Corrosion of metal containers for use in PCM energy storage

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SUMMARY

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 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.

Keywords: solar energy, thermal energy storage (TES), comfort building applications, phase change materials (PCM), metal corrosion.

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 ºC – 25 ºC 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, 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 PureTemp23 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.

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	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

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 Figure 1. The specimen size used was approximately 5 x 1 x 0.1 cm.

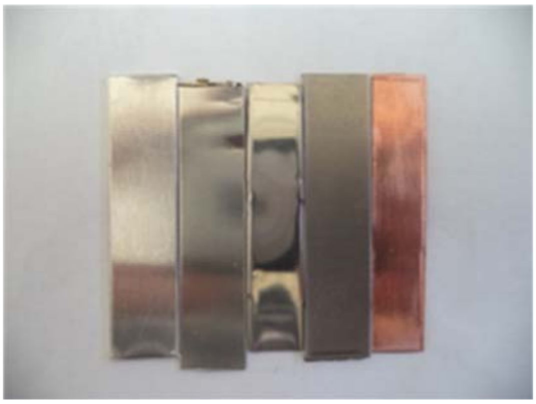

Figure 1. Metal specimens studied. From left to right: aluminium, stainless steel 316, stainless steel 304, carbon steel and copper.

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 ºC, they were kept in a stove at 38 ºC, 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, coloration 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.

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

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

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

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 4^{th} test week, with an evident increase on the colour intensity and bubbling in the test tubes. After the 12^{th} week of test, the coloration had turned into orange and the test tubes also presented bubbling, as shown in Figure 2. Surface degradation was also noticed at this point.

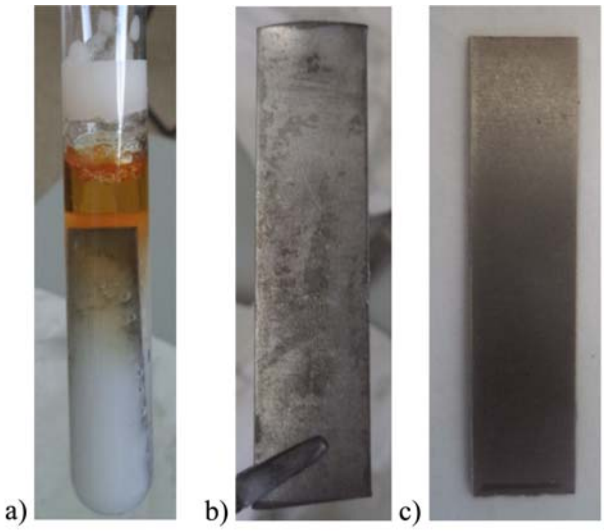

Figure 2. a) Carbon steel specimen immersed in SP21E after 12 weeks. b) The same carbon steel specimen once cleaned. c) Non tested carbon steel specimen.

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

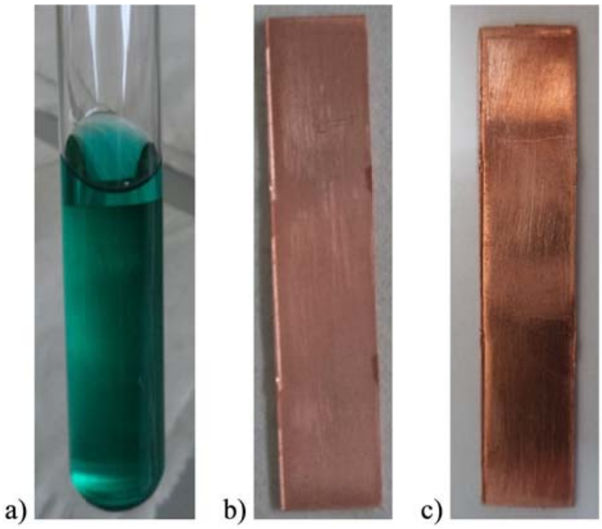

Figure 3. a) Copper specimen immersed in capric (75.2 %)/palmitic (24.8%) acid mixture after 12 weeks. b) The same specimen cleaned. c) Non tested copper specimen.

