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Molten nitrate salts containing lithium as thermal energy storage media: a short review

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Abstract:

Energy storage plays a crucial role in the development and progress of renewable energy sources. In the case of thermal energy, storage has been a step ahead since storage solutions already exist, unlike other conversion energy technologies. In this sense, the utilization of molten salts, mainly composed of mixtures of alkali/alkaline earth metals, in nitrate forms (sometimes also with nitrite), have been proposed and successfully applied. Molten salts have recognized advantages over other solutions namely in what concerns simultaneous use as heat transfer fluids and as storage media. Commercial utilization of molten salts has been tested essentially with the Na/K salt mixtures. Introduction of lithium nitrate in these formulation has been proposed, since can allow decreasing the melting point of the mixtures, thus providing safety concerning the risks of freezing in the tubes or tanks of the storage plant. This paper provides a short review on the utilization of lithium in molten salt mixtures used for thermal energy storage. Physical, chemical and thermal properties, as well as stability and decomposition issues are evaluated. Corrosion of stainless steels in contact with the salts is another crucial question that is also addressed.

Keywords:

Thermal energy storage, Molten salts, Lithium, Thermal stability.

1. Introduction

The climate change challenge addresses for global responses, the renewable energy sources (RES) being one of the essential pillars [1]. The total RES share in global energy in the European Union was 16% in 2014 [2], in spite of all efforts done. The breakdown by sectors for the RES is as follows: 43% electricity, 49% heating & cooling and 8% transport (biofuels). Production of heat from RES has increased significantly.

Regarding the electricity sector, the Concentrating Solar Power (CSP) Technology allows electricity production by converting sunlight to a heat source that transfers energy to a power block. When compared to other renewable sources, CSP has nowadays a clear advantage since allows incorporating a thermal energy storage process (TES), already in commercial stage, and thus providing electricity dispatchability. In a renewable energy system, energy storage is a key factor [3] and the technologies allowing such feature have high potential for implementation and success. Moreover, TES has much more applications than electricity conversion. It can be also used as: heat management in industry or buildings; store and reuse of waste heat; transport of heat. Although solar thermal sources for both electricity conversion and heating/cooling have nowadays a very narrow contribution to the overall energy consumption, its growing potential is enormous.

CSP technologies involve the integration of a solar field, a heat transfer/thermal storage zone and a power block. Concerning the solar field, the technologies are classified as parabolic trough, linear Fresnel, central receiver tower and parabolic dish [4]. Parabolic trough is already a commercially proven mature technology. Regarding heat transfer, several options can be applied, namely two-tank direct, indirect and single-tank thermocline, among other arrangements [5,6], including the use of several filler materials as storage media (e.g. concrete, quartzite rock). The first CSP processes have operated with oil as heat transfer fluid (HTF). Synthetic oil has, however, many disadvantages such as the low maximum operating temperature (<390 ºC), limiting the efficiency of the power block cycle), high vapor pressure and potential flammability. Molten salts, namely alkali nitrate mixtures, have been introduced as HTF/TES media, and are nowadays the most reliable TES technology [6]. Examples of its application can be found in Gemasolar Thermosolar Plant (Spain) with tower technology or in Archimede Plant (Italy) with parabolic trough technology.

The first developed mixtures involved sodium and potassium nitrates, such as the common Solar salt (60wt% $NaNO_3$ + 40wt% KNO_3). This mixture was successful since was found relatively stable until temperatures higher than 500 ºC. However its melting point is relatively high (240 ºC), which limits the efficiency of the plants and introduces a parasitic load due to the use of electric heating to ensure a minimum line temperature. Several other salt mixtures have been studied and developed in the last years, aiming at decreasing the melting points and also improving other important properties. Besides the binary mixtures, ternary and quaternary mixtures of metal nitrates have been proposed and tested. One of the alkali metals introduced in such mixtures has been lithium, and some of the proposed formulations have shown promising characteristics. In this paper, a short review on the development of nitrate salt mixtures for TES is presented, with particular emphasis, but not limited, to the inclusion of lithium. Thermal and physical properties are addressed, mainly respecting to the temperature working ranges. The interaction of the salts with the construction materials, namely in what concerns corrosion, is also a crucial topic when developing a formulation. All these issues are addressed in the ongoing NewSol research project and are discussed in the present paper.

