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A Multi-Criteria decision making (MCDM) methodology for high temperature thermochemical storage material selection using graph theory and matrix approach

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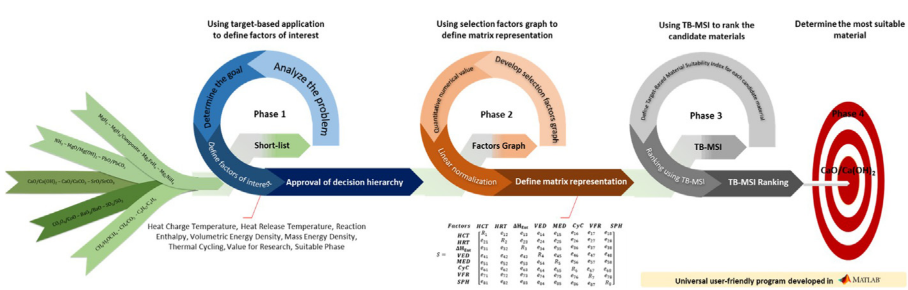
HIGHLIGHTS

- The application of a MCDM methodology based on Graph Theory and Matrix approach leads to selection of Cao/Ca$(OH)_2$ for high temperature thermochemical storage.
- Target based, universal and user-friendly MATLAB program based on MCDM methodology allows the simple selection of candidate materials.
- The MCDM tool is tested against a real-life situation, namely the capture of waste heat from Tata Steel UK Port Talbot steelworks.
- Practicality of proposed MCDM method is validated with selection of a suitable heat storage material for low-medium temperature application.
- Proposed method can be applied to other scenarios such as heat storage from high and low temperature coupled with solar thermal generators.

GRAPHICAL ABSTRACT



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ABSTRACT

Industrial waste heat is currently underutilized due to the techno-economic challenges, inherent variability and intermittency of this source. To overcome the existing barriers, reduce the emission of greenhouse gases and protect the global environmental conditions, energy recovery is one of the most effective strategies. In the design of heat storage systems, the material selection procedure plays an important role and requires complex interrelationships between the various factors and parameters to be elucidated toachieve the best candidate material for a given application. This paper presents a Multi-Criteria Decision Making (MCDM) methodology based on Graph Theory and Matrix approach for high temperature thermochemical storage (TCS) material selection. Furthermore, the presented approach has been used to select the suitable candidate material for recovering the high temperature waste heat (over 500 °C) in Port Talbot Steelworks.

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Graph Theory
Matrix Approach

1. Introduction

The application of MCDM methodologies is increasing to reduce the number of improper choices during the material selection procedure and to provide a systematic, logical, and repeatable approach for different applications. In general, the selection of suitable materials is based on user preference for a target operation and consists of a series of essential steps including ranking and choosing [1–3].

Liao [4] developed and proposed a fuzzy multicriteria decision-making method to support material selection decisions in engineering design applications based on trapezoidal fuzzy numbers and this requires much more computation when compared with a simple scoring method. Farag [5] studied a material selection tool including value engineering (VE), a technique for order preference by similarity to ideal solution (TOPSIS) and Cambridge material selector methods. Holloway [6], studied the environmental impact of improper material selection in mechanical design. This study showed that, the mechanical design for optimal environmental impact can be defined through the generation of material selection charts, along the lines of Ashby's method [7]. Ashby [8] presented a simple multi-objective method based on value functions (utility functions) in materials selection and design. Shanian and Savadogo [9] reported a new approach by criteria sensitivity analysis and producing a material selection decision matrix through the use of the ELimination and Choice Expressing the REality (ELECTRE) models. Dehghan-Manshadi et al. [10] studied a novel numerical method based on the weighting factor approach whilst also combining non-linear normalization with a modified digital logic method. Hambali et al. [11] presented analytical hierarchy process (AHP) for material selection procedure. Rao and Patel [12] introduced a novel multiple attribute decision making method for material selection by considering the subjective preferences of the decision maker and objective weights of the different attributes using fuzzy logic. In another study, Rao and Padmanabhan [1] proposed a methodology for the selection of a rapid prototyping process through evaluation and ranking of multiple viable rapid prototyping processes for manufacture of a given product. Karande et al. [13] introduced utility concept and desirability function approaches to material selection problems. The proposed methods are conceptually simple and strong mathematical techniques. Peças et al. [14] reviewed the existing methods for selecting materials and proposed a new comprehensive approach for informed life cycle-based materials selection. Jahan and Edwards [15] presented a novel VIKOR method by considering cost criteria for material selection problems based on interval numbers applied to three practical examples of materials selection. Peng and Xiao [16] studied preference ranking organization method for enrichment evaluations (PROMETHEE) combined with an analytic network process (ANP) to select the best material for a given application. Liu [17] proposed a new hybrid multiple criteria decision-making model for material selection with target-based criteria. In this study, DEMATEL-based ANP is employed to determine the degrees of influence among criteria and modified VIKOR is utilized for calculating the compromise ranking of alternatives. Sakthivel et al. [18] introduced a hybrid multi-criteria decision modelling approach integrated with analytical network process based on TOPSIS and VIKOR analysis for the selection of an optimum fuel mixture. Moreover, several real-world issues in field of chemistry have been addressed recently with the help of graph theory. In this field, graph theory allows scientists to focus on the physiochemical aspects of the molecular graph and provides a visual representation of chemical compounds [19–22].

In recent years, there has been a considerable amount of research on material selection procedure and the aforementioned studies provide useful methods and tools for this purpose [23,24]. However, most of them are unable to guide users in taking a proper decision in a simple, logical, and systematic scientific method. Most of the existing methods are still far from an ideal easy-to-use yet scientific tool. In addition, few studies have been conducted on decision making methodologies for material selection with focus on thermal energy storage materials. Loganathan and Mani [3], proposed a fuzzy based hybrid MCDM methodology combined with TOPSIS, VIKOR and PROMETHEE methods for phase change material (PCM) selection in an electronics cooling system and applied the model in the numerical example as well. Gaddala and Devanuri introduced a hybrid decision-making method for the selection of a PCM for low temperature thermal energy storage. The AHP method for measuring the subjective weights of the attributes and the TOPSIS method for ranking the candidate materials have been proposed by the researchers [25]. Baumann et al. [26] reviewed existing MCDM studies on energy storage systems and reported that most of the studies in this field have a limited orientation towards practical decision making and that a clear definition of the targeted application is missing. Another important output of this review refers to the lack of insight regarding the impact of proposed methods on relevant stakeholders and decision makers.

