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Corrosion of metal containers for use in PCM energy storage

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Abstract

In recent years, thermal energy storage (TES) systems using phase change materials (PCM) have been widely studied and developed for comfort building applications. The PCM are normally encapsulated in containers, hence the compatibility of the container material with the PCM has to be considered. Therefore, the main aim of this paper is to study the corrosion effect that four different PCM (one inorganic mixture, one ester and two fatty acid eutectics) have on five selected metals to be used in buildings comfort applications. Results showed corrosion on aluminium specimens immersed in SP21E, hence caution must be taken when selecting it as inorganic salt container. Despite copper has a corrosion rate range of 6-10 $mg/cm^2 \cdot yr$ 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 $mg/cm^2 \cdot yr$) and its use would totally be recommended with any of the studied PCM.

1. Introduction

Significant development on energy storage systems has been shown over the recent years. Comfort building installations and transportation are examples of applications that have been modified with thermal energy storage (TES) systems in order to improve the energy efficiency and decrease electricity consumption (Azzouz et al., 2008; Gin et al., 2010; Oró et al., 2012a. 2012b).

The heat storage in TES systems is based on the use of phase change materials (PCM), and more specifically, on the latent heat of the phase change, which provides high energy densities during the phase change, energy that can be stored or released depending on the needs. Its use in TES systems has been studied by many researchers and they are being implemented in different systems, active or passive, regarding cold, medium and high temperature storage as well as comfort building applications. In all these applications PCM are normally encapsulated in containers, therefore, the main interest remains on designing a non-corrosive, lightweight, high conductive and low cost container (Gil et al. 2010; Medrano et al. 2010).

Different material types are nowadays used in systems applied to comfort building applications. Organic mixtures, paraffins, salt hydrates, organic and inorganic eutectics are examples of materials that have been used as PCM due to its high latent heat values. However, inorganic materials are commonly corrosive to metals, thus an accurate selection of the material container is needed in each application.

The aim of the present paper is to study the compatibility of five different metals to be used as container materials of four different PCM for comfort systems in building applications.

2. Materials

2.1. Phase change materials

Four different PCM were used in this study, all of them with melting points in the range 20-24 ºC. Two of them were commercial PCM, SP21E by Rubitherm and PureTemp 23 by PureTemp, and the other two were fatty acid eutectics prepared at the University of Lleida based on formulations found in literature studies (Kenisarin et al. 2007). Table 1 shows the properties and composition of each formulation.

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

PCM composition	Family type	Composition type	Melting point (ºC)	Heat of fusion (kJ/kg)
SP21E	Salt	Inorganic mixture	21	160
PureTemp23	Organic	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

2.2. Metals

The metal container candidates selected were: stainless steel 316, stainless steel 304, carbon steel, copper and aluminium. The size of each specimen used was 5 x 1 x 0.1 cm.

3. Methodology

Metal specimens needed some pretreatment before combining them with each one of the selected PCM. These previous stages consisted on polishing the specimens and cleaning them with acetone to remove all the remaining oils and impurities from the cutting process. The next step was to weigh each metal specimen in a Mettler Toledo precision balance (4 decimals). At this point, the specimens were ready to be immersed in glass test tubes containing PCM so that each metal was combined with the four different PCM formulations. To avoid contact with environmental agents that could damage the specimens, the test tubes were covered with a plastic lid and kept in a stove at 38 ºC to ensure all PCM were at liquid state.

A total of 60 test tubes were prepared and placed in the stove in order to keep them at constant temperature. The corrosion rate with time was studied following the ASTM G1-03 standard (ASTM International G1-03. 2011), a methodology that implied analysing each metal-PCM combination after 1 week (7 days), 4 weeks (28 days) and 12 weeks (84 days) (Cabeza et al. 2001). Importance was also given to bubbles, colour changes, surface degradation, precipitation or pitting as qualitative corrosion signs. Every specimen was cleaned with the corresponding acid solution and polished with abrasive paper when necessary as the ASTM G1-03 standard recommends.

