

1 THERMAL ENERGY STORAGE FOR LOW AND MEDIUM TEMPERA- 2 TURE APPLICATIONS USING PHASE CHANGE MATERIALS 3 - A REVIEW

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11 ABSTRACT

13 A comprehensive review of phase change materials (PCMs) with phase transition temperatures be-
14 tween 0 and 250 °C is presented. From that review, organic compounds and salt hydrates seem more
15 promising below 100 °C and eutectic mixtures from 100 to 250 °C.

16 Practical indirect heat exchanger designs for latent heat storage systems were also assessed and feasi-
17 ble heat enhancement mechanisms reviewed. The focus on this temperature range is due to potential
18 CO₂ emissions reduction able to be achieved replacing conventional heating and cooling applications
19 in the domestic, commercial and public administration sectors, which represented around a quarter of
20 the UK's final energy consumption in 2015.

21

22 Keywords:

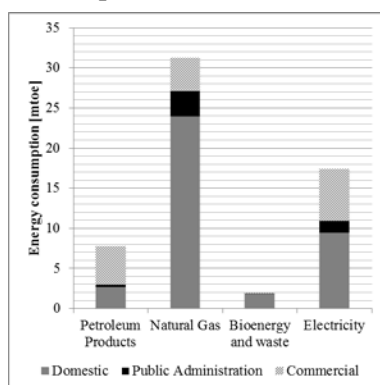
23 Phase change materials, Thermal Energy storage, Inorganic PCMs, Organic PCMs, Eutectic PCMs,
24 Latent Heat Storage.

25 1. INTRODUCTION

26

27 To date, the measures adopted to stabilize global temperature rise below the 2°C target, are likely to
28 be insufficient [1]. If this target is to be achieved, there must be an increased effort to de-carbonize
29 global energy consumption, which still relies heavily on fossil fuel sources.

30 Conventional heating and cooling in the domestic, commercial and public administration sectors had a
31 combined natural gas and petroleum products consumption of around 25% of the UK's final energy
32 consumption in 2014 [2]. The distribution per sector is presented in Figure 1.



33

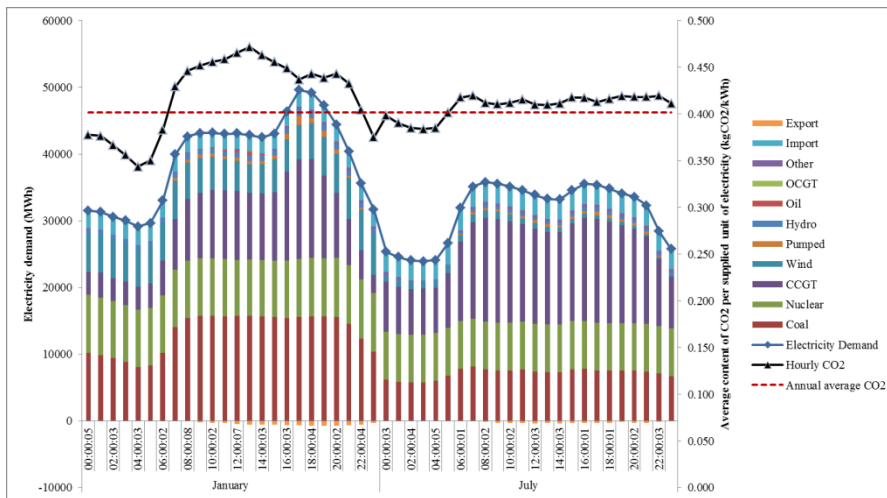
34 **Figure 1- The UK's final energy consumption aggregated values for 2014 [2] by source in the Domestic, Commercial
35 and Public Administration sectors.**

36

37 To reduce the CO₂ emissions in the domestic heating sector, heat pumps could be used as an alternative to current fossil fuel burning systems; however, their usage should be restricted to off peak times (between 22.00 and 07.00), in order not to greatly increase the UK's electrical grid peak demand [3], Figure 2, with local heat storage being used to meet heat demand at other times. .

41 The daily variation of CO₂ emissions per kWh of electricity consumed for the 15th of January and July of 2015 are presented in Figure 2, values were obtained for the generation mix for the UK national grid and CO₂ emission factors applied similar to those estimated by Hawkes et al [4]. In order to match the CO₂ emissions associated with grid electricity to natural gas used for space heating (204.9 gCO₂/kWh [2]), the minimum coefficient of performance (COP) required for heat pumps is approximately 2.

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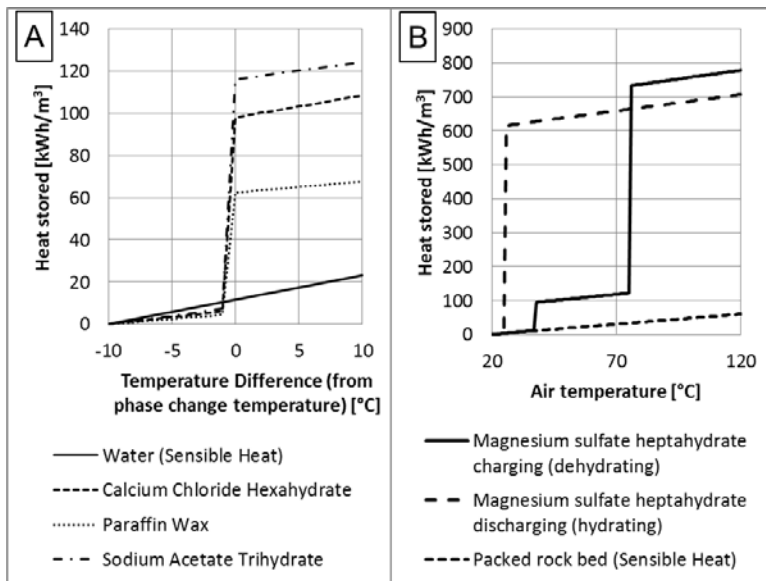
49 **Figure 2 – Seasonal and hourly variation of CO₂ emissions associated with the electricity supplied by the UK national grid - sample date: 15/01/2015 & 15/07/2015**[4], [5].

50

51
52 The use of solar thermal systems is another potential way of reducing CO₂ emissions associated with space and water heating, effective thermal energy storage will be essential to address the mismatch between the intermittent solar heat supply and the heat demand. [6], [7].

