

Thermal energy storage: “How previous findings determine current research priorities”

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ARTICLE INFO

Article history:

Received 1 November 2011

Received in revised form

11 January 2012

Accepted 13 January 2012

Available online 15 February 2012

Keywords:

Thermal energy storage

Heat transfer enhancement

PCM

Metal foam

Energy storage

Composite materials

ABSTRACT

Thermal energy storage is an expanding field within the subject of renewable energy technologies. After a listing of the different possibilities available for energy storage, this paper provides a comparison of various materials for High Temperature Thermal Energy Storage (HTTS). Several attributes and needs of each solution are listed. One in particular is using the latent heat as one of the most efficient ways to store thermal energy. The mixture of phase change material (PCM) embedded in a metal foam is optimising the thermal properties of the material for latent heat energy storage. The results of previous studies show that mechanical and thermal properties of foam were extensively studied separately. This paper highlights the potential for an advanced study of thermo-mechanical properties of metal foams embedded with PCM.

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1. Introduction

The efficient use of energy is of growing importance and developing highly effective energy saving solutions are paramount in the current energy demand context. The objective of the current paper is to review the available information on the thermal energy storage (TES), in order to define the priority research objectives to complete the fundamentals needed for their widespread application. The review part of the paper specifically focuses upon (i) the underlying storage mechanisms and its potential, (ii) the essential materials and properties that delineate temperature ranges of application, and (iii) the illustration of particular solutions to high temperature thermal energy storage. After a brief description of thermal energy storage, the advantages of storing both sensible and latent heat are discussed. As a specific case, we show the effectiveness of storage involving latent heat and how it leads to the selection of a phase change material (PCM) for specific applications, whilst highlighting its appropriate characteristics, its current

weaknesses, and the multiple solutions to improve the thermal properties of PCM. The selected solution involves a metal foam and a PCM, two materials that have been previously studied, mostly towards their applicability and advantages. From assessing these previous studies, it is clear that there is an urgent need to develop a thermo-mechanical modelling of such a composite, subject of the extensive research program currently carried out by the authors. The layout of the present paper is illustrated in Fig. 1. Each of the parallel topics is subsequently dealt with.

2. Energy storage

Energy Storage (ES) is the storage of some kind of energy that can be drawn upon at a later time and usefully re-applied in a given operation. It has the potential of increasing the effective use of energy equipment and is normally applied to balance the possible mismatch between the supply of, and demand for energy [1]. The imperativeness of ES results from the need of having the energy production decoupled from its supply and distribution, and to support the intermittent nature of producing alternative energy [2]. An energy storage process is based on three fundamental steps: charging (loading), storing and discharging (releasing) [1]. As a result, ES applications facilitate energy management, help bridging power supply/needs and power quality, and increase the

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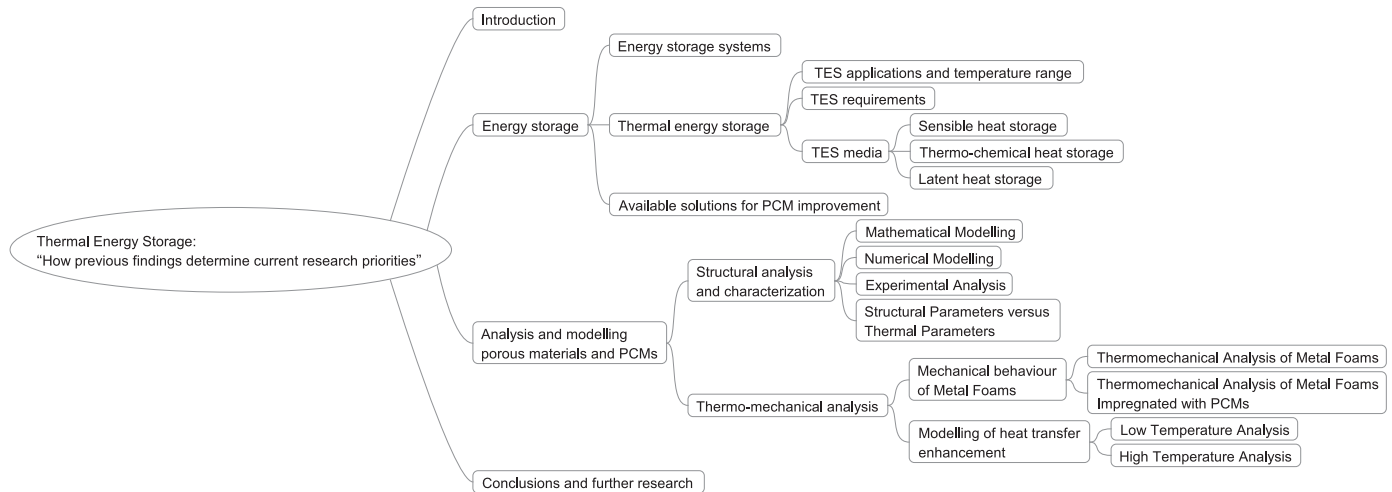


Fig. 1. Layout of the present paper.

system reliability [2]. Energy forms include mainly mechanical, chemical, electrical or thermal energy, and all of them can be stored using an appropriate method, system or technology as described below.

2.1. Energy storage systems

Every system or technology of ES had been developed in order to answer specific needs [2]. They are classified by the form of energy stored, as shown in Fig. 2.

Mechanical ES systems are either of potential or kinetic nature. Kinetic energy storage systems are usually flywheels with low or high rotational speeds (FES) [2]. Potential energy storage systems include pumped hydroelectric (PHS) and compressed air energy systems (CAES) at small and large scale [2]. The electrical ES is the only technology that charges, stores and returns electric energy: it uses standard electrostatic capacitors (CAP), electrochemical capacitors (super-capacitors) (ECC), and superconducting magnetic energy storage (SMES). Chemical ES groups three main types of batteries; i.e. the conventional, molten salt, and flow batteries [2]. The Thermal Energy Storage (TES) systems cover a large range of temperatures and applications [2] and are further detailed in this paper because of their expected high technological strength and market potential.

Several reviews have previously described ES technologies and systems [2,3]. Datas are collected in Table 1 by Bradbury [3]: the wide range of their characteristics, costs and efficiencies illustrates that development and application are at different stages. The comparison shows that each technology has a specific field of applications and answers a specific need. Thermal Energy Storage is presented here as a solution for numerous applications.

2.2. Thermal energy storage

With Thermal Energy Storage (TES), heat is transferred to storage media during the charging period, and released at a later stage during the discharging step, to be usefully applied e.g. in generating high-pressure steam for power block (Rankine cycle) in solar plants, or as heat carrier in high temperature industrial processes, such as metallurgical transformations [4]. In terms of storage media, a variety of choices exists depending on the storage media system selected, the temperature range and the specific application.

