

Phase Change Materials for Building Applications: A State-of-the-Art Review

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Abstract

Phase change materials (PCMs) are regarded as a possible solution for reducing the energy consumption of buildings. By storing and releasing heat within a certain temperature range, it raises the building inertia and stabilizes indoor climate. Within this work, a state-of-the-art review is given on the knowledge of PCMs today for building applications.

Keywords: Phase change material, PCM, Building application, State-of-the-art, Review.

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1. Background

Since the European Union decided to reduce their greenhouse gas emission by accepting the Kyoto-protocol of the UNFCCC - United Nations Framework Convention on Climatic Change in 1997, many serious steps have been taken. A promise was made that emissions 8 % lower as the levels in 1990 would be reached in 2008-2012 and levels 20 % lower in 2020 (United Nations 1998).

In 1999, the total energy consumption in Europe was 1 780 million tons of oil equivalent, for which 35 % was used in the residential and commercial sector. It became clear that reducing the heat losses of buildings or in general the total energy consumption of buildings can have a major impact on the total greenhouse gas emissions in Europe. Traditional insulation materials were and are being used in thicker or multiple layers in order to achieve higher thermal resistances, but resulting in more complex building details, an adverse net-to-gross floor area and possible heavier load bearing constructions. But simultaneously, another strategy won interest.

A certain performance of insulation is generally expressed in static terms as the thermal resistance or thermal transmittance of the exterior building envelope, describing the heat flow for a static temperature difference between two faces. However, such a static point of view can be extended by introducing a dynamical term, the heat storage coefficient K ($W/(m^2K)$), to come to the index of inertia. This heat storage coefficient depends on the thermal conductivity, the volumetric heat capacity and the seasonal heat flow wave. As a result, the index of inertia expresses the resisting ability of the building envelope to a periodical heat flow wave. Phase change materials have been addressed and studied widely to influence (i.e. increase) this index of inertia and as such result in a lower energy consumption for buildings.

In this work, an overview is given on the different kinds of phase change materials (PCMs) and their specific properties and possibilities for building applications. Several more PCMs are known, but only those suitable for building applications will be treated in the text. Secondly, an outline is given on current possible building applications of PCMs such as enhanced gypsum wallboards or concrete.

2. Introduction to phase change materials

The main property of phase change materials is the storage of heat energy in a latent form, leading to greater heat storage capacity per unit volume than that of conventional building materials. When the ambient temperature rises, the chemical bonds of the material will break up whereby the material will change from solid to liquid. This phase change is an endothermic process and as a result will absorb heat. As the ambient temperature drops again, the PCM will return to the solid state and give off the absorbed heat. This cycle stabilises the interior temperature, cuts off peak cooling loads and decreases heating loads, not by affecting the thermal resistance of the building envelope but by influencing the (surface) temperatures.

Including such phase change materials in building constructions, some specific thermal, physical, kinetic and chemical properties are desired:

- i.* From a thermal point of view, a suitable phase change temperature range, a high latent heat of fusion and a good heat transfer towards the PCM are desired. The desired phase change temperature will depend on climatic conditions and the desired comfort temperature.
- ii.* From a physical point of view, a favourable phase equilibrium, i.e. no phase segregation, a high density and small volume changes at the phase change are desired for easy incorporation in existing building materials or structures.
- iii.* From a kinetic point of view, no supercooling and a sufficient crystallization rate are desired to make optimal use of the properties and possibilities of PCMs. Supercooling, i.e. the process of lowering the temperature of a liquid below its freezing point without becoming a solid, could strongly affect the performance of the PCMs based on the chosen suitable phase change temperature by influencing this temperature.
- iv.* From a chemical point of view, a long-term chemical stability of the PCM despite cycling, compatibility with construction materials, non-toxicity and no fire hazard are desired.

Phase change materials can be divided into different subcategories based on their chemical composition. Three groups are commonly made: *(i)* organic compounds, *(ii)* inorganic compounds and *(iii)* inorganic eutectics or eutectic mixtures. The group of organics can be divided in paraffins and non-paraffins. Each group has its typical range of melting temperature and its range of melting enthalpy (see Fig.4.1) and an overview of common PCMs from each group is given in Table 4.1.

Research has until recently primarily been concerned on inorganic compounds, i.e. hydrated salts, which requires support and containment, and cannot be directly incorporated into a building material. One crucial question for these materials was which container was most suitable for the specific phase change material, because

degradation through time will occur due to cycling. However, the use of organic PCMs has been investigated in the last decade (Peippo *et al.* 1991, Feldman *et al.* 1993, Athienitis *et al.* 1997), demonstrating the possibility of impregnating porous building materials with it and in this way creating a direct-gain storage element (Kelly 1997).

2.1 Organic phase change compounds

Organic phase change materials are in general chemically stable, do not suffer from supercooling, are non-corrosive, are non-toxic and have a high latent heat of fusion. Organic PCMs can be subdivided in two groups: Paraffins (*i*) and non-paraffins (*ii*).

Commercial paraffin waxes (*i*) or $\text{CH}_3(\text{CH}_2)_n\text{CH}_3$ are inexpensive and have a reasonable thermal storage density of 120 up to 210 kJ/kg. Paraffins are available in a wide range of melting temperatures from approximately 20 up to about 70°C, they are chemically inert, have a low vapour pressure in the melt and do not undergo phase segregation. Differential scanning calorimetry (DSC) has also shown that technical grad paraffin waxes do not show any indication that thermal cycling can significantly degrade its thermal performance.

