International Journal of Applied Engineering Research ISSN 0973-4562 Volume 13, Number 11 (2018) pp. 9858-9867
© Research India Publications. http://www.ripublication.com

Experimental investigationon$CaCl_2.6H_2O$ for subcooling behavior and its correction for low temperature thermal energy storage

Hari Kumar Singh[1] **and D Buddhi**

Centre of Excellence - Renewable & Sustainable Energy Studies
Suresh Gyanvihar University, Mahal Jagatpura, Jaipur-302017, Rajasthan, India.

Abstract

In order to study thermophysical behavior of $CaCl_2.6H_2O$ as a phase change material (PCM) for thermal energy storage (TES) in buildings, accelerated thermal cycling test under constrained parameters have been conducted. A commercial grade PCM named as calcium chloride hexahydrate as base material was procured from Indian market for investigation. In the initialinvestigation, an average value of 12.2 degree of subcooling was detected during freezing cycle of phase change material sample. The PCM sample after mixing a nucleating salt 1n 1:100 was further investigated.It is concluded that the commercial grade PCM after prescribed improvedis useful for TES systems in building.

Keywords: Phase change materials, Subcooling, Thermal energy storage, thermal cycle test

INTRODUCTION

Space coolingandheating are the major sharing areas in theresidential building with an estimate of 54% of the total energy consumption in buildings[1,2]. According to the estimated studies, due to increasing demand for thermal comfort,the world energy demand will increase about 50% by 2030 [3]. It is indicatinga huge potential for enhancing energy efficiency of buildings to reduce the energy consumption.

Thermal energy storage (TES) in buildings has been gaining wide attention now days due to its huge potential to reduce the energy consumption or shifting the peak load demand of the energy. Phase change materials (PCMs)based energy storage systems have been identified as one of the potential technology to reduce energy consumption, with useful spectrum of categorization, by various researchers [4]. Life cycle time and chemical degradation are important parameters which governs economic feasibility of PCMs. Additionally, because of ease of availability and low price commercial grade PCMs are generally used for TES systems. Although the thermophysical properties of commercial grade PCMs varies from laboratory grade PCMs asmentioned in different literatures [5,6,7,8].

Therefore, it is essential to check the effect of thermal cycling on the PCM. PCM which undergoes melt and freeze cycle in a natural processas per the requirement is called ``normal cycle`` and if a storage material is investigated in simulated conditions for thermal cycles to investigate the behavior, it is called ``accelerated cycle``. Sharma et al. [5,7] performed a accelerated thermal test for 300 to 1500 periodic charging-discharging cycles of commercial grade paraffin wax, stearic acid and acetamide respectively. These materials cannot be used for building applications due to non-meeting of desired properties, and one of the objectives is to use night ambient air to create comfort conditions in the day time in hot and dry climate of India, which is represented by Jaiselmer.

SELECTION OF PCM

PCMs must manifest certain desirable requirementsfor their employmentas thermal energy storage and they are (i) thermal properties, (ii) physical properties, (iii) kinetic properties, (iv) chemical properties (v) economic and (vi) availability.

Calcium chloride hexa hydrate ($CaCl_2.H_2O$) which has melting/ freezing temperature of the order of 27 – 29 ^{0}C has been identified as a PCM for the study.Moreover, easy availability and economic considerations of these materials have to be kept in mind.$CaCl_2.H_2O$ has high energy storage density, thermal conductivity, low cost and easily available in the Indian market. $CaCl_2.H_2O$ has been studied for its thermal life cycles, however, no recent study has been noticed on subcooling behavior of commercial grade $CaCl_2.H_2O$. In this paper subcooling, its correction and thermal cycle effect has been studied.

SUBCOOLING BEHAVIOR OF PCMS

Subcooling is an undesirable effect caused by loss of sensible heat during freezing or solidification process of PCMs. It is all because of lack of self nucleation development particularly in freezing process. For example, temperature of distil water (pure form) sample can be reduced to -15 ^{0}C without being freeze it as compared to tap water (dissolve impurities) with 0^{0}C of freeing point temperature[9].If the amount of heat absorbed is much enough to push the boundaries limits of the supercooling temperature during freezing process, will reach to constant phase change temperature for long time and may be availed as high heat of fusion with little loss. The given phenomenon does not occur during melting process of PCMs and can be eliminated by adding self nucleation chemicals of appropriate properties.

Kumano et al. [9], discussed significant suppression in supercooling of tab water, pure water and ultra pure water by using 3 wt.% to 5 wt.% of poly-vinyl alcohols (PVAs) as an additive. Inaba et al. [10] in reference to the improvement of cold storage, handling and heat exchange studied different processes of using a small amount of desirable additives for preventing the aggregation and development of ice particles in water. They also remarked that the use of less than 1 wt.% anti-agglomeration additives in water are found to disperse ice particles in water devoid of any significant change in melting-freezing temperature.Yilmaz et al. [11], reviewed different cycling tests, performed in a temperature range of-24 to -10 ^{0}C for potassium chloride (KCl) and aqueous salt solutions of NaCl as PCM for cold storage systems and other cooling applications have been explained indetail.Eduard et al. [12], optimized the use of suitable additive concentration in PCMs by using DOE (design of experiment) as a tool (for low temperature storage applications of around -18 ^{0}C) for maximizing the latent heat of fusion and reducing subcooling and phase segregation with good technical, physical and economical properties. The study was focused on addition of different additive concentrations for two main objectives; altering the phase change temperature (NaCl or AlF_3) and increasing the viscosity of the material (CMC) that thereafter indicated good thermal and chemical stability following 100 melting -freezing cycles.Matsui et al. [13], explained that more than 15 wt.% sodium oleate or sodiumlaurate as an additive to the L–C acid limited the phase change temperature between 4 and 7 ^{O}C. They also analyzed, there was no degradation even after 200 charging-discharging cycles of PCM with these additives. Bi et al. [14] performed test on gas hydrate HCFC141b to decrease its subcooling by using various proportions of benzenesulfonic acid sodium salt and calcium hypochlorite as an additive. In addition to increase in its storage density and formation rate of gas hydrate they recorded a considerable decrease in supercooling.

Based on the above literaturesurvey it was pointed out that before designing of TES systems it is very important to identify thermophysical behavior of commercial grade PCM[15]. $CaCl_2.6H_2O$ (calcium chloride hexa hydrate) is an inorganic PCM has been identified as high potential for thermal energy storage applications particularly in buildingsof hot region [16]. It has vide varity of advantages including high latent heat of fusion, good thermal conductivity, low cost and large numbers of charging-discharging cycles with negligible deformation. Additionally, apart from these advantages it possesses some disadvantages like subcooling and high corrosiveness with some materials. No studies have been noticed which quantifies the sub-cooling of $CaCl_2.6H_2O$, therefore, the objective of this paper is to quantify the order of sub-cooling its thermal behavior. Few selected thermo-physical properties of commercial grade PCM have been tabulated in table 1.