55 Thermal energy storage can be achieved through 3 distinct ways: sensible; latent or thermochemical heat storage. Sensible heat storage relies on the material's specific heat capacity. Latent heat storage relies on the material's phase change enthalpy to store heat within a narrow temperature range, providing greater energy density [kWh_{th}/m³] than that achievable with sensible heat storage over the same temperature gradient; however, volumetric expansions during the melting process can reach 10 to 15% for some materials. Thermochemical heat storage is more energetic than latent heat storage, but since it relies on adsorption / desorption or other chemical reactions, reaction kinetics and reactor design significantly determine their actual performance, and require distinct charging and discharging temperatures [8] (usually between 100 and 300 °C, depending on the reaction), having potential interest for interseasonal storage applications. Figure 3 A shows, heat storage capacity [kWh_{th}/m³] of water sensible heat storage and 3 PCMs over a 20 °C temperature interval; the PCMs store around 2.5 to 6 times more energy than water.. Figure 3 B compares thermochemical heat storage to a packed rock bed heat storage system; the hydration of the thermochemical compound can theoretically release 25 times more energy than what achievable with 40°C of air temperature increase in a rock bed heat storage system, although temperatures up to 120°C are required for dehydration of the salt hydrate ;, such thermochemical heat storage materials may prove to be suitable candidates for inter seasonal thermal energy storage.

71



72
73 **Figure 3- Heat stored vs. Temperature diagrams for 3 PCMs and a sensible water heat storage system (A) and mag-**
74 **nesium sulphate heptahydrate (data retrieved from Zondag et al. [8]) compared to a conventional rock bed storage**
75 **system (B).**

76
77 Medium and large scale systems such as centralized cooling (absorption chillers [9], [10], [11]) and
78 district heating networks [12]-[13], used commonly in hospitals, commercial centres and office build-
79 ings could also benefit from latent heat storage systems, when supplied by solar thermal collectors.

80 Another potential application for latent heat storage would be integration into solar thermal driven
81 organic rankine cycles (ORC) [14]. The characterization of a compact ORC system for low grade
82 transient solar energy conversion was made by [15], and it was concluded that adding latent heat
83 thermal energy storage could potentially stabilize the system to short term weather irregularities
84 (clouds, fog, etc) or even depending on the storage size, be able to maintain daily production.

85 Latent heat energy storage may also have use in industry when integrated in some thermal batch pro-
86 cesses, potentially reducing sensible heat losses in the heating and cooling process necessary to
87 achieve optimum process temperatures [9], and allowing heat to be stored between cycles. Such batch
88 processes can be found in most of the food and beverages industry (beer, milk, chocolate, cheese, cof-
89 fee, canned food) and industrial drying processes. The possible integration of solar thermal collectors
90 into some common industrial applications in Cyprus was presented by Kalogirou [16].

91 For nominal operation of latent heat storage systems, the PCM must have a relative high latent heat of
92 fusion, stability in its molten state and be chemically inert with its enclosure. Another important re-
93 quirement would be a low degree of subcooling; else their enhanced heat capacity won't be fully real-
94 ised. One of the main properties of commonly used PCMs is their low thermal conductivity, usually
95 between 0.2 and 0.7 [W/m.K], requiring the use of complex heat exchanger geometries to obtain re-
96 quired heat transfer rates from latent heat storage containers. Conventional techniques to overcome
97 the low heat transfer characteristic rates would be the used of metal fins [17]; however novel promis-
98 ing techniques such as carbon cloths [18], shape stabilized PCMs with graphite [19], [20] microen-
99 capsulated-PCM slurries [21] and direct contact latent heat storage systems [22], [23] can also be used
100 to increase the global UA value of latent heat storage systems.

101
102 **2. PHASE CHANGE MATERIALS LITERATURE REVIEW**
103

104 In order to assess the potential of latent heat storage applications, a comprehensive review of the
105 PCMs physical properties during phase change is critical. For a comparative economic evaluation,
106 market prices for industrial grade materials were used to provide a common approach.

107

108 **i. ORGANIC PCMS**

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110 Organic compounds, characterized by having carbon atoms in their structure, generally have very low
 111 thermal conductivity (from 0.1 to 0.7 W/m.K), hence requiring mechanisms to enhance their heat
 112 transfer in order to achieve reasonable rates of heat output (W). Table 1 presents the thermophysical
 113 properties of the compounds identified for further analysis based on their relative low price, their
 114 quoted stability from the review and enthalpy of phase change. The Organic compounds reviewed
 115 that appeared to be promising in this temperature range are some of the saturated fatty acids [24]; sug-
 116 ar alcohols [25], [26], carboxylic acids [27], amides [28] and alkanes [29]. Urea [30], is not a promis-
 117 ing compound in its pure state, due to its instability when molten [31], but some of its eutectic mix-
 118 tures seem to have suitable properties for latent heat storage, with details presented in Table 3.

119

120 **Table 1 - Thermophysical properties of selected organic compounds**

Compound	T _m	ΔH _m	C _{p,s}	C _{p,l}	λ _s	λ _l	ρ _s	V _{exp}	E _{density}	Price		Ref.
	°C	kJ/kg	kJ/kg.K		W/m.K		kg/m ³	m ³ /m ³	kWh/m ³	£/m ³	£/kWh	
Formic Acid	8	277	1.00	1.17	0.30	0.27	1227	12.0	96	255	4.2	[32], [33]
Acetic Acid	17	192	1.33	2.04	0.26	0.19	1214	13.5	71	327	7.2	[32], [34]
Lauric acid	44	212	2.02	2.15	0.22	0.15	1007	13.6	66	276	6.5	[32], [34]
Stearic acid	54	157	1.76	2.27	0.29	0.17	940	9.9	49	345	11.0	[31], [33], [35], [36]
Palmitic acid	61	222	1.69	2.20	0.21	0.17	989	14.1	67	354	8.3	[32], [35], [37], [38]
Paraffin Wax	0 - 90	150 - 250	3.00	2.00	0.2		880 - 950	12 - 14	50 - 70	400 - 500	9.5 - 7.1	[9], [32], [39]
Acetamide	82	260	2.00	3.00	0.40	0.25	1160	13.9	93	1318	22.2	[32], [40]
Oxalic acid	105	356	1.62	2.73			1900		211	524	3.9	[27], [41]
Erythritol	117	340	2.25	2.61	0.73	0.33	1450	10.3	148	1287	13.6	[25], [31], [42]
HDPE	130	255	2.60	2.15	0.48	0.44	952		80	463	9.0	[32], [43]
Phthalic an- hydride	131	160	1.85	2.20			1530		85	2042	37.4	[44]
Urea	134	250	1.80	2.11	0.80	0.60	1320	16.7	97	189	3.0	[30], [31], [45]
Maleic acid	141	385	1.17	2.08			1590		184	1059	9.0	[31], [46], [47]
2- Chlorobenzoic acid	142	164	1.30	1.60			1544		83	1861	35.1	[48]
Adipic acid	152	275	1.87	2.72			1360	20.2	109	584	8.4	[49]
d-Mannitol	165	300	1.31	2.36	0.19	0.11	1490		139	1027	11.5	[25], [50]–[52]
Hydroquinone	172	258	1.59	1.64			1300		105	3415	50.9	[32], [53]

121

122 **ii. SALT HYDRATES**

123

124 Salt hydrates, formed by water absorption by the anhydrous salt at ambient temperatures, have a phase
 125 change enthalpy depending on the bond strength between the water molecules and the salt. Super
 126 cooling during crystallization [54], phase segregation [55] and corrosion with commonly used metals
 127 (copper, aluminium, stainless steel) [56], are the main issues inhibiting their use in latent heat energy
 128 storage systems. Table 2 presents the thermophysical properties for a selection of salt hydrates.

