

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

4 *Jose Pereira da Cunha, j.pereira-da-cunha@lboro.ac.uk, Centre for Renewable Energy Systems*
5 *Technology (CREST); Loughborough University, Loughborough (Leicestershire) LE11 3TU, United*
6 *Kingdom;*

7 *Philip Eames, p.c.eames@lboro.ac.uk, Centre for Renewable Energy Systems Technology (CREST);*
8 *Loughborough University, Loughborough (Leicestershire) LE11 3TU, United Kingdom;*

10 **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.

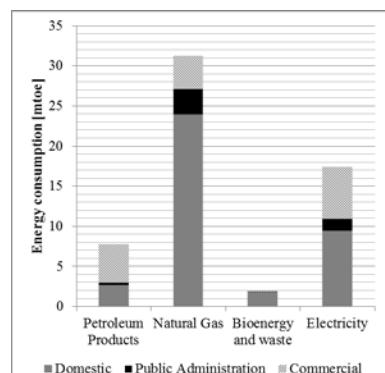
21 **Keywords:**

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

25 **1. INTRODUCTION**

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.

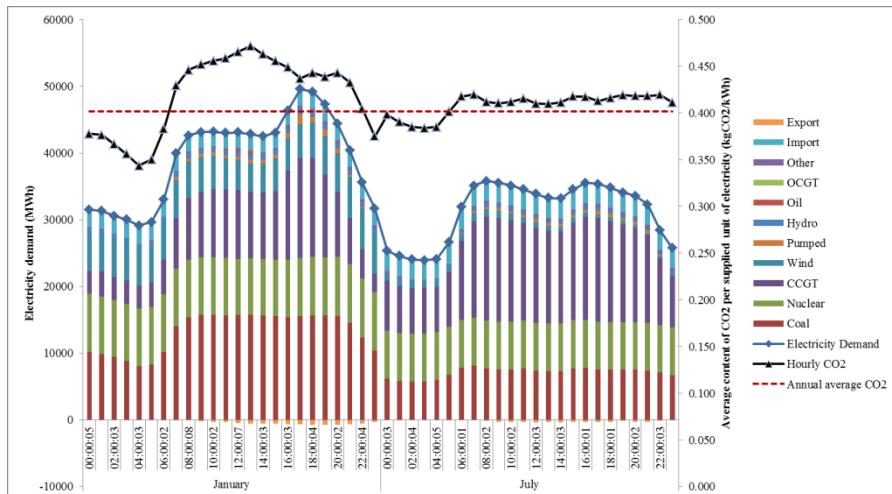
30 Conventional heating and cooling in the domestic, commercial and public administration sectors had a
31 combined natural gas and petroleum products consumption of around 25% of the UK's final energy
32 consumption in 2014 [2]. The distribution per sector is presented in Figure 1.



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

37 To reduce the CO₂ emissions in the domestic heating sector, heat pumps could be used as an alternative
 38 to current fossil fuel burning systems; however, their usage should be restricted to off peak times
 39 (between 22.00 and 07.00), in order not to greatly increase the UK's electrical grid peak demand [3],
 40 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
 42 July of 2015 are presented in Figure 2, values were obtained for the generation mix for the UK national
 43 grid and CO₂ emission factors applied similar to those estimated by Hawkes et al [4]. In order
 44 to match the CO₂ emissions associated with grid electricity to natural gas used for space heating
 45 (204.9 gCO₂/kWh [2]), the minimum coefficient of performance (COP) required for heat pumps is
 46 approximately 2.



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

52 The use of solar thermal systems is another potential way of reducing CO₂ emissions associated with
 53 space and water heating, effective thermal energy storage will be essential to address the mismatch
 54 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
 56 heat storage. Sensible heat storage relies on the material's specific heat capacity. Latent heat storage
 57 relies on the material's phase change enthalpy to store heat within a narrow temperature range, providing
 58 greater energy density [kWh_{th}/m³] than that achievable with sensible heat storage over the same
 59 temperature gradient; however, volumetric expansions during the melting process can reach 10 to
 60 15% for some materials. Thermochemical heat storage is more energetic than latent heat storage, but
 61 since it relies on adsorption / desorption or other chemical reactions, reaction kinetics and reactor
 62 design significantly determine their actual performance, and require distinct charging and discharging
 63 temperatures [8] (usually between 100 and 300 °C, depending on the reaction), having potential interest
 64 for interseasonal storage applications. Figure 3 A shows , heat storage capacity [kWh_{th}/m³] of water
 65 sensible heat storage and 3 PCMs over a 20 °C temperature interval; the PCMs store around 2.5 to
 66 6 times more energy than water.. Figure 3 B compares thermochemical heat storage to a packed
 67 rock bed heat storage system; the hydration of the thermochemical compound can theoretically re-
 68 lease25 times more energy than what achievable with 40°C of air temperature increase in a rock bed
 69 heat storage system, although temperatures up to 120°C are required for dehydration of the salt hy-
 70 drate ;, such thermochemical heat storage materials may prove to be suitable candidates for inter sea-
 71 sonal thermal energy storage.

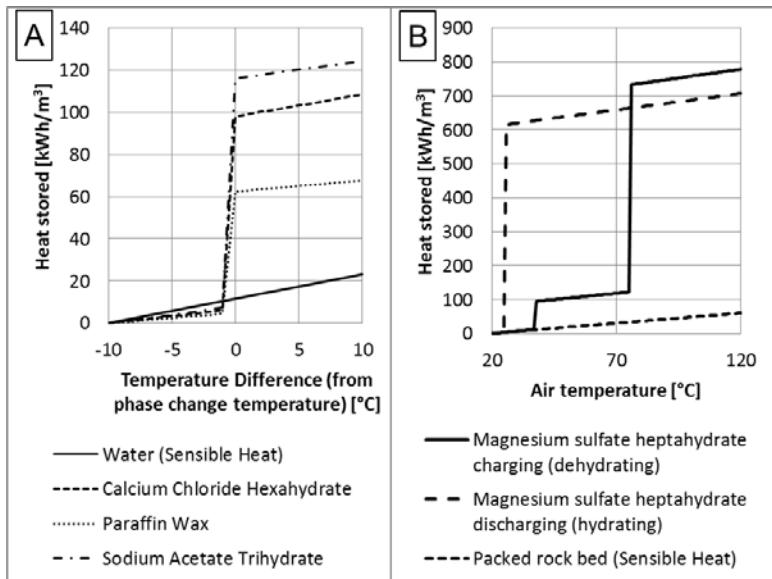


Figure 3- Heat stored vs. Temperature diagrams for 3 PCMs and a sensible water heat storage system (A) and magnesium sulphate heptahydrate (data retrieved from Zondag et al. [8]) compared to a conventional rock bed storage system (B).

