

Temperature Tailored Molten Salts for Sustainable Energy Storage

Marco Bernagozzi, Angad Panesar*, Robert Morgan

Advanced Engineering Centre, School of Computing, Engineering and Mathematics, University of Brighton,
United Kingdom

*Corresponding Author: A.S.Panesar@brighton.ac.uk

Abstract

The power generation sector is moving towards more renewable energy sources to reduce CO₂ emissions by employing technologies such as the concentrated solar power plants and the liquid air energy storage systems. This work was focused on the identification of new molten salt mixtures to act as both, the thermal energy store and the heat transfer fluid in such applications. Firstly, a selection process utilizing literature data and Aspen⁺ property package led to the identification of 5 nitrate-based mixtures offering suitable trade-off between melting point temperatures and volumetric heat capacities. Secondly, new salt compositions with improved volumetric heat capacities were created from the starting-point commercial molten salt mixtures, and then, experimentally tested for evaluating the melting point. Finally, volumetric heat capacity maps were created for the different temperature regimes, indicating 3 new temperature tailored molten salt mixtures, which use the same pure constituents as that of CaLiNaK and Quaternary.

1. Introduction

Global warming has increased the focus of the power generation sector to reduce CO₂ emissions by utilizing lesser fossil fuels and greater renewable energy sources. The European Union has set a target for renewable energy to constitute 20% of the total energy produced by 2020 [1]. The very nature of renewable energy sources carries a series of intrinsic complexities in balancing the energy network, such as less flexibility, intermittent operation and geographical dependency. This makes it complex to combine the most prominent renewable energy sources (Wind, Hydro and Solar) with the power grid, as generation and consumption need to be constantly matched. Electric energy storage can partially mitigate these issues, allowing to store energy when the production exceeds demand and to discharge it to the power grid when needed [2]. Amongst the technologies for sustainable energy production, two are gaining increasing interest from the research community: Concentrated Solar Power (CSP) and Liquid Air Energy Storage (LAES).

CSP plants use solar collectors that reflect direct sun irradiation to a thermal receiver system, hence, increasing the solar radiation flux density. This allows for higher temperatures and higher conversion efficiencies from optical energy to thermal energy [3]. Typically, there are two main groups of CSPs: line focusing, which comprise of parabolic trough and linear Fresnel reflector, and point focusing, which can be central receiver type or parabolic dish type.

Parabolic trough is characterized by the use of parabolic shaped mirrors to focus sunlight onto an evacuated absorber tube receiver, while mirrors and tubes follow the daily sun movement. This typology is the most diffused as it provides the highest efficiency. Linear Fresnel systems use individual planar mirrors to focus sunlight on a downward-facing tube receiver. Typical operating temperatures of linear Fresnel plants are between 290-390 °C with peak and annual average conversion efficiencies of 14-20% and 13-15%, respectively [4]. Furthermore, they can reduce the costs with respect to parabolic trough.

Point focusing systems are typically based on two-axial mirrors, called heliostats, systems that allow for high concentration ratios and higher temperatures in the receiver, which can be either a solar tower or a dish system, when compared to linear Fresnel systems. The high operation temperatures between 290-565°C results in higher peak of 23-35% and annual conversion efficiencies of 14-18% [5].

During day time operation, surplus energy generated is stored in a Thermal Energy Storage (TES), which is used to heat the working fluid of the thermal cycle during discharging, increasing the overall system efficiency [6]. Moreover, a TES can increase the system reliability and reduce the energy cost for the customer. It was estimated that a TES used to store energy produced in excess during day operation could improve the capacity factor from 20-25% to 60-85% [7].

An additional interesting solution for sustainable energy production is the Liquid Air Energy Storage (LAES) which is gaining interest due to its advantages such as: large volumetric energy density, no geographical dependency, no pollution and long operative life [8]. LAES working principle is threefold: electrical energy is used to liquefy air via compression and refrigeration; cold liquefied air is stored in low pressure insulated tanks; when the grid requires additional power, liquid is drawn from the tank, heated and expanded in a turbine connected to a generator [9]. Currently, there is only one MW-scale LAES plant in operation. This is located near Manchester (UK) and managed by Highview Power Storage Ltd. The LAES system is distinct from the Compressed Air Energy Storage (CAES) system, where the thermal medium is compressed air [10].

56 Similar to CSP plants, LAES can employ a TES system, especially for the recovery of excess heat during the
 57 charging process (i.e. air liquefaction). It has been reported that, there is a 20-40% excess heat of compression,
 58 which currently is not being used effectively [11], and can therefore be recovered. This thermal energy can be
 59 used to heat up the air during the discharging process (i.e. evaporation), hence increasing the overall system
 60 efficiency.

