Solar Energy Materials & Solar Cells ∎ (∎∎∎∎) ∎∎∎–∎∎∎

Contents lists available at ScienceDirect

Solar Energy Materials & Solar Cells

journal homepage: www.elsevier.com/locate/solmat

Thermal cycle testing of calcium chloride hexahydrate as a possible PCM for latent heat storage

V.V. Tyagi *, D. Buddhi

Thermal Energy Storage Laboratory, School of Energy and Environmental Studies, Devi Ahilya University, Indore 452017, India

ARTICLE INFO

Article history:
Received 12 July 2007
Received in revised form
6 February 2008
Accepted 17 February 2008

Keywords:
Phase change material (PCM)
Latent heat storage
Thermal cycle testing
Differential scanning calorimeter (DSC)

ABSTRACT

In order to study the changes in latent heat of fusion and melting temperature of calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$) inorganic salt as a latent heat storage material, a thousand accelerated thermal cycle tests have been conducted. The effect of thermal cycling and the reliability in terms of the changing of the melting temperature using a differential scanning calorimeter (DSC) is determined. It has been noticed that the $CaCl_2 \cdot 6H_2O$ melts between a stable range of temperature and has shown small variations in the latent heat of fusion during the thermal cycling process. Thus, it can be a promising phase change material (PCM) for heating and cooling applications for various building/storage systems.

1. Introduction

The storage of thermal energy in the form of latent heat in phase change materials (PCMs) represents an attractive option for low and medium temperature range energy applications. Wide ranges of PCMs have been investigated, such as paraffin wax, salt hydrates and non-paraffin organic compounds. The economic feasibility of employing a latent heat storage material in a system depends on the life span and cost of the storage materials. In other words, there should not be major changes in the melting point and the latent heat of fusion with time, due to thermal cycles of the storage materials. For latent heat storage, commercial grade PCMs are preferred due to various reasons, such as low cost and easy availability. The thermo-physical properties of commercial PCMs are found to be much different from those quoted in the literature [1] for laboratory grade PCMs. The matching of transition temperature range for the PCMs is to deliver the energy at a suitable temperature for a given application. This is one of the important aspects for a PCM-based energy storage system. Eliminating the problems of super cooling, phase separation and stability over a long period of application is an important criterion for the successful application of suitable PCMs for thermal energy storage systems.

A thermal energy system with latent heat storage undergoes at least one melt–freeze cycle per day, and can be called as normal cycle. If a number of melt–freeze cycles tests are conducted in the laboratory under controlled conditions, this can be called as the accelerated thermal cycle test, after a number of heating–cooling cycles, and some of the important studies are mentioned in this paper. Ting et al. [2] conducted the accelerated cycle tests of a latent heat storage unit having $Na_2SO_4 \cdot nH_2O$ as a possible PCM for the suitable temperature range. They [2] studied the effect of a thousand thermal cycles on the container tube but did not analyze the effect on the thermo-physical properties of the PCM. Fernanda [3] also studied the thermal reliability of salt hydrate PCMs having melting temperature between 15 and 32 °C for repeated thermal cycles by measuring the latent heat of fusion and melting temperature. Sharma et al. [4,5] conducted the accelerated thermal cycle test of commercial grade stearic acid, acetamide and paraffin wax for 300 and 1500 repeated melt–freeze cycles, respectively. They [4,5] concluded that acetamide and paraffin had shown good stability as compared to stearic acid, which melted over a wide range of temperatures. Jotshi [6] used ammonium alum/ammonium nitrate eutectic for solar space heating applications and also conducted the accelerated thermal cycle for the same eutectic. At the end of 1100 accelerated thermal cycles, the enthalpy change was found to be 5% lower than that of the initial value. Wada et al. [7] investigated the decreasing heat storage capacity of $CH_3COONa \cdot 3H_2O$ during thermal cycling and performed calorimetric measurements on three kinds of samples. They [7] also studied the effects of a thickening agent on the latent heat storage capacity of the sample and found a considerable improvement in the latent heat capacity after 500 thermal cycles. Cedeno et al. [8] studied the melting process of three fatty acids

---

* Corresponding author. Tel.: +91 9999926477.
E-mail addresses: vtyagi16@yahoo.co.in, vtyagi16@gmail.com (V.V. Tyagi).

0927-0248/$ - see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.solmat.2008.02.021

(palmitic, stearic and oleic) and their binary and ternary mixtures. On the other hand, investigations on the thermal and heat transfer properties of the inorganic and organic eutectics have been conducted in limited numbers. Hasan [9] has conducted an experimental investigation of palmitic acid as a possible PCM for thermal energy storage. The parametric study of phase change transition included transition time, temperature range and propagation of the solid–liquid interface, as well as the heat flow rate characteristics of the employed circular tube storage system. Zhang et al. [10] studied the solid–liquid phase transitions in lauric, palmitic, stearic acid and their binary systems and also investigated the stability of thermal properties after different times of heating–cooling cycles, such as 30, 50, 80 and 100.

Ahmet Sari [11,12] studied the thermal reliability of stearic, palmitic, myristic and lauric acid latent heat storage materials for a number of thermal cycles using a differential scanning calorimeter (DSC). The selected materials were of industrial grade (90–95%), and it was concluded that there is a change in melting temperature of about 0.07–7.87 °C, whereas the latent heat of fusion was found to be effected by −1.0% to −27.7%. Dimaano and Escoto [13] developed the capric and lauric acids mixture as a possible phase change media for low thermal energy storage systems. The properties of different combinations of acids were verified against existing literature data with the use of the DSC. Classical evaluation techniques were employed to determine the required thermodynamic, kinetic and other physical properties. The accuracy of the setup was determined and phase transitions were observed by performing a series of thermal cycles. To authenticate the long-term stability and reproducibility of the combination, 120 thermal cycles were carried out using a fabricated equilibrium cell.

