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Thermophysical and chemical characterization of induction furnace slags for high temperature thermal energy storage in solar tower plants

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ABSTRACT

An induction furnace is an electric furnace in which ferrous metal scrap and fluxes (e.g. silica, limestone) are melted using an electromagnetic field to produce steel or cast iron. This metallurgical process is accompanied by the generation of large amounts of wastes called slags, which are composed mainly of a non-metallic part as well as a small metallic part. At the end of the melting process the slags layer is removed from the furnace top, then it is air-cooled and stored prior to discharge. While blast furnace slags (**BFS**), electric arc furnace slags (**EAFS**), and ladle furnace slags (**LFS**) were characterized in earlier works for thermal energy storage up to 1000 °C, the induction furnace slags **(IFS)** have never been investigated for this application. Thus the aim of this paper is the thermophysical and chemical characterization of **IFS** to be used as high-temperature thermal energy storage materials (around 1000 °C) in packed bed TES system. Chemical investigation of this metallurgical waste was conducted using: Energy dispersive X-ray spectroscopy (EDS) coupled with the Scanning electron microscopy (SEM), and infrared spectroscopy (FTIR). Their thermal heat capacity was measured using Modulated differential scanning calorimetry (MDSC), while their bulk density was determined using the pycnometer method. It was found that they have a good specific heat capacity ($\boldsymbol{C_p \approx 700\ \mathrm{J/kg\,^\circ C}}$) and a good bulk density ($\rho \approx \mathbf{2583\ kg/m^3}$). The thermal stability of the IFS was assessed using thermogravimetric analysis (TGA) from room temperature up to 1000 °C; Three cycles of heating/cooling were applied on the IFS and their thermal stability was proved at the end of the first cycle. The obtained results suggest that **IFS** are good candidate materials for high-temperature thermal energy storage application (up to 1000 °C).

1. Introduction

Concentrated solar power (CSP) technology combined with thermal energy storage (TES) technology is considered as a promising option to ensure a green and dispatchable production of electricity on an industrial scale. Nowadays, the most mature TES technology used in current commercial CSP plants is two-tank molten salts technology [1,2]. However this latter present many techno-economical drawbacks which are related directly to the storage medium: (1) Limited maximum operating temperature (e.g. up to 393 °C for parabolic through plants and up to 565 °C for solar tower plants [1]), (2) high freezing temperatures of the used salts (120–220 °C [3]), (3) relatively high cost of the molten salts (around 700 euros/ton [3]), (4) huge amount of storage medium are needed to ensure dispatchability of a CSP plant (e.g. around 28,000 t of molten salts are used in the 50 MWe ANDASOL 1 plant to ensure 7.5 h of storage capacity [4]), (5) low availability of molten salts for the future targeted CSP plants [3]. All these disadvantages disqualify the current state of the art of TES technology to be integrated into the future generation of CSP plants [1,5–7], which will require high operating storage temperature (e.g. more than 650 °C according to the 2020 SunShot target [1]). Recently, to overcome the economical limitation of the two-tank TES configuration, a single thermocline TES concept has been investigated: in this two phases storage configuration a part of molten salts (i.e. fluid phase) is replaced by low-cost solid phase storage materials (e.g. Quartzite rocks), and its cost was estimated to be 35% less than that of the state of the art [8,9]. To deal with the technical problems of molten salts, other heat transfer fluids (HTFs) has been considered in the same single tank thermocline configuration (e.g. Air, and supercritical CO_2). Furthermore, other solid storage materials (e.g. Natural rocks, Refractories, etc.) has been

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Abbreviations: ACW, Asbestos containing wastes; CSP, Concentrated solar power; BFS, Blast furnace slags; EAFS, Electric arc furnace slags; EDS, Energy dispersive X-ray spectroscopy; HTF, Heat transfer fluid; IFS, Induction furnace slags; FTIR, Fourier transform infrared spectroscopy; MDSC, Modulated Differential Scanning Calorimetry; TES, Thermal energy storage; TGA, Thermogravimetric analysis

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Nomenclature

C_p	specific heat capacity (J/kg K)
d_c	caracteristic particle diameter (m)
k	thermal conductivity (W/m K)
ρ	density (kg/m^3)

studied experimentally and numerically in the same configuration [3,9–11]. The main aim of these investigations was to identify or develop suitable solid storage materials able to withstand the high operating temperature (more than 650 °C and up to around 1000 °C [1,6]), which is required by the new generation of CSP plants. Thus, these materials should have the following desirable properties [12]:

- *Thermophysical properties*: high energy density ρ × *cp* × *T* (per unit volume), high thermal conductivity *k*, and long-term thermal stability under thermal cycling.
- *Chemical properties*: long-term chemical stability under thermal cycling, and chemical compatibility with the heat transfer fluid (HTF) and the construction materials of the tank.
- *Mechanical properties*: high mechanical stability under thermal cycling, low coefficient of thermal expansion, high fracture toughness, and high compressive strength.
- *Economical properties*: cheap and abundant materials with low-cost of manufacturing into suitable shapes.
- *Environmental properties*: low manufacturing energy requirement and CO_2 footprint.

