



Review

Review on thermal energy storage with phase change: materials, heat transfer analysis and applications

Belén Zalba ^{a,1}, José M^a Marín ^a, Luisa F. Cabeza ^{b,*},
Harald Mehling ^{c,2}

^a *Dpto. Ingeniería Mecánica, Campus Politécnico, Universidad de Zaragoza, EUITIZ “EDIFICIO B.3”
María de Luna 3 (Actur), 50015 Zaragoza, Spain*

^b *Dpt.d’Informàtica i Enginyeria Industrial, Escola, Universitària Politècnica, Universitat de Lleida, CREA, Jaume II,
69, 25001 Lleida, Spain*

^c *ZAE Bayern, Division 1: Energy Conversion and Storage, Walther-Meissner-Str. 6, 85748 Garching, Germany*

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Abstract

Thermal energy storage in general, and phase change materials (PCMs) in particular, have been a main topic in research for the last 20 years, but although the information is quantitatively enormous, it is also spread widely in the literature, and difficult to find. In this work, a review has been carried out of the history of thermal energy storage with solid–liquid phase change. Three aspects have been the focus of this review: materials, heat transfer and applications. The paper contains listed over 150 materials used in research as PCMs, and about 45 commercially available PCMs. The paper lists over 230 references.

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Keywords: PCM, phase change materials; LTES, latent thermal energy storage; Heat transfer

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* Corresponding author. Tel.: +34-973-702742; fax: +34-973-702702.

E-mail addresses: bzalba@posta.unizar.es (B. Zalba), lcabeza@diei.udl.es (L.F. Cabeza), mehling@muc.zae-bayern.de (H. Mehling).

¹ Tel.: +34-976-762566; fax: +34-976-762189.

² Tel.: +49-89-32944222; fax: +49-89-32944212.

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1. Introduction

Thermal energy storage (TES) in general, and phase change materials in particular, have been a main topic in research for the last 20 years, but although the information is quantitatively enormous, it is also spread widely in the literature, and difficult to find.

The work described below falls within an area of international interest as it deals with energy saving, the efficient and rational use of available resources and the optimum use of renewable energies. Within this framework, TES provides solutions in very specific areas:

- The time delay and available power between production or availability of energy and its consumption in receiving systems (solar energy, cogeneration, etc.)
- Security of energy supply (hospitals, computer centres, etc.)
- Thermal inertia and thermal protection

In the first case, applications related with the use of renewable energies are common, in particular the use of solar energy among others, although applications are also found in cogeneration

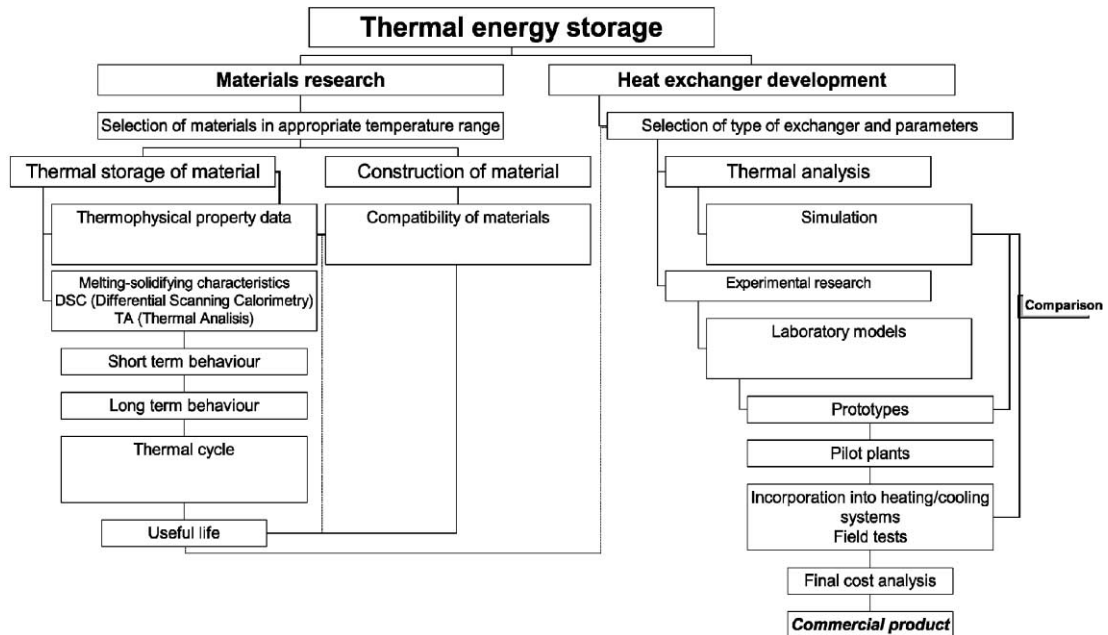


Fig. 1. Areas of research in thermal storage systems [1].

equipment or in installations with reduced prices for electrical energy consumed during off-peak hours. Nowadays, security of energy supply is often achieved with extra equipment. The use of phase change materials (PCMs) could either avoid or reduce this extra equipment. As it will be seen later in this paper, thermal inertia and thermal protection is the area where the PCMs have achieved a higher penetration in the market.

This paper provides a review of studies dealing with TES using phase change materials. The material in this review has been arranged within the main areas of work:

- Phase change materials
- Heat transfer analysis
- Applications

The first two areas cover the two fundamental aspects to be studied in a thermal storage system, the material and the heat-exchanger, as is shown in Fig. 1.

2. Phase change materials

2.1. Classification

In 1983 Abhat [1] gave a useful classification of the substances used for TES, shown in Fig. 2.

Among the most thorough references related with phase change materials, one can cite Abhat [1], Lane [2,3] and Dincer and Rosen [4]. These contain a complete review of the types of material

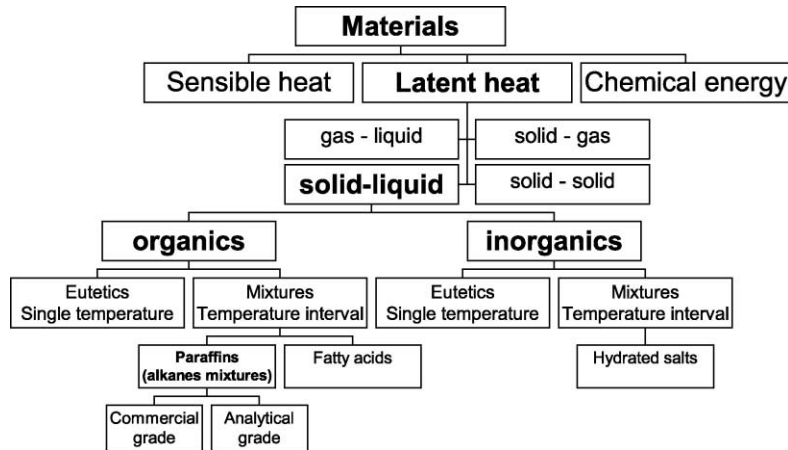


Fig. 2. Classification of energy storage materials [1].

which have been used, their classification, characteristics, advantages and disadvantages and the various experimental techniques used to determine the behaviour of these materials in melting and solidification.

2.1.1. Non-commercial/commercial materials

Many substances have been studied as potential PCMs, but only a few of them are commercialised as so.

Tables 1–6 present the different substances, eutectics and mixtures (inorganic, organic and fatty acids), that have been studied by different researchers for their potential use as PCMs. Some of their thermophysical properties are included (melting point, heat of fusion, thermal conductivity and density), although some authors give further information (congruent/incongruent melting, volume change, specific heat, etc.).

Table 7 shows a list of the commercial PCMs available in the market with their thermophysical properties as given by the companies (melting point, heat of fusion and density), and the company which is producing them.

2.1.2. Organic/inorganic materials

A comparison of the advantages and disadvantages of organic and inorganic materials is shown in Table 8.

Notable among inorganic materials are hydrated salts and their multiple applications in the field of solar energy storage [3,4]. In Chapter 1 of Lane [2] there is an extensive review of phase change materials and especially hydrated salts. Chapter 3 of the same work covers the different types of encapsulation and their compatibility with different materials.