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

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

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

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

2. PHASE CHANGE MATERIALS LITERATURE REVIEW

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

108 **i. ORGANIC PCMS**

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 alcohol [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.

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

| 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 | |
| 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 anhydride | 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] |

122 **ii. SALT HYDRATES**

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.

Table 2 - Thermophysical properties of selected salt hydrates;

| Compound | T _m | ΔH _m | C _{p_s} | C _{p_t} | λ _s | λ _t | 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] |

132 *a. PHASE SEPARATION*

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*

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.

145 *iii. EUTECTIC PCMs*

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 (Cp), 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-

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

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

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

$$Cp_{eutectic} = \sum_i Cp_i \times w_i \quad 3$$

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

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

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

Table 3 - Thermophysical properties of selected eutectic compounds

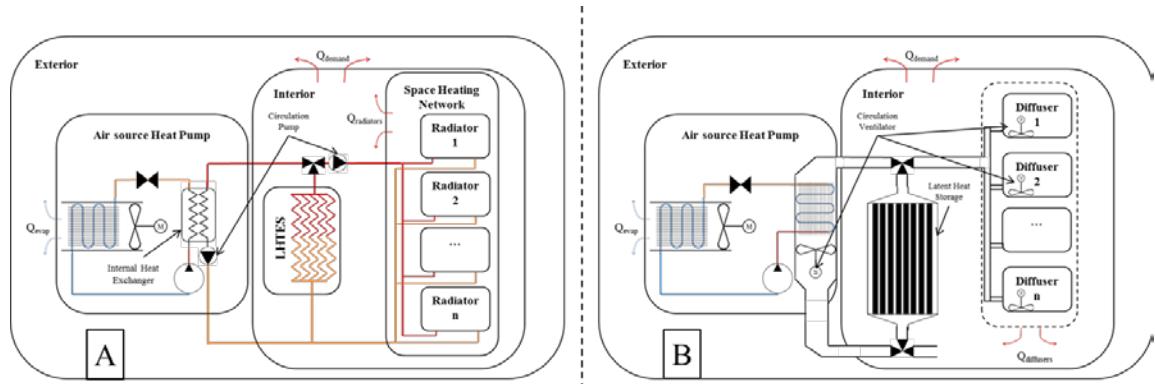
| Eutectic Compounds | Mass Ratio | T _m | ΔH _m | Cp _s | Cp _l | λ _s | λ _l | ρ _s | E _{density} | Price | | Ref |
|---|------------|----------------|-----------------|-----------------|-----------------|-------------------|--------------------|------------------|----------------------|------------|------------|------------|
| | | °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 | |
| Urea - LiNO ₃ | 82-18 | 76 | 218 | 1770 | 2020 | 850 | 600 | 1438 | 84 | 851 | 10.1 | [73] |
| 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 | |
| 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 | |
| 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 | |
| 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 | |
| NaNO ₂ - NaNO ₃ | 55-45 | 233 | 163 | 1310 | 2130 | 590 | 640 | 2210 | 97 | 382 | 3.9 | |
| CaCl ₂ - LiNO ₃ | 13-87 | 238 | 317 | 1500 | 1530 | 1370 | 690 | 2362 | 204 | 5325 | 26 | |
| LiCl - LiNO ₃ | 9-91 | 244 | 342 | 1580 | 1610 | 1370 | 640 | 2351 | 218 | 6019 | 28 | |
| NaNO ₃ - NaOH | 86-14 | 250 | 160 | 1190 | 1860 | 660 | 600 | 2241 | 97 | 339 | 3.5 | [32] |

186

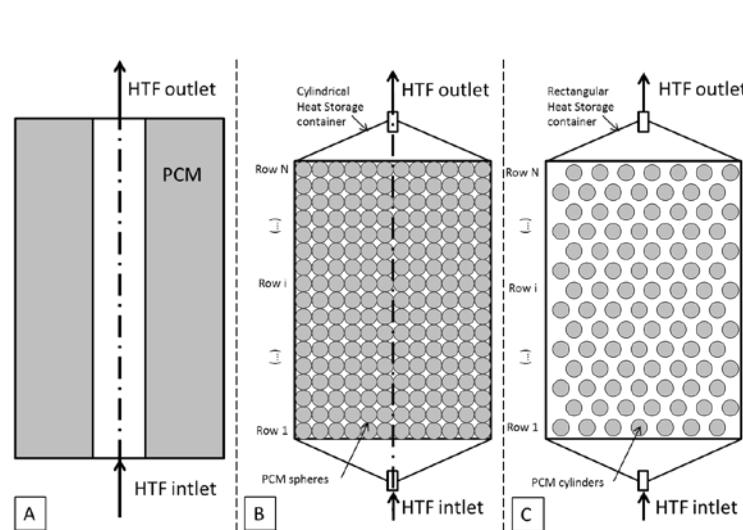
187 3. POTENTIAL APPLICATIONS FOR INDIRECT LATENT HEAT STORAGE CONTAINERS AND
188 SYSTEMS
189

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.



197
 198 **Figure 4 - Simplified diagrams of the integration of LHTES into water space heating systems (A) and centralized air**
 199 **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 in 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]. Encapsulated
 205 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.



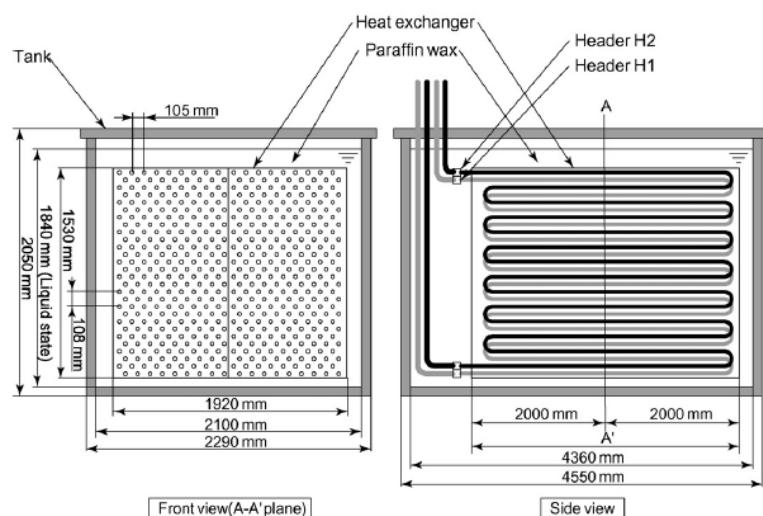
213
 214 **Figure 5 – Cross sections of a compact tube in tube (A), a encapsulated packed bed (B) and encapsulated staggered**
 215 **cylinders (C) latent heat storage containers.**