Based on the literature survey [1–13], it can be noted that a comprehensive knowledge of the thermal properties and thermal reliability of a PCM should be verified by thermal cycling life testing to ensure the longevity of the LHTES system in which it is used. Therefore, this study aims to measure the thermal properties of calcium chloride hexahydrate ($CaCl_2 \cdot 6H_2O$) inorganic salt as a latent heat storage material and to determine the effect of thermal cycling on its reliability in terms of the variations in the melting temperature using DSC analysis method. Besides, the probable causes for the variations in thermal properties of

Table 1
Specifications and limitations of the instrument used for life cycle testing

Specifications and limitations of the instrument used (DSC Q-100)	
Temperature range	−180 to 725 °C
Temperature accuracy	0.1 °C
Temperature precision	0.05 °C
Sensitivity	0.2 μW

Table 2
Some features of the calcium chloride hexahydrate salt

Properties of the PCM	Value
Melting point	24 °C[a]
Specific heat	
(I) Solid	1.4 kJ/kg °C
(II) Liquid	2.1 kJ/kg °C
Latent heat of fusion	140 kJ/kg[a]
Density (35 °C)	1470 kg/m^3 [b]
Thermal conductivity	
(I) Solid	1.09(W/m °C)
(II) Liquid	0.54(W/m °C)

[a] Measured by differential scanning calorimeter (DSC).
[b] Measured by hydrometer.

Table 3
Latent heat of fusion and melting temperature of calcium chloride hexahydrate at various thermal cycles by DSC

S. no.	No. of cycles	Melting temperature (°C)	Heat of fusion (kJ/kg)
1	1	23.26	125.4
2	10	26.85	138.1
3	100	27.14	117.9
4	200	24.62	130.3
5	300	24.79	130.0
6	400	24.34	135.3
7	500	24.54	130.1
8	600	24.41	127.1
9	700	24.26	129.5
10	800	24.15	129.6
11	900	23.95	122.3
12	1000	23.26	125.4

Fig. 1. A camera snap of differential scanning calorimeter.

Please cite this article as: V.V. Tyagi, D. Buddhi, Sol. Energy Mater. Sol. Cells (2008), doi:10.1016/j.solmat.2008.02.021

the inorganic salt with increasing number of melt/freeze cycles were investigated. Since there is not much data available on these subjects in the literature, the present work is an effort to provide some expanded experimental results.

2. Experimental setup

The experiments for the repeated melt/freeze cycles have been conducted in the Laboratory to study the changes in the

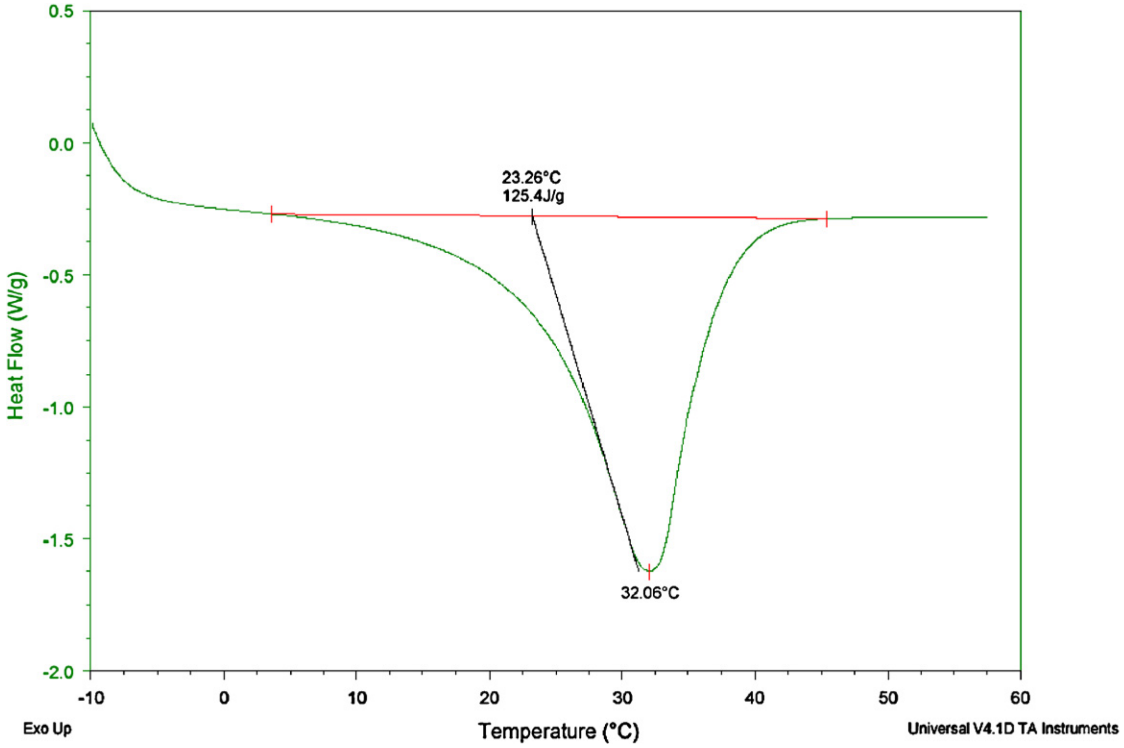

Fig. 2. DSC measurement curve of latent heat of fusion and melting temperature of $CaCl_2 \cdot 6H_2O$ at the 1st cycle.