2. Molten salts in TES: main characteristics

Designing a HTF of a thermal energy storage system involves a complex set of features. The most common important properties of molten salts regarding its use as HTF and TES are:

- Melting point: melting point is a reference for designing the minimum working temperature of the process (usually, a safety margin above, e.g. 20-30%). Lower melting points can be important for some technologies involving relatively low working temperatures, such as parabolic trough, in order to avoid freezing in the tubes and tanks. Melting points of nitrate salt mixtures vary considerably with the composition, typically from 90 to 240 ºC.
- Maximum temperature: maximum temperature is a key parameter and shall be chosen according to salt stability criteria. Salts with stability at high temperatures are particularly important for tower technologies, but are also relevant in the others. Besides chemical stability, other factors can be used to establish the upper limit of temperature, such as the degradability effects of the salt on the exposed materials. Maximum attainable temperatures for alkali nitrate mixtures are usually from 400 to 550 ºC.
- Operating temperature range: besides minimum and maximum temperatures, the temperature difference (ΔT) is a key factor for the success of a HTF/TES process. As much higher is the temperature range, higher will be the heat transferred per unit mass/volume. Typical values of ΔT for nitrate salt mixtures are from 290 to 420 ºC.
- Heat capacity: is an intrinsic property of a salt/salt mixture, and defines the heat transferred per unit of temperature changed. Higher heat capacities lead to higher heat transfer per unit mass, and thus to higher efficiency. Heat capacities of nitrate salt mixtures are commonly in the range 1.2-1.8 $J\ g^{-1}\ K^{-1}$ (average values, since heat capacity changes with temperature).
- Physical properties: density and viscosity of molten salts are important physical properties since are related with the efficiency of transport phenomena, in both mass and heat transfer. Both vary inversely with temperature. For molten nitrates, typical values of densities of 1.7-1.9 $g\ cm^{-3}$ are reported, while viscosities can be in the range of 0.002-0.06 Pa.s (in certain cases, even higher). Density varies linearly with temperature while viscosity has usually an

exponential-type relation with temperature, reason why the values of viscosity are substantially different according with that parameter.

- Volumetric heat capacity: not always considered, is however an important parameter for characterizing a HTF/TES process, since reveals the heat capacity per unit volume which is a significant issue for designing the plant capacity. It is defined as the product of the density by the heat capacity ($\rho \cdot C_p$).
- Thermal conductivity: an important property that affects the efficiency of the heat transfer rates in the plant (charging/discharging processes of TES). However, in this matter, other aspects are crucial and are not depending on the salt properties, such as the heat transfer coefficients of the materials of the heat transfer equipment, of the storage materials (e.g fillers), as well as depends on the equipment design. Typical values for alkali nitrate mixtures: 0.50-1.0 W m^{-1} K^{-1}.
- Chemical stability: the salt shall be stable at the temperature range of the usage, without occurrence of decomposition or other physical/chemical degradation phenomena. The stability shall be guaranteed in thermal cycles during long working periods. Usually, the higher temperatures promote decomposition and so the maximum temperature shall be carefully chosen. Other important factors are the atmosphere, the pressure, the salt impurities and the materials in contact with the melt.
- Compatibility with the construction materials: is a crucial issue when designing a thermal storage plant, since materials in contact with the fluids shall be compatible. The working conditions of the plant are decisive for the materials choice, such as the salt composition and, mostly, the temperature. Phenomena of physical and chemical degradation, such as corrosion, shall be avoided or reduced to minimum. This will be essential for the longevity of the salt and of the construction materials in contact with it.
- Cost is obviously a key factor with a close relation with the decision for a HTF/TES salt formulation.

Table 1 shows some thermal properties collected from the published literature [6-14] and other sources, for several selected salt mixtures.

After the development of the binary Solar salt, further investigations were centered on ternary mixtures, searching for formulations with the highest temperature range, namely melting points as low as 100 ºC and chemical stability at temperatures as high as 500 ºC. Quaternary mixtures have also been studied. The introduction of Li and Ca in nitrate formulations has been proposed and developed. These compounds can provide to the mixtures lower melting points, namely at eutectic points or close, but other aspects shall be taken into account [15] such as decomposition issues, viscosity and cost. In the case of calcium addition, is frequently accompanied by increase in viscosity. Lithium addition is usually associated with the search for decreasing melting temperature [16], reducing energy needs for maintaining the HTF above the freezing point, thus avoiding problems in the equipment (pipes/tanks), mainly in the “cool section” of the TES plant. High costs of lithium nitrate, when compared with other alkali nitrates, is however a drawback.

