Review

Molten Salts for Sensible Thermal Energy Storage: A Review and an Energy Performance Analysis

Adrián Caraballo [1,2], Santos Galán-Casado [1], Ángel Caballero [2],* and Sara Serena [2]

1   Department of Chemical and Environmental Engineering, ETSII, Universidad Politécnica de Madrid (UPM), 28006 Madrid, Spain; a.caraballo@alumnos.upm.es (A.C.); santos.galan@upm.es (S.G.-C.)
2   Department of Ceramics, Institute of Ceramics and Glass, Spanish National Research Council (CSIC), 28049 Madrid, Spain; serena@icv.csic.es
*   Correspondence: acaballero@icv.csic.es

Abstract: A comprehensive review of different thermal energy storage materials for concentrated solar power has been conducted. Fifteen candidates were selected due to their nature, thermophysical properties, and economic impact. Three key energy performance indicators were defined in order to evaluate the performance of the different molten salts, using Solar Salt as a reference for low and high temperatures. The analysis provided evidence that nitrate-based materials are the best choice for the former and chloride-based materials are best for the latter instead of fluoride and carbonate-based candidates, mainly due to their low cost.

Keywords: thermal energy storage; molten salts; concentrated solar power; sensible heat storage; nanofluids

1. Introduction

Electricity generation is one of the main contributors to greenhouse gas (GHG) emissions due to CO_2 being released from fossil fuels; additionally, electricity is also one of the energy vectors upon which many applications will be transformed in the near future [1,2]. As decarbonization is the objective of future energy systems, its stability and dispatchability at a reasonable cost must be ensured. Among all those available, solar energy is one of the most suitable alternatives: it is clean, abundant, and easily obtained anywhere on earth. Among the different alternatives, concentrated solar power (CSP) in combination with thermal energy storage (TES) allows for dispatched electricity to match peak demand and solves the supply−demand coupling problem, allowing energy release and its transformation to electricity whenever necessary and eluding the inherent instability of solar resource availability [3].

Although the International Energy Agency (IEA) estimates that CSP will provide 11% of all global electricity generated by 2050 [4], current plants in operation or in development mainly use sensible TES systems with nitrate-based materials. Other alternatives must be explored, since they have the potential to overcome several drawbacks of commercial TES materials in terms of cost reduction, thermal properties enhancement, and higher/broader operational. TES, together with CSP, still have a long road ahead of them to be considered consistent, robust, continuous, and competitive alternatives. Thus, the incorporation of both into future energy management and generation mix depends greatly upon the future developments of TES materials.

The authors of this work spot the need to present a comprehensive review of the most promising next generation TES materials in order to analyze their strengths and weaknesses, sum up the most relevant thermodynamical properties found in the narrative, and define and evaluate three different key performance indicators (KPIs) to help make the most suitable choice for a specific CSP application.

2. Thermal Energy Storage Materials

High-temperature TES is one of the cheapest forms of energy storage [5]. Although there are different alternatives, such as latent, thermochemical, or solid sensible heat storage [6–8], the most common TES materials are molten salts, which are classified as sensible heat storage [9]. Sensible storage implies that increasing the temperature of a substance increases its energy content; when the material is cooled, the stored energy is released, but without a phase change. The following characteristics are desirable in a TES material [10,11]:

- The energy storage density must be high for a compact design.
- For indirect TES systems, those where the energy storage medium is different from the heat transfer fluid (HTF) circulating through the solar field, a good heat transfer between HTF and TES material is needed to optimize the system's efficiency.
- The TES material should be thermally stable and possess a low vapor pressure in the operating temperature range to avoid undesirable side effects such as material ageing, performance decline of the system, or GHG emissions.
- A high thermal, chemical, and cyclic stability for extended plant life should be expected.
- A non-flammable and non-toxic nature are desirable.
- Inexpensive and abundant.