61 The TES medium proposed in the present work is molten salts because of their appealing features such as [12]:
 62 low melting point, ultra-low vapour pressure, high volumetric heat capacity, no spontaneous detrimental
 63 exothermic reactions, insensibility to radiations and the fact that they can be liquid over a wide operative
 64 temperature range. Moreover, they present good stability at high temperatures [13]. When compared against
 65 conventional coolants, they allow lower heat exchanger costs, as they provide volumetric heat capacities 25%
 66 higher than pressurised water and five times higher than liquid sodium. Furthermore, they have been utilised as
 67 TES fluid in several CSP plants, including, USA (Solar Two), Spain (CESA I-PSA) and France (THEMIS) [14].
 68 TES technology with molten salt can be either direct or indirect. In direct molten salt storage, the salt is used to
 69 directly heat the working fluid used for the energy conversion. In indirect molten salt storage, the salt is an
 70 intermediary as it heats a HTF, such as thermal oil, which will then heat the working fluid for the power generation
 71 [15]. Research recently is focusing on the development of lower melting point molten salts in order to reduce the
 72 usage of solutions such as heat tracing tapes, thermal insulation, and to reduce the risk of freezing inside the pipes
 73 [16]. This would reduce the initial capital investment as well as the running costs.

74 An interesting feature of such industrial applications is that, the molten salts are also being used as the Heat
 75 Transfer Fluid (HTF), thereby reducing the system complexity. In fact, molten salts have been used as coolants
 76 in the so-called Molten Salt Reactors (MSR), where a fluoride salt (FLiBe) is used as coolant. This offers several
 77 key benefits such as high degree of passive safety, atmospheric pressure operation, lower spent fuel per unit of
 78 energy, and high solubility of most fission products in molten salts [17].

79 This work is focused on the identification of new molten salt mixtures that offer low to medium melting
 80 temperatures and beneficial thermo-physical properties, in order to be used as both TES and HTF in CSP and
 81 LAES plants. Firstly, selection of low melting point molten salt mixtures using the published literature was
 82 conducted, resulting in the choice of 5 starting-point commercial salt mixtures for further investigation. Secondly,
 83 utilising the same constituents as the starting-point mixtures, several new salt compositions were evaluated in
 84 terms of volumetric heat capacity using the Aspen⁺ simulation platform employing an advanced simulation
 85 procedure. Subsequently, experimental investigations were conducted to identify the melting point of 13 new
 86 mixtures. Finally, three maps presenting melting temperature and volumetric heat capacity of the starting-point as
 87 well as the alternative mixtures, with particular focus on three different temperature ranges ($< 100^{\circ}\text{C}$, $100\text{-}150^{\circ}\text{C}$,
 88 $< 200^{\circ}\text{C}$) were created, with the aim to provide a better guide in selecting the correct molten salt for a particular
 89 application.

90 2. Salt Mixture Selection and Hybrid Simulation Procedure

91 The aim of the present work was to investigate new molten salt mixtures to be used for both TES and HTF. For
 92 the first phase of down-selection, the melting temperature of $< 200^{\circ}\text{C}$ was chosen, as it indicates the common
 93 range for CSP and LAES applications. Table I presents the starting-point salts and their melting point, as a result
 94 of the initial down-selection process performed following a comprehensive review of molten salts data. The nitrate
 95 and chloride salt families offered comparable average melting point temperatures (113 vs. 108°C). Note that, solar
 96 salt is only included as a reference due to its use in CSP plants [18].

97 Table I. Starting-point commercial molten salts (nitrate and chloride families) with low melting point temperature.

| Salt | Composition | T_m [$^{\circ}\text{C}$] | Ref |
|-----------------------------|---|------------------------------|------|
| HITEC | 7NaNO ₃ -40NaNO ₂ -53KNO ₃ (7-40-53) | 142 | [12] |
| LiNaK | 18NaNO ₃ -52KNO ₃ -30LiNO ₃ (18-52-30) | 120 | [19] |
| LiK | 68KNO ₃ -32LiNO ₃ (68-32) | 133 | [20] |
| Quaternary | 14.2NaNO ₃ -50.5KNO ₃ -17.5LiNO ₃ -17.8NaNO ₂ (14.2-50.5-17.5-17.8) | 99 | [21] |
| CaLiNaK | 24.6LiNO ₃ -13.6Ca(NO ₃) ₂ -16.8NaNO ₂ -15KNO ₂ (24.6-13.6-16.8-15) | 72 | [15] |
| NaCl-AlCl ₃ | 20NaCl-80AlCl ₃ (20-80) | 108 | [21] |
| KCl-AlCl ₃ | 22KCl-78AlCl ₃ (22-78) | 128 | [21] |
| KCl-AlCl ₃ -NaCl | 11KCl-78AlCl ₃ -11NaCl (11-78-11) | 89 | [21] |
| Solar Salt | 60NaNO ₃ -40KNO ₃ (60-40) | 222 | [12] |

