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New insights into the corrosion mechanism between molten nitrate salts and ceramic materials for packed bed thermocline systems: A case study for steel slag and Solar salt

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ABSTRACT

Thermal energy storage (TES) systems based on packed bed arrangements are proven to be a very promising route to decrease the levelized cost of electricity (LCOE) in concentrated solar power (CSP) plants. However, the compatibility between the TES material and the heat transfer fluid (HTF), which operate in direct contact, is known to be a major limitation for such configuration. In this regard, the compatibility between a molten nitrate salt (Solar salt) and a ceramic by-product from the steel production, the steel slag, is investigated in this work. The obtained results show that the standard criteria used for determining any chemical incompatibility phenomena like the formation of a corrosion layer or the appearance of structural modifications, are not enough to draw a conclusion on the materials compatibility. A deep analysis of the TES material and the HTF chemical compositions revealed a migration of cations from the slag to the salt, and the formation of nitrites in the latter boosted by the presence of the slag. These two mechanisms lead to the modification of the thermo-physical properties of the salt.

1. Introduction

The implementation of low cost and effective thermal energy storage (TES) systems (Zhang et al., 2016) in many applications such as concentrated solar power (CSP) (Liu et al., 2016), industrial waste heat recovery or adiabatic compressed air energy storage (ACAES) (Budt et al., 2016) is a promising way to increase the efficiency and competiveness of these technologies. In CSP plants, the TES system allows the electricity production during night or low irradiation periods and thus, increases the total number of working hours of the plant. On the other hand, in energy-intensive industries such as the steel, glass or cement production, the implementation of this type of systems allows the recovery of considerable amount of waste energy (Brückner et al., 2015; U.S. Department of Energy Industrial Technologies Program, 2008), typically released to the atmosphere, to be used in the process itself or in the electricity production. Finally, in ACAES plants, the TES unit is of vital importance for the global efficiency of the process. In this application, the TES system is used to cool down the air after the compression stage and before being stored in a cavern, and to heat the air before being fed to the turbine in the electricity production operation. A proper TES design can improve the ACAES technology competitiveness with traditional concepts like pumped-storage hydroelectricity (RWE Power AG, 2010; Ortega-Fernández et al., 2017).

The most mature thermal energy storage technology is based on a double tank solution of molten nitrate salts (typically a mixture of 60% of $NaNO_3$ and 40% of KNO_3, so-called “Solar salt”). Even if this technology has been implemented in many industrial applications, it presents as a main drawback the high cost due to the salt price (1.08 US $/kg (Zhang et al., 2016). Hence, it contributes to the increment of the levelized cost of electricity (LCOE) in CSP plants.

Aiming at the reduction of the total cost of a TES system, many research activities are being carried out in this field. For example, the formulation of new salts to increase the operational temperature range (Nunes et al., 2016; Serrano-López et al., 2013; Fernández et al., 2014), the addition of nanoparticles to increase the salt heat capacity and hence to reduce the required amount (Tiznobaik and Shin, 2013; Hentschke, 2016) or, the partial salt substitution by means of the implementation of a single-tank packed bed configuration in which, a low-cost solid filler material is used as storage media (Pacheco et al., 2002; Yin et al., 2017; Wu et al., 2016). This last approach consists of the use

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Fig. 1. Picture showing the general aspect of the studied EAF slag samples.

of sensible heat storage materials (SHSM) or encapsulated phase change materials (EPCM) in a packed bed configuration in which the heat transfer fluid (HTF) flows interstitially through the solid media packing. Although several authors introduced this heat storage concept (Pacheco et al., 2002; Ismail and Stugrinsky, 1999), its industrial deployment is still far from a full development. The large potential of the packed bed technology in the heat storage frame has extensively been studied (Zanganeh et al., 2012; Hoffmann et al., 2016; Cascetta et al., 2016). In this regard, many pilot plants have already being constructed and numerous research projects are ongoing to implement this concept at industrial level, such as the ORC-Plus (http), RESLAG (http), Airlight Energy Ait-Baha pilot plant (Airlight Energy) and ALACAES (Airlight Energy) projects, among others.

