Bjørn Petter Jelle, Arild Gustavsen, Phase change materials for building applications: A state-of-the-art review, 1361-68, Copyright 2010, with permission from Elsevier.*

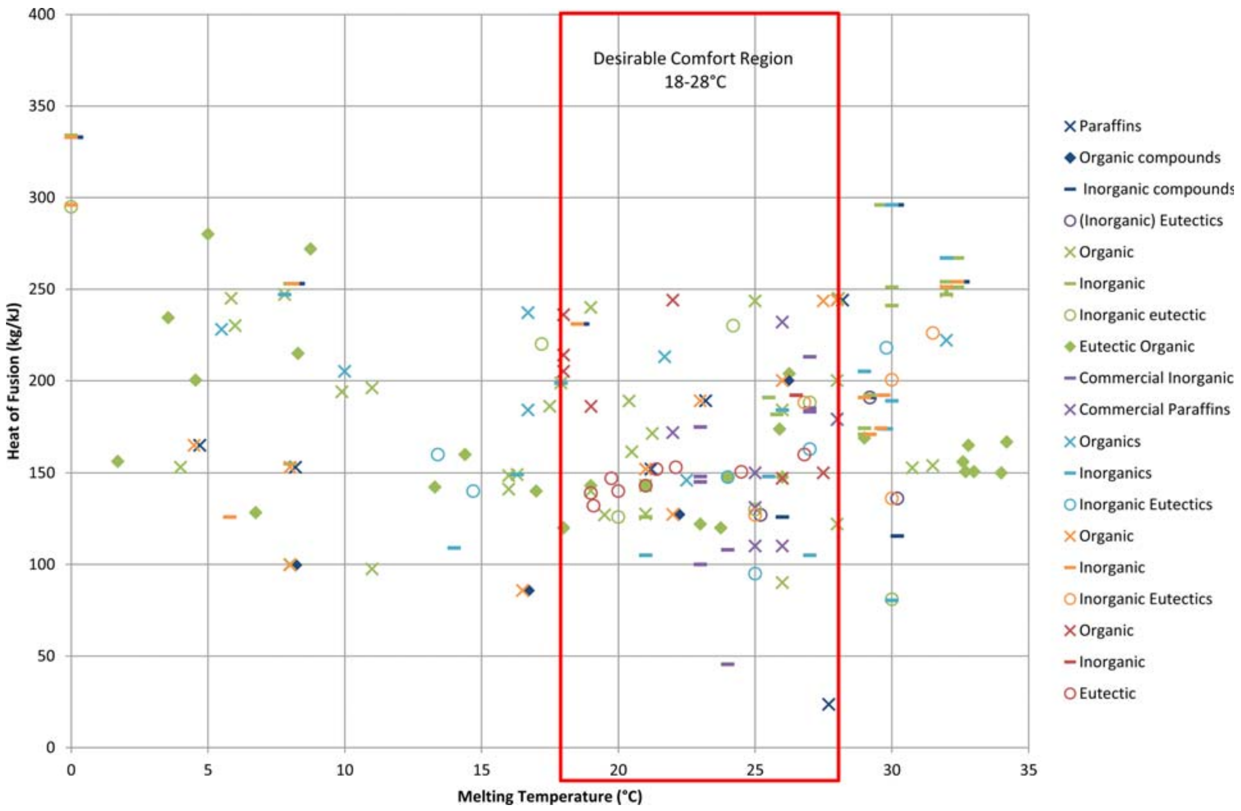

Figure 9. *Melting temperature versus enthalpy for known PCMs with melting points between 0 and 35°C.*

Table 2. *Commercially available PCMs with melting range between 18 and 28°C [11].*

Material	Type	Melting point (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m K)	Company source
RT 20	Paraffin	22	172	0.88	Rubitherm GmbH
Climsel C 23	Salt hydrate	23	148		Climator
E23	Salt hydrate	23	155	0.43	EPS Ltd.
Climsel C 24	Salt hydrate	24	108	1.48	Climator
TH 24	Salt hydrate	24	45.5	0.8	TEAP
RT 26	Paraffin	25	131	0.88	Rubitherm GmbH
RT 25	Paraffin	26	232		Rubitherm GmbH
STL 27	Salt hydrate	27	213	1.09	Mitsubishi Chemical
S27	Salt hydrate	27	207		Cristopia
AC 27	Salt hydrate	27	207	1.47	Cristopia
RT 27	Paraffin	28	179	0.87	Rubitherm GmbH

properties are graphically presented in Figure 9. On the chart, each marker type represents a different PCM category;