Table 1: Technical specifications of $CaCl_2.6H_2O$[15].

Property	**Value/Specifications**
PCM	Mixture of $CaCl_2.6H_2O$ & other additives
Melting Temp (°C)	29.0
Latent Heat (kJ/kg)	160
Liquid Density (kg/m^3)	1470
Solid Density (kg/m3)	1830
Liquid Specific Heat (kJ/kg^{0}C)	2.1
Solid Specific Heat (kJ/kg^{0}C)	1.4
Liquid Thermal Conductivity (W/m^{0}C)	0.54
Solid Thermal Conductivity (W/m^{0}C)	1.09
Base Material	Inorganic
Flammability	No
Thermal Stability (Cycles)	more than 1000
Max Operating Temperature (°C)	80
Appearance	Grey liquid Suspension

EXPERIMENTAL SETUP FOR MELT-FREEZE CYCLES

An experimental setup was designed for theaccelerated thermal cycling (freezing-melting) test to perform on $CaCl_2.6H_2O$ for observing its melt –freeze behavior. The experiment was conducted on a 100 g sample of PCM encapsulated in 100 ml airtight plastic container with 0.5 mm thickness as shown in figure 1. The temperature of the PCM was measured with a mercury thermometer of 0.1 ^{0}C accuracy,which was placed at the centre of the material. The PCM sample was exposed to air of 15-22 ^{0}C for freezing and 32 -37 ^{0}C for melting of the PCMfor analyzing its periodic patterns for freezing and melting cycles. The experiment was conducted for 100 charging-discharging cycles to find out the behavior of phase change temperature and latent heat of fusion, about one gram material was taken out at 0th and 10thcycle.The usedPCM $CaCl_2.6H_2O$was procured form Indian market.

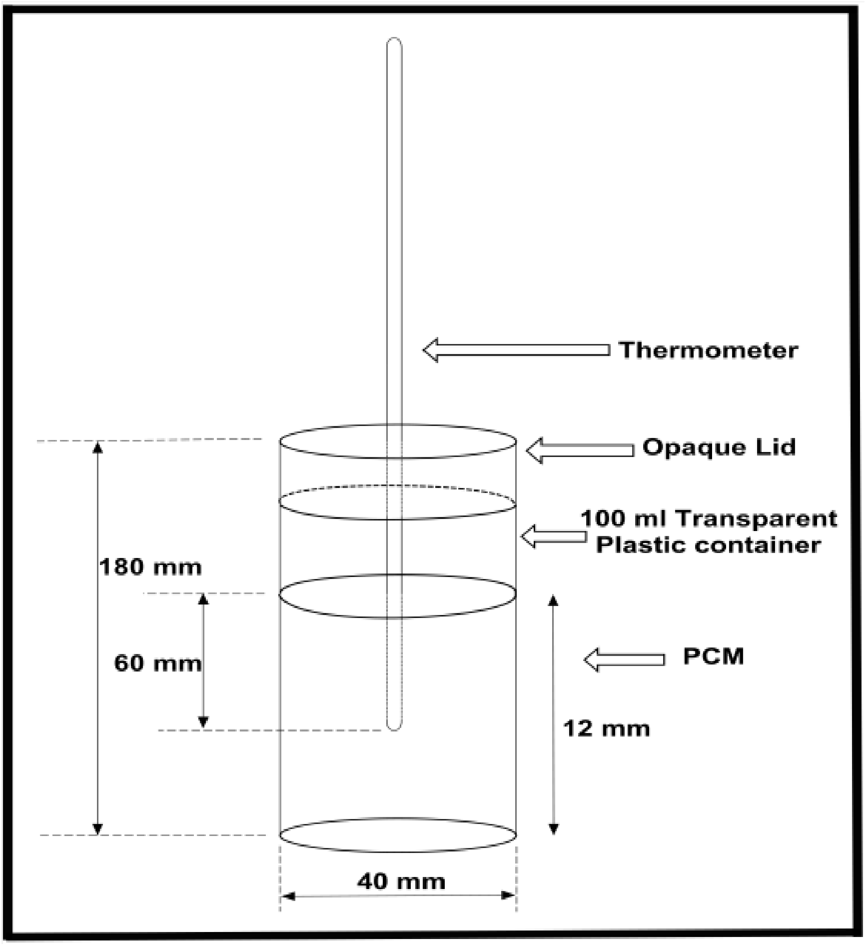

Figure 1: Laboratory Experimental setup for freeze melt cycle of PCM.

RESULTS& DISCUSSION

FREEZINGCYCLE OF PCM

The PCM procured from the market was exposed to the cold air of temperature of 15- 22 ^{0}C to study its freezing behavior. Test room temperature and cool air temperature were nearly constant at an average value of 30.5 and 16.5 ^{0}C respectively during the course of experiment.The initial temperature of the sample was 34.5 ^{0}C (higher than the freezing point) and started decreasing due to the cool air circulation across the sample container. However, a sharp decrease in temperature of PCM was noticed and reached to 16.8^{0}C without freezing i.e. it showed a subcoolingof 12.2^{0}C then attains an increase in temperature andreached nearly constant temperature of an average value of 27.5 ^{0}C for 85 minutes.PCM temperature, cool air temperature and room temperature were recorded using mercury thermometer of 0.1 ^{0}C accuracy and are plotted in figure 4. The experiments were repeatedup to 10 cycles and the behaviour was observed.The recorded subcooling during these cycles has been given in table 2.

Table 2: Sub-cooling during of PCM during different cycles.

S.No.	*No. of Cycles*	*Subcooling*
1.	First	9.5
2.	Third	11.2
3.	Fifth	11.5
4.	Seventh	12
5.	Tenth	12.2

MELTINGCYCLE OF PCM

The PCM was exposed to hot air of temperature of 15- 22 ^{0}C to study its melting behavior. Test room temperature and air outlet temperature are nearly constant at an average value of 29 and 37 ^{0}C respectively.The PCM remains at a nearly constant average value of 26.3 for long time the melting behaviour of the PCM is shown in figure 5 respectively.

