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Multiple-Criteria Decision Analysis and characterisation of phase change materials for waste heat recovery at high temperature for sustainable energy-intensive industry

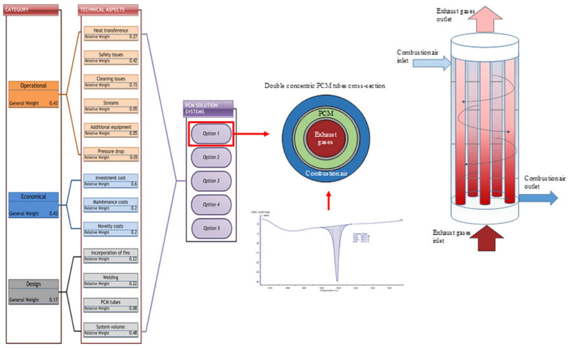
Patricia Royo [a,c,*], Victor J. Ferreira [a,c], Zafer Ure [b], Sam Gledhill [b], Ana M. López-Sabirón [a,c], Germán Ferreira [a,c,**]

[a] Research Centre for Energy Resources and Consumption (CIRCE), Parque Empresaria Dinamiza, Avenida Ranillas 63, Building 3D, 1st Floor, 50018, Zaragoza, Spain
[b] Phase Change Material Products Limited (PCMP) - Unit 32, Mere View Industrial Estate, Yaxley, Cambridgeshire, PE7 3HS, United Kingdom
[c] CIRCE Institute – Campus Río Ebro, Mariano Esquillor Gómez, 15, 50018, Zaragoza, Spain

HIGHLIGHTS

- A phase-change material system is proposed working at high temperature for waste heat recovery.
- Thermal characterisation and cycling were conducted on the candidate storage material.
- Two phase change materials are identified for the application with a high latent heat capacity and thermal stability.
- A multiple-criteria decision analysis defined shell and double concentric tubes storage as the most suitable configuration.

GRAPHICAL ABSTRACT



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ABSTRACT

A latent heat storage system based on Phase Change Materials (PCMs) is proposed to increase the energy and environmental efficiency by recovering and storing waste heat from combustion gases or other surplus sources at in the energy-intensive industries (EII), currently unused. The final configuration design is specifically adapted to the plant operational requirements, by means of a methodology combining the search of the best conceptual design and a proper selection of core PCMs. To that end, a selection of suitable PCM is carried out by using characterisation techniques and thermal stability testing. Furthermore, relevant key factors are weighted by an in-house Multiple-Criteria Decision Analysis (MCDA) to define the most promising design options to be implemented in two plants belonging to the EII sector. For the ceramic sector, the design resulted in a shell-and-tube system with 1188 kg of a PCM melting at 885 °C and encapsulated in double concentric tubes, involving a storage capacity of 227 MJ. Similarly, 1606 kg of PCM, whose phase-change temperature is 509 °C, is selected for the steel sector providing a PCM-TES system capable to store 420 MJ.

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* Corresponding author.
** Corresponding author.
E-mail addresses: proyo@fcirce.es (P. Royo), vferreira@fcirce.es (V.J. Ferreira), z.ure@pcmproducts.net (Z. Ure), sam.gledhill@pcmproducts.net (S. Gledhill), amlopezs@fcirce.es (A.M. López-Sabirón), germanf@unizar.es (G. Ferreira).

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1. Introduction

Currently, the energy-intensive industry (EII) is facing numerous requirements and initiatives aimed to meet environmental targets [1]. These EII sectors, composed by aluminium, cement, mineral, steel, iron, ceramic, glass, pulp, paper and chemical industries, among others, are making significant efforts to decarbonise their sectors following the 2050 roadmap for energy [2] and achieving the environmental challenges, i.e. those expressed in the Paris Agreement [3]. Meanwhile, industrial producers are conscious of energy costs, as these can be considerable in the overall production cost distribution. For instance, in the ceramic sector, the overall average energy cost can be as much as 30% of total production costs [4]. EII should grow while being economically competitive in terms of energy efficiency and environmental performance, towards exemplarity in a more sustainable industrial future. To do so, these industries aim for overall optimization, energy and resources efficiency, minimizing the residues and heat losses. This latter can be done by means of waste heat recovery (WHR), which is one of the next frontiers for EII in terms of energy efficiency [5,6].

Waste heat is usually wasted through flue gases from boilers, ovens, kilns, turbines, incinerators and furnaces and other EII processes. Some of waste heat losses are inevitable; however industrial facilities could reduce additional losses by improving the efficiency of their processes and equipment or incorporating WHR and storage technologies [7]. Waste energy in terms of heat can be recovered and reused in another plant process or even outside the plant. WHR has a direct effect on the efficiency of the process, and consequently, achieving reductions in consumption, in pollution, in equipment size and costs [8]. Despite all these benefits, approximately 4000 TWh of heat is wasted every year worldwide, whilst in Europe alone the reduction potential could be a total of 250 million tons CO_2 emissions per year [9].

Different WHR technological solutions are based on systems such as conventional heat exchangers, thermal energy storage (TES) systems, recuperators and regenerators, heat wheels, heat pumps, steam boilers, organic Rankine cycles, cold power production, thermo-chemical/biological reactions, etc. [7,10,11]. TES is the temporary storage of high or low temperature energy for later use. It bridges the time gap between energy requirement and energy use. Among them, Phase Change Materials (PCMs) combine latent and sensible energy storage capacities into a single storage unit, which makes them useful for advanced TES technologies [12]. In particular, latent heat based systems have emerged as an attractive option for managing the wasted thermal energy, since it increases energy efficiency through improved use of waste heat, thermal regulation as well as balancing intermittencies between the availability and demand of thermal energy [13]. Specifically, PCMs can be described as mixtures of chemicals having freezing and melting points above or below the water freezing temperature of 0 °C [14,15]. PCMs are able to store large amount of thermal energy when changing its phase (solid to liquid or vice versa) maintaining a constant temperature (melting temperature). When such material solidifies, it releases large amounts of energy in the form of latent heat of fusion. Conversely, when the material is melted, an equal amount of energy is absorbed from the immediate environment as it changes from solid to liquid. PCMs present high-energy storage density and a nearly isothermal nature of the storage process [16], by taking advantage of latent heat instead of sensible heat [17].

Therefore, it is essential to pinpoint the maximum amount of recoverable heat at the highest potential and to ensure the increase of efficiency by means of WHR systems [5]. The PCM system aims to take full advantage of heat going through the flue gases in order to improve the current energy thermal system from the facility, which has reached a technological limit using commercial solutions at high temperatures [18]. Hence, in general terms, the conceptual designs of the proposed solutions aim to increase the air flow temperature used for fuel burning and other preheating processes in order to improve the energy efficiency of the chain and reduce the overall environmental impact [19], both upstream and downstream.

Even though PCM-TES arises as a promising and innovative both WHR and storage solution, only about 5% of the final energy consumption is assumed to be recovered in industrial installations [20]. These systems are not widespread due to technical barriers such as chemical constituents in exhaust gases that interfere with heat exchange, compatibility and safety issues, the low stability of the physical and thermal properties of the materials and/or the corrosion between the PCM and the container [21,22]. PCM-TES have only been tested at lab scale [18,23,24], and very few PCM products meeting the strict requirements of high temperature levels are commercialized [25]. Furthermore, there remains a lack of research owing to the mentioned technical and economic implications under real conditions, no reports in the assessment of the energy savings and an unclear knowledge about the PCM thermal performance at high temperatures in industrial applications [18].

The present design assessment and material characterisation provide a key in the definition of a proper Latent Heat Storage (LHS) system to be fruitfully integrated for industrial WHR and storage at high temperatures [16,26], given the current scarcity of these systems at industrial scale implementation. On the one hand, a PCM characterisation using the Differential Scanning Calorimeter (DSC) machine will be carried out in order to define the most relevant thermo-physical properties of high temperature PCMs (i.e. phase change temperature and latent fusion heat). Currently, the only viable PCMs to use at high temperatures (>500 °C) are molten salts, metal alloys and other inorganic eutectic PCMs [27], from which there is still scarce available test data of thermo-physical properties. Thus, in order to identify the most appropriate high temperature PCM for the application, a range of both metal alloys and molten salts are investigated. On the other hand, an inhouse Multiple-Criteria Decision Analysis (MCDA) methodology is developed and applied in order to define the most promising design options to be integrated in two specific cases studies belonging to the EII sector. As a result, a technically feasible and suitable conceptual design is proposed taking into account the end-user requirements and the plant operation conditions, as well as overcoming the contextual operational restrictions, especially at high temperature levels.

In conclusion, this work deals with the development of new technological systems for increasing the energy efficiency. This topic is aligned with the scope and future thematic threads of the scientific and engineering community [28], such as the use of innovative and intelligent materials design to optimise performance of heat recovery and storage systems that absorb wasted energy; and also the assessment of the phase-change performance in relation to its design at industrial scale.

2. Challenges of PCM at high temperatures

Two study cases are chosen as representative of two of the most intensive energy consumer sectors (ceramic and steel) [29] and have a great potential for WHR [30]. The production processes of this kind of EII requires extremely high temperatures, over 600 °C and even up to 1650 °C [10]. Consequently, the high operating temperature ranges generates streams of products, by-products and/or waste released at high temperature ranges. Usually, the final products need to be cooled down by means of refrigeration, quenching or drying processes, which also consumed material and/or energy resources. Furthermore, the heat losses generated in these industries are even more crucial than in other one working at lower temperature levels, because of the higher exergy levels. Considering the quantity and temperature of the potential waste flows, those with better quality levels will be selected to work as the main waste heat source, these are the exhaust gases exiting the main furnace. The waste heat sources should be preferably stable, ample and with high exergy for activating and supporting the operation of the heat recovery systems [31]. The recovered energy could be used for electricity generation, combustion air preheating, furnace loads preheating, space heating, drying, curing, baking, hot water generation and even cooling purposes [9].

To this end, a material has to meet several criteria [32] to be considered as a useful PCM for a practical TES or WHR implementation:

- Release and absorb large amounts of energy when solidifying and melting.
- Have a fixed and well-defined phase change temperature (solidification/melting point).
- Avoid excessive super cooling and remain stable over many freeze/melt cycles.
- Be non-hazardous and non-corrosive to its encapsulating material.
- Be cost-effective for a given application.

Commercially available PCMs can broadly be arranged into seven categories [33], which are presented in Fig. 1: alcohol solutions, eutectics, hydrated salts, organics, solid-solids, molten salt materials and metal alloys.