- × Organics (e.g. paraffins),
- ◇ Organic eutectics (e.g. fatty acid mixtures),
- – Inorganics (e.g. salt hydrates),
- ○ Inorganic eutectics (e.g. salt mixtures)

Source data has been taken from [7,11,12,13 and 30] and is available on request. From Figure 9, it is clear that the PCMs with highest enthalpies are the salt hydrates; however, within the desirable comfort region, paraffin-based organics offer the highest fusion enthalpies.

4.3.3 *Commercial materials*

PCMs are available commercially from a range of suppliers. Table 2 lists the thermal properties of commercially available PCMs, with a melting point between 18 and 28°C. Rubitherm specializes in paraffin-based PCM production for application as a thermal storage medium [31]. The melting points of their products range from −10 to 100°C.

EPS Ltd specializes in PCMs, environmental chemicals and services. They have a wide variety of containers and applications to house the PCM or can fill any given container with the specified PCM. PCM's can operate in the temperature range from −114 to 164°C. Depending on the operational temperature range, PCMs are made up of a mix of non-toxic salts and organic compounds [32].

BASF offers Micronal® PCM, MPCM. The Micronal® PCM is suitable for mixing in fluid substances (paints or adhesives) or more densely in powder form, suitable for inclusion in construction mixes to produce 'Melting' dry walls. Micronal® PCM targets building applications offering products with a range of melting temperatures in the human comfort region, 21–26°C [33].

Further manufacturers include Teap, Cristopia, Climator, Mitsubishi Chemical, Doerken and Merck. Of these manufactures, the melting temperatures of PCMs offered range from −50 to 118°C [1].

4.4 Encapsulation

The method of encapsulation is integral to PCM application. Various companies have utilized different methods. EPS specialize in adaptable macro-encapsulation solutions [32]. Rubitherm has developed *in situ* bulk storage solutions [31], whereas BASF has produced microencapsulated PCMs [33]. To achieve heightened performance, PCM encapsulation technology continues to be refined. In each encapsulation method, it is important that the PCM and container material have no chemical interaction to maintain long-term stability and avoid corrosive mixes [11].

4.4.1 *Direct application*

Early research into IPCM focused largely on direct incorporation and direct immersion. For direct incorporation, PCMs in either liquid or powdered form are added to bulk building material mix during production. The attraction is its simplicity; however, problems with leakage and material compatibility hinder widespread applicability [9].

Direct immersion involves dipping prefabricated building materials in liquid PCMs. The building material surface absorbs PCMs via capillary elevation. Due to the exposed nature of the PCM on the material surface, significant leakage occurs during the lifetime of the technology [9].

4.4.2 *Bulk storage*

Bulk storage encases PCM in large tanks. This highly cost-effective method requires little processing of the materials. Issues have arisen from poor thermal conductivity, causing fluctuating performance. Effective methods of increasing heat transfer through agitation and by increasing the surface area have been explored [21].

4.4.3 *Macro-encapsulation*

Cabeza *et al.* [11] contains figures of macro-encapsulation methods offered commercially by EPS and TEAP. PCM is encapsulated in containers ranging from 10 cm to a few metres [32]. In each application, standard produced units are fitted within the technology to ensure maximum heat transfer. These macro-encapsulation units are anti-corrosive, enabling inorganic PCM encapsulation. Poor heat transfer throughout the contained PCM causes solidification on the edges, thereby limiting performance. The large scale makes flexible incorporation in building applications difficult [9].

4.4.4 *Microencapsulation*

Microencapsulated PCM (MPCM) contains PCM particles (core), a few microns in diameter, in a sealed membrane (shell). Methods for incorporating MPCM in applications range from uniform sealing in a solid matrix to suspension in heat transfer fluid (HTF). Most modern applications of PCM favour MPCM [30] because of the high surface area to volume ratio, reducing the effects of poor thermal conductivity. Due to the capsules small scale the overall thermal conductivity is significantly affected by the thermal conductivity of the shell. In MPCM, internal volume changes are tolerated by the shell and avoid bulk volume change.