Therefore, there is a need for a comprehensive, easy-to-use and target-related MCDM methodology for heat storage applications. To help fill the gaps, this study proposes universal user-friendly MATLAB program based on MCDM methodology for thermochemical storage material selection using graph theory and matrix approach. In this study, the impact of the proposed method has been evaluated through identifying the target waste heat recovery unit at Tata Steel Port Talbot Steelworks and selection of the most appropriate material for medium to high temperature heat storage based on real requirements and user preferences.

As a systematic and logical approach, graph theory deals with the connection between points (vertices/nodes) by edges/lines [2,27]. Graph theory is the analysis of objects (called graphs), defined by a set of vertices, each pair of which is allocated with an incidence relation represented by an edge. Graph theory has provided a particularly powerful and useful way of analyzing and modelling different systems and their associated problems in various scientific and technological fields [2,28,29]. In addition, to analyze the obtained graph models in a quick and efficient way the matrix approach is beneficial [1]. Therefore, graph theory and matrix approach are used in this paper for decision making and material selection for high temperature heat storage applications.

High temperature heat storage can be achieved by utilising various materials and several heat storage techniques [30]. The performance and application of any heat storage system depends upon several design parameters including, but not limited to, material, ambient psychrometric conditions, process, and reactor design [31]. In material selection procedure for heat storage, various key factors and criteria should be considered based on user preference, engineering design parameters and the final application.

2. Proposed Multi-Criteria decision making (MCDM) methodology for material selection

The proposed MCDM methodology consists of two fundamental stages prior to the selection procedure in MATLAB program: (1) define the material selection factors graph based on the favorable application-based criteria; (2) define the matrix representation of the material selection factors graph for each candidate material.

2.1. Target based identification of material selection factors graph

Tata Steel's Port Talbot integrated iron and steel works is located in South Wales (UK) and is capable of producing nearly 5 million tons of steel slab per annum[32]. This site has been previously reported to produce 15 % of Wales carbon emissions [33]. CO_2 emissions at this site totalled 6.1 Mt in 2020, based on a report made by EU Emissions Trading System (ETS) and 6.9 Mt in 2019 based on a report made by Worldsteel scope[32]. A Port Talbot exergy mapping and waste heat recovery opportunities report produced in 2010 showed that the sum of heat losses from sinter product in the sinter plant reaches 632.7 GWh/year (around 6.2 % of total heat loss in Port Talbot site) based on a discharge temperature of 650 °C and a sinter cooler discharge temperature of 550 °C. The respective exergy to available total waste heat ratio in the sinter plant (waste heat temperature source of 500–600 °C) is around 47 % (295 GWh/year), while this ratio for waste heat sources under 50 °C, 100–200 °C and 200–300 °C are 4 %, 24 % and 25 %, respectively [34]. The Port Talbot exergy mapping and waste heat recovery opportunities report data is used to illustrate energy flow by Sankey diagrams to identify potential areas of energy savings and waste heat recovery. 8 key processes (sectors) that take place in Tata Steel's Port Talbot were grouped under 9 ranges of temperature. A schematic of energy flows at different temperature level and related exergy ratio of each range is shown in Fig. 1.

The application of heat storage with waste heat or renewable energy sources can reduce greenhouse gas (GHG) emissions (specifically CO_2 emissions) and consequently the demand from primary energy generation via fossil-fuels [35]. Therefore, to reduce CO_2 emissions by storing waste heat based on a maximised available specific heat capacity at the specified temperatures (exergy ratio), the target waste heat recovery area (of the sinter plant) in Port Talbot Steelworks has been identified. In next step, the related material selection criteria and factors of interest have been considered. To be eligible as candidates, and to be compatible with high temperature waste heat recovery unit, the candidate materials must fit a set of criteria such as; high heat charge temperature, high enthalpy of reaction, high energy density, high reversibility of the reaction and the multi-cycle stability. Based on this, eight targeted material selection factors are considered in this paper. Table 1 shows the material selection factors of interest for a high temperature heat storage material that will for recover the high temperature waste heat (over 500 °C) in Port Talbot Steelworks. Factors of interest and type of attributes will be explained in section 4.1 and 3.3, respectively.

In order to model the material selection factors and their interrelationship, the material selection graph utilised is based on a set of nodes and a set of directed edges. The nodes and set of directed edges are defined as $N=\{n_i\}$, with $i = 1, 2, \ldots, N$ and $E=\{e_{ij}\}$, respectively. A factor that influences the selection of a material for a given application is called the material selection factor (MSF) [2]. Therefore, the number of MSFs is equal to the number of nodes (N) where the n_i is defined as a i-th material selection factor. In selection factors graph, the relative importance among the factors is defined by edges of the graph. If one of the material selection factors (node i) has relative importance over another material selection factor (node j), then the arrow (directed edge of e_{ij}) is drawn from node i to node j and when node j has relative importance over node i, the arrow (directed edge of e_{ji}) is drawn from node j to node i. Fig. 2 shows the target based material selection factors graph with nodes 1–8 presented in Table 1. To have quick visual analysis of the selection factors and their relative importance, the material selection factors graph is useful and can be represented in matrix