In order to guaranty economic feasibility, contents not much higher than 10wt% $LiNO_3$ are usually advised [15], but many other formulations have been proposed, as Table 1 shows. The selection of the fluid used as HTF/TES is crucial, namely for CSP plants where the high power requirements (e.g 100 MW) involve the use of large volumes of fluid [11]. Therefore the cost is a decisive factor.

Mixtures including nitrites have also been proposed, such as the so-called Hitec salt, including nitrite anion in the formulation (7wt% $NaNO_3$ + 53wt% KNO_3 + 40wt% $NaNO_2$). Addition of other alkali/alkaline earth metals, like calcium, has been attempted, the most known being the Hitec XL (15wt% $NaNO_3$ + 43wt% KNO_3 + 42wt% $Ca(NO_3)_2$).

The Li-containing formulations depicted in Table 1 show in fact that the melting points can be substantially reduced when compared with other salts based on Na-K. Values in the range 100-130ºC are usually found or even lower, such as a melting point of 75 ºC for a Li-Na-K-Ca with nitrate/nitrite formulation. Simultaneously, these systems did not show any visible decrease in the heat capacity, showing a potential for improving the energy density when compared with the current commercial salts. However, Table 1 also demonstrates that mixtures containing Li can result in a decrease of the maximum operating temperatures, due to premature decomposition, which can be deleterious for the design of the TES plant. So, achieving the highest feasible temperature is also an important issue to allow attaining higher energy densities.

Table 1. Properties of some selected salt mixtures proposed as HTF/TES.

Salt mixture (wt% of components)	Melting point (ºC)	Max. oper. temper. (ºC)	Heat capacity ($J\ g^{-1}\ K^{-1}$)	Volum. heat capacity ($J\ cm^{-3}\ K^{-1}$)	Source Refs.
Lithium mixtures					
$LiNO_3$-$NaNO_3$-KNO_3-$Ca(NO_3)_2$ (10-20-60-10)	132	553	1.518	-	[6,7]
$LiNO_3$-$NaNO_3$-KNO_3-$Ca(NO_3)_2.4H_2O$ (20-10-60-10)	88.6	>500	1.5	2.78	[6]
$LiNO_3$-$Ca(NO_3)_2$-$NaNO_2$-KNO_2 (24-14-17-45)	75	400	1.65	3.02	Internal report
$LiNO_3$-$NaNO_3$-KNO_3 (30-18-52)	120	435-540	1.6	2.85	Internal report
$LiNO_3$-$NaNO_3$-KNO_3 (20-28-52)	130	568	1.091	-	[6]
$LiNO_3$-$NaNO_3$-KNO_3 (26-20-54)	118	430	1.63	-	[6]
$LiNO_3$-$NaNO_3$-KNO_3 (30-15-55)	120	-	-	-	[9]
$LiNO_3$-$NaNO_3$-KNO_3 (27-33-40)	170	-	-	-	[8]
$LiNO_3$-$NaNO_3$-KNO_3 (23-17-59)	140	-	-	-	[8]
$LiNO_3$-KNO_3-$Ca(NO_3)_2$ (30-60-10)	132	560	1.395	-	[6,10]
$LiNO_3$-KNO_3-$Ca(NO_3)_2$ (22-58-20)	117		-	-	[8,11]
$LiNO_3$-$NaNO_3$ (49-51)	194	-	1.85	3.27	Internal report
$LiNO_3$-$NaNO_3$-KNO_3-$2KNO_3.Mg(NO_3)_2$ (17.7-15.3-36-31)	102	-	1.67	-	[6,12]
$LiNO_3$-$NaNO_3$-KNO_3-$NaNO_2$ (18-14-50-18)	94	430	1.66	2.85	[6,13]
$LiNO_3$-$NaNO_3$-KNO_3-KNO_2 (17.5-14.2-50.5-17.8)	99	-	-	-	[14]
Non-Li mixtures					
$NaNO_3$-KNO_3 (60-40), Solar salt	240	530-565	1.55	2.85	Internal report
$NaNO_3$-KNO_3-$NaNO_2$ (7-53-40), Hitec	142	450-540	1.54	2.76	Internal report
$NaNO_3$-KNO_3-$Ca(NO_3)_2$ (15-43-42), HitecXL	140	460-500	1.43	2.73	Internal report
$NaNO_3$-KNO_3 (46-54)	222	550	1.52	-	[6]
$NaNO_3$-KNO_3-$Ca(NO_3)_2$ (16-48-36)	133	550	1.67	2.80	Internal report,[8]