Table 4.1 Overview of the main phase change materials (Demirbas 2006).

Organic compounds	Paraffins	Inorganic compounds	(Inorganic) Eutectics
Polyglycol E 400	Paraffin C ₁₄	H ₂ O	58.7 % Mg(NO ₃) ₂ ·6H ₂ O +
Polyglycol E 600	Paraffin C ₁₅ -C ₁₆	LiClO ₃ ·3H ₂ O	41.3 % MgCl ₂ ·6H ₂ O
Polyglycol E 6000	Paraffin C ₁₆ -C ₁₈	Mn(NO ₃) ₂ ·6H ₂ O	66.6 % CaCl ₂ ·6H ₂ O +
Dodecanol	Paraffin C ₁₃ -C ₂₄	LiNO ₃ ·3H ₂ O	33.3 % MgCl ₂ ·6H ₂ O
Tetradodocanol	Paraffin C ₁₆ -C ₂₈	Zn(NO ₃) ₂ ·6H ₂ O	48 % CaCl ₂ + 4.3 % NaCl +
Biphenyl	Paraffin C ₁₈	Na ₂ CO ₃ ·10H ₂ O	0.4 % KCl + 47.3 H ₂ O
HDPE	Paraffin C ₂₀ -C ₃₃	CaBr ₂ ·6H ₂ O	47 % Ca(NO ₃) ₂ ·4H ₂ O +
Trans-1,4-polybutadiene	Paraffin C ₂₂ -C ₄₅	Na ₂ HPO ₄ ·12H ₂ O	53 % Mg(NO ₃) ₂ ·6H ₂ O
Propianide	Paraffin C ₂₃ -C ₅₀	Na ₂ S ₂ O ₃ ·5H ₂ O	60 % Na(CH ₂ COO)·3H ₂ O +
Naphtalene	Paraffin wax	Na(CH ₃ COO)·3H ₂ O	40 % CO(NH ₂) ₂
Erythitol	Octadecane	Na ₂ P ₂ O ₇ ·10H ₂ O	66.6 % Urea + 33.4 % NH ₄ Br
Dimethyl-sulfoxide		Ba(OH) ₂ ·8H ₂ O	
Capric acid		Mg(NO ₃) ₂ ·6H ₂ O	
Capricinic acid		(NH ₄)Al(SO ₄) ₂ ·6H ₂ O	
Laurinic acid		MgCl ₂ ·6H ₂ O	
Miristic acid		NaNO ₃	
Lakisol		KNO ₃	
Palmitic acid		KOH	
Stearic acid		MgCl ₂	
Acetamid		NaCl	
Propionamid		Na ₂ CO ₃	
		KF	
		K ₂ CO ₃	

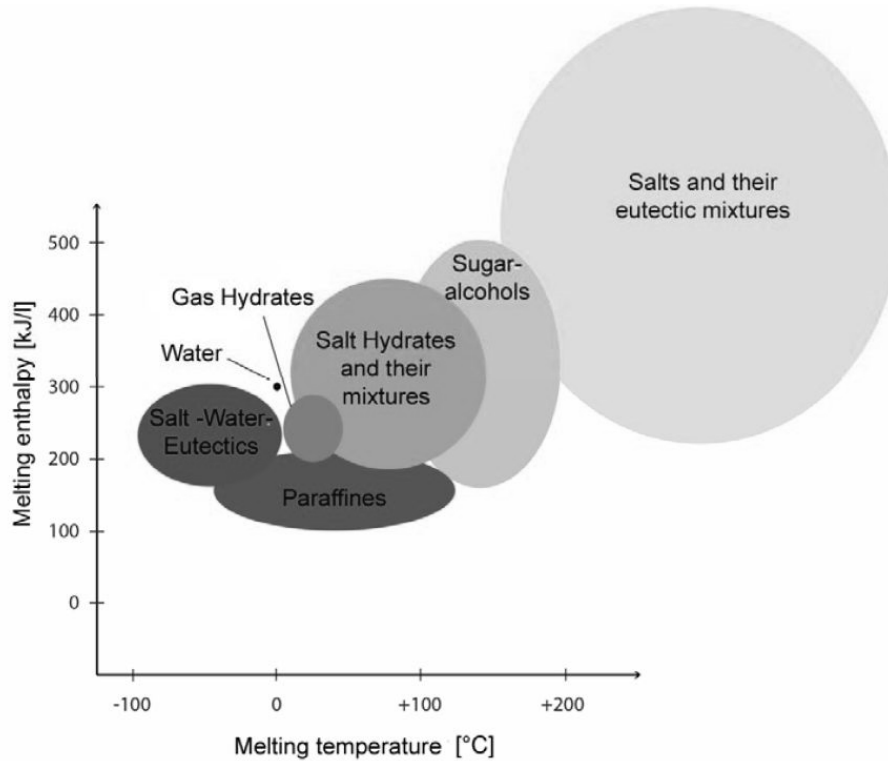


Fig.4.1. The melting enthalpy and melting temperature for the different groups of phase change materials (Dieckmann 2006).

