



# Improvement of the corrosion properties in ternary molten nitrate salts for direct energy storage in CSP plants



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## ABSTRACT

The corrosive effects of a molten nitrate mixture composed by 20% LiNO<sub>3</sub> + 28% NaNO<sub>3</sub> + 52% KNO<sub>3</sub> were appraised at 390 °C on a low-Cr alloy steel (T22) and a carbon steel (A1). The corrosion rates were determined using gravimetric analysis, which measures the weight gain over 2000 h in order to identify the corrosion products with scanning electron microscopy (SEM) and X-ray diffraction (XRD).

The observed behavior was compared with the corrosion ability produced by 58% KNO<sub>3</sub> + 11% Ca(NO<sub>3</sub>)<sub>2</sub> + 31% LiNO<sub>3</sub> mixture. The results shown improved behavior in the ternary molten salt with calcium nitrate content due to the reduction of chloride ion levels and the superior diffusion and formation of protective spinels, such as MgCr<sub>2</sub>O<sub>4</sub> and FeCr<sub>2</sub>O<sub>4</sub>, which were detected in ternary molten salt with Ca(NO<sub>3</sub>)<sub>2</sub> content.

The formation of certain stable compounds with salt impurities, such as carbonates and sulfates, was also observed.

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## 1. Introduction

The solar conditions in northern Chile, particularly in the Atacama Desert, which presents an annual global radiation value of approximately 2500 kW h/m<sup>2</sup> and an index of direct normal irradiance (DNI) of 3500 kW h/m<sup>2</sup>, are among the best worldwide for capturing and storing solar energy. These features are more relevant when considering the high concentrations of saline deposits that are found in this area.

Northern Chile contains the world's largest commercially exploited nitrate and iodine deposits and is the source of other natural nitrates, such as caliche ore (Fig. 1) (Ortega et al., 2010). The raw minerals reservoirs are found as solid deposits (caliches) and brines in vast salt flats called *Salares* with grades that are profitable when large extractions (30,000 tons/year) are targeted, such as for solar thermal storage applications (Ushak et al., 2015).

During the extraction process, the brines from salt reservoirs are pumped from beneath the saline crust in two different areas, obtaining a wide range of highly concentrated products. In one area, high concentration levels of potassium and lithium can be

observed (Cabeza et al., 2015), and in the other, the obtained brines contain high concentrations of sulfate and boron.

Chilean deposits have great potential to be exploited to obtain new molten nitrates with the possibility of improving the properties currently associated to the solar binary salt (60% NaNO<sub>3</sub> + 40% KNO<sub>3</sub>). To explore this potential, research and development in the solar energy sector is focused on reducing the high cost of the operation and maintenance of these plants (Wang et al., 2012a,b; Bradshaw and Meeker, 1990; Bradshaw, 2009; Bauer and Tamme, 2010).

Binary mixtures of alkali molten nitrates/nitrites present phase diagrams with a simple eutectic point. By adding one or more components, it is expected that the resulting mixture will have a lower melting point compared to the initial eutectic binary mixture.

In this direction, the design of multicomponent mixtures by the addition of alkali/alkaline earth nitrates could extend the working temperature range of thermal energy storage (Fernandez et al., 2014b; Mantha et al., 2013; Olivares, 2012; Peng et al., 2010; Kleppa and Meschel, 1963; Raade and Padowitz, 2010; Bradshaw and Clift, 2010; Cordaro, 2011; Raade et al., 2011; Bauer et al., 2011; Glatzmaier and Gomez, 2013). The additives that present greater potential to be used for solar energy storage are Ca(NO<sub>3</sub>)<sub>2</sub> and LiNO<sub>3</sub> because these salts decrease the melting point and improve the thermal stability, respectively.

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Fig. 1. Principal salt reservoirs in the North of Chile.

Fernandez et al. (2014b) proposed the study of molten salts of more than three components as a novel approach to achieve a synergic effect between the properties of  $\text{LiNO}_3$  and  $\text{Ca}(\text{NO}_3)_2$  additives and the components of the solar salt.

The most notable property of the molten salts using calcium and lithium nitrate is its energy density (based on the heat capacity), which represents an important improvement over the solar salt currently used. Based on this parameter, a smaller amount of salt could be used to store the same amount of energy.

However, there are not publications in the literature reporting the corrosion ability in these promising molten salts. In this study, we examined the behavior of ternary molten salts containing  $\text{LiNO}_3$  and  $\text{Ca}(\text{NO}_3)_2$  in contrast with the obtained results in the binary solar salt currently used in CSP plants, which was tested in a previous study (Fernández et al., 2012), using the same isothermal test conditions.