Most aqueous salt-based PCM solutions either have a tendency to absorb moisture from the atmosphere, meaning they are hygroscopic, or lose water through evaporation, and therefore they must be encapsulated in sealed containers [32]. Macrocapsules in the form of spheres, plates, or cylinders, as well as micro-encapsulated paraffins, are available industrially today and used in various applications [35]. Although organic solutions can be exposed to air as they are not water based, there are contamination and fire risks due to them having a low flash point, making it necessary for them to be encapsulated in sealed containers. Salt-based PCM solutions are corrosive and so, the most practical and economical method of encapsulation is to use plastic or metal containers [36]. However, plastic becomes soft and pliable at temperatures above 50 °C, which restricts their application range to temperatures below this level. As well as rigid plastic containers, a wide range of flexible pouches filled with various PCM solutions can be used for encapsulation, enabling a wide range of low-cost applications. Although plastics are economical, their heat transfer rate and limited temperature range can restrict their use. In order to extend the temperature range or improve the heat transfer rate, metal containers have been extensively used for special applications [32].

At high temperatures, there are two different PCM options, metallic PCMs and molten salts, which present both advantages and disadvantages. On the one hand, molten salts can often be difficult to integrate into TES systems due to their corrosiveness, so they require a protective encapsulation. In addition, they are often supplied in powder or granule form, meaning their volume can decrease by up to 50% when first melted, this can also result in difficulties when filling units with high temperature molten salts. Despite the previous technical limitations, molten salts are one of the most used PCMs at present due to their wide availability and the high energy density that these materials offer. On the other hand, metal alloys working as PCMs are characterized by a high thermal conductivity and volumetric energy density. Although metallic PCMs are easier to handle since they do not have issues with corrosion, their integration in systems is complex due to the thermal expansion issues and the implications of operating at high temperatures, that could risk the implementation of the system [37].

Under this premise, a MCDA methodology and the analysis of the thermo-physical properties of alternative PCM at high temperature are proposed in this study. This will help to customize a PCM-TES solution according to the plant specifications, for expanding and promoting its incorporation in the industrial sectors and in other valuable future applications.

3. Materials and Methods

3.1. System description

A PCM-based heat recovery system is going to be incorporated to absorb the wasted heat from the exhaust gases exiting the furnace, as shown in Fig. 2. During the PCM-TES charging, the high temperature exhaust gases transfer the heat to the PCM, which increases its temperature until the phase-change point. During the phase transition, the heat is stored in function of the latent heat capacity; while the PCM becomes liquid. This process lasts until almost all the PCM is completely melted. After that, the flue gas stream through the PCM-TES is closed and the air combustion flows during the discharging; while the PCM becomes solid again while releasing the heat. As a specific application, the main objective of the proposed WHR system consists of increasing the current temperature of the preheated combustion air (maximum temperature around 500 °C and 850 °C, depending on the sector) in order to improve the combustion efficiency and to reduce the fossil fuel consumption.

All the information related to the waste heat sources flows and temperatures of each industrial plant is summarised in Table 1. Additionally, the target temperature objectives for the combustion air preheating are also established.

3.2. Experimental section

The experimental section is devoted to gather valuable information by means of thermal performance characterisation and thermal stability

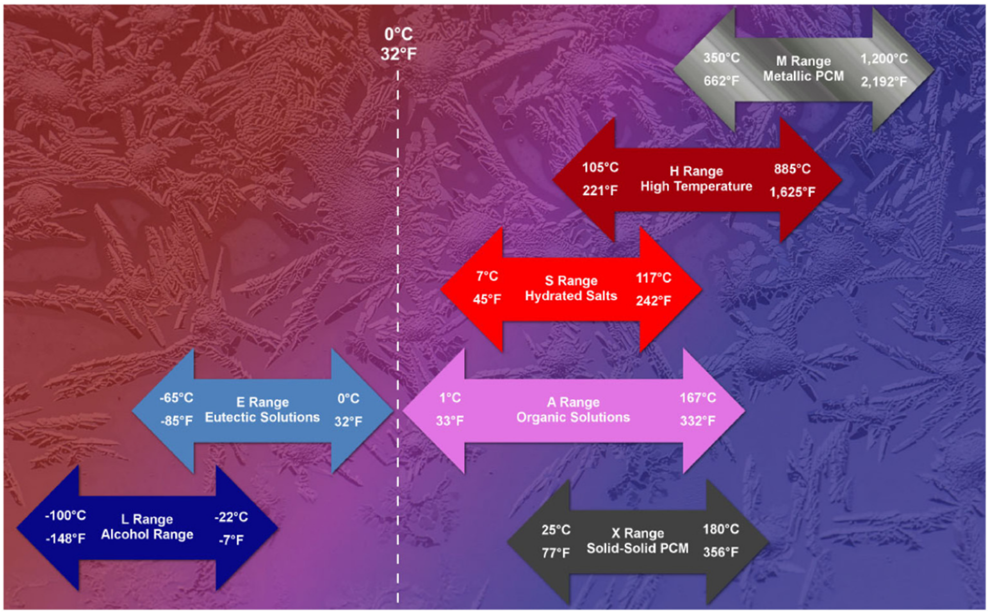

Fig. 1. Commercially available PCM and their temperature ranges PCM Products Ltd. [34].

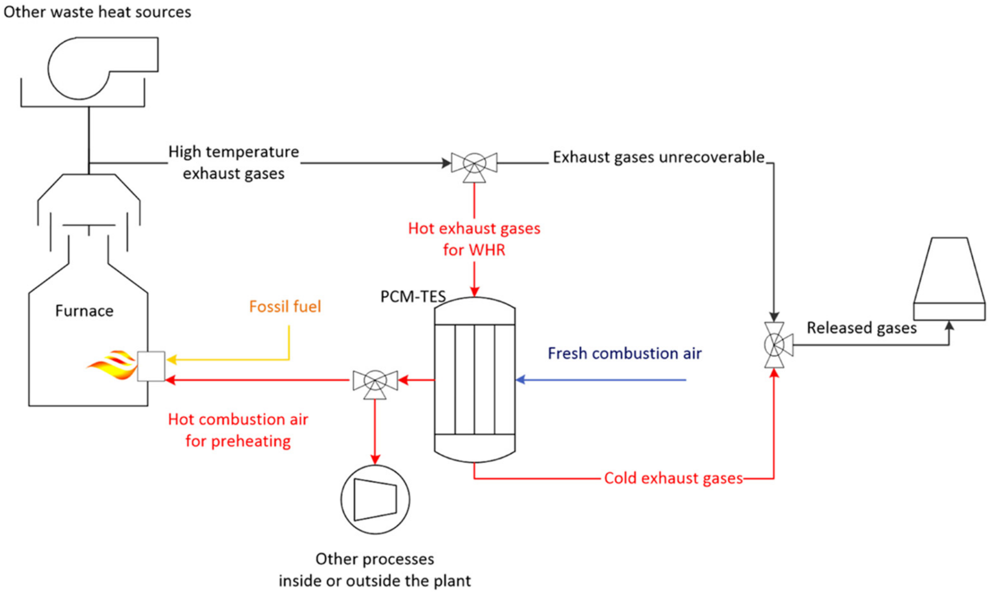

Fig. 2. General diagram flow of the PCM-TES integration to recover heat from an exhaust gas stream exiting an industrial furnace.

tests, in order to identify the most appropriate high temperature PCM investigated as potential medium material for the TES system for the applications specified in the system description.

3.2.1. Selection and preparation of PCMs

PCMs will be identified in order to select the most appropriate material and determine its thermal behaviour based on their thermo-physical properties. Two different categories of PCMs were mainly investigated in this study, molten salts and metal alloys and Table 2 summarises the properties of the identified high temperature PCMs. The PCM selection is focused on the combustion air and the flue gas temperatures that are required for their use in the steel and ceramic sectors. For the steel sector, it is desired to select a PCM with a temperature as close to 500 °C as possible, with the exhaust gas temperature being around 750 °C at the furnace outlet. Whereas, the hotter ceramic sector requires a combustion temperature of around 850 °C, with the furnace exhaust temperature being up to 1100 °C. The molten salts (prefix ‘H’) are mixes or pure forms of salt compounds; while the metallic PCMs (prefix ‘M’) are alloys based on zinc, magnesium and aluminium. Despite the presence of the argon blanket, oxidation issues were found with the magnesium and zinc-based alloys. All costs are estimated; these are not yet known for the metallic PCMs.

One of the most crucial criteria for the PCM selection is the phase change temperature (PCT), followed by its latent heat and cost. The key idea is to recover as much waste heat as possible, at high temperature levels, while being economically feasible. However, it should also be taken into account that the charge and discharge processes should not last very long and should have a good transference rate. In conclusion, the objective is to select the candidate PCMs with PCTs close to the specified targets and showing promising properties. H500 and M550 are the candidates for the steel sector; while, H845 and H885 will be tested as alternatives for the ceramic industry.

3.2.2. PCM characterisation and thermal stability testing

The candidate PCMs were synthesised in laboratory, characterized and evaluated by means of different thermal stability tests at temperatures above and below their PCT. The main goal is to analyse their suitability, stability and define their thermo-physical properties along different charge/discharge cycles. These properties are sometimes just based only on theoretical literature reviews, or experimental studies under very well controlled conditions. That is why, it is very important to ensure that a PCM is reliable thermally, chemically and physically stable after repeated high temperature cycling in the long-term [38]. However, the design of thermal cycling test has no common standard and depends on the researchers and the application [39]. Ferrer, Solé, Barreneche, Martorell and Cabeza [40] remarked the scarcity of available data, especially in high temperature PCM since it is more energy and time consuming. Furthermore, data discrepancy suggests that proper thermal characterisation is still not assessed in depth.

The molten salt PCMs were produced in a sample size of approximately 20 g by melting component salts in stainless steel crucibles within a VCG Ventura FE1N furnace at 1100 °C. This furnace has a 2-L volume and was fed with an argon blanket at 0.2 L/min. The temperature of the sample during this testing was recorded using a K-type thermocouple placed in the top of the furnace. For the synthesis of metallic PCMs, approximately 20 g of each alloy was produced in graphite crucibles in the furnace mentioned above.

Once the virgin PCM samples were prepared, DSC analysis was performed on each to determine their phase change temperature and latent heat capacity. The DSC scans, performed on a Mettler Toledo DSC823e, used 10 mg PCM samples within alumina crucibles for the characterisation and nitrogen was used as the purge gas. The heat flow was measured using a sensor with its 120 gold-gold/palladium

Table 1
Main parameters of the waste heat sources and expected preheating temperatures for the combustion air.

Industrial process description	Ceramic	Steel
Exhaust gases flow exiting the furnace (Nm^3/h)	782	643
Exhaust gases temperature exiting the furnace (°C)	1100	750
Combustion air flow to be preheated (Nm^3/h)	481	1600
Combustion air temperature to be preheated (°C)	650	50
Maximum temperature for combustion air (°C)	850	500
Minimum temperature for combustion air (°C)	700	300

Table 2
Summary of the identified potential high temperature PCMs from PCM Products Ltd. [34].

PCM	PCT (°C)	Density (kg/m^3)	Latent Heat Capacity (kJ/kg)	Cost (€/kg)
H485	483	2220	200	7.57
H500	509	2220	260	5.10
H500A	500	2140	140	0.70
H845	840	2530	146	1.41
H885	888	2700	191	2.29
M550	552	4770	251	–
M570	570	2650	428	–

thermocouples. The calorimetric data resolution of the DSC is 0.01 μW, the temperature accuracy is ±0.20 K, and its temperature precision is ±0.02 K. The accurate PCM characterisation data obtained using this procedure was used to identify the most suitable PCM for both sectors, the successful materials then proceeded to thermal stability testing.