216 **i. COMPACT LATENT HEAT STORAGE SYSTEMS**

217
 218 Compact latent heat storage systems can have much higher PCM volumetric ratios [$\text{m}^3_{\text{PCM}}/\text{m}^3_{\text{Container}}$]
 219 than encapsulated latent heat systems, providing in theory longer duration isothermal outputs; howev-
 220 er, low rates of thermal diffusion within the bulk PCM can be a major challenge, leading to lower
 221 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



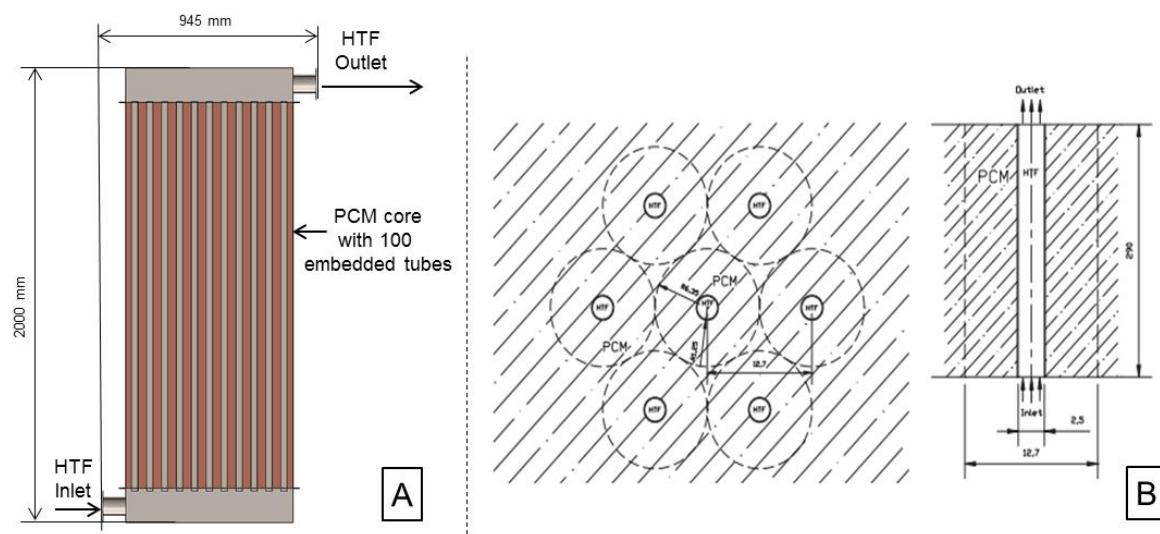
233

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.

244



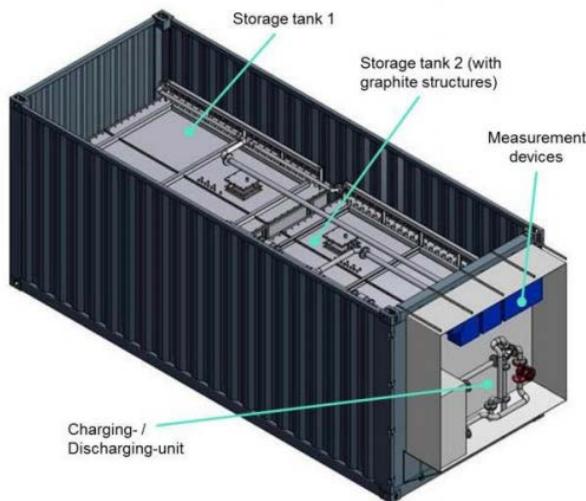
245

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].

248

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

260



261

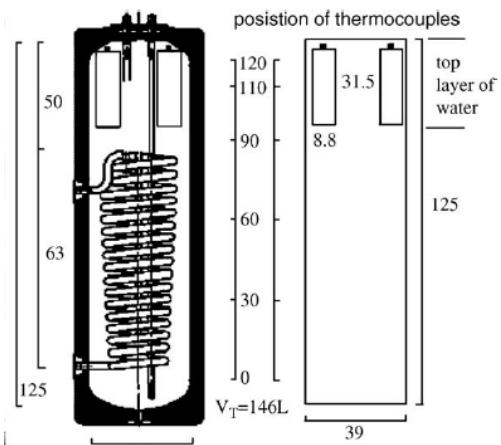
262 **Figure 8 – Structure of the prototype storage system developed by Deckert et al. [87] to meet the heat demands of a**
263 **district heating network.**

264

265 Systems using encapsulated PCMs offer higher heat transfer area per system volume [$m^2_{HT\ area}/m^3_{System}$], but have lower volumetric ratios [m^3_{PCM}/m^3_{System}]. Another advantage is the ease of ob-
266 taining leak-proof solutions [9], proving suitable for less stable materials. The ability to be used with
267 any given storage container provides great versatility, regardless of size; hence their popularity [86],
268 [88].

269 The geometries used vary significantly with the application, but they commonly have cylindrical or
270 spherically shaped capsules, which can be inserted into off the shelf storage containers. Cabeza et al.
271 [89], undertook a study in which two to six small cylinders containing a mixture of 90% sodium ace-
272 tate trihydrate + 10% graphite as the PCM were inserted in the upper part of a domestic hot water
273 tank, making good use of the tank's thermal stratification, Figure 9. The study concluded that, by add-
274 ing 2% by volume of PCM (2 tubes) to the top region of the store, they could achieve an increase of
275 40% in the thermal storage capacity; comparing to the common water tank over a temperature differ-
276 ence of 1K where the PCM solidifies (around 54 °C).
277