Equation (1) was followed to calculate the specimen mass loss, considering the initial mass, m(t0), and the weight obtained after 1, 4 and 12 weeks m(t), respectively.

$$\Delta m = m(t_0) - m(t) \qquad \text{eq. (1)}$$

The corrosion rate (CR) considers the mass loss (Δm), the metal sample surface area (A) and the experimental time (t0-t) and was calculated with equation (2).

$$CR = \frac{\Delta m}{A \cdot (t_0 - t)} \qquad \text{eq. (2)}$$

4. Results and discussion

4.1. Remarkable observations

Corrosion signs were noticed since week one in the carbon steel specimens immersed in SP21E. Yellow tonality in the test tubes was observed. This fact was also noticed after the fourth test week, this time with higher colour intensity and some bubbling in the test tubes. After twelve weeks, this coloration had turned into orange and bubbling and surface degradation of the metal specimen were also noticed, as shown in Figure 1.

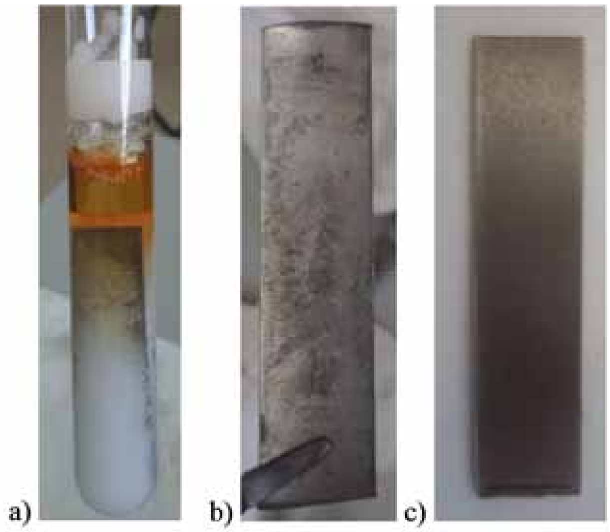

Figure 1. a) Carbon steel specimen immersed in SP21E after 12 weeks. b) The same carbon steel specimen once cleaned. c) Non tested carbon steel specimen.

Copper specimens immersed in the capric (75.2 %)/palmitic (24.8%) eutectic presented blue coloration of the PCM after the first week. The blue coloration gained intensity and turned into a greener tonality along the 12 experimental weeks. Brightness loss of the copper specimens was also noticed since week one, and it became more important with time.

The same phenomena was observed when copper was in contact with the capric/myristic eutectic. Blue coloration of the PCM was observed since week one and it became greener as weeks passed by. Brightness loss was also noticed, mainly in the specimen removed after the 12th week, as Figure 2 shows.

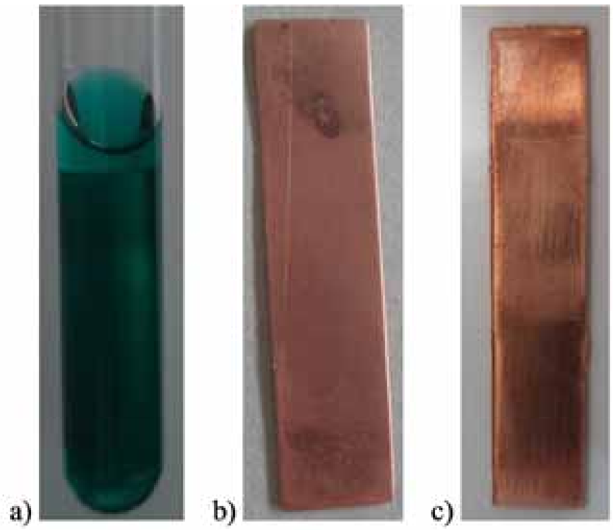

Figure 2. a) Copper specimen immersed in capric (73.5%)/myristic (23.5%) eutectic after 12 weeks. b) 12th week copper specimen after the cleaning process. c) Non corroded copper specimen.

