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Selection and characterization of recycled materials for sensible thermal energy storage

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ABSTRACT

Alternative low cost materials are evaluated through the valorization of by-products derived from mining and metallurgical industry for solid sensible heat based energy storage systems. They were used either as received or formulated as aggregates in mortars, and their thermal and mechanical properties were characterized. A selection methodology was applied in order to compare them with available materials found in the literature for applications as (STES) materials, and with materials from Cambridge Educational Software (CES) Selector database. It was demonstrated that these recycled materials have a high potential for these thermal energy storage applications.

1. Introduction

Last years have been characterized by an energy consumption increase as well as a constant rise in prices for energy. Assuming the necessity of more effective utilization of energy in all spheres of human activity, energy storage is a key element to improve the efficiency of energy utilization in different economical aspects. It is the way of bridging the time gap between the energy supply and the energy demand.

Thermal energy storage (TES) plays a significant role in improvement of energy efficiency. There are mainly three types of TES systems, chemical, latent and sensible storage, depending on the type of process or property of the material that is profitable. In latent heat storage (LTES) the property we are interested in is the energy that is required to change the phase of a material, usually between liquid and solid phases. In chemical energy storage storing heat is through the use of reversible chemical reactions. And the last one is the storage of sensible heat (STES), which uses the energy released (or absorbed) by materials when its temperature is decreasing or increasing. STES is classified on the basis of the heat storage media as liquid media storage (like water, oil based fluids, molten salts etc.) and solid media storage (like ceramics, metals and others) [1].These different types of TES mean a variety of working temperatures, capacities and heat transfer carriers used and thus, each heat store differs in the specific parameters required for its design [2,3].

For the application of a solid as a thermal energy storage media several properties like density (ρ), specific heat capacity (c_p), thermal conductivity (k), thermal expansion coefficient, and cyclic stability, as well as availability, cost and production methods have to be taken into account [4]. These properties are relevant because the higher the volumetric heat capacity ($\rho\ c_p$), the lower the volume per thermal unit is required; on the other hand, thermal conductivity improves the dynamics of charge/discharge of the system. Furthermore, a high cyclic stability is important for a long lifetime of the storage unit, and the thermal expansion coefficient is a design criterion needed to integrate the material in the energy storage system. If we consider only the thermal properties for the materials selection, the solid sensible heat storage is not the best option in terms of energy density as the highest values are for thermochemical storage. Otherwise, if other parameters such as cost, system complexity, embodied energy or production methods are also considered in the selection procedure, solid materials may become a feasible alternative. As an illustrative example, at the time of writing all large scale Concentrated Solar Plant (CSP) industrial TES are based on the sensible heat approach only.

When integrating the thermal storage in the energy system, economics are an important driven force. Because of the increase

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of the cost of storage materials, it is a very interesting issue to evaluate low cost alternative materials through the valorization of by-products derived from mining and metallurgical industry for solid sensible heat storage. Moreover, the expected extensive development of TES in the future could lead to a lack in TES materials availability and sometimes to major conflict of use with other applications.

The aim of this work is to evaluate the potential of several materials to be used as storage materials: by-products of the pyrometallurgical refining process of copper (Slag P and Slag B), the powder material produced during the steelmaking process in electric arc furnace (WDF), they are basically metal oxides. IB and WrutF are two by-products of the mineral industry. IB is a chloride (mainly sodium chloride) by-product of the potash production and WRutF is a derivative from ilmenite mining that contains mostly silica oxide.

These materials are compared with the materials described in the CES Selector database. CES Selector is software from GRANTA that combines the information on materials and process properties [5]. For this purpose, the methodology for materials selection applied in a previous paper [6] is used.

2. Experimental procedure

2.1. Materials

In order to evaluate the potential of the by-products used in this paper as thermal energy storage materials they were characterized. Previously the particle size was homogenized as the materials were supplied as granulates or powders. To do so, different jaw crusher steps were used obtaining particles size lower than 1 mm. Then, two approaches were followed to shape them. Two of them (IB, WDF) were prepared by compression and the others (Slag B, Slag P), for which compression or molding was not possible, were included as aggregate in different mortar formulations using either Portland, aluminous or phosphate cements, as binder. WRutF was not shaped and it was evaluated as powder.