BASF's Micronial® PCM uses MPCM technology, encapsulating a paraffin core with a vinyl shell [33]. The key to MPCM technology is the compatibility and stability of the core and shell. Typically, the shell membrane is made from a high-molecular-weight polymeric film that maintains the particle structure and protects against leakage. Good stability and minimal structural strength losses upon concrete incorporation have been reported [9]. The use of MPCM in building materials has alleviated the leakage losses seen with the direct incorporation method.

PCMs can be microencapsulated through a range of methods, both physical and chemical. Physical encapsulation methods include pan coating, air-suspension coating, centrifugal extrusion, vibration nozzle and spray drying. PCM is physically encapsulated via interfacial polymerization, *in situ* polymerization and matrix polymerization [30]. MPCMs are categorized based on their core structure and shell deposition process:

- Mononuclear, a single core with a single surrounding shell.
- Polynuclear, multiple cores surrounded with a single shell.
- Matrix encapsulation, core material is distributed homogeneously throughout the shell material.

MPCMs are produced following a four-stage process: emulsification, coacervation, cross linking and filtration [1].

4.4.5 *Shape-stabilized PCM*

PCMs dispersed homogeneously throughout a supporting material, such as HDPE, form a stable composite material. This composite material boasts high thermal conductivity, high stability and the ability to maintain solid shapes throughout the phase change process [9].

4.4.6 *Slurry*

Two methods have been reported for transporting PCM in thermally active fluids (slurries): that of microencapsulation (MPCM) and direct mixing of paraffin in water by use of immiscible fluids [1, 3]. In MPCM slurries, the core PCM is encapsulated by a molecular vinyl coating, allowing for expansion without leakage into the slurry. These encapsulated balls exist in suspension in the thermally active fluids.

Paraffin directly mixed in water makes use of appropriate surfactants to enable the solubility of paraffin in water [34]. Further work to understand the melting and solidification process in water is required to enable wider application of paraffin water slurries. Initial investigations show promise in comparison with MPCM slurries offering reduced cost, simpler production and more efficient heat transfer [34]. Stability of the mixture is questionable and requires further techniques to maintain a consistent density of paraffin throughout the liquid; Lu and Tassou [34] suggest some methods, including constant mixing and addition of thickening agents.

For both methods, the use of slurries opens new capabilities for PCM applications as thermally active fluid. By making use of their relatively high energy densities, the PCM slurries rival traditional coolant fluid applications. Careful consideration of the slurry transport medium will aid the thermal performance of the suspended MPCM [35]. Their functionality as fluids also enables transport to and from active centres through traditional liquid pumping methods.

4.5 Heat transfer

The specifics of PCM technology to meet performance requirements are found as heat transfer capabilities and requirements are considered. The rate of heat transfer is governed by thermal conductivity, exchange area and temperature difference of the PCM and heat transfer medium, the structural arrangement and operation of the PCM system [21].

All forms of heat transfer occur during operation of a PCM system. Convection occurs within the heating fluid, between the fluid and external surfaces and between the heating fluid and PCM containers. Conduction carries heat through PCM containers and throughout the encapsulated PCM. Depending on the system, radiation may occur from the container surface. When modelling packed bed systems, the effective conductivity and total heat transfer coefficient are most often used to express general thermodynamic performance [21].

4.5.1 *Enhancement*

PCM in bulk systems suffers from poor heat transfer due to low thermal conductivity [9]. Work to enhance the heat transfer capabilities has been done. Thermal conductivity was increased by the use of metal foams, Al powders, carbon fibre and expanded graphite (EG) structures [34, 36].

Early enhancement of macro-encapsulated PCM was achieved through increased voidage and surface area to volume ratio [21]. Heat transfer was still limited within containers during crystallization due to the solid layer formed on the boundary. The addition of metal fins and additives have been found to increase conductivity; however, the cost and incompatibility with certain PCM prohibits progress [17].