2.2.1. TES applications and temperature range

Low temperature thermal energy storage (LTTEs) operates in a temperature range below 200 °C and has been extensively investigated and developed. LTTEs applications can be found in building heating and cooling [5], in solar cooking, in solar water boilers and air-heating systems, and in solar greenhouses [6,7].

High temperature thermal energy storage (HTTES) plays a vital role in renewable energy technologies and waste heat recovery. There is a wide range of industrial applications where waste heat can be recovered, as in the manufacturing of construction materials (e.g. clay brick or cement kilns) mining and in the metallurgical industry in general [8,9]. Today, most HTTES usages are however focused upon applications of solar thermal energy [10,11].

TES applications are subject of constant innovative research and designs as shown in the numerous reviews [1–3,6,10,12–18]. The current paper presents a guideline in selecting a specific material as TES solution.

2.2.2. TES requirements

In order to make HTTES a more plausible and attractive alternative for improving the efficiency of industrial processes and solar engineering, some requirements must be fulfilled. HTTESs firstly need to stably operate in a high range of temperatures, which in the present context is specified from 200 °C to as high a temperature limit as possible. Secondly, the material used as storage media must be inexpensive, available in big quantities and compatible with a cost-effective system design [1]. Several additional facts need to be considered when deciding on the storage media for an HTTES, and the most important requirements are presented by Zalba et al. [18]:

- (i) Energy capacity: high energy density in the storage material;
- (ii) Efficiency: good transfer between the heat transfer fluid (HTF) and the storage medium;
- (iii) Mechanical and chemical stability of the storage material during the multiple charging/discharging cycles;
- (iv) Safety: compatibility between HTF, heat exchanger and/or storage medium;
- (v) Lifespan: complete reversibility in multiple charging/discharging cycles;
- (vi) Low heat losses;
- (vii) Ease of control;

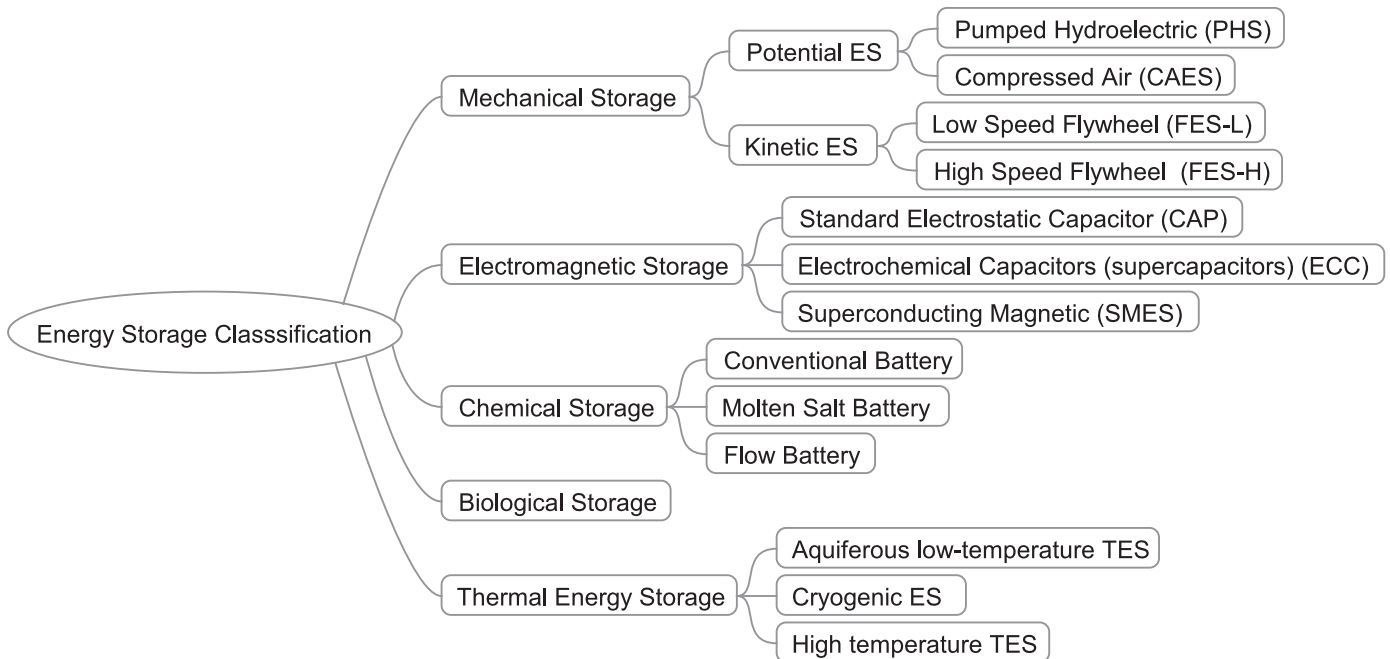


Fig. 2. Classification of energy storage systems [1].

- (viii) Adequate maximum load;
- (ix) Appropriate nominal temperature and;
- (x) Specific enthalpy drops in load.

Meeting all these requirements needs innovative engineering approaches, with a major impact attributed to the development and research into the fields of storage media. The latter is due to the difficulty of selecting an adequate and stable storage material that matches both (i) and (ii) requirements described above. The combination of high efficiency and high energy density requirements can lead to the development of a storage media that makes viable the design of cost-efficient HTTES, and it is a challenge that demands novel ideas and pioneering efforts.

2.2.3. TES media

An assertive material selection involves choosing an adequate form of thermal storage, which can be found in three types, being the thermal storage as sensible heat, the thermal storage as latent heat when phase transformations are accounted for, and the thermo-chemical storage as a result of combining endothermic and exothermic reactions occurring with the media. The energy released or absorbed by a material as its temperature is reduced or increased is called sensible heat, and the specific heat (c_p) is the relevant characteristic. The energy required to convert a solid into a liquid, or a liquid into a gas (material phase change) is called latent heat with e.g. heats of fusion and condensation recognised for their high value. The capacity of energy storage is significantly higher when latent heat storage complements the sensible heat storage. The third and less developed category of heat storage, the thermo-chemical heat storage, uses the reversible endothermic/exothermic reactions of some reactions as detailed below.

2.2.3.1. Sensible heat storage. Sensible heat storage materials undergo no phase change within the temperature range required for the storage application [19]. Table 2 summarizes the main characteristics of the most common solid and liquid sensible HTTS materials [19,20].