ELIMINATION OF SUBCOOLING OF THE CACL2.6H2O

A PCM having subcooling behavior of 10 to 12 ^{0}C cannot be used as a PCM as it requires low temperature environment than the required. Therefore, it becomes necessary to eliminate the subcooling effect of the PCM before employing it as a PCM. 1% Strontium chloride hexa hydrate ($SrCl_2.6H_2O$) was identified and added as nucleating agent in a sample of $CaCl_2.6H_2O$ to treat the subcooling. After this the treated PCM was again studied for melt and freeze cycles.

FREEZING BEHAVIOR OF THE TREATED PCM

The PCM was exposed to cold air of temperature of 15- 22. Test room temperature and air outlet temperature were nearly constant at an average value of 30.5 and 16.5 ^{0}C.Latent heat of fusion at nearly constant temperature of an average value of 26.5 ^{0}C was observed for 65 minutes. No subcooling was recorded up to 100 cyclesand freezing behaviour at 0th, 10th, 50th and 100th cycle are plotted in figure 4 to 11.

MELTING BEHAVIOR OF THE TREATED PCM

The PCM was exposed to hot air of temperature of 15- 22 ^{0}C. Test room temperature and air outlet temperature were nearly constant at an average value of 30 and 37.5^{0}C.Latent heat of fusion at nearly constant average value of 25.8 ^{0}C was observed for 65 minutes.

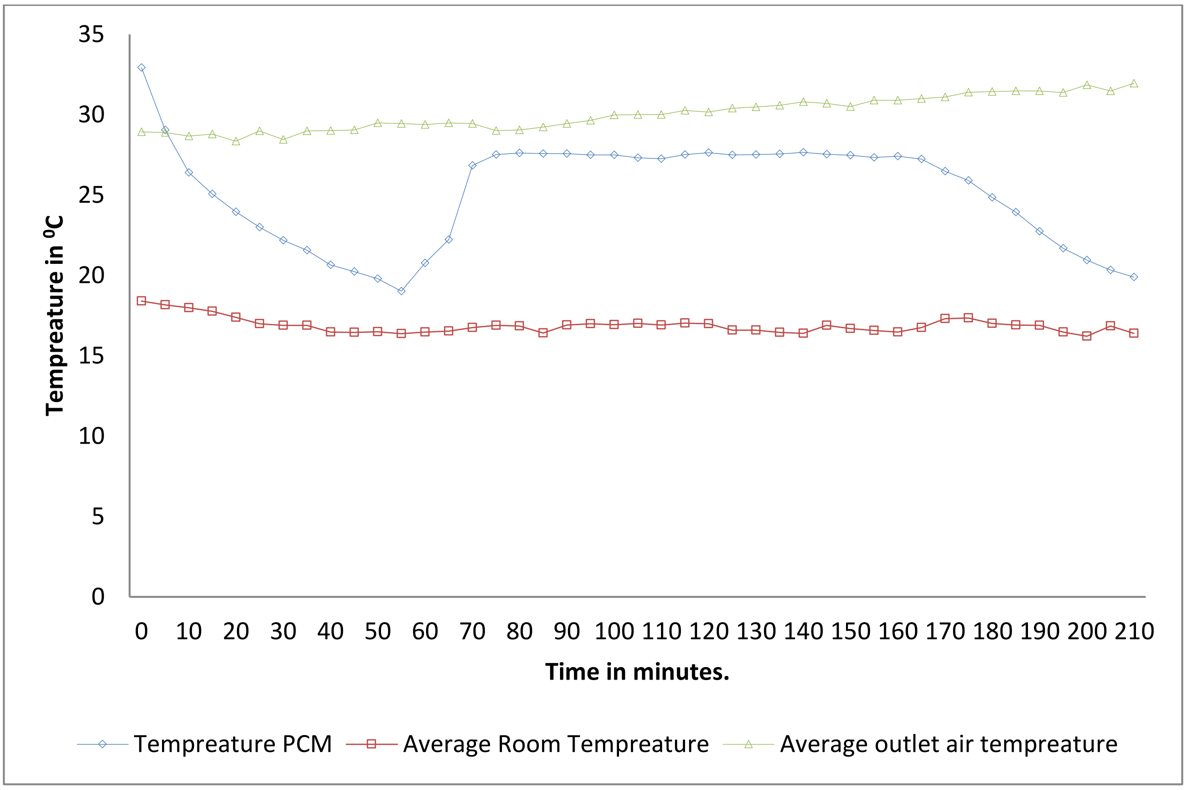

Figure 2: Freezing behavior of $CaCl_2.6H_2O$ at 0th cycle without nucleating material

