SELECTION AND CHARACTERIZATION OF RECYCLED MATERIALS FOR SENSIBLE THERMAL ENERGY STORAGE

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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 that we are interested for is the energy that is required to change the phase of a material. 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. It 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 rocks, metals and others) [1].These different types of TES carry to a variety of levels of working temperatures, capacities and heat transfer carriers used and thus, each heat store differs in the specific parameters [2].

For the application of a solid as a thermal energy storage media several properties like density (ρ), specific heat capacity (cp), thermal conductivity (k), thermal expansion coefficient (α) and cyclic stability as well as availability, cost and production methods are of great relevance[3]. These properties are relevant because the higher the heat capacity (ρ*cp), the lower the volume per thermal unit that is required. Also thermal conductivity improves the dynamics of the system. 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, embodied energy or production methods are also considered in the selection procedure solid materials may become a feasible alternative.

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

The aim of this work is to evaluate the potential of several materials to be used as storage materials: by-products of copper industry (Slag P and Slag B), steel industry (WDF), mineral industry (IB and WrutF), and to compare them with the materials described in the CES Selector database. For this purpose, the methodology for materials selection applied in a previous paper [4] is used.

2. Experimental

Starting materials are granulated or powders, and were first tested in this form. Then, two approaches were followed to shape them. First, they were molded by compression and mechanical integrity of the resulting shape was evaluated. If the resulting shape was considered fragile, they were included as aggregate in different mortar formulations using either Portland, alumina or phosphate cements, as binder.

2.1. Mortars formulation

Mortars were prepared either with Portland, alumina or phosphate cement as binder, and Slag P or Slag B 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. Mortar formulations were casted in prismatic moulds with dimensions of 40×40×160mm to perform mechanical properties. Specimens were left in their moulds for 24h 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 days.

Table 1. Mortars Formulation

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

2.2. Materials and mortars characterization

The specific heat capacity of the materials was evaluated by means of differential scanning calorimetry (DSC). DSC performed in nitrogen atmosphere using the dynamic method with a DSC-822e/40 Mettler Toledo, at a heating rate of $10°C\cdot min^{-1}$ from 30 to 600°C. For each experiment a mass of 15 mg ± 0.5 mg was used and the flow rate of gas was $50ml\cdot min^{-1}$. The density of powders and mortars was obtained with a Helium pycnometer Accupic 1330.

The thermal conductivity was measured with the device described by Olivès et al. (1999) [5].The steady-state measurement 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 (25×25×65 mm) of different materials with well-known conductivities. 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 ($\lambda=3\times10^{-2}$ $W\cdot m^{-1}\cdot K^{-1}$) 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 (25×25×25 mm) and the compacted and powder materials in a cylindrical shape (25mm diameter x25 mm height).

3. Results

In Table 2, the most important parameters for materials selection in STES including an estimation given by the materials producers of their cost are listed. In Table 3, the most important properties of some materials for sensible thermal energy storage described in the literature are summarized and compared with the well reported system of nitrate molten salts. The studied materials have similar or even higher conductivities compared to those described in the literature. Although some of them have lower specific heat capacities, they have higher densities and lower prices. Taking into account these materials properties, competitive alternative candidates in sensible thermal energy storage can be foreseen.

Table 2. Properties of different studied thermal energy storage materials

Compound	**λ (W/m·K)**	**Cp (kJ/kgK)**	**ρ (kg/m^3)**	**Cost (€/kg)**
Slag_P	0.8	0.6	3600	0.15
Slag_B	1.1	0.9	3700	0.15
IB	3 to 4	0.8	2100	0.007
WDF	0.7	0.8	3967	0.001
WRutF	0.8	0.9	4154	0.008
CBPC_B	1.6	1.2	2828	0.15
CBPC_P	1.5	0.9	2804	0.15
AB	1.4	0.9	3030	0.15
AP	1.4	0.7	2947	0.15
PP	1.4	0.65	2785	0.12
PB	1.8	0.8	2859	0.12

Table 1 Properties of materials described as thermal energy storage materials

	λ (W/m·K)	**Cp (kJ/kgK)**	**ρ (kg/m^3)**	**Cost (€/kg)**	**Cost/kWh**
Molten Salt[7]	0.52	1.6	1870	0.625	14.05
Cofalite[6]	2 to 1,5	0.9	3120	0.010	0.40
Castable Ceramics[7]	1.35	0.86	3500	4.5	188.22
High temperature Concrete[7]	1	0.916	2750	0.08	3.14

3.1. Case study

In a previous work a theoretical case study was analyzed using the CES Selector database [4]. The main objective of this manuscript is compare how do these alternative materials perform when the same methodology of selection is applied. Thus, the database was customized adding the data of these materials.

When looking for STES materials we are interested on maximizing the energy density and thermal conductivity. To reduce the universe of selectable materials we apply constrains previously used: limit the service temperature (lower limit for maximum service temperature is 400 ºC) and the cost per unit mass (maximum cost 5 €/kg). A plot of energy density vs. thermal conductivity chart including the studied materials is presented in Figure 1.