Within the indicated solids, concrete and cast ceramics have been extensively studied due to their low costs, good thermal conductivities and moderate specific heats [21,22]. In terms of liquids, molten salts are widely used in power tower systems [22,23], being liquid at ambient pressure, providing an efficient and low cost medium, having their operating temperatures compatible with current high-pressure and high temperature turbines (temperature range over 120 °C–600 °C), whilst being non-flammable and non-toxic. These molten salts are already used in the chemical and metallurgical industries as heat-transport fluid, hence providing experience and knowledge for their use in other fields than solar plants [24]. From Table 2, it is clear that the main candidates for liquid sensible heat storage are either a solar salt, i.e. a binary salt consisting of 60% of NaNO_3 and 40% of KNO_3 , that melts at 221 °C and is kept liquid at 288 °C in an insulated storage tank; or HitecXL, a ternary salt consisting of 48% $\text{Ca}(\text{NO}_3)_2$, 7% NaNO_3 , and 45% of KNO_3 operating beyond its melting point of 130 °C [25].

Sensible heat materials have been widely studied and are currently applied in solar thermal plant applications, despite important disadvantages that can affect the storage system design and stability. Kearny et al. [26] investigated molten salts and demonstrated such disadvantages. Most molten salts have a high freezing point (around 100 °C), and the high outlet temperature results in heat losses and in requiring more expensive piping and materials [26,27]. The high freezing point may be a problem for solar power plants because of the required heat trace during non-functioning periods. Furthermore, the sensible fraction of thermal energy is seldom fully recovered due to the required temperature difference as heat transfer driving force. Another important disadvantage consists in the low energy storage density of sensible heat materials, which are required in large volumes or quantities in order to deliver the amount of energy storage necessary for HTTES applications. The above mentioned problems can imply significant increments in the costs of sensible heat storage systems.

2.2.3.2. Thermo-chemical heat storage. The main advantage of the thermo-chemical heat storage systems consists in the potentially high energy density of the occurring reversible chemical reactions,

Table 1
Main characteristics of energy storage systems [3].

Parameter	Mechanical storage				
	PHS	CAES	FES-LS	FES-HS	
Roundtrip efficiency [%]	70–85	57–85	70–95	70–95	
Self-discharge [%energy/day]	~0	~0	100	1.3–100	
Cycle lifetime [cycles]	N/A	N/A	20k–100k	20k–100k	
Expected lifetime [years]	30–60	20–40	15–20	15–20	
Specific energy [Wh/kg]	0.5–1.5	30–60	10–30	10–30	
Specific power [W/kg]	0	0	400–1.5k	400–1.5k	
Energy density [kWh/m ³]	0.5–1.5	3–6	20–80	20–80	
Power density [kW/m ³]	0	0.5–2	1k–2k	1k–2k	
Costs					
Power cost [\$/kW]	600–2k	400–800	250–360	250–400	
Energy cost [\$/kWh]	0–23	2–140	230–60k	580–150k	
Balance of plant costs (BOP) [\$/kW]	270–580	270–580	110–600	110–600	
Power conversion system costs (PCS) [\$/kW]	0–4.8	46–190	0–120	0–1200	
Operation and maintenance (OM) fixed cost [\$/kW-y]	3–4.4	1.6–29	6–22	6–22	
Parameter	Electrical storage			SMES	
	CAP	ECC			
Roundtrip efficiency [%]	60–70	90–98		90–98	
Self-discharge [%energy/day]	40	20–40		10–15	
Cycle lifetime [cycles]	50k	10k–100k		100k	
Expected lifetime [Years]	5	20		20–30	
Specific energy [Wh/kg]	0.05–5	2.5–15		0.5–5	
Specific power [W/kg]	100k	500–5k		500–2k	
Energy density [kWh/m ³]	2–10	0		0.2–2.5	
Power density [kW/m ³]	100k	100k		1k–4k	
Costs					
Power cost [\$/kW]	200–400	100–360		200–350	
Energy cost [\$/kWh]	500–1k	300–94k		1k–83k	
BOP cost [\$/kW]	180–580	180–580		140–650	
PCS cost [\$/kW]	50–12k	50–12k		60–12k	
O&M fixed cost [\$/kW-y]	6–16	6–16		9.2–30	
Parameters	Chemical storage				
	Conventional battery			Molten salt battery	
	Lead acid	NiCd	Li-ion	NaS	ZEBRA
Roundtrip efficiency [%]	70–82	60–70	85–98	70–90	85–90
Self-discharge [%energy/day]	0.033–0.3	0.067–0.6	0.1–0.3	0.05–20	15
Cycle lifetime [cycles]	100–2k	800–3.5k	1k–10k	2.5k–2.5k	2.5k
Expected lifetime [Years]	3–20	5–20	5–15	5–15	10–14
Specific energy [Wh/kg]	30–50	50–75	75–200	150–240	100–120
Specific power [W/kg]	75–300	150–300	150–315	150–230	150–200
Energy density [kWh/m ³]	50–80	60–150	200–500	150–250	150–180
Power density [kW/m ³]	10–400	0	0	0	220–300
Costs					
Power cost [\$/kW]	175–600	150–1500	175–4000	150–3000	150–300
Energy cost [\$/kWh]	150–400	600–1500	500–2500	250–500	100–200
BOP cost [\$/kWh]	120–600	120–600	120–600	120–600	120–600
PCS cost [\$/kW]	58–180	50–180	0	0–120	0–120
O&M fixed cost [\$/kW-y]	1.8–52	6–32	12–30	23–61	23–61
Parameters	Chemical storage				
	Flow battery				
	ZnBr	Polysulfide-bromide		Vanadium Redox	
Roundtrip efficiency [%]	60–75	57–75		60–85	
Self-discharge [%energy/day]	0.24	~0		0.2	
Cycle lifetime [cycles]	2k	2k		12k–14k	
Expected lifetime [Years]	5–10	10–15		5–15	
Specific energy [Wh/kg]	30–50	10–50		10–30	
Specific power [W/kg]	0	0		0	
Energy density [kWh/m ³]	30–60	16–60		16–33	
Power density [kW/m ³]	0	0		0	
Costs					
Power cost [\$/kW]	175–2500	330–2500		175–1500	
Energy cost [\$/kWh]	150–1000	120–1000		150–1000	
BOP cost [\$/kWh]	120–600	120–600		120–610	
PCS cost [\$/kW]	0–120	60–120		36–120	
O&M fixed cost [\$/kW-y]	15–47	18–96		24–65	

Table 2
Main characteristics of sensible heat storage solid and liquid materials.