However, paraffins have a low thermal conductivity of about 0.2 W/(mK) which limits their application (Farid *et al.* 2004) and have a large volume change during the phase transition (Hasnain 1998). Metallic fillers and matrix structures are used to improve the thermal conductivity, while plastic containers and different geometries of containers are used to overcome the volume change during melting and freezing, but these issues remain to be solved for applying the paraffin PCMs in buildings.

The non-paraffin organics (*ii*) include a wide selection of organic materials such as fatty acids, esters, alcohols and glycols. They have generally excellent melting and freezing properties, but are about three times more expensive than paraffins (Hasnain 1998). Of most interest in this group are the fatty acids or palmitoleic acids, i.e. $\text{CH}_3(\text{CH}_2)_n\text{COOH}$, which have melting points in a relatively low temperature range, have a high latent heat of fusion, undergo small volume changes during phase transition and do not undergo supercooling during freezing. Most common useful fatty acids are divided in 6 groups: caprylic, capric, lauric, myristic, palmitic and stearic with respectively 8 up to 18 carbon atoms per molecule. Their melting points are in the range between 16 and 65°C and freezing points between 17 and 64°C, with a heat of fusion between 155 and 180 kJ/kg. However, there is a lack of materials with phase transition around the comfort temperature of 21°C.

2.2 Inorganic phase change compounds

Inorganic PCMs in general have a rather high heat of fusion, good thermal conductivity, are cheap and non flammable. However, most of them are corrosive to most metals, undergo supercooling and undergo phase decomposition. Most common inorganic PCMs are hydrated salts.

Hydrated salts are attractive materials for thermal energy storage due to their high storage density of about 240 kJ/kg, their relative high thermal conductivity of about 0.5 W/(mK) and their reasonable cost compared to paraffin waxes. Most known is *Glauber's salt* or $\text{Na}_2\text{SO}_4 \cdot \text{H}_2\text{O}$ with a melting temperature between 32 and 35°C and a high latent heat of 254 kJ/kg as one of the cheapest materials that can be used for thermal energy storage, but it is restricted in its applications because of supercooling and phase segregation (Farid *et al.* 2004). Furthermore, the high storage density of hydrated salts is hard to maintain during cycling: Hydrated salts will melt congruently with formation of lower salts, which makes the process irreversible and results into a decreasing storage capacity.

The salt/ceramic-based composite thermal storage media offers the potential of using PCMs in direct contact heat exchange and, as a result, shows a potential of cost improvement. This may be explained as a microencapsulated PCM within the submicron pores of a ceramic matrix, where the liquid salt is kept within the

solid network of the ceramic by surface tension and capillary forces. However, the salt/ceramic material not only represents a pure latent heat: Heat storage will occur as a combination of the latent heat of the PCM and as sensible heat of the basic ceramic.

Also solid-solid PCMs may have large latent heats if one of the states is much more disordered than the previous and may be used as potential candidates for space heating and heat process applications (Hasnain 1998; Jing-Cang & Peng-Sheng 2006). Examples here are pentaerythritol $C(CH_2OH)_4$, pentaglycerine $CH_3C(CH_2OH)_3$, polyethylene glycol and neopentyl glycol $(CH_3)_2C(CH_2OH)_2$ and their eutectic mixtures. Also a highly crystalline polymer such as high density polyethylene (HDPE) offers specific advantages if it is rendered stable by crosslinking as 98 % of the heat of fusion can be used by transition while retaining its shape. However, some of them are used as storage media, only a small number of solid-solid transitions are known and most of them occur at higher unfavourable temperatures, i.e. at 30 up to 600°C.

2.3 Eutectics

Eutectic mixtures or eutectics, i.e. a mixture of multiple solids in such proportions that the melting point is as low as possible, have in general sharp melting points and its volumetric storage density is slightly higher than that of organic compounds (see Fig.4.3). However, limited data are available on their thermal and physical properties. Eutectics may be divided in 3 groups according to the materials of which they consist: (i) organic-organic, (ii) inorganic-inorganic and (iii) inorganic-organic eutectics.

Pure acids and their eutectic compounds are characterized by a single peak in DSC thermograms, which is sharp and well-defined. Binary systems of fatty acids may form a single eutectic point for both melting and freezing, but mixtures with up to four peaks have been noticed (see Fig.4.2) (Feldman *et al.* 1989). The eutectic binary systems showed melting points between 18 and 51°C and freezing points between 16 and 51°C, with a heat of fusion between 120 and 160 kJ/kg. The organic eutectic capric-mauric acid seems to be the most suitable for passive solar storage with a melting point of 18°C, a freezing point of 17°C and a heat of fusion of 120 kJ/kg.

The application of these eutectic binary systems is further developed (Kauranen *et al.* 1991, Peippo *et al.* 1991, Rudd 1993, Shilei *et al.* 2006) for PCM-enhanced wallboards (see Ch.3.1.d).