129

130 **Table 2 - Thermophysical properties of selected salt hydrates;**

Compound	T_m	ΔH_m	C_{ps}	C_{pl}	λ_s	λ_l	ρ_s	V_{exp}	$E_{density}$	Price		Ref.
	°C	kJ/kg	kJ/kg.K	W/m.K	kg/m ³	m ³ /m ³	kWh/m ³	£/m ³	£/kWh			
Water	0	333	3.30	4.18	1.60	0.61	920	-8.7	109	0	0.0	[32], [57]
Calcium Chloride Hexahydrate	30	125	1.42	2.20	1.09	0.53	1710	11	64	93	2	[9], [32], [56], [58]
Sodium Sulphate Decahydrate	32	180	1.93	2.80	0.56	0.45	1485	4	82	48	1	[9], [32], [56]
Sodium Thiosulfate Pentahydrate	46	210	1.46	2.39	0.76	0.38	1666	6	103	199	3	[32], [43], [59]
Sodium Acetate Trihydrate	58	266	1.68	2.37	0.43	0.34	1450	3	113	233	3	[32], [60], [61]
Barium Hydroxide Octahydrate	78	280	1.34	2.44	1.26	0.66	2180	11	171	422	4	[32], [62], [63]
Magnesium Nitrate Hexahydrate	89	140	2.50	3.10	0.65	0.50	1640	5	74	131	3	[9], [32], [54]
Oxalic acid Dihydrate	105	264	2.11	2.89	0.90	0.70	1653	0	133	339	4	[31], [41]
Magnesium Chloride Hexahydrate	117	150	2.00	2.40	0.70	0.58	1570	8	72	56	1	[32], [54], [64]

131

132 *a. PHASE SEPARATION*

133

134 Water separation, related to poor molecular bonding [55], [64] is the main factor determining thermal
 135 stability in the molten phase. Suitable encapsulation could help reduce the effects of water segrega-
 136 tion, since it would prevent the release of partially evaporated water.

137 *b. SUPER COOLING*

138

139 The onset of solidification can occur at a significantly lower temperature than the melting point, nor-
 140 mally around 10 to 20 °C [37]. Adding other salts with similar crystal structures, increases nucleation
 141 points, and may reduce this phenomenon. A study of Magnesium chloride hexahydrate [64], proved
 142 that the addition of Strontium Carbonate, Strontium Hydroxide and Magnesium Hydroxide effectively
 143 reduced super cooling for this salt.

144

145 **iii. EUTECTIC PCMS**

146

147 Binary and ternary mixtures of inorganic salts have been widely studied for thermal storage applica-
 148 tions. Nitrate, chloride and sulphate salts of alkali and alkaline metals, such as magnesium, potassium,
 149 lithium and calcium, are the main compounds used to produce medium temperature eutectic mixtures,
 150 also known as ionic liquids [65].

151 Due to their higher density and stability in their liquid state, they have been used widely as ionic liq-
 152 uids in high temperature sensible thermal storage systems (thermonuclear energy, concentrated solar
 153 thermal power [66]–[68]).

154 Due to the lack of experimental data for some of the thermophysical properties of eutectic mixtures,
 155 weighting methods have been used to predict missing values [69], [70]. More developed techniques to
 156 predict thermophysical properties of eutectic mixtures do exist [71], [72], involving Van Der Waals
 157 volumes and surface areas of stable molecular combinations; however, more simplified correlations
 158 were used. The weighting correlations used to obtain the thermophysical properties, namely heat ca-
 159 pacity (C_p), density (ρ), thermal conductivity (λ) and melting enthalpy (ΔH_m), are presented in equa-
 160 tions 1 to 6, which use available properties of the mixture and its constituents, molar ratio (x_i), mass
 161 ratio (w_i) and volumetric ratio (z_i) and their melting point (T_m) to predict the unknown values. A
 162 comparison was made with some eutectic salts for which experimental data was available; the differ-
 163 ence between predictions and measurements was less than 10%. Table 3 presents the physical proper-

164 ties of the selected eutectic compounds in the 0-250 °C range, with the predicted latent heat values
 165 shown in bold.

166
 167
$$w_i = x_i \times M_i \times \left(\sum_i x_i \times M_i \right)^{-1} \quad 1$$

168
 169
 170
$$z_i = \frac{w_i}{\rho_i} \times \left(\sum_i \frac{w_i}{\rho_i} \right)^{-1} \quad 2$$

171
 172
 173
 174
$$Cp_{eutectic} = \sum_i Cp_i \times w_i \quad 3$$

175
 176
 177
$$\rho_{eutectic} = \sum_i \rho_i \times z_i \quad 4$$

178
 179
 180
$$\lambda_{eutectic} = \prod_i \lambda_i^{z_i} \quad 5$$

181
 182
$$\Delta H_{eutectic} = Tm_{eutectic} \times \sum_i \frac{\Delta H_i \times w_i}{Tm_i} \quad 6$$