Storage medium	Temperature		Average density (kg/m ³)	Average heat conductivity (W/m K)	Average heat capacity (kJ/kg K)	Volume specific heat capacity (kWh _t /m ³)	Costs per kg (US\$/kg)	Costs per kWh _t (US\$/kWh _t)
	Cold (°C)	Hot (°C)						
Solid storage medium								
Sand-rock-mineral oil	200	300	1700	1	1.3	60	0.15	4.2
Reinforced Concrete	200	400	2200	1.5	0.85	100	0.05	1
NaCl (solid)	200	500	2160	7	0.85	150	0.15	1.5
Cast iron	200	400	7200	37	0.56	160	1	32
Silica fire bricks	200	700	1820	1.5	1	150	1	7
Magnesia fire bricks	200	1200	3000	1	1.15	600	2	6
Liquid storage medium								
HITEC solar salt	120	133	1990	0.60	–	–	–	–
Mineral oil	200	300	770	0.12	2.6	55	0.3	4.2
Synthetic oil	250	350	900	0.11	2.3	57	3	42
Silicon oil	300	400	900	0.1	2.1	52	5	80
Nitrite salts	250	450	1825	0.57	1.5	152	1	12
Nitrate salts	265	565	1870	0.52	1.6	250	0.5	3.7
Carbonate salts	450	850	2100	2	1.8	430	2.4	11
Liquid sodium	270	530	850	71	1.3	80	2	21

which can be even higher than what is usually encountered for the other thermal storage processes [1,28]. Materials that have been mostly investigated for chemical storage are the SnO_x/Sn and ammonia system. In the former case, the metal oxide/metal reactions are possible and technically feasible, occurring at a temperature of 980 K, and SnO₂ (solid) is reduced with CH₄ while it floats on top of liquid Sn. For the latter case, ammonia is dissociated producing hydrogen and nitrogen. The exothermic reaction heat from ammonia synthesis is suitable for electric power generation in conventional Rankine Cycles. Despite its high energy density, thermo-chemical heat storage is considered to be an expensive alternative and is, at the present, at early stages of development [28].

2.2.3.3. Latent heat storage. Latent heat storage is based on the heat absorption or heat release that occurs when a storage material undergoes a phase change. Latent storage systems based on phase change materials (PCMs) with solid–liquid transition are considered to be very efficient in comparison to liquid–vapour and solid–solid transitions [7]. Liquid–gas transition requires a large volume recipient for the PCM and the solid–solid transition presents a low value of latent heat. Therefore these last two alternatives are not considered appropriated choices [29]. A large number of materials are known to melt with a high heat of fusion within different ranges of temperature. No material yet studied has all the optimal characteristics required for a PCM, and the selection of a PCM for a given application requires careful consideration of the properties of the various substances and/or mixtures [16]. The main characteristics required for PCMs are indicated in Table 3 [7]. As an example, commercial or potential substances used as PCM are shown in Tables 4, 5 and 6 [20].

Current experimented uses of PCMs for thermal storage involve low to moderate temperatures (10–100 °C) and include solar water-heating systems, solar air-heating systems, solar cookers, solar greenhouses (for curing and drying processes), building acclimatization as in a PCM Trombe wall, PCM wallboards [5], under-floor heating systems and ceiling boards [6,7]. Though PCMs usage in HTTES has been experimented for solar plant applications, it has not yet been commercially used in a solar plant [1,11].

The development of high temperature thermal storage using PCMs is of increasing interest since they are moderately expensive, have high energy density, can in the future be available in large quantities [18], and are able to store and release thermal energy at a constant temperature most of the times [6,7]. However, most of PCMs have a low thermal conductivity, leading to low charging and

discharging rates and sometimes non suitable field of temperature in the material. Therefore, using PCMs for energy storage in high temperature range applications requires considering new aspects of material selection and development. In addition to adapt PCM's melting points to a high temperature range, their characteristics need to be improved in order to increase the *efficiency of the charging and discharging* processes.

Based on this information, several studies or papers consider the development of novel phase change materials for high temperature purpose a very important subject of study, and the team of authors is engaged in an extensive programme of research to provide an adequate theoretical background and a description of the fundamentals. The successful completion of this research will help create fundamental and advanced knowledge on the subject, as well as support the development of cost-effective high temperature thermal storage systems oriented for the improvement of renewable energy technologies and energy-efficient industrial processes. The facts and findings of previous research form the guidelines to the research priorities, and are dealt with below.

2.3. Available solutions for PCM improvement

To improve the efficiency of the charging and discharging processes of PCMs, the most relevant parameter to be studied is their thermal conductivity. In order to increase the thermal conductivity of PCMs, several heat transfer enhancement techniques have been studied [15], such as:

Table 3
Main desirable characteristics of PCMs.

Thermal properties	Phase change temperature suitable within the desired operating range. High latent heat per unit mass. High specific heat. High thermal conductivity for both solid and liquid phases.
Physical properties	High energy density. Low-density variation during phase change. No supercooling during freezing.
Chemical properties	Chemical stability. No chemical decomposition. Compatibility with container materials construction (e.g. vessels and piping). Non-toxic, non-inflammable and non-explosive.
Economic Factors	Available in large quantities. Inexpensive

Table 4
Organic compounds for potential use as PCM.

Organic compounds	Melting point (°C)	Heat of fusion (kJ/kg)
Ammediol	112	285
Neopentyl glycol	125	45.3
Neopentylglycol diacrylate	126	44.3
Isomalt	147	275
Adipic acid	152	247
Dimethylol propionic acid	153	275
Tromethamine	172	27.6
Trimethylolethan	198	44.6
Pentaerythritol	260	36.9

- (i) the micro-encapsulation of PCMs using graphite [30], Silicon Carbide (SiC) [31], nickel film coating of PCM copper spheres [32];
- (ii) the use of metal carrier structures made of steel or stainless steel;
- (iii) a dispersion of high conductivity material i.e. copper, silver or aluminium particles, within the PCM;
- (iv) the use of high conductivity, low-density materials such as carbon fibres and paraffin composites; and
- (v) the impregnation of high conductivity porous materials, either as a metal foam (copper, steel or aluminium), or as porous material like graphite.

A general review of these techniques has been undertaken by the authors (Fig. 3), and the impregnation of metal foams in PCM was determined as being one of the most promising and suitable approaches at the present stage of the project investigation. As described below and explained in detail in the following sections, metal foams prove to be a non-expensive, easy to handle, abundantly available material that improves heat transfer rates in PCMs significantly, thus being an attractive approach for developing and improving latent heat storage media.

The reasons behind this selection are the result of the detailed assessment, which summaries as follows:

- (i) The thermal performance of *micro-encapsulated PCMs* is expected to exceed conventional PCMs since small PCM particles

provide larger heat transfer area per unit volume and will provide a higher heat transfer rate. Micro-encapsulated PCMs moreover add advantages like less reaction of PCM with container material, and the ability to withstand volume change during phase change [33]. This heat transfer enhancement technique has been widely studied for different combinations of PCMs and coating shells [30–37]. These studies mainly focused on the preparation and characterization of micro-encapsulated PCMs, without extensive comparison of the performance of micro-encapsulated PCM with that of pure PCM, and more comparative work is needed in order to assess the performance enhancement due to micro-encapsulation of commonly used PCMs. Such approach requires a great deal of experimental work, only at its incipient stage at present.