2.2. Mortars formulation

Mortars were prepared using three types of binders: Portland cement, CEM I 52,5R (according to EN-197–2000), calcium aluminate cement (according to EN-14647-CAC) aluminous and phosphate cements, ($KMgPO_4 \cdot 6H_2O$) [7], Slag P or Slag B were added as aggregates. Due to the different physicochemical characteristics of both by-products, different water/cement ratios were needed to have a comparable workability. The compositions of the different formulations are summarized in Table 1, that shows the solids ratios (%w/w), and also the water/cement ratio added to each mixture, necessary to complete the hydration reaction to form the mortar. Mortar formulations were casted in prismatic molds with dimensions of $40 \times 40 \times 160\ mm^3$ to evaluate later their mechanical properties. Specimens were left in their molds for 24 h in a curing chamber, at a constant temperature of 20 °C, and a relative humidity of 95%. Unmolded mortars were further cured in the same conditions up to 28 day.

Table 1
Mortars Formulation used for Slag P and Slag B.

	Acronym	Aggregate (%)	Cement (%)	Ratio H_2O/cement
Portland cement/Slag P	PP	75	25	0.58
Portland cement/Slag B	PB	75	25	0.52
Aluminous cement/Slag P	AP	75	25	0.52
Aluminous cement/Slag B	AB	75	25	0.48
Phosphate cement/Slag P	CBPC_P	80	20	0.58
Phosphate cement/Slag B	CBPC_B	80	20	0.68

2.3. Materials and mortars characterization

Samples for DSC and picnometer were prepared by crushing and milling the samples if required (for mortars). The specific heat capacity of the materials was evaluated by differential scanning calorimetry (DSC). DSC was performed in nitrogen atmosphere using the dynamic method with a DSC-822e/40 Mettler Toledo, at a heating rate of $10\ °C \times min^{-1}$ from 30 to 600 °C. For each experiment a mass of $15\ mg \pm 0.5\ mg$ was used and the flow rate of gas was $50\ ml \times min^{-1}$. The density of powders and mortars was obtained with a Helium pycnometer Accupic 1330. Flexural strength and compressive strength tests were performed on the molded samples, in a mechanical testing machine MUTC-200 from Incotecnic at a loading rate of $5\ kg \times s^{-1}$ [8].

The thermal conductivity was measured with the device described by Olivès et al. (2001) [9], see Fig. 1. The steady-state measurement is based on the ASTM C 518-04 Standard test method. The apparatus is composed of two plates, one heat source and one heat sink, made of copper which temperatures were regulated and two flux-meters made of rods ($25 \times 25 \times 65\ mm^3$) of different materials with well-known conductivities (a stainless steel AISI 304L, $14.5 W \times m^{-1} \times K^{-1}$, and Macor®, $1.4 W \times m^{-1} \times K^{-1}$). The axial temperature profile was measured by K-type thermocouples implanted in the two flux-meters and in the sample placed between them was recorded. A polystyrene foam ($\lambda = 3 \times 10^{-2} W \times m^{-1} \times K^{-1}$) was used as insulator in order to reduce the radial heat losses and to obtain a quasi one-dimensional heat flow. The mortars were tested in a cubic shape ($25 \times 25 \times 25\ mm^3$) and the compacted and powder materials in a cylindrical shape (25 mm diameter × 25 mm height).

The thermal stability was studied using a thermogravimetric analysis (TGA), at a heating rate of $5\ °C \times min^{-1}$ from 30 to 800 °C and air atmosphere.

3. Results

3.1. Thermal energy storage properties

In Table 2, the most important parameters for materials selection in STES are listed. Specific heat capacity results are listed at different working temperatures (100–300–500 °C), showing all

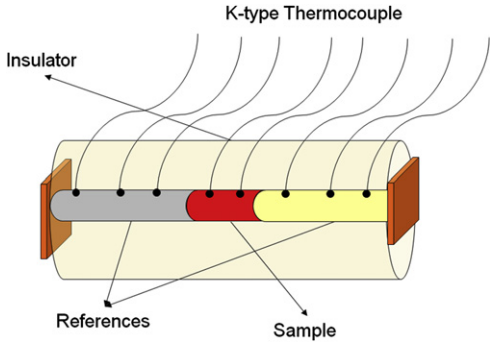

Fig. 1. Thermal conductivity measurement apparatus.