The studied materials perform quite well as they are located with the materials with highest energy density even though the thermal conductivity is moderate.

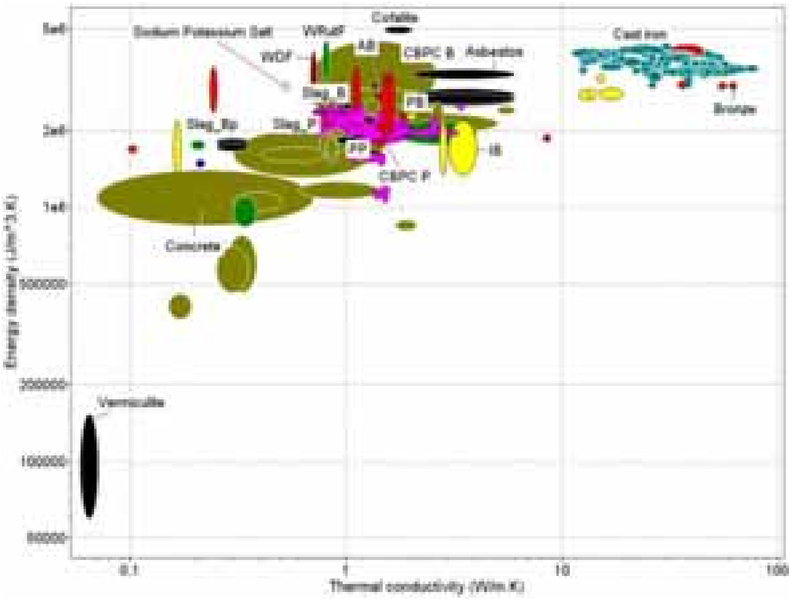

Fig. 1 Energy density vs. thermal conductivity

Also, the cost per unit mass of the studied materials may be considered and compared with those of the database, see Figure 2. Cofalite, WRutF and WDF show the better results as they are in the upper left of the graphic, and as expected, they show lower cost than most of the nontechnical ceramics considered (green bubbles).

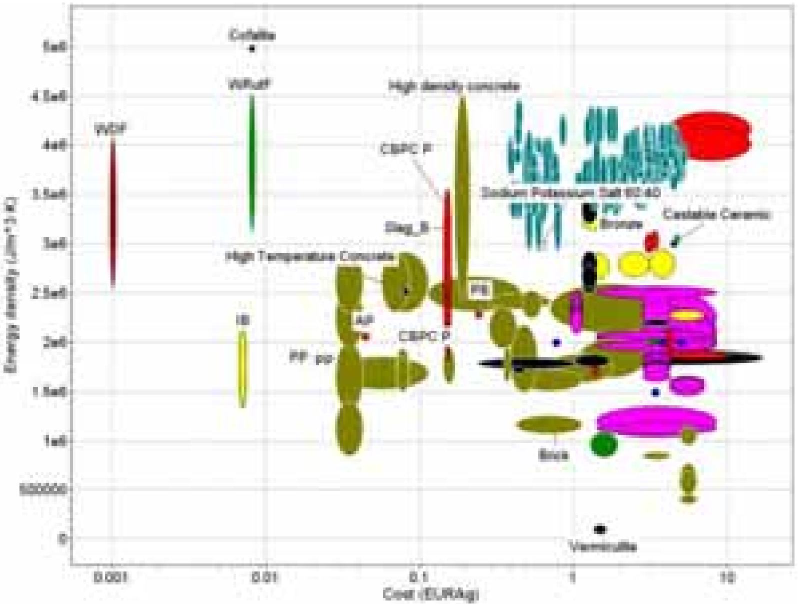

Fig. 2 Energy density vs. cost

A more exhaustive selection can be performed following the selection strategy [8].The performance of a material may be presented specified by three things: the functional requirements (the need to carry loads, transmit heat, store elastic or thermal energy, etc), the geometry, and the properties of the material of which it is made, including its cost. The performance can be described by an equation with the general form:

$$p = f[(\text{functional requirements}, F), (\text{Geometric parameters}, G), (\text{Material properties}, M)]$$

or

$$p = f[F, G, M]$$

Optimum design can be considered to be the selection of the material and geometry which maximize (or minimize) p. The optimization is subject to constraints, some of them imposed by the material properties. Table 4 summarizes the requirements in our case study for a sensible energy storage material.

Table 2 Material requirements for our case study

Function	Heat-storing medium
Objective	Maximize thermal energy stored per unit material cost
Constraints	Working temperature Tmax = 400°C and Price < 5 €/kg

As described by Fernández A.I. et al (2010), for a long term storage device, the energy per unit cost is maximized by maximizing M.

$$M = \frac{c_P}{C_m} \quad \text{(eq.1)}$$

where c_p is the specific heat capacity and C_m the cost per kg.