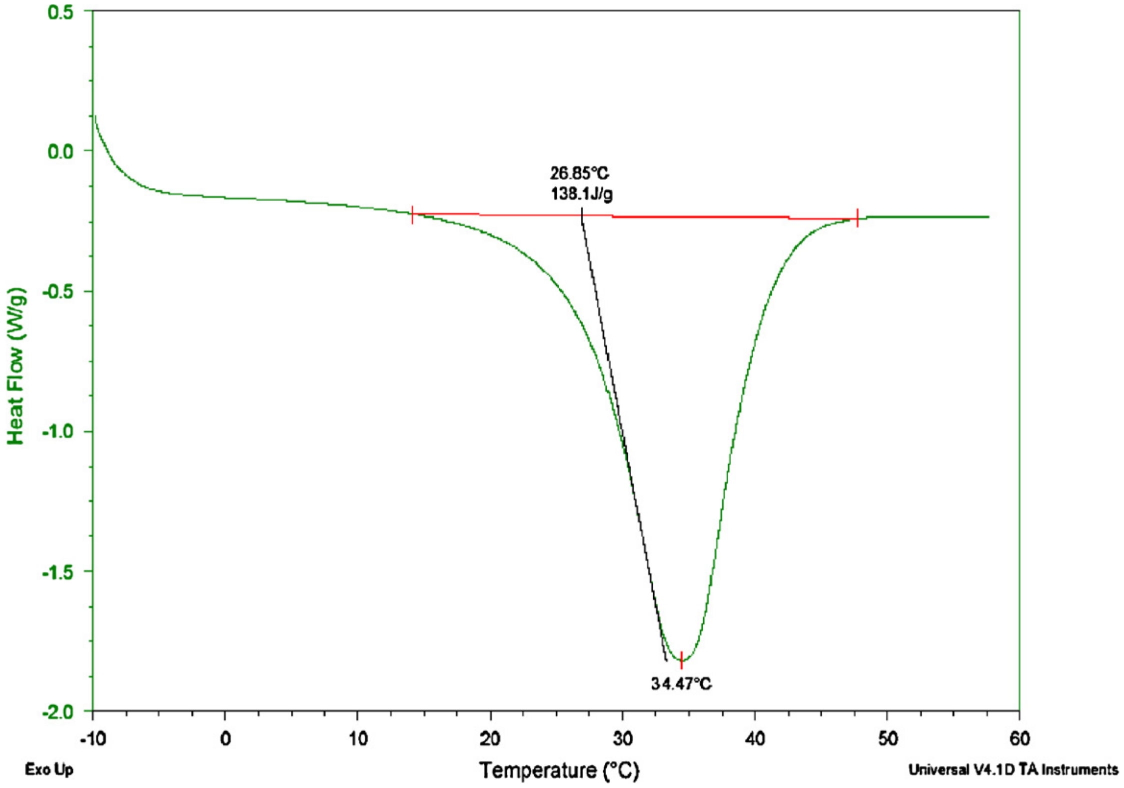

Fig. 3. DSC measurement curves of latent heat of fusion and melting temperature of $CaCl_2 \cdot 6H_2O$ at the 10th cycle.

Please cite this article as: V.V. Tyagi, D. Buddhi, Sol. Energy Mater. Sol. Cells (2008), doi:10.1016/j.solmat.2008.02.021

melting point and the latent heat of fusion for commercial grade calcium chloride hexahydrate salt. All the thermal cycle tests were conducted by DSC (Q-100) manufactured by TA instrument, USA, and used for measuring the latent heat of fusion and the melting temperature of selected PCM. The specifications of the instrument (Fig. 1) are given in Table 1. In DSC, the sample and reference materials are heated at a constant rate. The temperature difference between them is proportional to the difference in heat flow between the two materials. Alumina (Al_2O_3), the reference material recommended by the DSC manufacturer, was used. The latent heat of fusion was calculated using the area under the peak of the DSC curve, and the melting temperature was estimated by the tangent at the point of highest slope on the face portion of the peak. The sample was cycled in the DSC at 7 °C/min between −10 and 60 °C.

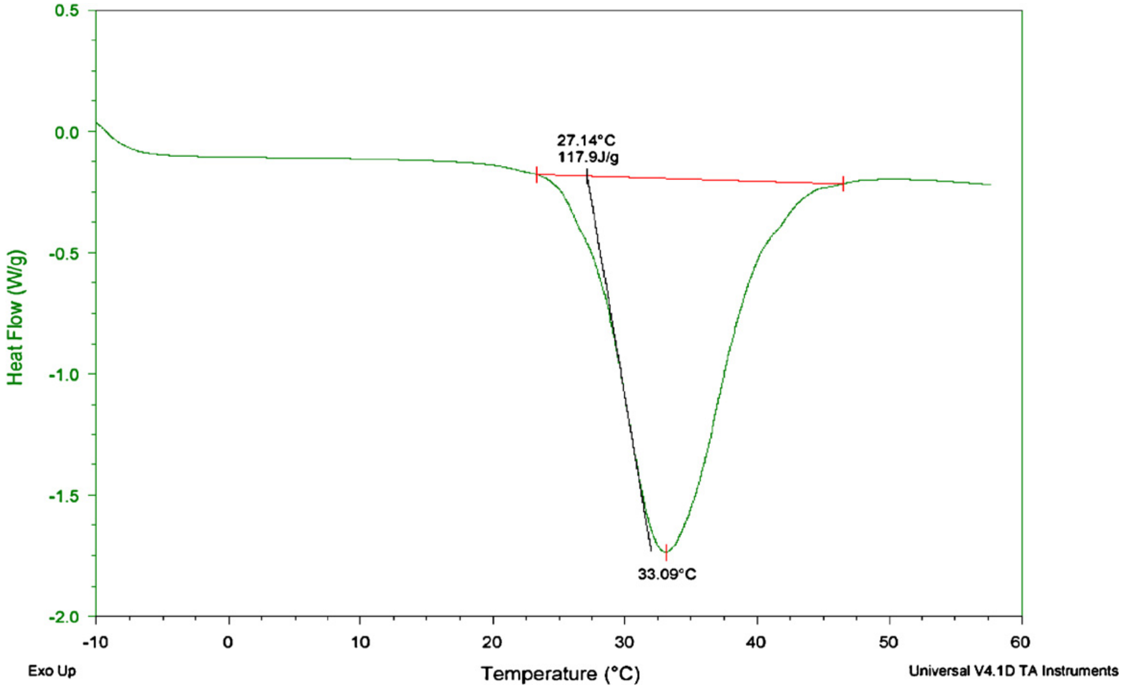

Fig. 4. DSC measurement curves of latent heat of fusion and melting temperature of $CaCl_2 \cdot 6H_2O$ at the 100th cycle.

