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Thermophysical characterization of a by-product from the steel industry to be used as a sustainable and low-cost thermal energy storage material

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ABSTRACT

In the metallurgical industry, large amounts of waste called slag are accumulated besides the production of iron and steel. One part, considered as by-product, is recycled but the other part, considered as waste, is still landfilled with potential bad consequences for environment. In this paper, two electric arc furnace slag samples (most common steel production technology in Europe), have been considered and characterized to be used in medium and high temperature thermal energy storage systems. These slags have demonstrated relevant properties to store thermal energy by sensible heat from ambient temperature up to 1000 °C, and their representativeness of the worldwide produced slag in a wide EAF (electric arc furnace) steelmaking process range. The objective is to develop sustainable and low-cost thermal energy storage systems for industry waste heat recovery and in renewable energy applications. At the same time, this new valuable market for slag in the energy field could solve a big part of the waste management problem in the iron and steel sector.

1. Introduction

In many power generation systems such as CSP (concentrated solar power) [1–3], adiabatic CAES (compressed air energy storage) [4] or, in industrial waste heat recovery applications [5], TES (thermal energy storage) is a noble solution to save energy and increase significantly the efficiency of different industrial processes. Focussing on the industrial waste heat, for example, in the United States is estimated that between 20 and 50% of the industrial energy input is lost as waste heat between 120 °C and 1700 °C [6]. In 2008, this represented a huge amount of energy of around 440 TWh [6]. This values display the large potential of heat recovery applications in different industrial processes, where their implementation could present clear economic and environmental benefits. So far, the development of innovative and efficient TES technologies in industrial waste heat recovery applications is still a challenge that needs to be successfully solved. In this regards, only a few and expensive TES systems (400 €/kWh [7]) are commercially available in the high temperature range (T > 400 °C). As a consequence, the majority of the waste heat is frequently released to the environment and hence, lost.

In the case of commercial CSP plants, the implemented TES solution is the use of a molten nitrate salts mixture called "Solar salt" [8] in a double-tank configuration. This mature technology requires thousand tons of the mentioned storage material for each power plant (e.g., 28,500 tons in the ANDASOL 1 (50 MWe) plant in Granada, Spain). However, even if this storage technology is a well-established solution, it presents several important limitations. The most important ones are the relatively high cost of the "Solar salt" (see Table 3), its high freezing point (220 °C), its limited maximum operating temperature (565 °C), and its low thermal conductivity value. Therefore, this makes necessary the search for new alternative storage materials and solutions. Overall, the selection of a successful storage material for solar thermal power generation might open new storage management and operation modes

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Nomenclature

α	thermal difussivity (mm^2/s)
λ	thermal conductivity ($W/m\cdot K$)
ρ	density (kg/m^3)
C_p	specific heat ($J/g\cdot K$)
l	thickness (mm)
T	temperature (K)

Abbreviations

CAES	compressed air energy storage
CSP	concentrated solar power
DSC	differential scanning calorimetry
EAF	electric arc furnace
EDX	energy-dispersive X-ray spectroscopy
ICP	inductively coupled plasma
LCOE	levelized cost of electricity
LFA	laser flash apparatus
OES	optical emission spectroscopy
SEM	scanning electron microscopy
TES	thermal energy storage
XRD	X-ray diffraction

according to the requirements involved on new generation concentrated solar power tower technologies [9], in the range of 300–800 °C or even higher.

With the decrease of fossil fuel resources and recent changes in environmental policies, the development of innovative, cost-effective and efficient TES systems have become a key issue in order to manage a global successful energetic solution. In this frame, the role of the storage material is decisive, as it represents one of the driving parameters of the thermal behaviour and economic cost of the storage unit [10]. Regarding the material, for a common application, it should satisfy among other the following constraints: low cost, large availability without any conflict of use, high heat capacity, suitable compatibility with usual heat transfer fluids and tank materials, and no-toxicity.