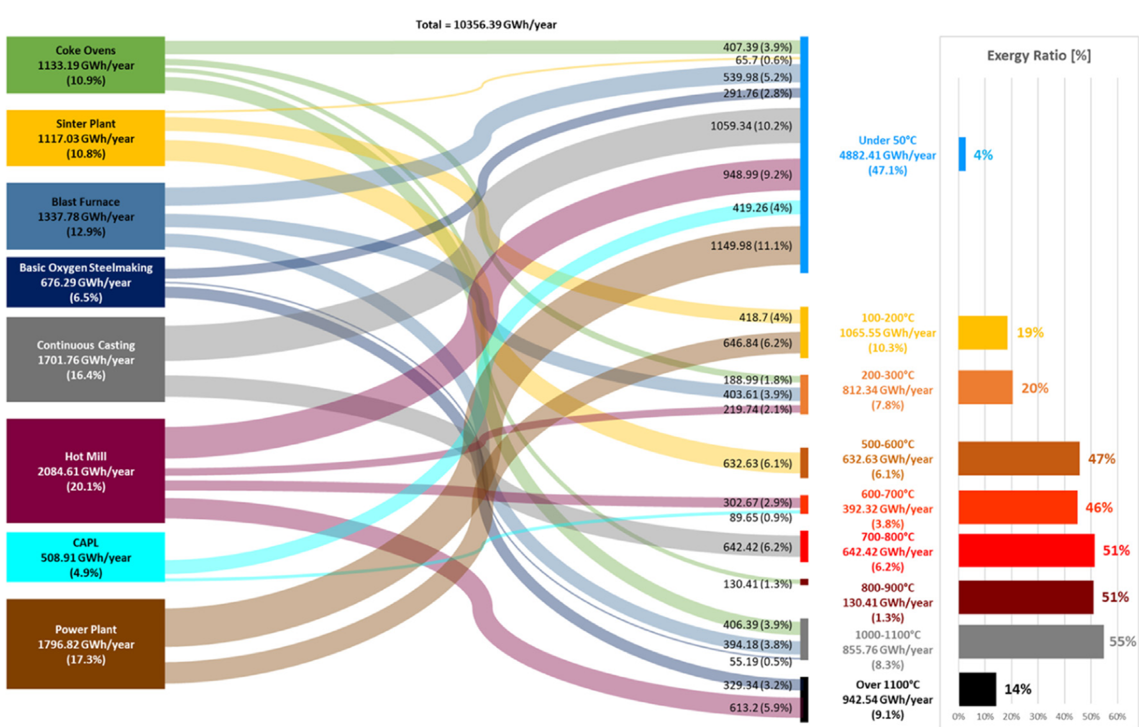

Fig. 1. Sankey diagrams of energy flows in Tata Steel's Port Talbot.

Table 1
Target based factors of interest for high temperature heat storage material.

Factor of interest	Abbreviations	Type of attributes	Number of Node
Heat Charge Temperature	HCT	Non-Beneficial	1
Heat Release Temperature	HRT	Beneficial	2
Reaction Enthalpy	ΔH_{Ent}	Beneficial	3
Volumetric Energy Density	VED	Beneficial	4
Mass Energy Density	MED	Beneficial	5
Thermal Cycling (Reversibility)	CyC	Beneficial	6
Value for Research	VFR	Beneficial	7
Suitable Phase	SPH	Beneficial	8

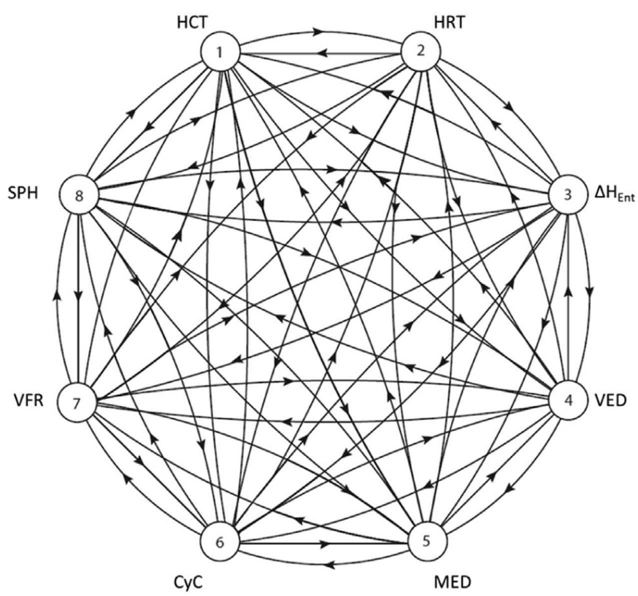

Fig. 2. Octagonal material selection factors graph for high temperature heat storage material.

form as well (see section 3.2). Relative importance between these 8 nodes (selection factors) can be represented by the connection between individual nodes and their direction. For instance, heat charge temperature (HCT) is equally important as heat release temperature (HRT) and therefore the relative importance exists between these two factors in both directions. Even though HCT is more important over the factor of value for research (VFR), the relative importance exists between HCT and VFR in both directions as well. The relative importance between two attributes (e_{ij} *and* e_{ji}) can be described based on a fuzzy conversion scale and will be explained in section 3.3.

2.2. Identification of matrix representation of the material selection factors graph

Matrix representation of the octagonal material selection factors graph is a square (N × N) matrix and can consider the normalized values of all 8 factors (R_i) and the relative importance between attributes (e_{ij} and e_{ji}). In this study, 18 different materials have been considered in the selection procedure and therefore for each single material there is a matrix representation called *S* for the octagonal material selection factor graph shown in Fig. 2. The matrix S, defined by formula (1).

$$S = \begin{array}{c} \textbf{Factors} \\ \textbf{HCT} \\ \textbf{HRT} \\ \Delta\mathbf{H_{Ent}} \\ \textbf{VED} \\ \textbf{MED} \\ \textbf{CyC} \\ \textbf{VFR} \\ \textbf{SPH} \end{array} \begin{array}{c} \begin{array}{cccccccc} \textbf{HCT} & \textbf{HRT} & \Delta\mathbf{H_{Ent}} & \textbf{VED} & \textbf{MED} & \textbf{CyC} & \textbf{VFR} & \textbf{SPH} \end{array} \\ \begin{bmatrix} R_1 & e_{12} & e_{13} & e_{14} & e_{15} & e_{16} & e_{17} & e_{18} \\ e_{21} & R_2 & e_{23} & e_{24} & e_{25} & e_{26} & e_{27} & e_{28} \\ e_{31} & e_{32} & R_3 & e_{34} & e_{35} & e_{36} & e_{37} & e_{38} \\ e_{41} & e_{42} & e_{43} & R_4 & e_{45} & e_{46} & e_{47} & e_{48} \\ e_{51} & e_{52} & e_{53} & e_{54} & R_5 & e_{56} & e_{57} & e_{58} \\ e_{61} & e_{62} & e_{63} & e_{64} & e_{65} & R_6 & e_{67} & e_{68} \\ e_{71} & e_{72} & e_{73} & e_{74} & e_{75} & e_{76} & R_7 & e_{78} \\ e_{81} & e_{82} & e_{83} & e_{84} & e_{85} & e_{86} & e_{87} & R_8 \end{bmatrix} \end{array} \tag{1}$$

