Thermal influence in corrosion properties of Chilean solar nitrates

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Abstract

Chile's Atacama Desert is one of the world's premier locations for the study and application of solar power. The typical impurities present in Chilean nitrates are Mg, SO_4^- and Cl^-, among others. Developing a heat treatment to eliminate impurities and optimise the quality of the salts from the solar flats of the Atacama Desert is one of the most important goals of the inorganic chemistry industry in northern Chile.

In this study, a full characterisation of the binary solar salt 60% $NaNO_3$ + 40% KNO_3 was performed by studying the influence of the most important impurities on the thermal processes and corrosiveness at the storage temperatures of the most important solar thermal plants.

Moisture is another parameter that is important for this technology. The corrosion test results improve after heat treatment.

The corrosion characteristics were determined using gravimetric tests, measuring the weight gain of three alloy steels with low Cr contents at 390 °C over 2000 h and identifying the corrosion products using scanning electron microscopy (SEM) and X-ray diffraction (XRD).

Fe_2O_3 and Fe_3O_4 were the most important corrosion products. Additionally, some stable compounds were formed from the impurities in the salt, such as magnesium ferrite ($MgFe_2O_4$).

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1. Introduction

The solar conditions in northern Chile and, in particular, the Atacama Desert, which has an annual global radiation value of 2500 kW h/m^2 and an index of direct normal irradiance (DNI) of 3500 kW h/m^2, are among the best in the world for capturing and storing solar energy (www.csptoday.com/Chile). These features are very important because there is a high concentration of saline deposits in this area. These salts are used in current solar technologies for fluid energy storage and provide significant benefits because this type of storage considerably increases the performance of solar plants and provides energy at night (Gil and Medrano, 2010). This characteristic is fundamental to the sustainable development of the mining industry in northern Chile, which requires energy 24 h per day.

Different mixtures of alkali nitrates have been used as the energy storage fluid at solar plants. The best mixture is called solar salt and is composed of 60% $NaNO_3$ and 40% KNO_3. This mixture melts at 223 °C, is thermally

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stable to approximately 600 °C, and offers a favourable combination of high density, low vapour pressure, moderate specific heat, low chemical reactivity, and low cost (Kearney and Kelly, 2004).

In addition to these features, this mixture of molten nitrates also satisfies other important requirements of solar plants, such as thermal conductivity, diffusivity and a low heat loss coefficient (Kolb, 1998). To have good efficiency, the heat storage fluid needs to have a low vapour pressure due to the heat exchanger in solar plants reaches a pressure of 20 bar, and this increase can cause heat losses.

The binary solar salt 60% $NaNO_3$ + 40% KNO_3 has been widely studied over the last 20 years. Its thermal properties have been reported by several authors (Dudda and Shin, 2012; Piemonte et al., 2010; Kamimoto and Tanaka, 1980; Pacheco and Showalter, 2002; Herrmann and Kelly, 2004; Hasuike et al., 2006; Bauer et al., 2011), which justifies its use as a storage fluid in CSP plants. However, few authors have evaluated its corrosiveness towards different steels (Fernández and Lasanta, 2012; Fernández and Rey, 2014; Goods, 1983; Goods and Bradshaw, 1999; Robert W. Bradshaw, 2003; Goods and Robert W. Bradshaw, 2003; Robert W. Bradshaw, 2010).

The goals of this paper are to evaluate the main parameters that influence the corrosiveness of these molten salts and to propose and evaluate a thermal treatment that is performed prior to the complete melting of the salt, which reduces the impurities that influence the corrosiveness of the salt. To achieve this goal, we performed a comparative study of the corrosion caused by the salt (with and without thermal treatment) in two carbon steels, A1 and T22; the latter has 2.25% Cr, and its behaviour was evaluated in a previous report (Fernández and Lasanta, 2012), so the experiments will be performed solely on the thermally pretreated salt. This study is focused on parabolic trough technology, where the solar storage temperature is 390 °C. Additionally, heat treatment effect was evaluated on two stainless steels, 304 and 430, in simulated storage conditions (550 °C) using central tower technology.