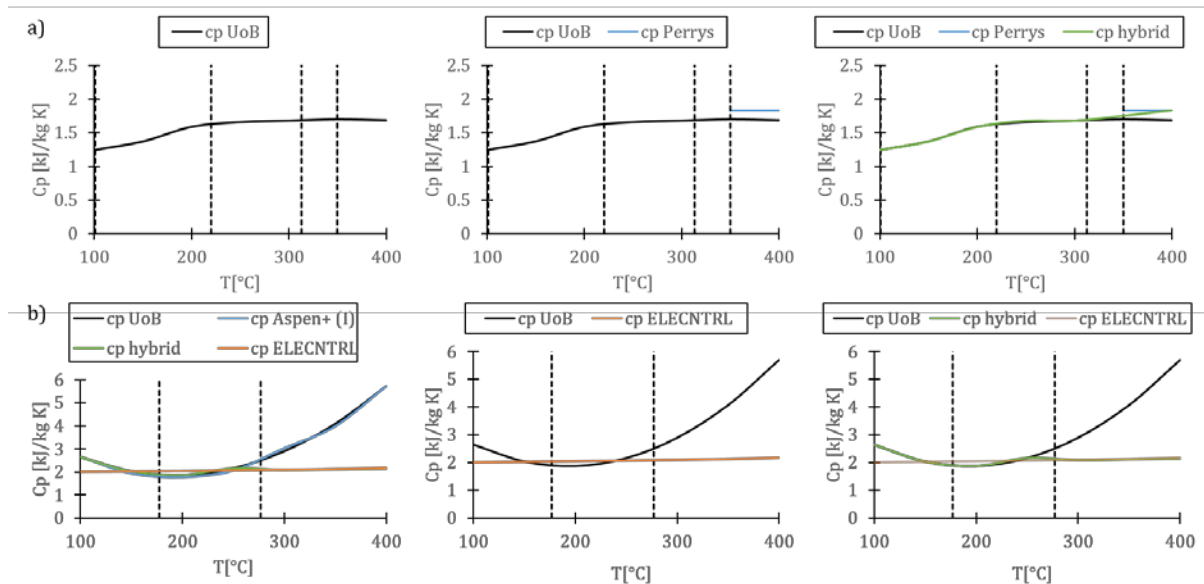
98
 99 In the second phase of down-selection, the critical thermo-physical property, i.e. the volumetric heat capacity,
 100 was considered. However, as highlighted by Nunes et al. [22], there is a noticeable fragmentation and ambiguity
 101 in the published data on salt properties, as diverging trends and incomparable temperature ranges have been

102 reported. Hence, a detailed literature review was conducted, and a database of the most relevant thermo-physical
 103 properties for all pure salts that make-up the starting-point mixtures reported in Table I was created.

104 2.1. Hybrid Simulation Procedure

105 To mitigate the challenges highlighted by Nunes et al. [22], a hybrid simulation procedure was developed. Firstly,
 106 the thermo-physical property database of pure salts were imposed in Aspen+. This allowed replication of the
 107 trends reported in the literature, regardless of their limited validity range. Secondly, in order to provide a
 108 continuous set of information over the interested temperature range (100°C to 400°C), different equations reported
 109 in the literature were coupled, including suitable Aspen+ property packages. Fig.1 reports two such hybrid
 110 procedure examples, for NaNO₃ and NaNO₂ respectively.

111



112

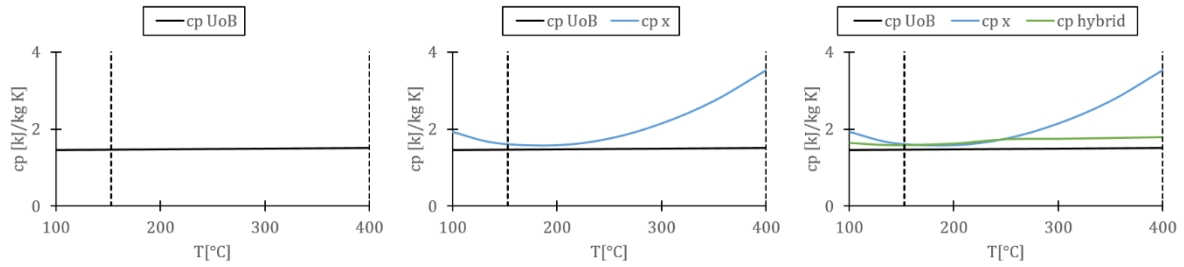
113 Fig.1. Hybrid simulation procedure applied to pure salts: a) NaNO₃ mass heat capacity and b) NaNO₂ mass heat capacity. UoB
 114 refers to the compiled database; Perrys refers to the Perry's Database; ELECNTL refers to the suitable Aspen+ Property
 115 Package; Hybrid refers to the advanced simulation procedure introduced herein.

