Passive latent heat thermal energy storage systems: PCMs-A review

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Abstract

In modern age, energy storage plays an important role in conserving available energy and improving its utilization, as most of the energy sources are confined within the fixed limit in nature. Globally, only buildings are responsible for 40% of the total world annual energy consumption which is responsible for one-third of green house gas emissions around the world, while the rest of 60% energy is utilized in other fields of life. A significant portion of this energy is used for lighting, heating, cooling, and air conditioning purposes in buildings. In most applications short term storage of energy is essential only for a few hours, while in some applications long term storage of energy for a few months may be required. One of the technologies which help to reduce energy consumption is the thermal energy storage by phase change materials (PCMs).Phase change materials (PCMs) are environmentally favorable salts or organic compounds with variable environmental credentials, which store and release latent heat by changing a phase transformation due to change in chemical bonds. During the phase transformation (solid-liquid and vice- versa) when PCMs reach melting point (phase change temperature) they absorb large amounts of heat without getting hotter. When the temperature of surroundings drops, the PCM solidifies with the release of its stored latent heat. PCMs absorb and emit heat while maintaining a nearly constant temperature.

This paper reviews how and where phase change materials (PCMs) are used in passive latent heat thermal energy storage (LHTES) systems. The main aim of this paper is to provide a comprehensive list of the different type of PCMs and main criteria that govern the selection of PCMs. The paper concludeswith some current problems that need to be adressed for further researchin this area.

Keyword : Phase change material (PCM), Latent heat thermal energy storage (LHTES); Passive *heating and cooling, Energy efficiency.*

Introduction

A phase-change material (PCM) is a substance having a high heat of fusion which,while melting and solidifying at a certain temperature is capable of storing and releasing large amounts of energy. When the material changes from solid to liquid and vice versa heat energy is absorbed or released. Hence, PCMs are characterized as latent heat storage (LHS) materials.

Fig.1: A sodium acetate heating pad

This can be achieved through solid–solid, solid–liquid, solid–gas and liquid–gas phase change. Practically only phase change used for PCMs is the solid–liquid change. Solid–solid phase changes are typically very slow and have a rather low heat of transformation. Liquid-gas or solid-gas phase change materials are not practical for use as thermal storage due to the large volumes or high pressures required to store the materials when in their gas phase. Liquid–gas transitions do have a higher heat of transformation than solid–liquid transitions. These material store, release or absorb heat as they oscillate between solid and liquid form eg., When the sodium acetate solution crystallises, it becomes warm as shown in Fig 1.

Such type of materials are very suitable for use in buildings because they can store a large amount of cold and heat. Solar energy is available only during the day time, so that the excess heat collected during sunshine hours requires an efficient thermal energy storage system that may be stored for later use during the night. Similar problems arise in heat recovery systems where the waste heat availability and utilization periods are different, requiring some thermal energy storage system. The same difficulties arise with electrical energy consumption which varies significantly during the day and night. In extremely hot and cold climate countries the major part of the variation is due to domestic space heating and air conditioning. Such variation leads to an off peak period, usually after midnight until early morning. Hence either power station have to be designed for capacities sufficient to meet the peak load or very efficient power distribution would be required. But if some of the peak load could be shifted to the off peak load period by some means than a better power generation management can be achieved. This has been achieved successfully by incorporating PCMs in passive latent heat thermal storage systems (LHTES) of heat or coolness. Here “passive” means that the phase-change processes without resorting to mechanical equipment.

Unlike conventional storage materials PCMs absorb and release heat while maintaining a nearly constant temperature. Within the human comfort range of approximately 16-25C PCMs latent heat thermal storage systems(LHTES) have been found to be very effective.PCMs store 5 to 14 times more heat per unit volume than sensible storage materials such as water masonry or rock. A large number of PCMs are known to melt with a heat of fusion in any required range. Thus PCMs can be used for any heating and cooling requirement in buildings, vehicles or fabrics, including insulation and engine cooling, refrigeration, process cooling or contributing to process heat, and combined heat and power systems.

Types of PCMs and main criteria that govern their selection

Materials to be used for phase-change TES (thermal energy storage) should posses melting/freezing temperature in the practical range of application and they must have a high latent heat of fusion and a high thermal conductivity. Moreover, to be used in the design of passive LHTES systems, PCMs should have desirable thermophysical, kinetic, chemical and economic properties as suggested by many authors. PCMs should also have desirable environmental properties to decrease the environmental impact of the systems during their lifecycle. The main criteria for selecting PCMs are given in Table 1.