The selected PCM for both sectors underwent temperature history analysis of high temperature freeze and melt cycling following the pyramid method [40], both with and without protective argon atmospheres. During these tests, small samples of the PCMs were analysed using DSC to determine if they suffered any loss in performance due to thermal degradation or evaporation. For the freeze and melt cycle, a PCM sample of 3 g was placed within a sealed ceramic crucible inside the VCG Ventura furnace. First, the samples were protected inside the furnace with an argon blanket. The furnace was then cycled to approximately 50 °C above and below the PCT of each sample for 20 freeze and melt cycles. Following every fifth cycle, a small sample around 3 mg was taken from the furnace and then analysed using DSC, and this was repeated up to the 20th cycle. This testing was then repeated without an argon blanket and with the PCMs in open alumina crucibles, thus more closely replicating the conditions that will be present during operation. This would allow for any degradation due to exposure to air become apparent. Following this test, the sample will have undergone 40 freeze and melt cycles. Any changes in the DSC results can then be used to identify any loss in performance or degradation.

Finally, the PCM selected for each sector was subjected to further repeatable high temperature cycling, in order to determine its maximum operating temperature. This cycling was performed 550 °C and 750 °C for the steel sector and between 940 °C and 1050 °C for the ceramic sector, with the sample exposed to air in a non-sealed alumina crucible, on each cycle the temperature was held at the maximum for 30 min. This testing replicates the maximum operating temperatures the system would reach in the ceramic sector. As before, small samples (3 mg) were taken from the main sample for DSC analysis after the 1st, 2nd, 5th, 10th, 15th and 20th cycle. In addition, the sample and crucible were weighed after each of the above melts to determine weight loss. If the sample loses weight during the testing, this would be due to either evaporation or thermal decomposition. If it were the latter, one would expect the latent heat of the remaining sample to change as the composition alters. This is because decomposition would result in the formation of gaseous by-products and solid metal oxides that would remain dissolved in the remaining PCM and alter its composition, thereby affecting its performance.

3.3. Design specifications

In order to determine the required storage capacity of the PCM-TES system, the procedure explained by Royo, P. et al. [41] is followed; where the heat demand (Q) of the combustion air preheating is quantified by means of Eq. (1). In this equation $m_{comb.\ air}$ is the flow of combustion air that will be preheated before entering the furnace or other inside/outside plant processes; c_p is the specific heat and $\Delta T_{comb.air}$ is the temperature increase in the combustion air due to the PCM-TES integration.

$$Q = m_{comb.air} \cdot c_p \cdot \Delta T_{comb.air} \tag{1}$$

The thermal energy transferred by the PCM (Q_{PCM}) during the charge/discharge process is governed by Eq. (2) [42], which is the equation for an arbitrary heat transfer process, $\Delta T_{HTF\text{-}PCM}$ is the HTF inlet and outlet temperatures and PCM melting temperature, heat exchange area (A) and global heat transfer coefficient (U).

$$Q_{PCM} = U \cdot A \cdot \Delta T_{HTF-PCM} \tag{2}$$

Furthermore, the following assumptions based on [43] will be considered for the PCM-TES design of the alternative solutions:

- The heat exchanger (HX) capacity is calculated in order to release an assumed heat (Q_{PCM}) to the air combustion stream in an hour autonomy, under an ideal heat transference rate.
- The net volume of the container, PCM density and the heat transference area will determine the final PCM mass and the tubes number to assure the desired Q.
- The surface and volume of the heat recovery system are estimated as a function of PCM mass.
- The difference between the linear thermal expansion of PCM and the container material must be considered because it might lead to structural stress with potential break of the system.
- The tubes height is recommended not to exceed 3.5 m, in order to ease dust extraction, PCM filling in and maintenance operation.

Finally, all the proposed systems were adapted to the use of PCMs encapsulated into tubes in order to avoid leakage issues during the operation. The encapsulation of PCMs in a tubular HX appears to offer a straightforward solution because heat loss from the shell and tube system is minimal and also it is a heat exchanger design well-known to engineers [44]. The encapsulation in multiple tubes presents a more homogenous distribution and prevents the melted PCM from leaking or spreading inside the container. Furthermore, when the PCM solidifies on the convective heat transfer surface, the solidified layer acts as an insulator [45]. This in turn decreases the heat transfer rate appreciably and causes a non-uniform rate of discharging characteristics in the storage tank, which may restrict the usage for any application.

For the conceptual design alternatives, two types of tubes for containing the PCM inside are considered in this study: single tubes and concentric double tubes. It may be easier to fill the first kind of tubes, but they only have one surface of contact to absorb and release heat. Thus, its thermal conductivity is a crucial parameter to ensure an efficient transference. Otherwise, by using concentric doubled tubes, hot and cold flows can circulate at the same time, and the charging/discharging stages could happen simultaneously if thermodynamic conditions are accomplished.

Moreover, there are three major concerns in the encapsulation of PCMs in tubes [46], and these issues must be well addressed in the conceptual design, material selection and the engineering of the proposed PCM solution system. Firstly, the tubes must be able to accommodate a large volumetric expansion of the PCM on melting. Secondly, the high temperatures and pressure build-up due to the expansion of air at such elevated temperatures during the start-up and charging of the TES system. The third concern is the reactivity of the molten PCM, as salts can be powerful oxidizers and highly reactive with a variety of metal, organic and inorganic materials.

In this vein, the high temperature is another technical issue, which made the tube material selection a difficult and challenging process [47]. In summary, the major compatibility and corrosion problems of this interaction are oxidation and de-alloying [48–50]. Special attention must be paid to the ceramic sector where the operating temperatures and the flue gases streams leave the furnace at very high temperature, increasing the corrosion and degradation issues. Thus, three major types of high temperature materials were regarded as candidates: nickel-based alloys, stainless steels and titanium-based alloys.

3.4. Conceptual design proposals of PCM-TES solutions at high temperature

This section is devoted to proposing and describing different conceptual alternative solutions focused on the PCM equipment configuration, all of them taking the design specifications explained above. A High Level Expert Panel (HLEP) was integrated by independent and international members of complementary expertise, involving engineering companies, PCM providers, academic and research centres and also industrial end-users of different sectors. Based on the knowledge and extensive experience provided by the HLEP, the alternative PCM-TES systems will be compared by identifying the advantages/disadvantages and considering the specific characteristics of the industrial processes

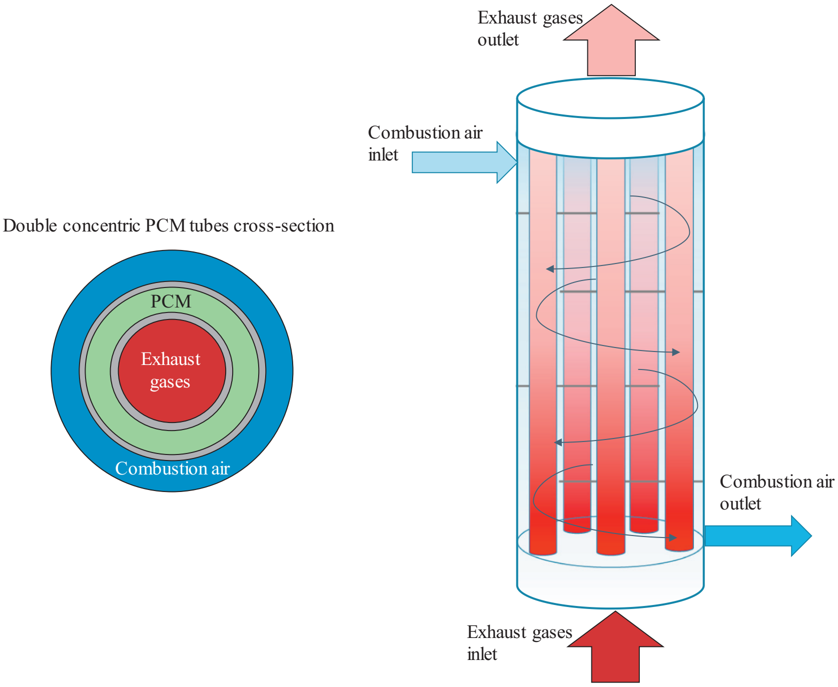

Fig. 3. Diagram of a shell-tube PCM-TES with PCM contained into double concentric tubes.

where they would be integrated. The alternatives are overall evaluated considering the adequacy to the application, the flexibility of the design and the configuration adaptation to accomplish a proper technical solution in combination with the storage material. Later on, all the gathered insights regarding the alternatives will set the basis for the evaluation and selection of the most suitable configuration solution. More specific design parameters, such us heat transference area, number of tubes, baffle integration among others, will be further considered in the preliminary sizing and cost analysis, described in section 4.4.

3.4.1. Option 1: shell and tube PCM-TES with PCM contained into double concentric tubes

In this first proposal, PCM is contained within concentric double tubes creating a ring where the flue gases circulate inside and the air to be preheated circulates on the outside. Flue gas flow is considered best to be in the inner tube because of maintenance issues. Besides, the cleaning process is easier in this configuration and the dust particles can be removed. The heat transference between PCM and flue gases might be enhanced by terms of removable helicoidal fins placed inside the tube, as can be seen in Fig. 3. Some of the most relevant advantages and disadvantages of this option are discussed in Table 3.

3.4.2. Option 2: PCM-TES system formed by two HX modules connected by a HTF

This proposal consists of a two-step system. Firstly, heat from flue gases is recovered using a tubular HX using a heat transfer fluid (HTF), such as synthetic oil, NaK or other. Secondly, the hot HTF is pumped towards the double tube PCM system (the HTF through the shell). Here, heat is transferred from the HTF to the PCM system in order to be then discharged to the combustion air (flowing inside the tubes) to increase its temperature. As in the first option, PCM is encapsulated within doubled concentric tubes, but in this case, the hot air is on the innermost part of tubes and HTF flows inside the shell. A graphical description of this system is shown in Fig. 4, as well as their advantages and disadvantages in Table 4.

3.4.3. Option 3: PCM-TES crossflow system in a double HX chamber (exhaust gases/combustion air) filled with PCM tubes

The concept consists on the transference of heat from one chamber to other (Fig. 5). This transference is carried out by means of metal tubes, sealed at both ends and filled with PCM, which will be able to absorb the waste heat from the exhaust gas stream and store it by changing its phase. By heat conduction throughout the tube, heat is transferred to the second chamber (at the top) where the air is preheated. Both the flue gases and the combustion air can flow at the same time because chambers are separated by plates. The advantages and disadvantages of this system were identified and collected in Table 5.