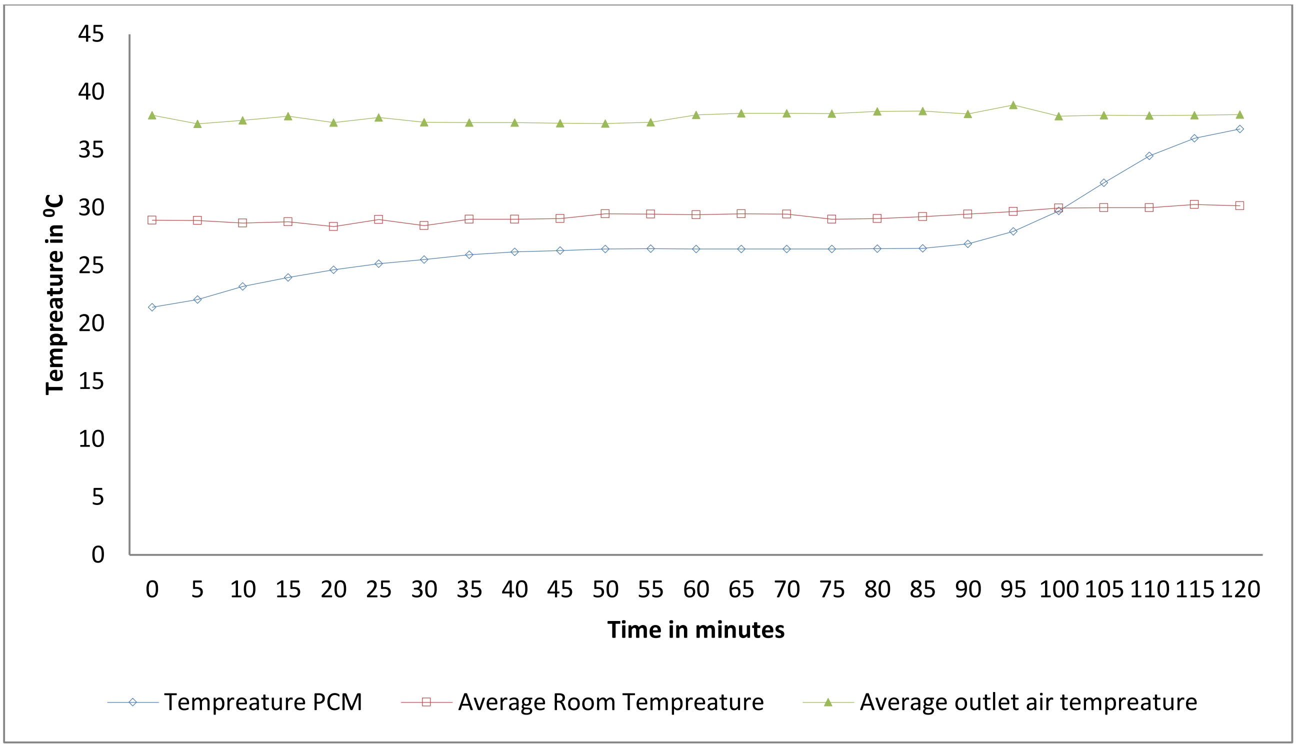

Figure 3: Melting behavior of $CaCl_2.6H_2O$ at 0th cycle without nucleating material

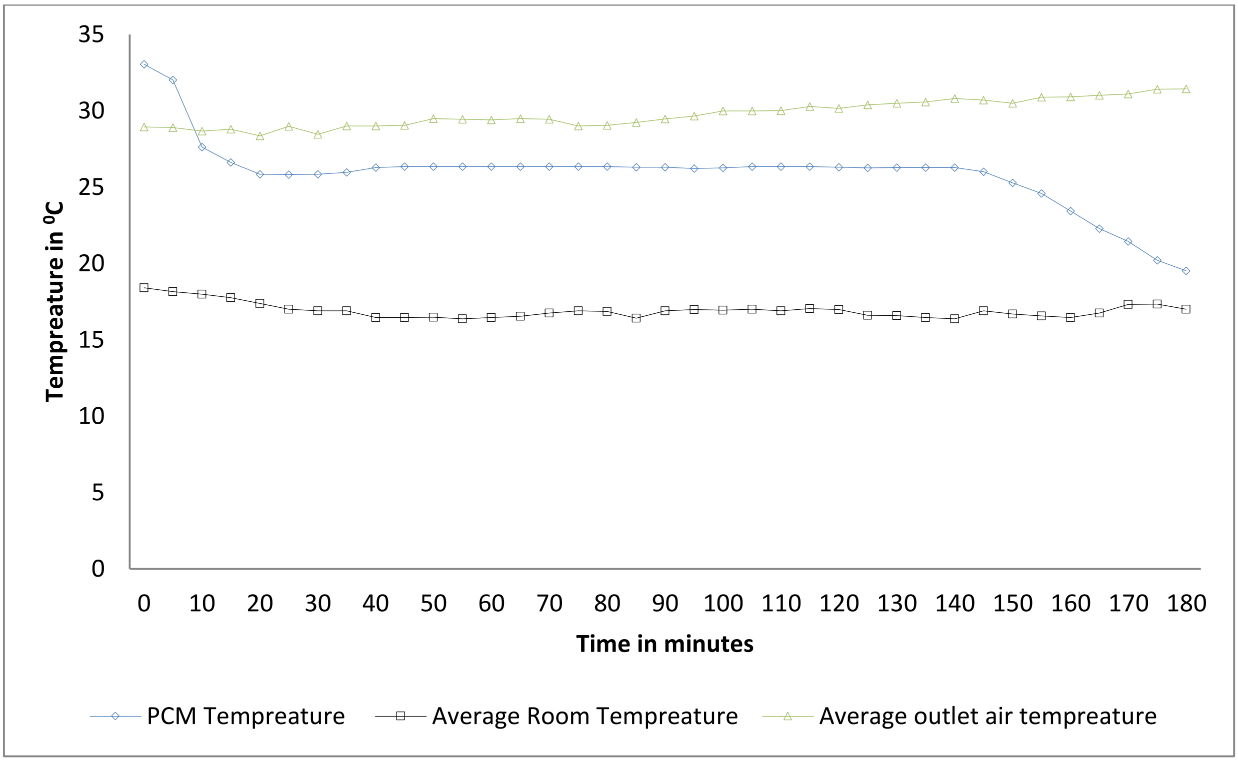

Figure 4: Freezing behavior of $CaCl_2.6H_2O$ at 10th cycle with nucleating material