Table 1: Main criteria for selecting PCMs

Thermal and physical properties	– Suitable phase-transition temperature in the desired operating temperature range
	– High thermal conductivity and good heat transfer
	– High latent heat of transition per unit mass
	– High specific heat and high density – Good heat transfer
	– Congruent melting and long term thermal stability
	– Favourable phase equilibrium and no segregation
	– Small volume change on phase-change
	– Small vapour pressure at operating temperature
Kinetic properties	– High nucleation rate and little or no supercooling of the liquid phase
	– High rate of crystallization
Chemical properties	– Complete reversible melt/freeze cycles
	– Long term chemical stability and no degradation after a large number of melt/freeze cycles
	– No corrosiveness and capability with construction materials
	– Nontoxic, non-flammable and non-explosive
Economic properties	– Abundant and available
	– Cost effective
Environmental properties	– Low embodied energy
	– Separation facility from the other materials and recycling potential
	– Low environmental impact and non-polluting

PCMs are classified as organic, inorganic and eutectic. These are available in any particular required temperature range. Organic PCMs are further divided as paraffins and non-paraffins. The non-paraffins include a wide selection of organic materials such as fatty acids, esters, alcohols and glycols. Inorganic PCMs are further divided as hydrated salts including Glauber salt (sodium sulphate decahydrate) and metallic (metals have too high melting temperatures for passive building applications). A eutectic is a minimum-melting composition of two or more components, each of which melts and freeze congruently forming a mixture of the component crystals during crystallization.

Eutectics PCMs are subdivided in organic–organic, organic–inorganic and inorganic–inorganic. Several authors have presented a comparison of the advantages and disadvantages of the different types of PCMs. The main advantages and disadvantages for each type are compared and summarized in Table 2.

Table 2. Comparison between different types of PCMs: advantage and disadvantages.

Classification	Advantages	Disadvantages
Organic: Paraffins and non-paraffins	– Availability in a large temperature range	– Low thermal conductivity
	– High latent heat of fusion (fatty acids have high heat of fusion values comparable to that of paraffins')	– Lower volumetric latent heat storage capacity, i.e. lower phase-change enthalpy
	– Freeze with little or no supercooling	Lower density
	– Congruent phase-change	– Flammable (possible to use fire-retardant additives)
	– Self-nucleation properties	– Non-compatibility with plastic containers
	– No segregation and good nucleation rate	– More expensive (commercial paraffins are cheaper and more available than pure paraffins and fatty acids are 2–2.5 times more expensive than technical grade paraffins)
	– Predictable and thermally and chemically stable, i.e. good stability of material properties during repeated thermal cyclings	– Relative large volume change (however some fatty acids could undergo small volume changes)
	– Low vapour pressure in the melt form	
	– Not dangerous, non-reactive and non-corrosive (fatty acids could be mild corrosive)	
	– Compatibility with conventional material of construction	
	– Recyclable	
Inorganic:	– Higher volumetric latent heat storage capacity, i.e. higher melting enthalpy	– Poor nucleating properties and supercooling problems
Hydrated salts	– Higher latent heat of fusion	– Incongruent melting and dehydration in the process of thermal cycling
	– Low cost and readily available	– Phase segregation during transition and thermal stability problems
	– Sharper phase-change	– Their application could require the use of some nucleating and thickening agents
	– Higher thermal conductivity	– Decomposition and phase separation
	– Non-flammable	– Non-compatible with some building materials
	– Lower volume change	– Corrosive to most metals and slightly toxic
	– Compatible with plastics	
	– It is better to use salt hydrates than paraffins to reduce the	

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Classification	Advantages	Disadvantages
	manufacturing/disposal environmental impact	
Eutectic	– Sharp melting temperature (could be used to deliver the desired melting temperature required)	– Limited data are available on their thermophysical properties
	– Volumetric thermal storage density slightly above organic compounds – No segration and congruent phase-change	– Some fatty eutectics have quite strong odour and therefore they are not recommended for use as PCM wallboard

The melting point and heat of fusion of few organic PCMs are given in Table3

Table 3: *Organic PCMs (typical values)*

PCM	Melting Point (°C)	Heat of Fusion (kJ/kg)
$CH_3(CH_2)_{16}COO(CH_2)_3CH_3$ Butyl stearate	19	140
$CH_3(CH_2)_{11}OH$ 1-dodecanol	26	200
$CH_3(CH_2)_{12}OH$ 1-tetradecanol	38	205
$CH_3(CH_2)_n(CH_3$.. Paraffin	20-60	200
45% $CH_3(CH_2)_8COOH$ 55% $CH_3(CH_2)_{10}COOH$ 45/55 capric-lauric acid	21	143
$CH_3(CH_2)_{12}COOC_3H_7$ Propyl palmitate	19	186