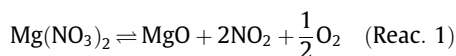
## 2. Influence of impurities in molten nitrates salts used in TES

Broad ranges of studies are informing that impurity levels tend to drive corrosion (Fernandez et al., 2014a). Kruizenga (2012) postulated that chlorine initially grows at surface of the oxide-metal interface. As the metal chloride diffuses toward the external surface, it is oxidized to form a non-protective oxide layer (Littlewood and Argent, 1961). Due to these assets, salt purification is critical for materials and for their corrosion properties. In the literature, purification was performed using the following approaches: a chlorinating process (the addition of  $\text{CCl}_4$ ,  $\text{HCl}$ , or another chlorinating compound); reduction of the salt using active metals, such as Mg or saturation of a salt with a liquid metal (i.e.,  $\text{LiCl}$  with Li metal) such that redox potential of the melt is lowered.

The impurities of Chilean nitrates with influence on the thermal behavior at elevated temperatures are the following (Gil et al., 2010):

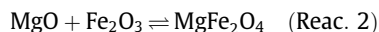
- $\text{SO}_4^{2-}$  and  $\text{CO}_3^{2-}$ : easily form calcium, magnesium, sodium and potassium compounds, which are frequently found in molten salts. The formation of these solid compounds can clog vessels, thus reducing the flowability of the mixtures through the pipes of the solar centrals. Corrosion-erosion problems arise in the connections, vessels as well as in propulsion pumps and heat exchangers.
- Mg: present in the form of magnesium nitrate, easily forms magnesium oxides, which can be found attached to the steel surface during the initial hours of exposure to the salt. In addition, note the integration of magnesium in the structure of hematite ( $\text{Fe}_2\text{O}_3$ , and other corrosion products present in steels) that leads to the development of magnesium ferrites ( $\text{MgFe}_2\text{O}_4$ ).
- $\text{Cl}^-$ : appears as a corrosion enhancing agent and is found in the form of perchlorates. Therefore, the study of the distribution and content of  $\text{Cl}^-$ , as well as its evolution in the salt, is important.

Medrano et al. (2010) noticed the presence of magnesium impurities in solar salt (60%  $\text{NaNO}_3$  + 40%  $\text{KNO}_3$ ), which add complexity to the melting process in commercial salts. These impurities start to decompose above  $480^\circ\text{C}$  with no interaction between Mg and the steels observed up to this temperature. Above this temperature, magnesium nitrate decomposes according to the following reaction:

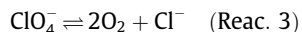


Therefore, the salt must be pretreated before usage to remove the  $\text{Mg}(\text{NO}_3)_2$ . This pretreatment could be accomplished by heating the salt mixture to  $552^\circ\text{C}$  for approximately 30 days followed by a venting process of the  $\text{NO}_x$  gas. However, in the vent stacks,  $\text{NO}_x$  and water vapor forms nitric and nitrous acid, which result in corrosion of the vent pipe (Wang et al., 2013); therefore, this process must be performed carefully.

The obtained magnesium compounds ( $\text{MgO}$ ) can interact with the regular iron corrosion products for the main nitrate application. Zimmol et al. (1997) studied the synthesis of  $\text{MgFe}_2\text{O}_4$ , establishing mutual solubility between  $\text{MgO}$  and  $\gamma\text{-Fe}_2\text{O}_3$ , which allows the formation of the spinel through the reaction:



Chlorine is another important impurity of these salts, which is generally found as perchlorate in the analyzed medium (Ebrahimifar and Zandrahimi, 2011; Li et al., 2012; Piemonte et al., 2011; Baraka and El Hosary, 1976; Singh and Sen, 1992; Grabke et al., 1995; Bradshaw and Clift, 2010). At high temperatures, the  $\text{ClO}_4^-$  perchlorate ion dissociates into oxygen and chloride via the reaction:



The presence of both oxygen and chlorine increases the corrosive capacity of these salts. Kleppa and Meschel (1963) determined the influence of steric hindrance in the formation of compounds of  $\text{ClO}_4^-$  and Na or K ions. The formation of  $\text{KClO}_4$  was favored due to the lower molecular size in potassium ions. The authors found more affinity in the formation of this compound, having measured the melting point at  $510^\circ\text{C}$ . However, in more recent studies (Lee, 2001; Pourmortazavi, 2006) performed using TGA for potassium perchlorate, more accurate signals were obtained for describing the behavior of this compound at high temperature, resulting in a solid state transition from a rhombic phase towards cubic phase at approximately  $300^\circ\text{C}$ , and compound melting at  $590^\circ\text{C}$ , with perchlorate decomposition resulting in oxygen and KCl.

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