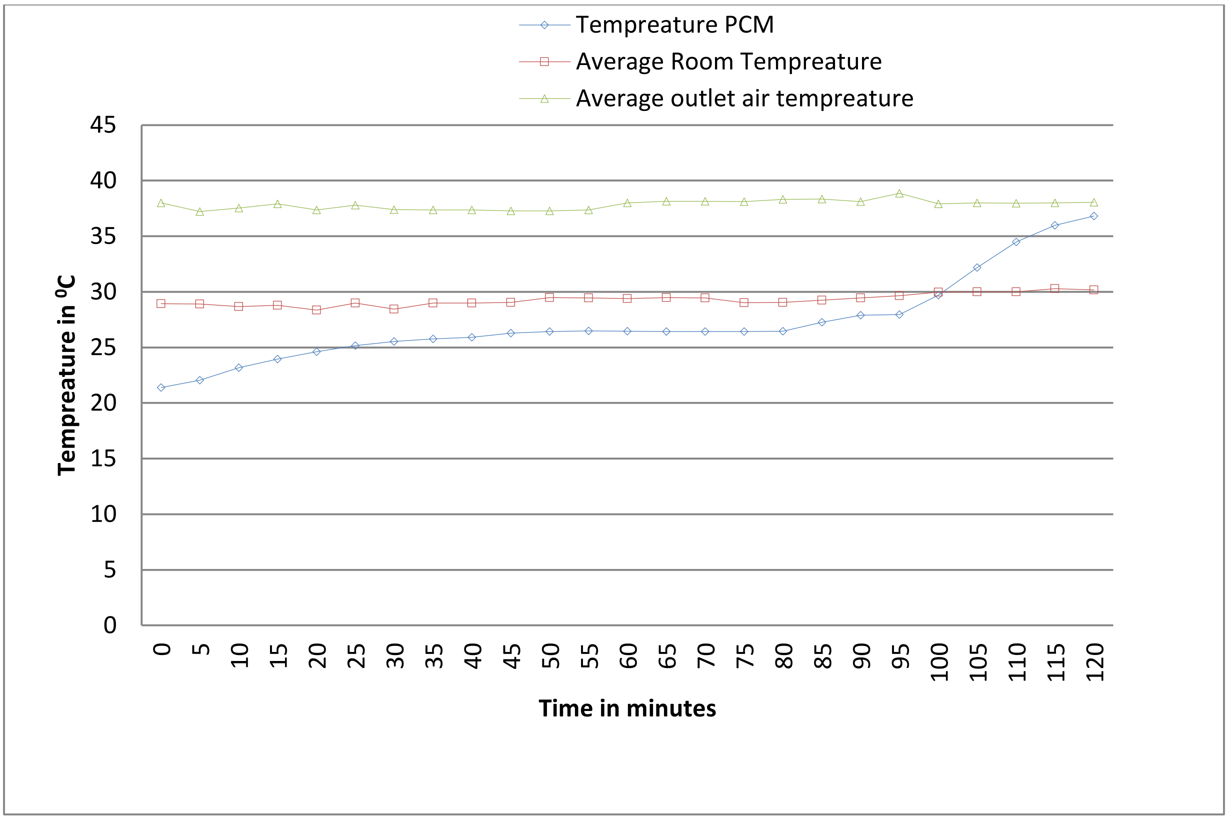

Figure 5: Melting behavior of $CaCl_2.6H_2O$ at 10th cycle with nucleating material

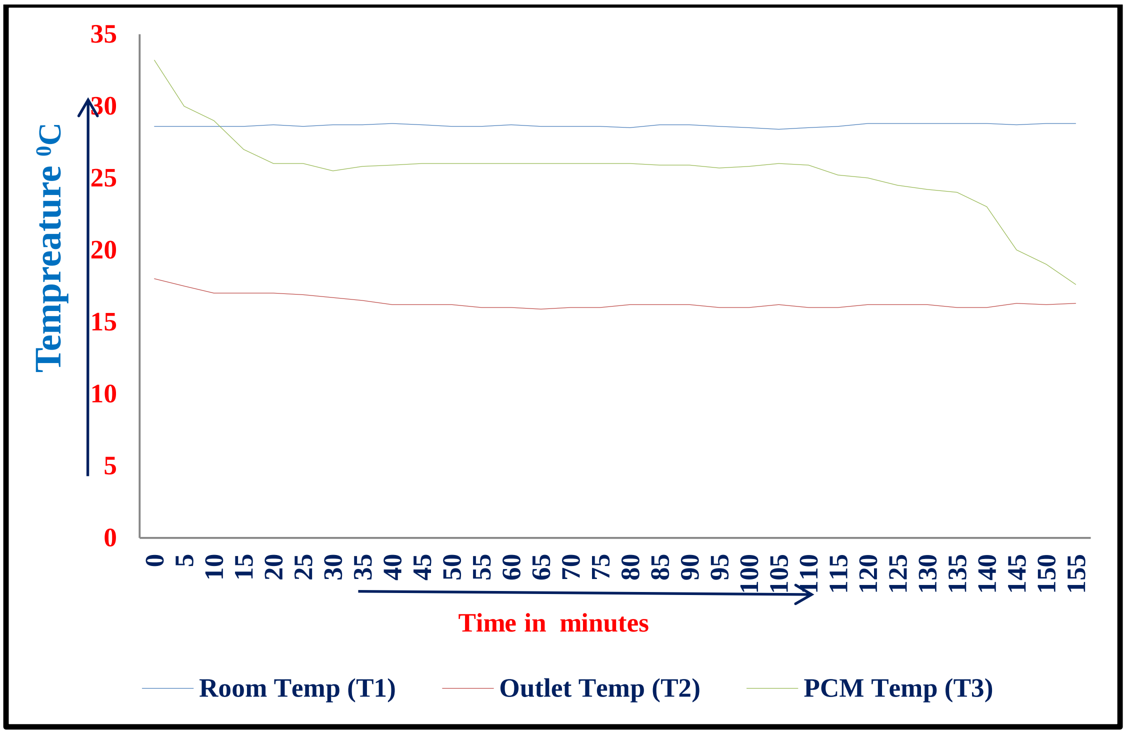

Figure 6: Freezing behavior of $CaCl_2.6H_2O$ at 50th cycle with nucleating material

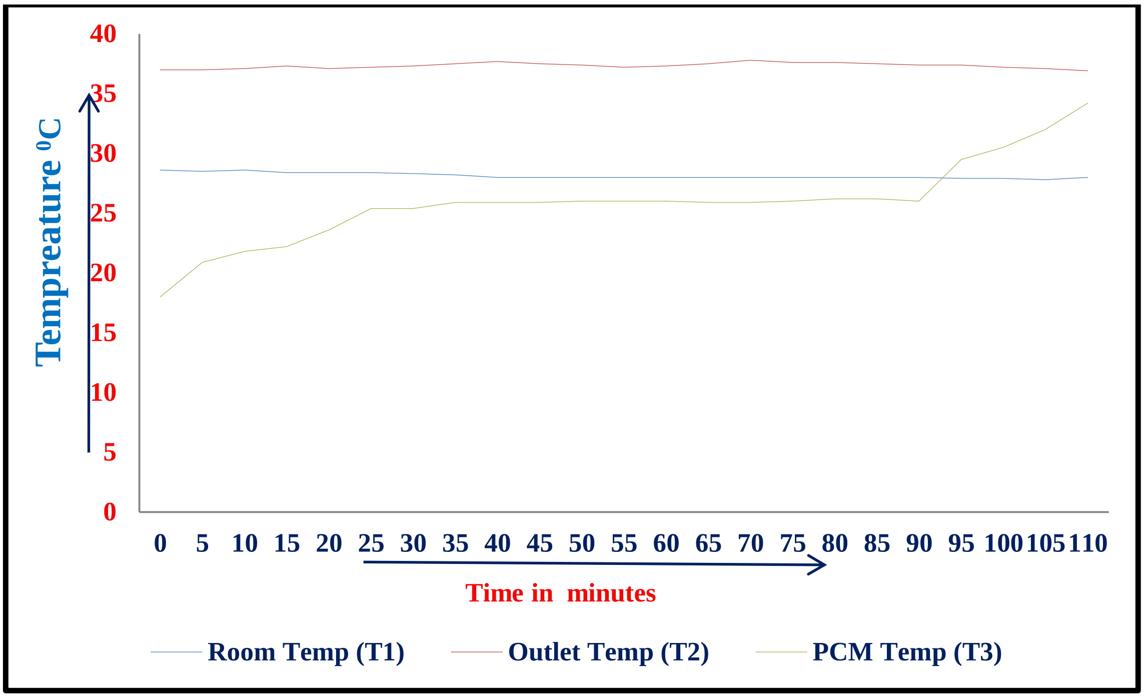

Figure 7: Melting behavior of $CaCl_2.6H_2O$ at 50th cycle with nucleating material