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 coloration 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 Figure 4.

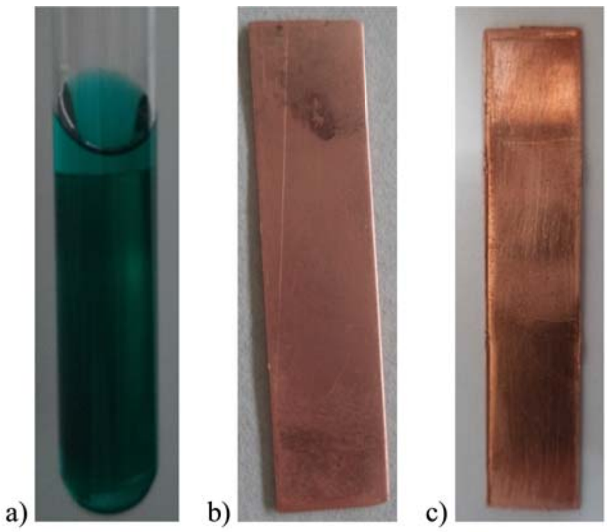

Figure 4. a) Copper specimen immersed in capric (73.5%)/myristic (23.5%) eutectic after 12 weeks. b) 12th week copper specimen after the cleaning process. c) Non corroded copper specimen.

The test tubes containing aluminium specimens immersed in SP21E showed grey coloration and bubbling from the 4th week on. After 12 weeks, the grey coloration 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 Figure 5.

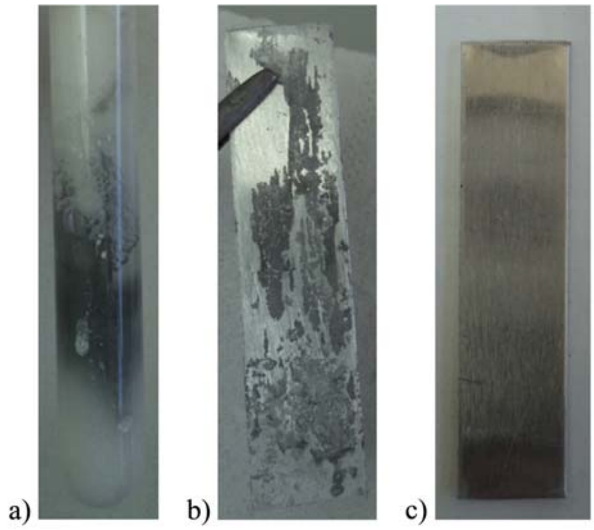

Figure 5. a) Aluminium specimen immersed in SP21E after 12 weeks. b) 12th week aluminium specimen once cleaned. c) Non tested aluminium specimen.

4.2. Results

Corrosion rates *(CR)* of all specimens were calculated. 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.

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

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

The enclosed Figure 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 1^{st} week until the 12^{th}. The exception is aluminium, which is corroded mostly after the 4^{th} 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 coloration 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.

