



# Corrosion of stainless steels and low-Cr steel in molten $\text{Ca}(\text{NO}_3)_2\text{--NaNO}_3\text{--KNO}_3$ eutectic salt for direct energy storage in CSP plants



A.G. Fernández<sup>a,b,c,\*</sup>, H. Galleguillos<sup>c</sup>, E. Fuentealba<sup>b,c</sup>, F.J. Pérez<sup>a</sup>

<sup>a</sup> Surface Engineering and Nanostructured Materials Research Group, Complutense University of Madrid, Avenue Complutense s/n, Madrid, Spain

<sup>b</sup> Energy Development Center, University of Antofagasta, Avenue Universidad de Antofagasta, 02800 Antofagasta, Chile

<sup>c</sup> Solar Energy Research Center (SERC-Chile), Avenue Tupper 2007, Piso 4, Santiago, Chile

## ARTICLE INFO

### Article history:

Received 28 November 2014

Received in revised form

9 April 2015

Accepted 4 May 2015

Available online 23 May 2015

### Keywords:

Molten salt

Heat transfer fluid

Thermal energy storage

Stainless steels

## ABSTRACT

The corrosive effects of a molten nitrate mixture of 48%  $\text{Ca}(\text{NO}_3)_2$  + 7%  $\text{NaNO}_3$  + 45%  $\text{KNO}_3$  were appraised at 390 °C on two different types of stainless steels (AISI 304, 430), a low-Cr alloy steel (T22) and a carbon steel (A1).

The corrosion rates were determined using gravimetric tests, which measured the weight gain during 2000 h to identify the corrosion products with scanning electron microscopy (SEM) and X-ray diffraction (XRD).

Studies on stainless steel revealed a better behaviour in corrosive environment, which mainly identifies the formation of  $(\text{K},\text{Na})\text{CrO}_4$  protective spinel.

$\text{Fe}_2\text{O}_3$  and  $\text{Fe}_3\text{O}_4$  were the other important products that were found in the tests performed at 390 °C; the formation of some stable compounds with salt impurities, such as carbonates and sulphates, was also observed.

© 2015 Elsevier B.V. All rights reserved.

## 1. Introduction

In recent years, renewable energy and its practical application have been increasingly studied. Solar energy is one of the most evolved types of renewable energy because of the development of energy storage systems that increases plant performance to function under unfavourable weather or night periods. An important component of a thermal-energy storage (TES) system is the choice of heat transfer fluids (HTF) in the solar plant. The general characteristics of molten salts are as follows:

- remaining in the liquid state over a wide range of temperatures;
- ability to dissolve a relatively large amount of many inorganic and organic compounds;
- low vapour pressure and stability at normal pressures;
- low viscosity because the ions are mutually independent for most cases;
- chemical inertness (no reaction with air or water); and
- high heat capacity per unit volume.

Because millions of kilograms of molten salts are required for energy storage and entail a high capital-investment cost, minimising that cost while maintaining a great heat transfer fluid performance is important.

From the technical viewpoint, the crucial requirements for the storage concept are as follows:

- High energy density (per-unit mass or per-unit volume) in the storage material.
- Good heat transfer between the heat transfer fluid (HTF) and the storage medium.
- Mechanical and chemical stabilities of the storage material.
- Compatibility among the HTF, heat exchanger and/or storage medium.
- Complete reversibility for a large number of charging/discharging cycles.
- Thermal losses.
- Ease of control.

The main energy storage system is based on *sensible* energy storage, which is designed with two tanks: a “cold” tank to collect solar heat and a “hot” tank to store thermal energy [1,2]. If the storage system in these tanks is direct, the heat transfer fluid also

\* Corresponding author.

E-mail address: [angel.fernandez@uantof.cl](mailto:angel.fernandez@uantof.cl) (A.G. Fernández).

serves as a storage medium, whereas in an indirect system, a second medium is used to store the heat [3].

The commercial parabolic trough plants use a mixture of organic compounds, diphenyl oxide and biphenyl, as the heat transfer fluid in the collector field. This oil offers the best combination of a low freezing point (12 °C) and upper temperature limit (393 °C) among the available heat transfer fluids [4,5]. However, to relax the temperature and pressure limitations of the synthetic oil, molten salt is required, which can be adopted as the heat storage fluid.

These inorganic molten fluids offer several favourable characteristics: upper temperature limits in the range of 500 °C, low unit cost and vapour pressure and satisfactory physical properties. Oil elimination to nitrate salt heat exchangers also reduces the unit storage system cost. However, the primary disadvantage of most molten salt formulation is its relatively high freezing point of approximately 230 °C [6]. Thus, multiple new formulations have been developed in the field of solar applications to avoid the nuisance in oil-to-salt heat transfers by using the same fluid in both collectors and storage tanks [7–11].

