Renewable Energy 76 (2015) 465–469

Contents lists available at ScienceDirect

Renewable Energy

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

Corrosion of metal containers for use in PCM energy storage

Gerard Ferrer [a, b, 1], Aran Solé [a, b, 1], Camila Barreneche [a, b, c, d, 1, 2], Ingrid Martorell [a, b, 1], Luisa F. Cabeza [a, b, *]

[a] GREA Innovació Concurrent, Universitat de Lleida, Edifici CREA, Pere de Cabrera s/n, 25001 Lleida, Spain
[b] Department of Materials Science & Metallurgical Engineering, Universitat de Barcelona, Martí i Franqués 1-11, 08028 Barcelona, Spain
[c] Department of Materials Science & Metallurgical Engineering, Universitat de Barcelona, Barcelona, Spain
[d] Martí i Franqués 1-11, 08028 Barcelona, Spain

ARTICLE INFO

Article history:
Received 21 July 2014
Accepted 13 November 2014
Available online

Keywords:
Solar energy
Thermal energy storage (TES)
Comfort building applications
Phase change materials (PCM)
Metal corrosion

ABSTRACT

In recent years, thermal energy storage (TES) systems using phase change materials (PCM) have been widely studied and developed to be applied as solar energy storage units for residential heating and cooling. These systems performance is based on the latent heat due to PCM phase change, a high energy density that can be stored or released depending on the needs. PCM are normally encapsulated in containers, hence the compatibility of the container material with the PCM has to be considered in order to design a resistant container. Therefore, the main aim of this paper is to study the corrosion effects when putting in contact five selected metals (aluminium, copper, carbon steel, stainless steel 304 and stainless steel 316) with four different PCM (one inorganic mixture, one ester and two fatty acid eutectics) to be used in comfort building applications. Results showed corrosion on aluminium specimens. Hence caution must be taken when selecting it as an inorganic salt container. Despite copper has a corrosion rate range of 6–10 mg/cm^2 yr in the two fatty acid formulations tested, it could be used as container. Stainless steel 316 and stainless steel 304 showed great corrosion resistance (0–1 mg/cm^2 yr) and its use would totally be recommended with any of the studied PCM.

1. Introduction

Energy policies are nowadays focused on using solar energy and reusing the waste heat of the industry to use them as a primary energy source. This way, fossil fuel and electricity consumption can be reduced, and consequently, CO_2 emissions too. To accomplish these aims, new technologies such as thermal energy storage (TES) systems have been designed to be implemented in applications such as cold storage systems, solar power plants or comfort building services [1,2,4,7,11,12,14].

TES systems present phase change materials (PCM) as one of the possible solutions to improve energy efficiency and reduce electricity consumption. These materials can provide high energy density due to the latent heat produced during the phase change, energy that can be released or stored depending on the needs. Some researchers have studied the addition of PCM in different thermal energy storage units. In all the possible applications PCM are normally encapsulated in containers, therefore the main interest remains on designing a lightweight, non-corrosive, high conductive and low cost container [6,9,10,17].

Different type of chemicals such as inorganic salts, organic mixtures, paraffins and water are nowadays used as PCM for different heat storage applications. This study is focused on selecting a metal container material for comfort building applications, thus PCM were selected according to their melting points, which needed to be in the 20 °C–25 °C range. It is widely known that most inorganic salts are corrosive to metals but less information could be found about the effect organic materials or fatty acids have on metals; hence an accurate selection of the PCM containers must be carried out during the design stage of the TES system.

The aim of the present paper is to study the corrosion experienced by five selected metals in contact with four different PCM (one inorganic mixture, one ester and two fatty acid eutectics) to be implemented as containers for thermal comfort systems in building applications. Stainless steel 316, stainless steel 304, carbon steel,

* Corresponding author. GREA Innovació Concurrent, Universitat de Lleida, Lleida, Spain. Tel.: +34 973 003576; fax: +34 973 003575.
E-mail addresses: c.barreneche@ub.edu (C. Barreneche), lcabeza@diei.udl.cat (L.F. Cabeza).
[1] Tel.: +34 973 003576; fax: +34 973 003575.
[2] Tel.: +34 934 021298.

http://dx.doi.org/10.1016/j.renene.2014.11.036
0960-1481/

copper and aluminium were the metals considered to be used as containers.