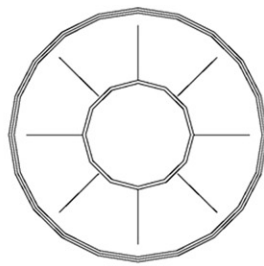
- (ii) *Incorporating metal structures into the PCM* has also been addressed as one of the thermal conductivity enhancement techniques by some researchers, who investigated metal structures made of steel or stainless steel in different geometries, such as cylindrical and spherical geometries, and in different arrangements [38–41]. In order to achieve a significant reduction of melting/solidification time, an important system volume is necessary, thus associated with an expected increase of costs and a limit of LTES system usages. Due to the constraints demonstrated by the review, this heat transfer enhancement technique does not fulfil our research interests.
- (iii) *Dispersion of high conductivity particles into the PCM* is a relatively simple technique to enhance the thermal conductivity of PCM. Studies involving dispersion of metal particles like copper, silver and aluminium have been undertaken [39,42,43]. They showed that, at any given condition, there is a range of optimum particle fractions and it is suggested to choose lower values in the band to ensure a high mass of PCM to increase the amount of energy stored. Hence, an appropriate combination of particle thermal conductivity and particle mass fraction is quite important when the conductive particles are to be dispersed in the PCM to enhance the performance of the unit. These results conclude that there is a limitation in terms of PCM/particle combination that could be applied, and further research is necessary.

Table 5
Inorganic substances for potential use as PCM and commercial compounds.

Inorganic compounds	Melting point (°C)	Heat of fusion (kJ/kg)	Density (kg/m ³)	Specific heat (kJ/kg K)	Thermal conductivity (W/m K)
Mg(NO ₃) ₂ ·2H ₂ O	130	275	n.a.	n.a.	n.a.
Hitec XL: 48%Ca(NO ₃) ₂ –45%KNO ₃ –7%NaNO ₃	140	n.a.	1992	1.44	0.519
Hitec: KNO ₃ –NaNO ₂ –NaNO ₃	142	84	1990	1.34	0.6
68%KNO ₃ –32%LiNO ₃	144	75	n.a.	n.a.	n.a.
Isomalt	147	252	n.a.	n.a.	n.a.
LiNO ₃ –NaNO ₃	195	n.a.	n.a.	n.a.	n.a.
KNO ₃ /NaNO ₃ eutetic	223	105	n.a.	n.a.	0.8
NaNO ₃	307/308	74	2260/2257	n.a.	0.5
KNO ₃ /KCl	320	116	2100	1.21	0.5
KNO ₃	333/336	266/116	2110	n.a.	0.5
KOH	380	149.7	2044	n.a.	0.5
MgCl ₂ /KCl/NaCl	380	400	1800	0.96	n.a.
NaCO ₃ –BaCO ₃ /MgO	500–850	n.a.	2600	n.a.	5
AlSi ₁₂	576	560	2700	1.038	160
AlSi ₂₀	585	460	n.a.	n.a.	n.a.
MgCl ₂	714	542	2140	n.a.	n.a.
80.5%LiF–19.5%CaF ₂ eutetic	767	790	2100/2670	1.97/1.84	1.7/5.9
NaCl	800/802	492/466.7	2160	n.a.	5
LiF	850	1800 MJ/m ³	n.a.	n.a.	n.a.
Na ₂ CO ₃	854	275.7	2533	n.a.	2
KF	857	452	2370	n.a.	n.a.
K ₂ CO ₃	897	235.8	2290	n.a.	2

Table 6
Inorganic substances for potential commercial compounds.

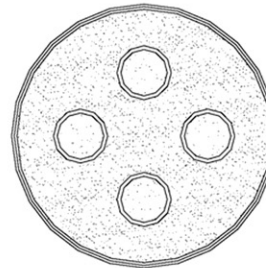
Commercial compounds	Melting point (°C)	Heat of fusion (kJ/kg)	Density (kg/m ³)	Specific heat (kJ/kg K)	Thermal conductivity (W/m K)
Paraffin RT110	112	213	n.a.	n.a.	n.a.
Inorganic E117	117	169	1450	2.61	0.7
Organic A164	164	306	1500	n.a.	n.a.



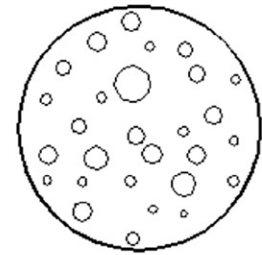
(i) Longitudinal or axial fins



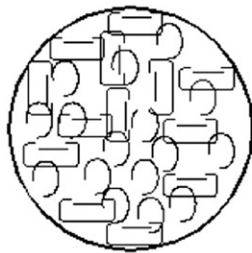
(ii) Circular fins



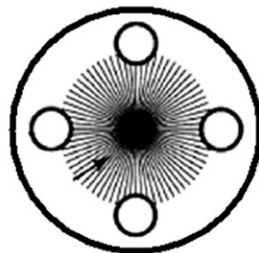
(iii) Multitubes or shell and tube



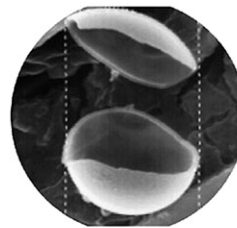
(iv) Bubble agitation



(v) Metal Rings



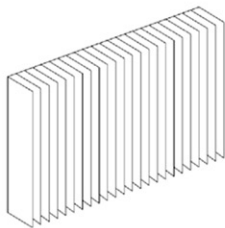
(vi) Multitubes and carbon brushes



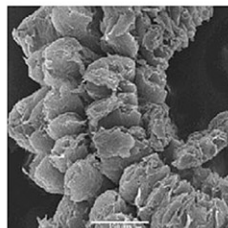
(vii) Encapsulation



(ix) Metal Matrix



(x) Finned Rectangular Container



(xi) Graphite flakes



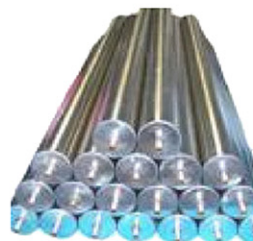
(xii) Steel metal ball capsules



(xiv) Polyolefine spherical balls



(xv) Polypropylene flat panel



(xvi) Module beam



(xvii) PCM-Graphite



(xviii) Compact flat panel

Fig. 3. Heat transfer enhancement methods employed in phase change material research [12].