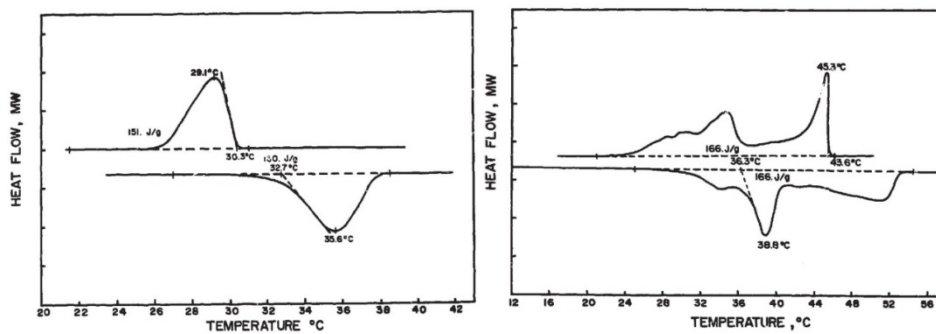


Fig.4.2. DSC thermograph for the eutectic binary system 80-20 mol% lauric-palmitic acid [left] and for the binary system 40-60 mol% lauric-palmitic acid [right] (Feldman *et al.* 1989).

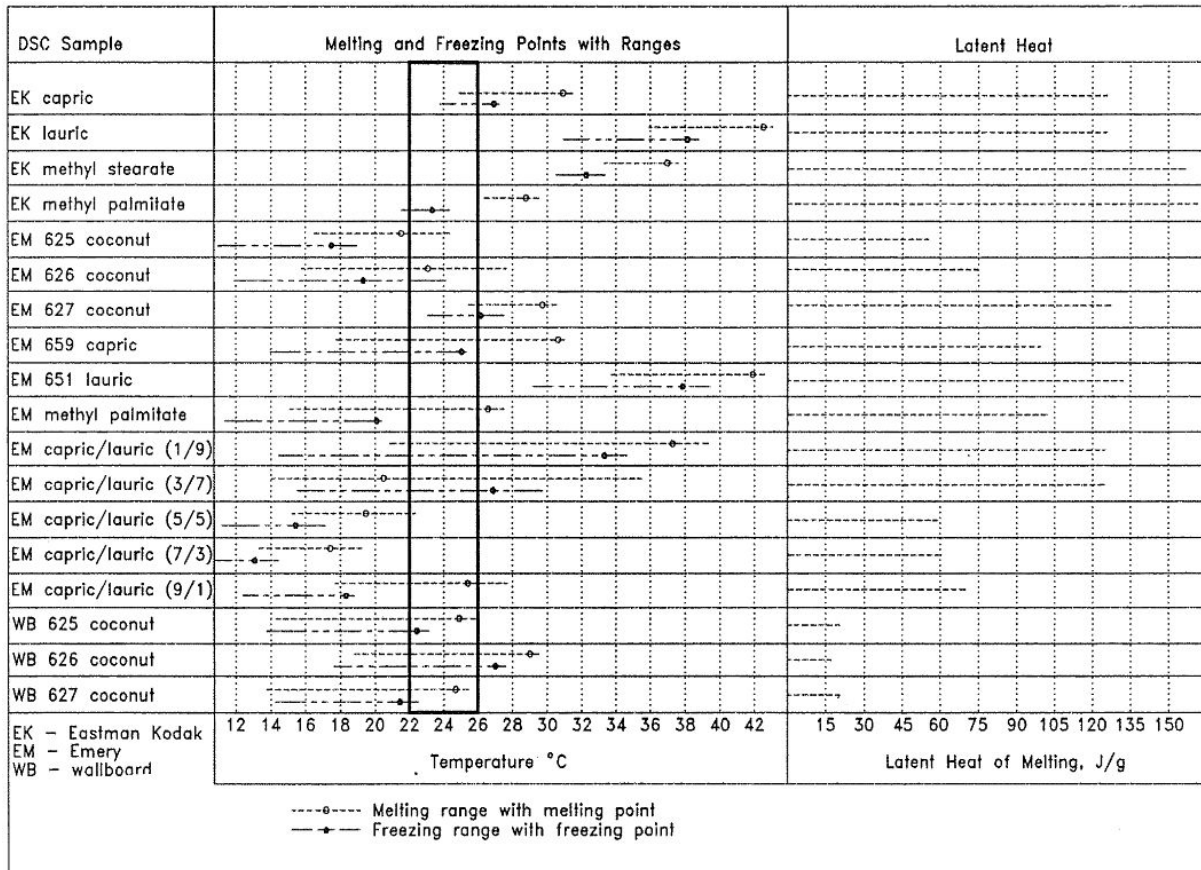


Fig.4.3. Graphical representation of DSC measurements on different fatty acids and their eutectics studied for applications in PCM-enhanced wallboards (Rudd 1993).

3. Test methods for phase change materials

Large-scale and small-scale tests were compared by Rudd (1993) to validate a differential scanning calorimeter (DSC) test as standard for the measurements of PCM performances. A DSC is an instrument that measures the heat capacity of small material samples with a typical size of 6.3 mm in diameter and 6.3 mm high. For PCMs, the DSC gives the melting and freezing curves and the associated heats. The principle of the test is to keep a temperature equilibrium between the test sample and a reference sample, i.e. mostly certified Indium metal, that is heated or cooled at a constant rate. The excess heat absorbed or emitted by the test sample is recorded as a function of the time and the total heat transition of the test sample between two temperatures is retrieved by integrating this recorded excess heat (Rudd 1993, Feldman & Banu 1996, Feldman *et al.* 1989).