Where e_{ij} is the relative importance of the *i*-th factor over *j*-th factor and R_i is the normalized value of the *i*-th factor represented by node n_i. The material selection factors function is defined by the permanent of the matrix *S*, called *Per(S)*, which can be obtained with equation (2).

$$Per(S) = \sum_{\sigma} a_{1\sigma(1)} a_{2\sigma(2)}, \cdots, a_{m\sigma(m)} \tag{2}$$

The sequence $a_{1\sigma(1)},\ldots,a_{m\sigma(m)}$ is called a diagonal of S and the product $a_{1\sigma(1)}\ldots a_{m\sigma(m)}$ is the diagonal product of S. Therefore, the sum of all diagonal products of S is called permanent of S [36]. Matrix permanents were first introduced in early 19th-century and are similar to the determinant of a matrix. The number of perfect matching in a bipartite graph can be described by the permanent and it has been used in combinatorial mathematics and in many other applications such as material selection factors. In permanents, all signs are taken as a positive and the sign of the permutations are not considered unlike the determinant of a matrix. The determinant is much easier to compute than the permanent since that, the permanent cannot be computed by using Gaussian elimination unlike determinant which can be computed in polynomial time by using Gaussian elimination. The permanent of matrices can be computed by the Ryser formula presented in equation (3) [2,36,37]. *Per(S)* can be calculated by using equation (2). An expanded version of this equation for matrix S is given in equation (3):

$$\begin{aligned} Per(S) = {} & \prod_{i=1}^{N} R_i + \sum_{i,j,\cdots,N} (e_{ij}e_{ji}) R_k R_l \cdots R_N \\ & + \sum_{i,j,\cdots,N} (e_{ij}e_{jk}e_{ki} + e_{ik}e_{kj}e_{ji}) R_l R_n \cdots R_N \\ & + \Big\{ \sum_{i,j,\cdots,N} (e_{ij}e_{ji})(e_{kl}e_{lk}) R_n R_m \cdots R_N \\ & + \sum_{i,j,\cdots,N} (e_{ij}e_{jk}e_{kl}e_{li} + e_{il}e_{lk}e_{kj}e_{ji}) R_n R_m \cdots R_N \Big\} \\ & + \Big[\sum_{i,j,\cdots,N} (e_{ij}e_{ji})(e_{kl}e_{ln}e_{nk} + e_{kn}e_{nl}e_{lk}) R_m R_o \cdots R_N \\ & + \sum_{i,j,\cdots,N} (e_{ij}e_{jk}e_{kl}e_{ln}e_{ni} + e_{in}e_{nl}e_{lk}e_{kj}e_{ji}) R_m R_o \cdots R_N \Big] + \cdots \end{aligned} \tag{3}$$

A universal user-friendly MATLAB program has been developed in order to calculate the value of the permanent of matrix S (*Per(S)*) for each candidate material based on 8 factors (R_i) and the relative importance between those attributes.

2.3. Target based material suitability index

The *Per(S)* function for each material is called the material selection factors function and the numerical value of this function is defined as a target-based material suitability index (TB-MSI). TB-MSI is a measure of extent or degree by which a high temperature heat storage material can be selected for a specific target (application). Evaluation of TB-MSI for each candidate material is based on a numerical value of the material selection factors (R_1-R_8, i.e., numerical value of heat charge temperature, heat release temperature, reaction enthalpy, volumetric energy density, mass energy density, thermal cycling, value for research, suitable phase) and their relative importance (e_{ij} and e_{ji}). The value of the material selection factors could be obtained from available quantitative data (heat charge temperature, heat release temperature, reaction enthalpy, volumetric energy density, mass energy density, thermal cycling) or estimated data adopted by a fuzzy conversion scale (value for research, suitable phase).

The available quantitative numerical value of the material selection factors is on different scales. In such cases, normalization of ratings (assigned normalized value of a factor) has been used in order to obtain a notionally common scale and enable the comparison between them.

Factors of interest (material selection factors) can be categorized into two attributes: beneficial and non-beneficial. Beneficial attributes are those attributes whose higher values are desirable, while non-beneficial criteria determine the lowest value as the desirable value [38]. Table 1 shows the type of the attributes for target-based factors of interest. The normalized value of factors (R) can be computed by linear normalization method (equation (4) and (5) for beneficial and non-beneficial attributes, respectively).

$$R_i = \frac{X_i}{Max(X_j)} \tag{4}$$

$$R_i = \frac{Min(X_j)}{X_i} \tag{5}$$

Within these equations X_i is the actual measure of the factor for the i-th alternative (candidate material), $Max(X_j)$ is the actual value of the factor for the j-th material which is having highest measure of the factor among the considered materials and $Min(X_j)$ is the actual value of the factor for the j-th material which is having lowest measure of the factor among the considered materials (e.g. if actual measure of the factor for the i-th alternative is the highest measure of the factor among the considered materials in this case the normalized value of factor is equal to 1).

A ranked value judgment on a fuzzy conversion scale has been adopted, allowing for quantitative data (e.g., value for research) that is not available or applicable. In this method, the value of the material selection factors (R_i) can be defined based on linguistic terms and then converted to related fuzzy numbers and eventually into a crisp score. In this paper, an eleven-point fuzzy scale is used for evaluation criteria scores for alternatives and the procedure proposed by Chen and Hwang [39] is used to convert fuzzy numbers (linguistic evaluations) into crisp scores. Fig. 3 shows the crisp scores conversion for qualitative (non-quantitative) alternatives to eleven-point scale linguistic terms (M_i). Similarly to quantitative alternatives, normalization of ratings has been used for qualitative alternatives based on an assigned value (fuzzy number conversation and related crisp score).

As with assigning the value on a fuzzy conversion scale to the qualitative attribute, the relative importance between attributes (e_{ij} and e_{ji}) can be described based on an eleven-point fuzzy scale and the value of e_{ij} can be obtained from decision makers. For the given high temperature heat storage material selection, the relative importance has been proposed to compare the relation between an attribute (i) with another attribute (j). In order to express and decide on the relative importance between target-based factors of interest for high temperature heat storage material, the procedure proposed by Chen and Hwang [39] is used as shown in Table 2. In this study the e_{ij} and e_{ji} are interrelated (inter influence of the criteria are equal) and therefore e_{ji} = 1-e_{ij}.