116 In Fig.1a, different correlations reported in the literature are merged together. The black dashed lines represent
 117 the validity ranges of the two different equations. The solid black line (UoB) is the result of the compiled database
 118 utilising [23] and is suitable between 100-220°C and 313-350°C. Furthermore, the solid blue line (Perrys) is the
 119 result of Perry's handbook [24] and is suitable for > 350°C. By merging these two results, the solid green line
 120 (hybrid) is produced, exploiting findings published over the years.

121 In Fig.1b, a correlation reported in the literature is merged together with the suitable Aspen+ Property Package. The
 122 solid black line (UoB) is the result of the compiled database utilising [25] and is suitable between 177-277°C.
 123 Furthermore, the solid orange line (ELECNTL) is the result of the existing property package in Aspen+ best
 124 matched to what is reported in the literature. By merging these two results, the solid green line (hybrid) is
 125 produced. This allowed improvements in the overall accuracy of the simulation, not only for pure salts, but also
 126 for mixtures, as detailed below.

127 The next step was to simulate and replicate the thermo-physical properties of the starting-point salt mixtures
 128 against the scarcely available data. Aspen+ is an advanced software that allows, once given the correct properties
 129 of the pure constituents, to correctly estimate thermo-physical properties of the mixtures. Fig.2 illustrates the
 130 advantage of using the hybrid simulation procedure for mixture modelling. The solid black line (UoB) represents
 131 the literature data for the HITEC mixture. The solid blue line (x) represents the result if the pure salts from the
 132 compiled database are utilized for the mixture. Whereas, the solid green line (hybrid) represents the result if the
 133 hybrid approach outcome of pure salts are utilized for the mixture in Aspen+. Hence, this advanced simulation
 134 procedure allowed reproduction of the key thermo-physical properties of mixtures with low errors of 0.4-13%
 135 over a wide temperature range.

136



137

138 Fig.2. Hybrid simulation procedure applied to salt mixtures (e.g. HITEC). Black line refers to the literature data; Blue line
 139 refers to the mixture obtained using the compiled database of pure salts; Green line refers to the mixture obtained by using the
 140 hybrid approach outcome of pure salts in Aspen⁺.

141 **2.2. Volumetric Heat Capacity**

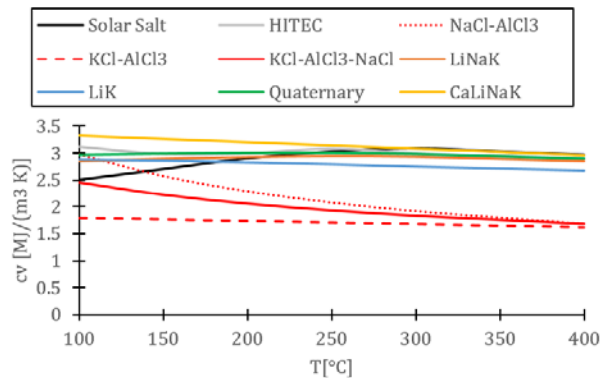
142 The ability to accurately reproduce the thermo-physical properties of the starting-point commercial salt mixtures,
 143 gave high confidence in estimating the thermo-physical properties not yet published in literature, for both the
 144 remaining commercial salt mixtures as well as their alternative weight compositions. This allowed to proceed with
 145 the second phase of the down-selection process, which was the evaluation of the thermo-physical properties in the
 146 temperature range of 100-400°C. The most relevant of these properties being the volumetric heat capacity, defined
 147 in eq.1. As maximizing this quantity reduces the size of vessels and heat exchangers, hence, reducing the cost and
 148 complexity of the plant.

149

$$c_v = c_p \rho \quad (1)$$

150

151 Fig.3 presents the variation in volumetric heat capacity for the starting-point commercial molten salt mixtures in
 152 the temperature range of application, obtained following the hybrid simulation procedure in Aspen⁺. It is evident
 153 how the chloride-based salt mixtures provided lower values of volumetric heat capacities compared to the
 154 nitrate-based salt mixtures (1.7-2.2 vs. 2.8-3.1 MJ/m³K). Hence, the chloride-based salt mixtures were disregarded
 155 from further consideration in the present work.



156

157 Fig.3. Volumetric heat capacity variation of the starting-point commercial molten salt mixtures.

158 A good compatibility of the chosen salts with the plant materials is vital [17]. Hence, information was compiled
 159 from several manufactures databanks (such as Cole Parmer, eFunda, Allorings, Trelleborg, Graco and Colder
 160 Products) concerning the compatibility with common materials of the pure salts which are constituents of the
 161 selected mixtures. Table II shows the results of this survey, ranking the compatibility on a scale from 1 (highly
 162 suitably) to 4 (zero suitability). This scale captures the swelling percentage in the case of the elastomer/plastic and
 163 the amount of μm lost over a year for metals. More importantly, the nitrate-based pure salts offered a wide
 164 compatibility.