183
 184
 185

Table 3 - Thermophysical properties of selected eutectic compounds

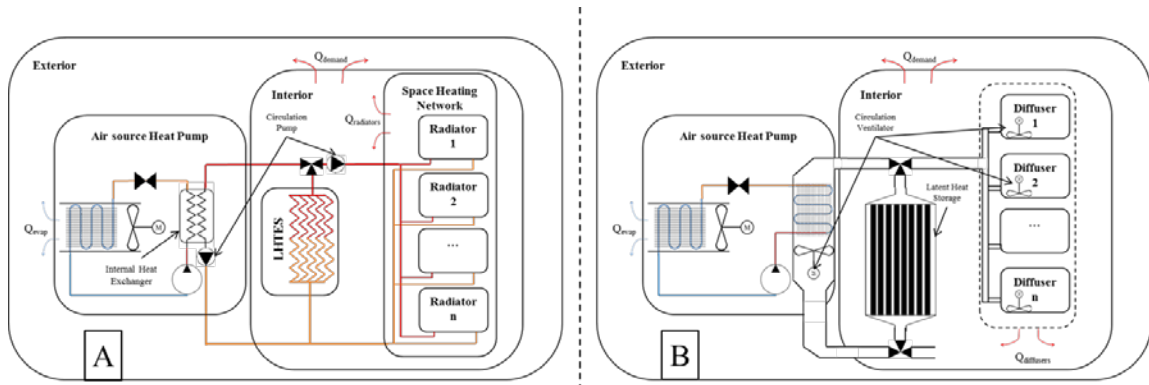
Eutectic Compounds	Mass Ratio	T _m	ΔH _m	C _{p,s}	C _{p,l}	λ _s	λ _l	ρ _s	E _{density}	Price		Ref
		°C	kJ/kg	J/kg.K		mW/m.K		kg/m ³	kWh/m ³	£/m ³	£/kWh	
CaCl ₂ ·(H ₂ O) ₆ - MgCl ₂ ·(H ₂ O) ₆	67-33	25	127	1620	2270	930	550	1661	57	80	1.4	[32], [43]
Urea - CH ₃ COONa·(H ₂ O) ₃	60-40	30	200	1750	2210	630	480	1370	74	206	2.8	[43], [73]
Mg(NO ₃) ₂ ·(H ₂ O) ₆ - NH ₄ NO ₃	61-39	52	125	2130	2670	590	500	1672	58	188	3.3	[43], [73]
Urea – Acetamide	38-62	53	224	1920	2660	510	340	1216	73	924	13	[58]
Stearic Acid - Palmitic Acid	36-64	53	182	1720	2230	234	169	971	46	351	8	[74]
Mg(NO ₃) ₂ ·(H ₂ O) ₆ - MgCl ₂ ·(H ₂ O) ₆	59-41	59	132	2290	2810	670	530	1610	58	99	1.7	[32], [43]
Stearic Acid - Acetamide	83-17	65	213	1800	2400	300	180	972	56	485	8.6	
LiNO ₃ - MgNO ₃ ·(H ₂ O) ₆	14-86	72	180	2380	2900	700	510	1713	84	718	8.5	[73]
Urea - LiNO ₃	82-18	76	218	1770	2020	850	600	1438	84	851	10.1	
Urea - NaNO ₃	71-29	83	187	1600	2030	750	590	1502	76	220	2.9	
Urea - NH ₄ Cl	85-15	102	214	1770	2090	760	580	1348	77	174	2.3	
Urea – K ₂ CO ₃	15-85	102	206	1660	2020	780	580	1415	78	269	3.4	
Urea - KNO ₃	77-23	109	195	1600	1910	810	580	1416	74	255	3.4	
Urea – NaCl	90-10	112	230	1720	2020	820	600	1372	85	180	2.1	

Urea - KCl	89-11	115	227	1690	1960	830	0.60	1370	83	197	2.4	
LiNO ₃ - NaNO ₃ - KNO ₃	30-18-52	123	140	1170	1440	790	530	2068	79	1979	25	[75], [76]
LiNO ₃ - KNO ₃	34-66	133	150	1170	1350	960	520	2018	82	2167	26	[75]-[77]
KNO ₃ - NaNO ₂	56-44	141	97	1180	1740	730	570	1994	52	504	9.7	[78, p. 778]
KNO ₃ - NaNO ₃ - NaNO ₂	53-6-41	142	110	1170	1730	720	570	2006	60	497	8.3	[32], [78, p. 786]
KNO ₂ - NaNO ₃	48-52	149	124	1050	1630	580	520	2080	70	994	14	[78]
LiNO ₃ - NaNO ₂	62-38	156	233	1570	1910	1120	660	2296	143	3816	27	[78]
LiNO ₃ - KCl	58-42	160	272	1260	1350	1310	590	2196	161	3409	21	[32], [79]
LiNO ₃ - NaNO ₃ - KCl	45-50-5	160	266	1320	1690	880	590	2297	166	2852	17	[32], [79]
HCOONa - HCOOK	45-55	176	175	1150	930	630	430	1913	92	421	4.6	[80]
LiOH - LiNO ₃	19-81	183	352	1600	2000	1330	690	2124	202	5165	26	[78]
LiNO ₃ - NaNO ₃	49-51	194	262	1350	1720	870	590	2317	165	3084	19	[32], [78]
LiNO ₃ - NaCl	87-13	208	369	1540	1560	1350	630	2350	235	5254	22	[32], [79], [81]
KNO ₃ - KOH	80-20	214	83	1030	1350	880	540	1905	43	611	14	[32]
KNO ₃ - NaNO ₃	55-45	222	110	1010	1490	730	510	2028	61	482	8.0	[32]
LiBr - LiNO ₃	27-73	228	279	1340	1380	1140	570	2603	196	6134	31	[78], [82]
LiOH - NaNO ₃ - NaOH	6-67-27	230	184	1300	2000	780	670	2154	107	538	5.0	[78], [82]
NaNO ₂ - NaNO ₃	55-45	233	163	1310	2130	590	640	2210	97	382	3.9	[78], [82]
CaCl ₂ - LiNO ₃	13-87	238	317	1500	1530	1370	690	2362	204	5325	26	[78], [82]
LiCl - LiNO ₃	9-91	244	342	1580	1610	1370	640	2351	218	6019	28	[78], [82]
NaNO ₃ - NaOH	86-14	250	160	1190	1860	660	600	2241	97	339	3.5	[32]

186

187 3. POTENTIAL APPLICATIONS FOR INDIRECT LATENT HEAT STORAGE CONTAINERS AND 188 SYSTEMS 189

190 The integration of latent heat storage containers into specific heating or cooling networks can be di-
191 vided by the heat transfer fluid used: air or liquid. Using water as the heat transfer fluid, latent heat
192 storage containers and systems could be integrated with conventional domestic central heating sys-
193 tems using water radiators, ideal to retrofit when changing a gas boiler for a heat pump [83], as illus-
194 trated in Figure 4 A. Using air as the heat transfer fluid, latent heat storage containers and systems can
195 be integrated into centralized ventilation systems, typical in large office areas and commercial build-
196 ings, as illustrated in Figure 4 B.



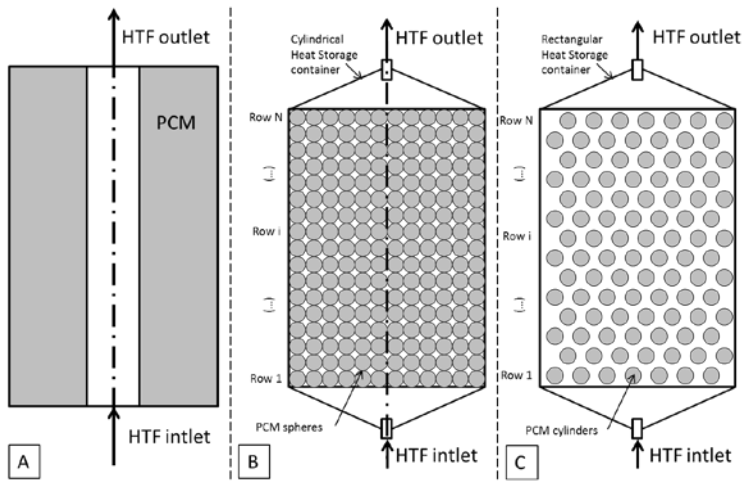
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Figure 4 - Simplified diagrams of the integration of LHTES into water space heating systems (A) and centralized air space heating systems (B).