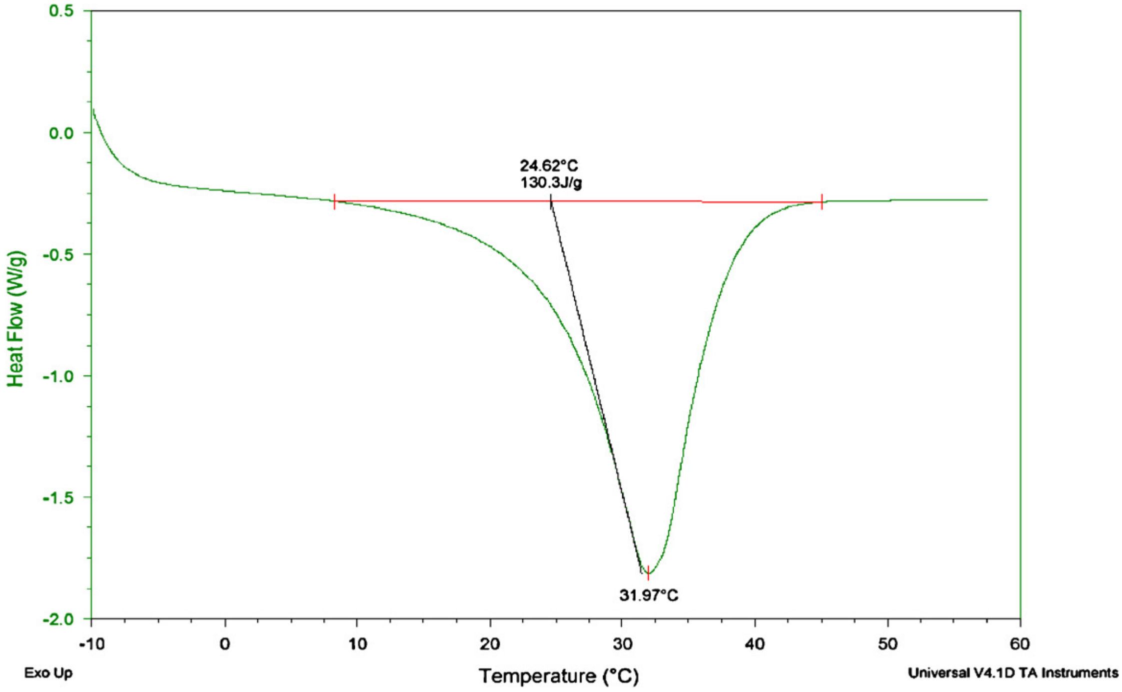

Fig. 5. DSC measurement curves of latent heat of fusion and melting temperature of $CaCl_2 \cdot 6H_2O$ at the 200th cycle.

Please cite this article as: V.V. Tyagi, D. Buddhi, Sol. Energy Mater. Sol. Cells (2008), doi:10.1016/j.solmat.2008.02.021

Thus, $CaCl_2 \cdot 6H_2O$ is used as a possible PCM for the repeated melt/freeze thermal cycles in this study and the properties are given in Table 2. The samples for $CaCl_2 \cdot 6H_2O$ were subjected to 1000 accelerated melt/freeze cycles. Around 26.38 mg of material was used on a selected melt/freeze test cycle to find the latent heat of fusion and the melting temperature. The time taken for this process was around 16.58 min. The PCM ($CaCl_2.6H_2O$) is being procured by an Indian company and nowadays is easily available in the Indian market.

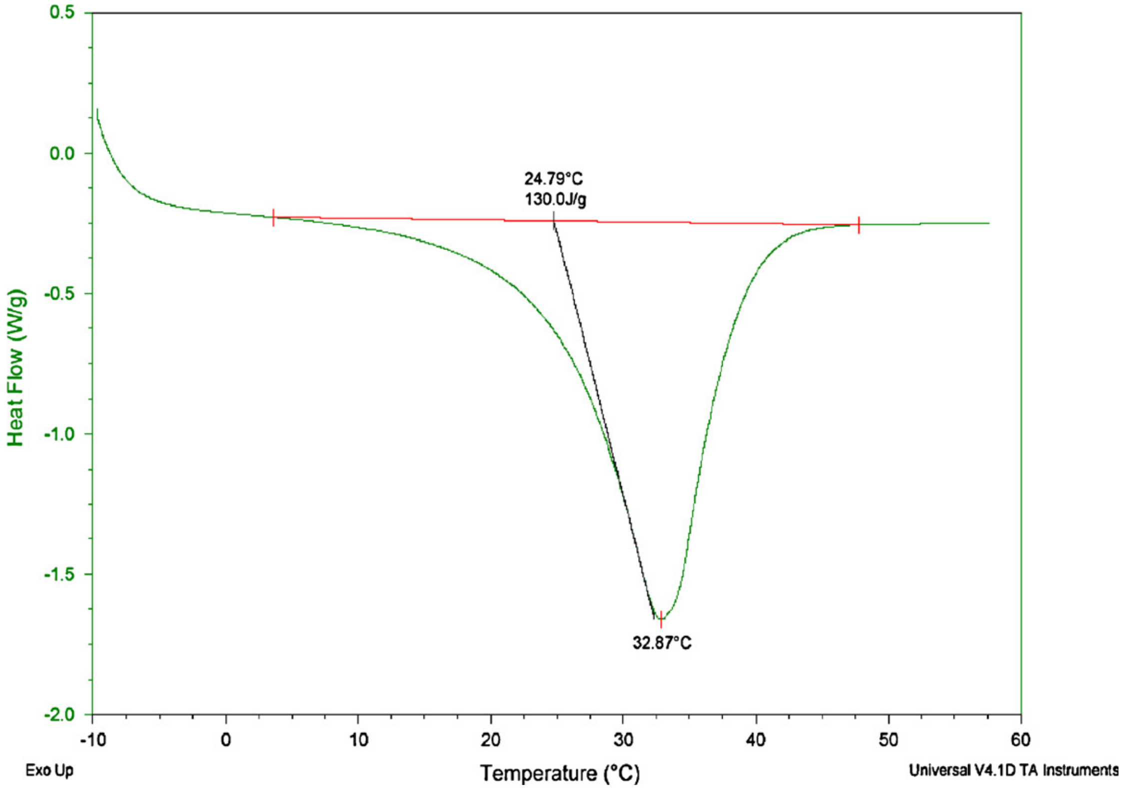

Fig. 6. DSC measurement curves of latent heat of fusion and melting temperature of $CaCl_2 \cdot 6H_2O$ at the 300th cycle.