The comparison between large scale and small scale tests (Rudd 1993) showed that both vary with only 8.7 % and where the DSC-test underestimates the results compared to the large scale tests. This indicates that small scale differential scanning calorimetry can adequately predict the performance of PCM enhanced products when installed in full-scale applications: Expensive large-scale testing is thus not required until the products are well along in development.

Large-scale tests will consist of two side-by-side test rooms heated with an electric resistance heater and equipped with air conditioning. For both rooms, the electrical energy use (kWh) and power draw (kW) are measured for the air conditioning and the room equipment. Because both rooms are placed side-by-side, both rooms are as a consequence influenced by the same climatic conditions. The performance of the PCM enhanced materials can be found by comparing the data from the room equipped with PCM enhanced materials with the data from the null-measurements of the second room, equipped with traditional materials (Rudd 1993, Athienitis *et al.* 1997, Stovall & Tomlinson 1995).

4. Building applications for phase change materials

The principle of latent heat storage can be applied to any porous building material, but current research primarily concerns on gypsum wallboards, concrete and insulation materials.

4.1 PCM enhanced wallboard

Wallboards are cheap and widely used in building applications, which makes them very suitable for the application of PCMs. Wallboards enhanced with PCMs will provide thermal storage distributed throughout the complete building, enabling passive solar design and off-peak cooling in traditional frame constructions with a typical low thermal mass.

The performance of the PCM enhanced wallboards will depend on several factors: the melt temperature of the PCM, the temperature range over which melting occurs, the latent capacity per unit area of the wall, how the PCMs are incorporated in the wallboard, the orientation of the wall, climatic conditions, direct solar gains, etc. However, because not all factors can be taken into account, most studies on PCM enhanced wallboards deal with the choice of the phase change material, the manufacturing methods and the method of testing.

4.1.a Manufacturing methods

Three different methods of enhancing the traditional wallboards with PCMs are found in literature: Impregnating wallboards with PCMs after manufacturing and direct incorporation of PCMs during the manufacturing of the wallboards.

The first method for enhancing wallboards with PCMs consists of adding PCM-filled pellets during the manufacturing. However, this method has been shown inappropriate due to its low surface to volume ratio.

The second method consists of impregnating PCMs into wallboards and is done in most researches (Kedl 1991, Rudd 1993, Athienitis 1997, Kauranen *et al.* 1991) because it makes it easy to apply a developed PCM in the laboratory. The procedure of impregnating is described by Feldmann *et al.* (1989a): A controlled heating bath is used for adsorption of PCM in aggregates. The PCM is heated in a flask and at controlled temperature and a weighted quantity of aggregate (the wallboard) is inserted for adsorption of the PCM under vacuum conditions. The aggregates are taken out, allowed to drain off excessive PCM and left for drying for 48 hours. Finally, the apparently dried but fully adsorbed wallboard are weighted and the percentage of adsorption can be calculated. It was observed that the best results were found if the PCM was impregnated at 70°C and under vacuum pressure of approximately 65 mbar during 30 minutes. Analysis (Farid 2004) shows that this immersion process has the potential of achieving higher storage capacity than adding filled pellets to wallboard during manufacturing.

The third fabrication method is proposed by Feldman *et al.* (1991) and is based on the industrial manufacturing of gypsum wallboards, achieved by mixing a slurry of calcinated gypsum $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ with water and other additives. The formed gypsum paste will be poured between two layers of paperboard, cut and dried to remove the excess water. Here, the PCM is introduced to the paste by mixing it into a homogenous mixture. However, the PCM will show a tendency to migrate to the surface of the paste and cause instability of the paste and a dispersing agent has to be added to ensure good dispersion of PCM in the matrix. Possible dispersing agents are poly(vinyl alcohol) or sodium salt. Results of this method indicate that PCMs can be easily applied into wallboards during manufacturing with comparable resulting mechanical and hygric properties as the traditional gypsum wallboards.

4.1.b Design methodology

The choice of the optimum PCM to enhance wallboards will depend on the optimal transition temperature for solar energy storage for a variety of circumstances. A phase change point outside the practical operational temperature range of the storage may make the wall completely useless as the temperature may never reach the melting point. This optimal transition temperature has been studied by Drake (1987) and Peippo *et al.* (1991) based on standard stud walls, depending on all conditions imposed to the wall. Different behaviour can be expected for internal and external walls, different weather conditions and the thermal resistance of the wall.

The optimal transition temperature $T_{PCM,opt}$ is estimated based on the amount of flux during the day and the amount of flux during the night, and is necessary to know to be able to give off all stored energy during the discharge cycle. The term is expressed by Drake (1987):

$$T_{PCM,opt} = \frac{1}{U + h} \left[h\bar{T}_i + U \frac{T_{e,d} + T_{e,n}}{2} + \frac{Q_{stor}}{t_{stor}} \right] \quad (1)$$

or analogously by Peippo *et al.* (1991), only considering charging of the element in the direct-gain room due to radiation and requiring the PCM slab to both melt and freeze during each single day:

$$T_{PCM,opt} = \bar{T}_i + \frac{Q_{abs,tot}}{t_{stor}h} \quad \text{where} \quad \bar{T}_i = \frac{t_d T_{i,d} + t_n T_{i,n}}{t_d + t_n} \quad (2)$$

where h is the heat transmission coefficient between the wall and the room, U the overall thermal heat transfer coefficient, where Q_{stor} (J) is the total amount of direct solar input to the wall over the diurnal cycle, t_{stor} (s) the diurnal storage cycle equalling t_d+t_n or 24 h, t_n and t_d the charging (day) and discharging (night) times and where $T_{i,d}$ & $T_{i,n}$ are the room temperatures at day and night. The equation shows the strong dependency of the T_{opt} on the amount of direct solar energy absorbed by the wallboard, the effect of the thermal insulation and the external weather conditions in case of an exterior wall. The critical temperature will be slightly higher for warm days compared to cold days, because the heat loss of the wall is smaller on mild days and the energy that should be discharged to the room side of the wall greater.