200

201 Most latent heat storage containers can be divided into two groups: compact and encapsulated. In
202 compact systems, the PCM is enclosed within a large container with an embedded heat exchanger
203 [84], a general configuration used is the shell and tube type, presented in Figure 5 A. Compact latent
204 heat storage systems are generally designed to integrate with water heating systems [18], [85]. Encap-
205 sulated systems are those in which the PCM is contained within small containers, over which the heat
206 transfer fluid flows, leading to a heat storage system that contains a greater component of sensible
207 heat storage than compact latent heat storage systems over the same temperature range [86]. Such en-
208 capsulated designs have the versatility to be integrated with both air and water heating networks, due
209 to their shape versatility and leak proof construction. Figure 5 presents cross sections of a selection
210 of 3 different types of latent heat storage containers suitable to be integrated with the heating net-
211 works described in Figure 4. A void fraction needs to be included in the PCM storage container to
212 allow for thermal expansion that occurs during the melt process.

213



214

Figure 5 – Cross sections of a compact tube in tube (A), a encapsulated packed bed (B) and encapsulated staggered cylinders (C) latent heat storage containers.

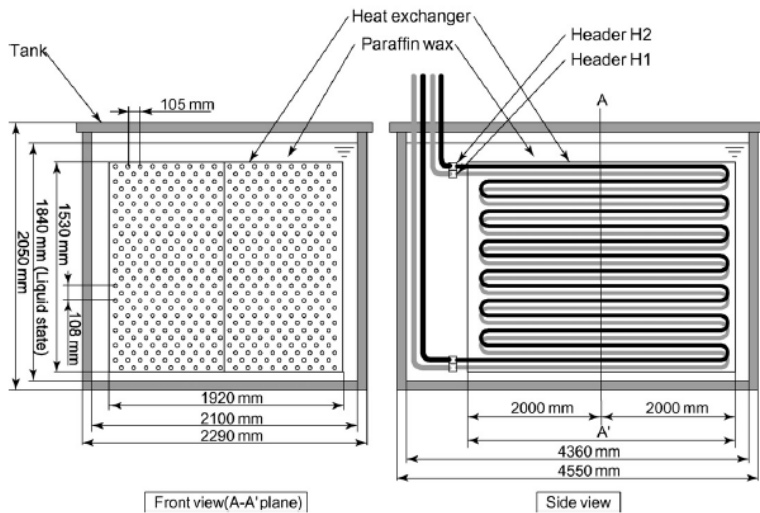
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i. COMPACT LATENT HEAT STORAGE SYSTEMS

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220 Compact latent heat storage systems can have much higher PCM volumetric ratios [$\text{m}^3_{\text{PCM}}/\text{m}^3_{\text{Container}}$]
221 than encapsulated latent heat systems, providing in theory longer duration isothermal outputs; howev-
222 er, low rates of thermal diffusion within the bulk PCM can be a major challenge, leading to lower
223 rates of heat output than can be achieved with encapsulated systems.

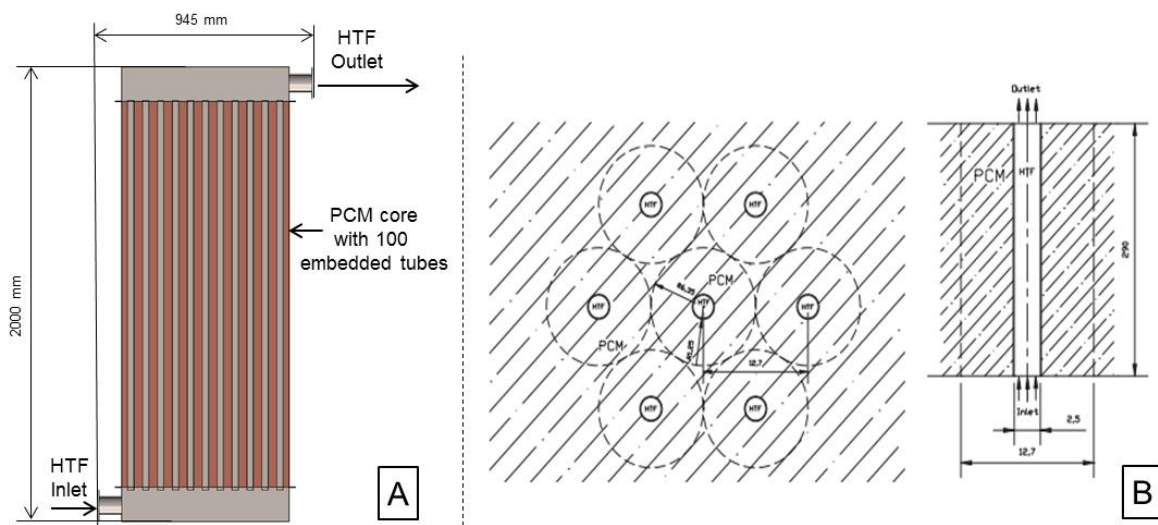
224 For domestic and small district water heating requirements, characterized by heating rates typically
 225 below 20 kW, more complex heat exchanger configurations can be used to obtain higher inlet-outlet
 226 temperature differentials, since flow head losses are not the main challenge. Figure 6 presents a sche-
 227 matic diagram of a 18 770 L PCM container modelled by Nakaso et al. [18], with a predicted thermal
 228 storage capacity using a paraffin wax with a melting temperature of 49°C (discharged from 53°C to
 229 40°C) of 516.7 kWh_{th}. He predicted numerically that without any thermal enhancement, the system
 230 could provide a constant 25 kW thermal power output for 80% of its total capacity, around 16h and 32
 231 minutes.
 232



233
 234 **Figure 6 – A schematic diagram of the 18 770L compact latent heat storage unit designed by Nakaso et al. [18], com-**
 235 **prised of 18 parallel 28mm copper tubes, each having 14 passes through the PCM volume.**

236
 237 For large process heating requirements, large parallel arrays of tubes should be used, to overcome the
 238 heat transfer limitation imposed by the PCMs low thermal conductivity [12], rather than using com-
 239 plex heat exchanging geometries [18]. This enables the heat transfer path length to be reduced, higher
 240 power outputs achieved, reduced heat transfer fluid volume flow rate, and lower frictional head losses.
 241 Figure 7 A, illustrates the cross section of a rectangular cross section container with 100 tubes running
 242 in parallel for the heat transfer fluid. The proposed system could contain up to 827 L of PCM within a
 243 container 2m high with a square cross section of 800mm x 800mm.