165 Table II. Compatibility of the pure salts which are constituents of the selected mixtures with common metal and plastics;
 166 Legend: 1 = Good; 2 = Fair; 3 = Poor; 4 = Bad. The below data refer to a 48hr exposure time at 21-22°C room temperature.

| Material | NaNO ₃ | KNO ₃ | NaNO ₂ | Ca(NO ₃) ₂ | LiNO ₃ |
|-----------------|-------------------|------------------|-------------------|-----------------------------------|-------------------|
| ABS plastic | | 2 | | | 1 |
| Aluminum | 2 | 2 | 1 | | 2 |
| Carbon graphite | 3 | 1 | | | 1 |
| Carbon Steel | 2 | 2 | | | 2 |
| Cast iron | 2 | 1 | 1 | | 2 |

| | | | | | |
|--------------------|---|---|---|---|---|
| Ceramic Al2O3 | 1 | 2 | | 1 | |
| Copper | 4 | 1 | | | |
| Ethylene-Propylene | 1 | 1 | 1 | 1 | 1 |
| Polycarbonate | | 1 | | 1 | |
| Polypropylene | 1 | 1 | 1 | 1 | |
| Polyurethane | 2 | 1 | 4 | 4 | |
| PTFE | 1 | 1 | 1 | 1 | |
| Silicone | 4 | 1 | 4 | 2 | 2 |
| SS 304 | 2 | 2 | 1 | 3 | |
| SS 316 | 2 | 2 | | 2 | |
| Teflon | 1 | 1 | 1 | 1 | |
| Titanium | 1 | 1 | | 2 | |

167
 168 The down-selection process summarised above resulted in the choice of HITEC, LiNaK, LiK, Quaternary and
 169 CaLiNaK as the 5 starting-point commercial salt mixtures for continued investigation. Table III details the
 170 compositions of these molten salt mixtures expressed in mass fraction.

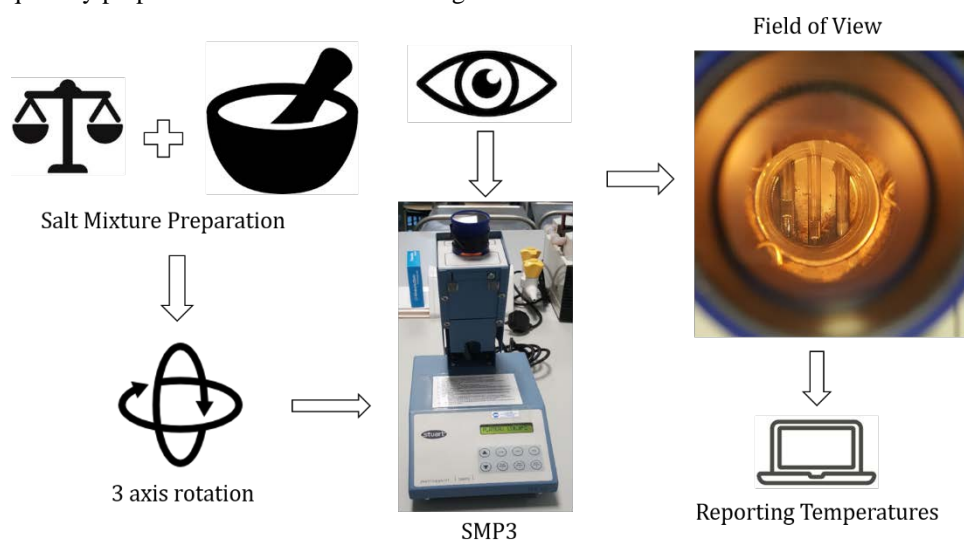
171 Table III. Chosen 5 starting-point molten salt mixture compositions expressed in mass fractions.

| Molten Salt Name | Composition |
|------------------|---|
| HITEC | 7NaNO ₃ -40NaNO ₂ -53KNO ₃ |
| LiNaK | 28NaNO ₃ -52KNO ₃ -20LiNO ₃ |
| LiK | 68KNO ₃ -32LiNO ₃ |
| Quaternary | 14.2NaNO ₃ -50.5KNO ₃ -17.5LiNO ₃ -17.8NaNO ₂ |
| CaLiNaK | 24.6LiNO ₃ -13.6Ca(NO ₃) ₂ -16.8NaNO ₂ -15KNO ₂ |

172 3. Experimental Melting Point

173 New molten salt mixtures were simulated in Aspen⁺ by varying the mass fractions of the pure salt constituents in
 174 the 5 chosen starting-point commercial salts. For the parametric analysis, the variable of interest was the
 175 volumetric heat capacity, as it was identified as an important parameter during the down-selection process. Two
 176 classifications of mixtures were considered: similar composition to starting-point salt mixtures, and noticeably
 177 different composition to starting-point salt mixtures but offering significantly higher volumetric heat capacity. As
 178 a result, a total of 13 out of 70 simulated alternative new molten salt mixtures were considered for experimental
 179 identification of melting point temperature. Mass fraction variations that provided volumetric heat capacity lower
 180 than its starting-point salt was disregarded from consideration.