A significant number of authors have based their work on organic materials such as alkanes, waxes or paraffins [46–52]. Within organic materials, there is a class called MCPAM (Phase change materials made up of molecular alloys), formed by alkane-based alloys which have the

Table 1
Inorganic substances with potential use as PCM

Compound	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m K)	Density (kg/m ³)
H ₂ O	0 [1,5]	333 [1] 334 [5]	0.612 (liquid, 20 °C) [1] 0.61 (30 °C) [5]	998 (liquid, 20 °C) [1] 996 (30 °C) [5] 917 (solid, 0 °C) [1]
LiClO ₃ · 3H ₂ O	8.1 [6,7]	253 [6]	n.a.	1720 [6]
ZnCl ₂ · 3H ₂ O	10 [8]	n.a.	n.a.	n.a.
K ₂ HPO ₄ · 6H ₂ O	13 [8]	n.a.	n.a.	n.a.
NaOH · 3½H ₂ O	15 [8] 15.4 [7]	n.a.	n.a.	n.a.
Na ₂ CrO ₄ · 10H ₂ O	18 [8]	n.a.	n.a.	n.a.
KF · 4H ₂ O	18.5 [1,6,7,9]	231 [1,6,9]	n.a.	1447 (liquid, 20 °C) [1] 1455 (solid, 18 °C) [1] 1480 [6]
Mn(NO ₃) ₂ · 6H ₂ O	25.8 [18]	125.9 [10]	n.a.	1738 (liquid, 20 °C) [10] 1728 (liquid, 40 °C) [10] 1795 (solid, 5 °C) [10]
CaCl ₂ · 6H ₂ O	29 [4,11] 29.2 [7] 29.6 [6] 29.7 [1,9] 30 [8] 29–39 [12]	190.8 [4,11] 171 [1,9] 174.4 [12] 192 [6]	0.540 (liquid, 38.7 °C) [4,11] 0.561 (liquid, 61.2 °C) [11] 1.088 (solid, 23 °C) [4,11]	1562 (liquid, 32 °C) [4,11] 1496 (liquid) [1] 1802 (solid, 24 °C) [4,11] 1710 (solid, 25 °C) [1] 1634 [12] 1620 [6]
LiNO ₃ · 3H ₂ O	30 [6]	296 [6]	n.a.	n.a.
Na ₂ SO ₄ · 10H ₂ O	32.4 [1,7,9] 32 [13] 31–32 [12]	254 [1,9] 251.1 [12]	0.544 [1]	1485 (solid) [1] 1458 [12]
Na ₂ CO ₃ · 10H ₂ O	32–36 [12] 33 [6,7]	246.5 [12] 247 [6]	n.a.	1442 [12]
CaBr ₂ · 6H ₂ O	34 [4,7,11]	115.5 [4,11]	n.a.	1956 (liquid, 35 °C) [4,11] 2194 (solid, 24 °C) [4,11]
Na ₂ HPO ₄ · 12H ₂ O	35.5 [8] 36 [12] 35[6,9] 35.2 [7]	265 [12] 280 [6] 281 [9]	n.a.	1522 [12]
Zn(NO ₃) ₂ · 6H ₂ O	36 [4,7,11] 36.4 [1,9]	146.9 [4,11] 147 [1,9]	0.464 (liquid, 39.9 °C) [4,11] 0.469 (liquid, 61.2 °C) [7]	1828 (liquid, 36 °C) [4,11] 1937 (solid, 24 °C) [4,11] 2065 (solid, 14 °C) [1]
KF · 2H ₂ O	41.4 [7]	n.a.	n.a.	n.a.
K(CH ₃ COO) · ½H ₂ O	42 [8]	n.a.	n.a.	n.a.
K ₃ PO ₄ · 7H ₂ O	45 [8]	n.a.	n.a.	n.a.
Zn(NO ₃) ₂ · 4H ₂ O	45.5 [8]	n.a.	n.a.	n.a.
Ca(NO ₃) ₂ · 4H ₂ O	42.7 [7] 47 [8]	n.a.	n.a.	n.a.
Na ₂ HPO ₄ · 7H ₂ O	48 [7]	n.a.	n.a.	n.a.

(continued on next page)

Table 1 (continued)

Compound	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m K)	Density (kg/m ³)
Na ₂ S ₂ O ₃ · 5H ₂ O	48 [1,6–8]	201 [1]	n.a.	1600 (solid) [1]
	48–49 [12]	209.3 [12] 187 [6]		1666 [12]
Zn(NO ₃) ₂ · 2H ₂ O	54 [8]	n.a.	n.a.	n.a.
NaOH · H ₂ O	58.0 [7]	n.a.	n.a.	n.a.
Na(CH ₃ COO) · 3H ₂ O	58 [6,13]	264 [14–20]	n.a.	1450 [6]
	58.4 [7,14–20]	226 [6]		
Cd(NO ₃) ₂ · 4H ₂ O	59.5 [7]	n.a.	n.a.	n.a.
Fe(NO ₃) ₂ · 6H ₂ O	60 [8]	n.a.	n.a.	n.a.
NaOH	64.3 [6]	227.6 [6]	n.a.	1690 [6]
Na ₂ B ₄ O ₇ · 10H ₂ O	68.1 [7]	n.a.	n.a.	n.a.
Na ₃ PO ₄ · 12H ₂ O	69 [7]	n.a.	n.a.	n.a.
Na ₂ P ₂ O ₇ · 10H ₂ O	70 [6]	184 [6]		n.a.
Ba(OH) ₂ · 8H ₂ O	78 [1,4,6,7,11,13]	265.7 [4,11]	0.653 (liquid, 85.7 °C) [4,11]	1937 (liquid, 84 °C) [4,11]
		267 [1]	0.678 (liquid, 98.2 °C) [11]	2070 (solid, 24 °C) [4,6,11]
		280 [6]	1.255 (solid, 23 °C) [4,11]	2180 (solid) [1]
AlK(SO ₄) ₂ · 12H ₂ O	80 [8]	n.a.	n.a.	n.a.
KAl(SO ₄) ₂ · 12H ₂ O	85.8 [7]	n.a.	n.a.	n.a.
Al ₂ (SO ₄) ₃ · 18H ₂ O	88 [7]	n.a.	n.a.	n.a.
Al(NO ₃) ₃ · 8H ₂ O	89 [8]	n.a.	n.a.	n.a.
Mg(NO ₃) ₂ · 6H ₂ O	89 [4,6,11] 90 [7,8]	162.8 [4,11] 149.5 [6]	0.490 (liquid, 95 °C) [4,11]	1550 (liquid, 94 °C) [4,11]
			0.502 (liquid, 110 °C) [11]	1636 (solid, 25 °C) [4,11]
			0.611 (solid, 37 °C) [4,11] 0.669 (solid, 55.6 °C) [11]	1640 [6]
(NH ₄)Al(SO ₄) · 6H ₂ O	95 [6,8]	269 [6]	n.a.	n.a.
Na ₂ S · 5½H ₂ O	97.5 [8]	n.a.	n.a.	n.a.
CaBr ₂ · 4H ₂ O	110 [8]	n.a.	n.a.	n.a.
Al ₂ (SO ₄) ₃ · 16H ₂ O	112 [8]	n.a.	n.a.	n.a.
MgCl ₂ · 6H ₂ O	117 [4,6,7,11] 115 [8] 116 [1]	168.6 [4,11] 165 [1,6]	0.570 (liquid, 120 °C) [4,11]	1450 (liquid, 120 °C) [4,11]
			0.598 (liquid, 140 °C) [11]	1442 (liquid, 78 °C) [1]
			0.694 (solid, 90 °C) [4,11] 0.704 (solid, 110 °C) [11]	1569 (solid, 20 °C) [4,11] 1570 (solid, 20 °C) [1]
Mg(NO ₃) ₂ · 2H ₂ O	130 [8]	n.a.	n.a.	n.a.
NaNO ₃	307 [21] 308 [22,23]	172 [21]	0.5 [22]	2260 [21]
		174 [23]		2257 [22]
		199 [22]		
KNO ₃	333 [22] 336 [23]	266 [22]	0.5 [23]	2.110 [23]
		116 [23]		
KOH	380 [22]	149.7 [22]	0.5 [22]	2.044 [22]
MgCl ₂	714 [21]	452 [21]	n.a.	2140 [21]
NaCl	800 [21]	492 [21]	5 [22]	2160 [21,22]
	802 [22]	466.7 [22]		

Table 1 (continued)

Compound	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m K)	Density (kg/m ³)
Na ₂ CO ₃	854 [22]	275.7 [22]	2 [22]	2.533 [22]
KF	857 [21]	452 [21]	n.a.	2370 [21]
K ₂ CO ₃	897 [22]	235.8 [22]	2 [22]	2.290 [22]

n.a.: not available.

advantage of being thermostable [53], that is, they allow alterations to the phase change temperature through their composition. There is abundant information on this subject in the literature [53–63].