2. Materials

2.1. Phase change materials

Four PCM formulations were under study in this paper. Two of them are commercial PCM: SP21E commercialized by Rubitherm and PureTemp 23 produced by PureTemp [15,16]. The other two were fatty acid eutectics prepared at the University of Lleida based on formulations available in literature studies [8] with similar phase change temperature ranges.

The composition of each formulation is shown in Table 1.

2.2. Metals

The five metals under study are samples of stainless steel 316 (SS-316), stainless steel 304 (SS-304), copper, aluminium and carbon steel, as shown in Fig. 1. The specimen size used was approximately 5 × 1 × 0.1 cm.

3. Methodology

All the metal specimens were polished and cleaned with acetone in order to remove all the oils and impurities from the cutting process. Afterwards, specimens were weighed in a Mettler Toledo precision balance (4 decimals) before starting the corrosion test. Once the specimens had been weighed, they were immersed in glass test tubes containing PCM to combine each metal specimen with the four different PCM formulations. All tubes were covered with a plastic lid to avoid contact with environmental agents and, as the phase change temperature of all the PCM was around 22 °C, they were kept in a stove at 38 °C, ensuring all PCM were always at liquid phase.

The methodology implies analysing the combination metal–PCM after 1 week (7 days), 4 weeks (28 days) and 12 weeks (84 days) [5]. A total of 60 tubes (20 per week considered) were prepared and placed in a stove in order that temperature remained constant. When removing the test tubes, the evolution of the corrosion rate with time was studied. Qualitative analyses were also performed seeking for bubbles, surface changes, colouration changes, precipitation and pitting. The ASTM G1-03 standard [3] was followed to treat the specimens, cleaning them with appropriate acid solutions and polishing with abrasive paper when necessary. After that, specimens were dried with soft paper and weighed.

The specimen mass change (Δm) and the corrosion rate (CR) were calculated to evaluate the experimental logged data. The mass loss was calculated following equation (1), considering the initial mass, $m(t_0)$, and the weight obtained after 1, 4 and 12 weeks $m(t)$, respectively.

Table 1
Composition of the PCM designed for cold storage applications.

PCM composition	Family type	Composition type	Melting point (°C)	Heat of fusion (kJ/kg)
SP21E	Salt	Inorganic mixture	21	160
PureTemp 23	Salt	Ester	23	200
Capric acid (73.5%) + myristic acid (26.5%)	Fatty acid	Eutectic	21.4	152
Capric acid (75.2%) + palmitic acid (24.8%)	Fatty acid	Eutectic	22.1	153

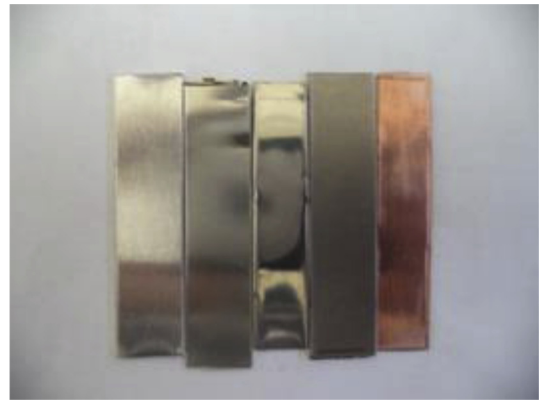

Fig. 1. Metal specimens studied. From left to right: aluminium, stainless steel 316, stainless steel 304, carbon steel and copper.

$$\Delta m = m(t_0) - m(t) \quad (1)$$

The corrosion rate (CR) considers the mass loss (Δm), the metal sample surface area (A) and the experimental time ($t_0 - t$) as equation (2) shows.

$$\mathrm{CR} = \frac{\Delta m}{A \cdot (t_0 - t)} \quad (2)$$

4. Results and discussion

As it has already been explained, the specimens were removed from the stove after 1, 4 and 12 weeks. The main qualitative observations are next exposed.