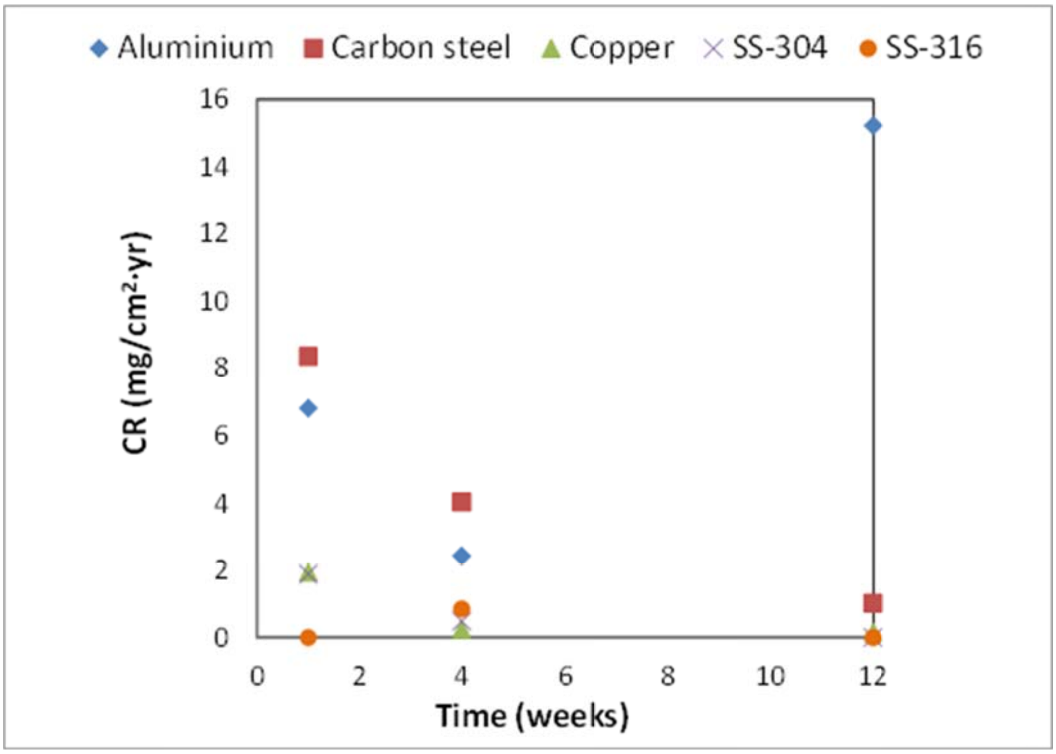

Figure 6. Corrosion rate vs time of all the metals immersed in SP21**E**.

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.

Figure 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 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 *CR*s 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 coloration 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.