As far as concerns the storage temperature or phase change, the heat transfer in accumulators can be improved choosing the PCM in such a way that its phase change temperature optimises the thermal gradient with respect to the substance with which the heat is being exchanged (Farid [46], Hassan [64], Strub [65]). For example, with paraffins and alkanes it is possible to vary the number of carbon atoms or form different molecular alloys which allows a practically continuous variation of the phase change temperature within certain ranges.

2.2. Thermophysical properties

It can be concluded from the information compiled that the main characteristics required of phase change materials are those indicated in Table 9.

2.2.1. Thermophysical properties determination

Speyer [66] gave a good overview of the thermal analysis methods in general, but also Eckert et al. [67] and should be mentioned. Naumann and Emons [7] and others [29,68] focussed their studies on thermal analysis methods for PCMs.

Analysis techniques used to study phase change are mainly conventional calorimetry, differential scanning calorimetry (DSC) and differential thermal analysis (DTA). Among studies relating to DSC, it is worth citing Flaherty [69] for characterisation of hydrocarbons and natural waxes, Giavarini [70] for characterisation of petroleum products and Salyer [47] for characterisation of paraffins.

As is mentioned in Gibbs [71], there is considerable uncertainty about the property values provided by manufacturers (who give values of pure substances) and it is therefore advisable to use DSC to obtain more accurate values.

Yinping [72] reviews the above-mentioned conventional methods of PCM property analysis and points out their limitations, of which the following stand out:

- Small quantities of sample are analysed (1–10 mg), although some behaviour of the PCMs depends on their quantity.
- The analysis instrumentation is complex and expensive.
- Phase change cannot be visually observed.

Table 2
Inorganic eutectics with potential use as PCM

Compound	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m K)	Density (kg/m ³)
66.6% CaCl ₂ · 6H ₂ O + 33.3% MgCl ₂ · 6H ₂ O	25 [6]	127 [6]	n.a.	1590 [6]
48% CaCl ₂ + 4.3% NaCl + 0.4% KCl + 47.3% H ₂ O	26.8 [1,6]	188.0 [6]	n.a.	1640 [6]
47% Ca(NO ₃) ₂ · 4H ₂ O + 33% Mg(NO ₃) ₂ · 6H ₂ O	30 [1]	136 [1]	n.a.	n.a.
60% Na(CH ₃ COO) · 3H ₂ O + 40% CO(NH ₂) ₂	31.5 [24] 30 [25]	226 [24] 200.5 [25]	n.a.	n.a.
61.5% Mg(NO ₃) ₂ · 6H ₂ O + 38.5% NH ₄ NO ₃	52 [11]	125.5 [11]	0.494 (liquid, 65.0 °C) [11] 0.515 (liquid, 88.0 °C) [11] 0.552 (solid, 36.0 °C) [11]	1515 (liquid, 65 °C) [11] 1596 (solid, 20 °C) [11]
58.7% Mg(NO ₃) ₂ · 6H ₂ O + 41.3% MgCl ₂ · 6H ₂ O	59 [11] 58 [6]	132.2 [11] 132 [6]	0.510 (liquid, 65.0 °C) [11] 0.565 (liquid, 85.0 °C) [11] 0.678 (solid, 38.0 °C) [11] 0.678 (solid, 53.0 °C) [11]	1550 (liquid, 50 °C) [11] 1630 (solid, 24 °C) [11]
53% Mg(NO ₃) ₂ · 6H ₂ O + 47% Al(NO ₃) ₂ · 9H ₂ O	61 [1]	148 [1]	n.a.	n.a.
14% LiNO ₃ + 86% Mg(NO ₃) ₂ · 6H ₂ O	72 [6]	>180 [6]	n.a.	1590 (liquid) [6] 1610 (solid) [6]
66.6% urea + 33.4% NH ₄ Br	76 [11]	161.0 [11]	0.331 (liquid, 79.8 °C) [11] 0.324 (liquid, 92.5 °C) [11] 0.649 (solid, 39.0 °C) [11] 0.682 (solid, 65 °C) [11]	1440 (liquid, 85 °C) [11] 1548 (solid, 24 °C) [11]
11.8% NaF + 54.3% KF + 26.6% LiF + 7.3% MgF ₂	449 [26]	n.a.	n.a.	2160 (liquid) [26]
35.1% LiF + 38.4% NaF + 26.5% CaF ₂	615 [26]	n.a.	n.a.	2225 (liquid) [26] 2820 (solid, 25 °C) [26]
32.5% LiF + 50.5% NaF + 17.0% MgF ₂	632 [26]	n.a.	n.a.	2105 (liquid) [26] 2810 (solid, 25 °C) [26]
51.8% NaF + 34.0% CaF ₂ + 14.2% MgF ₂	645 [26]	n.a.	n.a.	2370 (liquid) [26] 2970 (solid, 25 °C) [26]
48.1% LiF + 51.9% NaF	652 [26]	n.a.	n.a.	1930 (liquid) [26] 2720 (solid, 25 °C) [26]
63.8% KF + 27.9% NaF + 8.3% MgF ₂	685 [26]	n.a.	n.a.	2090 (liquid) [26]
45.8% LiF + 54.2% MgF ₂	746 [26]	n.a.	n.a.	2305 (liquid) [26] 2880 (solid, 25 °C) [26]
53.6% NaF + 28.6% MgF ₂ + 17.8% KF	809 [26]	n.a.	n.a.	2110 (liquid) [26] 2850 (solid, 25 °C) [26]
66.9% NaF + 33.1% MgF ₂	832 [26]	n.a.	n.a.	2190 (liquid) [26] 2940 (solid, 25 °C) [26]

% in weight; n.a.: not available.

Yinping proposes a simple method for determining phase change temperature, undercooling, enthalpy, specific heat, and thermal conductivity in solid and liquid phases. Temperature–time

Table 3
Non-eutectic mixtures of inorganic substances with potential use as PCM

Compound	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m K)	Density (kg/m ³)
H ₂ O + polyacrylamid	0 [5]	292 [5]	0.486 (30 °C) [5]	1047 (30 °C) [5]
50% Na(CH ₃ COO) · 3H ₂ O + 50% HCONH ₂	40.5 [27]	255 [27]	n.a.	n.a.
Mg(NO ₃) ₂ · 6H ₂ O/ Mg(NO ₃) ₂ · 2H ₂ O	55.5 [8]	n.a.	n.a.	n.a.
KOH · H ₂ O/KOH	99 [8]	n.a.	n.a.	
68.1% KCl + 31.9% ZnCl ₂	235 [21]	198 [21]	n.a.	2480 [21]
38.5% MgCl + 61.5% NaCl	435 [21]	328 [21]	n.a.	2160 [21]
Salt-ceramics NaCO ₃ –BaCO ₃ /MgO	500–850 [22]	415.4 [22]	5 [22]	2.600 [22]

% in weight; n.a.: not available.

graphs are drawn and properties evaluated for comparison with the graphs of the other known materials are used (usually pure water) as reference.

Marín et al. [73] developed a further evaluation procedure to determine specific heat and enthalpy as temperature dependent values. The results obtained are presented in the form of enthalpy–temperature curves, and an experimental improvement is proposed.