The following thermal and transport properties are essential for a suitable selection of the proper material that complies with most of the previously mentioned characteristics:

- Specific heat capacity: this property controls the capacity of the temperature rise that can be transferred or stored. It improves the TES system efficiency [12].
- Melting temperature: this is directly related to operating and maintenance (O&M) costs since higher melting points need antifreeze protection.
- Decomposition temperature: this is the theoretical maximum operating temperature that must not be exceeded in order to keep the TES material operative and in good condition; the higher the maximum operating temperature, the higher the TES system efficiency achieved.
- Thermal conductivity: this property is related to the heat transfer behavior. Higher values are preferred in order to achieve higher heat exchange efficiency.
- Viscosity: this is directly related to the cost of pumping energy through the system, and lower values are preferable. It is also linked to the previous property, and a compromise between them should be taken.
- Density: this directly affects the specific energy that a selected TES material can store per unit of volume. The amount of heat carried by the HTF at working temperature relates to the density of a material and its specific heat capacity. Higher values are recommended.

Sensible TES has other relevant properties: the specific heat, the temperature variation of the material (see Equation (1)), as well as conductivity, diffusivity, thermal stability, vapor pressure, and the cost and compatibility of materials. Its main drawbacks are the temperature stability and its energy storage density, which is lower than latent and thermochemical TES [13].

$$Q = mc_p\Delta T = \rho V c_p \Delta T \tag{1}$$

For high temperature applications, such as CSP, molten salts are the most widely used material. This is due to their high volumetric heat capacity, a high boiling point, high temperature stability, and their vapor pressure being close to zero. Additionally, they are relatively cheap, readily available, neither toxic nor flammable, and can act as an HTF as well as a TES material. However, they have certain disadvantages: they have a relatively high melting point (generally > 200 °C), which results in them solidifying in pipes in the absence of a heat source and thus necessitates the installation of antifreeze systems; they also have high viscosity and low thermal conductivity compared to other fluids [9,13].

Focusing on reducing the levelized cost of electricity (LCOE) for CSP plants, which is currently slightly higher than other renewable alternatives [14], there is presently a strong interest in developing higher temperature power systems (around 700 °C) with better efficiency, such as supercritical CO_2 Brayton cycles [15]. Current CSP plants are limited to relatively low temperatures (below 600 °C), which means they are enough for parabolic through collector (PTC) or linear Fresnel reflector (LFR) plants. However, they are inadequate for higher temperatures (up to 950 °C) that can be achieved in central tower (CT) plants [16]. Hence, there is substantial potential to increase the operating temperatures (increasing the Carnot efficiency) and the heat-to-electricity efficiency for the next CSP generation. Replacing commercial nitrate-based molten salts with other TES materials such as chloride, fluoride, or carbonate-based materials will achieve this [17,18]. Tables 1 and 2 summarize the TES materials analyzed in the present work along with their thermal properties.

Table 1. Composition, fusion, and decomposition temperatures for selected molten salt thermal energy storage (TES) materials.

	%Weight	Fusion Temperature (°C)	Decomposition Temperature (°C)	References
	Nitrate-based			
Solar Salt	60 $NaNO_3$–40 KNO_3	240	565	[19]
Hitec	7 $NaNO_3$–53 KNO_3–40 $NaNO_2$	142	450	[20]
Hitec XL	15 $NaNO_3$–43 KNO_3–42 $Ca(NO_3)_2$	130	450	[21,22]
LiNaKNO3	30 $LiNO_3$–18 $NaNO_3$–52 KNO_3	118	550	[23,24]
LiNaKCaNO3	15.5 $LiNO_3$–8.2 $NaNO_3$–54.3 KNO_3–22 $Ca(NO_3)_2$	93	450	[25]
LiNaKNO3NO2	9 $LiNO_3$–42.3 $NaNO_3$–33.6 KNO_3–15.1 KNO_2	97	450	[26]
	Chloride-based			
KMgCl	62.5 KCl–37.5 $MgCl_2$	430	>700	[27]
NaKMgCl	20.5 $NaCl$–30.9 KCl–48.6 $MgCl_2$	383	>700	[27,28]
NaMgCaCl	39.6 $NaCl$–39 $MgCl_2$–21.4 $CaCl_2$	407	650	[29–31]
NaKZnCl	7.5 $NaCl$–23.9 KCl–68.6 $ZnCl_2$	204	>700	[31,32]
KMgZnCl	49.4 KCl–15.5 $MgCl_2$–35.1 $ZnCl_2$	356	>700	[31,32]
	Fluoride-based			
LiNaKF	29.2 LiF–11.7 NaF–59.1 KF	454	>700	[33]
NaBF	3 NaF–97 $NaBF_4$	385	>700	[34]
KBF	13 KF–87 KBF_4	460	>700	[35]
KZrF	32.5 KF–67.5 ZrF_4	420	>700	[34]
	Carbonate-based			
LiNaKCO3	32.1 Li_2CO_3–33.4 Na_2CO_3–34.5 K_2CO_3	397	670	[36]