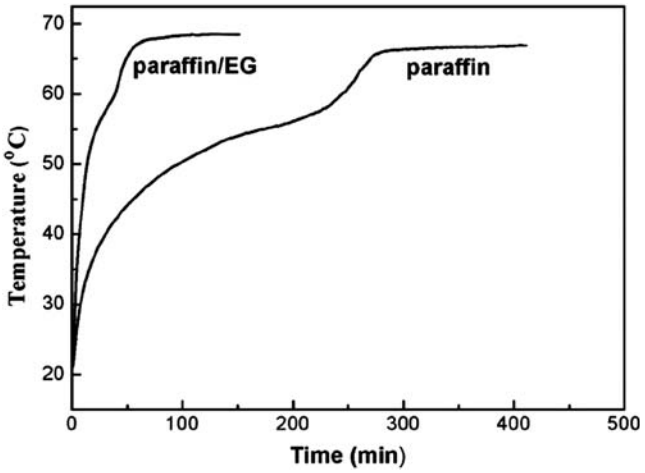

Figure 10. *Temperature versus time graph displaying the different rates of heat transfer in paraffin and paraffin/EG [17]. Reprinted from Applied Energy 91(1), Zhengguo Zhang, Ni Zhang, Jing Peng, Xiaoming Fang, Xuenong Gao and Yutang Fang, Preparation and thermal energy storage properties of paraffin/expanded graphite composite phase change material, 426–431, Copyright 2012, with permission from Elsevier.*

Table 3. *Properties of MPCM slurry and components [3].*

Material	Density (kg/m^3)	Specific heat (J/kg K)	Thermal conductivity (W/m K)	Latent heat (kJ/kg)
Hexadecane (solid)	780	1805	0.4	224
Hexadecane (liquid)	770	2221	0.21	
Urea–formaldehyde	1490	1675	0.433	
Water (at 20°C)	998	4183	0.599	
MPCM particle (solid)	829	1789	0.382	196
MPCM particle (liquid)	819	2153	0.203	
MPCM slurry (mass fraction)				
$\varphi = 0.1$	987	3945	0.575	19.6
$\varphi = 0.2$	976	3707	0.551	39.2
$\varphi = 0.3$	933	3470	0.528	58.8
$\varphi = 0.4$	911	3232	0.505	78.4

EG has shown great potential for enhancement of paraffin-based systems (Figure 10) [17]. EG demonstrates high thermal conductivity, high stability, good compatibility and lower density than metal promoters. EG paraffin with 92wt% PCM produced minimal loss of latent heat while speeding up the conduction rate by over 250 min [17]. Work has been carried out [17] to develop EG in a more efficient manner through microwave irradiation.

Microencapsulation- and emulsion-based PCM slurries improve heat transfer by the utilization of convection, and minimal conduction poor bulk conduction rates are avoided [34, 36]. The performance of emulsion slurries can vary due to surface interactions, increasing the undesirable effects of supercooling [37].

Table 3 [3] shows the promising physical property enhancement when MPCM was suspended in a slurry. A 60% loss of latent heat is the main drawback, reducing the heat storage density, though significant enhancement of specific heat (80%) and thermal conductivity (32%) increases the capability of MPCM as a heat transfer medium.

4.5.2 *Modelling heat transfer*

Modelling PCM systems requires understanding of the PCM transition process, heat transfer and fluid flow. Thus, various research teams have endeavoured to produce easily replicable formulae. Regin *et al.* [21] catalogue many of the mathematical models that have been developed for modelling PCM heat transfer. Two categories are identified: those of the single model and double model. The categorical distinction is on the inclusion of apparent change that occurs during phase change.

Difficulties in modelling have occurred due to the thermal gradients occurring within encapsulated PCM. During heat extraction, the liquid core solidifies first on the outer boundaries of PCM. This solidification creates a crystalline PCM shell that must be permeated for the centrally contained heat to be extracted. The thermal conductivity of PCM is typically low; thus this crystalline layer significantly impedes heat transfer, limiting the system. For this reason, many commercial systems have produced lower than expected performance during the product lifetime.

Modelling performance is further limited by the diversity of PCMs and applications. Regin *et al.* [21] discuss methods being explored to increase the models accuracy. Dolado *et al.* [22] investigated a theoretical model carrying out uncertainty propagation analysis on various inputs. The findings increased the realistic nature of model results.