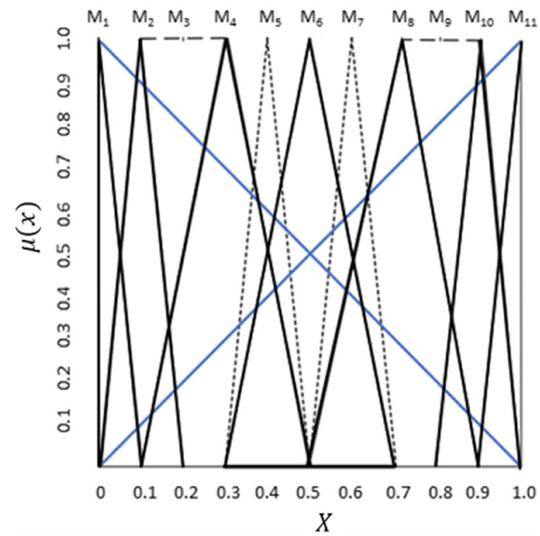

Fig. 3. Crisp scores conversion for qualitative (non-quantitative) alternatives to eleven-point scale linguistic terms (M_i) [39].

Table 2
Relative importance between target-based factors of interest for high temperature heat storage material (11-point scale).

Class definition	Relative importance	
	r_{ij}	r_{ji} = 1-r_{ij}
One attribute is exceptionally less important over the other	0.045	0.955
One attribute is extremely less important over the other	0.135	0.865
One attribute is very less important over the other	0.255	0.745
One attribute is less important over the other	0.335	0.665
One attribute is slightly less important over the other	0.410	0.590
Two attributes are equally important over the other	0.500	0.500
One attribute is slightly more important over the other	0.590	0.410
One attribute is more important over the other	0.665	0.335
One attribute is highly important over the other	0.745	0.255
One attribute is extremely more important over the other	0.865	0.135
One attribute is exceptionally more important over the other	0.955	0.045

3. High temperature heat storage material selection based on MCDM methodology

The proposed methodology to select most suitable material among the candidates consists of four basic phases: (1) Using target-based application to define factors of interest; (2) Using selection factors graph to define matrix representation; (3) Using TB-MSI to rank the candidate materials and (4) Determine the most suitable material. The process of MCDM methodology is schematically shown and described in Fig. 4.

3.1. Phase 1

The given target application is defined by analysis of the problem and subsequent determination of solution(s) in the first phase of MCDM methodology. As explained in section 3.1, the generation of high CO_2 emissions in Port Talbot Steelworks is the targeted problem and this is to be addressed via waste heat recovery in the sinter plant (waste heat temperature source of 500–600 °C) The targeted application will provide the anticipated reduction of CO_2 emissions by storing and reusing waste heat on site, consequently reducing primary energy consumption. The first three

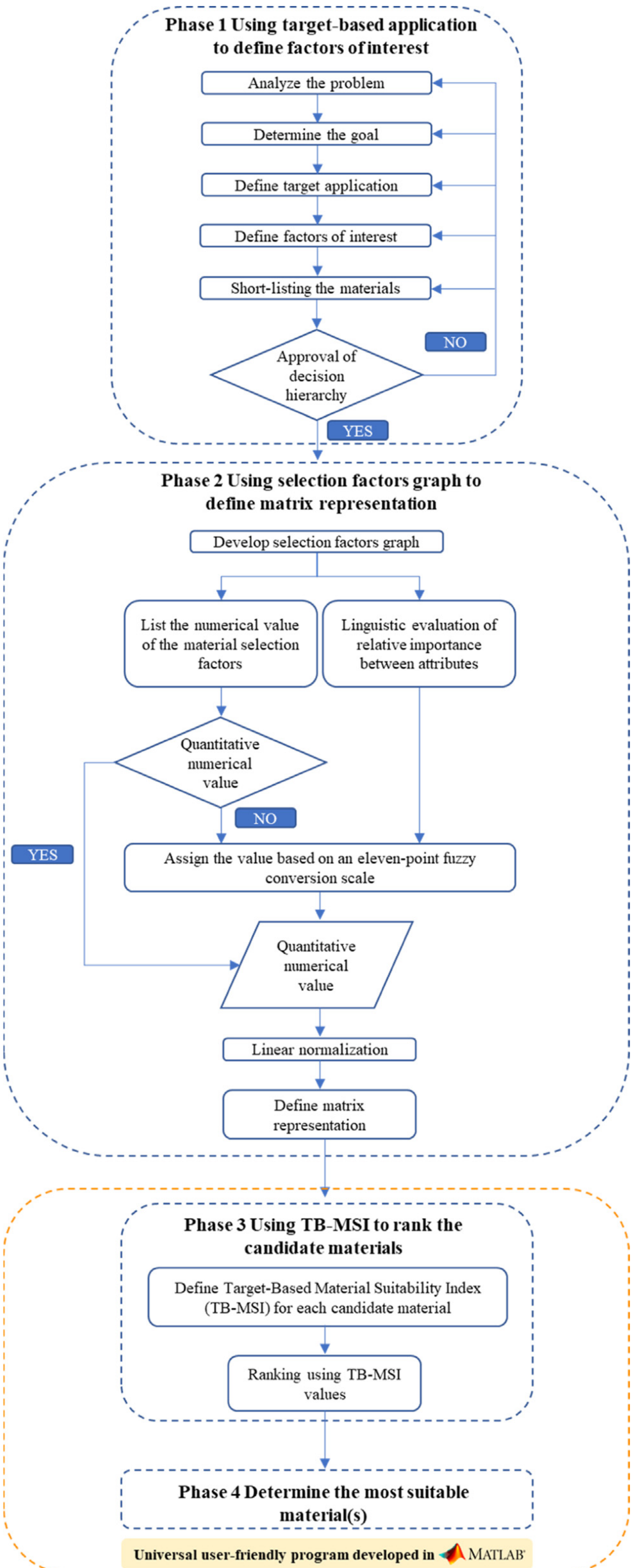

Fig. 4. Flowchart of the proposed MCDM methodology for high temperature heat storage material selection.