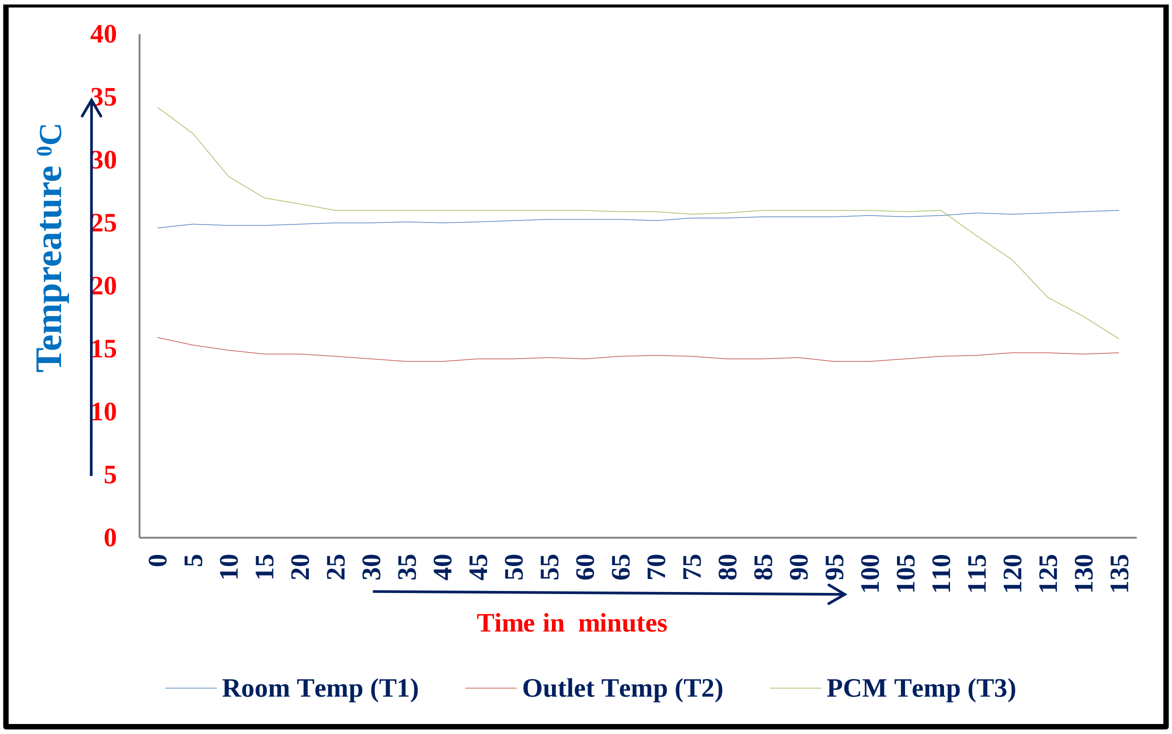

Figure 8: Freezing behavior of $CaCl_2.6H_2O$ at 100th cycle with nucleating material

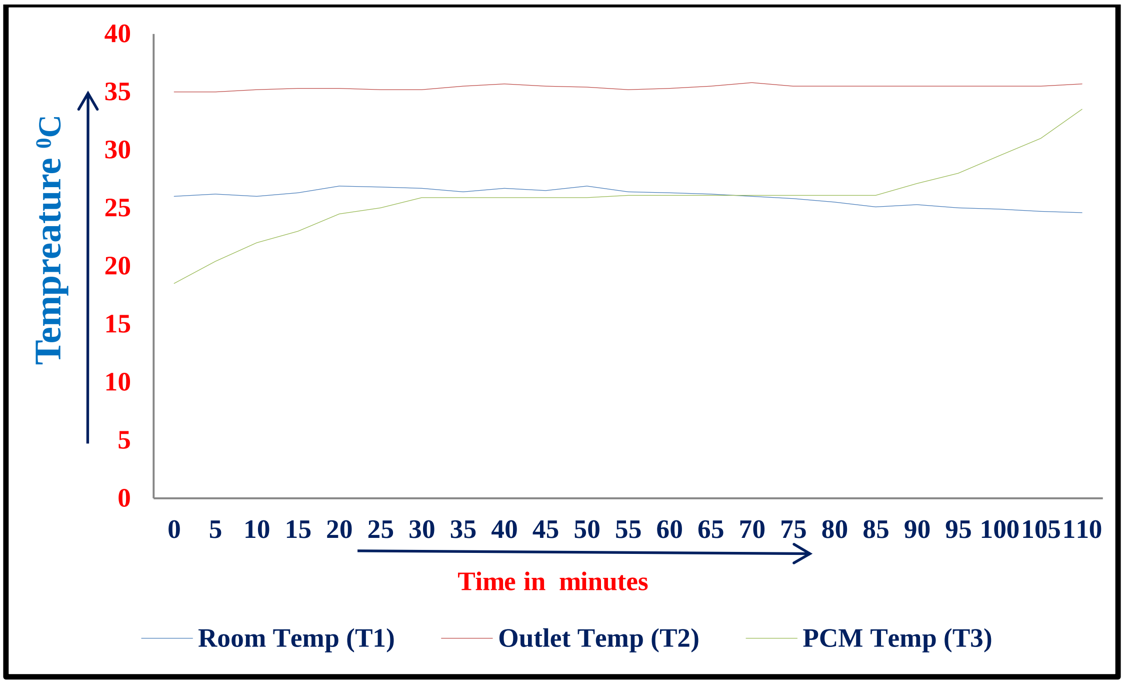

Figure 9: Melting behavior of $CaCl_2.6H_2O$ at 100th cycle with nucleating material