278



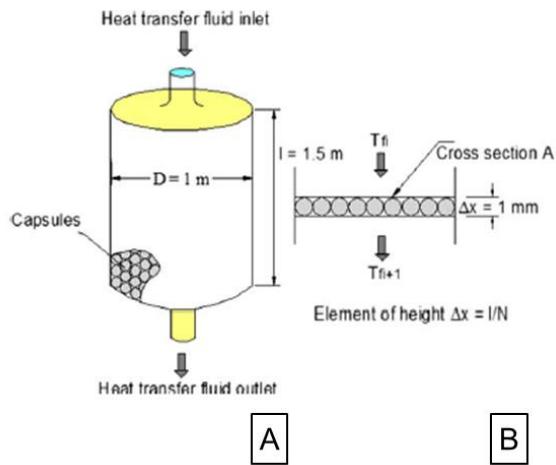
279

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

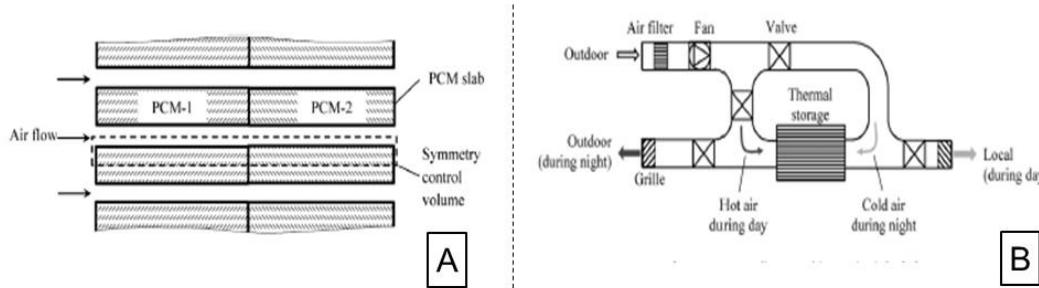


289

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].**

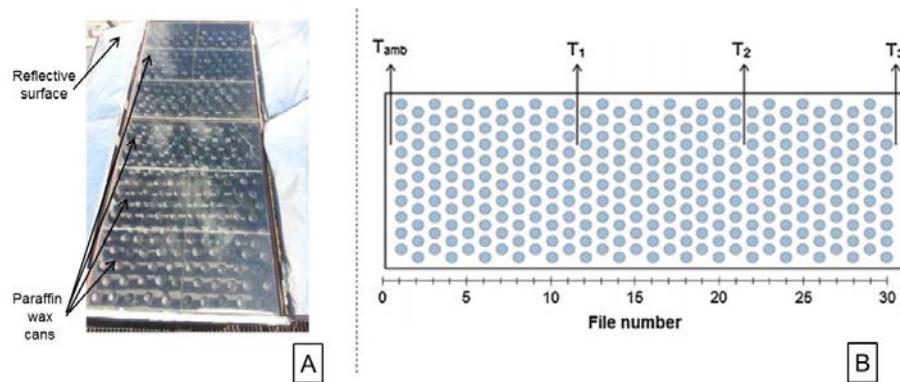
292

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.



302
303 **Figure 11 – Detailed view of the heat transfer arrangement inside the PCM module (A) and schematic representation**
304 **of the container integration into the ventilation system studied by Mosaffa et al. [92].**

305
306 Another possible application for an encapsulated latent heat storage system was studied in [94] and is
307 illustrated in figure 12. Heat from solar thermal collectors is stored in an array of cylinders filled
308 with paraffin wax, air is used as the heat transfer fluid. Due to the poor convective heat transfer ob-
309 tained to the outer shell of the capsules, aluminium strips were used to increase the effective heat
310 transfer area of the cylinders, providing a substantial increase in the latent heat storage system's effec-
311 tiveness and the global solar collector system efficiency.



312
313 **Figure 12 – Picture of the solar air absorber (A) and schematic diagram of the absorber presenting the thermocou-
314 ple positions for the experimental work performed by Reyes et al. [94].**

315 *a. MICRO ENCAPSULATION OF PCM*

316
317 Micro capsules with a diameter varying from around $1-1000 \mu\text{m}$ [32] have been used to encapsulate
318 PCMs, such micro capsules when introduced into a liquid, form a slurry, effectively increasing the
319 thermal storage capacity of the working fluid and potentially its convective heat transfer properties.
320 Current production methods for micro encapsulated PCMs are: coacervation, suspension and emul-
321 sion polymerization, poly-condensation and polyaddition. Huang et al. [21], undertook a study in which
322 a cylindrical container filled with a PCM slurry was heated and cooled using a helical coil heat ex-
323 changer. The slurry varied between 25, 35 and 50 % composition by volume of PCM capsules to car-
324 rier fluid. It was concluded that higher volumetric ratios (50 % respectively) reduced natural convec-
325 tion heat transfer within the storage container. Another characteristic of using PCM filled microcap-
326 sules was the low PCM volumetric ratios per capsule, normally around 50%, which when multiplied
327 by the slurry volumetric ratio leads to a very low PCM volumetric ratio which reduces the typical
328 heat capacity increase obtained when using PCMs.
329
330

331
332 *ii. HEAT TRANSFER ENHANCEMENT METHODS*

333

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.

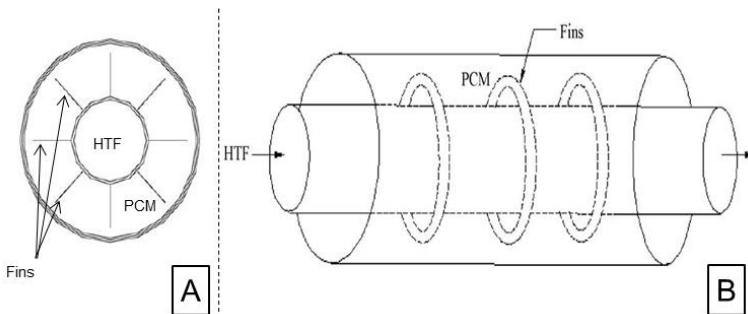
339

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].**

353

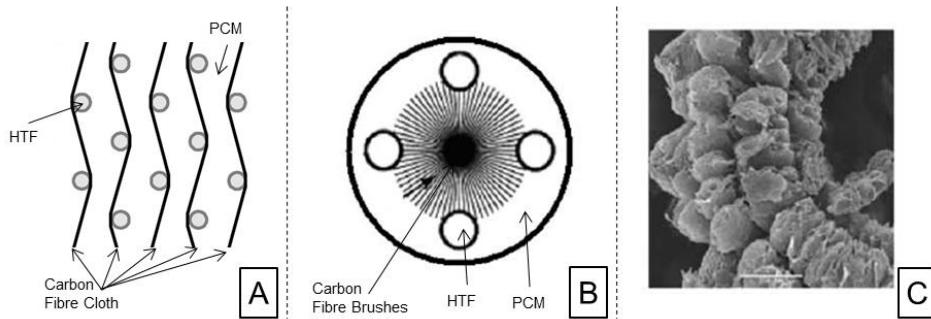
354 *b. HEAT TRANSFER ENHANCEMENT USING CARBON*

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].

