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A Review on Thermal Properties of Building Material Containing PCMs

Birendra Sahu[1], Ajay Singh Paikra[2], Dilbag Mondloe[3]

[1]M.Tech Researcher, Dept. of Mechanical Engineering, GEC Jagdalpur, Chhattisgarh, India.
[2]Assistant professor, Dept. of Mechanical Engineering, GEC Jagdalpur, Chhattisgarh, India.
[3]Assistant professor, Dept. of Mechanical Engineering, GEC Jagdalpur, Chhattisgarh, India.

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Abstract - *Phase change materials (PCMs) are high thermal energy storing materials. Adding PCMs into building materials is reported to give high thermal mass which gives higher energy efficiency. Researches show that effective thermal conductivity of concrete reduces with increasing PCM content in concrete. Energy efficiency and heat capacity of PCM-concrete are reported to be higher than plain concrete. In this paper thermal properties of PCM-concrete product are reviewed along with some mechanical properties. Incorporating PCM into concrete is found to lower the peak temperature and retards the time of occurrence of this peak temperature. PCM absorbs high heat which reduces cooling as well as heating load in building which in turn reduces the risk of thermal cracking. This review paper assembles thermal properties of PCM-concrete with mechanical properties to understand the complete behavior of concrete when PCMs are employed.)*

Key Words: Phase change materials (PCM), Thermal energy storage, Thermal properties, Thermal cracking, building materials.

1. INTRODUCTION

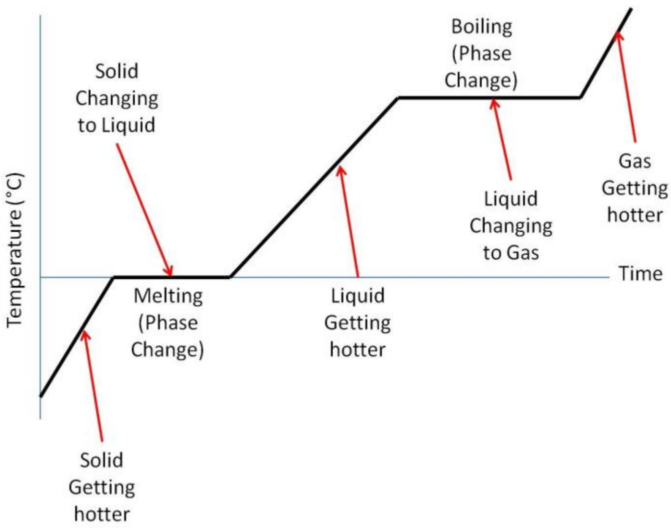
Phase change materials (PCMs) are thermal energy storing materials which store energy in the form of both sensible and latent heat. Many researches show that adding PCM in building elements like concrete [6], gypsum board [4], plaster [5], increases thermal mass of building due to which energy efficiency of the building is increased [11,15] and so energy demands for cooling and heating is decreased [13,14]. Thermal energy storage in PCM can be classified in two ways: first as sensible heat storage system heat is stored/released with temperature change and the phase remains same, hence a large volume needs to be handled whereas for latent heat storage system heat is stored/released as heat of fusion or heat of solidification, hence a large energy can be stored[1].

Some thermal characteristics of materials such as effective thermal conductivity and heat capacity are essential criteria to understand thermal behaviour of buildings and designs. Researches also show that embedding phase change materials in concrete reduces the risk of thermal cracking [9,12]. Adding PCMs in concrete is found to give more thermal comfort while saving energy for heating and cooling. This review paper is concerned with the thermal characteristics of PCM embedded building materials with the help of various researches.

1.1 Phase change theory

In nature all matters are found in three states: solid, liquid, gas and the state of matters is a function of temperature & pressure of the system in which matter is placed. The phase change of any thermodynamic system can be defined as transformation of its one phase to another due to change in temperature or pressure and thus the physical property like density, volume etc. are changed.