4.1. Remarkable observations

The carbon steel specimens immersed in SP21E showed corrosion signs since week one. The test tubes containing the specimens presented yellow tonality after the first week of test, fact that was also observed after the 4th test week, with an evident increase on the colour intensity and bubbling in the test tubes. After the 12th week of test, the colouration had turned into orange (in the web version) and the test tubes also presented bubbling, as shown in Fig. 2. Surface degradation was also noticed at this point.

The capric (75.2%)/palmitic (24.8%) eutectic test tubes where copper specimens were immersed presented blue colouration after the 1st week of test, colouration that gained in intensity and turned into a greener tonality as weeks passed by. Some brightness loss was also noticed since the 1st week removal, becoming more important with time. Fig. 3 illustrates the explained on the copper sample removed after 12 weeks.

The copper specimens immersed in the capric (73.5%)/myristic (23.5%) eutectic experienced the same phenomena as the ones immersed in the other fatty acid formulation. Blue colouration was observed in the tests tubes since the 1st week, gaining intensity and green tonality with time. Brightness loss was also noticed, mainly in the specimen removed on the 12th week of experimentation, as shown in Fig. 4.

The test tubes containing aluminium specimens immersed in SP21E showed grey colouration and bubbling from the 4th week on. After 12 weeks, the grey colouration and bubbling were notorious, and there was partial solidification of the PCM and the corroded metal. Surface degradation and pitting were evident on the specimen's surface as displayed in Fig. 5.

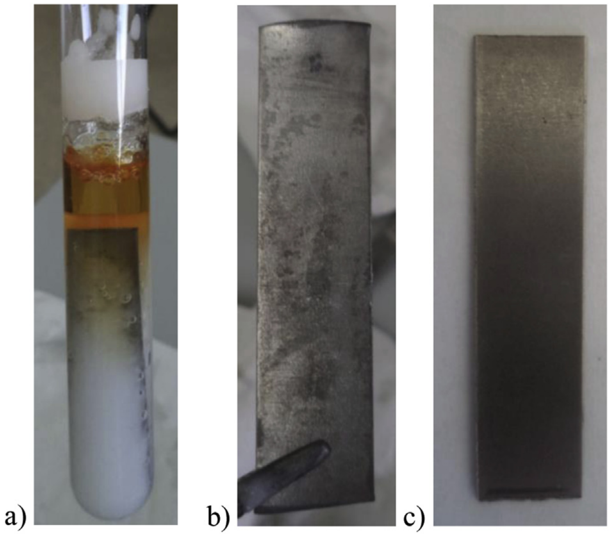

Fig. 2. a) Carbon steel specimen immersed in SP21E after 12 weeks. b) The same carbon steel specimen once cleaned. c) Non-tested carbon steel specimen.

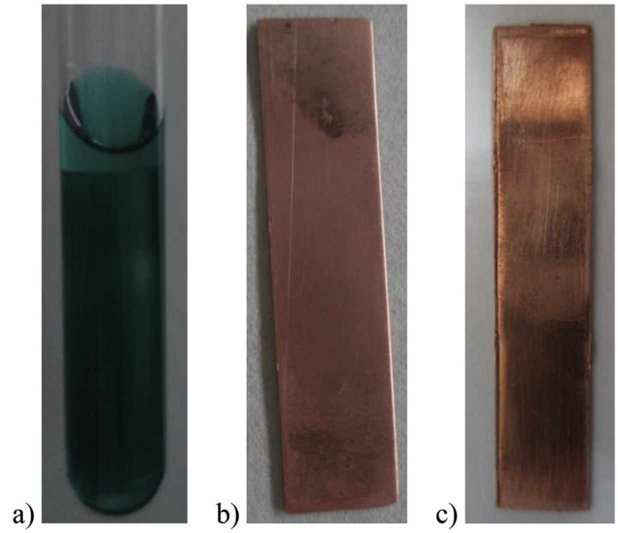

Fig. 4. a) Copper specimen immersed in capric (73.5%)/myristic (23.5%) eutectic after 12 weeks. b) 12th week copper specimen after the cleaning process. c) Non-corroded copper specimen.

