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Industrial Waste Materials and By-products as Thermal Energy Storage (TES) Materials: A Review

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Abstract. A wide variety of potential materials for thermal energy storage (TES) have been identify depending on the implemented TES method, Sensible, latent or thermochemical. In order to improve the efficiency of TES systems more alternatives are continuously being sought. In this regard, this paper presents the review of low cost heat storage materials focused mainly in two objectives: on the one hand, the implementation of improved heat storage devices based on new appropriate materials and, on the other hand, the valorisation of waste industrial materials will have strong environmental, economic and societal benefits such as reducing the landfilled waste amounts, reducing the greenhouse emissions and others. Different industrial and municipal waste materials and by products have been considered as potential TES materials and have been characterized as such. Asbestos containing wastes, fly ashes, by-products from the salt industry and from the metal industry, wastes from recycling steel process and from copper refining process and dross from the aluminium industry, and municipal wastes (glass and nylon) have been considered. This work shows a great revalorization of wastes and by-product opportunity as TES materials, although more studies are needed to achieve industrial deployment of the idea.

INTRODUCTION

The industrial growth and negative impact because of CO₂ emissions to the atmosphere, demands new sources of energy besides the traditional sources which have been mainly used up to now. Renewable energies have enormous potential for this purpose, such as wind, solar, geothermal and others. As some of these energy sources are not continuously available, is necessary to store them while the sources are available to use them when demand require it. Solar energy seems the most a promising source to fill these requirements but is necessary to evaluate the economic and technical feasibilities of thermal energy storage (TES) systems. Also efficient and low cost devices are needed to be competitive with traditional sources [1]. TES systems can also represent a breakthrough concept in
industrial heat recovery applications. According to the report of US DOE [2], there are large heat recovery opportunities in different industrial processes. These applications require a particular research and development in order to adapt the heat production to the storage. A wide variety of potential heat storage materials have been identified depending on the implemented TES method: sensible, latent or thermochemical. The particular application also limits the suitable materials as a function of the operation temperature range, storage capacity, power and other requirements [3-5]. Overall, although no ideal storage material has been identified, several materials have shown a high potential depending on the mentioned considerations. In addition, the increase of industrial activities worldwide, mentioned before, leave different and important amount of waste materials with any applications up to date. The accumulation of these wastes can have negative environmental impact when they decompose, react with atmosphere gases or where they have contact with water. In order to reduce this negative impact, different industrial waste materials have been considered as potential TES materials and have been characterized as such. Asbestos containing wastes, fly ashes, by-products from the salt industry and from the metal industry, wastes from recycling steel process and from copper refining process and dross from the aluminum industry, and municipal wastes (glass and nylon) have been considered. The aim of this review is to show that the revalorization of wastes or by-products as TES materials is possible, and that more studies are needed to achieve industrial deployment of the idea.

**SENSIBLE HEAT THERMAL ENERGY STORAGE (SHTES) BASED ON INDUSTRIAL WASTES**

A wide range of materials for SHTES have been extensively studied and design during the last decades. Some of them are now being produced and marketed to be applied in commercial systems achieving considerable results [6-8]. However, the authors of this review, decided to evaluate the potential of some industrial wastes materials as SHTES, obtaining promising results at different ranges of temperature as are show below:

### High Temperature SHTES Materials

*Asbestos Containing Wastes (ACW)*

- Thermophysical and Mechanical Characterization and Compatibility Studies

  There were two types of materials from melted ACW, glass and ceramic. The ACW comes from various demolishing sources, which currently produce in France 250,000 tons of waste per year, guaranteeing a huge amount of available raw material. Both ACW were characterized focused on thermophysical properties important for TES applications. Initial composition of ACW can be seen as highly fluctuating, however the main major involved compounds are O 32%wt, Ca 21wt, Si 23%wt, Fe-Mg-Al 13%wt which changed with the temperature increasing. This behavior was study by X-Ray diffraction at different temperatures (See Fig. 1a). It can be seen that at 900°C the glass crystallizes to form ceramic made of Wollastonite (Ca(Ca, Mn) Si₂O₆), Akermanite (Ca₂MgSi₂O₇) and Augite (Ca (Mg, Fe)Si₂O₆). This new structure obtained is stable under repetitive cycles heating and cooling from room temperature to 1000°C. This clearly demonstrates that recycled ACW ceramic is able to resist cycles of heating and cooling at high temperatures.