365

366



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

384
385 *d. USING CONDUCTIVE POWDERS*

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

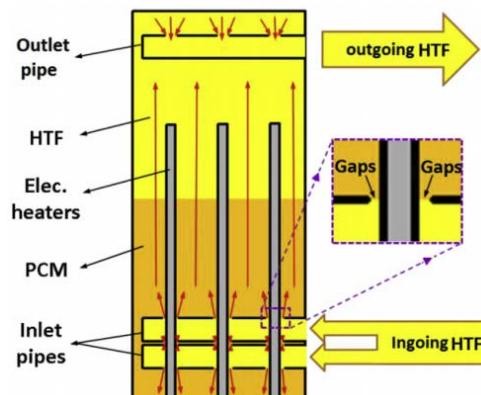
393
394
395
396 *e. DIRECT HEAT TRANSFER TECHNIQUES*

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 melting
 401 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 container
 403 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.



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].**

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.



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

4. CONCLUSIONS

421 Phase change materials have the potential to store large amounts of energy within a smaller tempera-
 422 ture range when compared to common sensible heat storage materials. Due to the low thermal con-
 423 ductivities of many PCMs, poor rates of thermal diffusion within the PCM can seriously affect the
 424 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 properties of the materials having the most appropriate properties presented. Below 100 °C, organic
428 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 1250 °C eutectic mixtures of inorganic
430 salts appear the most promising PCMs. A mixture of sodium and potassium fomates 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

440 **Acknowledgements**

441 The research presented in this paper is funded by the EPSRC through Grant reference EP/K011847/1,
442 Interdisciplinary centre for Storage, Transformation and Upgrading of Thermal Energy (i-STUT)E
443 and a Loughborough University funded PhD studentship.

444

445 **5. REFERENCES**

- 446 [1] International Energy Agency, “World Energy Outlook 2013,” 2015.
- 447 [2] K. Harris, A. Annut, and I. MacLeay, *Digest of United Kingdom Energy Statistics 2015*, vol. b.
448 2015.
- 449 [3] A. D. Hawkes, “Long-run marginal CO₂ emissions factors in national electricity systems,”
450 *Appl. Energy*, vol. 125, pp. 197–205, Jul. 2014.
- 451 [4] A. D. Hawkes, “Estimating marginal CO₂ emissions rates for national electricity systems,”
452 *Energy Policy*, vol. 38, no. 10, pp. 5977–5987, Oct. 2010.
- 453 [5] National Grid, “UK Future Energy Scenarios 2014,” *Energy*, no. July, p. 220, 2014.
- 454 [6] D. Haillot, E. Franquet, S. Gibout, and J.-P. Bédécarrats, “Optimization of solar DHW system
455 including PCM media,” *Appl. Energy*, vol. 109, pp. 470–475, Sep. 2013.
- 456 [7] M. Ibáñez, L. F. Cabeza, C. Solé, J. Roca, and M. Nogués, “Modelization of a water tank
457 including a PCM module,” *Appl. Therm. Eng.*, vol. 26, pp. 1328–1333, 2006.
- 458 [8] H. Zondag, B. Kikkert, S. Smeding, R. de Boer, and M. Bakker, “Prototype thermochemical
459 heat storage with open reactor system,” *Appl. Energy*, vol. 109, pp. 360–365, Sep. 2013.
- 460 [9] F. Agyenim, N. Hewitt, P. Eames, and M. Smyth, “A review of materials, heat transfer and
461 phase change problem formulation for latent heat thermal energy storage systems (LHTESS),”
462 *Renew. Sustain. Energy Rev.*, vol. 14, pp. 615–628, 2010.

- 463 [10] A. Gil, E. Oró, G. Peiró, S. Álvarez, and L. F. Cabeza, “Material selection and testing for
464 thermal energy storage in solar cooling,” *Renew. Energy*, vol. 57, pp. 366–371, 2013.
- 465 [11] A. Gil, C. Barreneche, P. Moreno, C. Solé, A. Inés Fernández, and L. F. Cabeza, “Thermal
466 behaviour of d-mannitol when used as PCM: Comparison of results obtained by DSC and in a
467 thermal energy storage unit at pilot plant scale,” *Appl. Energy*, vol. 111, pp. 1107–1113, Nov.
468 2013.
- 469 [12] F. Colella, A. Sciacovelli, and V. Verda, “Numerical analysis of a medium scale latent energy
470 storage unit for district heating systems,” *Energy*, vol. 45, no. 1, pp. 397–406, Sep. 2012.
- 471 [13] J. Kensby, A. Trüschel, and J.-O. Dalenbäck, “Potential of residential buildings as thermal
472 energy storage in district heating systems – Results from a pilot test,” *Appl. Energy*, vol. 137,
473 pp. 773–781, Jan. 2015.
- 474 [14] J. Vivian, G. Manente, and A. Lazzaretto, “A general framework to select working fluid and
475 configuration of ORCs for low-to-medium temperature heat sources,” *Appl. Energy*, vol. 156,
476 pp. 727–746, Oct. 2015.
- 477 [15] A. R. Higgo and T. J. Zhang, “Characterization of a Compact Organic Rankine Cycle
478 Prototype for Low-grade Transient Solar Energy Conversion,” *Energy Procedia*, vol. 69, pp.
479 1113–1122, May 2015.
- 480 [16] S. Kalogirou, “The potential of solar industrial process heat applications,” *Appl. Energy*, vol.
481 76, no. 4, pp. 337–361, Dec. 2003.
- 482 [17] S. Jegadheeswaran and S. D. Pohekar, “Performance enhancement in latent heat thermal
483 storage system: A review,” *Renew. Sustain. Energy Rev.*, vol. 13, no. 9, pp. 2225–2244, 2009.
- 484 [18] K. Nakaso, H. Teshima, A. Yoshimura, S. Nogami, Y. Hamada, and J. Fukai, “Extension of
485 heat transfer area using carbon fiber cloths in latent heat thermal energy storage tanks,” *Chem.
486 Eng. Process. Process Intensif.*, vol. 47, no. 5, pp. 879–885, 2008.
- 487 [19] G. Q. Qi, C. L. Liang, R. Y. Bao, Z. Y. Liu, W. Yang, B. H. Xie, and M. B. Yang,
488 “Polyethylene glycol based shape-stabilized phase change material for thermal energy storage
489 with ultra-low content of graphene oxide,” *Sol. Energy Mater. Sol. Cells*, vol. 123, pp. 171–
490 177, 2014.
- 491 [20] W. Wang, X. Yang, Y. Fang, J. Ding, and J. Yan, “Preparation and thermal properties of
492 polyethylene glycol/expanded graphite blends for energy storage,” *Appl. Energy*, vol. 86, no. 9,
493 pp. 1479–1483, 2009.
- 494 [21] M. J. Huang, P. C. Eames, S. McCormack, P. Griffiths, and N. J. Hewitt, “Microencapsulated
495 phase change slurries for thermal energy storage in a residential solar energy system,” *Renew.
496 Energy*, vol. 36, pp. 2932–2939, 2011.
- 497 [22] W. Wang, S. He, S. Guo, J. Yan, and J. Ding, “A combined experimental and simulation study
498 on charging process of Erythritol–HTO direct-blending based energy storage system,” *Energy
499 Convers. Manag.*, vol. 83, pp. 306–313, Jul. 2014.
- 500 [23] S. Guo, J. Zhao, W. Wang, G. Jin, X. Wang, Q. An, and W. Gao, “Experimental study on
501 solving the blocking for the direct contact mobilized thermal energy storage container,” *Appl.
502 Therm. Eng.*, vol. 78, pp. 556–564, Mar. 2015.