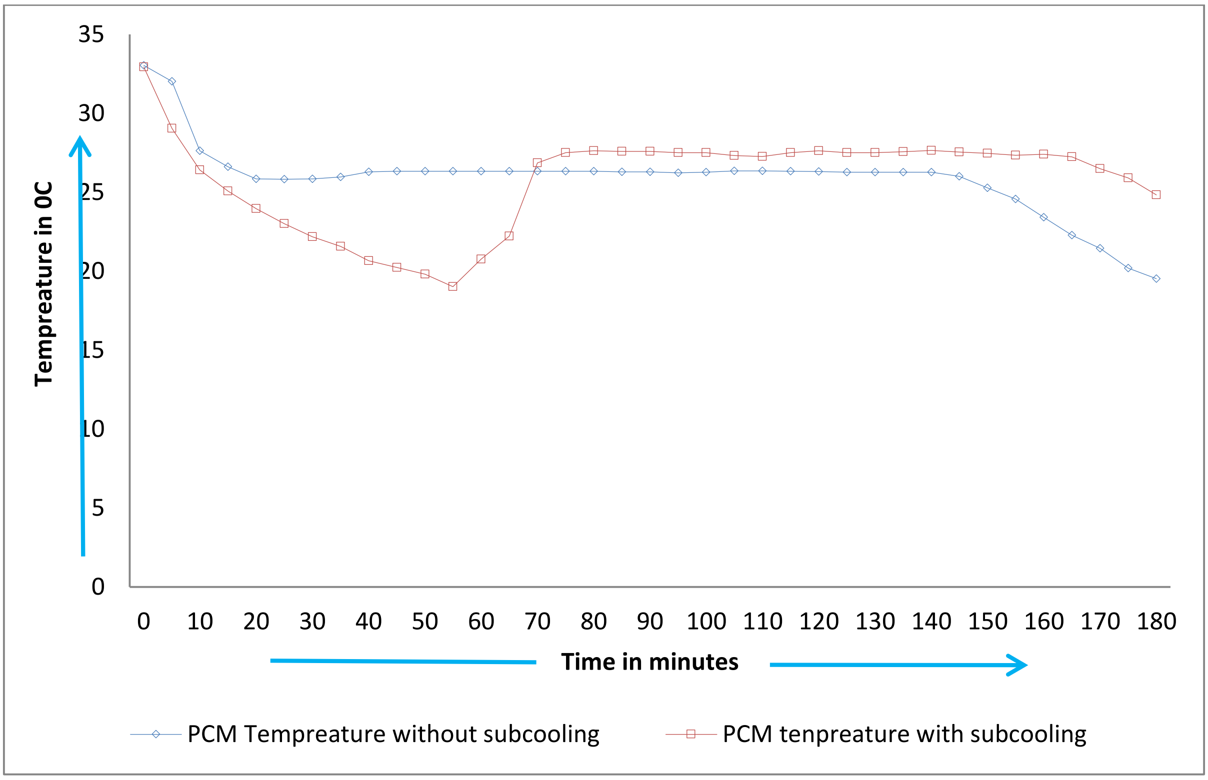

Figure 10: Acomparative PCM temperature profile subcooling and without subcooling**.**

MEASUREMENT OF LATENT HEAT OF FUSION & MELTING TEMPERATURE

DIFFERENTIAL SCANNING CALORIMETER TEST OF CACL2.6H2O

A differential scanning calorimeter (DSC), manufactured by Rheometric ScientificLtd., UK, was used for measuring the latent heat of fusion and melting temperature the PCM samples. The DSC was tested using standard materials provided by the manufacturer, and thelatent heat results were reproduced within ±2%. The DSC was tested using standard reference material (alumina, Al_2O_3) provided by the manufacturer and the latent heat results were reproduced within 72%. In DSC, sample and reference materials are heated from 10^0C to 50^0C at a constant rate of 5^0C/m. The temperature difference between them is proportional to the difference in heat flow between the two materials and the plot between heat flow and temperature is the DSC curve. Latent heat of fusion was calculated using the area under the peak and melting temperature was estimated by the tangent at the point of greatest slope on the face portion of the peak. About 14 mg of material was withdrawn on a selected melt/freeze test cycle for each material to find the latent heat of fusion and melting temperature. Tominimize the effect of surrounding moisture, the samples were kept in desiccators.In The PCMsamples heat flow against peak temperature was observed 85 to 90 mW while testing of PCM samples with nucleating agentheat flow against peak temperature was observed 55 to 75mW.The results of the PCM samples with and without treatment for 0th and 10th cycles are tabulated in Table 3&4 and the DSC curves are plotted in figure 10- 13.

Table 3: Melting point Temperature & latent heat of fusion of $CaCl_2.6H_2O$

S.No.	No. of cycle	Melting Temperature in ^{0}C	Heat of fusion in J/g
1.	0th	27.03	154.58
2.	10th	26.75	159.29

Table4 : Melting point Temperature & latent heat of fusion of the treated PCM

S.No.	No. of cycle	Melting Temperature in ^{0}C	Heat of fusion in J/g
1.	0th	27.88	140.09
2.	10th	27.56	166.98

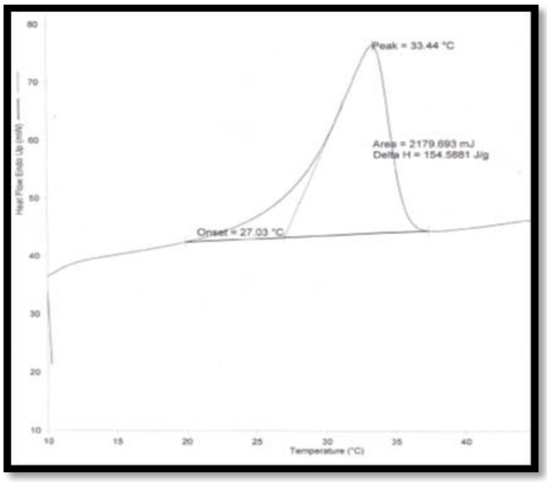

Figure 9. DSC curve of $CaCl_2.6H_2O$ at 0th cycle without nucleating material

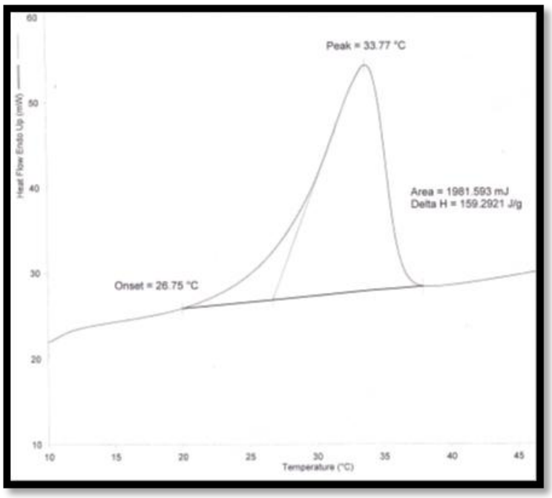

Figure 10. DSC curve of $CaCl_2.6H_2O$ at 10th cycle without nucleating material

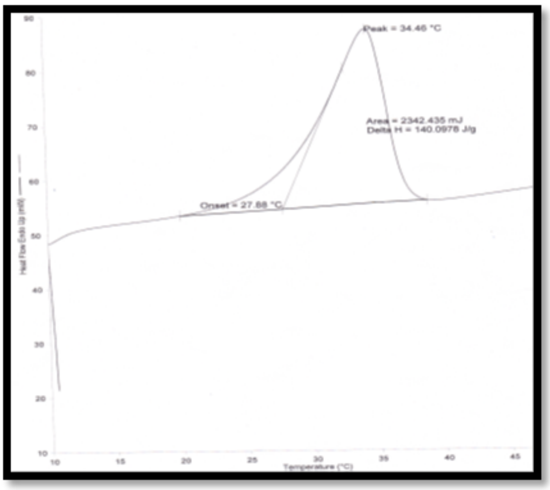

Figure 11. DSC curve of $CaCl_2.6H_2O$ at 0th cycle with nucleating material.