In nature materials can be classified as a pure material and a mixture. the substance which has a fixed chemical composition in every phase is known as pure substance e.g. water, carbon dioxide etc. Let us understand phase change of



pure materials:

Fig-1: Temperature-time diagram of pure substance

At the beginning when the solid changes to liquid, materials behave like sensible heat storage (SHS) materials; They absorb heat and so their temperature rises. When material reach the temperature at which they change their phase (i.e. melting point temperature) they absorb large amounts of heat at an almost constant temperature. The materials (PCM) continues to absorb heat without a significant rise in temperature until all the material is transformed to the liquid phase. At this stage heat is absorbed as latent heat storage (LHS) system. When the ambient temperature around a liquid material falls, the PCM solidifies and releases its stored latent heat.

1.2 Phase change materials (PCM)

A PCM is a substance which melts and solidifies at a certain temperature and has high heat of fusion. Thus, PCM can store and release large amounts of heat energy while material changes from solid to liquid state and vice versa; so, PCMs may be called as latent heat storage (LHS) units. LHS in PCMs can be achieved through solid to gas, solid to liquid, liquid to gas and liquid to solid phase changes. But only solid to liquid and liquid to solid phase changes are feasible for PCMs because the gaseous phase of material requires high volume and pressure which makes solid to gas or liquid to gas phase change transformation impractical for PCM.

Many PCMs are available in the temperature range of −5°C to 190 °C. Also, for the human comfort range between 20–30 °C, some PCMs are available with a good effectiveness. These PCMs store about 5 to 14 times more heat per unit volume than conventional storage materials such as water, masonry or rock. The use of PCMs in building envelopes and in concrete is coming into existence from last two to three decades.

1.3 Classification of phase change materials

There are many organic and inorganic chemical materials available for any required temperature range, which are identified as PCMs. Which are categorized and identified according to the melting temperature and latent heat of fusion. The classification of PCM is shown below:

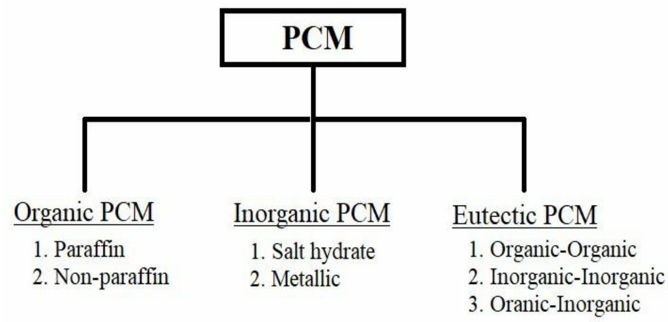


Fig -2: Classification of PCM

(1) Organic phase change materials: -

Organic phase change materials are further classified as paraffin and non-paraffin. Organic phase change materials are further classified as follows:

(a) Paraffin

Paraffin wax are mixture of straight chain n-alkanes (C_nH_{2n+2}). The crystallization of this chain releases large amount of latent heat. In paraffin wax as the carbon content or chain length increases, latent heat and melting point of fusion also increase.

Paraffin can be used as energy storage materials due to its availability in a large temperature range. Paraffin is reliable, non-corrosive, less expensive and safe then non-paraffin. Paraffins are chemically inert and stable up to sufficiently in high temperature range. Paraffin have low vapor pressure in the melt form and shows little volume changes in melting. Due to these properties paraffin can be used for longer melt-freeze cycle. It shows few undesirable properties like: (a) non-compatibility with the plastic container, (b) moderately flammability and (c) low thermal conductivity. But all these effects can be eliminated up to some existence.