- (iv) High conductivity particles *should also be compatible with all PCMs*. Due to the relatively high density, the metal particles/metal structures may settle at the bottom of the TES container and add considerable weight to the system. According to Fugai et al. [44], not all metal particles are compatible with all PCMs. For example, paraffin and aluminium are compatible, while copper and nickel are not compatible. Similarly, aluminium and copper are not compatible with some salt hydrates. Hence, there has been a search for *low-density high conductivity additives which should be compatible with all PCMs*. Since the densities of carbon fibres are lower than those of metals and the thermal conductivities are almost equal to that of aluminium and copper, carbon fibres can be better alternatives to enhance the thermal performance of LTES systems. This heat transfer enhancement technique has been widely studied, as previously mentioned [42,45–48]. The review has revealed that both the phase change and/or the charging and discharging rate (melting/solidification) can be increased considerably by adding high conductivity substances. In general, however, these additives may lead to the loss of storage capacity of pure PCM. The loss in storage capacity limits the mass/volume fraction of additives. It should therefore be mentioned that this technique has a limited potential for developing LTES systems for industrial applications, where a high storage capacity of PCMs is needed to accomplish the industrial requirement of non-intermittent high temperature steam production.
- (v) In view of the above mentioned constraints, *impregnation of high conductivity porous materials in PCMs* constitutes an attractive alternative for improving the heat transfer processes in PCMs. The use of a porous matrix has gained increasing attention because of its light weight and high specific surface area for heat transfer [49]. Porous structures can be even matrices made of aluminium, copper, etc., or naturally available porous materials such as graphite. Since the porous material is impregnated in the PCM, the problem of particle segregation at the bottom of the TES container is reduced. The main challenge of this approach would be to develop a compatible and efficient combination of the PCM and porous material, suitable for high temperature purposes. More specifically, the research should provide a proper modelling of copper foam structures embedded in selected salts as PCM. Therefore, *structural* and *thermo-mechanical* parameters need to be studied in conjunction with a *charging/discharging efficiency analysis* of PCMs impregnated in metal foams.

3. Preliminary analysis and modelling of composites metal foam/PCM to be applied as HTES material

3.1. Structural analysis and characterization

Several studies of isolated metal foam structures have been undertaken over the past years. Efforts have been made to determine the proper modelling of aluminium alloys. However, there are no studies attempting to develop a model specifically to a copper foam structure. The present review presents a few interesting approaches to the micro-structural characterization of metal foams and porous materials in general, which provide starting points for further investigations related to copper foam structures.

3.1.1. Mathematical modelling

Micro-structural modelling of metal foams has been done for tetrakaidecahedron geometry [50–52] and octahedral geometry [53]. The first investigations are considered to be a good approximation to aluminium structures (Fig. 4). The last one states that

metallic struts constituting the porous body can be regarded to be regularly connected by the way of diagonals of cubes and, thereby, form a great deal of octahedral units in the form of close-packed Body Centered Cube.

3.1.2. Numerical modelling

Numerical models of metal foams can be found for tetrakaidecahedron geometry [51,52]. The first one was developed in order to predict the heat transfer enhancement capability of a channel filled with metal foam; the last one was generated for estimating the crushing behaviour of dynamically loaded metal foam-filled square columns.

For a spherical geometry [54], an incompressible, hardening, visco-plastic matrix material has been modelled, and the growth of a void in metallic media has been analysed. This approach, similar to the ones described above, is designed to be used in either mechanical or thermo-mechanical evaluations of metal foams structures. In this case specifically, the purpose was the analysis of constitutive relations, shearing and volumetric viscosities for plastic deformation of a porous material.

3.1.3. Experimental analysis

In order to validate the modelling of metal foams structures, Raj et al. [55] have experimentally analysed the microstructure of an aluminium alloy, FeCrAlY, and compared the results with previously modelled geometries.

According to the above mentioned research, modelling of foam cell structures fall into two broad categories: (i) idealized topological models based on minimizing the ratio of the surface free energy to volume free energy that can fill a three-dimensional (3D) space; and (ii) engineering models based on the actual reconstruction of the 3D foam microstructures. Among the several possible idealized topological representations of the foam microstructures [56], the three-dimensional, space-filling Kelvin tetrakaidecahedron [56,57] is often favoured for modelling the foam cellular network. This cell has 14 faces consisting of 6 square and 8 hexagonal faces. In other words, about 43% of the faces are squares, 0% faces are pentagonal and 57% of the faces are hexagonal. Elsewhere, other topological models like Williams and Weaire–Phelan models have been proposed, where pentagonal faces are incorporated in the cell geometry [58,59].

The Raj et al. research [55], belonging to the second category above listed, determined quantitative information on ligament (or struts) dimensions, cell face dimensions, area fractions of open and closed faces, geometric shapes of the cell faces and distribution of ligament [60]. The paper specifically reports statistical data on the geometrical features of the cells faces to determine the validity of the Kelvin [61] and other theoretical space-filling models [57,59,62] in a comprehensive manner.

The shapes of cell faces of the alloy were evaluated by approximating the faces by regular polygons. It was observed that between 24 and 28% of the cell faces were quadrilateral, 50–57% pentagonal and 15–22% hexagonal in morphology. The results agreed with Matzke's observations [63], which suggested that the FeCrAlY foam cells had a total of 11 faces with 3 quadrilateral, 6 pentagonal and 2 hexagonal faces. Both sets of results do not agree with the 14-hedra Kelvin tetrakaidecahedron model [61], which only has 43 and 57% quadrilateral and hexagonal faces, respectively. Neither do the results agree with the Williams and Weaire–Phelan models [58,59]. Their calculations show that the 3–6–2 cell, which probably best describes the FeCrAlY foam cells, has 27 edges and 18 vertices [55]. The Raj et al. studies [55,60] are a very important support for the structural characterization that will be carried out in our further research. However, it will be necessary to analyse if the results need to be taken strictly into account for the investigation of copper foam as a storage material. It could instead be found that the Kelvin model