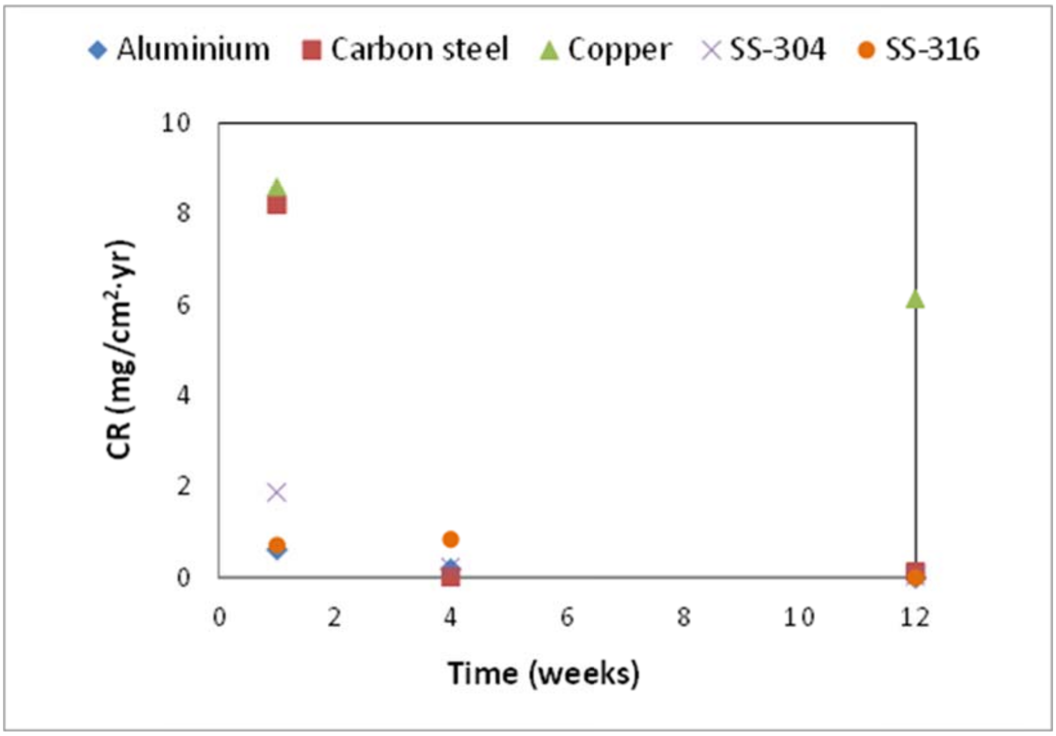

Figure 7. Corrosion rate vs time of all the metals immersed in the capric (75.2 %)/palmitic (24.8%) acid mixture.

The experimental data logged for the capric (73.5%)/myristic (23.5%) eutectic is presented in Figure 8. A common pattern is found on the copper and carbon steel curves as their *CR*s 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 coloration 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 coloration 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.

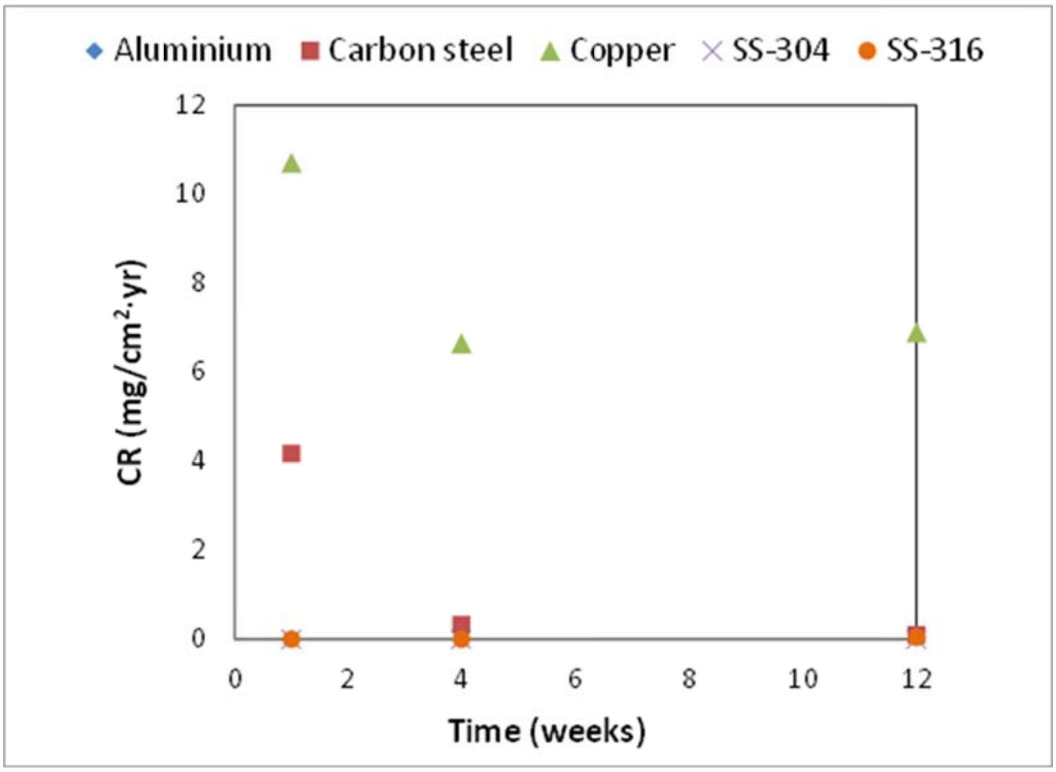

Figure 8. Corrosion rate vs time of all the metals immersed in the capric (73.5%)/myristic (23.5%) acid mixture.

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.

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.

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.

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