In this context, abundant and low-cost natural rocks have been investigated by many authors and they have shown good thermophysical properties (ρ, *cp*, and *k*) [10,11,13]. However, their thermal stability was proved under thermal cycling only up to temperatures between 550 °C and 600 °C [11,13,14]. Moreover, their non-homogenous mircostructure and mineral composition induce an unequal rate of contraction and expansion of the component minerals under thermal cycling [12,13], and these natural rocks may disintegrate due to microcracks. Thus, it has been noted that the unpredictable thermo-mechanical behaviors of natural rocks under thermal cycling introduce technical uncertainties with respect to their durability [15], as well as to their destructive effect (e.g. thermal ratcheting) on the storage vessel [16]. Refractories have been investigated because of their good thermal and mechanical stability under high operating temperatures (more than 1000 °C). Howbeit, instead of their good sensible storage properties their main drawback was their high cost (e.g. Magnesia bricks (2000 US $/ton) [17], and Castable ceramics (4500–9000 €/ton) [3,18,19]).

Recently, the trend of research in this topic was the valorization of industrial wastes into ceramics to be used as high-temperature (up to 1000 °C) thermal energy storage (TES) materials. The main motives of this trend are the huge amount of generated industrial wastes around the world, and the environmental emergency to recycle them into inert materials. Thus these latters are generally characterized by their low-cost. In this scope, X. Py et al. [3], have studied the inhertized asbestos-containing wastes (IACW) and they have found that they are:

- no longer toxic,
- thermally stable up to 1200 °C,

and they have:

- good storage properties (λ = 1.4 W m^{-1} K^{-1}, ***Cp*** = 1025 J/kg K, ρ = 3100 kg/m^3)
- a cheap cost (8 €/ton).

Using the same vitrification process, coal fly ashes wastes obtained from coal-fired power plant were neutralized and the obtained materials were characterized for high-temperature TES application [20,21]. The obtained crystallized and inhertized coal fly ashes (**ICFA**) had good thermal properties (λ = 1.3–2.1 W m^{-1} K^{-1}, ***Cp*** = 735–1300 J/kg K, ρ = 2600 kg/m^3) [20], and their thermal stability has been proven up to 1000 °C [21]. One drawback of the previously obtained storage materials is their high cost (1200 €/ton) of heat treatment at 1400 °C in the plasma torch furnace [22].

Other interesting high-temperature TES materials were obtained from the iron and steel making processes by-products known by slags [4,20,23,24]. There are various types of slags depending on the used furnace technology, but they are mainly composed of silica (SiO_2), lime (CaO), alumina (Al_2O_3), iron oxides (Fe_2O_3), and magnesia (MgO). Depending on their cooling rate the obtained solid slags are either glassy or crystalline [4]. The main advantage of crystalline slags is that they have rock-like shape and they can be used directly as received in the storage application without any further heat treatment [4]. Nevertheless, remelting of slags is mandatory when their original form is glassy, brittle, or when they should be manufactured into suitable regular shapes [24,25]. The slags that have been investigated for high-temperature TES application are: Blast furnace slags (**BFS**) [20], Electric arc furnace slags (**EAFS**) [4,20,25,26], and Ladle furnace slags (**LFS**) [26]; All the studied slags have shown good storage properties, and their thermal stability has been demonstrated up to 1000 °C.

Another type of slags (**IFS**) is produced in induction furnaces, which are good alternatives to **EAF**, because of their clean process and their high efficiency [27]. For example, in India about 30% of the steel production is based on the use of this type of furnace which generates huge amounts of slags (about 450,000 t per year [28]). According to our knowledge, induction furnace slags (**IFS**) have never been considered for high-temperature TES application. Consequently, the main aim of this article is the characterization of this waste for this application. The organization of this scientific article is as follows: in a first place, a description of the process of **IFS** is given. In a second place the **IFS** have been characterized in term of their chemical composition,

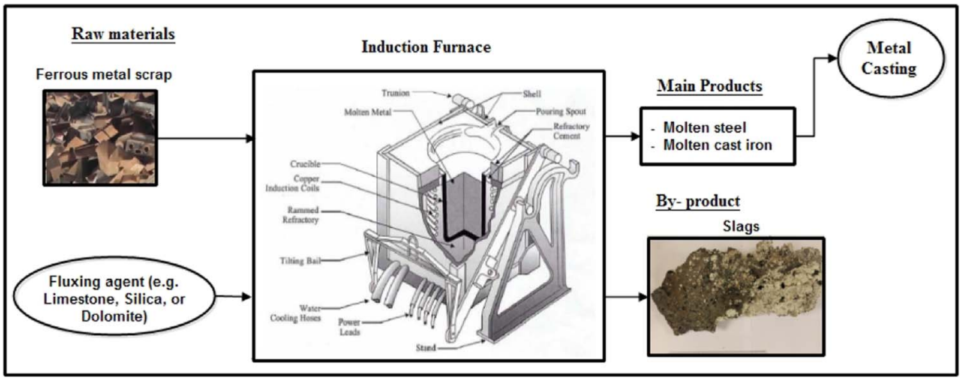

Fig. 1. Steel production in induction furnace.