steps of phase one are followed by the factors of interest identification based on user quantitative or qualitative evaluation for limiting the acceptance value or threshold value for a given target application. The material selection factors of interest for high temperature heat storage materials recovering waste heat (over 500 °C) in Port Talbot Steelworks are listed in Table 1. Within this application, high heat release temperature, reaction enthalpy, energy density, and reversibility are favorable. The heat charge temperature is considered as a non-beneficial factor in this study. In addition, solid–gas reaction is more favorable than liquid–gas and gas reactions due to its easier reaction control. Finally, value for research is defined based on an in-depth literature review covering available heat storage materials and their potential for high temperature applications. In the final step of phase one, 18 sets of materials based on previous criteria have been considered (Table 3). The aforementioned review of the various candidate materials that are applicable for high temperature heat storage concluded that the main targeted materials should be; 1. hydride systems (metal hydride and ammonia systems), 2. metal oxide systems (hydroxide, carbonate and redox systems), 3. Organic systems (methane reforming, cyclohexane dehydrogenation and thermal dissociation of sulfur trioxide) and 4. metal sulfate systems [30,40–42].

3.2. Phase 2

Based on the obtained information in phase one (selection factors and their relative importance), a target-based material selection factors graph is developed with nodes 1–8 presented in Table 1. The number of nodes is equal to the number of selection factors and the edges and their directions are determined from relative importance between the factors as shown in Fig. 2. The quantitative values of the material selection factors (factors of interest) for 18 alternative materials are given in Table 3, and are subsequently required to be normalized. Among the quantitative values *HRT*, ΔH_{Ent}, *VED* and *MED* are considered to be beneficial factors and *HCT* is considered a non-beneficial factor. The values of these five quantitative factors are normalized, as described in section 3.3, and given in Table 4. *VED* is defined as the increase in the air sensible heat and is calculated from the difference in temperature between the inlet and outlet air to the thermochemical system. *MED* is defined based on the mass of water lost from the sample and enthalpy of the reaction in the mass of the sample [43]. In this study *CyC*, *VFR* and *SPH* are considered as qualitative beneficial values and their assigned values based on an eleven-point fuzzy scale conversion and are normalized utilising equation (4) and (5) and are presented in Table 4.

In order to define the matrix representation of the material selection factors graph, the relative importance of factors (e_{ij} and e_{ji}) is also assigned as described in section 3.3. In this paper, based on the targeted application, *HCT*, *HRT* and ΔH_{Ent} are equally important over each other ($e_{12} = e_{21} = e_{31} = e_{13} = e_{32} = e_{23} = 0.5$). *VED*, *MED* and *SPH* are slightly more important over *HCT* and *HRT* ($e_{41} = e_{42} = e_{51} = e_{52} = e_{81} = e_{82} = 0.59$) and because the inter-influence of the criteria are equal. *HCT* and *HRT* are slightly less important over *VED*, *MED* and *SPH* ($e_{14} = e_{24} = e_{15} = e_{25} = e_{18} = e_{28} = 0.41$). *VFR* is less important over *HCT*, *HRT* and ΔH_{Ent} ($e_{71} = e_{72} = e_{73} = 0.335$) and slightly less important over *VED*, *MED* and *SPH* ($e_{74} = e_{75} = e_{78} = 0.41$). Other relative importance values are assigned similarly based on the targeted application and are shown in (6) as a MCDM matrix representative for high temperature heat storage material selection. For other purposes and alternative end user requirements (defined by decision maker depending on target application) the assigned relative importance values could be different from this paper. In the matrix representative shown in (6), normalized material selection factors (R1-R8, i.e., numerical value of heat charge temperature, heat release temperature, reaction enthalpy, volumetric energy density, mass energy density, thermal cycling, value for research, suitable phase) are different for each material and can be replaced by values reported in in Table 4.

Table 3
Quantitative data of material selection factors for candidate materials.

Material		Factors of interest (Material Selection Factors) - Quantitative Factors				
		HCT	HRT	ΔH_{Ent}	VED	MED
		[°C]	[°C]	[kJ/mol]	[kWh/m^3]	[kWh/kg]
1	MgH_2 [41,42]	380	230	75	580	0.80
2	MgH_2/Composite [41,44,45]	380	230	60	580	0.80
3	Mg_2FeH_6 [30,42]	590	510	77	650	0.54
4	Mg_2NiH_4 [30]	330	220	62	295	0.25
5	NH_3[41,42]	450	450	66.9	745	1.09
6	$MgO/Mg(OH)_2$ [30,40–42]	150	100	81	380	0.39
7	$CaO/Ca(OH)_2$ [41,42]	450	400	104	437	0.39
8	$CaO/Ca(OH)_2$/Inner Material [46–48]	450	400	104	693	0.49
9	$CaO/CaCO_3$ [30,40–42]	1000	700	178	437	0.39
10	$CaO/CaCO_3$/Inner Material [41,49–51]	860	880	178	692	0.49
11	$PbO/PbCO_3$ [30,40–42]	450	300	88	303	0.09
12	$SrO/SrCO_3$ [40]	1100	1000	125	390	0.39
13	Co_3O_4/CoO [40–42]	850	700	205	295	0.24
14	BaO_2/BaO [40,42]	1027	400	77	328	0.13
15	CH_4/H_2OCH_4 [41,42]	950	530	250	7.8	4.34
16	CH_4/CO_2 [41,42]	950	530	247	7.7	4.28
17	C_6H_{12}/C_6H_6 [42]	317	397	206	530	0.68
18	SO_3/SO_2 [42,52]	800	500	98	646	0.34

Table 4
Normalized data of material selection factors for candidate materials.