3.4.4. Option 4: interchangeable crossflow PCM-TES with finned PCM tubes storage

In this conceptual design, the interchangeability between both flows (flue gases and combustion air) can be achieved by means of valves that guide the streams in a bidirectional pipe. This option could be applied,

Table 3
Technical issues of PCM-TES alternative option 1.

Advantages	Disadvantages
Avoiding gravity and compatibility issues with PCM encapsulated inside tube	Cleaning system to be defined in order to avoid corrosion and inefficiency
Adaptable design by varying capacity, volume, tubes number, configuration, PCM type, etc.	Partial sealing of the concentric tubes with PCM inside
Helicoidal fins can increase the heat transference, if included	Possible problems derived from the introduction of PCMs into hollow tubes
Dirtiness, volatiles and dust can be easily cleaned	Condensation and corrosion could be an issue
Modular HX concept divided with baffles to increase heat transference	Pressure drop across the flue stream could be an issue
Large heat exchange area that offers better PCM melting and solidification cycle	

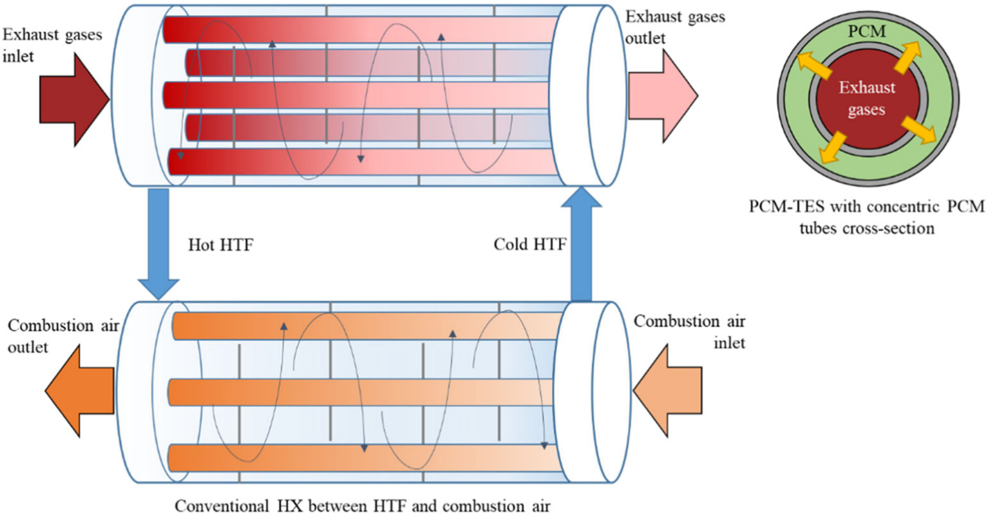

Fig. 4. Diagram of a PCM-TES system formed by two HX modules connected by a HTF.

Table 4
Technical issues of PCM-TES alternative option 2.

Advantages	Disadvantages
Avoiding gravity and compatibility issues with PCM encapsulated inside tube	Conventional synthetic oil working as HTF undergoes degradation at high temperatures
Adaptable design by varying capacity, volume, tubes number, configuration, PCM type, etc.	Other alternative HTF can be used such as NaK, but safety problems can occur (reactive, explosive, flammable, etc.)
Flat fins can be placed around the tubes to increase the heat transference	Cleaning system to be defined in order to avoid corrosion and inefficiency
Efficient heat transfer	Expensive system with 2 HXs and 3 fluids. Increase of investment, operational and maintenance costs
Control capacity by managing the HTF flows	Partial sealing of the concentric PCM tubes
	Greater volume, more difficult to handle and find a location at plant

for example, in the steel/aluminium sectors, since it is considered that there are not severe problems with the dust content in the exhaust gases, unlike the ceramic sector. Furthermore, there is the possibility of working with different modules in series and/or parallel (or independent exchangers). By this way, while exhausted gases are giving heat to the PCMs of one module, combustion air can be heated up in the other section. An example including plate fins for improving heat transfer is shown in Fig. 6, and its advantages and disadvantages in Table 6.

3.4.5. Option 5: crossflow PCM-TES with simultaneous flows (exhaust gas and combustion air streams) and filled PCM tubes

Similarly to option 4, a crossflow HX is proposed in order to recover heat contained in flue gases using PCM tubes and transmit the heat to combustion air. In this configuration, both streams can circulate simultaneously in the same module, because the streams are divided alternatively between the plate void. PCM is placed into compact tubes sealed at both ends. The number of modules can be adapted to match the heat

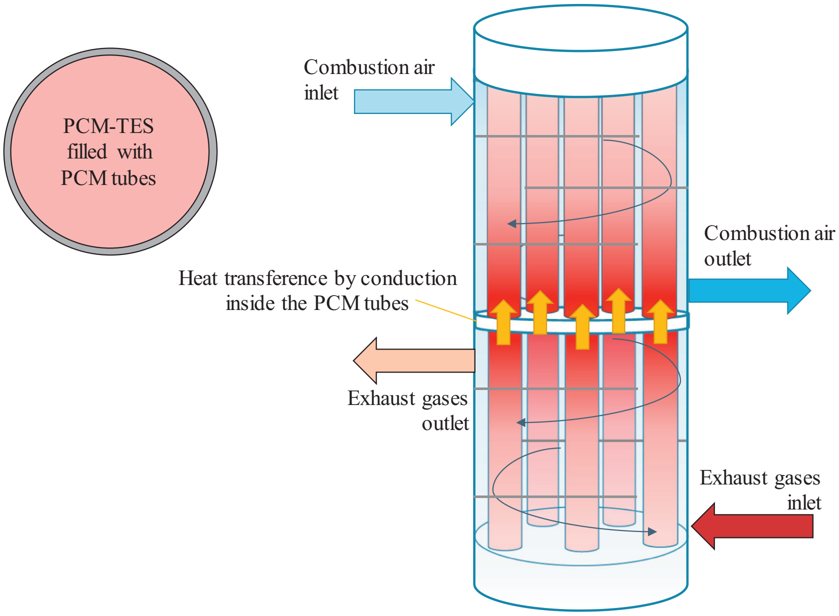

Fig. 5. Diagram of a PCM-TES based on a double HX chamber filled with PCM tubes.

Table 5
Technical issues of PCM-TES alternative option 3.

Advantages	Disadvantages
Avoiding gravity and compatibility issues with PCM encapsulated inside tube Tubes filled just with PCM are more easily sealed (physical and thermally) Adaptable design by varying capacity, volume, tubes number, configuration, PCM type, etc. Large heat transfer surface results in high heat transfer efficiency Dynamic heat pipe or doping material may offer fast acting heat recovery	Severe thermal conductivity problems along the PCM tubes and temperature gradient Inefficient heat transference that may make the system not feasible Relative dirt and dust problems interfering in the HX configuration. Difficulties while cleaning.

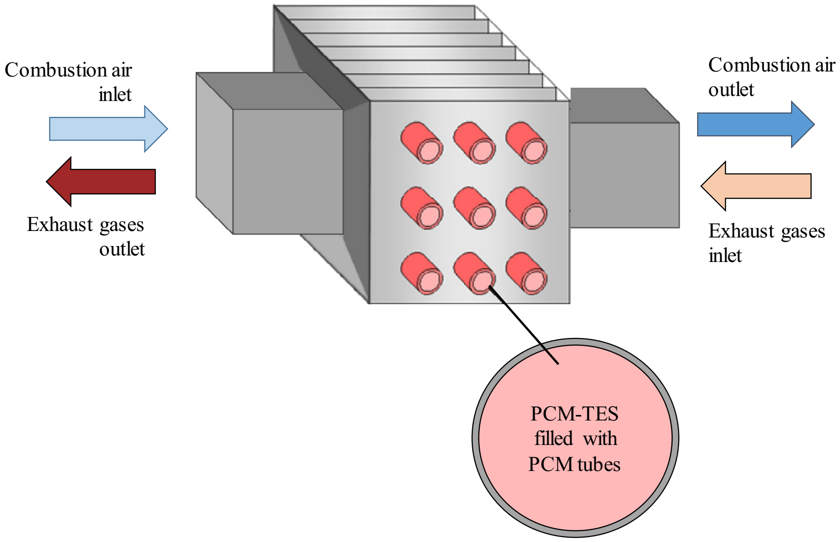

Fig. 6. Diagram of a crossflow PCM-TES with finned PCM tubes storage.

capacity requirements. Unlike what happen in option 3, this crossflow HX solution is not so strongly dependent on the PCM conductivity. A scheme of this proposal is shown in Fig. 7. Advantages and disadvantages of this option, which are included in Table 6, can also be applied to this configuration, but in this case, the thermal conductivity and the efficiency are enhanced.

3.5. Multiple-Criteria Decision Analysis (MCDA) methodology for the best configuration selection

After gathering and interpreting all the above information, it is needed an overall approach which allows accounting explicitly for a variety of criteria, perspectives, stakeholders, values, uncertainties and intra and inter-generational considerations [51]. Due to the complexity involving the operation at high temperature ranges and the need to provide a path towards the design of an efficient and feasible PCM-TES solution, the selection must be taken in a structured, transparent and reliable way. In order to select which of the previous PCM-TES system alternatives is the most suitable configuration as the one with the greatest potential to be installed on each specific industrial site, a MCDA matrix will be performed in order to weight a set of technical, economic and operational decision criteria. To do so, a methodology based on the Analytic Hierarchy Process (AHP) proposed by Thomas Saaty, which is one of the more widely applied MCDA [52], will be used mixed with a rating score including positive/negative values in order to enhance the beneficial/detrimental characteristics of the proposed alternatives. The AHP is a compensatory method that decomposes complex structures into their components and arranges these variables into a hierarchical structure. For applying the MCDA, the following steps will be followed according to Department for Communities and Local Government [53]:

1. Establish the decision context and design the socio-technical system, which is set by the challenge and needs of PCM-TES design.
2. Identify the options and alternatives to be appraised, ensuring that they are comparable, real, practical and feasible (which were defined in the previous sub-section).
3. Identify criteria for assessing the consequences of each option and cluster them under higher/lower-level objectives in a hierarchy. These criteria have been selected according to the authors' own experience and a literature review [54]. As there is a notary quantity of aspects to take into account, the AHP is appropriate to categorize

Table 6
Technical issues of PCM-TES alternative options 4 and 5.