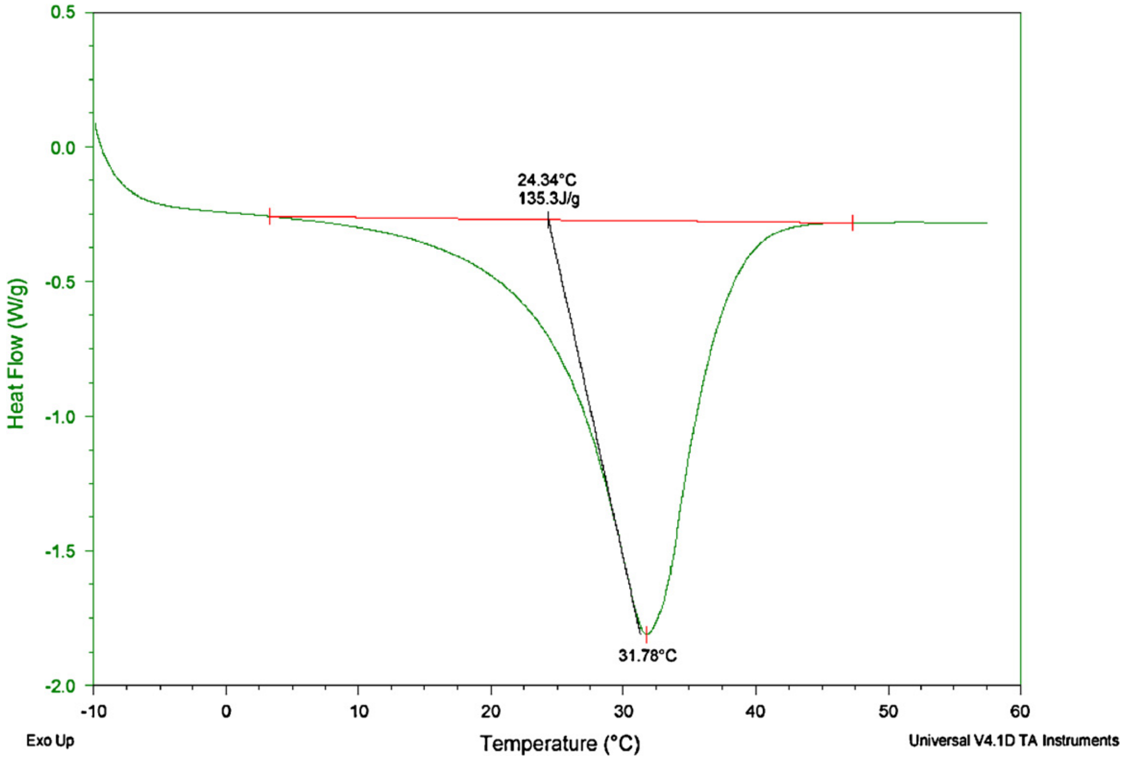

Fig. 7. DSC measurement curves of latent heat of fusion and melting temperature of $CaCl_2 \cdot 6H_2O$ at the 400th cycle.

Please cite this article as: V.V. Tyagi, D. Buddhi, Sol. Energy Mater. Sol. Cells (2008), doi:10.1016/j.solmat.2008.02.021

3. Results and discussion

The latent heat of fusion and freezing temperature of $Cacl_2\cdot6H_2O$ was measured between 0–1000 test cycles (0th, 100th, 200th, 300th, 400th, 500th, 600th, 700th, 800th, 900th and 1000th) and are given in Table 3. The value at the zeroth cycle was taken as the reference value. The DSC curves of the 1st to 1000th cycles showing variation of heat flow rate against temperature of $Cacl_2\cdot6H_2O$ are shown in Figs. 2–13.

As one can see from Table 3, the latent heat of fusion of $CaCl_2\cdot6H_2O$ has a variation of 10.4% (10th cycle) and −6.4% (100th cycle) in respect of the 1st cycle value. It may be due to the fact that a small amount of sample was used while no major variations were observed after 100th cycle. Melting temperature variations have been recorded from Figs. 2–13, i.e. 3.59 °C after the 10th cycle, 3.88 °C after the 100th cycle, 1.36 °C after the 200th cycle, 1.53 °C after the 300th cycle, 1.06 °C after the 400th cycle, 1.28 °C after the 500th cycle, 1.15 °C after the 600th cycle, 1.0 °C after the

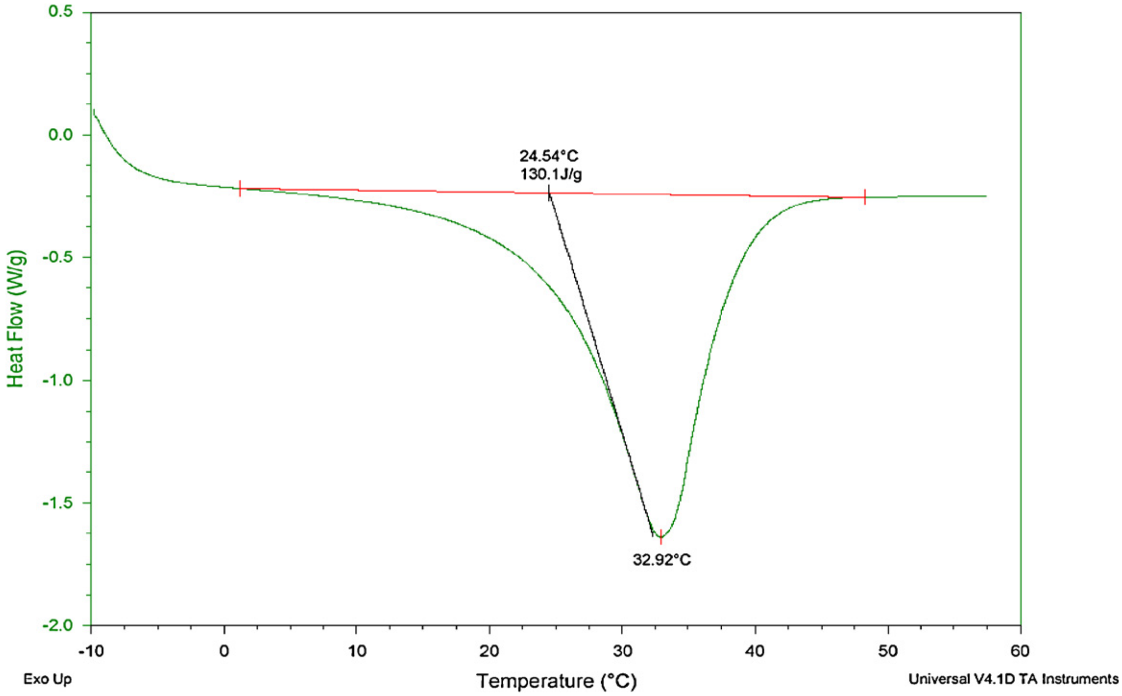

Fig. 8. DSC measurement curves of latent heat of fusion and melting temperature of $CaCl_2\cdot6H_2O$ at the 500th cycle.