Material		Normalized Value of factors of interest (Material Selection Factors)							
		HCT	HRT	ΔH_{Ent}	VED	MED	CyC	VFR	SPH
1	MgH_2	0.395	0.230	0.300	0.779	0.184	0.255	0.665	0.745
2	MgH_2/Composite	0.395	0.230	0.240	0.779	0.184	0.665	0.745	0.745
3	Mg_2FeH_6	0.254	0.510	0.308	0.872	0.124	0.665	0.500	0.745
4	Mg_2NiH_4	0.455	0.220	0.248	0.396	0.058	0.665	0.500	0.745
5	NH_3	0.333	0.450	0.268	1.000	0.251	0.335	0.665	0.410
6	$MgO/Mg(OH)_2$	1.000	0.100	0.324	0.510	0.090	0.665	0.500	0.745
7	$CaO/Ca(OH)_2$	0.333	0.400	0.416	0.587	0.090	0.500	0.665	0.745
8	$CaO/Ca(OH)_2$/Inner Material	0.333	0.400	0.416	0.930	0.113	0.665	0.745	0.745
9	$CaO/CaCO_3$	0.150	0.700	0.712	0.587	0.090	0.410	0.665	0.745
10	$CaO/CaCO_3$/Inner Material	0.174	0.880	0.712	0.929	0.113	0.665	0.745	0.745
11	$PbO/PbCO_3$	0.333	0.300	0.352	0.407	0.021	0.255	0.665	0.745
12	$SrO/SrCO_3$	0.136	1.000	0.500	0.523	0.090	0.255	0.500	0.745
13	Co_3O_4/CoO	0.176	0.700	0.820	0.396	0.055	0.500	0.500	0.745
14	BaO_2/BaO	0.146	0.400	0.308	0.440	0.030	0.255	0.500	0.745
15	CH_4/H_2OCH_4	0.158	0.530	1.000	0.010	1.000	0.355	0.500	0.410
16	CH_4/CO_2	0.158	0.530	0.988	0.010	0.986	0.355	0.500	0.410
17	C_6H_{12}/C_6H_6	0.473	0.397	0.824	0.711	0.157	0.255	0.500	0.500
18	SO_3/SO_2	0.188	0.500	0.392	0.867	0.078	0.255	0.500	0.500

$$
S = \begin{array}{c} \textbf{\textit{Factors}} \\ \textbf{\textit{HCT}} \\ \textbf{\textit{HRT}} \\ \boldsymbol{\Delta H_{Ent}} \\ \textbf{\textit{VED}} \\ \textbf{\textit{MED}} \\ \textbf{\textit{CyC}} \\ \textbf{\textit{VFR}} \\ \textbf{\textit{SPH}} \end{array}
\begin{array}{c}
\begin{array}{cccccccc} \textbf{\textit{HCT}} & \textbf{\textit{HRT}} & \boldsymbol{\Delta H_{Ent}} & \textbf{\textit{VED}} & \textbf{\textit{MED}} & \textbf{\textit{CyC}} & \textbf{\textit{VFR}} & \textbf{\textit{SPH}} \end{array} \\
\begin{bmatrix}
R_1 & 0.500 & 0.500 & 0.410 & 0.410 & 0.500 & 0.665 & 0.410 \\
0.500 & R_2 & 0.500 & 0.410 & 0.410 & 0.500 & 0.665 & 0.410 \\
0.500 & 0.5 & R_3 & 0.500 & 0.500 & 0.500 & 0.665 & 0.410 \\
0.590 & 0.590 & 0.500 & R_4 & 0.500 & 0.590 & 0.590 & 0.410 \\
0.590 & 0.590 & 0.500 & 0.500 & R_5 & 0.590 & 0.590 & 0.41\,0 \\
0.500 & 0.500 & 0.500 & 0.410 & 0.410 & R_6 & 0.500 & 0.410 \\
0.335 & 0.335 & 0.335 & 0.410 & 0.410 & 0.500 & R_7 & 0.410 \\
0.590 & 0.590 & 0.590 & 0.590 & 0.590 & 0.590 & 0.590 & R_8
\end{bmatrix}
\end{array}
\quad (6)
$$

3.3. Phase 3

Due to a need for a comprehensive, easy-to-use and target-related MCDM methodology, a universal non-commercial MATLAB program has been developed. The target-based material suitability index (TB-MSI) for each material is calculated by the above mentioned program using matrix representation of S defined by (1) (the normalized values of material selection factors and relative importance between attributes). The developed program can receive the matrix input for each material from an excel file,calculate the TB-MSI value for each alternative material and outputthe TB-MSI values, in ascending order, in a separate excel file.. The TB-MSI values for high temperature heat storage materials are given in Table 5 in ascending order.

The program is able to receive any square matrix (depending on number of material selection factors and relative importance

Table 5
TB-MSI values for candidate materials for high temperature heat storage application.

Material		TB-MSI
1	BaO_2/BaO	107.49
2	$PbO/PbCO_3$	114.57
3	SO_3/SO_2	120.23
4	Mg_2NiH_4	120.51
5	MgH_2	128.91
6	NH_3	134.09
7	$SrO/SrCO_3$	134.24
8	$CaO/Ca(OH)_2$	135.44
9	C_6H_{12}/C_6H_6	138.01
10	CH_4/CO_2	139.54
11	Co_3O_4/CoO	139.64
12	$MgO/Mg(OH)_2$	140.28
13	CH_4/H_2OCH_4	140.34
14	Mg_2FeH_6	143.01
15	MgH_2/Composite	143.24
16	$CaO/CaCO_3$	145.89
17	$CaO/Ca(OH)_2$/Inner Material	156.80
18	$CaO/CaCO_3$/Inner Material	181.89

between them) for any number of candidate materials defined by the user and calculate the TB-MSI value for each of them. Furthermore, the proposed MCDM methodology can be used for any type of target-based application and decision-making situation.

3.4. Phase 4

From the TB-MSI values presented in Table 5, it is identified that $CaO/Ca(OH)_2$ and $CaO/Ca(OH)_2$ with inner materials are the correct material choice for a high temperature heat storage material within the targeted application. Although, $CaO/Ca(OH)_2$ has a lower theoretical energy storage density in comparison with $CaO/CaCO_3$, $CaO/Ca(OH)_2$ the required lower temperature during a charging/discharging cycle in comparison to $CaO/CaCO_3$ (For $CaO/CaCO_3$: 900 °C for calcination vs 500–550 °C for dehydration) is clearly beneficial. In $CaO/Ca(OH)_2$ system, heat can be released at a temperature ranging from room temperature to 500 °C under atmospheric pressure and by changing the water vapor pressure, heat can be stored at around 500 °C. Therefore, $CaO/Ca(OH)_2$ has been selected from thermodynamic point of view for further studies and possible application for storing/recovering the high temperature waste heat (over 500 °C) in Port Talbot Steelworks. In addition, $CaO/Ca(OH)_2$ is commercially available at low cost [53]. The outcome from the proposed MCDM methodology in the selection of material is in line with the recent research trends on $Ca(OH)_2/CaO$ system for high temperature thermochemical storage [54–60].