Advantages	Disadvantages
Heat transference rate can be high since flue gases and air go by the same pipe Tubes filled with PCM can be physical and thermally sealed and avoid gravity issues Flat fins can be used to increase the heat transference The use of two systems in parallel can increase the flexibility and adaptability to batched demands Adaptable design by varying capacity, volume, tubes number, configuration, PCM type, etc.	Cleaning system to be defined in order to avoid corrosion and inefficiency The need of sealing the PCM tubes with numerous flat fins can increase costs High maintenance costs Only suitable when exhaust gases are clean (low dirt, low dust) because they flow in the same pipe as the combustion air entering the furnace Pressure drop for the flue gases could be an issue

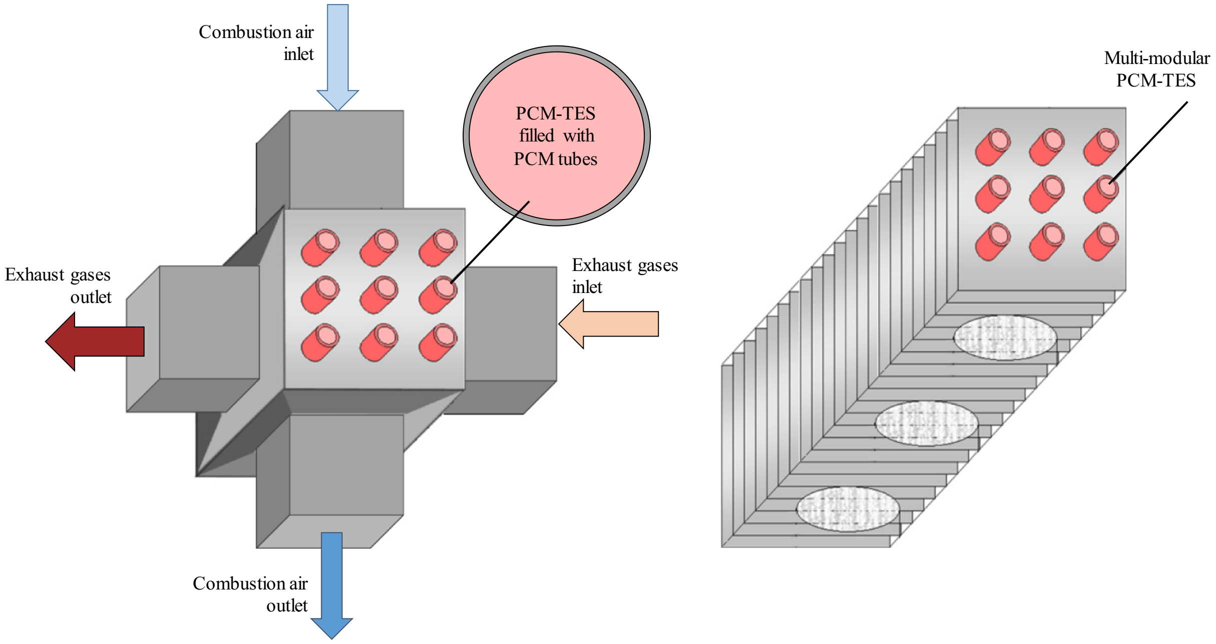

Fig. 7. Diagram of a crossflow PCM-TES with simultaneous flows and filled PCM tubes.

these technical aspects into three main criteria: operational, economic and design criteria (Fig. 8).

4. Assign weights for each of the criterion to reflect their relative importance to the decision. To do so, Saaty's ratio scale [55] is the basis for pair wise comparison of importance of weights of criteria/alternatives covering the entire spectrum of the comparison (from 1 for equal importance, up to 9 defining an extreme importance). Furthermore, it is checked the consistency ratio (being always less than 5%) to ensure a satisfactory decision and avoid incongruities during scoring step, else the procedure is repeated until these values lie in a desired range.
5. Scoring the expected performance of each option against the rest of criteria. These technical aspects were grouped under the rating levels presented in Table 7 in order to quantify which are the most suitable configurations for the PCM-TES solution, depending on the EII where the WHR system is meant to be integrated. The beneficial and favourable aspects to find the suitable and optimal conceptual design are highlighted with a positive value. Otherwise, the major or crucial drawbacks will be scored with a negative value in order to discard the unfeasible options from the technical or economic perspective or with major difficulties in the performance or assembly. Finally, a neutral weight with value of 0 is attributed to the average performances or characteristics.
6. Method of aggregation, which combines the weights and scores for each option at each level in the hierarchy to derive the overall scores. Depending on this structure and their relative importance, a general weight (GW) for the category balancing is given. In this line, the technical aspects belonging to each category are also presented with their respective relative weight (RW).
7. Interpretation and examination of the results will be discussed in the following section. The total score for the different options will be normalized on a −100 to +100 point scale.
8. Conduct a sensitivity analysis to assess how the weights and scores affect the overall values and create new options if needed, before repeating the process until a clear and consistent result is obtained.

The above process provides a mixed methodology to calibrate the numeric scale for the measurement of quantitative as well as qualitative performances. The basic idea of the approach is to convert subjective assessments (qualitative criteria) to a set of overall quantitative hierarchical weights (scores), as illustrated in Fig. 8.

4. Results and discussion

4.1. PCM selection and characterisation results

4.1.1. Steel sector

Firstly, a molten salt PCM with a PCT of approximately 500 °C was identified, H500. The DSC result of the virgin sample for this PCM is shown in Fig. 9, which shows the signs of a PCM with great potential and a latent heat of approximately 260 kJ/kg and a confirmed PCT of 509 °C.

As the PCM will be encapsulated within metal tubes in the heat exchanger design options, it would be required to work out the least corrosive options. An identified alternative to H500 is the metallic PCM M550. The DSC for M550 in Fig. 10 shows a well-defined latent heat peak around 251 kJ/kg. Furthermore, good melting and freezing plateaus can clearly be seen for the PCM at 550 °C.

Table 8 summarises the key data for both candidate materials for the steel sector.

Overall, M550 represents an excellent option; due to its high density, its volumetric latent heat capacity is very high compared to many other PCMs, including H500. In addition, due to being a metal alloy, it presents a higher thermal conductivity than H500 and no issues with corrosion. However, the lack of suitable materials in the desired temperature range alongside the time it would take to bring metallic PCMs to market ruled these out as candidate materials. Thus, selecting an appropriate encapsulating for molten salt material to avoid compatibility problems is a much more straightforward process [56], mainly due to the advances in the material commercial readiness. Therefore, molten salts are suggested as best option despite their strong corrosive attack they have at high temperatures, an issue that can be solved using resistant metal tubes for encapsulating the molten salt. Because this, H500 was selected as the most appropriate PCM to apply in the steel sector.

4.1.2. Ceramic sector

The ceramic sector requires a PCM with a PCT much higher than that in the steel sector because the exhaust gases can reach temperatures

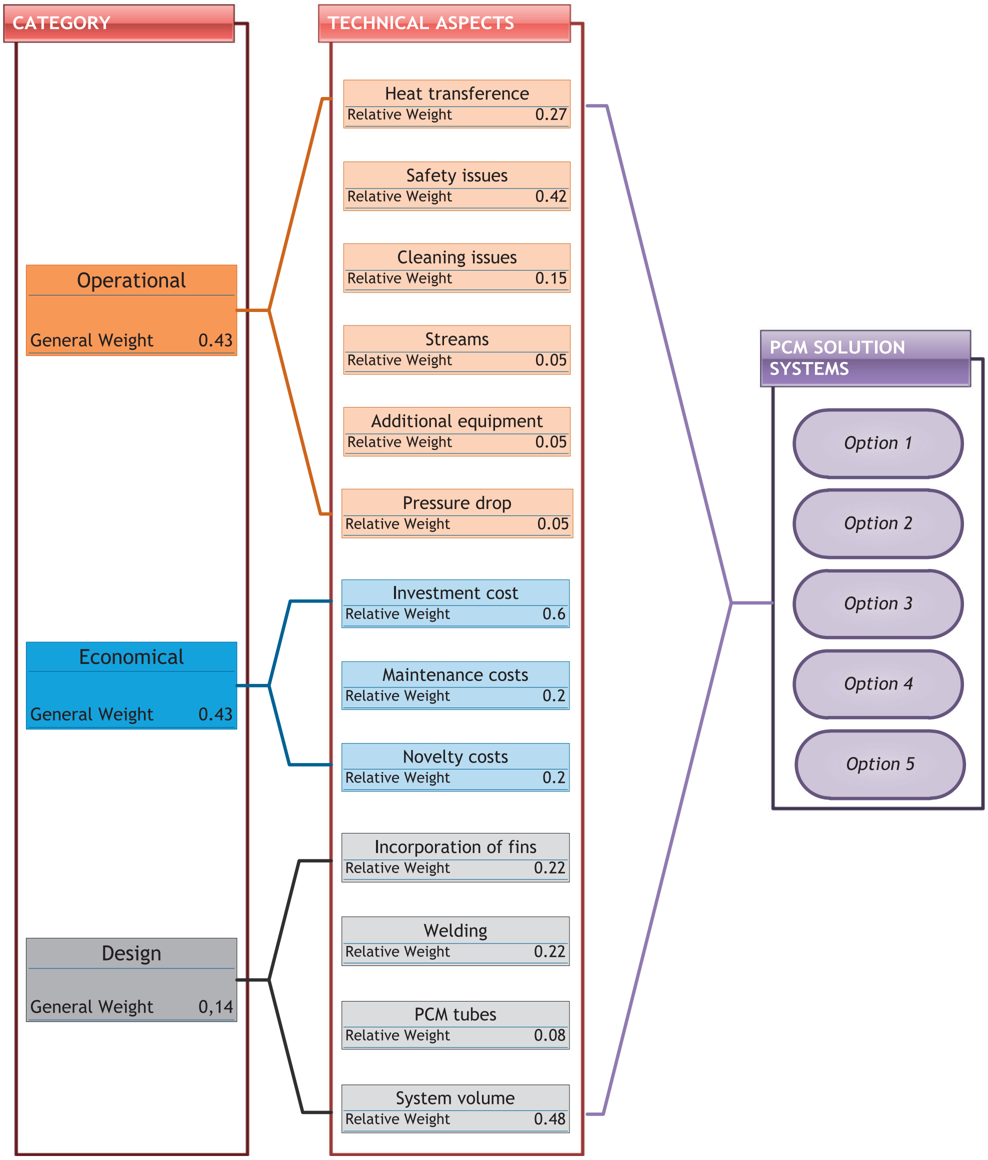

Fig. 8. Hierarchical structure for the technical aspects included in the main categories, with their general and relative weights, for the evaluation of the PCM-TES alternative solutions.

over 1000 °C. No metallic PCMs were available at this extremely high range; however, two molten salts, H845 and H885 were identified as potential candidates. Fig. 11 and Fig. 12 show the DSCs and freeze and melt profiles for these two PCMs after repeated cycles of phase changing in order to analyse the behaviour along time and a possible variation of the thermo-physical properties.

Both H845 and H885 show clear latent heat peaks in their DSC results, however, the peak for H845 is slightly lower than expected (at 840 °C). In addition to this, the freeze and melt profile for H845 show no clear freezing or melting plateaus, suggesting poor PCM performance and an uncertain PCT. The results for H885 show much better repeatable behaviour. Table 9 summarises the experimental key data obtained for both PCMs.

The higher PCT, which is even over 885 °C, and the improved performance of H885 is more desirable for the ceramic furnace system, making the H885 molten salt the most suitable PCM to use in this case.

4.2. PCM thermal stability

As H500 and H885 were identified as the most appropriate PCMs for each sector, they underwent more rigorous thermal stability testing in order to confirm that they are suitable to be used in the heat recovery

Table 7
Rating score values for MCDA matrix.