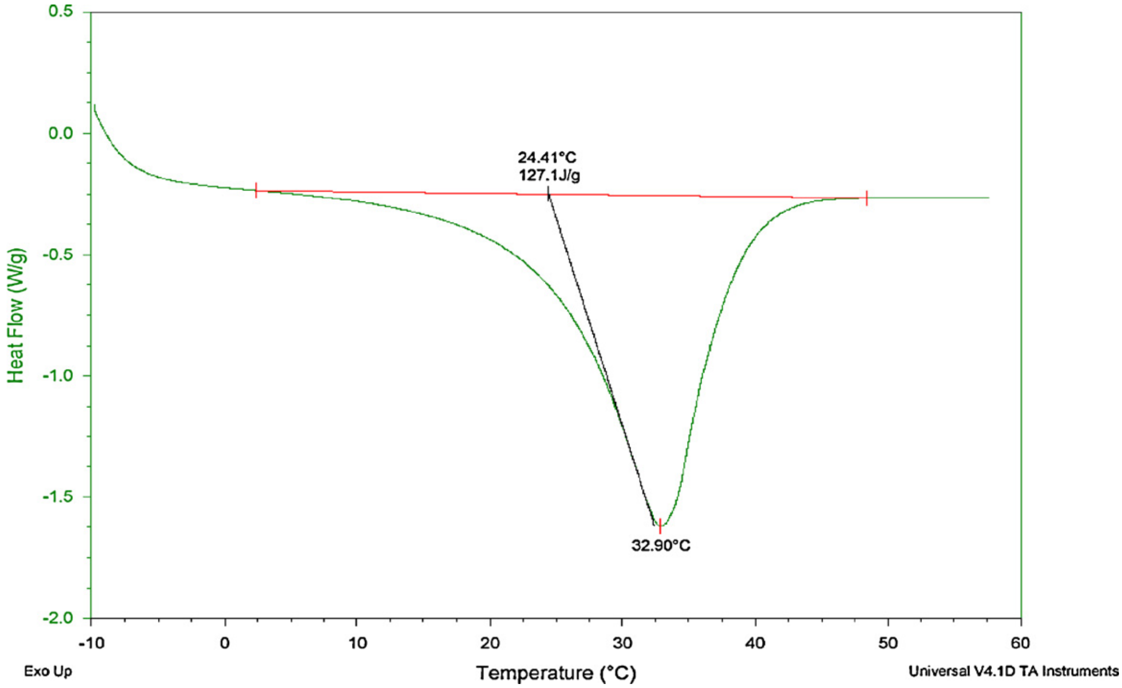

Fig. 9. DSC measurement curves of latent heat of fusion and melting temperature of $CaCl_2\cdot6H_2O$ at the 600th cycle.

Please cite this article as: V.V. Tyagi, D. Buddhi, Sol. Energy Mater. Sol. Cells (2008), doi:10.1016/j.solmat.2008.02.021

700th cycle, 0.89 °C after the 800th cycle, 0.69 °C after the 900th cycle, and did not show any variation in the 1000th cycle for the $CaCl_2 \cdot 6H_2O$ with respect to the 1st cycle melting temperature value. All the results of melting temperatures are given in Table 3.

These results indicate that the change in melting temperature of the $CaCl_2 \cdot 6H_2O$ with the increasing number of thermal cycles is not regular. However, no major change in the melting temperature of the $CaCl_2 \cdot 6H_2O$ was noticed. Variation in the range of 1–1.5 °C temperature has been noticed after the 1000th cycle. Also, it can be noted that the changes in the melting temperature of the tested PCM after approximately a 3.5-year utility period corresponds to about 300 melt/freeze cycles in a year, which is at an accepted level for a PCM which will be used in a latent heat energy storage system.

Table 3 depicts the effect of thermal cycling on the thermal stability of the $CaCl_2 \cdot 6H_2O$ in view of the changes in its latent heat of fusion. It can be observed from Table 3 and Figs. 2–13 that latent heat of fusion (ΔH_{fusion}) has variations of 10.4%, −6.4%, 4%, 4%, 8%, 4%, 1.6%, 3.6%, 3.7%, −2.2% and 0.3% after the 10th, 100th, 200th, 300th, 400th, 500th, 600th, 700th, 800th, 900th and

