

# Corrosion properties of a ternary nitrate/nitrite molten salt in concentrated solar technology



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## ABSTRACT

The enhancements in the storage systems developed by solar thermal power plants have provided to renewable energy a considerable increase in efficiency. Thermal Energy Storage (TES) using HITEC mixture could be used as Heat Transfer Fluid (HTF) in concentrated solar linear technology.

In this research, the corrosive effects of HITEC mixture composed by 40 wt% NaNO<sub>2</sub> + 7 wt% NaNO<sub>3</sub> + 53 wt% KNO<sub>3</sub> were assessed at 390 °C on a carbon steel (A516) and on low-Cr alloy steels (T11 and T22). The corrosion rates were determined by gravimetric tests, measuring the weight gain during 2000 h, identifying the corrosion products via scanning electron microscopy and X-ray diffraction. T22 steel shows a corrosion layer of 6.05 microns, with a protective layer formed in the inner zone to the material, identified through DRX as the K<sub>2</sub>CrO<sub>4</sub> protective spinel.

Fe<sub>2</sub>O<sub>3</sub> and MgO were the others important products found on the tests performed at 390 °C, being observed also the formation of some stable compounds with the impurities of the salt, as carbonates.

The use of the HITEC mixture in solar technology would provide a less aggressive behaviour for materials in contact with it, providing an increase in operational life cycles in current solar technology.

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## 1. Introduction

Molten salt are widely applied as heat transfer media in Concentrating Solar Power (CSP) plants. An important component of Thermal Energy Storage (TES) systems is the choice of heat transfer fluids used in a solar plant. The main challenges to making electrical power generation from solar thermal plants more profitable are the following:

- Reducing the investment, operational and maintenance costs;
- Extending the hours of operation and energy supply;
- Increasing the temperatures in the thermal cycle;
- Increasing the lifetime of power plants.

Research and development in the solar energy sector has focused on reducing the high cost associated with the operation

and maintenance of these plants. One of the most important lines of research in this regard is the study, design and characterisation of the salts that are used as energy storage fluids.

The thermal properties of the HITEC mixture, a molten salt composed of 40 wt% NaNO<sub>2</sub> + 7 wt% NaNO<sub>3</sub> + 53 wt% KNO<sub>3</sub>, are highly suited to its use as storage fluid in CSP plants [1].

This ternary mixture was first proposed for use as a storage fluid in the THEMIS experimental solar plant in France in the 1980s [2,3]. It is worth noting that one of the disadvantages of this mixture is the need to use a protective layer of inert gas at temperatures above 350 °C to avoid the oxidation of the nitrites upon contact with the oxygen in the atmosphere. This is the main reason which prevents at present the widespread use of this salt on thermoelectric solar plants.

However the use of the HITEC mixture in solar technology is once again under consideration, albeit for specific applications only. A number of research projects are currently seeking to improve the physical properties of the mixture to a point in which the mixture enhanced properties could compensate its higher costs.

To this end, M. Xi Ho and R. Olivares [1,4] tried to improve the mixture's thermal properties as well as its thermal stability under

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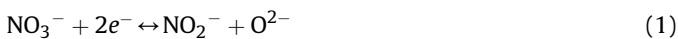
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different atmospheres, to allow for its use as Heat Transfer Fluid in concentrated linear solar technologies (Parabolic Trough Collectors and Linear Fresnel).

The present research introduces a new parameter to be taken into account when using the mixture as solar energy storage fluid, the corrosion potential. This is parameter seldom reported in the bibliography but of vital importance when developing a new generation of solar plants that are both cheaper and profitable. The present study shows the results of an isothermal corrosion study at 390 °C (the storage temperature in solar plants using parabolic trough collectors) in a number of carbon steels and with low Cr content. The objective of this study is to establish the influence of the Cr additions in commercial steels, for which a comparative study was carried out in the commercial steel A516, which is currently used as a building material in CSP technology.