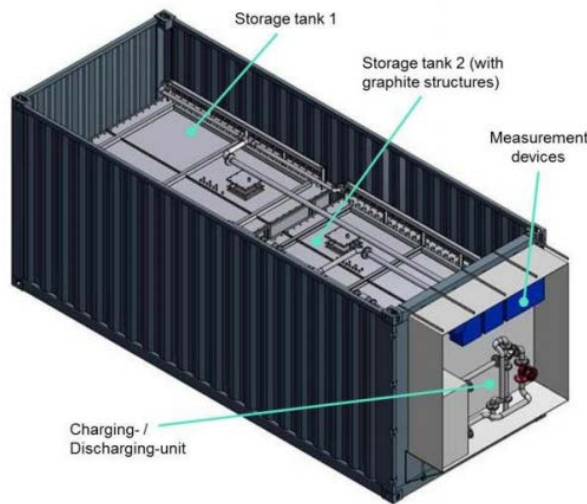
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 246 **Figure 7 – Proposed design for a 827L compact latent heat storage container for process heating applications (A), and**
 247 **the geometrical arrangement and tube spacing (B), studied by Collela et al. [12].**

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Latent heat storage for use with district heating networks has been studied by Colella et al. [12], and compared to hot water storage which is commonly used in many district heating systems. Due to the high energy density of latent heat storage systems, portable containers charged from industrial waste heat streams could be of potential interest in providing heat to the nearby district heating networks. Figure 8 presents the design of a prototype thermal storage system for use with a district heating system housed in a 20 foot long cargo container tested by Deckert et al. [87]; the system can store a maximum capacity of 1758 kWh_{th}, using sodium acetate trihydrate between 90 and 25 °C; being the heat supplied by a biogas plant located 6km from the district heat network with the charged store being physically transported between locations. Limiting the practical storage capacity to 80%, the compact latent heat storage system could provide 40kW of nearly constant thermal output over a discharge time of 38 h.

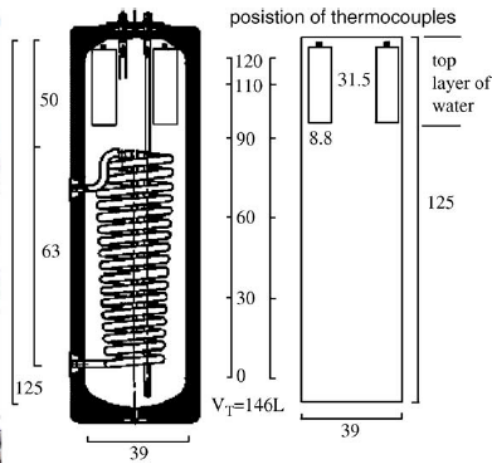


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Figure 8 – Structure of the prototype storage system developed by Deckert et al. [87] to meet the heat demands of a district heating network.

Systems using encapsulated PCMs offer higher heat transfer area per system volume [$m^2_{HT\ ar.} / m^3_{System}$], but have lower volumetric ratios [m^3_{PCM} / m^3_{System}]. Another advantage is the ease of obtaining leak-proof solutions [9], proving suitable for less stable materials. The ability to be used with any given storage container provides great versatility, regardless of size; hence their popularity [86], [88].

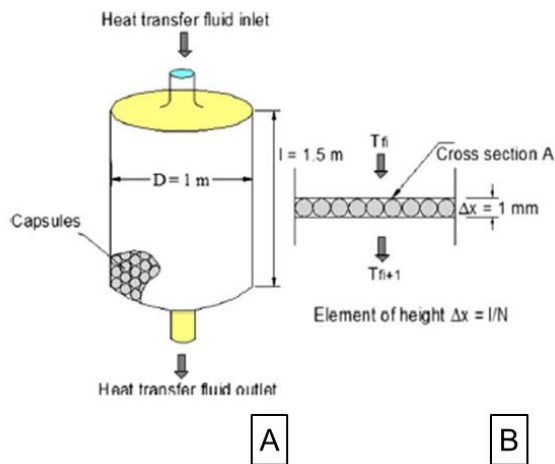
The geometries used vary significantly with the application, but they commonly have cylindrical or spherically shaped capsules, which can be inserted into off the shelf storage containers. Cabeza et al. [89], undertook a study in which two to six small cylinders containing a mixture of 90% sodium acetate trihydrate + 10% graphite as the PCM were inserted in the upper part of a domestic hot water tank, making good use of the tank's thermal stratification, Figure 9. The study concluded that, by adding 2% by volume of PCM (2 tubes) to the top region of the store, they could achieve an increase of 40% in the thermal storage capacity; comparing to the common water tank over a temperature difference of 1K where the PCM solidifies (around 54 °C).



279
 280 **Figure 9 – Schematic representation illustrating the location of the encapsulated PCM modules inside the water tank**
 281 **of the experimental work undertaken by Cabeza et al. [89];**

282
 283 Encapsulating a PCM into spherical capsules, Figure 10, provides closer packing within the storage
 284 system [90]. This approach benefits from higher mixing of the heat transfer fluid and consequently
 285 better convective heat transfer coefficients [86] than in the vertical cylinders illustrated in Figure 9.
 286 However, lower rates of thermal diffusion within the spherical capsules can reduce their effectiveness
 287 in exchanging heat to and from the heat transfer fluid [91].

288



289
 290 **Figure 10 – Simplified drawing of the modelled container (A) and cross section view of a nodule (B) of the packed bed**
 291 **model used by Regin et al. [91].**

292
 293 Direct space cooling applications in which the charging of the store occurs during the night and dis-
 294 charge occurs during the day to cool office areas have been studied by Mosaffa et al. [92] and Jiao et
 295 al. [93]. Air was used as the heat transfer fluid with the PCM encapsulated in rectangular cross section
 296 slabs with $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ as PCM. Figure 11 illustrates the modelled system studied by Mosaffa et al.
 297 [92] with a PCM store in an office air duct. The storage unit was composed by 80 rectangular slabs
 298 with 10mm thickness, 500mm width and 1.3m length, with air gaps of 3.2 mm thickness. The model-
 299 ling results demonstrated that the system could provide a constant heat output rate between 5 and 3
 300 kW, with the air flow varying rate from 1600 to 800 m^3/h respectively; for an inlet air temperature of
 301 36 °C, the system's predicted coefficient of performance was around 7.