  The range of temperature to characterize other properties was from room temperature to 1000°C results obtained are show in **TABLE 1**:

**TABLE 1** Thermophysical properties of ACW in the range of temperature from room temperature to 1000°C.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Density</th>
<th>Thermal Capacity</th>
<th>Thermal Conductivity</th>
<th>Coefficient of Thermal Expansion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Units</td>
<td>[kg/m³]</td>
<td>[kJ/kg K]</td>
<td>[W/m K]</td>
<td>[1/K]</td>
</tr>
<tr>
<td>Values</td>
<td>3120</td>
<td>0.800 – 1.034</td>
<td>2.1 – 1.4</td>
<td>8.8·10⁻⁶</td>
</tr>
</tbody>
</table>

In addition, an innovative ultrasonic pulse echography was applied evaluate the behavior of the Young modulus, from room temperature to 1000°C. Results of two cycles of heating and cooling are showed in Fig. 1b for Cofalit ® (COF), where it can be seen the refractory behavior of those ceramics and their ability to resist several thermal cycles. The obtained ACW ceramic was studied for several heat transfer fluids (HTF) commonly used in TES applications such as; molten salts, hot air, compressed hot air, oil, hot water and atmospheric steam. Results showed
that only nitrates present good compatibility with this cofalit®, the other molten salt tested didn’t have promising results [10-13]. The rest of materials mentioned were compatible but more extensive studies are needed [14, 15].

**FIGURE 1**
(a) XRD diagrams of the ACW glass and ceramics under two cycles of heating and cooling from room temperature to 1000°C. (b) Young modulus and linear expansion of the ACW ceramics under thermal cycling [9].
Lab scale Experiences

TESM were tested at lab scale, in two forms: granular packing (oil as HTF) and shaped packing (hot air as HTF see Fig. 2a). Hundreds of cycles of heating and cooling were performed at different operating conditions (adiabatic compressed air energy storage) ACAES 50°C to 650°C; linear CSP 200°C to 400°C; central receiver CSP 400°C to 800°C.

The TESM at the end of the experiments were characterized and compared with initial properties. No changes of structure or properties were noticed.

Fly Ashes

Fly ashes are micron-size particles present in gaseous effluents produced by industrial combustions such as coal fired power plants or municipal solid wastes incinerators. They are composed mainly of SiO₂, Al₂O₃, and CaO, for this reason they can be used to produce ceramics. The power plant fly ash (CFA see Fig. 2b) and the municipal solid waste fly ash (MSWFA See Fig. 2c) are mainly amorphous and crystallized respectively. Both are collected by electrostatic filters from the industrial gas effluents and available in the form of light powder. Only some countries concerned by environmental issues, recycle these materials and use for other applications like concrete production or in the construction of roads.

![Figures 2a, 2b, 2c](image)

**FIGURE 2** (a) Flat and corrugated plates of ACW ceramics tested under hot air up to 800°C [9]. SEM picture of Coal Fly ash particles (b), SEM pictures of MSWI Fly Ash particle (c) [14].

Treatment Technologies

Thermal treatment was performed for Municipal solid waste incinerator fly ash (MSWIFA), up to 1400°C, melting wastes. This way it was possible to obtain glass plates of about 2 mm in thickness, which were used as raw material for direct characterization and for subsequent crystallization followed by characterizations. The characterization results showed that pollutants such as heavy metals are fixed within the material and no lixiviation effect was detected. Results of thermophysical properties are shown in **TABLE 2**.

**TABLE 2** Thermophysical properties of MSWIFA in the range of temperature from room temperature to 1000°C.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic and glass</td>
<td>2962 – 2896</td>
<td>0.714 – 1.122</td>
<td>1.16 – 1.59</td>
<td>8.7·10⁻⁶</td>
</tr>
</tbody>
</table>
Also measurements by DSC method were performed, from 0 to 1100°C. Thermal behavior of both materials, glass (dash line) and ceramic (continuous line), are show in Fig. 3.

![Figure 3: DSC characterization of MSWIFA made products, from glass (dash line), from ceramic (continuous line) [9].](image)

On the one hand Glass transition can be observed at about 650°C for the glass and the crystallization peak at 900°C. On the other hand, the ceramic behaves stable during the whole range of temperature.