Grey coloration was observed from the fourth week on in the test tubes were aluminium specimens were immersed in SP21E. Bubbling was notorious on week twelve, when partial solidification of the PCM and the corroded metal could also be observed. Surface degradation and pitting were evident as shown in Figure 3.

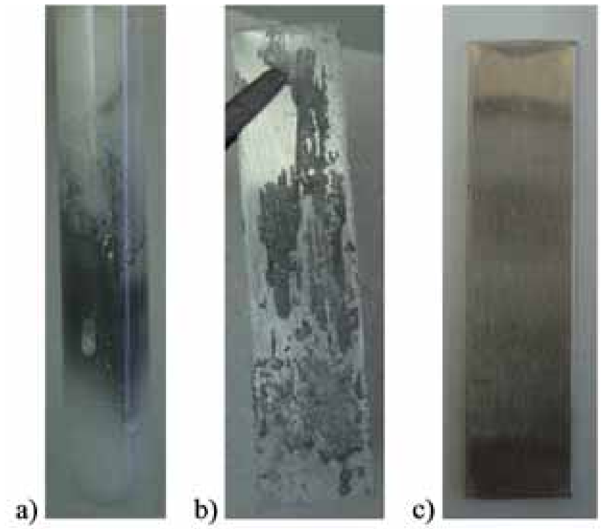

Figure 3. a) Aluminium specimen immersed in SP21E after 12 weeks. b) 12th week aluminium specimen once cleaned. c) Non tested aluminium specimen.

4.2. Results

Corrosion rates *(CR)* of all specimens were calculated according to the guide for corrosion weight loss used in industry (Table 2), which was the one followed as reference to evaluate the results. It is important to point out here that the following numerical results are given as indicative 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.

Table 2. Guide for corrosion weight loss used in the industry (Sastri et al. 2007)

mg/cm^2yr	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

Low positive *CR* values in the range 0-1 $mg/cm^2 \cdot yr$ were obtained for all the metals in contact with PureTemp 23. These values are in accordance to the null corrosion signs observed on any of the metal specimens and can be considered result of surface cleaning. Therefore, all metals are suitable to be used as PureTemp 23 container.

Figure 4 shows the *CR* evolution of the metals immersed in SP21E. All metal curves present a similar pattern but the aluminium one. As shown in the figure, aluminium is corroded mostly after the fourth week of test, reason why, along with the surface degradation and pitting marks observed caution would be recommended on its application as container. Carbon steel shows higher *CR* values after the first week of test, observed as yellow coloration of the PCM, but despite the decrease of the following values, caution must be taken when choosing carbon steel as container material for SP21E in long term service applications. Copper and the two stainless steels tested do not show important *CRs* at all, thus they are suitable to be used as long term container materials.