4.2. Results

Corrosion rates (CRs) of all specimens were calculated. The guide for corrosion weight loss used in industry (Table 2) is followed as reference to evaluate the results obtained [12]. It is important to point out here that the following numerical results are given as approximate results and are tied to the experimental limitations of the standard followed to do the experimentation. However, these values allow recommending the useful metal specimens due to the low levels or no evidences of corrosion, which indeed is the main goal of this study.

The enclosed Fig. 6 shows the CR evolution of the metals immersed in SP21E. A common pattern is seen in all metal curves but aluminium. In general, CRs decrease in a similar way from the 1st week until the 12th. The exception is aluminium, which is corroded mostly after the 4th week of test, thus according to the CR values achieved as well as to the surface degradation and pitting observed, caution would be recommended on its application as container. Copper and the two stainless steels do not show important CRs and their tendencies would recommend its use for long term services. Carbon steel presented higher CR values after 1 week of test (observed as the yellow colouration of the solution) than after 4 and 12 weeks. However, this tendency is not enough to recommend this material as SP21E container, hence caution must be taken when selecting it for long term uses.

The data obtained for PureTemp 23 agrees with the lack of corrosion traces explained on the former paragraphs and do not show corrosion on any of the metals. The low positive values obtained, which are in the 0–1 mg/cm^2 yr range, are considered result of surface cleaning. Therefore, all metals would be recommended to be used as PureTemp 23 containers for long term services.

Fig. 7 presents the CR evolution with time of all the metals immersed in the capric (75.2%)/palmitic (24.8%) eutectic formulation. The mass loss and CR obtained for the metal specimens immersed in this acid mixture showed that copper is the only material that experienced a remarkable weight loss during the 12 weeks of test. It is important to point out here that copper's CR at

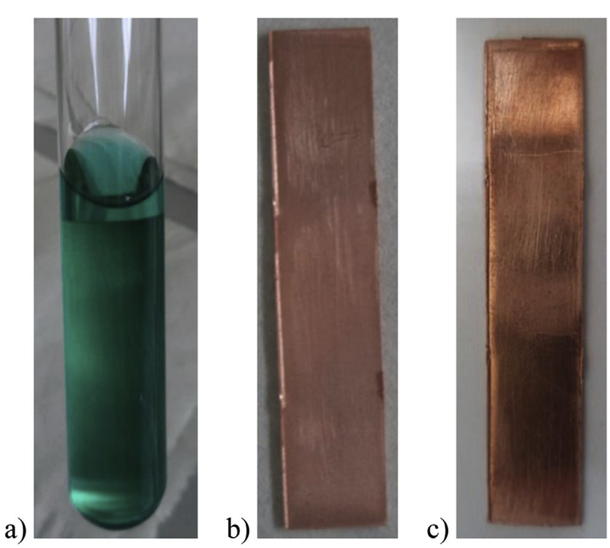

Fig. 3. a) Copper specimen immersed in capric (75.2%)/palmitic (24.8%) acid mixture after 12 weeks. b) The same specimen cleaned. c) Non-tested copper specimen.