Table 2. Properties of selected molten salt TES materials.

	Density (kg/m³)	Specific Heat Capacity (J/kg°C)	References
	Nitrate-based		
Solar Salt	$2090 - 0.636T$	$1443 + 0.172T$	[37]
Hitec	$1938 - 0.732T$	$1560 - 0.001T$	[34,38]
Hitec XL	$2240 - 0.827T$	$1542.3 - 0.322T$	[39]
LiNaKNO3	$2088 - 0.612T$	1580	[40]
LiNaKCaNO3	$1993 - 0.700T$	1518	[41,42]
LiNaKNO3NO2	$2074 - 0.720T$	$1135.3 + 0.071T$	[26]
	Chloride-based		
KMgCl	$2125.1 - 0.474T$	999	[32,43]
NaKMgCl	$1899.2 - 0.4253T$	1023.8	[27]
NaMgCaCl	$4020.57 - 2.7697T$	$12,382.2 + 0.040568T^2 - 42.78T$	[29,30]
NaKZnCl	$2625.44 - 0.926T$	$911.4 - 0.0227T$	[32,44]
KMgZnCl	$2169.6 - 0.5926T$	866.4	[27]

Table 2. *Cont.*

	Density (kg/m³)	Specific Heat Capacity (J/kg°C)	References
	Fluoride-based		
LiNaKF	$2530 - 0.73T$	$976.78 + 1.0634T$	[33,45]
NaBF	$2252.1 - 0.711T$	1506.0	[34]
KBF	$2258 - 0.8026T$	1305.4	[35]
KZrF	$3041.3 - 0.6453T$	1000	[34]
	Carbonate-based		
LiNaKCO3	$2270 - 0.434T$	1610	[36]

2.1. Nitrate-Based Materials

The most popular TES material used in CSP is Solar Salt: a non-eutectic mixture of 60% $NaNO_3$–40% KNO_3 (wt%), which has been investigated since the 1980s [46,47]. However, there are other candidates, mostly derived from Solar Salt. The main reasons for its popularity are its relatively low cost, its good chemical safety (it is neither toxic nor flammable), and its reasonable material compatibility which allows standard stainless steels to be used without incurring high corrosion rates [48,49]. However, its operating temperature range is restricted by a crystallization temperature of around 240 °C and a maximum operating temperature of around 565 °C, after which decomposition and salt degradation reactions begin [19,50]. In general, when considering an alkaline and alkaline earth nitrate generic mixture, the following main decomposition reactions can occur [21,51]:

$$MNO_3 \leftrightarrow MNO_2 + \frac{1}{2}O_2 \tag{2}$$

$$5\,MNO_2 \rightarrow 3\,MNO_3 + M_2O + N_2 \tag{3}$$

$$M'(NO_3)_2 \rightarrow M'O + N_2 + \frac{5}{2}O_2 \tag{4}$$

$$M'(NO_3)_2 \rightarrow M'O + NO_2 + NO + O_2 \tag{5}$$

Being M alkaline and M′ alkaline earth metals. Oxides can be produced [20] and nitrates can in turn react with the atmospheric humidity and carbon dioxide:

$$M_2O + H_2O \leftrightarrow 2MOH \tag{6}$$

$$M_2O + CO_2 \leftrightarrow M_2CO_3 \tag{7}$$

$$M'O + H_2O \rightarrow M'(OH)_2 \tag{8}$$

$$M'(NO_3)_2 + CO_2 \rightarrow M'CO_3 + N_2 + \frac{5}{2}O_2 \tag{9}$$

A realistic principle to determine the stability of nitrate mixtures is to measure the occurrence of reactions (3), (4) and (6)–(9) where oxides, hydroxides, and carbonates are produced [52]. In fact, the formation of nitrites from the equilibrium in reaction (2) does not prejudice neither the thermophysical properties of the mixtures nor the compatibility properties [51]. On the other hand, the solubility of oxides, hydroxides, and carbonates is limited so solids can be produced and, moreover, the corrosion phenomena from the thermal fluid are more acute [21]. From several investigations of different mixtures of alkaline and alkaline earth nitrates, the following considerations can be made:

- If only sodium and potassium nitrates are present, the thermal stability limit is around 600 °C [51,53–57].
- The presence of lithium nitrate leads to a thermal stability limit between 550 and 600 °C [51,58].
- The addition of calcium nitrate produces a drastic decrease in long-term stability; an upper temperature value of around 450 °C has been proposed [21,22].

- The presence of nitrites limits the thermal stability at about 450 °C under air atmosphere [59,60].
- The decomposition kinetics depends on the concentration of chemical species; with respect to the nitrate mole fraction, a first order kinetics was found for sodium and potassium nitrates' decomposition into nitrites [53,57].
- The kinetics degradation is also related to the surrounding atmosphere, its humidity, and CO_2 content [52].

Little effort has been devoted to increasing the stability limit of the upper temperature of nitrates, the chemical nature of the stability loss, nor the long periods of time in which the maximum temperature must be maintained. In addition, the results obtained using other cations different from alkali metals lead to a decrease in thermal stability [52,61,62]. To overcome this problem, some authors have proposed confinement of the molten salt in a controlled atmosphere that allows for an increase of the partial pressure of oxygen and for a shift to the nitrate side the reaction number 2 in order to decrease the nitrite concentrations at the same temperature [63]. Nonetheless, the current research into these materials is focused on decreasing the crystallization points of the mixtures and adding other alkali (i.e., lithium) or alkaline earth (i.e., calcium) cations, or other anions (i.e., nitrite) [51].

Regarding lithium nitrate, mixtures have been proposed in combination with sodium and potassium nitrates whose crystallization points can be found below 130 °C and report thermophysical properties comparable to those presented by Solar Salt [47,51,58,64–67]. Concerning calcium nitrate, several formulations related to its addition to sodium and potassium nitrates have been proposed [47,62,67,68]. The most researched is the one marketed as Hitec XL (15% $NaNO_3$–43% KNO_3–42% $Ca(NO_3)_2$ wt%), which closely corresponds to the ternary eutectic point of the published phase diagrams [68,69]. However, the presence of $Ca(NO_3)_2$ makes it difficult to accurately determine the crystallization point by calorimetric methods (around 130 °C) given the presence of slow transitions with low enthalpies [68], which explains the uncertainties and disparities presented in the literature. Similarly, the maximum operating temperature presents discrepancies in the published articles due to decomposition reactions [62,67,68]. On the other hand, $Ca(NO_3)_2$ increases the viscosity up to three times in comparison to the reference values of Solar Salt and this compromises the application of these mixtures at very low temperatures [62]. Both previously described nitrates have also been proposed to be used together, especially in ternary mixtures that include KNO_3 [22,58,65,67].

The only anion proposed for these mixtures and applications with nitrate is nitrite, mainly sodium nitrite in a ternary mixture with sodium and potassium nitrates, and the composition most widely studied and used is the eutectic one (7% $NaNO_3$–53% KNO_3–40% $NaNO_2$ wt%), also known as Hitec [20]. The use of nitrites leads to a decrease in the melting point of the liquid, but its presence limits the thermal stability at about 450 °C under air atmosphere due to decomposition and degradation reactions, limiting its application to mid-temperature applications [59,60].