- 503 [24] I. Johansson, "AMIDES , Fatty Acid," *Kirch-Othmer Encycl. Ind. Chem.*, vol. 2, 2000.
- 504 [25] a. Raemy and T. F. Schweizer, "Thermal behaviour of carbohydrates studied by heat flow
505 calorimetry," *J. Therm. Anal.*, vol. 28, pp. 95–108, 1983.
- 506 [26] H. Schiweck, A. Bär, R. Vogel, E. Schwarz, M. Kunz, C. Dusautois, A. Clement, C. Lefranc,
507 B. Lüssem, M. Moser, and S. Peters, "Sugar Alcohols," in *Ullmann's Encyclopedia of
508 Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2012, pp. 2–32.
- 509 [27] B. Cornils and P. Lappe, "Dicarboxylic acids. Aliphatic," in *Ullmann's Encyclopedia of
510 Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2008.
- 511 [28] D. H. Kerridge, "The chemistry of molten acetamide and acetamide complexes," *Chem. Soc.
512 Rev.*, vol. 17, p. 181, 1988.
- 513 [29] M. M. Kenisarin, "Thermophysical properties of some organic phase change materials for
514 latent heat storage. A review," *Sol. Energy*, vol. 107, pp. 553–575, 2014.
- 515 [30] I. Mavrovic, a. R. Shirley, and G. R. Coleman, "Urea," *Kirk-Othmer Encycl. Chem. Technol.*,
516 vol. 2, pp. 1–21, 2010.
- 517 [31] D. Haillot, T. Bauer, U. Kröner, and R. Tamme, "Thermal analysis of phase change materials
518 in the temperature range 120-150 °c," *Thermochim. Acta*, vol. 513, no. 1–2, pp. 49–59, 2011.
- 519 [32] N. R. Jankowski and F. P. McCluskey, "A review of phase change materials for vehicle
520 component thermal buffering," *Appl. Energy*, vol. 113, pp. 1525–1561, 2014.
- 521 [33] A. P. Miller, "Lange's Handbook of Chemistry," *Am. J. Public Heal. Nations Heal.*, vol. 31,
522 no. 12, p. 1324, 1941.
- 523 [34] S. Harish, D. Orejon, Y. Takata, and M. Kohno, "Thermal conductivity enhancement of lauric
524 acid phase change nanocomposite with graphene nanoplatelets," *Appl. Therm. Eng.*, vol. 80,
525 pp. 205–211, Apr. 2015.
- 526 [35] Y. Yuan, N. Zhang, W. Tao, X. Cao, and Y. He, "Fatty acids as phase change materials: A
527 review," *Renewable and Sustainable Energy Reviews*, vol. 29, pp. 482–498, 2014.
- 528 [36] F. Tang, L. Cao, and G. Fang, "Preparation and thermal properties of stearic acid/titanium
529 dioxide composites as shape-stabilized phase change materials for building thermal energy
530 storage," *Energy Build.*, vol. 80, pp. 352–357, Sep. 2014.
- 531 [37] M. M. Farid, A. M. Khudhair, S. A. K. Razack, and S. Al-Hallaj, "A review on phase change
532 energy storage: Materials and applications," *Energy Convers. Manag.*, vol. 45, pp. 1597–1615,
533 2004.
- 534 [38] M. Silakhori, H. Fauzi, M. R. Mahmoudian, H. S. C. Metselaar, T. M. I. Mahlia, and H. M.
535 Khanlou, "Preparation and thermal properties of form-stable phase change materials composed
536 of palmitic acid/polypyrrole/graphene nanoplatelets," *Energy Build.*, vol. 99, pp. 189–195, Jul.
537 2015.
- 538 [39] "Website of Rubitherm GmbH," *Rubitherm GmbH*, 2016. [Online]. Available:
539 <http://www.rubitherm.eu/>.

- 540 [40] J. G. Dunn, H. G. Smith, and R. L. Willix, "The supercooling of acetamide," *Thermochim. Acta*, vol. 80, no. 2, pp. 343–353, Oct. 1984.
- 542 [41] W. Riemenssneider and M. Tanifuji, "Oxalic Acid," in *Ullmann's Encyclopedia of Industrial Chemistry*, 25th ed., Wiley-VCH Verlag GmbH & Co. KGaA, 2012, pp. 543–600.
- 544 [42] B. Tong, Z. C. Tan, J. N. Zhang, and S. X. Wang, "Thermodynamic investigation of several natural polyols (III): Heat capacities and thermodynamic properties of erythritol," *J. Therm. Anal. Calorim.*, vol. 95, no. 2, pp. 469–475, 2009.
- 547 [43] K. Pielichowska and K. Pielichowski, "Phase change materials for thermal energy storage," *Prog. Mater. Sci.*, vol. 65, pp. 67–123, 2014.
- 549 [44] P. Lorz, F. Towae, W. Enke, R. Jäckh, N. Bhargava, and W. Hillesheim, "Phthalic acid and Derivates," in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2012, pp. 35–154.
- 552 [45] K. Muraishi and Y. Suzuki, "The thermal behaviour of dicarboxylic acids in various atmospheres," *Thermochim. Acta*, vol. 232, pp. 195–203, 1994.
- 554 [46] K. Lohbeck, H. Haferkorn, W. Fuhrmann, and N. Fedtke, "Maleic and Fumaric Acids," in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, 2005, pp. 413–454.
- 557 [47] T. Felthouse, J. Burnett, B. Horrell, M. Mommey, and Y.-J. Kuo, "Maleic Anhydride , Maleic Acid , and Fumaric Acid," in *Kirk-Othmer Encyclopedia of Industrial Chemistry*, no. 10, John Wiley & Sons, Inc., 1933.
- 560 [48] T. Maki and K. Takeda, "Benzoic Acid and Derivatives," in *Ullmann's Encyclopedia of Industrial Chemistry*, vol. 60, 2012, pp. 329–342.
- 562 [49] T. Hasl and I. Jiricek, "The prediction of heat storage properties by the study of structural effect on organic phase change materials," *Energy Procedia*, vol. 46, pp. 301–309, 2014.
- 564 [50] G. Barone, G. Della Gatta, D. Ferro, and V. Piacente, "Enthalpies and entropies of sublimation, vaporization and fusion of nine polyhydric alcohols," *J. Chem. Soc. Faraday Trans.*, vol. 86, no. 1, p. 75, 1990.
- 567 [51] A. Solé, H. Neumann, S. Niedermaier, I. Martorell, P. Schossig, and L. F. Cabeza, "Stability of sugar alcohols as PCM for thermal energy storage," *Sol. Energy Mater. Sol. Cells*, vol. 126, pp. 125–134, 2014.
- 570 [52] G. Krishna Bama, R. Anitha, and K. Ramachandran, "On the thermal properties of aqueous solution of D-mannitol," *Nondestruct. Test. Eval.*, vol. 25, no. 1, pp. 67–75, Oct. 2009.
- 572 [53] A. Gil, E. Oró, L. Miró, G. Peiró, Á. Ruiz, J. M. Salmerón, and L. F. Cabeza, "Experimental analysis of hydroquinone used as phase change material (PCM) to be applied in solar cooling refrigeration," *Int. J. Refrig.*, vol. 39, pp. 95–103, Mar. 2014.
- 575 [54] G. a. Lane, "Phase change materials for energy storage nucleation to prevent supercooling," *Sol. Energy Mater. Sol. Cells*, vol. 27, pp. 135–160, 1992.