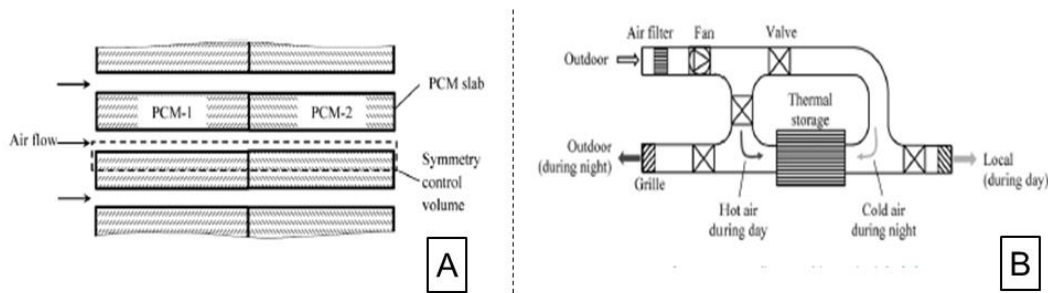


Figure 11 – Detailed view of the heat transfer arrangement inside the PCM module (A) and schematic representation of the container integration into the ventilation system studied by Mosaffa et al. [92].

Another possible application for an encapsulated latent heat storage system was studied in [94] and is illustrated in figure 12. Heat from solar thermal collectors is stored in an array of cylinders filled with paraffin wax, air is used as the heat transfer fluid. Due to the poor convective heat transfer obtained to the outer shell of the capsules, aluminium strips were used to increase the effective heat transfer area of the cylinders, providing a substantial increase in the latent heat storage system's effectiveness and the global solar collector system efficiency.

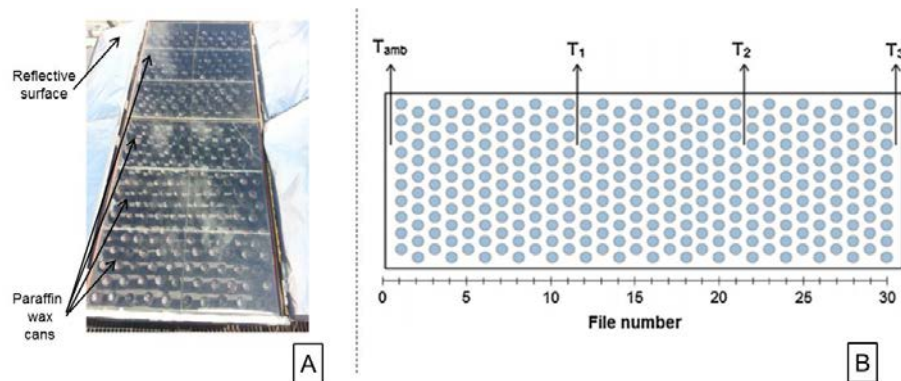


Figure 12 – Picture of the solar air absorber (A) and schematic diagram of the absorber presenting the thermocouple positions for the experimental work performed by Reyes et al. [94].

a. MICRO ENCAPSULATION OF PCM

Micro capsules with a diameter varying from around 1-1000 μm [32] have been used to encapsulate PCMs, such micro capsules when introduced into a liquid, form a slurry, effectively increasing the thermal storage capacity of the working fluid and potentially its convective heat transfer properties. Current production methods for micro encapsulated PCMs are: coacervation, suspension and emulsion polymerization, poly-condensation and polyaddition. Huang et al. [21], undertook a study in which a cylindrical container filled with a PCM slurry was heated and cooled using a helical coil heat exchanger. The slurry varied between 25, 35 and 50 % composition by volume of PCM capsules to carrier fluid. It was concluded that higher volumetric ratios (50 % respectively) reduced natural convection heat transfer within the storage container. Another characteristic of using PCM filled microcapsules was the low PCM volumetric ratios per capsule, normally around 50%, which when multiplied by the slurry volumetric ratio leads to a very low PCM volumetric ratio which reduces the typical heat capacity increase obtained when using PCMs.

ii. HEAT TRANSFER ENHANCEMENT METHODS

334 Most PCMs have low thermal conductivity, which can seriously affect the storage system charge and
335 discharge rates. To address this limitation, extended metal surfaces [84], conductive powders [17] or
336 conductive matrices [18] have proven to be effective in increasing the PCMs heat transport properties,
337 leading to a more uniform temperature within the PCM and better charge and discharge effectiveness
338 for the latent heat storage container/system.

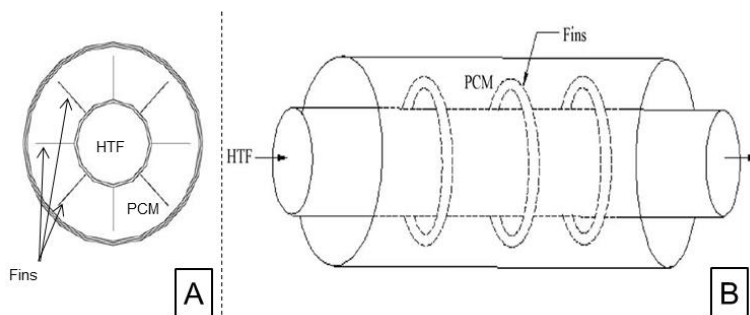
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340 a. EXTENDED METAL SURFACES

341

342 One of the most widely used heat transfer enhancement techniques used is to increase the heat trans-
343 fer area by adding extended metal surfaces, fins. Various studies have been made on modelling the
344 phase change process with different fin geometries [95], [96]. A study made by Agyenim et al. [9],
345 tested a compact horizontal tube in tube container using erythritol as the PCM, using axial fins to en-
346 hance heat transfer. They found for this system melting/solidifying properties that would provide a
347 suitable a heat source for driving an absorption cooling system. Figure 13 illustrates two common fin
348 geometries widely used in the literature [17].

349



350

351 **Figure 13 – Cross section of a tube in tube heat storage unit with longitudinal fins from Agyenim et al. [9], and a**
352 **schematic representation of a tube in tube heat storage unit with annular fins from Jegadeeswaran et al. [17].**

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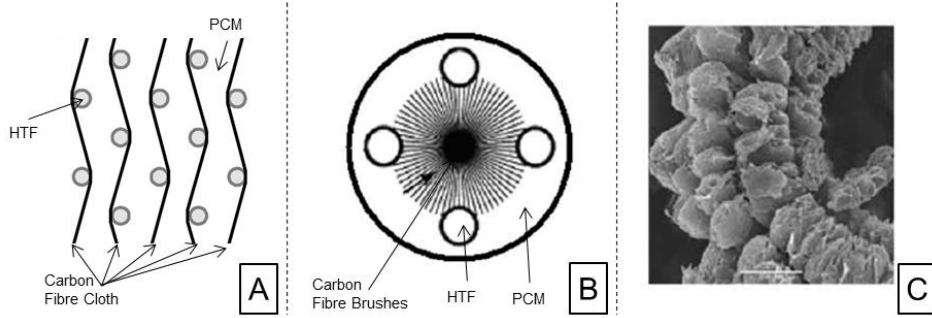
354 b. HEAT TRANSFER ENHANCEMENT USING CARBON

355

356 Exfoliated graphite, also known as expanded graphite (EG), with a thermal conductivity ranging from
357 24 to 470 W/m.K, has the potential to increase the global PCM thermal conductivity [17], with low
358 volume ratios (usually around 10-15% [32]). EG is generally obtained from the oxidation of natural
359 graphite with a mixture of nitric and sulphuric acid, followed by drying in an oven and rapid heating
360 in a furnace at 800 to 900°C to obtain rapid expansion. The PCM is impregnated into the EG under
361 vacuum, this prevents the formation of air gaps within the EG/PCM composite [17], [43]. This tech-
362 nique is the most effective procedure currently used to enhance the PCM thermal conductivity [97]. It
363 also provides a shape-stabilized (SS) form to the PCM since the pore cavities can withstand the ther-
364 mal expansion typical during phase change and prevent leakage of molten PCM [43].