Other high-order mixtures constituted by alkaline nitrates [20,26,47,58] or nitrate−nitrite mixtures [25,26,65] have been proposed, but they have received little attention, and as of yet there is no evidence of any commercial application.

2.2. Chloride-Based Materials

Molten mixtures of chlorides have been considered as coolants in nuclear reactor designs where fluids operate at about 525 °C and are stable at temperatures above 800 °C [45,70,71]. Due to their low cost, high decomposition temperatures, and natural abundance, molten chlorides are considered good TES material candidates even if their melting temperatures are generally higher than those of nitrate salts, but typically lower than fluoride and carbonate-based TES materials [72]. In recent years, research has focused on the development of multicomponent mixtures of lithium, sodium, potassium, magnesium, calcium, and zinc chlorides. Nonetheless, although lithium and zinc chlorides

offer the mixtures the lowest melting point, their high cost implies a major disadvantage [15,72,73].

Regarding binary mixtures, the KCl–MgCl$_2$ eutectic composition has the lowest melting temperature among all possible binaries considered above [27,74] and has been widely studied as a primary coolant in nuclear power [75]. Its vapor pressure is very low, even at high temperatures, resulting in good thermal stability [43]. In addition, if NaCl is added to the mixture, the melting temperature of the ternary eutectic is about 50 °C lower, which allows the thermal properties to remain almost unchanged [28].

The NaCl–MgCl$_2$–CaCl$_2$ mixture has been proposed due to its relatively low-temperature melting point (424 °C) and because it has a heat capacity higher than all the alkaline and alkaline earth chloride binary mixtures, excluding the ones with lithium chloride [29]. Moreover, the addition of potassium chloride to the latter mixture diminishes the melting point to 385 °C and increases the heat capacity by more than 25% [76]. By contrast, calcium chloride mixtures lack the same thermal stability as other chlorides, resulting in an operating temperature gap lower than other chloride mixtures [29].

Mixtures containing zinc chloride are very interesting due to the low melting temperature achieved. The NaCl–KCl–ZnCl$_2$ mixture is one of the most promising candidates given its eutectic has a very low melting temperature of 204 °C [32]. The KCl–MgCl$_2$–ZnCl$_2$ mixture eutectic also has a reasonably low melting temperature of 356 °C [62] and high thermal stability of up to 730 °C [77]. However, as was mentioned earlier, the high cost of zinc chloride makes these mixtures less attractive.

Nevertheless, their main drawback is corrosion: the corrosion mechanisms are complex, with different interactions between atmosphere, molten salts, outer and inner corrosion layers, and the matrix of metallic alloys [78–81]. Chloride melts facilitate corrosion of steels in air, and this fact should be considered in the development of corrosion mitigation methods, such as inert atmospheres and gas purification of the melts prior to its operation [82]. Container materials should be nickel-based superalloys which have better corrosion resistance than stainless steels [83]. However, this leads to a more expensive solution for nitrate-based TES materials and should be taken into account for future applications.

2.3. Fluoride and Carbonate-Based Materials

Fluoride-based molten salts have been used as nuclear coolant fluids due to their relatively high specific heat capacity, thermal conductivity, and thermal stability compared to other molten salts, including experimental reactors on a megawatt scale and in test loops for hundreds of thousands of hours [33,71]. On the other hand, carbonate-based materials are widely used in fuel cells, operating between 600–700 °C [84], and for cleaning and processing uranium-containing alloys in the nuclear power industry [85].

In general, fluorides tend to be better HTF than chlorides and carbonates [45,70] and possess almost the same thermal stability over 700 °C [86]. It has been stated that at operating temperatures, the thermophysical properties of liquid fluoride-based salts are similar to those of room temperature water except for their very low vapor pressure [33]. However, carbonate-based TES materials are generally more stable; a limit decomposition temperature under air of 670 °C, 700 °C under argon, and no sign of decomposition under CO$_2$ atmosphere, even at 1000 °C, has been reported [86].