181 The experimental method, depicted in Fig.4 included the preparation of alternative salt mixture concentrations
 182 using the pure salts (KNO₃, NaNO₃, NaNO₂, LiNO₃, CaNO₃•4H₂O, 99% purity, Merck[®]). To ensure fine
 183 homogenous mixture, mass fractions were prepared using Kern[®] weighing scale (resolution 0.1 mg) and mixed
 184 using Camlab[®] vortex mixer. To limit sensibility errors relating to small weight fractions of pure salts, the
 185 minimum quantity prepared for salt mixtures was 5 grams.



186
 187 Fig.4. Concentration preparation and homogenous mixing followed by observation and measurement of melting point.

188 For measuring the melting point, the Stuart[®] SMP3 was used. It was observed that, due to the small diameter of
 189 the capillary tubes, the preparation of a fine mixture was important, as well as ensuring a proper mixing.

190 Otherwise, clusters of single salt were observed in the tube, resulting in an incomplete melting of the mixture. In
 191 order to ensure the correct implementation of the experimental procedure, thermal cycling was performed on the
 192 samples, resulting in the same melting temperature in majority of the test cases. In those test cases where the
 193 melting point had varied, the result was disregarded.

194 This allowed the simultaneous testing of three capillary samples (Stuart® OD/ID 1.9mm/1.3mm) with a fine
 195 control ($\pm 0.1^\circ\text{C}/\text{min}$) of the heating ramp rate. During testing of each mixture, a fast $5^\circ\text{C}/\text{min}$ ramp rate was
 196 applied until the plateau temperature was reached, which was set at 30°C lower than the melting temperature of
 197 the starting-point commercial salt mixture. Once the plateau temperature was reached, a slower $1^\circ\text{C}/\text{min}$ ramp rate
 198 was applied. In order to gain enough precision, for each salt mixture, three tests were conducted and the mean
 199 values are reported. The melting temperature was calculated using the standard approach [26]:

$$T_m = \frac{T_{m,1} + T_{m,2}}{2} \quad (2)$$

200 where $T_{m,1}$ is the temperature at which the onset of melting was observed and $T_{m,2}$ is the temperature at which
 201 the samples were noted to be in a complete liquid state.

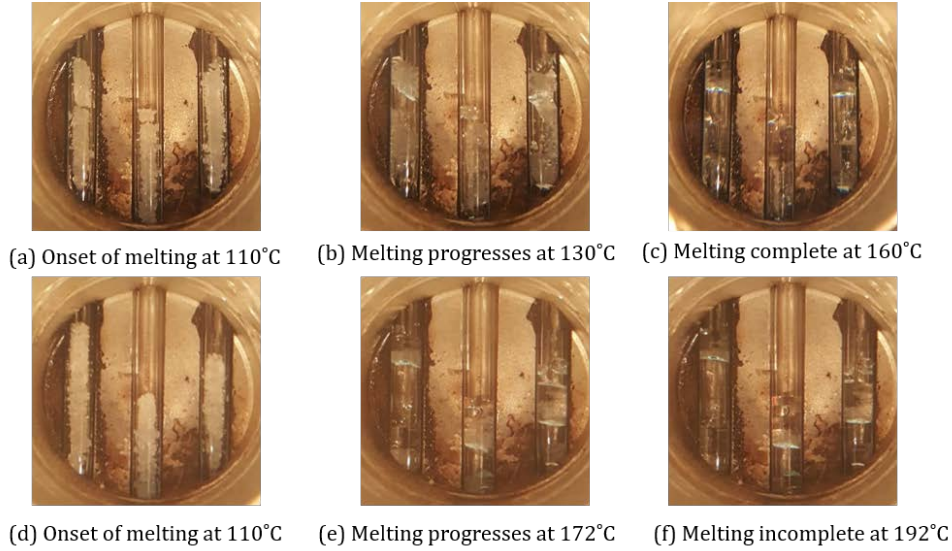
202 Particular attention was given to avoid air gaps and to ensure equal quantity of salt mixtures inside the tubes. The
 203 small tube size assured a favourable heat transfer to the salt mixtures due to the low thermal inertia. However, on
 204 occasions, this hindered the homogeneity of the sample, as some single salt clusters were observed separating
 205 from the salt mixture during testing.

206 Firstly, a validation of the experimental procedure was performed, with the aim of reproducing the melting points
 207 of the starting-point commercial salt mixtures reported in the literature. Table IV presents the experimental data
 208 for validation using the 5 chosen starting-point commercial salt mixtures. The HITEC, LiK and LiNaK results
 209 were reproduced within $1\text{-}3^\circ\text{C}$ of the published values. However, a greater discrepancy was noted for the
 210 quaternary mixtures, with errors of $11\text{-}19^\circ\text{C}$. This may be attributed to a three-fold challenge. Firstly, the precision
 211 required for the individual components (e.g. mass fraction of 14.2 for NaNO_3 in Quaternary). Secondly, the
 212 complexity associated with an increased number of individual mixture components. Thirdly, due to the individual
 213 components purity being 99% (rather than 99.99%) to ensure an economical molten salt TES and HTF solution.