**Steel Slags**

This material is generated, essentially during the melting process of the iron ore and about 10% to 20% of slags is produced per ton of steel. This process generates different types of steel slag depending on the furnace technology used. In general, the slag is partially vitreous by-products of melting ore due to separating of the metal fraction from the worthless fraction. Also some heavy metals are present in the composition of these wastes, which can generate hazardous problems. Even if slags are from now non-officially considered non-hazardous waste in Europe, dumping slag should not be considered as a long term solution of waste management.

The European Slag Association [16] classified the slag in different families depending on their nature as shown in TABLE 3.

<table>
<thead>
<tr>
<th>Families</th>
<th>From</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granulated Blast furnace Slag (GBS)</td>
<td>Production of iron by thermochemical reduction in a blast furnace</td>
</tr>
<tr>
<td>Air-cooled Blast furnace Slag (ABS)</td>
<td></td>
</tr>
<tr>
<td>Basic Oxygen furnace Slag (BOS)</td>
<td>Solidification of the steel in a basic oxygen furnace and generated by addition of limestone and/or dolomite.</td>
</tr>
<tr>
<td>Electric Arc furnace Slag for Carbon and Stainless steel (EAF A and EAF S respectively)</td>
<td>Melting of scrap in an electric arc furnace</td>
</tr>
<tr>
<td>Steelmaking slag (SMS)</td>
<td>Steel production process to the subsequent treatment of crude steel.</td>
</tr>
</tbody>
</table>

Treatment technologies developed for slags are related with the posterior applications of this by-product. According to the normative, the treatment of each slag will vary depending on its slag family (See TABLE 4).
The revalorization as TES material was evaluated for steel slags. Thermophysical properties of ferrous slag, indicate very appropriate values for the use of this material in TES applications according the IEA criterions. In addition slag shows an extended thermal stability range, up to 1200°C, limited by the melting process of this material. This allows a high operation temperature, suitable for a wide range of heat storage applications, from thermo-solar power generation to industrial heat recovery. On both applications, the potential implementation of a ferrous slag based packed-bed storage solution could be successful. On one hand, on the CSP frame, the substitution of large amounts of molten salt by this low-cost by-product in a single storage tank could lead to a substantial cost reduction of the storage system, and hence, of the produced electricity.

On the other hand, the main drawback using slag as TES material may be the compatibility between the by-product and the HTF or the container material. Positive results may permit a direct contact between the slag and the fluid, which the subsequent elimination of sophisticated heat exchangers.

It has been reported by other authors an experimental characterization of as received and re-melted EAF S slag (as received slag melted and solidified again to obtain a desired shape) coming from steel production process [12, 18]. TGA results shown no mass loss between 300 °C and 1200 °C under Argon, and a small mass gain when dry air is used as purge gas due to the oxidation of metal iron (3.15 %) still contained in the waste.

Some thermal properties of black slag were measured, such as heat capacity, from 200°C - 750°C, showing values between 0.600 and 0.800 kJ/ kg K, as shown in Fig. 4a. Thermal conductivity results were from 1.7 W/m K at 50 °C to 1 W/m K at 900 °C (Fig. 4b). This relatively small value imposes to increase the heat exchange surface between the HTF and the TES material to obtain satisfactory heat transfer in the future storage system.

![Figure 4a](image1.png) ![Figure 4b](image2.png)

**FIGURE 4** Thermal properties determined for black slag. (a) Cp of a sample of as-received black slag (Room T to 700 °C ) measured with Netzsch LFA 452 and DSC TA Q2000, (b) Thermal conductivity of the re-melted sample (Room T to 900 °C )[18]

**Aluminium and Nylon Composites**

Furthermore, dross from the aluminium industry were studied. Results showed thermal stability up to 500°C. Finally, Reinforced concrete with Nylon coming from municipal wastes were characterized, promising properties up to 450°C. Also heat capacity and thermal conductivities where measured at 300°C, obtaining 0.63 kJ/kg K and 1.16 W/mK respectively [19, 20].
Medium and Low Temperature SHTES Materials

There have been also studied some industrial wastes for SHTES at medium and low temperature potential applications. A summary of thermophysical characterization results are shown in Table 5, including the methods or equipment used for these measurements.

**Table 5** Thermophysical properties of SHTES materials based on industrial wastes, potential to be applied at medium and low temperature.