The first fluoride material presented in this work is the ternary eutectic mixture of LiF–NaF–KF, which has good thermal properties, but a high melting temperature (see Table 2). This is also a problem for other fluoride-based mixtures, but fluoroborates mixtures can slightly decrease the melting temperature and maintain other thermal properties [34,35]. In addition, compositions based on zinc fluorides can reduce the temperature even further and present figures similar to those of chloride-based salts [34,35]. Other fluorides, such as beryllium fluoride, demonstrate good performance and different mixtures have been proposed, but their high cost makes them inappropriate for this application [87].

Single and binary mixtures of carbonate salts have high melting points above 500 °C [88]. However, the ternary eutectic mixture Li_2CO_3–Na_2CO_3–K_2CO_3 has been proposed as a TES material with a melting temperature of 397 °C [36]. In particular, the richer the potassium carbonate mixtures are, the higher the temperature value they will have (more than three times that of Solar Salt) [18]. Finally, some authors suggest mixtures of fluorides with carbonates or other fluorides, carbonates, and chlorides, but they have received little attention [89,90].

The main drawback for fluoride-based molten salt is corrosion, which is much lower in carbonate and chloride salt mixtures. They should be thermodynamically stable relative to the confinement materials because they tend to rapidly dissolve many of their oxide protective layers, which limits choices [33,91]. By contrast, it has been stated that carbonates are much less corrosive than fluorides and commercial stainless steels can be used in most practical situations [18,92]. Nevertheless, viscosity is their main problem, as it is higher in general than the other proposed salt mixtures in this work and therefore, its suitability for this application, due to pumping issues, must be revised [93].

3. Molten Salts Properties Enhancement

One of the main reasons to advocate for the use of the molten salts in CSP plants and other industrial facilities is their properties' enhancement. This can be done by adding nanoparticles (NPs) to the fused system in order to create a nanofluid (NF) [94]. The basis for this solution is simple: the NPs can increase the specific heat capacity, precisely one of the main properties that is relatively low in all molten salts in comparison with other fluid-sensible materials like water or liquid metals, and therefore, it enhances the overall CSP efficiency [95–97]. However, the rheological behavior of NFs is a limiting factor because the viscosity of particulate suspensions increases as a function of particle volume fraction. Consequently, a maximum number of NPs can be added to the fluid without compromising the performance of the system exits [98,99].

Because of the high operating temperatures and aggressive nature of molten salts, the main requirements of NP are to be stable at high temperatures and to have a strong affinity to the adsorbate [100]. In addition, it is essential that they do not suffer deformations and/or chemical degradation in order to conserve the NF design features.

NFs' complex nature implies that many factors affect their thermal behavior [101–105]:

- Particle concentration, typically lower than 2%;
- Particle size, from 2 to 90 nm;
- Particle shape, mainly spherical or cylindrical;
- Particle type, oxides being the most popular, followed by carbon-based materials such as graphite or multi-walled carbon nanotubes (MWCNTs) and solid metals;
- Interaction between liquid and particles.

Among nitrate-based molten salts, Solar Salt is the most investigated base fluid. Different types and sizes of NPs like alumina, silica, iron, titanium, and copper or zinc oxides been investigated [106–109], reporting a maximum specific heat capacity enhancement of 31.1% with 0.5%wt of silica NP [110]. Other nitrated-based mixtures mentioned in this work have also been studied, mainly silica NPs, and the authors reported similar enhancements compared to those obtained in the Solar Salt case [94,100–112].

Two different chloride-based NFs have been proposed. First, $BaCl_2$–$NaCl$–$CaCl_2$ mixtures with 1%wt of silica 20–30 nm NPs, which obtain a specific heat capacity enhancement of about 14.5% [94]. Second, KCl–$CaCl_2$–$LiCl$ mixtures have been proposed with 1%wt of silica 10 nm NPs that give a specific heat capacity enhancement of about 7.6% [113].

Regarding carbonate-based molten salts, the most investigated is the Li_2CO_3–K_2CO_3 eutectic mixture. It has been enhanced with silica, MWCNT, alumina, graphite, and TiO2 NPs [99,100,114–120] with different types and sizes. There is reportedly a very low specific heat capacity increase of about 1–2% in various composition ranges with silica, but up to 17% in mixtures containing ≥0.5% of MWCNT NPs [99,121]. Until now, no fluoride-based materials have been reported in the literature as NF candidates.