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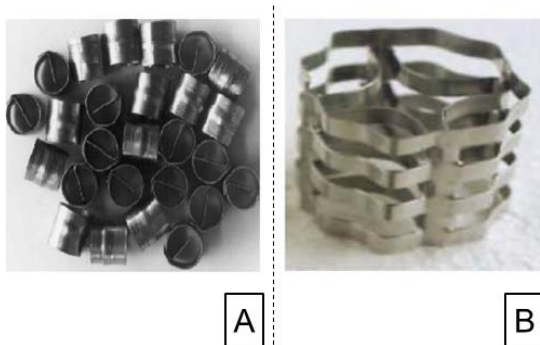


367
368 **Figure 14 -Cross-section diagram of a carbon fibre cloth (A), a carbon fibre brush (B) and EG viewed with a SEM**
369 **microscope Jegadeeswaran et al. [17].**

370
371 The container studied by Nakaso et al. [18] presented in Figure 6 was predicted to double its heat
372 output (from 25 to 50 kW_{th}) if a carbon fibre cloth of 0.8% v/v was incorporated into the system. The
373 system would then provide a nearly constant heat output of 50kW for around 10h and 20 minutes.

374
375 *c. THERMAL CONDUCTIVITY ENHANCEMENT USING METAL MATRICES*

376
377 Using sparse metal matrices is another effective way to increase thermal conductivity within a PCM
378 container, structure that would also provide multiple nucleation points. Steel wool is a more feasible
379 method of improving thermal conductivity of a PCM, compared to expandable graphite, but does not
380 provide a shape stabilized solution; since it is not as compactable as graphite. Figure 15 presents 2
381 approaches used to effectively enhance heat transfer within a PCM.



382
383
384 **Figure 15 – Stainless steel (A) and aluminium lessing rings (B) from Agyenim et al. [9].**

385
386 *d. USING CONDUCTIVE POWDERS*

387
388 Including small percentages by volume of metallic particles (aluminium, copper, silver, nickel), or
389 graphite [17] can also increase thermal diffusion within low thermal conductivity PCMs. It would also
390 have the added benefit of increasing the number of potential nucleation points, potentially enhancing
391 crystallization within the PCM. However, the conductive material could lose its miscibility when the
392 PCM is in the molten state (due to differences in density), separating from the storage material and
393 sinking to the base of the container. This could be prevented by including gelling agents in the PCM
394 [43], with a consequent reduction in the PCM volume ratio.

395
396
397 *e. DIRECT HEAT TRANSFER TECHNIQUES*

398

399 Another technique to increase the heat transfer would be to provide direct contact between the heat
400 transfer fluid and the PCM. This would provide an effective increase in heat transfer during the melt-
401 ing process since the convective nature of the heat transfer fluid would act directly on the solid PCM
402 phase [20]. Weilong et al. [22] studied the performance of a direct contact latent heat storage contain-
403 er using erythritol and an heat transfer oil, Figure 16; and it concluded that at the beginning of the
404 melt process the oil has a low flow rate due to the block of solid erythritol, the top surface of the
405 PCM melts faster than the bottom due to the higher heat transfer rate and the melting time varies sig-
406 nificantly with the oil flow rate.

407



(a) initial stage

(b) middle stage

(c) final stage

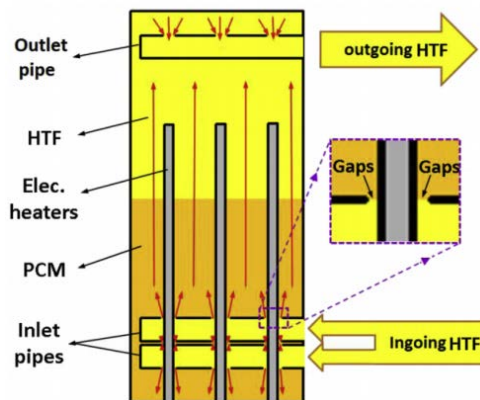
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409 **Figure 16 - Temporal variation of the melting process in a direct contact heat transfer container using erythritol as**
410 **the PCM and oil as the heat transfer fluid, from Weilong et al. [20].**

411

412 To overcome the initial blocking of the fluid flow path when the PCM is in the solid state, Shaopeng
413 et al. [23] studied the insertion of electric heaters, Figure 17, and concluded that the overall energy
414 spent on melting the initial flow pathways was 5% of the total thermal energy stored.

415



416

417 **Figure 17 - Schematic cross section showing the locations of the electric heaters in the inlet pipes, studied by**
418 **Shaopeng et al. [23].**

419

420 4. CONCLUSIONS

421

422 Phase change materials have the potential to store large amounts of energy within a smaller tempera-
423 ture range when compared to common sensible heat storage materials. Due to the low thermal con-
424 ductivities of many PCMs, poor rates of thermal diffusion within the PCM can seriously affect the
425 storage system charge and discharge rates that can be achieved.

426 A comprehensive review of PCMs melting between 0 and 250°C has been made and the thermophysical
427 cal properties of the materials having the most appropriate properties presented. Below 100 °C, organ-
428 ic compounds and salt hydrates are the most interesting materials. Eutectic mixtures with Urea seem
429 promising around 100 °C, and in the range from 130°C up to 250 °C eutectic mixtures of inorganic
430 salts appear the most promising PCMs. A mixture of sodium and potassium formates melting around
431 170 °C appears attractive due to its relatively low price and moderate latent heat of fusion.

432 A review of potential indirect latent heat storage containers and systems suitable for integration with
433 various process heating and cooling networks is also reported. Due to its geometrical versatility, en-
434 capsulated systems seem more feasible since they can be integrated to any existing system without
435 major technical constraints, although they have lower PCM volume ratios. Compact systems offer
436 larger isothermal stages due to their higher PCM volume ratios; however, heat transfer enhancement
437 among the PCM is imperative to achieve reasonable thermal power output rates, since PCMs thermal
438 conductivity can be a major issue.

439

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