Several reports mentioned this nitrate mixture, which is commercially available under the name Hitec XL, and a recent paper studied the preparation, handling considerations and characterisation of this ternary molten salt mixture [12,13].

However, no publication in the open literature has reported the corrosion ability in this promising molten salt. In this study, we examined the behaviour of the calcium ternary mixture in comparison with the obtained results of the currently used solar salt in CSP plants, which was tested in a previous study [14].

The corrosive effect of this salt is based on the following reduction reaction:



That reaction oxidises iron atoms, which diffuse from the material [15]:



To understand the process in alkaline nitrates, it is important to note the formation of different (several) oxide ions during the corrosion tests.

The experiments of Singh et al. [16] indicate the existence of  $\text{O}^{2-}$  oxide,  $\text{O}_2^{2-}$  peroxide and  $\text{O}_2^-$  superoxide ions, which formed from unstable oxide ions in the nitrate melt as described in the following reactions:



Several authors studied the formation of these oxides in the corrosive process [17–19], highlighting that the ions  $\text{K}^+$  and  $\text{Na}^+$  have different affinities for the formed ions in reactions 4 and 5 as follows:



The formation of these oxides hinders the required electronic movement to generate a cathodic reaction and decreases the corrosive ability of the salt. The moisture effect in these reactions has also been studied by the aforementioned authors and establishes the following reaction intermedium:



**Table 1**  
Impurity levels of Hitec XL salt.

Parameter	Initial values
$\text{Cl}^-$ (%)	0.078
$\text{SO}_4^{2-}$ ( $\mu\text{g/g}$ )	290.29
Ca ( $\mu\text{g/g}$ )	90033.08
Cr ( $\mu\text{g/g}$ )	< 1
Fe ( $\mu\text{g/g}$ )	< 1
Mg ( $\mu\text{g/g}$ )	69.36
Humedad (%)	4.83769
$\text{NO}_2^-$ ( $\mu\text{g/g}$ )	8.015



In this environment, the potassium and sodium oxides are more solvable, which allows a better course of the cathodic reaction and increases the salt corrosive ability [20,21].



The concentration of oxide ions can affect the corrosive effects in melts that have been subject to hydrolysis through contact with atmospheric moisture. Based on this phenomenon, it can be inferred that the formation of alkali oxides and their inhibitory activity in nitrate reduction is not effective in salts containing water.

The corrosion reaction proceeds primarily by oxidation, which is followed by the dissolution of metal oxides in the melt. Molten salts often act as fluxes and remove oxide layers on the container materials, which generally may be protective.

This paper aims to evaluate the main parameters that affect the corrosiveness of Hitec XL molten salt. To achieve this goal, we compared the corrosion caused by the salt in two carbon steels: A1 and T22.

This study has been focused on the parabolic-trough technology, where the solar storage temperature was 390 °C. In addition, the corrosion ability was evaluated on two stainless steels: AISI 304 and 430.

## 2. Materials and methods

The specimens that were analysed in the gravimetric corrosion tests have dimensions of 20 mmx10 mmx2 mm and were prepared using a disc impregnated with diamond powder and were subsequently grinded with silicon carbide (SiC) abrasive paper with a P1000 (SiC particle size: 18.3  $\mu\text{m}$ ) granulometry, which produced a homogeneous surface of the sample and eliminated possible oxides and small imperfections where corrosion could locate. The samples were subsequently washed with acetone in an ultrasound bath to eliminate any remaining dirt on the specimen. The sample dimensions were measured with an electronic calibre and weighed with an analytical balance with a 0.00001 g (10  $\mu\text{g}$ ) responsiveness. Then, the samples were placed in alumina crucibles with the saline mixture and heated in a resistance oven at 390 °C.

Gravimetric measurements were taken at 24, 48, 150, 350, 500, 675, 850, 1000, 1250, 1500, 1750 and 2000 h of the assay for the isothermal immersion test.

After the samples were removed from the oven, they were slowly cooled in warm distilled water to eliminate the salt in which they were immersed. Then, they were dried and weighed, and the average value was obtained from five weight values. The formula (Eq. (1)) to calculate the mass gain over time is

$$\frac{\Delta m}{S_0} = \frac{m_i - m_f}{S_0} \quad (1)$$

Download English Version:

<https://daneshyari.com/en/article/77719>

Download Persian Version:

<https://daneshyari.com/article/77719>

[Daneshyari.com](https://daneshyari.com)