Regarding the filler material, a proper SHSM or EPCM has to accomplish different requirements to be used in this configuration. Among them, it needs to have balanced thermal properties in terms of energy density and thermal conductivity, appropriate mechanical properties, stability with thermal cycling and compatibility to operate in direct contact with the HTF. In addition to the previous requirements, a candidate filler material for a packed bed TES system should have low price to improve the competitiveness of this technology in comparison to the current molten salt double tank solution. With this ambitious objective, many research works have already been published, proposing different low cost materials such as natural rocks (Allen et al., 2014; Tiskatine et al., 2016; Jemmal et al., 2016; Grosu et al., 2017), high performance concretes (Laing et al., 2006; Hoivik et al., 2016), sand (Diago et al., 2015) or industrial by-products (Gutierrez et al., 2016; Grosu et al., 2018). Even though these materials have been widely studied in terms of their thermo-physical properties, few works are available dealing with corrosion studies between the filler material and HTFs like synthetic thermal oils (Grosu et al., 2018; Fasquelle et al., 2016) or molten nitrate salts (Grosu et al., 2018; Guillot et al., 2012; Motte et al., 2015; Calvet et al., 2013; Brosseau et al., 2005; Pacheco et al., 2002; Bonk et al., 2017). These works mainly apply techniques such as X-ray diffraction (XRD) or Scanning Electron Microscopy (SEM) to identify possible corrosion phenomena. However, it is demonstrated in this work that, even if with these techniques is possible to detect macroscopic corrosion mechanisms, i.e. corrosion/passivation layers, degradation of crystallographic phases (above ~5%), they do not guarantee the perfect compatibility between both materials. In this regard, very few works are available analysing, for example, possible variations in the thermophysical properties of the HTF (Bonk et al., 2017) caused by the cation/anions exchange or by the loss/gain of oxygen.

This work addresses a deep compatibility study between the steel slag and the most common molten nitrate salt used in CSP plants, the so-called Solar salt. The suitability of the steel slag in the TES frame has been already demonstrated in terms of its thermal properties and its cost-effectiveness (Ortega-Fernandez et al., 2015; Grosu et al., 2018). Taking this into account, the main goal of this work is the study of the possible chemical interaction behaviour of the steel slag in direct contact with Solar salt. For this purpose, long-term corrosion analyses have been performed, followed by a complete superficial, chemical and thermal properties characterization.

2. Materials and methods

2.1. Materials

Three electric arc furnace (EAF) slag samples from different

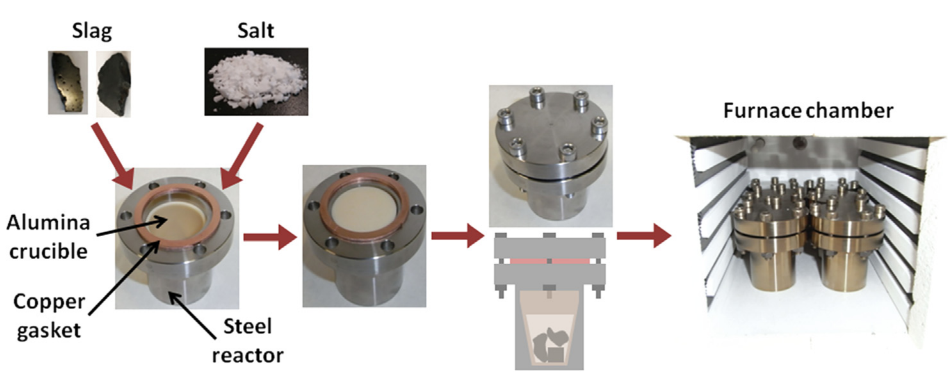

Fig. 2. Protocol followed in the preparation of the compatibility experiments.