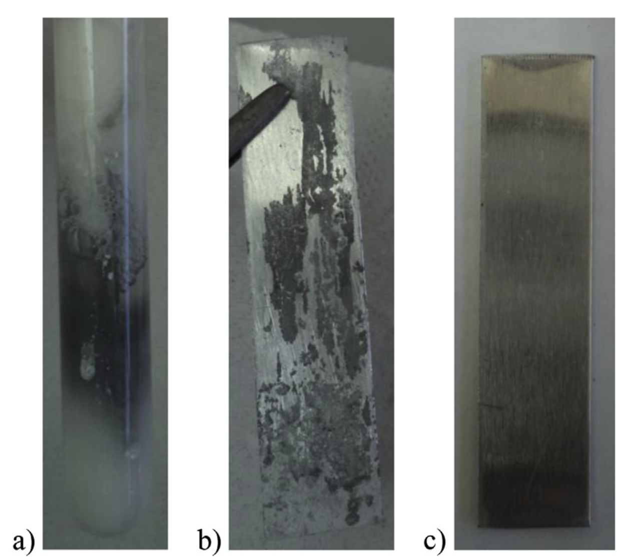

Fig. 5. a) Aluminium specimen immersed in SP21E after 12 weeks. b) 12th week aluminium specimen once cleaned. c) Non-tested aluminium specimen.

Table 2
Guide for corrosion weight loss used in the industry [13].

mg/cm^{2}yr	Recommendation
>1000	Completely destroyed within days
100–999	Not recommended for service greater than a month
50–99	Not recommended for service greater than 1 yr
10–49	Caution recommended, based on the specific application
0.3–9.9	Recommended for long term service
<0.2	Recommended for long term service; no corrosion, other than as a result of surface cleaning, was evidenced

week four could not be calculated due to experimental problems during tests, but the twelve week value is relevant enough to draw the corresponding conclusions. A similar CR profile to the one obtained in the capric (73.5%)/myristic (23.5%) eutectic should be expected. Carbon steel presented remarkably high CR value after 1 week compared to the other weeks, but this first high value should be taken with caution. Some passivation may be happening in this early stage of the test, but no further chemical analyses were conducted to determine the concrete phenomena happening there as it was not included in the ASTM standard followed, thus we cannot say there is passivation and we take it as a limitation of the experimental process. No corrosion traces are observed on the 4th and 12th week results and the CRs obtained are below 0.2 mg/cm^2 yr, therefore they are not taken as corrosion evidence. Further, according to the obtained values and also to the blue colouration observed in the copper test tubes, caution would be recommended in copper's long term use as a container while carbon steel could be profitable for long period services. The other three metals under study, stainless steel 304, stainless steel 316 and aluminium, showed really low or null CR values during the 12 experimental weeks result of the cleaning processes when removing them from the test tubes. Consequently, they are considered as useful containers for the capric (75.2%)/palmitic (24.8%) eutectic formulation.

The experimental data logged for the capric (73.5%)/myristic (23.5%) eutectic is presented in Fig. 8. A common pattern is found on the copper and carbon steel curves as their CRs step down from the 1st week on, keeping a quite constant value after the 4th week test point. Copper is the only evident corroded metal, which is in accordance with the blue colouration the test tubes presented. Again, the 1st week value for carbon steel could be due to passivation but, as explained in the former paragraph, it is taken as a limitation of the process. Moreover, no corrosion evidences were observed on the 4th and 12th week carbon steel specimens, thus carbon steel mass losses during this last 8 week period are explained as sample cleaning consequences. Due to its low and null CR values and the tendency they followed with time, carbon steel along with aluminium and both stainless steels would be recommended as PCM containers for long term use services. However, the values achieved by the copper specimens along with the remarkable blue colouration observed in the test tubes are considered enough to recommend caution on its use depending on the application it is thought to be implemented in.