4. Energy and Cost Analysis of TES Materials

Many economic assessments have been made elsewhere both for CSP plants and TES systems [114,115,117,119,122–124], and it has been demonstrated that a CSP plant is more cost-effective if it has a TES system [125,126]. There are many key parameter indicators (KPIs) that can be used to carry out the techno-economic analysis for TES materials, and in this work, the following were used:

- Specific mass energy density E^m (in MJ/kg): quantifies the amount of energy stored by the TES material in its operating temperature range and is defined in Equation (9).
- Specific volumetric energy density E^v (in MJ/m^3): quantifies the same energy as the previous KPI, but in terms of volume (its definition is given in Equation (10)). This is helpful when estimating other KPIs in the TES system (i.e., confinement, land-area dimensions, and cost) and is useful in determining the flow rate and if it was going to be used as HTF.
- Energy storage cost E^c (in $/MJ): represents the direct cost of the stored energy and is defined in Equation (11).

$$E^m = \int_{T_{fus}}^{T_{dec}} c_p dT \tag{10}$$

$$E^v = \int_{T_{fus}}^{T_{dec}} \rho c_p dT \tag{11}$$

$$E^c = \frac{C}{E^m} \tag{12}$$

where T_{fus} and T_{dec} are the fusion and decomposition temperatures (in °C), ρ is the density (in kg/m^3), c_p is the specific heat (in J/kg °C), and C is the cost (in $/kg) of the molten salts. In this analysis, the temperature range considered will always be higher than real ones and narrower due to safety considerations such as avoiding solidification and decomposition. The values for the selected TES materials in this work are presented in Table 3. In this analysis, Solar Salt was used as a reference for comparison issues, and 700 °C was considered the maximum temperature allowed.

Table 3. Specific cost and energy of selected molten salt TES materials.

	Specific Cost $/kg	E^m MJ/kg	E^v MJ/m^3	E $/MJ	References
			Nitrate-based		
Solar Salt	1.3	0.491	901.1	2.65	[127]
Hitec	1.93	0.480	826.9	4.02	[127]
Hitec XL	1.66	0.464	928.1	3.58	[127]
LiNaKNO3	1.1	0.683	1285.7	1.61	[56]
LiNaKCaNO3	0.7	0.542	977.1	1.29	[56]
LiNaKNO3NO2	N/A	0.408	764.9	N/A	-
			Chloride-based		
KMgCl	0.35	0.271	431.3	1.29	[48]
NaKMgCl	0.22	0.325	541.6	0.68	[48]
NaMgCaCl	0.17	0.289	739.7	0.57	[128]
NaKZnCl	0.8	0.447	986.6	1.79	[48]
KMgZnCl	1	0.298	553.4	3.36	[48]
			Fluoride-based		
LiNaKF	2	0.391	824.1	5.11	[128]
NaBF	4.88	0.474	885.4	10.29	[129]
KBF	3.68	0.313	833.3	11.75	[129]
KZrF	4.85	0.280	750.3	17.32	[129]
			Carbonate-based		
LiNaKCO3	2.02	0.448	9912	4.15	[18]

It is clear that for low temperature applications like PTC or LFR, nitrated-based TES materials are the only ones suitable, while the rest are reserved for high temperature CT plants operating up to 700 °C. Figures 1 and 2 gathers KPIs comparison for selected candidates.
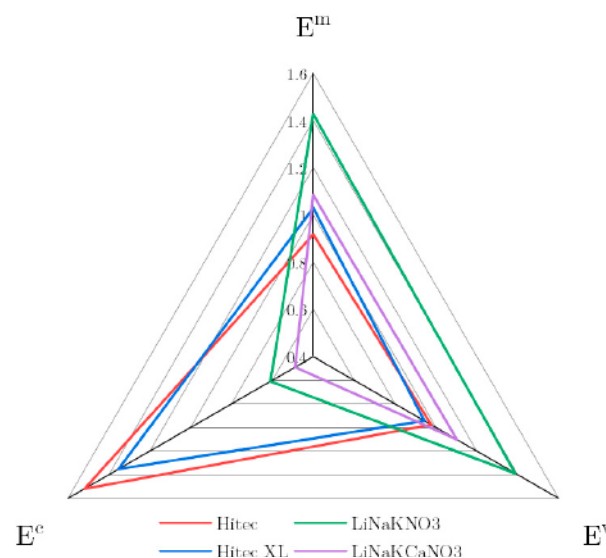