214 Table IV. Experimental validation of melting point of the 5 chosen starting-point commercial salt mixtures using published
 215 literature.

| Molten Salt Name | Literature [T_m °C] | Experiment [T_m °C] | [ΔT °C] |
|------------------|------------------------|------------------------|------------------|
| HITEC | 142 | 143 | 1 |
| LiK | 133 | 132 | -1 |
| LiNaK | 120 | 123 | 3 |
| Quaternary | 99 | 118 | -19 |
| CaLiNaK | 72 | 86 | -11 |

216
 217 Following the validation of the experimental procedure, tests were conducted on the two classifications of
 218 alternative salt mixtures. Fig.5 (a-c) presents the field of view images during the successful testing of an alternative
 219 composition of LiNaK constituents. However, in limited number of cases, testing was discontinued as complete
 220 melting was not observed below 200°C . Thus, making the salt mixture unsuitable for the considered CSP and
 221 LAES applications. Fig.5 (d-f) presents such an unsuccessful testing example of an alternative composition of
 222 HITEC constituents.



223

224 Fig.5. Example of melting temperature field of view images in case of a successful test (a-c, LiNaK-5) and in a discontinued
225 test (d-f, HITEC-8).

226 Table V details the composition of the 13 alternative new molten salt mixtures, their average volumetric heat
227 capacities between 100-400°C and the experimentally identified melting point. Also included are the, variation in
228 volumetric heat capacity and melting temperature compared to the respective starting-point commercial molten
229 salts. It can be noted that, most of the alternative salt mixtures with different compositions and higher values of
230 volumetric heat capacities (10-24%) also resulted in a noticeable increase in the melting point temperature
231 (62-107°C) with respect to the starting-point mixtures. Whereas, the alternative salt mixtures with similar
232 compositions resulted in a compromised solution, with small increases in volumetric heat capacities (1-15%) and
233 melting point temperature (17-46°C) with respect to the starting-point mixtures. More importantly, two alternative
234 mixtures (CaLiNaK 11 and 4), which were associated with higher volumetric heat capacity improvements
235 (15-19%), were identified to give a preferred trade-off, resulting in only moderate increases in melting point
236 temperature (20-30°C) with respect to the starting-point mixture.
237

238 Table V. Summary of the 13 alternative new molten salt mixtures, including mass composition, change in volumetric heat
239 capacity and change in experimental melting point (- means that complete melting was not observed below 200°C)

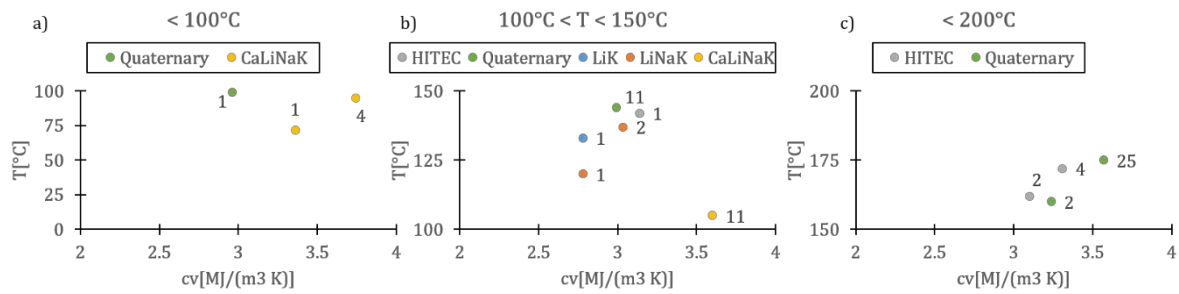
| Salt Name | ID | Composition | $c_v \left[\frac{MJ}{m^3K} \right]$ | $\Delta c_v \left[\frac{MJ}{m^3K} \right]$ | $T_m \text{ [}^\circ\text{C]}$ | $\Delta T \text{ [}^\circ\text{C]}$ | σ |
|------------|----|-------------|--------------------------------------|---|--------------------------------|-------------------------------------|----------|
| HITEC | 5 | Different | 3.32 | 10% | - | - | - |
| | 8 | Different | 3.52 | 17% | - | - | - |
| | 2 | Similar | 3.10 | 3% | 162 | 20 | 5.7 |
| | 4 | Similar | 3.31 | 10% | 172 | 30 | 3.3 |
| LiK | 3 | Different | 3.27 | 18% | - | - | - |
| | 5 | Different | 3.26 | 13% | - | - | - |
| LiNaK | 2 | Similar | 3.04 | 5% | 137 | 17 | 2.3 |
| | 25 | Different | 3.57 | 20% | 175 | 76 | 2.3 |
| Quaternary | 11 | Similar | 2.99 | 1% | 145 | 46 | 2.5 |
| | 2 | Similar | 3.24 | 9% | 160 | 61 | 3.1 |
| | 4 | Different | 3.74 | 19% | 95 | 20 | 7.9 |
| CaLiNaK | 17 | Different | 3.88 | 24% | - | - | - |
| | 11 | Similar | 3.60 | 15% | 105 | 30 | 7.2 |