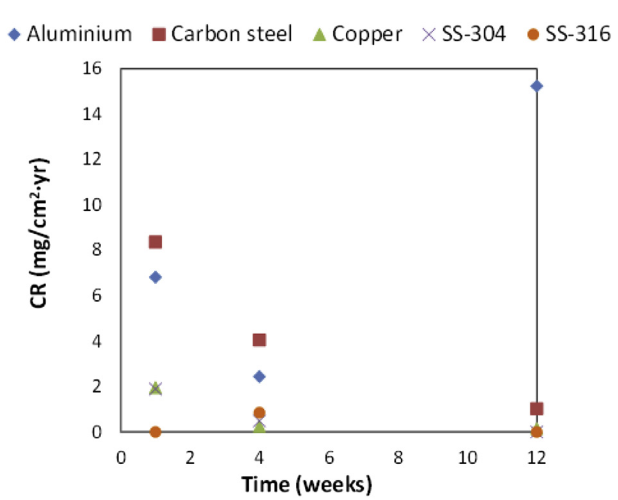

Fig. 6. Corrosion rate vs time of all the metals immersed in SP21E.

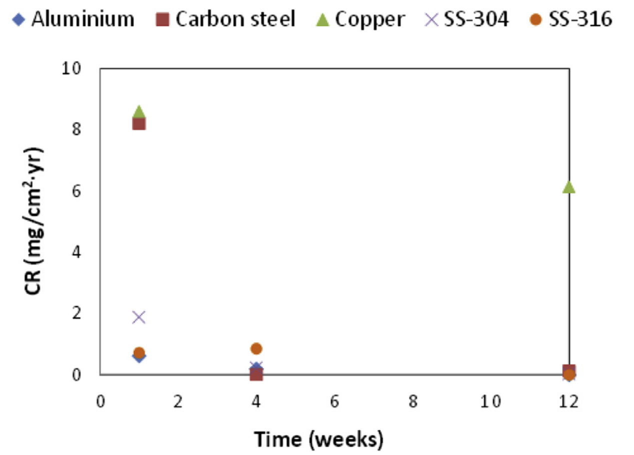

Fig. 7. Corrosion rate vs time of all the metals immersed in the capric (75.2%)/palmitic (24.8%) acid mixture.

5. Conclusions

This study analyses the suitability of five different metals to contain four different PCM formulations, considering the corrosion degradation through time that specimens of these metals suffer when they are immersed in the PCM during 12 weeks. In addition, visual phenomena such as bubbling, colouration, surface degradation and pitting were also analysed.

The first conclusion drawn from the displayed results is that the ester PureTemp 23 is the only PCM to which all the studied metals are resistant to. Therefore all of them can be used in long term service installations to contain this PCM.

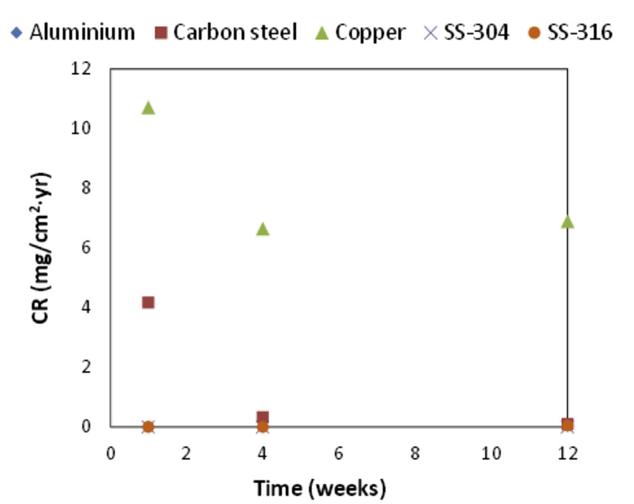

Fig. 8. Corrosion rate vs time of all the metals immersed in the capric (73.5%)/myristic (23.5%) acid mixture.

The inorganic salt SP21E has a non-despicable corrosive effect on aluminium, reason why caution is recommended on its application as this PCM container. However, its use should be avoided as better matches have been found. In addition, the corrosion rates obtained for carbon steel were not remarkably high, however corrosion signs could be observed on the carbon steel specimens, hence caution is recommended to be taken when applying it for long term service installations. The other three metals under study, stainless steel 304, stainless steel 316 and copper, showed great resistance to this salt's corrosive effects so its suitability to be used as this inorganic salt container is ensured.