In Figure 3 the selection graphic where c_p is plotted versus C_m in a logarithmic scale is plotted. A line with slope 1 should be moved in this figure to find the materials that perform better with the objective to minimize cost. In this case WDF performs better, followed by Cofalite, IB and WRutF. With materials with the same material index M (lying in the same line), other parameters have to be considerer to select one of them.

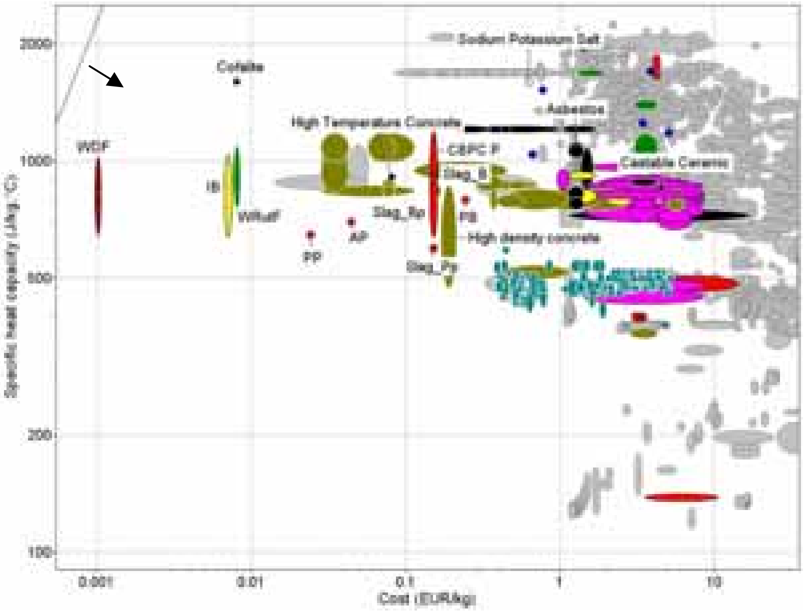

Fig.3 Specific heat capacity vs. cost

For short term storage, the material index to be optimized is:

$$M = \frac{1}{(\alpha)^{1/2} \rho C_m} \quad \text{(eq.2)}$$

If α vs ρC_m is plotted in a logarithmic scale, the materials with the highest material index will be those in the bottom left of the chart because of the negative slope and negative *y* intercept. A line of slope -2 should be moved in Figure 4 getting the best performance, for WDF followed by Halite (natural NaCl), IB, Cofalite, WRutF, non technical ceramics (concretes) and the prepared mortars formulations. The figure also shows the corresponding values for nitrate molten salts that have been used in liquid sensible heat storage during the last 30 years, showing that the studied solids perform better for this example of short term storage.

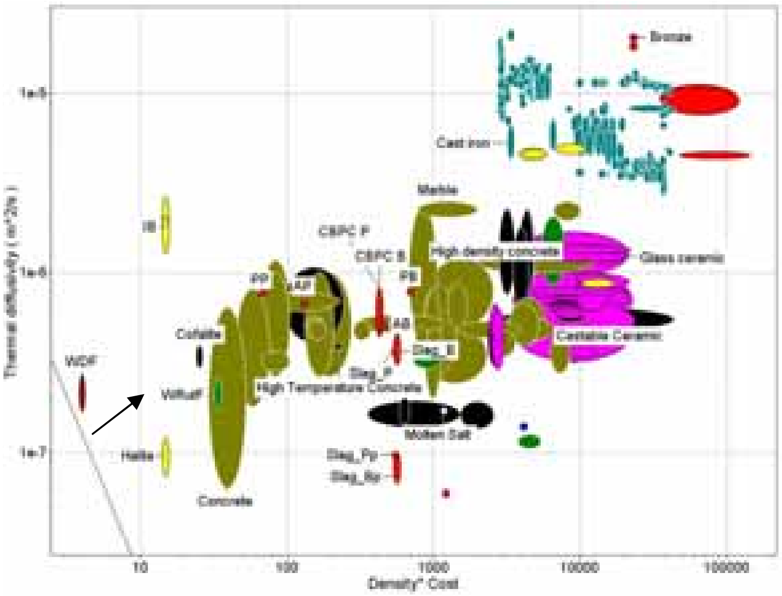

Fig. 4 Diffusivity vs. density x Cost

4. Conclusions

In this paper several materials have been evaluated to be used as solid sensible heat storage materials, and compared with CES Selector database as well as materials reported in literature. Although it has been shown that there are materials with higher thermal properties suitable for STES than the studied ones, an exhaustive selection has been performed following the selection strategy. It is demonstrated that WDF, IB, Cofalite, WRutF and the mortars formulations are promising materials in this application. Further studies need to be done concerning other properties that are relevant when incorporating the materials to the storage systems, as mechanical properties, thermal expansion and resistance to thermal cycles.

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