Source: Feldman *et al.* 1993

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Table 4: *Salt hydrate PCMs (typical values)*

PCM	Melting Point (°C)	Heat of Fusion (kJ/kg)
$KF \cdot 4H_2O$ Potassium flouride tetrahydrate	18.5	231
$CaCl_2 \cdot 6H_2O$ Calcium chloride hexahydrate	29.7	171
$Na_2SO_4 \cdot 10H_2O$ Sodium sulphate decahydrate	32.4	254
$Na_2HPO_4 \cdot 12H_2O$ Sodium orthophosphate dodecahydrate	35.0	281
$Zn(NO_3)_2 \cdot 6H_2O$ Zinc nitrate hexahydrate	36.4	147

Source: Feldman *et al.* 1993

Fig.2

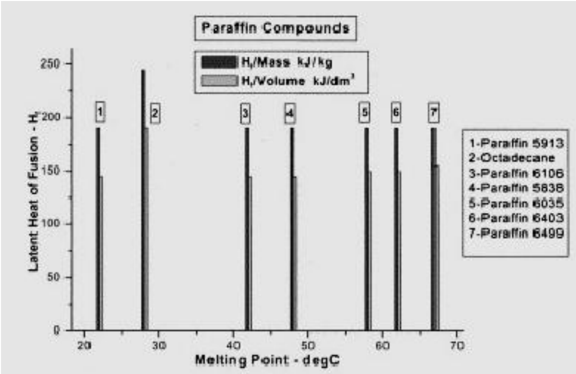


Fig.3

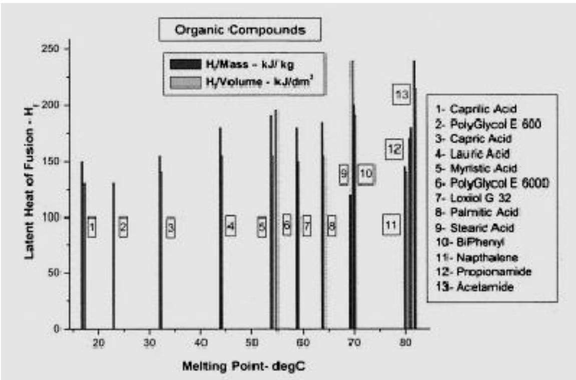


Fig.4

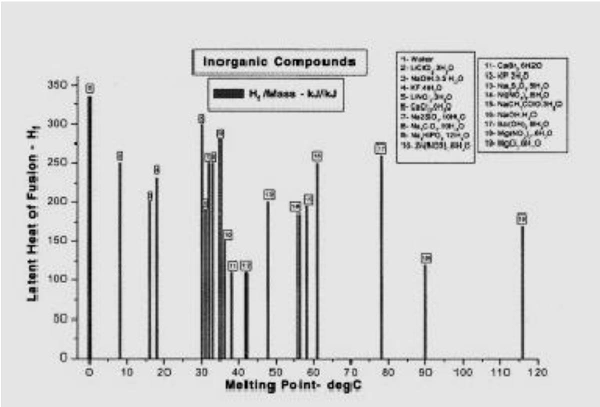


Fig.5

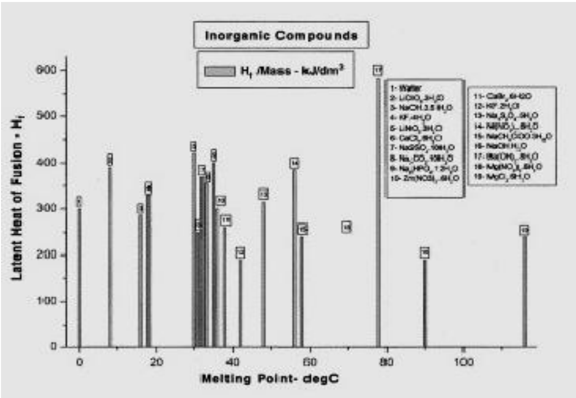
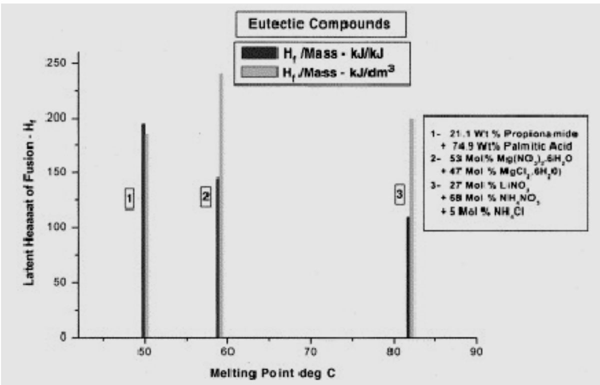