The valorisation of different industrial by-products as heat storage materials could be a possible satisfactory approach with a double objective: first, to obtain a viable and cost-effective TES material and second, to reduce the industrial environmental impact. In this field, some solutions have been proposed such as inert ceramics obtained from the treatment of the asbestos waste (Cofalit) [11], fly ashes from the incineration of municipal solid waste [12] or, ashes from coal thermal power plants [13].

Another alternative material for thermal storage, proposed in this work and suggested in the 90's by Tayeb [14] and Hasnain [15], is one of the most representative by-products of the iron and steel industry, the steel slag. A typical steel slag is mostly composed by oxides of aluminium, calcium, iron, magnesium and silicon. Once cooled down, the slag forms a ceramic material that, depending on the cooling rate, could range between amorphous and crystalline structural nature.

According to Álvarez et al. [16], about 10% of slag is produced per ton of steel. In 2004, the European steel industry generated around 15 million tons of slag [17] while in 2010, the slag production raised up to 21.8 million tons [18]. As reported by Euroslag [18], around 76% of produced slag is reused on several applications such as road construction, cement production, hydraulic engineering and others. However, the other 24% is still landfilled or stored at site in the steelmaker itself. Attending to the announced CSP growth previsions [19], this slag amount might be enough to provide storage material for the CSP plants planned for construction until 2050. As a consequence, the valorisation of steel slag for heat storage applications represents a huge potential for this material.

In this context, a new application window in energy recovery or energy production fields will allow to offer a high-value outlet for the slag. As mentioned above, the heat storage material is one of the critical aspects in order to obtain a competitive and efficient TES system. However, the final technological solution where steel slag is implemented as storage material is also crucial and it must be carefully analysed. In these regards one possible solution is the use of packed bed storage systems based on the so-called "thermocline" temperature stratification phenomena. This alternative has shown large potential in the thermal energy storage frame as demonstrated by the increasing interests shown by the international scientific and technological community [20–22]. The main goal of this work is to demonstrate the suitability of steel slag as a heat storage material in a packed bed arrangement.

In this paper, thermophysical and structural characterization of two different worldwide representative EAF (electric arc furnace) slag types has been performed. The results have demonstrated the viability of this material for different thermal energy storage applications on a wide range of temperatures up to 1000 °C. In addition, a preliminary and qualitative techno-economic viability analysis has also been done showing immediate benefits of the proposed heat storage system.

2. Materials and methods

2.1. Materials

Electric arc furnace technology is one of the most common production method used in the steel-making plants [18]. In the later, the ferrous material introduced in the furnace, usually steel scrap or wrought iron, together with the slag precursors, typically alumina, silica and lime, are directly melted under the energy supplied by the electric arc. The melting includes some steps like oxidation to remove manganese and silicon impurities, the dephosphorization and the formation of a foaming slag where all the impurities are accumulated. Apart from these functions, the slag also protects the molten steel from oxidation and maintains the temperature of the liquid steel. Once the process is finished, the slag is discharged to a ladle where it is cooled down.

In this work, two different slags supplied by two of the biggest steelmakers located in Spain, are studied. Both slag types correspond to the EAF steelmaking process. The main difference between them is their cooling procedure: the Slag 1 was obtained by fast cooling rate using water while the Slag 2 was produced by low open air cooling rate. Fig. 1 shows pictures of both raw EAF slag samples.

2.2. Characterization techniques and methodology

2.2.1. ICP-OES (Inductively coupled plasma – optical emission spectroscopy)

The chemical composition of both samples was studied by ICP-OES with an Ultima 2 equipment from Horiba Scientific. For these measurements, fine powder of both EAF slags was obtained and fused with 99.9% lithium metaborate in high purity graphite crucibles and later dissolved with diluted HNO_3 (trace metal grade nitric acid and ultrapure Milli-Q© water were used to prepare the dissolution). The solution obtained was directly analysed by using the accepted standard practice reported in Ref. [23]. The analysis was carried out for the predominant chemical components (Al, Ca, Fe, Mg, Mn, Si, and Ti).