Another method for determining thermal conductivity in PCM at temperatures around phase change temperature is established in Delaunay [74]. This method is based on analysing one-dimensional conduction in a cylinder. Various alternatives are proposed in the literature for the enhancement of thermal conductivity such as increasing the heat transfer surface, inserting metallic fins (Sadasuke [75]) or adding metallic additives (Bugaje [76]). In Manoo [77] there are some interesting charts relating to variations in conductivity, density and enthalpy against temperature for some paraffins.

2.3. Long term stability

Insufficient long term stability of the storage materials and containers is a problem that has limited widespread use of latent heat stores. This poor stability is due to two factors: poor stability of the materials properties due to thermal cycling, and/or corrosion between the PCM and the container.

2.3.1. Stability of the PCM-container system

A relevant aspect is the useful life of these systems, and the number of cycles they can withstand without any degrading of their properties. Hadjieva [48] uses three paraffin mixtures; the lack of effect of the cycles on the properties of paraffin is verified. Other authors, such as Gibbs [71], also confirm that neither the cycles nor contact with metals degrade the thermal behaviour of paraffin and that they therefore have excellent thermal stability.

Table 4
Organic substances with potential use as PCM

Compound	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m K)	Density (kg/m ³)
Paraffin C ₁₄	4.5 [1]	165 [1]	n.a.	n.a.
Paraffin C ₁₅ –C ₁₆	8 [1]	153 [1]	n.a.	n.a.
Polyglycol E400	8 [4,11]	99.6 [4,11]	0.187 (liquid, 38.6 °C) [4,11] 0.185 (liquid, 69.9 °C) [11]	1125 (liquid, 25 °C) [4,11] 1228 (solid, 3 °C) [4,11]
Dimethyl-sulfoxide (DMS)	16.5 [28]	85.7 [28]	n.a.	1009 (solid and liquid) [28]
Paraffin C ₁₆ –C ₁₈	20–22 [29]	152 [29]	n.a.	n.a.
Polyglycol E600	22 [4,11]	127.2 [4,11]	0.189 (liquid, 38.6 °C) [4,11] 0.187 (liquid, 67.0 °C) [11]	1126 (liquid, 25 °C) [4,11] 1232 (solid, 4 °C) [4,11]
Paraffin C ₁₃ –C ₂₄	22–24 [1]	189 [1]	0.21 (solid) [1]	0.760 (liquid, 70 °C) [1] 0.900 (solid, 20 °C) [1]
1-Dodecanol	26 [9]	200 [9]	n.a.	n.a.
Paraffin C ₁₈	28 [1] 27.5 [30]	244 [1] 243.5 [30]	0.148 (liquid, 40 °C) [30] 0.15 (solid) [1] 0.358 (solid, 25 °C) [30]	0.774 (liquid, 70 °C) [1] 0.814 (solid, 20 °C) [1]
1-Tetradecanol	38 [9]	205 [9]		
Paraffin C ₁₆ –C ₂₈	42–44 [1]	189 [1]	0.21 (solid) [1]	0.765 (liquid, 70 °C) [1] 0.910 (solid, 20 °C) [1]
Paraffin C ₂₀ –C ₃₃	48–50 [1]	189 [1]	0.21 (solid) [1]	0.769 (liquid, 70 °C) [1] 0.912 (solid, 20 °C) [1]
Paraffin C ₂₂ –C ₄₅	58–60 [1]	189 [1]	0.21 (solid) [1]	0.795 (liquid, 70 °C) [1] 0.920 (solid, 20 °C) [1]
Paraffin wax	64 [4,11]	173.6 [4,11] 266 [6]	0.167 (liquid, 63.5 °C) [4,11] 0.346 (solid, 33.6 °C) [4,11] 0.339 (solid, 45.7 °C) [11]	790 (liquid, 65 °C) [4,11] 916 (solid, 24 °C) [4,11]
Polyglycol E6000	66 [4,11]	190.0 [4,11]	n.a.	1085 (liquid, 70 °C) [4,11] 1212 (solid, 25 °C) [4,11]
Paraffin C ₂₁ –C ₅₀	66–68 [1]	189 [1]	0.21 (solid) [1]	0.830 (liquid, 70 °C) [1] 0.930 (solid, 20 °C) [1]
Biphenyl	71 [4,11]	119.2 [4,11]	n.a.	991 (liquid, 73 °C) [4,11] 1166 (solid, 24 °C) [11]
Propionamide	79 [11]	168.2 [11]	n.a.	n.a.
Naphthalene	80 [4,11]	147.7 [4,11]	0.132 (liquid, 83.8 °C) [4,11] 0.341 (solid, 49.9 °C) [4,11] 0.310 (solid, 66.6 °C) [11]	976 (liquid, 84 °C) [4,11] 1145 (solid, 20 °C) [4,11]
Erythritol	118.0 [31]	339.8 [31]	0.326 (liquid, 140 °C) [31] 0.733 (solid, 20 °C) [31]	1300 (liquid, 140 °C) [31] 1480 (solid, 20 °C) [31]
HDPE	100–150 [32]	200 [32]	n.a.	n.a.
Trans-1,4-polybutadiene (TPB)	145 [33]	144 [33]	n.a.	n.a.

n.a.: not available.

2.3.2. Corrosion of the materials

Most references on corrosion tests using salt hydrates were performed with diluted salt hydrates, as typically used in the chemical industry, and only a few presented results, usually based

Table 5
Organic eutectics with potential use as PCM

Compound	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m K)	Density (kg/m ³)
37.5% Urea + 63.5% acetamide	53 [1]	n.a.	n.a.	n.a.
67.1% Naphthalene + 32.9% benzoic acid	67 [11]	123.4 [11]	0.136 (liquid, 78.5 °C) [11] 0.130 (liquid, 100 °C) [11] 0.282 (solid, 38 °C) [11] 0.257 (solid, 52 °C) [11]	n.a.

% in weight; n.a.: not available.

on observation over experimental set-ups [78,79]. Porisini [80] tested the corrosion of four commercially available salt hydrates used as PCMs in 1988. Recently, Cabeza et al. [81–84] studied corrosion resistance of five common metals (aluminium, brass, copper, steel and stainless steel) in contact with molten salt hydrates (zinc nitrate hexahydrate, sodium hydrogen phosphate dodecahydrate, calcium chloride hexahydrate, sodium carbonate, potassium hydrogen carbonate, potassium chloride, water, sodium acetate trihydrate, and sodium thiosulphate pentahydrate) in an immersion corrosion test.

Some investigations have been concerned with corrosion of molten salts at high temperature. Already in 1980, Heine et al. [21] studied the corrosion performance of six molten salts melting between 235 and 857 °C vs. four metals used at these temperatures.

2.3.3. Encapsulation of the materials

The encapsulation of the PCM has developed interest in several researchers. Advantages and disadvantages of different geometries of PCM encapsulation with different materials and their compatibility was discussed by Lane [3]. The freezing and melting processes of water contained in spherical elements was studied experimentally by Eames et al. [85], proposing semi empirical equations that allow the mass of ice within a sphere to be predicted at any time during the freezing or melting processes. Earlier, Bedecarrats et al. [86,87] and Alloncle [88], studied the crystallization process of an organic eutectic in a spherical encapsulation.

For the use of PCM in buildings applications, an encapsulation of PCM (50–80%) with unsaturated polyester matrix (45–10%), and water (5–10%) was studied by Morikama et al. [89]. Polymerisation of PCMs has been also studied for other applications, like insulation materials for use in clothing or bedding articles [90]. In the same area, Inaba [91] and Lee and Choi [92] propose using the storage substance integrated with the building materials without encapsulation (“Shape-stabilised paraffin”: 74% paraffin + 26% high-density polyethylene (HDPE)). Structural stability is achieved using HDPE which retains the paraffin when in liquid phase.

Revankar et al. studied the presence of concentrated voids in encapsulated PCM use for space-based heat exchangers [93].