(b) Non-paraffin

The non-paraffin organic PCMs are mainly fatty acids $\{CH_3(CH_2)_{2n}COOH\}$ and some are esters, alcohols, glycols etc. Many non-paraffin organic PCMs are available with large variation in their properties. Some practical features of these organic materials are: (i) low thermal conductivity, (ii) high heat of fusion, (iii) low flash points, (iv) less toxicity, (v) nonflammability and(vi) reproducible melting and freezing behaviour without supercooling. The drawback of these PCMs is price, which are 2–2.5 times higher than that of technical grade paraffin and these PCMs are little corrosive in nature. The melting and freezing properties of these non-paraffin organic PCMs are also good and are thermally stable for large number of cycles.

(2) Inorganic phase change materials: -

Inorganic phase change materials are classified as salt hydrates and metallics.

(a) Salt hydrates

Salt hydrates are formed by salt and water molecules. In salt hydrate salt and water molecules are combined at higher temperature when it melts it breaks into salt and few moles of water molecules. Salt hydrates have some good properties like:

a. Salt hydrates have high latent heat of fusion and higher thermal conductivity which is required for any PCM as energy storage unit.
b. On melting change in volume is sufficiently small which makes these materials easy for handling.
c. These materials are non-corrosive, less toxic.
d. These are compatible with plastic containers.
e. These materials are not expensive.

Apart from these good properties salt hydrates have few drawbacks as:

a. For salt hydrates the rate of nucleation is very low at the fusion temperature.
b. The salt hydrates melt incongruently and n mole of water present in the hydrates is not enough to dissolve the one mole of salt.
c. Other problem may include degradation and inoperative characteristic after a greater number of cycles.

(b) Metallics

Metallics are usually not considered for PCM usage and not much research has been carried out for this, because use of metallics is concerned with various engineering problems. Although metallics have some good properties like:

a. High thermal conductivity.
b. Low vapor pressure as compared to others.
c. High heat of fusion per unit volume.

(3) Eutectics: -

A eutectic is a mixture of two or more components, which has a minimum melting temperature of composition. The most important feature of this mixture is that its components melt and freeze congruently. Since this melt congruently without segregation hence can be utilized for the purpose of energy storage. A eutectic can be a mixture of (a) Organic-organic, (b) Inorganic-inorganic or (c) Organic-inorganic.

1.4 Incorporation techniques of PCM in concrete

PCM may be incorporated in concrete by several methods which can be categorized in two ways:

(1) Traditional methods:

Traditionally three techniques are mostly employed, and these techniques are:

(i) Direct mixing method: -

In this method liquid or powdered PCMs are directly mixed in building material. PCMs are added in a definite amount to the material as other ingredients are added to the material. This is very simple method but leakage of PCM might occur.

(ii) Immersion method: -

In this practice the porous products are immersed into melted PCM. So, the products absorb PCM into the pores and products are left for some time to soak PCM. The soaking capacity depends on absorption capacity, temperature at which soaking is to be done and type of the PCM used. The main problem with this technique is leakage of PCM.

(iii) Impregnation method: -

In this practice firstly the porous or light weight aggregate is evacuated, then dipped into liquid PCM. This is left for some time for soaking in a controlled environment. After that this PCM soaked aggregate is added to building materials.

(2) Newly developed methods:

Newly developed procedures are some special techniques which are developed to prevent leakage of PCM and to retain properties of PCMs after long period of use. Some of the special techniques are:

(i) Microencapsulation: -

Microencapsulation is an adjustment in direct mixing technique. In this procedure, PCM particles are firstly enclosed in a capsule of thin and high molecular weight polymers which prevents chemical reaction of PCM with building materials and helps to prevent leakage of PCM while phase changing. Some common courses to encapsulate organic PCMs are in-situ polymerization, Interfacial polymerization, spray drying emulsion polymerization, etc. Microencapsulated PCM developed by BASF as Micronal ® PCM is shown in figure below:

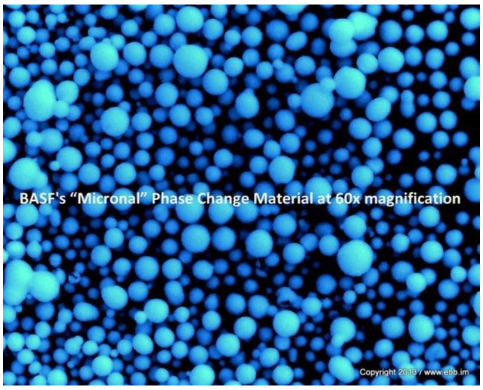


Fig -3: BASF's Micronal® PCM at 60×magnification

(ii) Shape-stabilized PCM: -

Shape-stabilized PCM is set by mixing liquid PCM with a secondary material and cooled down until this becomes solid. The most common secondary material used is styrene butadiene styrene (SBS) and high-density polyethylene (HDPE). The selection of supporting material is important because it supports PCM for long term of use.

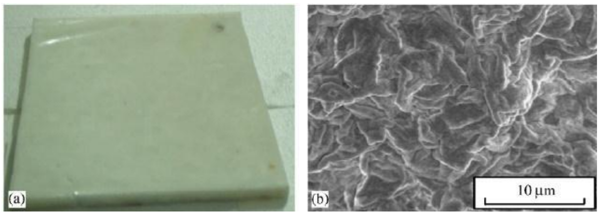


Fig -6: (a) shape-stabilized PCM plate (b) SEM (Scanning Electron Microscope) view of this PCM

1.5 Stability of PCM in concrete

For incorporation of PCM, it is important that they must be stable after long term of use in any application. When we use PCM in building materials it is important to check alkalinity level of concrete because every PCM is not suitable for use. Many investigations have been done to check for alkalinity of various types of concrete. Hawes [20] investigated for the alkalinity of various types of concrete. He found that concrete block with increasing alkali content were regular concrete block, autoclaved concrete block, lightweight concrete with expended shale aggregate and pumice concrete. He also found that butyl stearate, 1-tetradecanol, 1-dodecanol, levied less alkalinity than paraffin wax.

Hawes [20] examined for the fire resistance of concrete containing PCM and conducted fire test. As a conclusion he found that concrete product may be flammable if PCMs are directly mixed in high concentration.

(1) Thermal stability test for organic PCMs

The most used instrument for performance thermal stability test is differential scanning calorimeter (DSC). This method is used to obtain melting temperature and heat of fusion of PCM samples. It also includes product stability and phase change crystallization. As organic PCMs are classified into paraffin and non-paraffin, the thermal stability tests have been performed for both groups by many researchers as:

(a) Test in paraffin wax: -

Hadjieva et al. [21] did DSC test for paraffin wax of technical grade with formula $C_{22}H_{44.1}$. They found initial and final melting point as 47.1 and 46.6˚C with initial and final latent heat as 166 and 163kJ/kg for 300 numbers of thermal cycles.

Sharma et al. [22] patterned for stability of commercial grade paraffin wax. They found initial and final melting point as 53 and 53˚C with initial and final latent heat as 184 and 165kJ/kg for 300 numbers of cycles.

Shukla et al. [23] did test for paraffin wax 58-60. It was found that initial and final melting points were 58.27 and 55˚C with initial and final latent heat as 129.8 and 102kJ/kg for 600 numbers of cycles.

Silakhori et al. [24] showed DSC test for microencapsulated paraffin wax 53 (0.1 g)/ polyaniline (0.9 g). It was found that initial and final melting points were 53.2 and 53.4˚C with initial and final latent heat as 31 and 30.5kJ/kg for 1000 numbers of cycles.

(b) Test in non-paraffin materials: -

Sharma et al. [22] carried out test for Acetamide. It was found that initial and final melting points were 82 and 81˚C with initial and final latent heat of fusion as 263 and 241kJ/kg for 300 numbers of cycles.

El-Sebaii et al. [25] showed test for Acetanilide. Initial and final melting points were found to be 113 and 106˚C with initial and final latent heat of fusion as 169.4 and 154kJ/kg for 500 numbers of cycles.