When the optimal transition temperature is known or approximated as function of the application conditions, it should be able to define an optimal PCM. However, before it is possible to enhance wallboards with PCMs, the storage system has to be sized appropriately. The latent heat storage capacity should be large enough to accommodate the amount of energy it will receive during the day cycle. A minimum thickness t of the wallboard as function of the $T_{PCM,opt}$ can be approximated as by Drake (1987). However, an undersized storage capacity does not adversely affect the performance of the system. If there is not enough storage, the energy in effect spills over the storage and the temperature of the PCM will rise, creating higher losses to the outside air (for exterior walls):

$$t_{min} = \frac{1}{\rho H} \left[Q_{stor} - 12h(T_{PCM,opt} - T_{i,d}) + 12U(\bar{T}_{e,stor} - T_{PCM,opt}) \right] \quad (3)$$

or analogously by Peippo *et al.* (1991), only considering charging of the element in the direct-gain room due to radiation and requiring the PCM slab to both melt and freeze during each single day:

$$t_{opt} = \frac{t_n h}{\rho \Delta H} (T_{PCM,opt} - T_{i,n}) \quad (4)$$

where ρ is the density of the material, H (J/m²) the latent heat of fusion, h the heat transmission coefficient between the wall and the room, U the overall heat transfer coefficient and $\bar{T}_{e,stor}$ the average exterior temperature of one cycle.

The equations on optimal transition temperature $T_{PCM,opt}$ and the minimum/optimal thickness of the PCM slab are based on static daily conditions and can not necessarily be directly applied to maximize the energy storage over a succession of days with varying solar irradiance. Therefore, the heat transfer equations have to be solved numerically. Models on this numerical solution are proposed in several papers (Charach *et al.* 1987, Peippo *et al.* 1991, Athienitis 1997, Neepser 1999).

4.1.c Possible PCMs to enhance wallboards and their results

As previously mentioned is a proper phase change point (or phase change temperature range) one of the most important criteria for selecting PCMs for the application considered. The PCM should also be simple and inexpensive, have good crystallization properties, be thermally and chemically stable non-toxic and non-flammable.

- i. The 0.73/0.26 eutectic mixture capric / myristic is introduced for wallboard applications in Stockholm¹, which has an optimal transition temperature of 21.5°C, in a study on PCM storage with adjustable melting temperature (Kauranen *et al.* 1991, Peippo *et al.* 1991). The mixture has a measured eutectic temperature of 21.4°C and a heat of fusion of 152 kJ/kg. When a 13 mm thick wallboard is impregnated with 30_{mass}% PCM content, a heat of fusion ΔH of 540 kJ/m² is reached. Numerical simulations have been done (Peippo *et al.* 1991) for a 120 m² house on the application of such PCM-enhanced wallboards and the results can be found in Table 4.2. The proposed PCM wall reduces the supplementary heating energy by approximately 2 GJ/yr or about 6 % for the climatic conditions as they are in Helsinki. This means an annual benefit of

¹ Stockholm (Sweden) [59°17'N 18°3'E] enjoys 1 981 hours of sunshine annually. Summers have average daytime temperatures between 20 and 23°C and night temperatures of approximately 15°C. Winters have temperatures ranging from -3 to 1°C. Daylight varies widely from more than 18 hours around midsummer to only around 6 hours in midwinter.

\$ 34 for a present cost of heat of approximately 17 \$/GJ, resulting in a payback time of 18 yrs assuming a cost of 1.5 \$/kg for industrial grade fatty acids.

- ii. The 0.75/0.25 eutectic mixture palmitic / myristic is introduced for wallboard applications in Madison (Wisconsin)², which has an optimal transition temperature of 22.0°C (Kauranen *et al.* 1991, Peippo *et al.* 1991). The mixture has a measured eutectic temperature of 22.1°C and a similar heat of fusion of 153 kJ/kg. When a 13 mm thick wallboard is impregnated with 30_{mass}% PCM content, a heat fusion ΔH of 540 kJ/m² is reached. Numerical simulations show that such a proposed PCM wall reduces the supplementary heating energy by approximately 3 GJ/yr or about 15 % (Peippo *et al.* 1991) for the climatic conditions as they are in Madison (Wisconsin), resulting in a payback time of 9 yrs for a material cost of 1.5 \$/kg for industrial grade fatty acids and a cost of heat of approximately 17 \$/GJ.
- iii. A capric / lauric eutectic mixture is applied by Shilei *et al.* (2006) but little is known on the achieved properties.
- iv. An octadene paraffin impregnated enhanced wallboard is simulated by Kedl (1991) . The paraffin has a measured eutectic temperature of 23.3 ± 1.8°C and a heat of fusion of 195 kJ/kg, resulting in a heat fusion ΔH of 805 kJ/m² for a 13 mm thick, 35_{mass}% impregnated wallboard.
- v. Many different fatty acids were tested (Rudd 1993) for wallboard applications, for which an average heat of fusion of 22 ± 3 kJ/kg was found. All different acids were applied in ratios of 25_{mass}% resulting in a simulated heat fusion ΔH of 360 kJ/m², but for (unrealistic) interior temperature variations between 18.3 and 29.4°C.
- vi. A new kind of PCM is introduced (Chen *et al.* 2008) with a theoretical transition temperature between 22 and 24°C and a heat of fusion of 60 kJ/kg. It was concluded that the PCM with a $T_{PCM,opt}$ of 23°C and applied in a layer of 30 mm could lead to an energy-saving rate of 17 % in the heating season. However, nothing is published about the true material properties.