### 1.1. Corrosion processes in molten nitrate salts

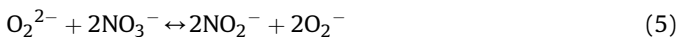
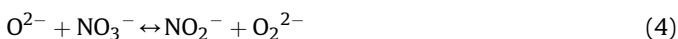
The corrosive effect of these salts is based on the following reduction reaction:



which results in the oxidation of iron atoms that diffuse from the material [5,6]:



To understand this process in alkaline nitrates, it is important to note the formation of several different oxidized ions during the corrosion tests. Experiments performed by I.B. Singh et al. [7] indicate the existence of  $\text{O}^{2-}$  (oxide),  $\text{O}_2^{2-}$  (peroxide) and  $\text{O}_2^-$  (superoxide), which arise from unstable oxide ions in the nitrate melt, as described by the following equations:



Several authors have studied the formation of these oxides in these salts during the corrosion process [8,9], which results in the formation of  $\text{Na}_2\text{O}$  and  $\text{KO}_2$ ; the  $\text{K}^+$  and  $\text{Na}^+$  ions have different affinities for the ions formed in equations (5) and (6).



The formation of these oxides hinders the electronic movement required to generate the cathodic reaction, which decreases the corrosiveness of the salts.

The salt mixtures studied in this paper are commercial grade, so impurities will be a factor to consider in the analysis and discussion of the thermal properties and corrosion potential. The common oxidant in molten salts, which accelerate corrosion, are  $\text{O}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{H}^+$  and  $\text{OH}^-$  [10]

Furthermore, water may dissociate into  $\text{H}^+$  and  $\text{OH}^-$ , and  $\text{Cl}_2$  can be present in the molten salt after reacting with oxygen:



Perchlorates are present in commercial molten nitrates as impurities; these impurities need to be controlled during the melting

**Table 1**

Chemical composition of HITEC salt.

Parameter	Initial values
$\text{Cl}^-$ (%)	0,0795
$\text{SO}_4^{2-}$ (µg/g)	431,57
Ca (µg/g)	35,76
Cr (µg/g)	<1
Fe (µg/g)	<1
Mg (µg/g)	70,14
Moisture (%)	0,14737
$\text{NO}_2^-$ (µg/g)	268001,4

process to reduce as much as possible their content in the melt. When the temperature increases, the perchlorate ion starts to dissociate into oxygen and chloride, which exponentially increases the corrosion of materials in contact with this environment.

The amount of perchlorate ( $\text{ClO}_4^-$ ) can be reduced by increasing the amount of chlorides in the melt. It is important to note that the perchlorate ion is an impurity present in the commercial salts used in this research.



The presence of both, oxygen and chlorine, increases the corrosion ability of these salts. Kleppa et al. [11] determined the influence of steric hindrance on the formation of compounds of  $\text{ClO}_4^{2-}$  with Na or K ions. The formation of  $\text{KClO}_4$  was favoured because K ion is smaller, which a melting point of 510 °C.

The objective of this study is to establish the corrosion ability in HITEC mixture in order to evaluate the most appropriate materials as well to determine the plant's life cycle.

## 2. Material and methods

The saline nitrates that were used in the research were  $\text{NaNO}_2$ ,  $\text{NaNO}_3$  and  $\text{KNO}_3$  (Sigma–Aldrich 98%). The impurity content of tested Hitec salt is shown in Table 1 and was determined using the Volhard procedure ( $\text{Cl}^-$ ), Gravimetry (% moisture,  $\text{SO}_4^{2-}$ ), UV–Vis spectroscopy ( $\text{NO}_2^-$ ) and ICP-OES (Mg).

The importance of the studied parameters is based on the following factors:

- $\text{Cl}^-$ : Appears as a corrosion enhancing agent. A slight increase from the initial value is due to the decomposition reaction of the perchlorate in the mixtures.
- $\text{SO}_4^{2-}$ : An important parameter to follow because sulphates are able to form insoluble compounds that can clog pumps and pipes, which affects the circulation of the salt in the solar power plant.
- Mg is an important impurity in the salt that forms oxides and is able to form magnesiumferrite, a very stable compound formed by the interaction between Mg and hematite ( $\text{Fe}_2\text{O}_3$ ).

The corrosion tests were performed on commercial steels with the compositions shown in Table 2 at storage temperature used in parabolic trough solar power plants (390 °C).

**Table 2**

Chemical composition of carbon steels studied.

Steel	Weight %						
	Si	Mn	Cr	P	Mo	C	S
A516	0.1	0.93		0.035		0.27	0.035
T11	0.79	0.44	1.2	0.008	0.5	0.1	0.002
T-22	0.3	0.4	2.25	0.3	1	0.12	0.3

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