Shukla et al. [23] showed test for Erythritol. The initial and final melting points were found to be 117 and 119˚C with initial and final latent heat of fusion as 339 and 305kJ/kg for 1000 numbers of cycles.

Hasan and Sayigh [26] did test for Myristic acid. The initial and final melting points were found to be 50.4 and 49.8˚C with initial and final latent heat of fusion as 189.4 and 163.5kJ/kg for 450 numbers of cycles.

Sari [27] completed DSC test for Lauric acid. The initial and final melting points got were 42.6 and 41.3˚C with initial and final latent heat of fusion as 176.6 and 156.6kJ/kg for 1200 numbers of cycles.

(2) Thermal stability test for inorganic PCMs

Inorganic PCMs are classified as salt hydrates and metallics.

(a) Test in salt hydrates: -

Kimura and Kai [28] completed test for calcium chloride hexahydrate. For this melting point got was 29.8˚C with latent heat of fusion as 190.8kJ/kg for 1000 numbers of cycles. For test directed in Sodium acetate trihydrate the melting point obtained was 58˚C with latent heat of fusion as 252kJ/kg for 100 numbers of cycles. They also conducted test for Trichlorofluoromethane heptadecahydrate. The melting point obtained was 8.5˚C with latent heat of fusion as 219kJ/kg for 100 numbers of cycles.

Marks [29] achieved test on Glauber's salt. Melting point obtained was 32.4˚C with latent heat of fusion as 238 for 320 numbers of cycles.

Porisini [30] completed test on Glauber's salt and obtained melting point 32˚C for 5650 cycles. For $NaOH.3.5H_2O$ the melting point obtained was 15˚C and for $Na_2SO_4.0.5NaCl.10H_2O$ melting point was 20˚C with same number of cycles.

El-Sebaii et al. [25] made test for Magnesium chloride hexahydrate. The melting point obtained was 111.5˚C with latent heat of fusion as 155.11kJ/kg for 500 cycles.

(b) Test in metallic: -

Sun et al. [31] performed test for Al-34%Mg-6%Zn alloy. Melting point obtained was 454˚C with latent heat as 314.4kJ/kg for 1000 cycles.

(3) Thermal stability test for eutectics

Eutectics are classified as: (a) organic-organic eutectics, (b)inorganic-inorganic eutectics and (c) organic-inorganic eutectics. The stability test performed in organic and inorganic eutectics are shown below:

Table -1: Thermal stability for organic eutectics

Thermal stability cycle for organic eutectics				
PCM	Melting point (˚C)	Latent heat(kJ/kg)	No. of thermal cycles	Reference
Butyl stearate (49wt%)+Butyl palmitate (48wt%)+other (3wt%)	17	138	100	Feldman et al. [33]
Ammonium alum (15%) + ammonium nitrate (85%)	53	170	1100	Jotshi et al. [32]

Capric acid (73.5wt%) + myristic acid (26.5wt%)	21.4	152	5000	Shilei et al. [35]
Capric acid (83wt%) + stearic acid (17wt%)	24.68	178.64	5000	Karaipekli et al. [36]
Capric acid (65mol%) + lauric acid (35mol%)	13	116.76	120	Dimaano & Escoto [34]

Table -2: Thermal stability for organic eutectics

Thermal stability cycle for Inorganic eutectics				
PCM	Melting point (˚C)	Latent heat (kJ/kg)	No. of thermal cycles	Reference
$CaCl_2.6H_2O$(80mol%)+$CaBr_2.6H_2O$(20mol%)	20	117	1000	Kimura and Kai [28]
$CaCl_2.6H_2O$ (93wt%) + $Ca(NO_3)_2.4H_2O$ (5wt%)+$Mg(NO_3)_2.6H_2O$ (2wt%)	24	125	1000	Kimura and Kai [28]
$CaCl_2.6H_2O$(96wt%) + NH_4NO_3(2wt%)+ NH_4Br (2wt%)	20	141	1000	Kimura and Kai [28]
$NaCH_3COO.3H_2O$ (90wt%)+$NaBr.2H_2O$ (10wt%)	51	175	1000	Kimura and Kai [28]
$NaCH_3COO.3H_2O$ (85wt%)+$NaHCOO.3H_2O$ (15wt%)	49	170	1000	Kimura and Kai [28]
$Mg(NO_3)_2.6H_2O$ (93wt%)+$MgCl_2.6H_2O$ (7wt%)	78	152.4	1000	Nagano et al. [37]