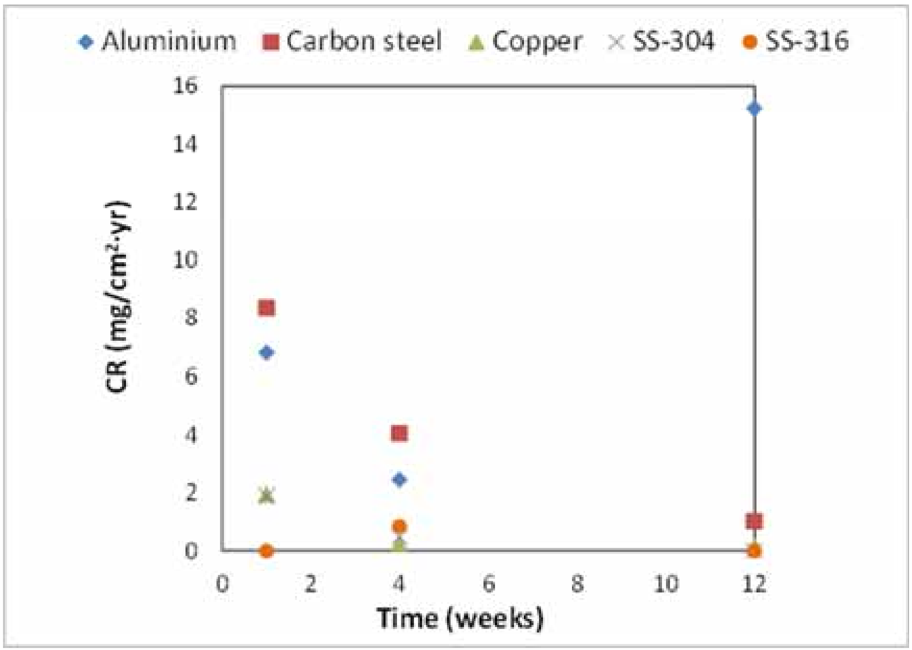

Figure 4. Corrosion rate vs time of all the metals immersed in SP21E.

Figure 5 shows the *CR* evolution with time of all the metals when immersed in the capric (75.2 %)/palmitic (24.8%) eutectic mixture. Copper experienced remarkable weight loss during the twelve weeks and its quite constant *CRs* along with the blue coloration observed in the test tubes lead to recommend caution when applying this metal as a container. Carbon steel presented remarkably high *CR* value after one week compared to the *CR* below 0.2 mg/cm2·yr obtained after four and twelve weeks. For this reason, first week results should be taken with caution and experimental limitations may explain them, thus they are not considered as corrosion evidence. Consequently, as no corrosion signs were observed on the samples and considering the low/null *CR* values obtained at the end of the tests, carbon steel would be a suitable material to be used as this eutectic container. Stainless steel 304, stainless steel 316 and aluminium presented really low or null *CR* values during all the experimentation, thus, all three metals are considered as useful container materials for the capric (75.2 %)/palmitic (24.8%) eutectic.

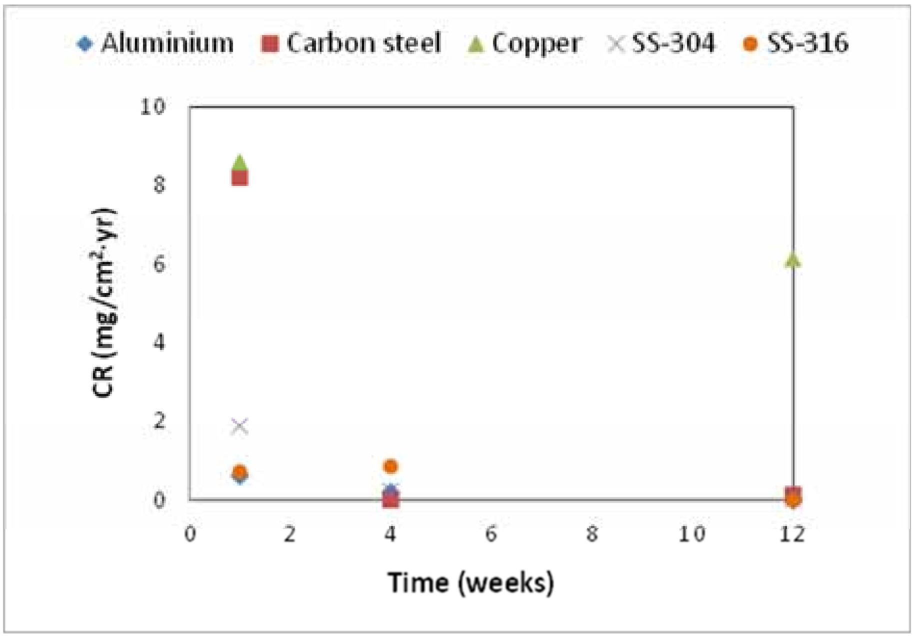

Figure 5. Corrosion rate vs time of all the metals immersed in the capric (75.2 %)/palmitic (24.8%) acid mixture.

