Corrosion evaluation of eutectic chloride molten salt for new generation of CSP plants. Part 1: Thermal treatment assessment

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ARTICLE INFO

Keywords:
Concentrated solar power
Thermal energy storage
Corrosion mitigation
Chloride molten salt
Thermal purification treatment

ABSTRACT

The operating temperature of a steam turbine is limited to 565 °C by the molten nitrate heat-transfer fluid; therefore, a new molten salt chemistry is needed to increase the maximum operating temperature in the new generation of CSP plants and improve the thermal-to-electrical energy conversion efficiency in the turbine block, such as chloride molten salts. Nevertheless, the prevention of high-temperature corrosion on containment materials using chlorides plays a critical role and a corrosion mitigation plan is needed to achieve the target plant lifetime of 30 years. This paper presents a corrosion mitigation strategy focused on different thermal treatments performed in the eutectic ternary chloride molten salt composed by MgCl₂/NaCl/KCl (55.1 wt.%/24.5 wt. %/20.4 wt.%). Corrosion rates were obtained through linear polarization resistance technique in a conventional commercial stainless steel (AISI 304) at 720 °C during 5 h of immersion after the different thermal treatments carried out. Scanning electron microscopy and XRD analysis were used to confirm the corrosion rates and corrosion layer proposed by electrochemical techniques, obtaining a minimum corrosion rate of 6.033 mm/year for the best thermal treatment performed.

1. Introduction

During the last years the cost of CSP technology was reduced, but an additional effort is necessary to compete with other renewables technologies as PV. On average, the projected cost for a CSP plant dropped by about 9 eUSD/kWh cents per kilowatt hour, from 21 eUSD/kWh in 2010 to 12 eUSD/kWh in 2015 and anticipated to reach 10 eUSD/kWh in 2017 [1]. To continue these cost reductions in solar technologies, US department of energy (DOE) recently established cost targets for 2030 that would make to this renewable energy, one of the lowest-cost sources of electricity provided by CSP technology. The new targets correspond to a levelized cost of electricity (LCOE) in 2030 of $0.05/ kWh for a dispatchable, high-capacity factor CSP-TES plant configuration [2]. Past and future cost reductions of CSP are tied to improve system wide performance. Particularly, increasing the maximum operating temperature and thereby the thermal to electric conversion efficiency reduces the required capacity of the entire plant strongly influencing cost reduction.

The selection of a high-temperature molten-salt chemistry is needed, as well as the need to understand its impact on containment materials, to achieve acceptable strength, durability, and cost targets at these high temperatures [3]. Table 1 shows the molten salt candidates that were analyzed in this direction.

Carbonates and fluoride salts need to include lithium in their formulations in order to reduce their melting points to levels below 500°C, increasing the final cost for the thermal energy storage material [5]. On the other hand, chloride molten salts are considered a feasible option due to their low cost and high decomposition temperature [6].

One of the most studied mixtures is composed by MgCl₂/NaCl/KCl (55.1 wt.%/24.5 wt. %/20.4 wt. %) since it has a melting point of 380 °C, thermal stability up to 800 °C, higher heat capacity compared to chloride salts containing ZnCl₂, and low vapor pressure [4]. This last parameter is one of the main drawbacks using ZnCl₂ due to their important increase at 530 °C [3]. But these molten salts introduce a set of technological and engineering challenges because of their very corrosive nature on typical containment materials. Corrosion mitigation approaches were investigated trying to achieve a corrosion rate around 20 µm/year or lower for the containment materials, thus providing a lifetime of 30 years or longer [7,8]. Nevertheless, this scope is still far and corrosion mitigation strategies are needed to reduce corrosion to these levels. One of these strategies is the performance of thermal purification treatments before corrosion tests using chloride molten salts.

The aim of this paper is to analyze different thermal purification treatments to reduce corrosive impurities and hence corrosion rates obtained in a conventional austenitic stainless steel (AISI 304).
HCl gas while the undecomposed portion dissociates to form hydroxychloride partially decomposes to its corresponding oxide and HCl gas at high temperature. At higher temperatures, the droxychlorides are formed via hydrolysis when MgCl2 is dried such that the chlorides with hydrated H2O molecules form hydroxychloride and oxide such as H2O, OH−, O2, and H+ since it can destabilize passive surface oxide films. One of the main important impurities present in molten chlorides, especially in MgCl2, are hydroxychlorides. Vilnyansky and Bakina, confirmed that MgO is practically insoluble in MgCl2–NaCl and Ozeryanaya et al. reported that oxygen (Ks = 10−8 mol/cm3), chlorine (Ks = (0.03−4.62) × 10−6 mol/cm3), and hydrogen chloride (Ks = (0.19–3.16) × 10−6 mol/cm3) possess a low solubility in molten alkali and alkaline-earth chlorides at temperatures between 650 °C and 950 °C. However, the oxidizing gases dissolved in molten chlorides cause corrosion and Fe2+,Cr2+ and Ni2+ ions can form low solubility oxides with oxygen ions in the molten salt.

