

Corrosion of metals and salt hydrates used for thermochemical energy storage



Aran Solé ^{a,1}, Laia Miró ^{a,1}, Camila Barreneche ^{a,b,1}, Ingrid Martorell ^{a,1}, Luisa F. Cabeza ^{a,*}

^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

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ABSTRACT

Solar energy can be efficiently used if thermal energy storage systems are accordingly designed to match availability and demand. Thermal energy storage by thermochemical materials (TCM) is very attractive since these materials present a high storage density. Therefore, compact systems can be designed to provide both heating and cooling in dwellings. One of the main drawbacks of the TCM is corrosion with metals in contact. Hence, the objective of this study is to present the obtained results of an immersion corrosion test following ASTM G1 simulating an open TCM reactor, under humidity and temperature defined conditions. Four common metals: copper, aluminum, stainless steel 316, and carbon steel, and five TCM: CaCl₂, Na₂S, CaO, MgSO₄, and MgCl₂, were studied. Aluminum and copper show severe corrosion when combined with Na₂S, aluminum corrosion is more significant since the specimen was totally destroyed after 3 weeks. Stainless steel 316 is recommended to be used as a metal container material when storing all tested TCM.

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1. Introduction

Solar energy is one of the most promising renewable energies to be used worldwide for house heating and domestic hot water applications and contributes in decreasing fossil fuel consumption, thus greenhouse gases emissions. The main drawback of solar energy is the mismatch between the availability and the demand, then thermal energy storage (TES) is needed to match it.

Up to now, there are mainly three known TES methods. Sensible TES systems store energy by applying a temperature gradient to the storage medium, for instance molten salts, water, ceramics, etc. Latent TES systems are based on the energy implied in a physical state change of a substance. These two methods have been widely studied and several commercial applications can be found [1–3]. Latent TES works with phase change materials (PCM), which are mainly divided into several groups as paraffin, fatty acids or salts. It is well known that salts will act corrosively with conventional metals used as vessel materials or in heat exchangers and corrosion behavior of them have been studied as an aqueous dissolution [4]. Several corrosion tests have been performed between salt hydrates

as PCM and metals in the liquid phase and 100% concentrated [5–9]. Moreover, the third method for thermal energy storage is thermochemical storage which is under research and a better understanding is needed for the further development of the technologies implementing thermochemical materials (TCM). TCM cover different chemical and physical processes. Those are based on adsorption, absorption process and reversible chemical reactions being exothermic in one direction (discharging process) and endothermic in the other (charging process).

TCM are based on adsorption materials like zeolites, silica gel, etc., absorption processes concerning concentrated and diluted salt solution and chemical reactions with salt hydrates such as magnesium chloride, aluminum sulfate, etc. [10].

One of the main advantages that TCM present is their theoretical energy storage density, which makes the development of compact systems for dwellings applications, be viable. Energy densities of some TCM based on reversible chemical reactions are shown in Table 1 [11], which are one order of magnitude larger than water (sensible heat storage).

Furthermore, despite the need to heat the TCM up to reach the discharging reaction temperature, heat losses when storing are almost zero. This last makes TCM suitable for long-term storage also known as seasonal storage [10]. Also, a life cycle analysis (LCA) study of a thermochemical based system shows that it provides a

* Corresponding author. Tel.: +34 973 003576; fax: +34 973 003575.

E-mail address: lcabeza@diei.udl.cat (L.F. Cabeza).

¹ Tel.: +34 973 003576; fax: +34 973 003575.

better solution for reduction of negative environmental impact by using solar energy when compared to conventional solar heating system and traditional fossil fuel based heating system [12].

On the other side, these systems are more complex to design than latent and sensible TES since TCM involve more than heat transfer. TCM systems design must consider also mass transfer and kinetics. A complete study on solid reactants and products is missing when designing a technology based on TCM, which could lead to a lower storage capacity [13]. Also, another big drawback is corrosion due to that a big part of TCM under research for building applications is solid salt hydrates reacting with water vapor.

Several prototypes are being tested at lab scale [14–16]. For instance, de Boer et al. [14], presented the Sweat module with $\text{Na}_2\text{S}\cdot\text{H}_2\text{O}$ salt hydrate used as the TCM. They highlighted the corrosive effect of the $\text{Na}_2\text{S}\cdot\text{H}_2\text{O}$ when this TCM is put in contact with metal. Cuypers et al. [15] showed preliminary experiments of a glass lab-scale zeolite reactor containing copper heat exchangers, where one of the downsides is the corrosion produced by the TCM. Furthermore, Schmidt et al. [16] published experimental results of a 25 kg reactor based on $\text{Ca}(\text{OH})_2$ which was first tested at lab scale where no corrosion was detected.

No data is found regarding corrosion test between solid salt hydrates under real conditions of the system design considering the working temperature, the relative humidity as well as pressure. These results are totally necessary for the optimal development of a TCM system and to resolve practical aspects to make them viable for market implementation [17].

Therefore, the main objective of the present paper is to perform immersion corrosion test of common metals used as a vessel material and as reactor components and TCM under research at defined operating conditions. These results are useful to select the optimal metal of the TCM container when transported, stored and reaction takes places.