2. THERMAL PROPERTIES OF PCM-CONCRETES

Thermal properties of concrete containing PCMs are analysed by mixing different PCMs in concrete by various scholars.

L.F. Cabeza et al. [8] examined the use of microencapsulated PCM in concrete walls for energy savings. Their results showed that wall with microencapsulated PCM had improved thermal inertia than wall without PCM.

D.P. Bentz and R. Turpin [9] proved potential applications of PCM in concrete technology. They found that PCM was good in enhancing the act of concrete knowledge in several applications. They established that PCM mortar under semi-adiabatic curing condition could be used to limit the temperature rise.

C. Voelker et al. [10] investigated for temperature reduction due to the application of PCM. They found that utilization of PCM in buildings increases the thermal mass and contributes to an improvement of the thermal protection in summer.

M. Hunger et al. [11] analysed the behaviour of self-compacting concrete containing micro-encapsulated PCM. Their results for thermal conductivity measurements are presented in figure below.

From the graph the addition of PCM particles into the mass of the concrete results in a reduction of thermal conductivity due to increased air content and material like paraffin.

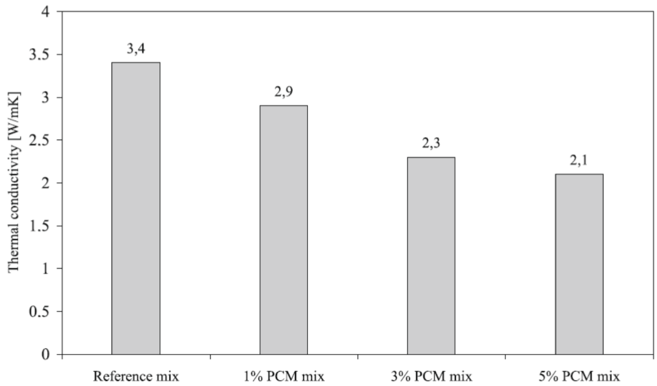


Chart -1: Thermal conductivity of PCM mixes measured by M. Hunger et al.

For specific heat capacity, they prepared four samples (200 mm×200 mm×30 mm) of four different mixes. The samples were introduced in a device and the temperature of the device during the heating process was maintained constant at 32˚C. The temperature and the heat flux were calculated as shown in chart 2 and 3.

Heat flux on the side of the sample corresponding to the indoor wall surface is measured. Temperatures and heat fluxes on both surfaces of the same samples as the ones used for the specific heat capacity were recorded. The heat flux measurement with respect to time is represented in chart 4. The heat flux measurements of below chart demonstrate an up to 11% variation. The calculated energy corresponds to the energy required by an air-conditioning system to maintain the indoor temperature constant at 23.5˚C.

F. Fernandes et al. [12] investigated for using phase change materials to lessen thermal cracking in cementitious materials. They found that during cooling period that PCM inclusion reduces cool down period which consequently reduces the peril of thermal cracking.

A.M. Thiele et al. [13] completed diurnal thermal analysis of microencapsulated PCM-concrete composite walls. They found that increasing the PCM volume fraction significantly reduced the heat transfer through the wall.

A.M. Thiele et al. [14] made annual energy analysis of concrete containing PCM for building envelopes. They detected that adding microencapsulated PCM to the concrete wall decrease the amplitude of heat flux throughout the year.