Additionally, Grabke et al. analyzed the presence of SO2 in chloride molten salt and concluded that it causes a minor increase of active corrosion by sulfation of chlorides and generation of chlorine. According to this, one of the key efforts in molten chloride corrosion mitigation has focused on reducing the corrosive impurities by suppressing the side reactions of hydrolysis during salt heating. In the molten salt proposed, MgCl2 (from raw material) is in the form of hexahydrate, and some authors identified the formation of MgOHCl through the following reaction at 167 °C:

\[ \text{MgCl}_2 \cdot 6\text{H}_2\text{O} \rightarrow \text{MgOHCl} \cdot \text{HCl} \cdot 2\text{H}_2\text{O} \]


impered in the ternary MgCl2/NaCl/KCl (55.1 wt.%/24.5 wt. %/20.4 wt.%) molten salt during 5 h at 720 °C using linear polarization resistance technique.

2. Corrosive impurities present in chloride molten salts

Corrosion in molten chlorides is driven by the impurities in the salt, such as H2O, OH−, O2, and H+ since it can destabilize passive surface oxide films. One of the main important impurities present in molten chlorides, especially in MgCl2, are hydroxychlorides. Hydroxychlorides are formed via hydrolysis when MgCl2 is dried such that the chlorides with hydrated H2O molecules form hydroxychloride and HCl gas at high temperatures. At higher temperatures, the hydroxychloride partially decomposes to its corresponding oxide and HCl gas while the unde decomposed portion dissociates to form OH−, which can remain in the molten chloride.

Although no solubility of MgOHCl in molten MgCl2 was reported, its dissolution in molten MgCl2-containing salts is believed to involve the formation of complex molecules between Mg2+ ion and MgOH− ion or a dimer structure with two MgOHCl molecules. Thermal decomposition of MgOHCl was reported to occur between 415 °C and 555 °C, which produces MgO and HCl:

\[ \text{MgOHCl} \rightarrow \text{MgO} + \text{HCl} \]

Table 1

<table>
<thead>
<tr>
<th>Molten salt composition (wt.%)</th>
<th>Melting point (°C)</th>
<th>Thermal stability limit (°C)</th>
<th>Density (g/cm3)</th>
<th>Heat capacity (kJ/kg K)</th>
<th>Material cost (USD/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60NaNO3/40KNO3</td>
<td>223</td>
<td>565</td>
<td>1.8 (400°C)</td>
<td>1.5 (400°C)</td>
<td>0.8</td>
</tr>
<tr>
<td>32 K2CO3 + 35 Li2CO3 + 33 Na2CO3</td>
<td>397</td>
<td>&gt;650</td>
<td>2.0 (700°C)</td>
<td>1.9 (700°C)</td>
<td>2.5</td>
</tr>
<tr>
<td>59 KF + 29 LiF + 12 NaF</td>
<td>454</td>
<td>&gt;700</td>
<td>2.0 (700°C)</td>
<td>1.9 (700°C)</td>
<td>&gt;2</td>
</tr>
<tr>
<td>23.9 KCl + 7.5 NaCl + 68.6 ZnCl2</td>
<td>204</td>
<td>850</td>
<td>2 (600°C)</td>
<td>0.8 (300-600°C)</td>
<td>0.8</td>
</tr>
<tr>
<td>20.4 KCl + 55.1 MgCl2 + 24.5 NaCl</td>
<td>380</td>
<td>800</td>
<td>1.7 (600°C)</td>
<td>1.0 (500-800°C)</td>
<td>&lt;0.35</td>
</tr>
</tbody>
</table>

Table 2

Chemical composition of ternary chloride salt tested.

<table>
<thead>
<tr>
<th>K (%)</th>
<th>Mg (%)</th>
<th>Na (%)</th>
<th>Mn (ppm)</th>
<th>SO4 (ppm)</th>
<th>Cl (%)</th>
<th>H2O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20.6</td>
<td>11.9</td>
<td>3.4</td>
<td>1.8</td>
<td>162</td>
<td>60</td>
<td>5</td>
</tr>
</tbody>
</table>

The dehydration of the monohydrate occurs at 235 °C and also produces MgO:

\[ \text{MgCl}_2 \cdot \text{H}_2\text{O} \rightarrow \text{MgO} + \text{H}_2\text{O} \]

3. Experimental procedures

The molten salt tested was the eutectic mixture 20.4 KCl + 55.1 MgCl2 + 24.5 NaCl (Sigma Aldrich 99%) at 720 °C under inert atmosphere (N2). Some analysis were carried out in the commercial salts used in this research (Table 2):

A two electrodes arrangement was used, composed by a working electrode (WE) and reference-counter (RE-CE) electrodes, that were immersed in the molten salt (electrolyte), and the open circuit potential (OCP) was measured using a potentiostat (Gamry 1010E). The experimental set up is shown in Fig. 1.