1.1. Corrosion processes in molten nitrate salts

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

$$NO_3^- + 2e^- \Longleftrightarrow NO_2^- + O^{2-} \tag{1}$$

which results in the oxidation of iron atoms that diffuse from the material (Baraka et al., 1976; De Jong and Broers, 1976):

$$Fe + O^{2-} \Longleftrightarrow FeO + 2e^- \tag{2}$$

$$3FeO + O^{2-} \Longleftrightarrow Fe_3O_4 + 2e^- \tag{3}$$
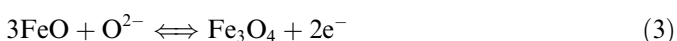
To understand this process in alkaline nitrates, it is important to note the formation of several different oxidized ions during the corrosion tests. Experiments performed by Singh (1993) indicate the existence of

O^{2-} (oxide), O_2^{2-} (peroxide) and O_2^- (superoxide), which arise from unstable oxide ions in the nitrate melt, as described by the following equations:

$$O^{2-} + NO_3^- \Longleftrightarrow NO_2^- + O_2^{2-} \tag{4}$$

$$O_2^{2-} + 2NO_3^- \Longleftrightarrow 2NO_2^- + 2O_2^- \tag{5}$$
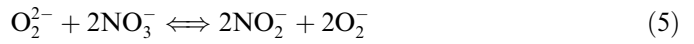
Several authors have studied the formation of these oxides in these salts during the corrosion process (Desimoni and Palmisano, 1977; Palmisano et al., 1978), which results in the formation of Na_2O and KO_2; the K^+ and Na^+ ions have different affinities for the ions formed in Eqs. (4) and (5):

$$2Na^+ + O^{2-} \rightarrow Na_2O \tag{6}$$

$$2K^+ + 2O_2^- \rightarrow KO_2 \tag{7}$$

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

The effect of moisture was also studied by the previously mentioned authors, and they described the following reaction intermediates (Zambonin and Cardetta, 1970; Singh, 1995):

$$H_2O + NO_3^- \rightarrow HONO_2 + OH^- \tag{8}$$

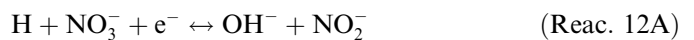$$HONO_2 + 2e^- \rightarrow NO_2^- + OH^- \tag{9}$$

In this environment, the oxides of potassium and sodium are more soluble, which increases the rate of the cathodic reaction and the corrosiveness of the salt.

$$H_2O + NO_3^- + 2e^- \rightarrow NO_2^- + 2OH^- \tag{10}$$
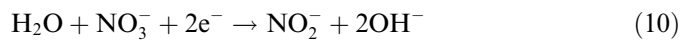
The influence of the water content in the salt was evaluated by several authors; (Zambonin and Cardetta, 1970) analyzed the influence of water in molten nitrates and their interaction at elevated temperature. They examined the process in two stages: Stage 1
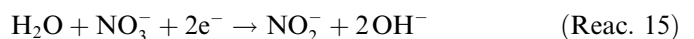
$$H_2O + e^- \leftrightarrow OH^- + H \tag{Reac. 11}$$

Stage 2

$$H + NO_3^- + e^- \leftrightarrow OH^- + NO_2^- \tag{Reac. 12A}$$

$$\frac{1}{2}(H + H \leftrightarrow H_2) \tag{Reac. 12B}$$

where reaction 12A is generated by reactions 13 and 14:

$$H + NO_3^- \leftrightarrow OH + NO_2^- \tag{Reac. 13}$$

$$OH + e^- \leftrightarrow OH^- \tag{Reac. 14}$$

Stages 11 and 12A yield reaction 15, which involves two electrons per mole of water:

$$H_2O + NO_3^- + 2e^- \rightarrow NO_2^- + 2OH^- \tag{Reac. 15}$$

In contrast, if the net reaction is described by 11 and 12B, the following reaction is obtained:

$$H_2O + e^- \leftrightarrow OH^- + \frac{1}{2}H_2 \tag{Reac. 16}$$