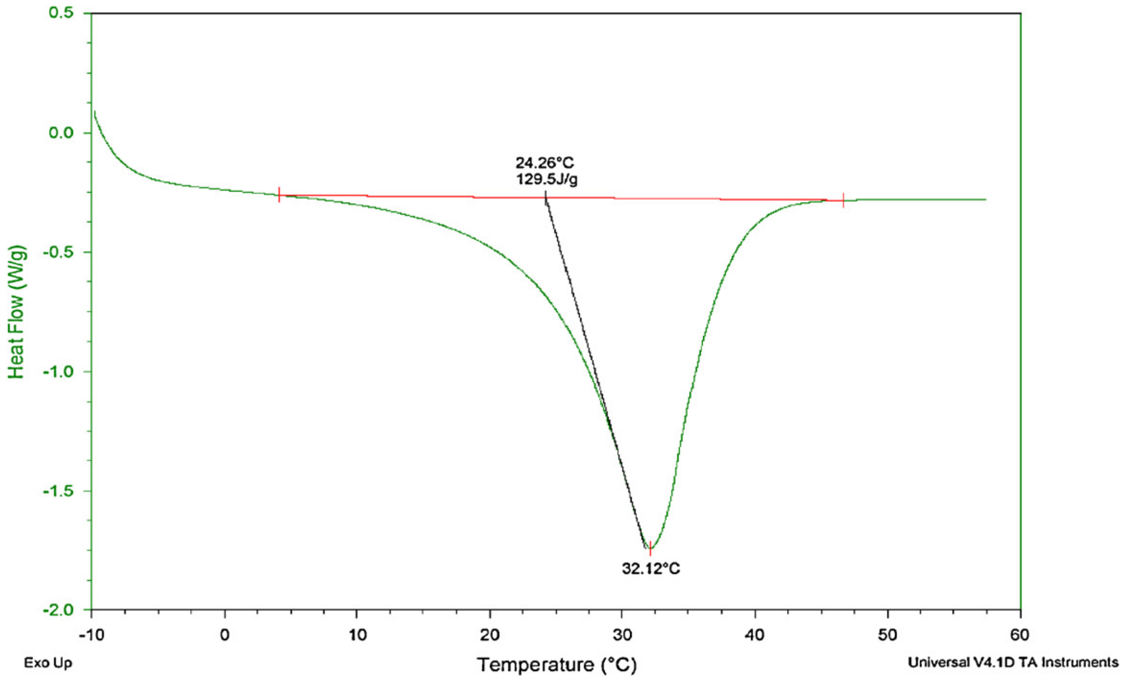

Fig. 10. DSC measurement curves of latent heat of fusion and melting temperature of $CaCl_2 \cdot 6H_2O$ at the 700th cycle.

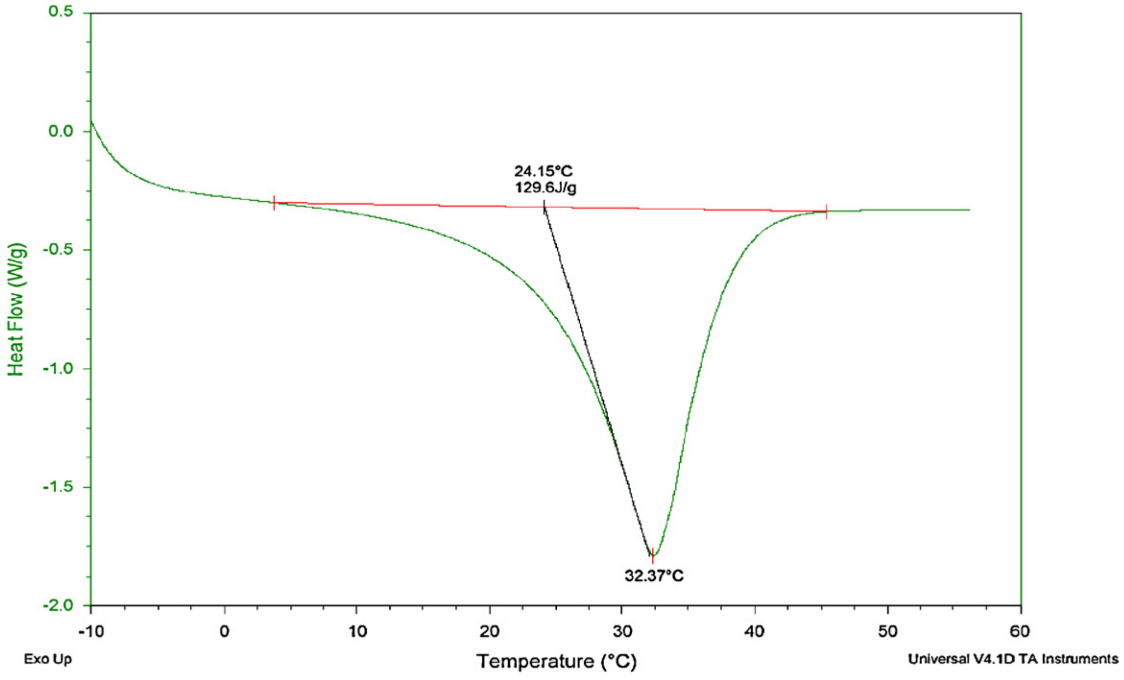

Fig. 11. DSC measurement curves of latent heat of fusion and melting temperature of $CaCl_2 \cdot 6H_2O$ at the 800th cycle.

Please cite this article as: V.V. Tyagi, D. Buddhi, Sol. Energy Mater. Sol. Cells (2008), doi:10.1016/j.solmat.2008.02.021

1000th cycles, respectively, in respect of the 1st cycle for the $CaCl_2 \cdot 6H_2O$. The positive and negative results show the higher and lower latent heat of fusion in comparison to the 1st cycle test result, i.e. $CaCl_2 \cdot 6H_2O$ has no regular change with the increasing number of the thermal cycles.

4. Conclusion

After repeated accelerated thermal cycles, experimental results show a good stability of thermal properties i.e. the latent heat of fusion and the melting temperature. The variation in latent heat of