3. Melting points, thermal stability and decomposition

Maximum and minimum operating temperatures of a HTF/TES allows defining the working temperature range and has a direct influence on the energy density of a system. The establishment of the melting temperature and the decomposition temperature are therefore two key parameters in the development of a molten salt mixture.

3.1 Phase diagrams and liquidus temperatures

For the definition of the melting temperature of a mixture, two situations can be found, depending on the composition. For the eutectic composition, the melting occurs at a set temperature. For other compositions, the melting occurs in a range of temperatures where a mixture of solid and liquid phases (with different compositions) coexist, until reaching a final temperature where all the material melts. This final temperature is the liquidus temperature, which is the melting temperature that effectively counts for this purpose.

The stability phase diagrams, expressing the liquidus temperature lines as a function of the composition, are significant tools for designing the appropriate mixtures. For the system Li-Na-K/NO_3, the literature provides several studies where these diagrams were modelled and validated by experimental determinations. The techniques used are TG-DTA (thermogravimetry - differential thermal analysis) and DSC (differential scanning calorimetry).

For understanding the importance of phase diagrams when developing mixtures, Fig. 1 shows the binary diagrams for the three combinations of alkali (Li-Na-K) nitrates. These figures contain plot trends and were constructed from data published by Coscia et al. [9], based on experimentation and mathematic models generated from thermodynamic presumptions. It is clear that the choice for binary mixtures allows attaining substantial decrease in melting points, specially when considering the eutectic point compositions: 222 ºC for Na-K/NO_3; 183 ºC for Li-Na/NO_3; 122 ºC for Li-K/NO_3. It is also observed that the use of lithium in the mixtures is advantageous for reducing the mixture melting points.

Regarding the ternary mixtures, the diagrams presented in Fig. 2 show three different combinations, each one changing the composition of two components with a constant value of the third one. This figure was also constructed from the data of the same publication referred for binary mixtures [9]. The constant composition values selected in each diagram corresponded to the eutectic point of the ternary mixture. The plots show an abrupt variation of the liquidus temperature when compositions approach to the eutectic one. As an example (Fig. 2c) the increase in the Li nitrate content from 15 to 30wt% corresponds to a drop in temperature from 190 to 122 ºC. The minimum temperature expected for this ternary mixture is around 120 ºC.