4. Practicality of proposed MCDM method

An additional example is included in this section to illustrate the approach and validate the proposed methodology. This practicalexample is related to the selection of a suitable heat storage material for low-medium temperature waste heat (under 200 °C). 5 alternative candidate materials are shortlisted for this example ($CaCl_2$, $LiNO_3$, $MgCl_2$, $MgSO_4$ and $SrBr_2$) [61–64], mainly based the authors' previous work on salt impregnated desiccant matrices for open thermochemical energy storage [61,62,62,65,66]. The factors considered in this example are selected among the targeted material selection factors described in section 3.1 and these are: Heat Charge Temperature (*HCT*), Heat Release Temperature (*HRT*), Reaction Enthalpy (ΔH_{Ent}) and Volumetric Energy Density (*VED*). The first three steps of phase 1 are followed by the factors of interest identification, which is based on user quantitative or qualitative evaluation for limiting the acceptance value or threshold value for low-medium temperature heat storage applications.

Similarly to the previously described steps in section 4.2 and based on obtained information in phase one, a target-based material selection factors graph and matrix representation of it are developed for this example. The quantitative values of the material selection factors (factors of interest) for 5 alternative materials are adopted from [67] and presented in Table 6.

Relative importance values are assigned like section 4.2 based on targeted application and values of quantitative factors are normalized (shown in (7)).

$$S = \begin{array}{c} \textbf{\textit{Factors}} \\ \textbf{\textit{HCT}} \\ \textbf{\textit{HRT}} \\ \boldsymbol{\Delta H_{Ent}} \\ \textbf{\textit{VED}} \end{array} \begin{array}{c} \begin{array}{cccc} \textbf{\textit{HCT}} & \textbf{\textit{HRT}} & \boldsymbol{\Delta H_{Ent}} & \textbf{\textit{VED}} \end{array} \\ \begin{bmatrix} R_1 & 0.500 & 0.500 & 0.410 \\ 0.500 & R_2 & 0.500 & 0.410 \\ 0.500 & 0.500 & R_3 & 0.500 \\ 0.590 & 0.590 & 0.500 & R_4 \end{bmatrix} \end{array} \quad (7)$$

The TB-MSI values for low-medium temperature heat storage materials obtained from developed MATLAB program are given in Table 7 in ascending order.

From the TB-MSI values presented in Table 7, it is identified that $LiNO_3$ is the correct material choice among 5 proposed alternative candidates for low-medium temperature heat storage material at targeted application based on proposed selection criteria and relative importance between factors of interest. Hence, even the general application of a proposed target based MCDM methodology in a practical example could lead to a relatively reliable conclusion. Several studies have proposed $LiNO_3$ as a promising candidate in a composite sorbent for heat storage applications driven by heat sources with low temperature potential [64,68,69]. In addition, the outcome fromMCDM methodology are in line with the results of previous studies of this group as well [61,62,62,65,66]. The considered factors of interest in the practical example are limited to

Table 7
TB-MSI values for candidate materials for practicality example.

Material		TB-MSI
1	$MgSO_4$	1.79
2	$CaCl_2$	1.92
3	$MgCl_2$	1.95
4	$SrBr_2$	2.22
5	$LiNO_3$	2.63

Table 6
Quantitative data of material selection factors for candidate materials for practicality example [67].

Material		Factors of interest (Material Selection Factors) - Quantitative Factors			
		HCT	HRT	ΔH_{Ent}	VED
		[°C]	[°C]	[kJ/mol]	[kWh/m^3]
1	$CaCl_2$	41	35	54.8	238.9
2	$LiNO_3$	34	28	55.6	591.7
3	$MgCl_2$	72	65	52.0	222.2
4	$MgSO_4$	29	24	59.6	111.1
5	$SrBr_2$	61	52	43.0	491.7

five factors for demonstration purposes. Therefore, the correct material selection for low-medium temperature heat storage application would require consideration of more candidate materials as well as more factors of interest. For example, commercial factors such as the relative cost of lithium and strontium compared to calcium and magnesium may result in a revised TB-MSI values. In addition, the assigned relative importance values in this example are for demonstration purpose and would be required to be modified further for a more accurate outcome from MCDM methodology in actual practice. The end user should make decisions based on the targeted application and design requirements within the local environment.

As mentioned earlier, the proposed method can guide users in taking a proper decision using a simple, logical, and systematic scientific method for material selection with focus on thermochemical storage materials. Limited studies have covered material selection for thermochemical storage and most of the existing methods are still far from an ideal easy-to-use yet scientific tool.

5. Conclusion

Within this body of work a multi criteria decision making tool is proposed for the selection of heat storage materials that utilise industrial waste heat as the capture source. The method draws on graph theory and matrix approach and considers both qualitive and quantitative data sets within a MATLAB programme to produce a target based material suitability index that allows the simple selection of candidate materials. This methodology allows for the relative importance of each selected factor to be accounted for and considers this via both objective and subjective routes.

The MCDM tool is tested against a real life situation, namely the capture of waste heat from Tata Steel UK Port Talbot steelworks. Two scenarios are assessed, with the waste heat temperature ranges selected being 500–600 °C and < 200 °C. In the higher temperature range a total of eight targeted material selection factors are used whereas the lower temperature range only considers five materials selection factors. In the higher temperature region variants of the $CaO/CaCO_3$ and $CaO/Ca(OH)_2$ are the selected variants whereas $LiNO_3$ is the selected choice from the (more limited) lower temperature range. Both material sets are appropriate when compared to current literature and ongoing studies within the field.

The methodology developed through this work will enable the refined selection of candidate materials for thermal storage systems. Whilst in this body of work the focus has been upon industrial waste heat recovery within the steel industry, the method can be applied to other scenarios such as heat storage from high and low temperature solar thermal generators. Hence, as the number candidate systems for Thermochemical storage is already quite large, this methodology may be used as a quick and simple method for future research activities to refine their material choices.

Data availability

Data will be made available on request.

Data availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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