For many applications, PCMs are microencapsulated, and this has been studied by several researchers [94] and developed by companies like BASF [95]. Nevertheless, the potential use of microencapsulated PCMs in various thermal control applications is limited to some extent by

Table 6
Fatty acids with potential use as PCM

Compound	Melting temperature (°C)	Heat of fusion (kJ/kg)	Thermal conductivity (W/m K)	Density (kg/m ³)
Propyl palmitate	10 [9]	186 [9]	n.a.	n.a.
Isopropyl palmitate	11 [34]	95–100 [34]	n.a.	n.a.
Capric–lauric acid + pentadecane (90:10)	13.3 [35]	142.2 [35]	n.a.	n.a.
Isopropyl stearate	14–18 [34]	140–142 [34]	n.a.	n.a.
Caprylic acid	16 [4,11]	148.5 [4,11]	0.149 (liquid, 38.6 °C) [4,11]	901 (liquid, 30 °C) [4,11]
	16.3 [1]	149 [1]	0.145 (liquid, 67.7 °C) [11]	862 (liquid, 80 °C) [1]
			0.148 (liquid, 20 °C) [1]	981 (solid, 13 °C) [4,11]
				1033 (solid, 10 °C) [1]
Capric–lauric acid (65 mol%–35 mol%)	18.0 [36]	148 [36]	n.a.	n.a.
Butyl stearate	19 [9]	140 [9] 123–200 [34]	n.a.	n.a.
Capric–lauric acid (45–55%)	21 [9]	143 [9]	n.a.	n.a.
Dimethyl sabacate	21 [34]	120–135 [34]	n.a.	n.a.
34% Mistic acid + 66% Capric acid	24 [11]	147.7 [11]	0.164 (liquid, 39.1 °C) [11]	888 (liquid, 25 °C) [11]
			0.154 (liquid, 61.2 °C) [11]	1018 (solid, 1 °C) [11]
Vinyl stearate	27–29 [34]	122 [34]	n.a.	n.a.
Capric acid	32 [4,11]	152.7 [4,11]	0.153 (liquid, 38.5 °C) [4,11]	878 (liquid, 45 °C) [4,11]
	31.5 [1]	153 [1]	0.152 (liquid, 55.5 °C) [11]	886 (liquid, 40 °C) [1]
			0.149 (liquid, 40 °C) [1]	1004 (solid, 24 °C) [4,11]
Methyl-12 hydroxy-stearate	42–43 [34]	120–126 [34]	n.a.	n.a.
Lauric acid	42–44 [1] 44 [11]	178 [1] 177.4 [11]	0.147(liquid, 50 °C) [1]	862 (liquid, 60 °C) [11] 870 (liquid, 50 °C) [1] 1007 (solid, 24 °C) [11]
Myristic acid	49–51 [37] 54 [1]	204.5 [37] 187 [1]	n.a.	861 (liquid, 55 °C) [11] 844 (liquid, 80 °C) [1]
	58 [11]	186.6 [11]		990 (solid, 24 °C) [11]
Palmitic acid	64 [4,11]	185.4 [4,11]	0.162 (liquid, 68.4 °C) [4,11]	850 (liquid, 65 °C) [4,11]
	61 [38,39]	203.4 [38,39]	0.159 (liquid, 80.1 °C) [11]	847 (liquid, 80 °C) [1]
	63 [1]	187 [1]	0.165 (liquid, 80 °C) [1]	989 (solid, 24 °C) [4,11]
Stearic acid	69 [4,11]	202.5 [4,11]	0.172 (liquid, 70 °C) [1]	848 (liquid, 70 °C) [4,11]
	60–61 [39,40] 70 [1]	186.5 [39,40] 203 [1]		965 (solid, 24 °C) [4,11]

% in weight; n.a.: not available.

their cost. However, because the performance of thermal control for space applications is so important and because costs are less important, several authors believe that the development of such PCMs could be a milestone for space technology [96].

Table 7
Commercial PCMs available in the market

PCM name	Type of product	Melting temperature (°C)	Heat of fusion (kJ/kg)	Density (kg/m ³)	Source
SN33	Salt solution	−33	245	1.24	Cristopia [41]
TH-31	n.a.	−31	131	n.a.	TEAP [42]
SN29	Salt solution	−29	233	1.15	Cristopia [41]
SN26	Salt solution	−26	268	1.21	Cristopia [41]
TH-21	n.a.	−21	222	n.a.	TEAP [42]
SN21	Salt solution	−21	240	1.12	Cristopia [41]
STL-21	Salt solution	−21	240	1.12	Mitsubishi Chemical [43]
SN18	Salt solution	−18	268	1.21	Cristopia [41]
TH-16	n.a.	−16	289	n.a.	TEAP [42]
STL-16	n.a.	−16	n.a.	n.a.	Mitsubishi Chemical [43]
SN15	Salt solution	−15	311	1.02	Cristopia [41]
SN12	Salt solution	−12	306	1.06	Cristopia [41]
STLN10	Salt solution	−11	271	1.05	Mitsubishi Chemical [43]
SN10	Salt solution	−11	310	1.11	Cristopia [41]
TH-10	n.a.	−10	283	n.a.	TEAP [42]
STL-6	Salt solution	−6	284	1.07	Mitsubishi Chemical [43]
SN06	Salt solution	−6	284	1.07	Cristopia [41]
TH-4	n.a.	−4	286	n.a.	TEAP [42]
STL-3	Saltsolution	−3	328	1.01	Mitsubishi Chemical [43]
SN03	Saltsolution	−3	328	1.01	Cristopia [41]
ClimSel C 7	n.a.	7	130	n.a.	Climator [44]
RT5	Paraffin	9	205	n.a.	Rubitherm GmbH [45]
ClimSel C 15	n.a.	15	130	n.a.	Climator [44]
ClimSel C 23	Salt hydrate	23	148	1.48	Climator [44]
RT25	Paraffin	26	232		Rubitherm GmbH [45]
STL27	Salt hydrate	27	213	1.09	Mitsubishi Chemical [43]
S27	Salt hydrate	27	207	1.47	Cristopia [41]
RT30	Paraffin	28	206	n.a.	Rubitherm GmbH [45]
TH29	Salt hydrate	29	188	n.a.	TEAP [42]
ClimSel C 32	Salt hydrate	32	212	1.45	Climator [44]
RT40	Paraffin	43	181	n.a.	Rubitherm GmbH [45]
STL47	Salt hydrate	47	221	1.34	Mitsubishi Chemical [43]
ClimSel C 48	n.a.	48	227	1.36	Climator [44]
STL52	Salt hydrate	52	201	1.3	Mitsubishi Chemical [43]
RT50	Paraffin	54	195	n.a.	Rubitherm GmbH [45]
STL55	Salt hydrate	55	242	1.29	Mitsubishi Chemical [43]
TH58	n.a.	58	226	n.a.	TEAP [42]
ClimSel C 58	n.a.	58	259	1.46	Climator [44]
RT65	Paraffin	64	207		Rubitherm GmbH [45]
ClimSel C 70	n.a.	70	194	1.7	Climator [44]
PCM72	Salt hydrate	72	n.a.	n.a.	Merck KgaA [6]
RT80	Paraffin	79	209	n.a.	Rubitherm GmbH [45]
TH89	n.a.	89	149	n.a.	TEAP [42]
RT90	Paraffin	90	197	n.a.	Rubitherm GmbH [45]
RT110	Paraffin	112	213	n.a.	Rubitherm GmbH [45]

n.a.: not available.

Table 8
Comparison of organic and inorganic materials for heat storage

Organics	Inorganics
Advantages No corrosives Low or none undercooling Chemical and thermal stability	Advantages Greater phase change enthalpy
Disadvantages Lower phase change enthalpy Low thermal conductivity Inflammability	Disadvantages Undercooling Corrosion Phase separation Phase segregation, lack of thermal stability

Table 9
Important characteristics of energy storage materials

Thermal properties	Physical properties	Chemical properties	Economic properties
Phase change temperature fitted to application	Low density variation	Stability	Cheap and abundant
High change of enthalpy near temperature of use	High density	No phase separation Compatibility with container materials	
High thermal conductivity in both liquid and solid phases (although not always)	Small or no undercooling	Non-toxic, non-flammable, non-polluting	

3. Heat transfer

3.1. Theory and simulation

As regards the thermal gradient, information about the analysis of irreversibilities and the application of the second principle of thermodynamics can be found in articles by Strub [65] and Bejan [97], and a whole review in Chapter 9 of Dincer and Rosen [4]. Studies of these latter authors show that the use of exergy is very important in developing a good understanding of the thermodynamic behaviour of TES systems, and for rationally assessing, comparing and improving their efficiencies. In particular, the use of exergy analysis is important because it clearly takes into account the loss of availability and temperature of heat in storage operations, and hence it more correctly reflects the thermodynamic and economic value of the storage operation.