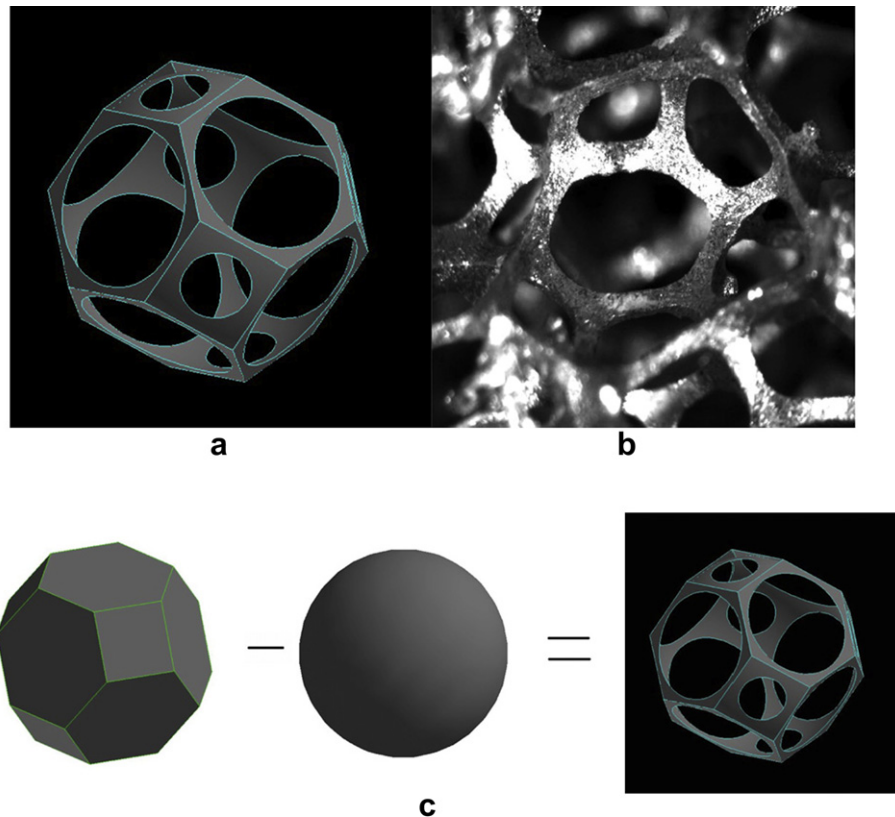


Fig. 4. Comparison of single cell model with actual foam structure, (a) Single cell model used in this study, (b) SEM photo of aluminium foam and (c) Geometry creation of a single cell [51].

assumption (where all cells are of the same size and volume so it can be determined the cell shape that can pack 3D space resulting in a system with the lowest free energy) provides a reasonable approximation. In this case, the mathematical and numerical studies previously mentioned in the other items of this section can be used as reference to evaluate the effects of those approximations in thermo-mechanical analysis results.

3.1.4. Structural parameters versus thermal parameters

The study of the relation of structural parameters with thermal conductivity, thermal diffusivity and latent heat in a porous material impregnated with PCM was done for a graphite foam integrated with paraffin wax [64,65]. The research determined:

- (i) an almost linear relation between thermal conductivity and the bulk density of the graphite matrix, as well as between the latent heat of the composite and the mass ratio of the paraffin wax in the matrix;
- (ii) a small pore-size and thicker ligament in the matrix resulted in a higher thermal diffusivity;
- (iii) a large pore-size and thinner ligament in the matrix resulted in a larger latent heat. A similar analysis relating structural and thermal parameters will be carried out in our research, which will instead consider a metal foam matrix structure impregnated with a selected salt submitted to a high temperature.

3.2. Thermo-mechanical analysis

The thermo-mechanical behaviour analysis is important to predict the effect of various cycles of charging and discharging of

thermal energy when the PCM is subjected to high and low temperatures. It also provides information about how this condition influences the stress parameters. The purely mechanical behaviour of isolated porous structures in absence of temperature variation has been widely studied [51–53,66,67] to determine the tensile properties of these materials. The authors consider the understanding of the mechanical behaviour of metal foams a first step to later combine with thermal analysis; therefore the review of particularly relevant literature on this subject has been undertaken. Additionally, the thermo-mechanical review for both isolated porous material and in composite with PCM has also previously been presented.

3.2.1. Mechanical behaviour of metal foams

A mathematical modelling of an octahedral metal foam structure was built to determine how the characteristic parameters, like porosity, are related to the maximum nominal shearing stress [53]. The results show that, when the porous body endures the fracture resulting from shearing loads or from torsion, the maximum nominal shearing stress and the nominal torque for the porous component can be related to the porosity and the inherent characteristic parameters of the metal foam itself. From these mathematical relations, the loading criterions may be directly and conveniently achieved for these materials under the corresponding loads, respectively.

The tetrakaidecahedron geometry, which is the closest approximation used for an aluminium foam, has been mathematic and numerically modelled in order to study the metal's crushing behaviour [52]. An existing fully self-similar Deshpande and Fleck [68] constitutive model for metallic foams is modified assuming

a non-associated plastic flow rule and incremental proportional straining under proportional stressing concept. The research determined a force–deformation curve, a mean force and a folding pattern. The output of the numerical modelling has been compared with available experimental data and the results were found reliable.

3.2.1.1. Thermo-mechanical analysis of metal foams. An experimental and analytical study of the thermal conductivity of compressed expanded graphite (EG) foam was carried out in order to study the density relationships of thermal conductivity and elasticity modulus of compact EG [66]. The compacted EG critical density corresponding to the observed jump in the thermal conductivity coefficient and elasticity modulus was shown to depend on the expandable graphite preparation method, EG bulk density, and degree of dispersion.

A mathematical modelling and numerical simulation of a tetra-kaidecahedron open-cell was undertaken for the modelling and simulation of heat transfer enhancement and corresponding pressure drop [51]. A simplified analytical model based on diamond-shaped unit cells has been developed to predict the heat transfer capability of a foamed channel. The heat transfer rates predicted by the analytical model have been compared with available experimental data from other researchers [4] and favourable agreement has been obtained.

3.2.1.2. Thermo-mechanical analysis of metal foams impregnated with PCMs. The thermo-mechanical analysis of porous graphite impregnated with PCMs was also performed in order to develop of a mathematical model [67] of porous materials plastic behaviour. This research is focused on help understanding salt melting within the graphite matrices and for proposing reliable ways for composite materials improvement. The mathematical modelling was able to determine the relation between the pore-elastic-plastic deformation versus temperature and pressure time history, as well as liquid–crystals equilibrium conditions. An important observation was that, under melting, the salt volume expansion will be constrained by the graphite matrix and pressure in pores will thus increase. Main consequences of this pressurization are a progressive increase of the salt melting temperature and a progressive reduction of its latent heat. For melting progress, materials have to be heated up to a melting point which is continuously increasing. Hence, a significant part of the energy supplied to the material will be used to heat it up (sensible heat instead of latent heat). Control of graphite densification during materials elaboration would be an easy way for increasing porosity (voids) within the graphite matrix skeleton and hence to reduce its rigidity and to increase the pore wall thickness. However, this will also lead to a reduction of the effective thermal conductivity. Even though the porous material of this previous study slightly differs from a metal foam, the results could be considered as a preliminary approach of the interaction between the PCM and the embedded foam.

3.2.2. Modelling of heat transfer enhancement

In order to predict how different parameters influence the heat transfer rate in porous materials-PCMs composites, efforts in modelling the thermal conductivity can be divided into three categories: firstly, the mathematical, numerical and experimental modelling of graphite and metal foams in a low temperature range; secondly, mathematical modelling of graphite foam in a high temperature range; and finally, experimental research of metal foams in a high temperature range.

3.2.2.1. Low temperature analysis. The behaviour of graphite and metal foams impregnated with PCMs has been the subject of

a variety of studies in the last few years. The discussion of thermal conductivity, diffusivity, convection and radiation has been carried out in order to define the role of structural parameters in the heat transfer rate. Analytical studies found results indicating that the thermal conductivity of the composites can be 28–180 times higher than of the pure paraffin wax [64]. It was moreover found that the thermal diffusivity of the Paraffin-GF can be enhanced 190, 270, 500, and 570 times as compared with that of pure PCM [65].