2. Experimental section

Five salt hydrates TCM were selected among the most used ones in research to carry out corrosion test: CaCl_2 , Na_2S , CaO , MgCl_2 , and MgSO_4 (see Table 2, component A). The TCM were all lab grade purity and solid powder form. Reaction enthalpy of each TCM before corrosion test was analyzed by 822e DSC Mettler-Toledo in GREA lab.

The vessel metals under study are the most common metals to build up reactors, heat exchangers, piping, etc.: copper, aluminum, stainless steel 316, and carbon steel. Metal pieces of $5\text{ cm} \times 1.1\text{ cm} \times 0.01\text{ cm}$ were tested (see Fig. 1). The surface of the metal samples was polished with silicon carbide paper and cleaned with acetone before testing.

Each metal specimen was immersed in each component A from Table 2. All test tubes containing the combinations were placed in a humidity chamber controlling the temperature and humidity. Temperature was set at $60\text{ }^\circ\text{C}$ above most of discharging/hydration temperatures [12] to let the reactions listed in Table 2 take place. Humidity was 99%. The corrosion test methodology was performed simulating an open TCM reactor where the H_2O vapor and the salt react to form an upper hydrate while releasing heat.

Table 1
Energy density of some TCM [11].

A	B	C	Energy storage density of A (GJ/m^3)
$\text{MgSO}_4\cdot 7\text{H}_2\text{O}$	MgSO_4	$7\text{H}_2\text{O}$	2.8
FeCO_3	FeO	CO_2	2.6
$\text{Fe}(\text{OH})_2$	FeO	H_2O	2.2
$\text{CaSO}_4\cdot 2\text{H}_2\text{O}$	CaSO_4	H_2O	1.4

Table 2
Selected TCM for the corrosion test.

Reaction $A + B \rightarrow C + \text{heat}$			Purity of component A (%)	Company	Reaction enthalpy (kJ/kg)
A	B	C			
$\text{CaCl}_2\cdot 2\text{H}_2\text{O}$	$4\text{H}_2\text{O}$	$\text{CaCl}_2\cdot 6\text{H}_2\text{O}$	n.a.	Sigma–Aldrich	682
$\text{Na}_2\text{S}\cdot x\text{H}_2\text{O}$	$5\text{H}_2\text{O}$	$\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$	n.a.	Sigma–Aldrich	1254
CaO	H_2O	$\text{Ca}(\text{OH})_2$	95.0–100.5	Panreac	n.a.
MgCl_2	$6\text{H}_2\text{O}$	$\text{MgCl}_2\cdot 6\text{H}_2\text{O}$	98.0–101.0	Panreac	1082
MgSO_4	$7\text{H}_2\text{O}$	$\text{MgSO}_4\cdot 7\text{H}_2\text{O}$	99.0–100.5	Panreac	918

Where n.a. stands for not available.

Metal samples are removed after 1, 4 and 12 weeks of test. Quantitative analyses of metal corrosion were done following Eq. (1) [17]:

$$\text{CR} = \frac{\Delta m}{A \cdot (t_0 - t)} \quad (1)$$

Corrosion rate CR ($\text{mg cm}^{-2} \text{ yr}^{-1}$) takes into account the mass loss (Δm), the area of the metal specimen (A), and the time of exposure ($t_0 - t$). Three CR values are obtained for each metal and TCM combination. Three specimens of the same metal are placed at the same time ($t = 0$), each one in one test tube with the TCM. Then, after one week ($t = 1$) one tube and metal are removed and the metal is evaluated. This procedure is repeated with the second sample at week four and finally with the third sample at week twelve ($t = 12$). At first removal one piece of metal is evaluated, and it is compared visually with the two others that will remain, until week four and twelve, respectively. In order to calculate the mass loss, the metal specimens were weighted, previously and after each test, in a precision balance ($\pm 0.01\text{ mg}$) from Mettler-Toledo, AG135. To prepare, clean and evaluate the metal specimen, ASTM G1 [18] has been followed.

Qualitative data are also important to draw conclusions. Therefore, a detailed analysis of the solution appearance is carried out in order to detect changes in color, appearance of bubbles, and formation of precipitates. Furthermore, the specimens were analyzed using Vision SX45 microscope with Pixel-fox v5.0 digital camera checking for pitting corrosion.

3. Results and discussion

Corrosion rate results of the experiments with calcium chloride (CaCl_2) and the four metals under study are shown in Fig. 2.

Stainless steel specimens in combination with CaCl_2 did not show corrosion or changes in the solution appearance. Carbon steel, aluminum and copper specimens presented a decreasing tendency of corrosion rate values after 4 weeks in contact and then remained

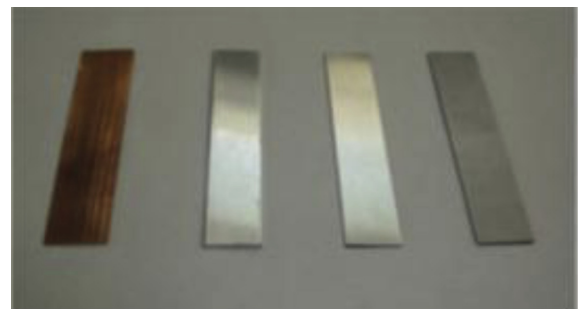


Fig. 1. Initial metal specimens from left to right: copper, stainless steel 316, aluminum, and carbon steel [5].

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