Fig.6

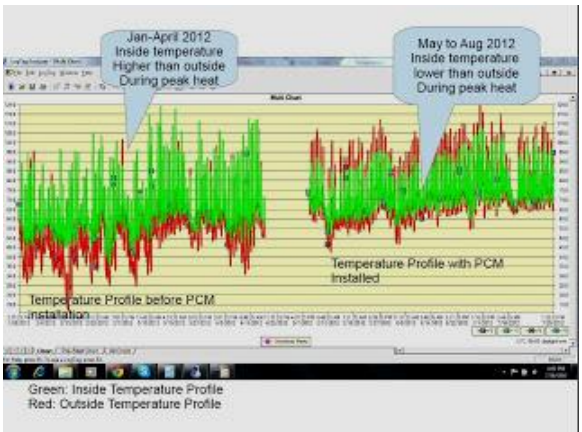


Applications

The LHES method has attracted a large number of applications in several fields of life.

1. Thermal energy storage (TES) is most often used as an effective means of shifting electrical peak load used from daytime peak periods to less expensive periods of the day or at nights, saving money, stabilizing load on power plants and increasing over all power generation and distribution system efficiency.
2. Protection from extreme environment has always been a critical requirement of textile industries. Clothing that protects from water, extreme winter intensive heat, open fire, high voltage, propelled bullets, toxic chemicals, nuclear radiations and biological toxins, etc. are some of the examples. These clothing finds application as a sportswear, fire fighting wear, defence wear, bulletproof jackets and other professional wear. Textile products can be made more comfortable when the properties of textile material adapt to the environment. One of such important intelligent material at the present is Phase Change Material (PCM), which absorb, stores or release heat according to the change of temperature during Phase Change Process is most frequently used in the manufacturing of smart textiles.
3. Initially Phase Change Material (PCM) were employed for building space suits for astronauts for space programs. These suits kept astronaut warm in a black void of space and cool in a solar glare.
4. Some of these PCMs change phase within a temperature range just above and below human skin temperature. This property of certain substance is used for making protective all season outfits, and for abruptly changing climatic conditions. Fibre, fabric and foam with built-in PCMs store the warmth of body and then release it back to the body, as it needs it. Moreover, phase change material are used, but never get used up.
5. In green house passive heating and cooling is also used. In Fig. 7 the light color represent the inside temperature of the Sycamore greenhouse while the dark color represents the temperature outside the greenhouse. The left side of the graph exhibits temperatures inside and out of the greenhouse before the PCM installation. From the end of January to mid-April, 2012, when its hot outside, its even hotter inside the greenhouse. In the right side of Fig. 7, a PCM 22P was installed at the end of April shows how phase change materials (PCMs) passively control temperature inside the greenhouse. Considerable good results observed that temperatures from January to April are cooler than in mid-summer. Without the PCM installation, greenhouse temperatures would've been much hotter during the summer months. The fact that temperatures inside the greenhouse are consistently

Fig.7-Green House Effect



15-20 degrees lower with the PCM than without it, is significant and exciting.

6. Now a days pizza continues to be one of the favorite food and staple in India and several other countries for youngest to the oldest. The most pizza chains strive to make deliveries within 30 - 45 minutes by using insulated delivery bags to ensure their pizzas stay hot as food temperature is important. But due to bad traffic, cold weather and GPS failure, it is a challenge to keep pizza hot. American students made some bottles with PCMs, the results were amazingly good. Two bottles at 53C / 127F and two more at 58C/136F were inserted into the pizza box. After 2 hours the pizza recorded at 46C/115F still deliciously hot while the pizza in insulated box without PCM checked at approximately 31C/88F

Conclusion

This paper provides a comprehensive review on previous studies related to the different types of phase change materials (PCMs), criteria of selection and where PCMs are used in passive LHTES systems. It is also concluded that PCM passive LHTES systems can contribute in different aspects of life:

- Provide thermal comfort in buildings during the whole year with a minimum auxiliary energy for heating.
- Decrease the conditioning power needed (reduction of the heating and cooling peak loads.
- Reduce energy consumption.
- Take advantage of off-peak energy savings.
- Contribute for the reduction of CO_2 emissions associated to heating and cooling.
- Keep food warm or cool on delivery depending on requirement.
- Used In textile industry.
- Employed in making space suits for astronauts for space programs.
- Maintain temperature in green house.

There may be several more applications of PCMs. But the challenge to greater use of PCMs is their packaging, cost and knowledge, both technical and among potential customer and user communities.

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