Tay *et al.* [38] proposed a simplified design method quantifying PCM performance in effective number of transfer units (εNTUs). Building upon experimental validation of PCM thermal storage units [39], thermal resistance of a PCM system [40] and a simplified slurry crystallisation model [41], the methodology for quantifying εNTUs was undertaken. εNTU was found to predict performance within 23% of experimental data with greater accuracy for higher heat transfer areas. The method is capable of designing storage systems based on required temperature conditions.

4.6 Cost optimization

After meeting the technical requirements, the financial cost is reviewed. The economic impact, commonly quantified in payback time, will be optimized against environmental and technical performance. The operation of the whole PCM system will be reviewed against competitive technologies in the market. If extra expense is required for innovative technology, the technical benefits felt through either increased comfort or financial and environmental savings must far outweigh the increased capital investment.

The price of commercially available PCM varies in the range of 0.5–10 €/kg [11, 42].

5 SUMMARY

PCM demonstrates that competitive energy storage densities are only surpassed by methanol and hydrogen. A wide range of PCM has been tested around the indoor comfort temperature region. Organic PCMs, especially paraffins, appear to be the most viable due to their long-term stability. Inorganics are hindered by unwanted sub-cooling and toxicity. Improved methods of encapsulation have enhanced performance and opened new avenues of research. There is a growing knowledge of PCM modelling, though refinement is necessary. Applications of PCM in the built environment are reviewed in Part II.

REFERENCES

[1] Dincer I, Rosen MA. *Thermal Energy Storage Systems and Applications*, 2nd edn. Wiley & Sons, 2011.

[2] Monodraught Ltd. *Monodraught Cool-Phase Mark 2 Brochure*. High Wycombe, 2011.

[3] Wang X, Niu J. Performance of cooled-ceiling operating with MPCM slurry. *Energy Convers Manage* 2009;**50**:583–91.

[4] Winwood R, Benstead R, Edwards R. Advanced fabric energy storage I: review. *Building Serv Eng Res Technol* 1997;**18**:1–6.

[5] Olesen BW, Parsons KC. Introduction to thermal comfort standards and to the proposed new version of EN ISO 7730. *Energy Build* 2002;**34**:537–48.

[6] Bonte M, Stuyfzand PJ, Hulsmann A, *et al.* Underground thermal energy storage: environmental risks and policy developments in the Netherlands and European Union. *Ecol Soc* 2011;**16**.

[7] Demirbas MF. Thermal energy storage and phase change materials: an overview. *Energy Sources, Part B: Econ Plann Policy* 2006;**1**:85–95.

[8] Dieckmann J. *Latent Heat Storage in Concrete*. Technische Universität Kaiserslautern, 2008.

[9] Zhou D, Zhao CY, Tian Y. Review on thermal energy storage with phase change materials (PCMs) in building applications. *Appl Energy* 2012; **92**:593–605.

[10] Baetens R, Jelle BP, Gustavsen A. Phase change materials for building applications: a state-of-the-art review. *Energy Build* 2010;**42**:1361–8.

[11] Cabeza LF, Castell A, Barreneche C, *et al.* Materials used as PCM in thermal energy storage in buildings: a review. *Renew Sustain Energy Rev* 2011;**15**:1675–95.

[12] Sharma A, Tyagi VV, Chen CR, *et al.* Review on thermal energy storage with phase change materials and applications. *Renew Sustain Energy Rev* 2009;**13**:318–45.

[13] Zalba B, Marín JM, Cabeza LF, *et al.* Review on thermal energy storage with phase change: materials, heat transfer analysis and applications. *Appl Thermal Eng* 2003;**23**:251–83.

[14] Mehling H, Cabeza LF. *Heat and Cold Storage with PCM: An Up-to-date Introduction into Basics and Applications*. Mewes D, Mayinger F (eds). Springer, 2008.

[15] Dean JA. *The Analytical Chemistry Handbook*. McGraw Hill, Inc., 1995.

[16] Buddhi D, Sawhney RL, Sehgal PN, *et al.* A simplification of the differential thermal analysis method to determine the latent heat of fusion of phase change materials. *J Phys D Appl Phys* 1987;**20**:1601–5.

[17] Zhang Z, Zhang N, Peng J, *et al.* Preparation and thermal energy storage properties of paraffin/expanded graphite composite phase change material. *Appl Energy* 2012;**91**:426–31.

[18] Yingping Z, Jiang Y. A simple method, the T-history method, of determining the heat of fusion, specific heat and thermal conductivity of phase-change materials. *Measur Sci Technol* 1999;**10**:201–5.