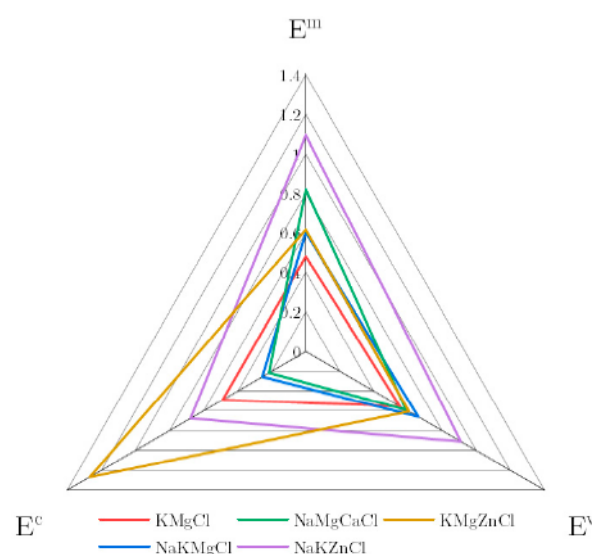**Figure 1.** Nitrate-based TES materials KPIs comparison (Solar Salt = 1).

Figure 2. Chloride-based TES materials KPIs comparison (Solar Salt = 1).

Regarding specific mass energy density, values for nitrate-based materials are the most attractive closely followed by carbonates, whereas chlorides and fluorides are in general relatively less interesting. It is worth to point out that Solar Salt has one of the highest values, only surpassed by nitrate mixtures containing lithium or lithium and calcium. In the case of other mixtures, LiNaKCO3, NaKZnCl, and NaBF have very close values to those reported for Solar Salt, giving high-temperature applications almost the same mass energy density. For specific volume energy density, the values are very similar to the previous ones; however, fluoride-based materials enhance their figures, almost to the same level as the nitrates, whereas LiNaKCO3 has an improved performance compared to Solar Salt. Finally, KPIs of previous chloride-based materials perform poorly in comparison to the other candidates, but its specific energy costs are more than half the Solar Salt ones, even achieving a reduction over 75%. This makes them one of the best choices for future high-temperature applications over fluorides and carbonate-based materials.

5. Conclusions

A comprehensive review of different thermal energy storage (TES) materials for concentrated solar power (CSP) has been completed: fifteen selected materials have been studied and compared and their nature, thermophysical properties, and economic impact have been considered. Three energy key performance indicators (KPIs) have been defined in order to evaluate the performance of the different molten salts by using Solar Salt as a reference.

The results of this analysis reveal that the most popular and sensible TES material, Solar Salt, scores reasonably well in comparison with other nitrate-based materials in terms of energy density and cost for its temperature interval of operation. However, other nitrate-based materials achieve almost the same figures, but their broader temperature ranges have the potential to be more interesting for very low-temperature applications.

In general, the studied chloride-based materials seem to be the favorite candidates for high-temperature applications compared to other fluoride and carbonate-based options. This is due to their very attractive low cost (excluding KMgZnCl), as even their energy KPIs give lower values than Solar Salt (except NaKZnCl).

For low-temperature applications, nitrate-based materials are more suitable due to their low melting temperature and good energy KPIs. On the other hand, for high-temperature applications, chloride-based materials are better choices over fluorides and carbonates, mainly due to their lower cost. However, the drawback that still remains is the corrosion of these materials, and this must be solved if they are to be the next generation of TES materials.

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