It is necessary to purify and refresh the gas release from the reactor (2). For this purpose, a MgO trap (11) is included to remove water content and a NaOH trap (13) to neutralize H+ that could be produce during the experiments. Linear polarization tests were carried out from a potential of −0.6 V to 0.4 V of the OCP voltage using a scanning range of 0.005 V/s with steps of 0.00244 V. A specific thermal treatment during the melting process must be defined in order to reduce the corrosive impurities present in commercial chloride molten salts, especially in MgCl2. The easiest way to prevent the contamination of O2 and H2O is to thoroughly dry the hygroscopic MgCl2 salt. The temperatures at each drying stage were determined from the vapor pressure curves in Fig. 2.
Some authors [23–25] proposed a multi-step heating to purify MgCl₂ salts and to reduce the formation of MgOHCl. In this research we have analyzed different thermal treatments, at different dwelling times at each temperature, to compare those available in the literature as well as new ones proposed in this study, with a more specific stepwise heating at T1-T5 shown in Fig. 2. Specific conditions for thermal treatments performed are shown in Table 3.

Vidal and Klammer [26] established different key temperatures (treatment #1) using long dwelling times for each temperature, but heating ramps were not reported. On the other hand, Ding et al. [23] established a quick thermal treatment only using a heating step at 200 °C, using a heating ramp of 5 °C/min. After this step, no heating ramps or additional temperature steps were reported before reaching the testing temperature (700 °C).

Additionally, other two heat treatments (#2 and #4) were carried out, following a more specific stepwise heating through MgCl₂ water molecules release and using a heating ramp of 10 °C/min, according to Fig. 2. In the last thermal treatment proposed (#4), dwelling times were reduced compared to thermal treatment #2.

The salts were carefully handled and mixed to avoid water absorption in a dry box containing desiccants and after the thermal purification treatment the salt was solidified and the bottom part was removed, with the insoluble impurities.

The corrosion behavior after thermal treatments was evaluated in the same alloy, AISI 304, with a chemical composition shown in Table 4.

Corrosion evaluation assessment were carried out using linear polarization resistance technique. To quantify the polarization resistance $R_p$, it is important to take into account the potential drop attributed to the electrolyte resistance (molten salts). The relationship between polarization resistance and corrosion current density $i_{corr}$, is given by Eq. (1):

![Fig 2. Vapour pressure of H₂O and HCl curve on MgCl₂·7H₂O.](image-url)
where $B$ is an electrochemical constant calculated theoretically according to the Eq. (2):

$$B = \frac{\beta_c^2 n \rho_{alloy}}{2,3 \cdot n(\beta_a + \beta_c)}$$

where $\beta_c$ and $\beta_a$ are the cathodic and anodic Tafel slope, respectively.

The $B$ parameter must be used to convert the $R_p$ values into corrosion current densities, so it is necessary to make a derivation of the polarization curves according to Eq. (3):

$$R_p = \frac{\Delta E}{\Delta i} = \frac{B}{i_{corr}} = \frac{\beta_c^2 n \rho_{alloy}}{i_{corr} \cdot 2,3 \cdot n(\beta_a + \beta_c)}$$

The corrosion density current $i_{corr}$ and the corrosion potential $E_{corr}$ were determined from the extrapolation of the Tafel curve.

The corrosion rate (CR) can be estimated through the Butler-Volmer equation showed in Eq. (4):

$$CR = \frac{i_{corr} \cdot K}{\rho_{alloy} \cdot \sum (\frac{f_i}{MW_i})}$$

where $K$ is a correlation constant that defines the units of CR (3272 for CR in mm/year), $\rho_{alloy}$ is the alloy density (g/cm$^3$), $f_i$ is the mole fraction of the element $i$ in the alloy, $n_i$ is the number of electrons that are transferred in element $i$ and $MW_i$ is the atomic weight of element $i$.

Finally, after the corrosion test, the metal specimens were analyzed by scanning electron microscopy (SEM) and x-ray diffraction (XRD) to detect the corrosion produced. The XRD device used was the PANalytical X’Pert PRO model, and measures were taken from 5 to 120° with a step size of 0.017°, while the SEM model used was the Quanta 250, Thermofisher.