3.1.1. Moving boundary problems

The analysis of heat transfer problems in melting and solidification processes, called moving boundary problems in scientific literature, is especially complicated due to the fact that the solid–liquid boundary moves depending on the speed at which the latent heat is absorbed or lost at the

boundary, so that the position of the boundary is not known a priori and forms part of the solution.

A review on analytical/numerical and experimental work in the area of phase change, specifically freezing and melting processes was carried out by Eckert et al. in 1994 [67]. They divided the review in melting and freezing of spheres, cylinders and slabs; Stefan problems; ice formation in porous materials; contact melting; and solidification during casting.

When the substance that solidifies is pure, the solidification occurs at a single temperature, while in the opposite case (with mixtures, alloys and impure materials) the solidification takes place over a range of temperatures, and therefore there appears a two-phase zone (a “mushy region”) between the solid and liquid zones. In this latter case, it is appropriate to consider the energy equation in terms of enthalpy which, if the advective movements in the inner of the liquid are disregarded, is expressed mathematically as:

$$\rho \frac{\partial h}{\partial t} = \nabla \cdot (\lambda \cdot \nabla T)$$

The solution of this equation obviously requires knowledge of the enthalpy–temperature functional dependency, which for an impure substance is as shown in Fig. 3. Similarly, it is necessary to know the function relating the thermal conductivity and the temperature.

The main advantages of this procedure are:

- The equation is directly applicable to the three phases.
- The temperature is determined at each point and the value of the thermophysical properties can be evaluated.
- Finally, according to the temperature field, it is possible to ascertain the position of the two boundaries if so desired, although as indicated above this is not necessary.

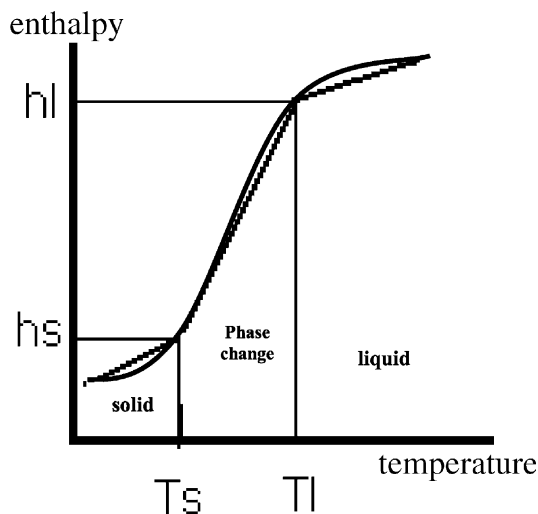


Fig. 3. Enthalpy variation with temperature.

3.1.2. Numerical solution considering only conduction

Although the dominant heat transfer mechanisms are conduction and natural convection in liquid phase, the earliest literature analyses heat transfer basically by considering one-dimensional conduction in pure substances. The first studies were by Lamé and Clapeyron in 1831 and Stefan in 1891, concerning ice formation. In 1912 the results of F. Neuman were published, establishing precise solutions to more general phase change problems. In 1943, London and Seban [98] analysed the process of ice formation for different geometries (cylinder, sphere, and flat plate). This study is very interesting although it was later disputed by Shamsundar [99] who asserted that London's one-dimensional formulation led to errors increasing with the progress of the solidification process and proposed a two-dimensional formulation for cylinders.

In 1970, Lazaridis [100] put forward a study of the relative importance of conduction and convection. Shamsundar and Sparrow [101] demonstrated the equivalence between the energy conservation equation applied in the three zones (solid, liquid, and solid/liquid) and the enthalpy model. These are solved through a finite differential method and the solidification is analysed in a square plate cooled by means of convection. This method is valid both for phase change in a single temperature and for phase change in a range of temperatures (mixtures or alloys). Among the hypotheses in this work, it can be pointed out that the authors do not consider convection in the melting phase and assume the solid and liquid densities to be equal and uniform. Later [102], they evaluated the effects of density change. In their conclusions, the relation between the heat transfer speed and the Biot number, linked with convection of the heat-carrier fluid, was already presented. Goodling [103] resolved a one-dimensional geometry outward solidification in a cylinder with a constant heat flow in the inner wall, the solution being given by the finite difference method applied to the temperature.

Meyer [104] studied the problem of phase change conduction, establishing that the classic Stefan problem implied the resolution of the temperature range and carrying out a review and comparison of explicit and implicit methods. The same year, Marshall published a work [105] studying natural convection effects in an annular geometry using hydrated salts and waxes/paraffins. He showed that the existence of natural convection significantly reduced the time necessary for melting, and gave recommendations for making use of natural convection especially with substances of low thermal conductivity (paraffins).

Bathelt [106] worked with heptadecane ($C_{17}H_{36}$) and studied solidification around a horizontal cylinder. Using photographs, he showed the important role of natural convection, which increases with time and produces an increase in the average radius of solidification (non-concentric). This two-dimensional behaviour for this geometry has also been confirmed by other authors [30,107].

Shamsundar and Srinivasan [108] analysed a heat exchanger of shell and tubes, and proposed a two-dimensional analysis [99], also taking into consideration the axial variation of the temperature, thus approaching a three-dimensional analysis. In 1981 Sparrow [109] analysed solidification on the outside of a tube carrying coolant inside, and confirmed the influence of the axial temperature variation of the coolant. He proposed an analytical solution providing initial values for the numerical method in which the moving boundary is immobilized by a transformation of coordinates. As a continuation of previous works, Shamsundar in 1981 [110] studied the influence of change in volume on phase change in the range of 10–20%. This involves the formation of cavities in the top part through which it is supposed there is no heat transfer (an additional adiabatic wall), so the usefulness of the methodology is therefore justified although there is density change

in the solidification. The same author in 1982 [111] developed analytical solutions and evaluated the resulting formulation using results obtained with numerical methods given in previous articles [109].

In 1983 Achard et al. [112] carried out a thermal storage experimental study on a test bench, using an immersed tubular heat exchanger in the PCM, both with salt hydrates and with fatty acids. They also developed a theoretical study using the enthalpy method and solved by means of finite differences, disregarding the convection effect. In the conclusion the theoretical and experimental results were compared and significant discrepancies found in the melting. It was therefore deduced that it is necessary to consider natural convection in the liquid.

Hunter in 1989 [113] and Amdjadi in 1990 [114] confirmed that the enthalpy method is the most suitable for real substances provided that there is no alteration to the numerical scheme in the boundary. Amdjadi added that if the material has hysteresis, it is necessary to rearrange or adjust the method. In this later work the finite differences method is used with a variable time step, adjusting it at each moment according to the stage of the phase change process. In 1999, Banaszek et al. [115,116] studied experimentally and numerically solid–liquid phase change in a spiral TES unit.

3.1.3. Numerical solution considering also convection

The first publications that include the convection heat transfer mechanism are Sparrow et al. [117] and Bathelt et al. [118]. An interesting article about convection is by Gobin [119] whose objective is to determine the influence of natural convection on the melting process. To model these processes, some articles [120–122] include the influence of the convection considering an effective thermal conductivity:

$$\frac{\lambda_e}{\lambda_l} = cRa^n$$

Özsisik [123] includes a classification of the various solution methods:

1. Exact solutions, limited to a few idealised situations.
2. Integral method. One-dimensional: solution of an integral equation to localise the boundary [124].
3. Heat moving source method.
4. Perturbation method [124].
5. Electrical analogy (this is being replaced by numerical methods owing to the availability of powerful computers).
6. Finite differences method.
7. Finite elements method.