Copper was corroded following a very similar pattern by both own fatty acid formulations but, despite the corrosion rate values being quite low in both cases and due to the observations done during the whole experimentation, caution is recommended to be taken when applying this metal as a long term container of any of these two eutectic formulations. On the other hand, none of the other metals are considered to be corroded by any of the fatty acid eutectics, hence, its use would totally be recommended for long term services.

Acknowledgements

The work is partially funded by the Spanish Government (ENE2011-28269-C03-02 and ENE2011-22722). The authors would like to thank the Catalan Government for the quality accreditation given to their research groups GREA (2014 SGR 123) and research group DIOPMA (2014 SGR 1543). Aran Solé would like to thank the Departament d'Universitats, Recerca i Societat de la Informació de la Generalitat de Catalunya for her research fellowship. The research leading to these results has received funding from the European Union's Seventh Framework Programme (FP7/2007-2013) under grant agreement n° PIRSES-GA-2013-610692 (INNOSTORAGE).

References

[1] International Energy Agency (IEA). Technology roadmap. Energy storage 2014.
[2] Zhao W, France DM, Yu W, Kim T, Singh D. Phase change material with graphite foam for applications in high-temperature latent heat storage systems of concentrated solar power plants. Renew Energy 2014;69:134–46.
[3] ASTM International G1-03. Standard practice for preparing, cleaning and evaluating corrosion test specimens. 2011.
[4] Azzouz K, Leducq D, Gobin D. Performance enhancement of a household refrigerator by addition of latent heat storage. Int J Refrig 2008;31:892–901.
[5] Cabeza LF, Illa J, Roca J, Badia F, Mehling H, Hiebler S, et al. Immersion corrosion tests on metal-salt hydrate pairs used for latent heat storage in the 32 to 36 °C temperature range. Mater Corros 2001;52:140–6.
[6] Gil A, Medrano M, Martorell I, Lázaro A, Dolado P, Zalba B, et al. State of the art on high temperature thermal energy storage for power generation. Part 1 – concepts, materials and modelization. Renew Sustain Energy Rev 2010;14:31–55.
[7] Gin B, Farid MM. The use of PCM panels to improve storage condition of frozen food. J Food Eng 2010;100:372–6.
[8] Kenisarin M, Mahkamoc K. Solar energy storage using phase change materials. Renew Sustain Energy Rev 2007;11:1913–65.
[9] Keles S, Kaygusuz K, Sari A. Lauric and myristic acids eutectic mixture as phase change material for low-temperature heating applications. Int J Energy Res 2005;29:857–70.
[10] Medrano M, Gil A, Martorell I, Potau X, Cabeza LF. State of the art on high-temperature thermal energy storage for power generation. Part 2 – case studies. Renew Sustain Energy Rev 2010;14:56–72.
[11] Oró E, Miró L, Farid MM, Cabeza LF. Improving thermal performance of freezers using phase change materials. Int J Refrig 2012;35(4):984–91.
[12] Oró E, Miró L, Farid MM, Cabeza LF. Thermal analysis of a low temperature storage unit using phase change materials without refrigeration system. Int J Refrig 2012;35(6):1709–14.
[13] Sastri VS, Ghali E, Elboujdaini M. Corrosion, prevention and protection. Practical solutions. John Wiley & Sons; 2007.
[14] Stritih U, Butala V. Energy saving in building with PCM cold storage. Int J Energy Res 2007;31:1532–44.
[15] Rubitherm datasheet. Available online, 15/10/2013. http://www.rubitherm.de/english/.
[16] PureTemp datasheet. Available online, 15/10/2013. http://www.puretemp.com/technology.html.
[17] Cabeza LF, Castell A, Barreneche C, de Gracia A, Fernández AI. Materials used as PCM in thermal energy storage in buildings: a review. Renew Sustain Energy Rev 2011;15:1675–95.