The combination of an experimental and analytical model was undertaken in order to evaluate the influence of radiation on the heat transfer performance. The analysis showed that radiation accounts up to 50% to the apparent foam conductivity [69,70]. Reduced natural convection was spotted in water-saturated metal foams [58], leaving conduction and buoyant advection as the dominant modes of heat transfer. Suppressed natural convection was also identified in PCM-metal foam composites [71]. The suppression mechanism was given [71]: the PCM was of high viscosity and low thermal expansion coefficient, resulting in both a large resistance force and weak driving force of natural convection. However, relevant studies, combining experiments and numerical modelling demonstrated an opposite tendency in air-saturated metal foams and claimed that natural convection was very significant, accounting for up to 50% of the effective foam conductivity obtained at ambient pressure [72]. These findings are not contradictory, because air tends to have a lower flow resistance and higher buoyancy force due to its low viscosity and high thermal expansion coefficient.

For low temperature analysis, recent research additionally provides experimental, numerical and mathematical modelling of graphite and/or metal foams impregnated with paraffin. Main interest of those studies consists of improving the feasibility of porous material for heat transfer enhancement. A numerical modelling for copper foams was developed and showed that the addition of this type of metal structure to paraffin wax can increase the heat transfer rate in comparison to the pure PCM [73] by 3–10 times. An experimental study comparing copper and graphite foams performances showed that, for a heat storage system of given volume, the PCMs embedded with metal foams usually have higher heat storage capacities than the composites made of PCMs and expanded graphite, since expanded graphite is very low in density [74]. In addition, metal foam composites appeared to have better heat transfer performance than graphite composites, because metal foam composites have continuous inner structures to help evenly distribute heat in PCMs. The research demonstrated that the volumetric heat of fusion decreases with the increase of relative density of metal foam and the mass ratio of expanded graphite.

Finally, an interesting comparison of methods was provided for the mathematical modelling of an aluminium foam embedded in paraffin [75]. The study determined that the heat transfer modelled with a two-temperature model is a better method to predicting the behaviour of energy flux in the metal foam instead of previous studies assuming local thermal equilibrium.

3.2.2.2. High temperature analysis. There are a reduced number of investigations that focus on heat transfer through a porous material embedded in PCMs at high temperature. As occurred in low temperature based studies, the core interest of the investigations resides in proving the feasibility of porous material for increasing heat transfer rates through PCMs subjected to high temperature. Moreover, some of the research aims at establishing a comparison between graphite and copper foam performances for the above mentioned purpose.

A large scale experimentation of graphite and salt composite applied to a thermal solar plant showed a very relevant result [4]; salt leakage was observed during the first cycles of charging/

discharging of the PCM and, therefore, all contact surfaces between PCM and graphite foam were lost. An analysis showed that, under thermal cycling, salt leakage can be mainly attributed to impurities and remaining mechanical stresses. The result points to potential problems that shall be considered in the present and further investigations of metal foams behaviour at high temperatures.

A mathematical model especially relevant for our research was developed for a graphite and salt composite [67]. The methods used for this research were based on energy conservation equations, pressure-dependent liquid–crystal equilibriums, linear elasticity laws and Poiseuille-like flow. The model provided a broad poro-elasto-plastic analysis and was able to determine required actions for achieving more desirable properties of the composite, which are the reduction of the pore wall rigidity, the increase of the pore walls thickness, increasing pores connectivity or, in general, creating void space.

Two very recent high temperature based studies carried out experimentations using both graphite and copper foams filled with NaNO_3 . A significant advantage of copper foams over graphite in terms of improving heat transfer rates was identified [76]. The performance of the addition of porous materials was proved to increase heat transfer 2–5 times in comparison with pure PCM [49]. Both studies investigated the problem of suppression of natural convection in the liquid region and showed that corrosion stress problems are more intense for copper than for graphite foams.

From this literature review, it is clear that thermo-mechanical and structural parameters play an important role in the heat transfer behaviour of metal foam-PCM composites. However, the few existing approaches lack mathematical modelling to predict how the interaction of those particular parameters will affect the stability and energy flux through the composite subjected to high temperatures.

The present research addresses these issues and tries to present a novel approach to the thermal conductivity predictions by developing a model that incorporates all of the crucial aspects mentioned above and which influence the efficiency of charging and discharging processes of PCMs.

4. Conclusions and further research

The aim of this review was to critically examine the current state of art in order to delineate the required further development of a high temperature model of metal foam embedded with PCM. The parameters involved in the process of loading and releasing of thermal energy have to be investigated and adjustments to improve the material's heat flux behaviour have to be determined.

This paper is leading to focus on the study of one major thermal storage parameter: the rate of loading and releasing of energy in PCMs impregnated in metal foams, and the logical extension of this general work results in the study of (i) the metal foam structure characterization (ii) the analysis of the composites' thermo-mechanical behaviour, and (iii) the combination of these two particular topics to accurately analyse and predict heat transfer processes through copper foam structures embedded in PCMs.

Current research related to heat transfer enhancement by impregnating metal foam to PCMs at high temperatures relies only on experimental studies that were developed without the powerful aid of a mathematical and numerical modelling.

In order to achieve our objectives, research must analyse the thermo-mechanical stress in metal foam structures in order to quantify the influence of stress boundary effects on the effective heat flux. The stress analysis should define conductivity maps as function of pore-size and thickness. Additionally, it has to determine the latent heat storage response to a copper-like micro-structural characterization subjected to high temperature heating

conditions during normal operation of loading and releasing of thermal energy in salts. The research has to be carried out by linking each methodology duly selected and adapted for the above mentioned analysis, to then improve the knowledge and insight of heat transfer processes in metal foams impregnated with PCMs.

Metals have in general a good thermal conductivity, but it is not enough to consider metals as good materials because graphite has excellent conductivity also. Then we can consider also the good mechanical properties as elasticity of metals to support high volume expansion without cracking which is one problem of graphite matrix. Manufacturing metals as foams is correct way to profit better their thermo-mechanical properties.

Acknowledgements

This work is supported by the Centre for the Innovation in Energy (UAI, Chile), FONDECYT Chile (project number:1120490), UK Engineering and Physical Science Research Council (EPSRC grant number: EP/F061439/1), by the National Natural Science Foundation of China (Grant Nos: 51176110 and 51071184). The authors gratefully acknowledge support and advices from Dr. C.Y. Zhao of the School of Mechanical Engineering, Shanghai Jiaotong University, Shanghai 200240, China, and from Mr Y. Tuan of School of Engineering, University of Warwick, Coventry CV7 4AL, UK.

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