The experimental data logged when the metals were immersed in the capric (73.5%)/myristic (23.5%) eutectic is presented in Figure 6. Copper and carbon steel share *CR* pattern, as they step down from the first week on, keeping a quite constant value after week four. However, the difference on the quantitative *CR* values is important enough to consider the carbon steel first week data as consequence of the cleaning process, hence, it is not considered as corrosion evidence and its use as container material would be useful for long term services. Oppositely, copper achieved *CR* values high enough to, along with the blue coloration observed in the test tubes, recommend caution on its application as container material. Regarding the other three tested metals, all of them showed mostly null *CR*, thus, they are suitable to be used as container materials for long term services.

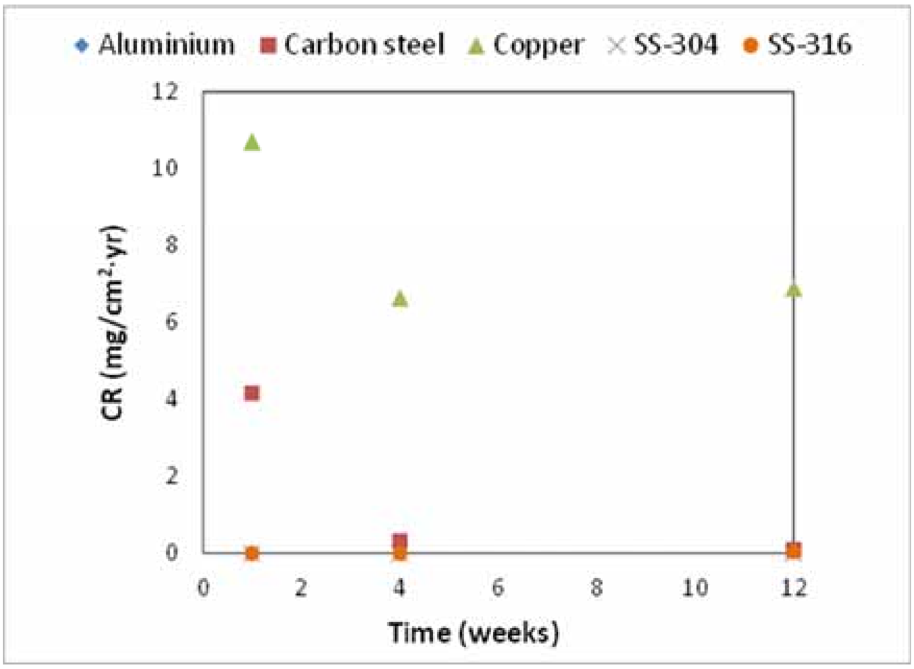

Figure 6. Corrosion rate vs time of all the metals immersed in the capric (73.5%)/myristic (23.5%) acid mixture.

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, coloration, surface degradation and pitting were also analysed.

Results show that PureTemp 23 is the only PCM to which all the studied metals are resistant to. Thus, the five metals are suitable to be used as material containers of this formulation for long term service applications.

Aluminium experiences evident corrosion when immersed in the inorganic salt SP21E, thus caution is recommended on its use as container material. However, its use should be avoided as better matches have been found. Although the CR obtained for carbon steel were not remarkably high, corrosion signs were observed on the specimens, thus caution is also needed when considering this material for container use. Stainless steel 304, stainless steel 316 and copper showed great resistance to this salt and no corrosion was noticed on the specimens as well as on their CR patterns, hence, its suitability to be used as SP21E container is total.

Copper experiences corrosion when immersed in both fatty acid eutectic formulations. Despite the CR being quite low, the observations done during the whole experimentation lead to recommend caution when choosing it as the material container of these two fatty acid mixtures. On the other hand, stainless steel 304, stainless steel 316 and aluminium did not show corrosion evidences during the twelve test weeks, therefore, its suitability to be used as fatty acid container materials for long term service applications is total.

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