Performance or Characteristic	Score Value
Beneficial performance: Very efficient, safety, easy or no cleaning, low or medium costs, adaptability, crossflow, use of compatible fins, low surface for welding, simplicity, modular approach, no extra accessories, complete sealing, no gravity issues, very compact, no pressure drop.	Positive value + 1
Average performance: Efficient, easy of cleaning, high costs, medium surface for welding, medium volume, compact.	Neutral value 0
Drawbacks or challenging performance: Low efficiency, danger or risks, difficulties for cleaning, too high costs, inadaptability or new implementation, great surface for welding, concentric tube, counterflow, extra accessories, partial sealing, gravity issues, large volumes or pressure drop.	Negative value −1

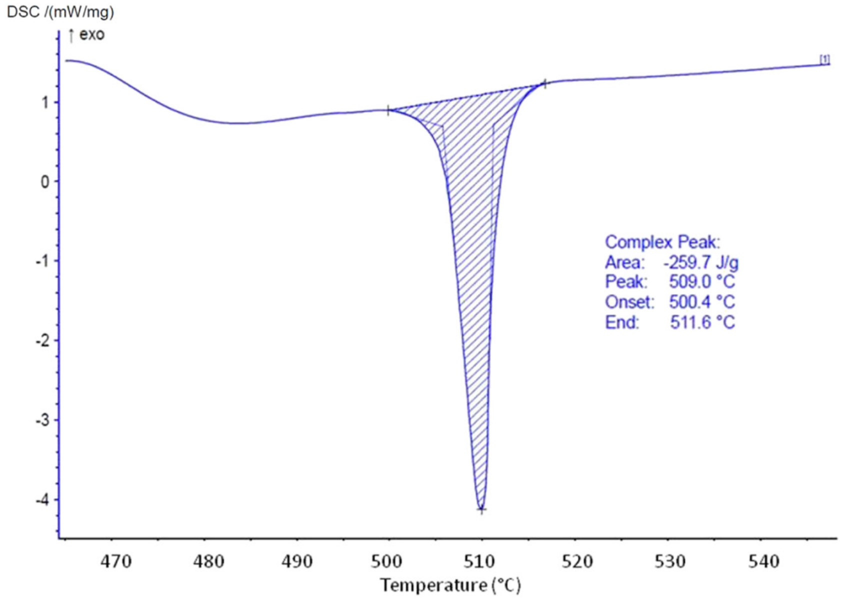

Fig. 9. DSC results for H500 molten salt PCM freeze and melt profile.

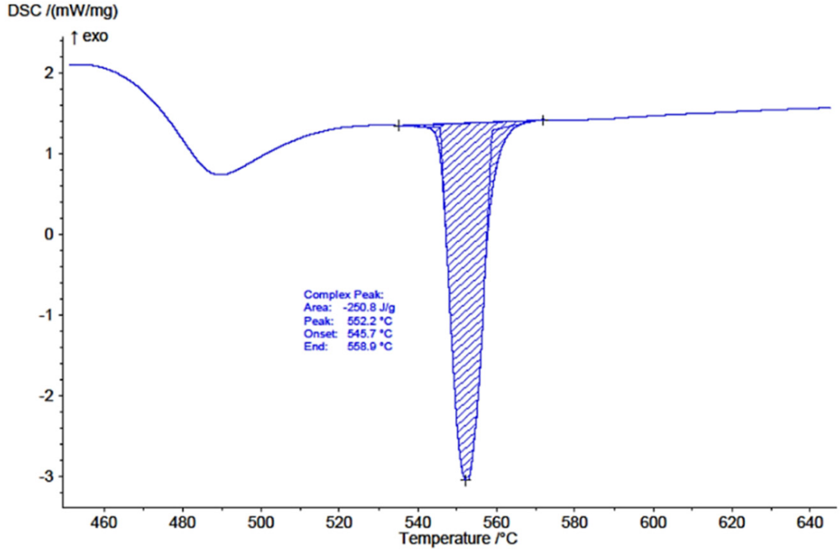

Fig. 10. DSC results for M550 metallic PCM freeze and melt profile.

systems. The first of the thermal stability tests involved subjecting H500 and H885 to twenty freeze and melt cycles between 400-590 °C and 840–950 °C, respectively. For these runs, the same PCM samples were used as for the previous thermal stability tests using argon within ceramic crucibles.

Fig. 13 and Fig. 14 show the DSCs from the 1st and 20th cycle for H500 and H885, correspondingly. It can be observed that the thermophysical properties of the PCM may slightly vary after several freeze and melt cycling. Moreover, it can be concluded from the figure's comparison that the PCT range from the onset to the end becomes even narrower as they go through cycles; which is beneficial for achieving a uniform thermal behaviour.

Table 8
Key data obtained for both candidate PCMs for the steel sector.

PCM	PCT (°C)	Latent Heat Capacity (kJ/kg)	Volumetric Heat Capacity (MJ/m^3)
M550	552	251	1197
H500	509	260	577

The testing results show just a 3.7% deviation in latent heat capacity and a 2.1 °C deviation in PCT of the tested samples for H885. These deviations are small and can be attributed to experimental error and compositional differences between the samples selected for DSC. For H500, the latent heat varies by up to 12% and the peak PCT by a maximum of 2.1 °C. Although the latent heat deviations are larger than for H885, they can still be attributed to compositional differences in the samples; any degradation in the PCM would see much more drastic characteristic deviations. This suggests that both H500 and H885 are thermally stable under the tested laboratory conditions.

Continuing with the thermal stability study, testing on H500 and H885 was performed in a different environment. This testing was performed with the samples exposed to air in alumina crucibles. For these runs, the same PCM samples were used as for the previous

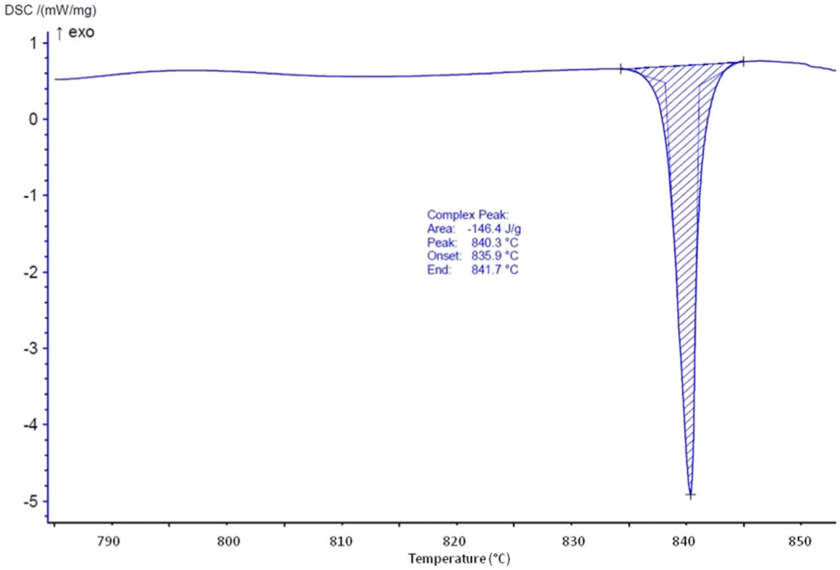

Fig. 11. DSC results for H845 molten salt PCM freeze and melt temperature profile.

thermal stability tests using argon; therefore, at the end of this experiment the samples had undergone 40 freeze/melt cycles, 20 with an argon atmosphere and 20 without. Table 10 shows the results of H500 after every fifth freeze and melt cycle for the full 40 cycles performed. The difference between the onset and end of the PCT peak (less than 10 °C in average for H500) is maintained at a nearly constant range along the cycling test, even in air atmosphere.

Table 11 summarises the thermal properties of H885 after every fifth freeze/melt cycle for the full 40 cycles. The latent heat capacity and the PCTs deviate little throughout the cycles, suggesting H885 is stable up to 950 °C and is stable even in the presence of air. Furthermore, the onset and end of the PCT peak always maintained a nearly-constant range, independently of the cycle number and the atmosphere. This value is 6.5 °C in average for H885; showing to have a fixed and well-defined phase change temperature.

According to the testing results, it can be concluded that both H885 and H500 are stable in the presence of air during their phase change processes. This suggests that the material does not decompose in the presence of air; its melting temperature also remains nearly unchanged. Comparing to studies concerning the operation of PCM at high temperatures, the previously presented tendencies and deviations reported are acceptable. There is some deviation in latent heat and phase change temperature, however this deviation follows no noticeable trend [39,40]; and it can be attributed to experimental errors and minute composition differences in samples taken. This is supported by the differences in the baseline of some of the DSCs, this baseline is not impacted by the latent heat storage of the PCM, but it can lead to differences in the calculation of the latent heat capacity of a sample.

The final testing on the PCMs involved cycling them to temperatures above their phase change temperature in order to see that they can cope with the higher temperatures that they might be exposed to in the system. H500 was cycled between 550 °C and 750 °C for 20 cycles whilst exposed to air. Samples were taken for DSC analysis following the 1st, 2nd and every 5th cycle, Table 12 shows the results of this DSC analysis. This showed no noticeable loss in performance of the PCM at this higher temperature. Although there are slight fluctuations in the latent heat capacity and peak PCT, there are no trends indicating a loss in performance, furthermore, the obtained values are very similar to the

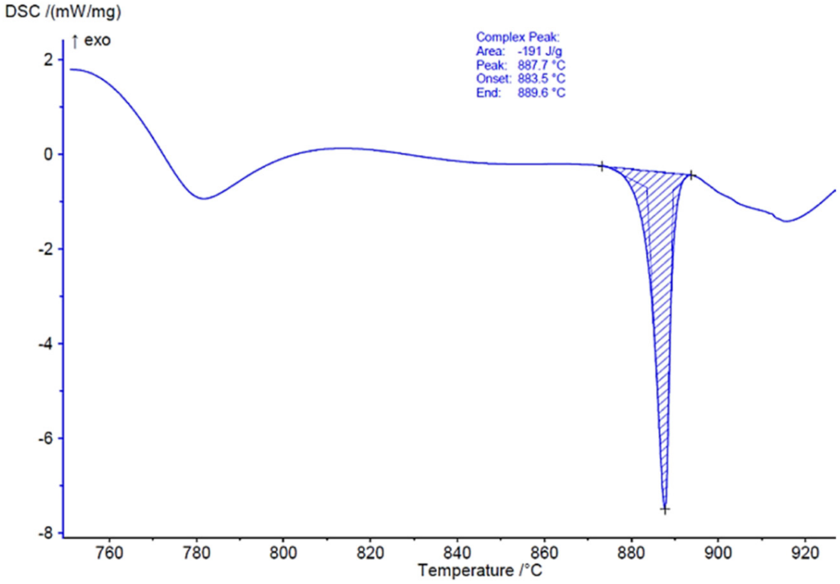

Fig. 12. DSC results for H885 molten salt PCM freeze and melt temperature profile.