Completing this classification, Ismail et al. [125] compare the results obtained with four different numerical methods, that is, the continuous solid phase models, Schumann's model, the single phase models and the thermal diffusion models or models with thermal gradient inside the particles. The authors evaluate the models in relation to the computational time consumed to solve a specific test problem and then compare them in relation to the influence to different factors. Also Ismail et al. in another publication [126] divide the numerical methods for the

solution of phase change problems into two groups: fixed grid methods based on the enthalpy concept, and moving grid methods utilizing the interface immobilization technique. Furzerland [127] compared the two methods for the solution of a specific test problem of one dimension and heat transfer by pure convection. One of this conclusions is that the enthalpy method is easy to program and more suitable for PCM with a range of fusion temperatures.

3.1.4. Numerical simulation in different heat exchanger geometries

Dincer and Rosen [4] deal with the problems of heat transfer with phase change materials in simple and complex geometries and around isothermal finned cylinders. The results are presented and validated with actual and existing data.

Lacroix [128,129] solved the problem of fusion in a rectangular cavity including the natural convection effects using a methodology similar to the front immobilization technique. He used a system of coordinates adjusted to the body obtained normally from the solution of differential equations, where the irregular domain is transformed into a simpler one. As this process is done for each time interval, an algebraic generator was used for the new system. Later Lacroix and Voller [130] performed a study comparing methods of solution of thermal phase change problems in a rectangular cavity. They compared the finite volume method with the enthalpic formulation and the method of body-fitted coordinates. As a result they concluded that the enthalpic method may require a fine grid in problems of phase change in a single temperature (such as water), while the limiting factor in the body-fitted coordinate method is the need to use a coordinate generator at each time increment, which would be complicated in cases of complex geometries.

The complexity of the equations means that the only generally applicable mathematical approach is that of numerical methods. One of the methods that appears more regularly in the literature is finite differences. Shamsundar and Sparrow [101,102] apply this method to the resolution of the enthalpy equation in the solidification of a flat plate. A much more comprehensive review of these methods can be found in Shamsundar [99,131,132] where they are applied to the case of a square geometry.

Works by Costa et al. [133] study numerically a two-dimensional rectangular area, using energy equations in solid and liquid phases, continuity, momentum and Stefan's equation in the boundary. Three PCM are analysed: paraffin (*n*-octadecanol) and metals (gallium and tin). They put forward a numerical resolution method called SIMPLEC (semi-implicit method for pressure-linked equations consistent) and compare the results with those obtained in the literature. In the case of octadecanol, there is poor agreement with the experimental results in the upper zone where the liquid which melts at the sides fills the upper empty cavity and accelerates melting in this area. Costa [133,134] indicates that the reasons of the discrepancies between the experimental and theoretical results are due to thermal inertia, instability in the systems, thermal losses, lack of reliable information about the physical properties of the materials, three-dimensional behaviour, consideration of constant thermophysical properties, variations in density, long calculation periods and significant variations in viscosity with the temperature.

Another group of articles in the literature simulates the global behaviour of the system, for example Carey [135] in "The control of ice storage systems" integrates the behaviour of the building, the storage and the cooling machine.

As Lacroix states in Dincer and Rosen [4], the mathematical complexity of the heat transfer models augments as the emphasis is placed on the physical phenomena occurring inside the PCM.

In the porous medium approach, models focus on the overall thermal behaviour of the latent heat TES system. The details of the heat transfer and phase change phenomena inside individual PCM capsules are ignored (or lumped into empirical coefficients), and the resulting mathematical models are very simple. At the other end of the spectrum, models on convection dominated phase change attempt to predict the heat transfer and the buoyancy driven flows inside the PCM capsules. The resulting mathematical models are, in this case, far more elaborated. Both approaches are very useful as they provide complementary information to the designer. An example in using two complementary approximations can be found in Lacroix et al. [136–139]. In spite of the impressive number of articles published on the subject over the last 15 years, modelling LHTES systems remains a challenging task.

3.2. Heat transfer enhancement

There are several methods to enhance the heat transfer in a latent heat thermal store. The use of finned tubes with different configurations has been proposed by various researchers such as Abhat et al. [140], Morcos et al. [141], Sadasuke [75], Costa et al. [142], Padmanabhan [143], Velraj [144,145] and Ismail et al. [146] use finned tubes in thermal storage systems.

Several other heat transfer enhancement techniques have been reported. Siegel [147] studied the improvement in solidification rate in molten salt dispersed with high conductivity particles. Another method used is to embed the PCM in a metal matrix structure [32,148–151]. The use of thin aluminium plates filled with PCM was developed by Bauer and Wirtz [152].

Mehling et al. [153–156] and Py et al. [157] proposed a graphite-compound-material, where the PCM is embedded inside a graphite matrix. The main advantage of such a material is the increase in heat conductivity in the PCM without much reduction in energy storage, but other advantages are the decrease in subcooling of salt hydrates and the decrease of volume change in paraffins.

The use of graphite as heat transfer enhancement material has also been studied by other researchers, such as Fukai et al. [158–160]. They developed brushes made of carbon fibres. The feature of this method is that the volume fraction of the fibres is accurately and easily controlled and that the fibres with low volume fraction are entirely dispersed in the PCM. Xiao et al. [161] developed a composite based on paraffin, styrene–butadiene–styrene triblock copolymer and exfoliated graphite. They claimed that in the composite paraffin undergoes solid–liquid phase change, and there is no leakage of it even in the state of melting. The composite exhibits high thermal conductivity and nearly 80% of the latent heat of fusion per unit mass of the paraffin.

4. Applications

Table 10 lists some of the different applications found in the literature. It should be pointed out that Dincer and Rosen [4] give a wide overview of different latent TES, cold TES and seasonal storage systems.

These applications can be divided into two main groups: thermal protection or inertia, and storage. One difference between these two substantial fields of application relates to the thermal conductivity of the substance. In some cases of thermal protection it is appropriate to have low conductivity values, while in storage systems such low values can produce a real problem since

Table 10
PCM-TES applications

Application	References
Thermal storage of solar energy	[3,12,25,32,46,88,140,141,204,205,224–229]
Passive storage in bioclimatic building/architecture (HDPE + paraffin)	[9,34,89,91,92,181,188–194,200–203]
Cooling: use of off-peak rates and reduction of installed power, ice-bank	[29,171,181,195–199,210–217,219]
Heating and sanitary hot water: using off-peak rate and adapting unloading curves	[54,87,120,142,206–209]
Safety: temperature maintenance in rooms with computers or electrical appliances	[220]
Thermal protection of food: transport, hotel trade, ice-cream, etc.	[54,56,173,181,218]
Food agroindustry, wine, milk products (absorbing peaks in demand), greenhouses	[189,221–223]
Thermal protection of electronic devices (integrated in the appliance)	[54,172,173,178]
Medical applications: transport of blood, operating tables, hot-cold therapies	[54,172]
Cooling of engines (electric and combustion)	[178–180,182–187]
Thermal comfort in vehicles	[230]
Softening of exothermic temperature peaks in chemical reactions	[189]
Spacecraft thermal systems	[96]
Solar power plants	[232–237]

there can be sufficient energy stored but insufficient capacity to dispose of this energy quickly enough.

4.1. Ice storage

In the past, the earliest works basically concentrated on analysing pure substances, often water (for ice stores). Studies that can be cited include London [98], Goodman [162], Lazaridis [100] and Saitoh [163]. In subsequent years, and even quite recently and due to the implementation on a commercial and industrial scale of the so-called ice storage systems, abundant information relating to water as a storage substance has also appeared in the literature.