A. Ricklefs et al. [15] made test to find out thermal conductivity of cementitious composites which contained microencapsulated PCM. They used a guarded hot plate apparatus to find out operative thermal conductivity of simple OPC paste and cement mortar both comprising microencapsulated PCM up to 30% volume fraction. They found that thermal conductivity remained nearly constant between temperature range of 10-50˚C and decreased as the microencapsulated PCM volume portion increased. The thermal conductivity was larger for composites made up of cement mortar (1.2-1.8 W/mK) than of simple cement paste (0.8- 1.2 W/mK).

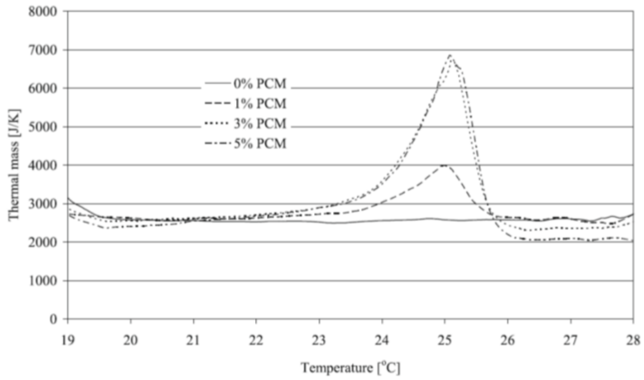


Chart -2: Thermal mass of PCM mixes with temperature measured by M. Hunger et al.

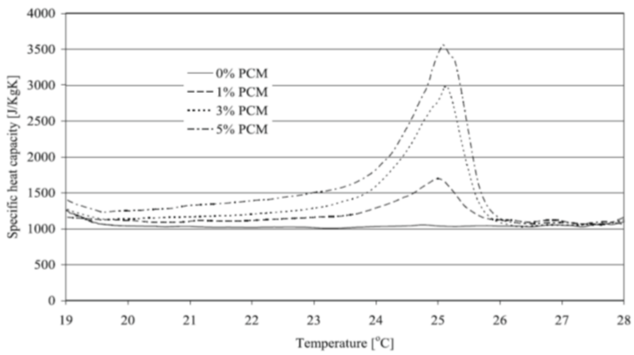


Chart -3: Specific heat capacity of PCM mixes with temperature measured by M. Hunger et al.

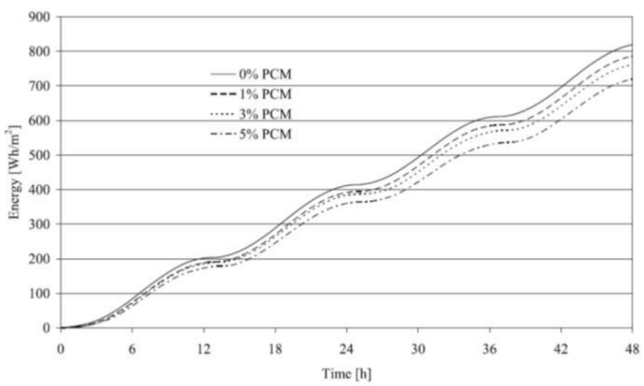


Chart -4: Energy required for maintaining indoor temperature stable at 23.5˚C

3. CONCLUSIONS

This review paper is prepared for analyzing thermal and some mechanical characteristics of concrete containing PCMs. Based on the reviewed research papers following conclusions can be drawn:

a) Incorporating PCM in concrete has a potential to increase thermal mass.

b) PCM incorporated in concrete gives reduction and delays the time of occurrence of peak temperature in summer days.

c) So, it reduces the risk of thermal cracking.

d) Thermal conductivity decreases and Specific heat capacity of concrete increases as the dosage of PCM is increased in the concrete mix.

e) Heat flux inside the concrete block reduces by incorporating PCM.

f) Reduces the cost of maintaining low temperature inside building containing PCM in its materials.

g) The coefficient of thermal expansion for plain concrete and PCM mixed concrete are almost same.

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