Table 9
Key data obtained for both candidate PCMs for the ceramic sector.

PCM	PCT (°C)	Latent Heat (kJ/kg)	Volumetric Heat Capacity (MJ/m^3)
H845	840	146	370
H885	888	191	516

previous testing, summarised in Table 10. Thus, H500 can therefore be considered safe to use at 750 °C for long periods.

Correspondingly, H885 was cycled between 940 °C and 1050 °C, whilst exposed to air; close to the upper operating temperatures of the ceramic WHR system. As before, small samples (3 mg) were taken from the main sample for DSC analysis melt. Table 13 shows data extracted from the DSC tests that were taken at the specified intervals during the 20 cycles. There is a slight fluctuation in latent heat and PCT values for the first few cycles, however after this point the values settle around the average 212 kJ/kg. When compared to the DSC results from the cycling tests between 840 °C and 950 °C, shown in Table 11, it can be seen that there is a similar trend in terms of values fluctuating for the first few cycles before settling down. The average values shown in both tables are also very similar, suggesting there is no loss in performance following any of the high temperature freeze and melt cycles.

At the end of the twenty cycles, the H885 sample was shown to only lose 5.5% of its original weight. The sample appeared almost unchanged visually, however a small area of yellow colouration on the crucible wall was noted, this yellow colouration is likely due to the presence of elemental sulphur. The consistent performance of the material as a PCM suggested this weight loss was due to evaporation as opposed to decomposition; suggesting that H885 is stable even at 1050 °C. However, the yellow colouration on the wall of the crucibles should act as warning that the PCM is on the limit of degradation. Therefore, the PCM should ideally be kept below 950 °C if possible and it should not be directly exposed to air above 1050 °C.

4.3. MCDA matrix for decision making for the design configuration

According to the methodology explained before, the five alternative PCM-TES options are assessed by a total of thirteen decision criteria, which are divided into three main categories (operational, economic and design). During the selection of the design, the alternatives are overall evaluated considering the adequacy to the application, the flexibility of the design and the configuration adaptation to accomplish a proper technical solution in combination with the storage material. The resulting MCDA matrix (Table 14) converts the technical and

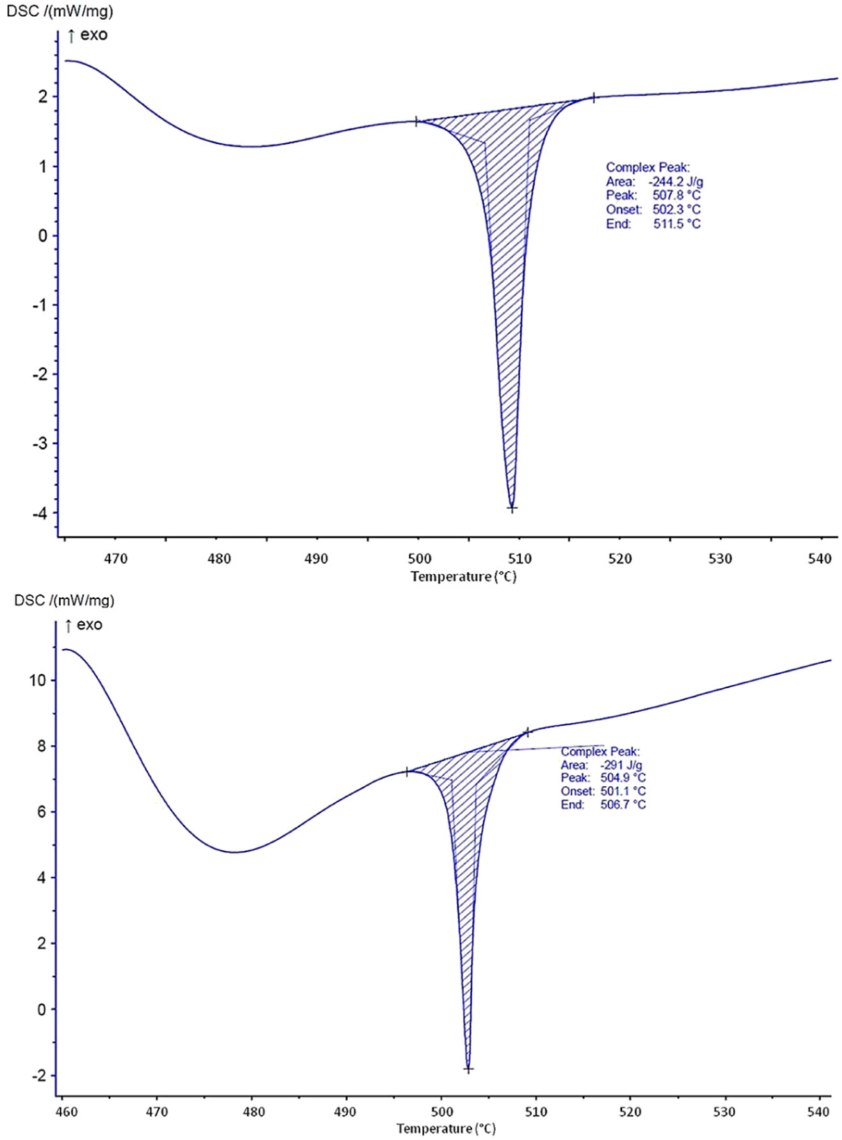

Fig. 13. H500 DSC results after one freeze/melt cycle (up) and twenty freeze/melt cycles (down).

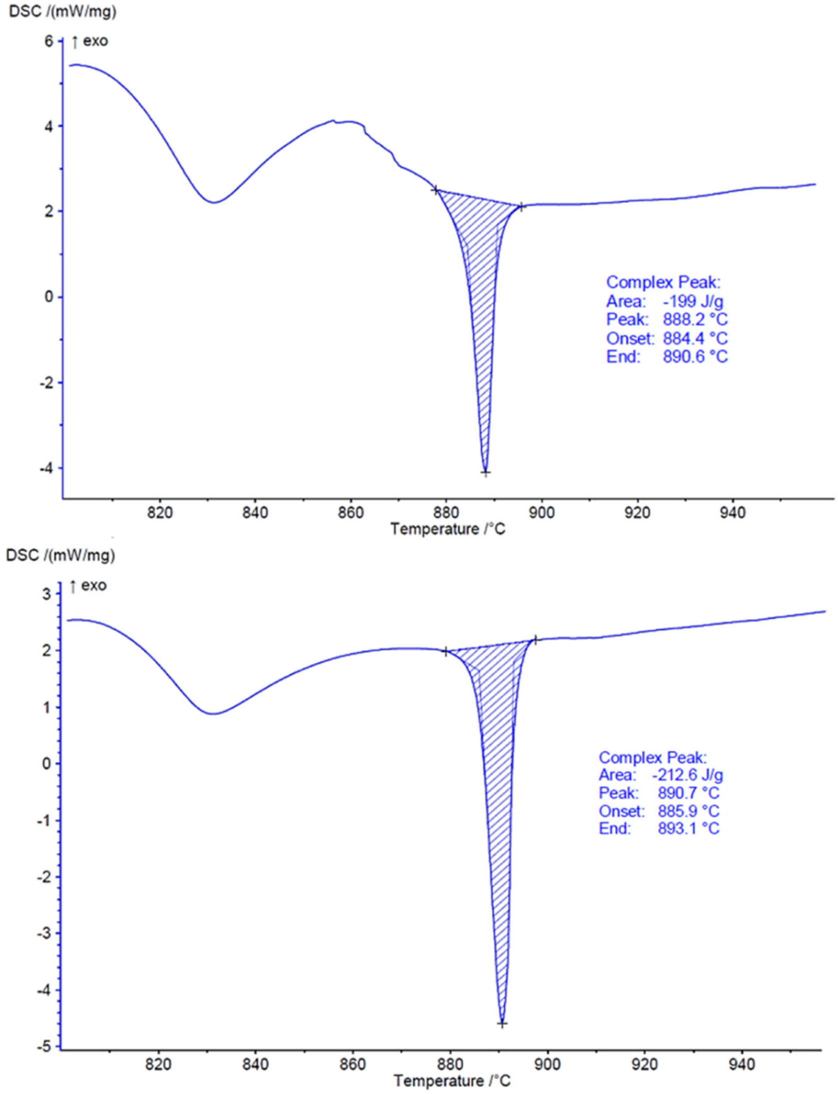

Fig. 14. H885 DSC results after one freeze/melt cycle (up) and twenty freeze/melt cycles (down).

economic performance into quantifiable values, according to the information provided by the HLEP about the conceptual design descriptions of the proposed PCM-TES solutions under study. All the gathered insights regarding the alternatives will set the basis for the evaluation and selection of the most suitable configuration solution. After the scoring, a method of multiplicative aggregation combines the RW and GW weights along with the scores for each option, considering the hierarchy at each level, resulting in an overall value. Later on, in the following section 4.4, more specific design parameters, such us the heat transference area, number of tubes, volume and cost of system among others, will be further considered in the preliminary sizing and cost analysis.

Table 10
Summary of the thermal properties of H500 after every fifth freeze/melt cycle for the full 40 cycles.

Freeze/Melt Cycles	Atmosphere	Latent Heat (kJ/kg)	Peak PCT (°C)	Onset PCT (°C)	End PCT (°C)
1	Argon	244.2	507.8	502.3	511.5
5		259.7	509	500.4	511.6
10		251.6	507	501.2	510.1
15		233.8	506.4	497.5	508.8
20		291	504.9	501.1	506.7
25 (5)	Air, without	208.5	507.5	501.6	510.1
30 (10)	Argon	234.4	510.5	505.1	514
35 (15)		234.8	514.1	505.9	518.6
40 (20)		241.8	510.3	502.2	512.7
Average	Argon	256.1	507	500.5	509.7
	Air	229.9	510.6	503.7	513.9
	Total	244.4	508.6	501.9	511.6

Table 11
Summary of the thermal properties of H885 after every fifth freeze/melt cycle for the full 40 cycles.

Freeze/Melt Cycles	Atmosphere	Latent Heat (kJ/kg)	Peak PCT (°C)	Onset PCT (°C)	End PCT (°C)
1	Argon	199	888.2	884.4	890.6
5		204.3	890.2	886.9	893.1
10		210.7	890.8	887	893.1
15		206.8	890.7	886.6	892.5
20		212.6	891.7	885.9	893.1
25 (5)	Air, without	213.4	891.6	883.1	893.9
30 (10)	Argon	211	892.2	887.3	893.5
35 (15)		228.2	893.2	889.5	893.8
40 (20)		216.6	891.9	888.9	894.5
Average	Argon	206.7	890.3	886.2	892.5
	Air	217.3	892.2	887.2	893.9
	Total	211.4	891.2	886.6	893.1

Table 12
DSC results from H500 cycling between 550 °C and 750 °C.