### 4. Results and discussions

The different thermal treatments were carefully addressed before reaching the testing temperature (720 °C). After that, linear polarization technique was carried out after 5 h of immersion of AISI 304 in the ternary MgCl$_2$/NaCl/KCl (55.1 wt.%/24.5 wt.%/20.4 wt.%%) molten salt. All Tafel curves for the different experiments carried out in this study are shown Fig. 3.

The corrosion rate results obtained from Fig. 3, according to Eq. (4), are shown in Table 5.

As expected, the highest corrosion rate was obtained in the steel without a previous thermal treatment in the salt, followed by Treat #1 > 3 > 4 > 2. The lowest corrosion rate was obtained in thermal treatment #2, which corresponds to the more specific stepwise heating (Table 1) proposed in this study.

These results were confirmed by scanning electron microscopy (SEM). Fig. 4 shows the superficial top-view (left) and cross-sectional image (right) for the different thermal treatment performed in the chloride salt, after immersion in chloride molten salt during 5 h at 720 °C. Results also include an energy dispersive x-ray analysis (EDX) in the corrosion layer found in the cross sectional study.

Micrographs are in concordance with corrosion rate values obtained by linear polarization resistance technique (Table 3). The sample without thermal treatment (Fig. 4a) showed the highest corrosion
average layer thickness (470 µm) with potassium, chloride and oxygen as main components. XRD analysis (Table 5) confirmed the compounds detected in this layer and MgOHCl, MgO and KCl were obtained. It is important to highlight that MgOHCl was pointed in the literature as one of the most corrosive impurities present in chloride salts [4,23, 24, 25].

In the following tests with the different thermal treatments performed (Fig. 4b–e) before the corrosion test, this compound was reduced, obtaining lower content in chloride from the EDX carried out in the steel surface. The lowest corrosion layer thickness corresponds to thermal treatment #2 (22.22 µm) in concordance with corrosion rates obtained by linear polarization resistance (LPR) (Table 5). This treatment was developed following a more specific stepwise heating according to vapor pressure curve on MgCl$_2$·7H$_2$O.

EDX analysis carried out in the steel surface showed the elements detected in the corrosion layer. Chromium content was detected in the protective layer of thermal treatment #2, #3 and #4 but it is important to highlight that the diffusion coefficient in Cr is lower compared to Fe. Additionally, an uniform corrosion mechanism was observed in the micrographs shown in Fig. 4.

In order to complete the corrosion characterization in the stainless steel tested, XRD analysis were performed in the stainless steels. Fig. 5 shows the XRD obtained in AISI 304 after the corrosion test in MgCl$_2$/NaCl/KCl (55.1 wt.%/24.5 wt.%/20.4 wt.%) with thermal treatment #2.

In this case, a protective layer composed by MgCr$_2$O$_4$ was detected as well as magnetite (Fe$_3$O$_4$) and MgO as the main corrosive compounds formed in the steel surface. All the XRD results obtained in the alloys immersed in chloride molten salts along with the different thermal treatment performed are shown in Table 6.

In this case, corrosion products containing magnesium, chloride and oxygen were detected in the experiments with thermal treatments that corresponds to higher corrosion rates. In this direction, corrosion test without a previous purification treatment showed the presence of MgOHCl, as the main aggressive impurity present in chloride molten salts.

5. Conclusions

A specific purification treatment is necessary to reduce the corrosive impurities in chloride molten salts to be used in the new generation of...
A viable method for drying and purifying chloride salts is proposed in this paper. The thermal treatment selected could be applied in the commercial application in a cost-effective way minimizing times involved for drying/heating energy requirements.

An important corrosion rate reduction was obtained after thermal treatment selected in this research, reducing this parameter 68%, from 19.66 mm/year to 6.33 mm/year.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Angel G. Fernández wants to acknowledge the financial support from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant No 712949 (TECNIOspring PLUS) and from the Agency for Business Competitiveness of the Government of Catalonia. This work was partially funded by the Ministerio de Ciencia, Innovación y Universidades de España (RTI2018-093849-B-C31). The authors would like to thank the Catalan Government for the quality accreditation given to their research group GREIA (2017 SGR 1537). GREIA is a certified agent TECNO in the category of technology developers from the Government of Catalonia. This work is partially supported by ICREA under the ICREA Academia programme.

Supplementary materials


References

[24] W. Ding, H. Shi, Y. Xia, A. Bonk, A. Weisenburger, A. Jizana, T. Bauer, Hot corrosion treatment selected in this research, reducing this parameter 68%, from 19.66 mm/year to 6.33 mm/year.