Because both mixtures capric-palmitic and capric-myristic have the same heat of fusion and have been investigated with the same model (Peippo *et al.* 1991), conclusions on the performance of a phase change material can be made based on environmental conditions. Firstly, one noticed that the energy savings are higher in houses with maximum temperature control with a reduction of temperature fluctuation between 1 and 2°C. Secondly, climatic conditions such as the available solar irradiance levels significantly affect the performance of storage. Finally, increased energy savings up to a factor 2 are noticed for badly insulated structures while lower values have been found for proper insulated dwellings.

Table 4.2 Annual energy balance of the simulated houses in Stockholm and Madison (Wisconsin). House type 1 denotes a reference house, where type 2 denotes a house with PCM enhanced plasterboard [$\Delta H = 540$ kJ/m²]. The simulated *conventional* house has an average thermal transfer coefficient U of 0.23 W/(m²K) and windows of 1.8 W/(m²K), while both the passive and reference house types have an average thermal transfer coefficient U of 0.12 W/(m²K) and windows of 1.3 W/(m²K). The mentioned T_r denotes the room temperature during the night and the day (Peippo *et al.* 1991).

		$T_r = 19-21$ °C		$T_r = 18-26$ °C	
		1	2	1	2
Helsinki, passive	Heating energy (backup) (GJ)	26.6	24.9	22.4	20.9
	Overheating energy (GJ)	17.1	29.3	9.3	13.4
	Maximum heating power (kW)	4.4	4.2	4.2	4.2
Madison, passive	Heating energy (backup) (GJ)	18.2	15.2	13.4	10.7
	Overheating energy (GJ)	38.0	35.5	25.0	21.1
	Maximum heating power (kW)	4.4	3.8	4.2	3.7
Helsinki, conventional	Heating energy (backup) (GJ)	52.5	51.1	46.9	46.2
	Overheating energy (GJ)	10.1	8.5	3.4	2.7
	Maximum heating power (kW)	7.2	7.1	7.1	7.0
Madison, conventional	Heating energy (backup) (GJ)	39.3	37.7	34.2	33.4
	Overheating energy (GJ)	18.1	16.3	7.4	6.6
	Maximum heating power (kW)	7.1	7.0	6.9	6.8

² Madison, Wisconsin (USA) [43°4'N 89°24'W] has an average temperature of -9°C in January and 22°C in July.

4.2 PCM-enhanced concrete

Another possibility for applying PCMs in building constructions is PCM-enhanced concrete or the so-called Thermocrete and PCM-enhanced clay tiles. Thermocrete is a heat storage medium combining an appropriate PCM with a concrete matrix or open-cell cements to produce low cost storage materials with structural and thermostatic properties.

4.2.a Manufacturing methods

A first possibility for enhancing concrete with phase change materials can be found in internal curing of concrete (Bentz & Turpin 2007, Weber 1996). Pre-wetted lightweight aggregates in concrete serve as internal reservoirs to supply extra water needed by the cement and the pozzolanic components of the concrete during their hydration processes. Due to their porous nature and reasonably high absorption capacity, these aggregates can also be filled with other materials like PCMs. Such a lightweight aggregate with a absorption capacity of 20 vol% could provide 350 kg/m³ of PCM in a typical concrete. Porous lightweight aggregates have been successfully impregnated with butyl stearate and this technique has been commercialized (Niesing 2004) in aerated concrete blocks using wax-filled spheres. The application of PCMs during curing has another advantage: The PCMs will reduce the temperature rise experienced during early-age curing of massive concrete structures, due to melting of the wax by absorbing energy. However, concrete strengths were significantly reduced by application of the PCMs (Bentz & Turpin 2007, Castellon 2006) because higher curing temperatures will accelerate hydration and strength gain at early ages, while it may lead to lower long term concrete strengths (Schindler & McCullough 2002).

A second possibility for enhancing concrete with PCMs can be found in the mechanisms of absorption to achieve diffusion of the desired amount of PCM in concrete (Khudhair & Farid 2004). The same technique has been used to impregnate Na₂S₂O₃·5H₂O (Hadjieva *et al.* 2000) into concrete. The conclusion was that the large absorption area of porous concrete serves as a good matrix for the incongruently melting PCM: It was possible to absorb up to 57 vol% of PCMs into a concrete composite.