240

241 Fig.6 presents the trade-off maps to compare the volumetric heat capacity and the melting point for all the relevant
242 experimentally tested mixtures, concerning three different temperature ranges, namely < 100°C, 100-150°C, and
243 < 200°C. Points are labelled with the corresponding ID number reported in Table V, or 1 when referring to the
244 starting-point commercial salt mixtures. The three graphs of Fig.6 shows how the present work has introduced in
245 all the different temperature ranges, at least one appealing alternative mixture composition which, in most cases,
246 provides a comparable melting point but higher volumetric heat capacity.

247 In Fig.6a, together with the starting-point mixtures of Quaternary and CaLiNaK, alternative CaLiNaK 4 has
248 similar melting point but significantly higher volumetric heat capacity. In Fig.6b, the alternative CaLiNaK 11 is
249 attractive due to its lower melting point and noticeably higher volumetric heat capacity. Fig.6c consists of

250 alternative mixtures only. However, Quaternary 25 provides the greatest increase in the volumetric heat capacity
 251 compared to the starting-point mixture.



252
 253 Fig.6. Experimental melting point temperature vs. volumetric heat capacity map, for the chosen 5 starting-point commercial
 254 salt mixtures and the alternative new salt mixtures.

255 These three trade-off maps have identify temperature tailored 3 new molten salts for application such as CSP and
 256 LAES. Namely CaLiNaK 4 and 11, and Quaternary 25, which offer low melting temperatures and beneficial
 257 thermo-physical properties. Table VI details the composition of these 3 new potential salt mixtures as future
 258 candidates for use as both thermal energy storage and heat transfer fluid.

259 Table VI. Composition of 3 new potential molten salt mixtures to act as both thermal energy storage and heat transfer fluid.

| Salt ID | Composition (wt%) |
|---------------|--|
| Quaternary-25 | 25NaNO ₃ -5KNO ₃ -5LiNO ₃ -65NaNO ₂ |
| CaLiNaK-4 | 45NaNO ₃ -25KNO ₃ -5LiNO ₃ -25Ca(NO ₃) ₂ |
| CaLiNaK-11 | 25NaNO ₃ -45KNO ₃ -5LiNO ₃ -25NaNO ₂ |

260 4. Conclusions

261 This work was focused on the identification and evaluation of low temperature molten salt mixtures as the feasible
 262 common medium for both the thermal store and the heat transfer fluid for sustainable energy systems. The
 263 parameters for evaluation were the melting point temperature and the volumetric heat capacity. Two
 264 classifications of mixtures were considered: similar compositions and noticeably different compositions to the
 265 starting-point commercial salts. The significant findings of the present work are as follows:

- 266 1. Nitrate-based salt mixtures were identified for detailed investigation as they offered higher volumetric
 267 heat capacities (2.8-3.1 vs. 1.7-2.1 MJ/m³K) and comparable average melting point temperatures
 268 (113 vs. 108°C) compared to the chloride-based salt mixtures.
- 269 2. The considered experimental procedure provided a low variation in melting point temperature against
 270 the published literature. For example, HITEC, LiK and LiNaK results were reproduced within 1-3°C.
- 271 3. Experimental investigations identified the melting point of 8 alternative new molten salt mixtures in the
 272 range of 95-175°C (Table V).
- 273 4. Melting temperature and volumetric heat capacity trade-off maps were produced using the starting-point
 274 commercial molten salts and the alternative new salt mixtures for different temperature ranges (< 100 °C,
 275 100-150°C, < 200 °C). These maps offer a guide in the selection of suitable molten salts, depending on
 276 the temperature requirements, to improve the overall system efficiency and feasibility.
- 277 5. Three alternative new molten salt mixtures, which included two from the CaLiNaK family (CaLiNaK 11
 278 and 4), were identified as preferred candidates due to higher improvements in volumetric heat capacity
 279 (15-19%) and only moderate increases in melting point temperature (20-30°C) compared to CaLiNaK.

280 Acknowledgement

281 This work was funded by INNOVATE UK “Development of High Grade Heat Storage for integration with Liquid
 282 Air Energy Storage” (Ref 133465) project. The Authors’ would like to acknowledge the support of the industrial
 283 partner Highview Power Storage Ltd. (Johnny Cochrane and Edward Scrase) and the School of Pharmacy and
 284 Biomolecular Sciences (Dr. Petra Kristova).

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