Cycle	Latent Heat (kJ/kg)	Peak PCT (°C)
1	246.3	509.4
2	251.9	508.2
5	239.5	510.1
10	235.7	513.6
15	241.1	511.2
20	251.8	510.4
Average	244.4	510.5

In light of the above, option 1 shows the best overall result (53.9 out of 100 points). It is compact, less expensive and presents a simple configuration. In addition, it does not present safety risks and the system could be cleaned more easily. Conversely, option 2 has been discarded (−46.9 points) mainly due to safety issues, high investment costs and the complexity of the configuration. Synthetic oil is the most used HTF but its degradation occurs about 420 °C. Other HTFs could be used such as eutectic alloys of sodium and potassium, which works at higher temperature, but they are very expensive and have safe operation issues (explosion risks). In regard to option 3, its implementation seems unfeasible (−4 points) mainly due to too high investment costs, low conductivity and inefficient performance. Moreover, it requires a large surface area to be welded and it would be difficult to clean Option 4 accounts for a positive result (19.4 points) due to the average costs, efficient thermal performance, safety and adaptability of design. However, the fact that the exhaust gas and combustion air streams have to go through the same piping makes implementation in the ceramic sector impossible due to fouling problem and dirtiness. Finally, option 5 presents the lowest overall score among the positive results (6.2 points), because it is very similar to option 3 and some of the disadvantages are the same. In conclusion, the options with a negative overall score will be discarded, while the most positive overall value will be further assessed in the design configuration and sizing calculations.

4.4. Preliminary sizing and costs of the proposed PCM-TES

Based on the above selection, preliminary sizing and material calculations are then performed for the best alternative (option 1, see Fig. 3) in order to guide decision making for its integration on each industrial application. To this end, material and energy balances of the furnace systems with the PCM solution incorporated was useful to calculate the main operating parameters, namely the mass of PCM required, the design configuration of the system and the sizing of the PCM-TES system, based on the reference Nardin, Meneghetti, Dal Magro and Benedetti [57].

The most suitable PCMs for each sector were selected based on the experimental and testing results along with the requirements reported in the system description. In short, Table 15 summaries some relevant thermo-physical and economic properties [34] of PCM H885, for ceramic sector, and H500, for steel sector.

Taking the PCM properties, shown in Table 15, into account, it is possible to determine the most relevant sizing parameters, such as PCM mass and the system volume. The volumes of the overall PCM-TES

Table 13
DSC results from H885 cycling between 940 °C and 1050 °C.

Cycle	Latent Heat (kJ/kg)	Peak PCT (°C)
1	190	890
2	234	892
5	214	891
10	204	891
15	214	891
20	220	891
Average	212.6	891

Table 14
MCDA matrix for weighting and scoring the PCM-TES system options.

PCM solution alternatives - Weighted Criteria Matrix																			
Category weighting				Option Scoring															
Cat	GW	T.Criteria	RW	Option 1	Score		Option 2	Score		Option 3	Score		Option 4	Score		Option 5	Score		
Operational	0.43	Heat transference	0.27	Efficient	1	11.7	Efficient	1	11.7	Low Efficiency	−1	−11.7	Efficient	1	11.7	Average	0	0.0	
		Safety issues	0.42	Average	0	0.0	Dangerous	−1	−18.1	Average	0	0.0	Average	0	0.0	Average	0	0.0	
		Cleaning issues	0.15	Difficult inside tubes	−1	6.4	Difficult inside tubes	−1	6.4	Difficult inside the shell	−1	−6.4	Difficult between plates	−1	−6.4	Difficult between plates	−1	−6.4	
		Streams	0.05	Crossflow	1	2.2	Counter/crossflow + HTF	0	0.0	Crossflow	1	2.2	Crossflow	1	2.2	Crossflow	1	2.2	
		Additional equipment	0.05	No need	1	2.2	Pumping, piping and HTF	−1	−2.2	No need	1	2.2	No need	1	2.2	No need	1	2.2	
		Pressure drop	0.05	May happen	−1	−2.2	May happen	−1	−2.2	–	0	0.0	–	0	0.0	–		0.0	
Economic	0.43	Investment cost	0.60	Medium	1	25.7	Too high	−1	−25.7	High	0	0.0	High	0	0.0	High	0	0.0	
		Maintenance costs	0.20	High	0	0.0	Too high	−1	−8.6	High	0	0.0	High	0	0.0	High	0	0.0	
		Novelty costs	0.20	Medium	1	8.6	Medium	1	8.6	Medium	1	8.6	Medium	1	8.6	High	0	0.0	
Design	0.14	Incorporation of fins (if possible)	0.22	Helicoidal	1	3.1	Flat and helicoidal	1	3.1	Flat	1	3.1	Flat	1	3.1	Flat	1	3.1	
		Welding	0.22	Low surface	1	3.1	Medium surface	0	0.0	Great surface	−1	−3.1	Great surface	−1	−3.1	Great surface	−1	−3.1	
		PCM tubes	0.08	Concentric double tubes	−1	−1.1	Single/Concentric double tubes	0	0.0	Single tube	1	1.1	Single tube	1	1.1	Single tube	1	1.1	
		System volume	0.49	Compact	1	7.0	Very large	−1	−7.0	Large	0	0.0	Large	0	0.0	Compact	1	7.0	
		TOTAL SCORE		Option 1	→	53.9	Option 2	→	−46.9	Option 3	→	−4.0	Option 4	→	19.4	Option 5	→	6.2	

Table 15
Main properties of the PCM required on each specific sector ranges.

Properties	H885-Ceramic Sector	H500-Steel Sector
PCT (°C)	888	509
Density (kg/m^3)	2700	2220
Latent heat capacity (kJ/kg)	191	260
Volumetric heat capacity (MJ/m^3)	516	577
Specific Heat Capacity (kJ/kgK)	0.90	1.55
Thermal conductivity (W/m·K)	0.50	0.57
Cost by capacity (€/MJ)	12	19.5

Table 16
Technical parameters needed to perform the conceptual design.

Design Parameter	Ceramic Sector	Steel Sector
Q demand (MJ/h)	220	316
Mass of PCM (kg)	1188	1606
Volume of PCM (m^3)	0.44	0.73
Volume of PCM-TES system (m^3)	13.5	15.5
Total storage capacity (MJ)	227	420
Cost of the PCM (€)	2720	8190

systems are calculated considering the design specifications detailed in the “Materials and Methods” section and based on a shell and tube configuration with the PCM encapsulated in double concentric tubes. In Table 16, the main parameters for the design configuration can be found for both PCM-TES systems for WHR in the two study cases:

Moreover, a complete analysis for the melting and solidification processes and the heat transference can be found in Royo, Acevedo, Ferreira, García-Armingol, López-Sabirón and Ferreira [41], where the thermal performance of the proposed PCM-TES design and material for the ceramic study case is shown. Those results prove, by means of computational simulations, the achievability of very high temperature levels from the recovered thermal energy.

5. Conclusions

Molten salts and metal alloys were considered to store waste heat from the EII sector, with focus on steel and ceramic industries. The waste heat recovered from flue gases exits at high temperatures (750–1100 °C), suitable PCMs with appropriate thermal characteristics around PCT of 500 °C for the steel sector and 850 °C for the ceramic sector. The main challenge was to identify a PCM that would be both technically acceptable and economically viable at these temperatures.

In the case of the ceramic industry, testing on H885 presented a higher latent heat (191 kJ/kg) and has the most desirable PCT (888 °C) for the application. The stability tests revealed that the material is stable and does not show a loss of performance when both sealed and when exposed to the air atmosphere at temperatures below 950 °C. However, early signs of thermal degradation were observed when the material was heated to 1050 °C, so it is recommendable not to expose the PCM directly exceed over that level. For the steel industry, H500 PCM was considered the most suitable PCM since testing revealed to have an appropriated PCT to be used in this sector, this PCM was also shown to be safe at temperatures up to 750 °C. Aside from molten salt PCM options, the aluminium alloys (M550) might be considered as a possible metal PCM option when fully commercially available.

A full summary of the PCM data including experimentally obtained in this study and other relevant thermo-physical properties measured during the PCM characterisation by the developers is given in Table 17, regarding both EII sectors analysed in the study cases.

PCM-TES proposals were evaluated by means of a MCDA matrix. The most promising options to be integrated in the study cases are namely: a shell and double concentric tubes PCM-TES (option 1) which would be suitable for both sectors. Interchangeable crossflow TES with PCM-filled single tubes (option 4) is more suitable for metal sectors, where the exhaust gases do not present so much degree of fouling. As a result, preliminary sizing, costs and conceptual design configuration were presented as an example of integration at industrial scale. For the ceramic sector, a PCM-TES system with a storage capacity of 227 MJ would involve 13.5 m^3 of volume and 1188 kg of H885 PCM. For the steel sector, a total of 1606 kg of H500 PCM and a volume of 15.5 m^3 would be required to store 420 MJ. The resulting conceptual design and material selection offer the opportunity to adapt the PCM-TES integration to increase the combustion air temperature, which would allow for the reduction of fossil fuels in EIIs and make for a more energy and resource efficient process. Overall, the complete methodology that addresses technical and engineering aspects provides a design is fully adapted to the operating framework of the EII sector.

CRediT authorship contribution statement

Patricia Royo: Methodology, Investigation, Writing - original draft, Validation, Writing - review & editing. **Victor J. Ferreira:** Writing - original draft, Validation, Writing - review & editing. **Zafer Ure:** Validation, Writing - review & editing. **Sam Gledhill:** Writing - original draft, Validation, Writing - review & editing. **Ana M. López-Sabirón:** Methodology, Investigation, Validation, Writing - review & editing. **Germán Ferreira:** Methodology, Investigation, Validation, Writing - review & editing.

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List of abbreviations

AHP	Analytical Hierarchy Process
A	Heat exchange area
c_p	Specific heat
DSC	Differential Scanning Calorimeter machine
GW	General Weight
HLEP	High Level Expert Panel
HTF	Heat Transfer Fluid
HX	Heat eXchanger
LHS	Latent Heat Storage
MCDA	Multiple Criteria Decision Analysis
$m_{comb.air}$	Combustion air flow
PCM	Phase Change Material
PCT	Phase Change Temperature
Q	Heat demand

Table 17
Summary of relevant thermo-physical properties for both PCMs, H500 and H885, selected as core storage material for the PCM-TES integrated in steel and ceramic sector, respectively.

PCM	PCT (°C)	Density (kg/m^3)	Latent Heat (kJ/kg)	Volumetric Heat Capacity (MJ/m^3)	Specific Heat Capacity (kJ/kg·K)	Thermal Conductivity (W/m·K)	Maximum Operating Temperature (°C)
H500	509	2220	260	577	1.55	0.57	750
H885	888	2700	191	516	0.90	0.50	1050

Q_{PCM}	thermal energy transferred by the PCM-TES system
RW	Relative Weight
TES	Thermal Energy Storage
U	Global heat transfer coefficient
WHR	Waste Heat Recovery
$\Delta T_{comb.air}$	Temperature increase in the combustion air
$\Delta T_{HTF\text{-}PCM}$	Temperature gradient between HTF and PCM melting temperature

Declarations of interest

None.

Data availability statement

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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