4.2.b Results

Test cubicles with PCM-enhanced concrete were installed in Spain³ (Castellon 2006). The PCM had a melting point of 26°C and a heat of fusion of 110 kJ/kg and lead to a lower inner temperature and an increased inertia of the test cubicles: The concrete surfaces had a temperature 3°C lower than that of non-PCM-enhanced cubicles and the peak temperature occurred 2 hours later, which forms a strong opportunity for possible air-conditioning energy savings in buildings. Also concrete with PCM-enhanced lightweight aggregates have been tested (Bentz & Turpin 2007). Five different PCMs were successfully applied into aggregates and tested: three different types of polyethylene glycol, octadecane and a paraffin wax. Here, simulations have been performed on PCM-enhanced traffic roads, showing a strong reduction of the annual freeze/thaw cycles from 19 up to 100 % for different American regions.

Different PCMs have been applied in 19 mm thick floor tiles (Hittle 2002) and it was concluded that encapsulated octadecane has the highest potential as solid state phase change material. Annual heating savings of 24 % were found by static analysis for a test building for the conditions of Denver⁴.

However, one may question the profit of concrete enhanced with a phase change material. PCMs are applied in buildings in order to increase the thermal mass, a purpose that is achieved by applying PCMs into gypsum wallboards which are usually used in light-weight constructions such as traditional wood-frame buildings. Compared to these wallboards, the overall benefits of PCMs in concrete seems more doubtful, because concrete buildings are yet generally known to have a high thermal mass. However, the possible profit of thermocrete may be shown by a simple comparison:

- i. Gypsum plasterboard has a heat capacity of 840 J/(kgK), a density of 950 kg/m³ and a typical thickness of 12.5 mm, resulting in an overall capacity of approximately 10 kJ/(m²K). Having in mind the numbers cited in Ch.4.3.1.c, enhancing gypsum plasterboards with PCMs results in an overall heat capacity of 550 up to 800 kJ/(m²K) at the phase change temperature.

³ Puigverd de Lleida (Spain) [41°54'N 0°73'E] has an average temperature of 6°C in January and 25°C in July and August.

⁴ Denver, Colorado (USA) [39°45'N 105°1'W] has an temperature of -9 to 8°C in January and of 13 up to 31°C in July and August.

- ii. On the other hand, concrete has a heat capacity of 1 000 J/(kgK), a density of 2 300 kg/m³, resulting in an overall capacity of 552 kJ/(m²K) if applied as a slab with a typical thickness of 24 cm, i.e. yet equalling the heat capacity a PCM-enhanced gypsum plasterboard. Having in mind the numbers cited in Ch.4.3.2.a, enhancing concrete with PCMs results in an overall heat capacity of approximately 8 000 kJ/(m²K) at the transition temperature, i.e. 10 times the value achieved for gypsum plasterboards.

This small comparison shows that, however concrete buildings do yet have a relatively high thermal mass, enhancing concrete with PCMs may mean a significant increase of thermal capacity of the building. Though, one must question whether the result is worth the (currently) high cost of PCMs applied in such a high amount.

4.3 PCM-enhanced building insulation materials

Studies on PCM-enhanced PU-foam (Kosny *et al.* 2007a, 2007b, 2008a) and cellulose (Kosny *et al.* 2005, 2008a, 2008b, 2008c) have been performed during the last decade.

The PCM-enhanced open-cell PU-foam was commonly installed in two layers of 6 mm between three low-emittance aluminium foils and installed on top of the mineral wool insulated studs. The PU-foam contained 0.49 kg/m² PCM with a melting point of 25.5°C and a maximum enthalpy of 140 kJ/kg. Hot-box measurements showed that it takes 3 hours to fully charge the PCM and that thermal excitations of 22°C were reduced with 1.6°C. Comparison of heat fluxes with traditional constructions showed also a potential reduction of 40 % in the wall-generated peak-hour cooling load. The same method has been applied on attic constructions, which resulted in a decreased attic summer air temperature from 43°C to 32°C.

Microencapsulated paraffin PCMs have been mixed with conventional loose-fill cellulose insulation at a rate of 22 weight% and installed in residential wall cavities without major modifications of the manufacturing or installation processes. The measured results of pilot projects are strongly depending on wall orientation and the location. Nevertheless, clear reductions of both cooling and heating loads are noticed.

4.4 Other building applications

Other different possible building applications for PCMs have been studied, especially trying to improve the performances of technical installations such as hot water heat stores (Morrison & Abdel-Khalik 1978, Mehling *et al.* 2008), cool thermal energy storage (He 2001, Zalba *et al.* 2004, Zalba *et al.* 2005) and latent heat thermal storage systems (Velraj *et al.* 1999, Stritih 2003). In addition, the improvement of double facades with PCMs has been studied (Athienitis *et al.* 2005) to achieve a better control of the cavity temperature.

5. Conclusions

The principle behind phase change materials is promising. Excess energy at elevated temperatures is stored and given back at a certain temperature, resulting in an increased thermal mass in a narrow temperature range. Relatively high (potential) energy savings have been achieved in literature, but current properties of the available phase change materials do not yet seem optimal for wide-spread building applications. Only few materials are known with a transition around comfort temperature, and those existing do have a relatively low heat of fusion.

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