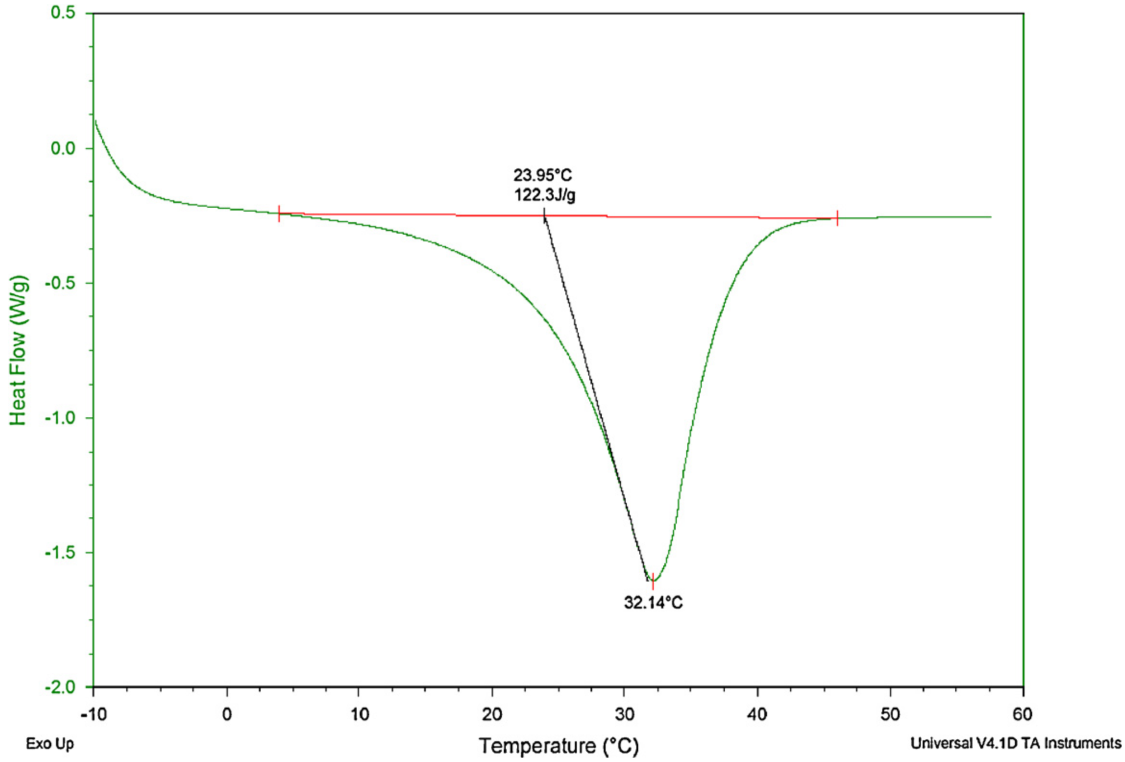

Fig. 12. DSC measurement curves of latent heat of fusion and melting temperature of $CaCl_2 \cdot 6H_2O$ at the 900th cycle.

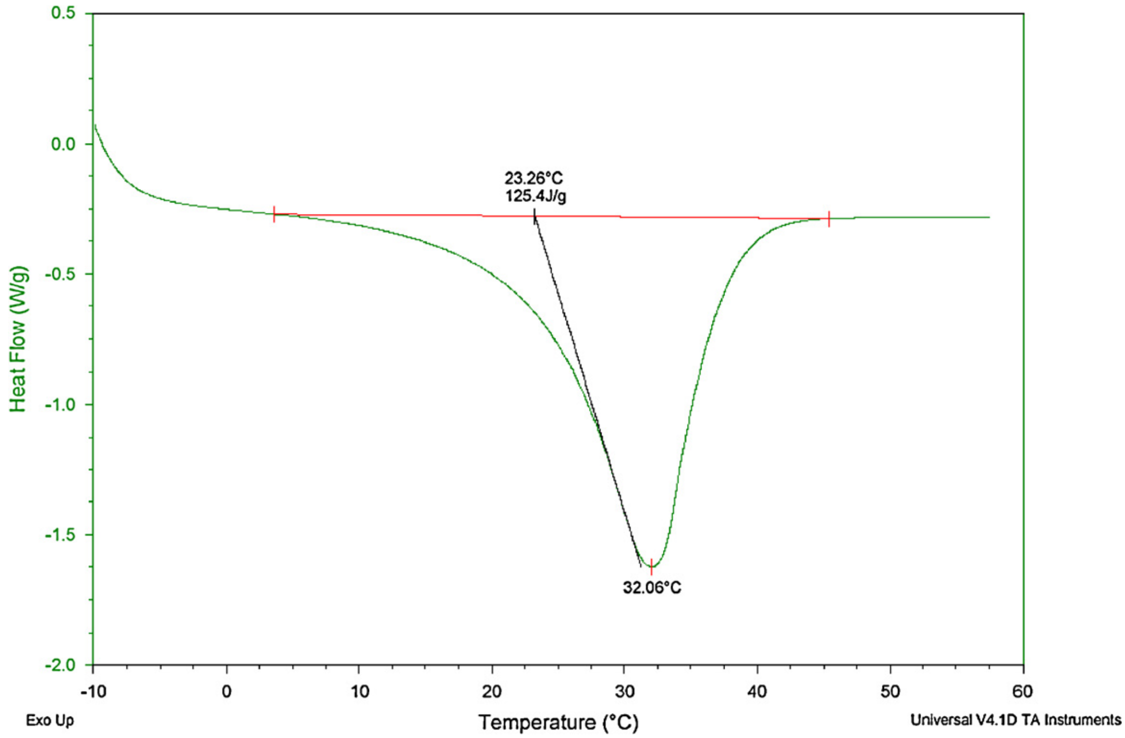

Fig. 13. DSC measurement curves of latent heat of fusion and melting temperature of $CaCl_2 \cdot 6H_2O$ at the 1000th cycle.

Please cite this article as: V.V. Tyagi, D. Buddhi, Sol. Energy Mater. Sol. Cells (2008), doi:10.1016/j.solmat.2008.02.021

fusion and melting temperature may be due to improper crystallization of the PCM as only a few milligrams quantity was used. Based on laboratory tests, calcium chloride hexahydrate is found to be a promising PCM for heating and cooling process in building applications.

References

[1] B. Zalba, J. Marın, L.F. Cabeza, Appl. Therm. Eng. 23 (2003) 251.
[2] K.C. Ting, P.N. Giannakakas, S.G. Gilbert, Sol. Energy 39 (2) (1987) 79.
[3] G.P. Fernanda, Sol. Energy 41 (2) (1988) 193.
[4] S.D. Sharma, D. Buddhi, R.L. Sawhney, Sol. Energy 66 (1999) 483.
[5] A. Sharma, S.D. Sharma, D. Buddhi, Energy Convers. Manage. 43 (2002) 1923.
[6] C.K. Jotshi, Int. J. Sol. Energy Eng. 120 (1998) 20.
[7] T. Wada, R. Yamamoto, Y. Matsuo, Sol. Energy 33 (3–4) (1984) 373.
[8] F.O. Cedeno, M.M. Prieto, A. Espina, JR. Garcia, Thermochim. Acta 369 (2001) 39.
[9] A. Hasan, Sol. Energy 52 (1994) 143.
[10] J.J. Zhang, JL. Zhang, SM. He, KZ. Wu, XD. Liu, Thermochim. Acta 369 (2001) 157.
[11] A. Sari, Energy Convers. Manage. 44 (2003) 2277.
[12] A. Sari, A. Omar, H. Sari, Energy Convers. Manage. 45 (2004) 365.
[13] M. Dimaano, A. Escoto, Energy 23 (1998) 421.

Please cite this article as: V.V. Tyagi, D. Buddhi, Sol. Energy Mater. Sol. Cells (2008), doi:10.1016/j.solmat.2008.02.021