<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[°C]</td>
<td>[kg/m³]</td>
<td>[kJ/kg K]</td>
<td>[W/m K]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Salt A</td>
<td>100 – 200 (sample 59kg)</td>
<td>1384</td>
<td>0.738</td>
<td>0.33</td>
<td>Salt Industry</td>
<td>[21]</td>
</tr>
<tr>
<td>Salt B</td>
<td>100 – 200 (sample 59kg)</td>
<td>2050</td>
<td>0.738</td>
<td>2.84</td>
<td>Salt Industry</td>
<td>[21]</td>
</tr>
<tr>
<td>Astrakanite</td>
<td>0 – 100 (DSC Method)</td>
<td>n/a</td>
<td>0.9 – 1.2</td>
<td>n.a.</td>
<td></td>
<td>[22]</td>
</tr>
</tbody>
</table>

LATENT HEAT THERMAL ENERGY STORAGE (LHTES) MATERIALS

High Temperature LHTES Materials

There have been studied wastes materials coming from different industries. Results showed significant potential to apply them at high temperature for LHTES. Astrakanite ($\text{Na}_2\text{SO}_4\cdot\text{MgSO}_4\cdot4\text{H}_2\text{O}$), is a waste material from non-metallic industry which naturally precipitates in the evaporation ponds during the process to obtain sodium nitrate. As it doesn’t have any application up to date, the composition of this material is not monitored. In this study, Astrakanite was synthesize from $\text{Na}_2\text{SO}_4$ and $\text{MgSO}_4$. Promising thermophysical properties were obtained for this material at low temperature (see Table 5). But it was also found that a heat treated material from Astrakanite (dehydrated) have potential to be applied as a LHTES material at high temperature showing a cycle melting and solidification phenomena in the range of temperature from 550°C to 750°C, and $C_p$ below 450°C 1.2 to 2.1[22]. So that is necessary to perform deeply studies.

Medium and Low Temperature LHTES Materials

Finally, there are also available results of thermophysical characterization of wastes materials at low temperature from industries such as salt, oil and gas industries and Municipal wastes. Summarized results are show in Table 6.

**Table 6** Thermophysical properties of PCM potential to be applied at low temperature.

<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>[°C]</td>
<td>[kJ/kg]</td>
<td>[kg/m³]</td>
<td>[kJ/kg K]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bischofite</td>
<td>98.9 (DSC Method)</td>
<td>120.2</td>
<td>1686 – 1841</td>
<td>1.6 – 3.0 (Ratio Method)</td>
<td>Salt Industry</td>
<td>[23]</td>
</tr>
<tr>
<td>Paraffins</td>
<td>20 – 60 (DSC Method)</td>
<td>&gt;200</td>
<td>n.a.</td>
<td>n.a.</td>
<td>Oil and gas industry</td>
<td>[24 25]</td>
</tr>
<tr>
<td>Glass</td>
<td>25.0 - 26.9 (DSC Method)</td>
<td>18.97 - 18.95</td>
<td>n.a.</td>
<td>n.a.</td>
<td>Municipal waste</td>
<td>[26]</td>
</tr>
<tr>
<td>Composite</td>
<td>21 (DSC Method)</td>
<td>100</td>
<td>n.a.</td>
<td>n.a.</td>
<td>Metal Industry</td>
<td>[27]</td>
</tr>
</tbody>
</table>
CONCLUSIONS

All studied wastes and by-products have been thoroughly chemically characterized and most of them are today categorized to be landfilled or reused. This review also shows that some of this materials already undergo required treatments before landfilling, therefore, when considered as TES material the cost of this pre-treatment does not need to be included in the TES material as is, since it needs to be carried out to the original waste anyway. When possible, the review also presents a short overview related to the revalorization of the waste material or by-product, for example in slags from the metal industry.

It is important to highlight that all the wastes and by-products listed in this paper have an availability or year production high enough to be considered in the TES industry without fear of shortage. The cost is usually very difficult to have and has been reported in very few cases. Finally, as expected all of the wastes and by-products considered have their own strengths and weaknesses when considered to be revalorized as TES materials.

It is very interesting to notice that all the materials have been well characterized with a good thermophysical characterization and most of the cases with compatibility studies. Most cases, only lab characterization has been carried out, and only a few times pilot plant test and modelization can also be found in the literature.

This review shows that the revalorisation of wastes or by-products as TES materials is possible, and that more studies are needed to achieve industrial deployment of the idea.

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