[19] Hong H, Kim SK, Kim Y-S. Accuracy improvement of T-history method for measuring heat of fusion of various materials. *Int J Refrig* 2004;**27**:360–6.

[20] Peck JH, Kim J-J, Kang C, *et al.* A study of accurate latent heat measurement for a PCM with a low melting temperature using T-history method. *Int J Refrig* 2006;**29**:1225–32.

[21] Regin AF, Solanki SC, Saini JS. Heat transfer characteristics of thermal energy storage system using PCM capsules: a review. *Renew Sustain Energy Rev* 2008;**12**:2438–58.

[22] Dolado P, Mazo J, Lázaro A, *et al.* Experimental validation of a theoretical model: uncertainty propagation analysis to a PCM-Air thermal energy storage unit. *Energy Build* 2012;**45**:124–31.

[23] Abhat A. Low temperature latent heat thermal energy storage: heat storage materials. *Solar Energy* 1983;**30**:313–32.

[24] Peippo K, Kauranen P, Lund PD. A multicomponent PCM wall optimized for passive solar heating. *Energy Build* 1991;**17**:259–70.

[25] Kuznik F, Virgone J, Noel J. Optimization of a phase change material wallboard for building use. *Appl Thermal Eng* 2008;**28**:1291–8.

[26] Xu X, Zhang Y, Lin K, *et al.* Modeling and simulation on the thermal performance of shape-stabilized phase change material floor used in passive solar buildings. *Energy Build* 2005;**37**:1084–91.

[27] Neeper DA. Thermal dynamics of wallboard with latent heat storage. *Solar Energy* 2000;**68**:393–403.

[28] Drake JB. A study of the optimal transition temperature of PCM wallboard for solar energy storage. Oak Ridge National Laboratory, 1987.

[29] Lane G. *Solar Heat Storage: Latent Heat Materials. Background and Scientific Principles*, **Vol. I**. CRC: Press Inc., 1983.

[30] Tyagi VV, Kaushik SC, Tyagi SK, *et al.* Development of phase change materials based microencapsulated technology for buildings: a review. *Renew Sustain Energy Rev* 2011;**15**:1373–91.

[31] Rubitherm Technologies GmbH. The Company. Berlin. http://www.rubitherm.com/english/index.htm.

[32] Environmental Process Systems Ltd. *Product Summary*, 2004.

[33] BASF. *Micronial (r) PCM: Intelligent Temperature Management for Buildings*. BASF, 2008.

[34] Lu W, Tassou SA. Experimental study of the thermal characteristics of phase change slurries for active cooling. *Appl Energy* 2012;**91**:366–74.

[35] Ma X, Omer SA, Riffat SB, *et al.* Investigation of energy transportation capability of a phase change slurry through a cold storage-cooling coil system. *Int J Energy Res* 2009;**33**:999–1004.

[36] Agyenim F, Hewitt N, Eames P, *et al.* A review of materials, heat transfer and phase change problem formulation for latent heat thermal energy storage systems (LHTESS). *Renew Sustain Energy Rev* 2010;**14**:615–28.

[37] Huang L, Günther E, Doetsch C, *et al.* Subcooling in PCM emulsions—Part 1: experimental. *Thermochim Acta* 2010;**509**:93–9.

[38] Tay NHS, Belusko M, Bruno F. An effectiveness-NTU technique for characterising tube-in-tank phase change thermal energy storage systems. *Appl Energy* 2012;**91**:309–19.

[39] Halawa E, Saman W. Thermal performance analysis of a phase change thermal storage unit for space heating. *Renew Energy* 2011;**36**:259–64.

[40] Belusko M, Bruno F. Design methodology of PCM thermal storage systems with parallel plates. In: *EuroSun Conference*, Lisbon, Portugal, 2008.

[41] Royon L, Guiffant G, Perrot P. Forced convection heat transfer in a slurry of phase change material in an agitated tank. *Int Commun Heat and Mass Transfer* 2000;**27**:1057–65.

[42] Mehling H, Cabeza L. Phase change materials and their basic properties. In Paksoy HÖ (ed.) *Thermal Energy Storage for Sustainable Energy Consumption*. Springer, 2007, 257–77.