A compilation of these processes can be found in the ASHRAE Handbook HVAC Applications [164] where the different geometries used are described: spheres, ice on coils containing water with glycol, or over an evaporator. These geometries are used by the various manufacturers and commercial brands such as Sedical (Cryogel) [165], Ciat (Cristopia) [41], Baltimore Aircoil (Ice Chiller) [166] or Calmac (Ice bank) [167]. Scientific studies found in this context include Dumas [168,169]. Among the main problems dealt with in these studies are those related to the random character of crystallisation and the delay in the start of solidification (undercooling), as well as the different techniques used to avoid the latter (nucleating agents or partial melting process). In addition, detailed heat transfer studies related to each of the geometries most widely used in the commercial sector have been studied. Cheng [170], using experimental data, analyzed the density inversion zone of water at 4 °C. Ismail et al. [171] presented studies about ice storage in bank geometry with finned tubes, studying the influence of parameters like inlet fluid temperature, initial temperature of PCM, and thermal conductivity of the tube, in the solidification front.

4.2. *Conservation and transport of temperature sensitive materials*

When transporting food, in many cases the food temperature must be kept above a certain temperature or if it is frozen food defrosting must be avoided. The situation is similar when transporting temperature sensitive medications. Both applications are suitable to apply PCM, because the PCMs capability to store heat and cold in a range of only several degrees can be used very well. This application can already be found in the market with many companies commercialising transport boxes for sensitive materials [54,172,173]. Several companies could be named: va-Q-tec GmbH [174], Rubitherm GmbH [45], Sofrigam [175], TCP RELIABLE [176], PCM Thermal Solutions [177], Bio Trans [54], etc.

Electronic components tend to age and finally fail very fast when their operating temperature rises beyond a critical limit. The application of PCM to restrict the maximum temperature of electronic components seems very promising, especially as they act as passive elements and therefore do not require any additional source of energy [178–180]. Several applications can be found in the market already [172], commercialised by, for example, TEAP [42], Climator [44], and EPS [181].

When engines and hydraulic machines are started from low temperatures, energy consumption and abrasion are high. Therefore, several companies have already investigated and developed latent heat stores for motor vehicles [182–186]. In this application, the heat store is heated up by the cooling fluid while the engine is running. When the engine is stopped, the heat is stored and can be used to preheat the engine on a new start. Using the heat store it is possible to reach an optimised working temperature within the engine in a much shorter time than without heat store [187].

4.3. *Building applications*

The use of PCMs for thermal storage in buildings was one of the first applications studied, together with typical storage tanks. The first application of PCMs described in the literature was their use for heating and cooling in buildings, by Telkes in 1975 [12], and Lane in 1986 [3]. The use of building structural components for thermal storage was pointed out already in 1975 by Barkmann and Wessling [188], and later by other authors [9,89,92].

One very important subject in applications like the use of PCMs in buildings, is that of safety. An article by Salyer [189] reports on reaction to fire and the possible fire-retardant additives (organic halogenous compounds) that improve the response to fire of the material. This paper covers an important number of applications in the field of heating and cooling, and sets out a review of materials, advantages, disadvantages and characteristics of a series of PCM substances applicable to thermal storage in buildings. Of the four possible PCM analysed, those with the greatest advantages were of the paraffin type (hydrocarbons; -60 to 80 °C) whose origin can be from the polymerisation of ethylene or as a by-product of petroleum. Among the suppliers cited are Shell, Exxon, Gulf, Sun Oil, and Witco. The trade names and prices of various paraffins are also given.

An important disadvantage of light weight buildings is their low thermal mass. They tend to have high temperature fluctuations, which result in a high heating and cooling demand. The

application of PCM in such buildings is, because of their capability to smooth temperature variations, very promising [190,191].

An interesting possibility in building applications is the impregnation of PCMs into porous construction materials, such as plasterboard, to increase thermal mass [192–194].

The use of PCMs to store coolness have been developed for air conditioning applications, where cold is collected and stored from ambient air during night, and its relieved to the indoor ambient during the hottest hours of the day. This concept is known as free-cooling [29,195–197].

Another application of PCMs in buildings is thermoelectric refrigeration. Omer et al. [198,199] have integrated a phase change material in the thermal diode to improve effectiveness of the heat sink.

In order to diminish the solar gain in buildings, Ismail et al. [200,201] studied the possibility of using a window with a PCM curtain. This window is double sheeted with a gap between the sheets and an air vent at the top corner; the gap can be filled with PCM that upon freezing would prevent the temperature of the internal ambient from decreasing. Similarly, Merker et al. [202,203] have developed a new PCM-shading system to avoid overheating around the window area.

4.4. *PCM tanks vs. water tanks*

In the field of solar energy storage, Cassedy [204] claims that today PCMs do not offer economic savings for thermal storage at low temperatures (50–100 °C), since these systems (paraffin) cost about the double of the cost of hot water systems. He does, however, point out the advantages associated with materials like paraffin, such as low corrosion, and chemical stability. Similar results were reported previously by Farid [46].

Especially the high storage density at small temperature changes can be a significant advantage in solar applications and utilization of waste heat [32,205].

Mehling et al. studied the possibility of including a PCM-module at the top of a stratified water tank. Their results stated and increase of energy storage and a better performance of the tank [206,207].

Esen et al. [208] studied theoretically the effects of various thermal and geometric parameters on the whole PCM melting time for different PCMs and tank configurations. The configurations were those of a tank with PCM packed in cylinders and the heat transfer fluid flows parallel to it; the second is a tank where pipes containing the fluid are embedded in the PCM. Another configuration used for many year is the inclusion of the PCM in spherical containers, and those in the water tank [87,209].

4.5. *Other applications*

Although there is a time coincidence between solar radiation and air conditioning, some heat storage is necessary for uninterrupted operation of the chiller or to expand the operation time, so Safarik et al. [210] developed a solar climatisation system using an ammonia/water absorption chiller with a paraffin-latent heat storage.

Similar concept has been developed in heating, where a PCM-TES is linked to a heat pump and heat distribution system, and significant reduction in the capacity of the heat pump and system annual running costs can be made [211–213].

The use of ice for cold storage is widely commercialised. Companies like Calmac International have a wide range of products to store cold at different temperatures with the use of additives in the water. Many cold storage tanks incorporated in air conditioning systems in buildings have been built and studied [214–216]. A review on cool thermal storage technologies as a demand side management tool for electric load management and a supply side management tool for efficient and economical power production was published by Hasnain in 1998 [217].

Cold storage is also developed for other applications like vegetable cooling (Kowata et al. [218]), pre-cooling inlet air in a gas turbine [219], or temperature maintenance in room with computers or electrical appliances [220].

The use of PCMs for energy savings and management in greenhouses has been widely studied. Kürklü [221–223] presented a review. The investigation showed that the types of heat exchangers, stores and the amounts of phase change materials per square meter of greenhouse ground area were different in each study.

Including PCM in a solar collector was first presented by Sokolov and Keizman [224], but has lately been considered by other researchers like Rabin et al. [225], Enibe [226,227], and Tey et al. [228].

Another application of PCMs has been its inclusion in solar cookers to extend their usage time [229]. The use of a PCM storage for increasing thermal comfort in vehicles has been implemented by companies like BMW [230]. A PCM storage has been included in a paint-drying system to recover exhaust heat [231].

The use of PCMs in solar power plants has been investigated. A survey by Pilkington Solar International [22] outlines that systems with phase change materials were considered to have a higher risk than sensible heat molten salt systems before 1990. After this date, some research has been carried out. Hunold et al. [232–234] investigated the heat transfer mechanism of different PCM salts during phase change and of liquid salts, using one storage module. They showed that phase change storage is technical feasible and proposed a storage design. However, Michels [235,236] said that one can only take full advantage of PCM storage by connecting several modules with different salts and different melting points in series. A new development was proposed by Ratzesberger et al. [237], where a combined configuration of one sensible heat storage module, like concrete, and of two PCM modules at each end is used.

5. Summary

A review of TES using solid–liquid phase change has been carried out. The information obtained is presented divided into three parts: materials, heat transfer and applications. Materials used by researchers as potential PCMs are described, together with their thermophysical properties. Commercial PCMs have also been listed. Different methods of thermal properties determination can be found. Problems in long term stability of the materials and their encapsulation are discussed. Heat transfer is considered mainly from a theoretical point of view, considering different simulation techniques. Many applications of PCMs can be found, divided in ice storage, building applications, conservation and transportation of temperature sensitive materials, water tanks vs. PCM tanks, and others.

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