- 577 [55] G. M. Habashy and G. A. Kolta, "Thermal decomposition of the hydrates of barium hydroxide,"
578 *J. Inorg. Nucl. Chem.*, vol. 34, no. 1961, pp. 57–67, 1972.
- 579 [56] F. C. Porisini, "Salt hydrates used for latent heat storage: Corrosion of metals and reliability of
580 thermal performance," *Sol. Energy*, vol. 41, no. 2, pp. 193–197, 1988.
- 581 [57] W. E. Acree, "Thermodynamic properties of organic compounds: enthalpy of fusion and
582 melting point temperature compilation," *Thermochim. Acta*, vol. 189, pp. 37–56, 1991.
- 583 [58] B. Zalba, "Review on thermal energy storage with phase change: materials, heat transfer
584 analysis and applications," *Appl. Therm. Eng.*, vol. 23, no. 3, pp. 251–283, 2003.
- 585 [59] M. Hadjieva, R. Stoykov, and T. Filipova, "Composite salt-hydrate concrete system for
586 building energy storage," *Renew. Energy*, vol. 19, no. 1–2, pp. 111–115, Jan. 2000.
- 587 [60] B. Sandnes and J. Rekstad, "Supercooling salt hydrates: Stored enthalpy as a function of
588 temperature," *Sol. Energy*, vol. 80, no. 5, pp. 616–625, May 2006.
- 589 [61] J. B. Johansen, M. Dannemand, W. Kong, J. Fan, J. Dragsted, and S. Furbo, "Thermal
590 Conductivity Enhancement of Sodium Acetate Trihydrate by Adding Graphite Powder and the
591 Effect on Stability of Supercooling," *Energy Procedia*, vol. 70, pp. 249–256, May 2015.
- 592 [62] P. Patnaik, *Handbook of Inorganic Chemicals*. McGraw-Hill, 2003.
- 593 [63] L. Zhongliang, M. Chongfang, and L. Jing, "An experimental study on the stability and
594 reliability of the thermal properties of barium hydroxide octahydrate as a phase change
595 material," *Proc. 7th Expert Meet. Work. IEA Annex 17 Adv. Therm. Energy Storage trough
596 Phase Chang. Mater. Chem. React. – Feasibility Stud. Demonstr. Proj.*, pp. 63–69, 2004.
- 597 [64] R. Pilar, L. Svoboda, P. Honcova, and L. Oravova, "Study of magnesium chloride hexahydrate
598 as heat storage material," *Thermochim. Acta*, vol. 546, pp. 81–86, 2012.
- 599 [65] T. Bauer, D. Laing, and R. Tamme, "Recent progress in alkali nitrate/nitrite developments for
600 solar thermal power applications," *Molten Salts Chem. Technol.* ..., no. June, pp. 1–10, 2011.
- 601 [66] J. C. Gomez, N. Calvet, A. K. Starace, and G. C. Glatzmaier, "Ca(NO₃)₂ — NaNO₃ — KNO₃
602 Molten Salt Mixtures for Direct Thermal Energy Storage Systems in Parabolic Trough Plants,"
603 *J. Sol. Energy Eng.*, vol. 135, no. May 2013, p. 021016, 2013.
- 604 [67] J. G. Cordaro, N. C. Rubin, and R. W. Bradshaw, "Multicomponent Molten Salt Mixtures
605 Based on Nitrate/Nitrite Anions," *J. Sol. Energy Eng.*, vol. 133, no. February 2011, p. 011014,
606 2011.
- 607 [68] M. Yamada, M. Tago, S. Fukusako, and A. Horibe, "Melting point and supercooling
608 characteristics of molten salt," *Thermochim. Acta*, vol. 218, pp. 401–411, May 1993.
- 609 [69] J. . Rowlinson, "Molecular thermodynamics of fluid-phase equilibria," *The Journal of
610 Chemical Thermodynamics*, vol. 2, no. 1. pp. 158–159, 1970.
- 611 [70] Y. Yanping, T. Wenquan, C. Xiaoling, and B. Li, "Theoretic prediction of melting temperature
612 and latent heat for a fatty acid eutectic mixture," *J. Chem. Eng. Data*, vol. 56, no. 6, pp. 2889–
613 2891, 2011.