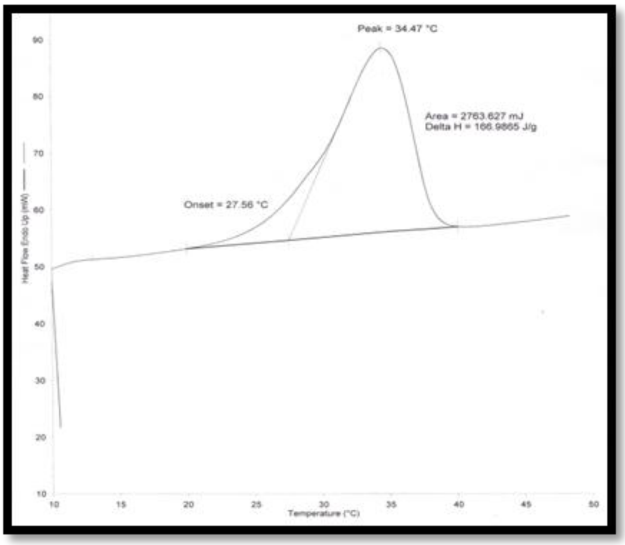

Figure 12. DSC curve of $CaCl_2.6H_2O$ at 10th cycle with nucleating material.

CONCLUSION

Thermal behavior of $CaCl_2.6H_2O$ has been studied experimentally with and without nucleating agent. Commercial grade calcium chloride hexa hydrate has been used for investigationand procured from the Indian market. In the initial investigation, an average value of 12.2 degree of subcooling was detected during freezing cycle of phase change material sample. The PCM sample after mixing 1% nucleating salt. It is concluded that the commercial grade $CaCl_2.6H_2O$ can be used as PCM after corrections in thermal energy storage systems in buildings in particular for hot and dry climatic conditions using free cooling.

REFERENCES

[1]. Rincón, R., Castell, A., Pérez, G., Solé, C., Boer, L., and Cabeza., LF., 2013, `` Evaluation of the environmental impact of experimental buildings with different constructive systems using Material Flow Analysis and Life Cycle Assessment,`` Applied Energy., 109, pp. 544-552.

[2]. El-Sawi, A., Haghighat, F., and Akbari, H., 2014, ``Assessing long-term performance of centralized thermal energy storage system,`` Appl Therm Eng., 62(2), pp.313–321.

[3]. US Department of Energy., (2011, March 1), Energy Efficiency and Renewable Energy Chapter 2: Residential Sector. Retrieved July 27, 2011, from Buildings Energy Data Book: http://buildingsdatabook.eren.doe.gov/ChapterIntro2.aspx

[4]. Menoufi, K., Castell, A., Navarro, L., Perez, G., Boer, D., and Cabeza, L.F., , 2012, ``Evaluation of the environmental impact of experimental cubicles using life cycle assessment: a highlight on the manufacturing phase,`` Appl Energy., 92, pp. 534–544.

[5]. Halawa, E., Saman, W., and Bruno, F.,2010,`` A phase change processor method for solving a one-dimensional phase change problem with convection boundary``, Renewable Energy., 35 (8), pp. 1688-1695.

[6]. Sharma, S.D., Buddhi, D., and Sawhney, R.L., 1999, ``Accelerated thermal cycle test of latent heat-storage materials,`` Solar Energy., 66(6), pp. 483-490.

[7]. Tyagi, V. V., and Buddhi, D., 2007, `` PCM Thermal Storage in Buildings: A state of art, Renewable and Sustainable Energy Reviews,`` 11(6), pp.1146 – 1166.

[8]. Sharma, A., Tyagi, V.V., Chen, C.R., and Buddhi**,** D., 2009, `` Review on thermal energy storage with phase change materials and applications,`` Renewable and Sustainable Energy Reviews., 13(2), pp. 318-345.

[9]. Tyagi, V.V., Buddhi, D., Kothari, R., Tyagi, S.K., 2012,`` Phase change material (PCM) based thermal management system for cool energy storage application in building: An experimental study,`` Energy and Building., 51, pp. 248-254.

[10]. Kumano, H., Hirata, T., and Kudoh, T., 2009,``Effects of poly-vinyl alcohol on supercooling phenomena of water,`` International Journal of Refrigeration., 32(3), pp. 454–61.

[11]. Inaba, H., Inada, T., Horibe, A., Suzuki, H., and Usui, H., 2005,``Preventing agglomeration and growth of ice particles in water with suitable additives.`` International Journal of Refrigeration., 28(1), pp. 20–26.

[12]. Yilmaz, S., Sheth, F., Martorell, I., Paksoy, HO., and Cabeza, F., 2010,``Salt-water solutions as PCM for cooling applications. `` In Proceedings of EuroSun international conference on solar heating, cooling and,buildings.

[13]. Eduard, O., Camila, B., Mohammed, M., Luisa, F., and Cabeza, F., 2013, ``Experimental study on the selection of phase change materials for low temperature applications,`` Renewable Energy., 57, pp.130-136.

[14]. Matsui, T., Yoshida, M., Yamasaki, H., and Hatate, Y., 2007, `` Thermal properties of multi component fatty acids as solid–liquid phase change materials for cooling applications,`` Chem Eng Commun., 194(4), pp. 129–39.

[15]. Bi, Y., Guo, T., Zhu, T., Zhang, L., and Chen, L., 2006 ``Influences of additives on the gas hydrate cool storage process in a new gas hydrate cool storage system, ``Energy Conversion and Management., 47(18), pp. 2974–82.

[16]. Tyagi, V.V., and Buddhi, D., 2008,`` Thermal cycle testing of calcium chloride hexahydrate as a possible PCM for latent heat storage,`` Solar Energy Materials & Solar Cells., 92(8), pp. 891–899.

[17]. Shukla, A., Buddhi, D., and Sawhney, R.L., 2008, `` Thermal cycling test of few selected inorganic and organic phase change materials, `` Renewable Energy., 33(12), pp. 2606–2614.