- 614 [71] J. Gmehling, J. Li, and M. Schiller, “A modified UNIFAC model. 2. Present parameter matrix
615 and results for different thermodynamic properties,” *Ind. Eng. Chem. Res.*, vol. 32, no. 1, pp.
616 178–193, 1993.
- 617 [72] G. Diarce, I. Gandarias, Á. Campos-Celador, A. García-Romero, and U. J. Griesser, “Eutectic
618 mixtures of sugar alcohols for thermal energy storage in the 50–90°C temperature range,” *Sol.
619 Energy Mater. Sol. Cells*, vol. 134, pp. 215–226, Mar. 2015.
- 620 [73] A. Sharma, V. V. Tyagi, C. R. Chen, and D. Buddhi, “Review on thermal energy storage with
621 phase change materials and applications,” *Renew. Sustain. Energy Rev.*, vol. 13, pp. 318–345,
622 2009.
- 623 [74] G. Baran and A. Sari, “Phase change and heat transfer characteristics of a eutectic mixture of
624 palmitic and stearic acids as PCM in a latent heat storage system,” *Energy Convers. Manag.*,
625 vol. 44, no. 20, pp. 3227–3246, Dec. 2003.
- 626 [75] R. I. Olivares and W. Edwards, “LiNO₃-NaNO₃-KNO₃ salt for thermal energy storage:
627 Thermal stability evaluation in different atmospheres,” *Thermochim. Acta*, vol. 560, pp. 34–42,
628 2013.
- 629 [76] F. Roget, C. Favotto, and J. Rogez, “Study of the KNO₃-LiNO₃ and KNO₃-NaNO₃-LiNO₃
630 eutectics as phase change materials for thermal storage in a low-temperature solar power plant,”
631 *Sol. Energy*, vol. 95, pp. 155–169, 2013.
- 632 [77] B. Y. Gamataeva, R. M. Bagomedova, and a. M. Gasanaliev, “Differentiation of the
633 Li_xNa_yK_zNO₂NO₃ quaternary reciprocal system and phase formation in its stable partitioning
634 tetrahedron LiNO₂-NaNO₂-KNO₂-KNO₃,” *Russ. J. Inorg. Chem.*, vol. 59, no. 2, pp. 134–140,
635 2014.
- 636 [78] G. J. Janz and R. P. T. Tomkins, “Molten Salts: Volume 5, Part 2. Additional Single and
637 Multi-Component Salt Systems. Electrical Conductance, Density, Viscosity and Surface
638 Tension Data.” New York, 1983.
- 639 [79] A. M. Gasanaliev and B. Y. Gamataeva, “Heat-accumulating properties of melts,” *Russ. Chem.
640 Rev.*, vol. 69, pp. 179–186, 2007.
- 641 [80] L. Dante, B. Mario, C. Augusto, and F. Paolo, “Molten Mixtures of K, Na Formates with
642 Alkali Halides. Note I,” *Zeitschrift für Naturforschung A*, vol. 25. p. 52, 1970.
- 643 [81] M. M. Kenisarin, “High-temperature phase change materials for thermal energy storage,”
644 *Renew. Sustain. Energy Rev.*, vol. 14, pp. 955–970, 2010.
- 645 [82] G. J. Janz and R. P. T. Tomkins, “Molten Salts: Volume 5, Part 1 Additional Single and Multi-
646 Component Salt systems. Electrical Conductance, Density, Viscosity and Surface Tension
647 Data.” New York, 1980.
- 648 [83] N. J. Hewitt, “Heat pumps and energy storage – The challenges of implementation,” *Appl.
649 Energy*, vol. 89, no. 1, pp. 37–44, Jan. 2012.
- 650 [84] F. Agyenim, P. Eames, and M. Smyth, “Experimental study on the melting and solidification
651 behaviour of a medium temperature phase change storage material (Erythritol) system
652 augmented with fins to power a LiBr/H₂O absorption cooling system,” *Renew. Energy*, vol. 36,
653 no. 1, pp. 108–117, 2011.

- 654 [85] A. Trp, "An experimental and numerical investigation of heat transfer during technical grade
655 paraffin melting and solidification in a shell-and-tube latent thermal energy storage unit," *Sol. Energy*, vol. 79, no. 6, pp. 648–660, Dec. 2005.
- 657 [86] a. Barba and M. Spiga, "Discharge mode for encapsulated PCMs in storage tanks," *Sol. Energy*, vol. 74, no. February, pp. 141–148, 2003.
- 659 [87] M. Deckert, R. Scholz, S. Binder, and A. Hornung, "Economic Efficiency of Mobile Latent
660 Heat Storages," *Energy Procedia*, vol. 46, pp. 171–177, 2014.
- 661 [88] M. N. a Hawlader, M. S. Uddin, and H. J. Zhu, "Encapsulated phase change materials for
662 thermal energy storage: Experiments and simulation," *Int. J. Energy Res.*, vol. 26, no. January
663 2001, pp. 159–171, 2002.
- 664 [89] L. F. Cabeza, M. Ibanez, C. Sole, J. Roca, and M. Nogues, "Experimentation with a water tank
665 including a PCM module," *Sol. Energy Mater. Sol. Cells*, vol. 90, no. 9, pp. 1273–1282, 2006.
- 666 [90] M. Wu, C. Xu, and Y.-L. He, "Dynamic thermal performance analysis of a molten-salt
667 packed-bed thermal energy storage system using PCM capsules," *Appl. Energy*, vol. 121, pp.
668 184–195, May 2014.
- 669 [91] a. Felix Regin, S. C. Solanki, and J. S. Saini, "An analysis of a packed bed latent heat thermal
670 energy storage system using PCM capsules: Numerical investigation," *Renew. Energy*, vol. 34,
671 no. 7, pp. 1765–1773, 2009.
- 672 [92] A. H. Mosaffa, L. Garousi Farshi, C. A. Infante Ferreira, and M. A. Rosen, "Energy and
673 exergy evaluation of a multiple-PCM thermal storage unit for free cooling applications,"
674 *Renew. Energy*, vol. 68, pp. 452–458, Aug. 2014.
- 675 [93] F. Jiao and P. Xu, "Simulation and Feasibility Analysis of PCM Based Passive Cooling
676 Technique in Residential House," *Procedia Eng.*, vol. 121, pp. 1969–1976, 2015.
- 677 [94] A. Reyes, L. Henríquez-Vargas, R. Aravena, and F. Sepúlveda, "Experimental analysis,
678 modeling and simulation of a solar energy accumulator with paraffin wax as PCM," *Energy
679 Convers. Manag.*, vol. 105, pp. 189–196, Nov. 2015.
- 680 [95] J. Shon, H. Kim, and K. Lee, "Improved heat storage rate for an automobile coolant waste heat
681 recovery system using phase-change material in a fin–tube heat exchanger," *Appl. Energy*, vol.
682 113, pp. 680–689, Jan. 2014.
- 683 [96] A. Sciacovelli, F. Gagliardi, and V. Verda, "Maximization of performance of a PCM latent
684 heat storage system with innovative fins," *Appl. Energy*, vol. 137, pp. 707–715, Jan. 2015.
- 685 [97] K. Merlin, D. Delaunay, J. Soto, and L. Traonvouez, "Heat transfer enhancement in latent heat
686 thermal storage systems: Comparative study of different solutions and thermal contact
687 investigation between the exchanger and the PCM," *Appl. Energy*, vol. 166, pp. 107–116, Mar.
688 2016.