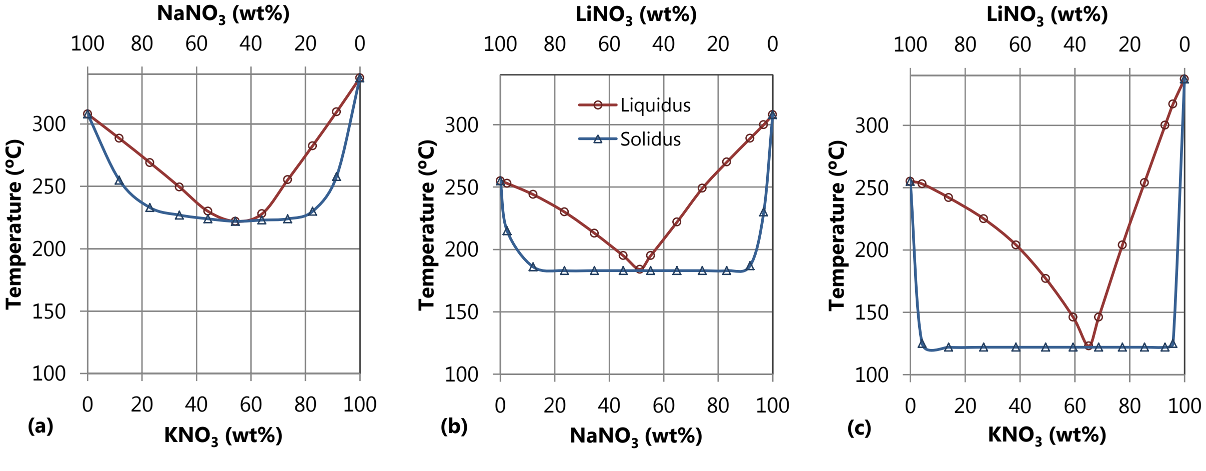

Fig. 1. Phase diagrams (temperature/ wt. composition) for the binary mixtures (a) Na-K/NO_3; (b) Li-Na/NO_3; (c) Li-K/NO_3.

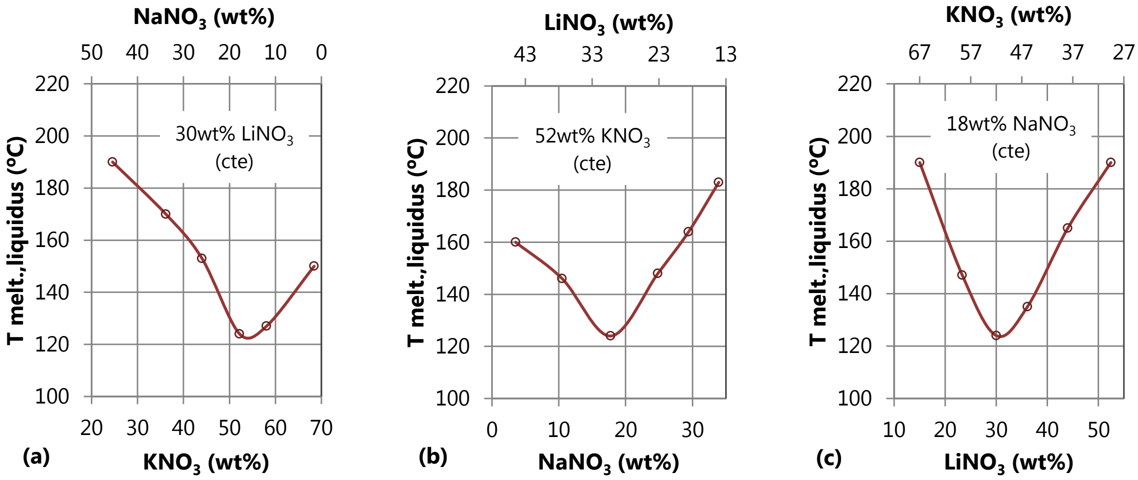

Fig. 2. Phase diagrams (liquidus temperature/ wt. composition) for the ternary mixture Li-Na-K /NO_3: (a) Na-K variation for constant Li; (b) Li-Na variation for constant K; (c) Li-K variation for constant Na.

3.2 Stability and decomposition

Stability of the molten salts is an important issue when designing a sensible heat TES system. There are many forms of salt degradation: interaction with the construction materials (with possible oxidation/reduction/dissolution reactions), interaction with the surrounding atmosphere, and decomposition/vaporization (with chemical transformation and/or release of gaseous substances). Thermal stability of nitrate salts depends on temperature, being usually more pronounced as the temperature increases. So, the maximum allowable operating temperature is normally associated with decomposition of the salt, and is frequently checked by TG techniques. Weight losses above 3wt% are commonly considered for establishing a bulk decomposition point. In order to better understand transformations, gas analysis by chromatography/mass spectrometry can be coupled to the TG tests.

The most important reactions of nitrate melts that affect stability are: nitrate decomposition to nitrite; oxide and carbonate formation; vaporization of the melt. For the nitrate/nitrite equilibria, the following equation is valid:

$MNO_{3\ (l)} = MNO_{2\ (l)} + ½\ O_{2\ (g)}$ (1)

where M represents an alkali metal. Once formed, nitrites can react to produce oxides,

$2\ MNO_{2\ (l)} = M_2O_{\ (s)} + NO_{\ (g)} + NO_{2\ (g)}$ (2)

and/or,

$5\ MNO_{2\ (l)} = M_2O_{\ (s)} + N_{2\ (g)} + 3\ MNO_{3\ (l)}$ (3)

and these ones can eventually react with carbon dioxide to generate carbonates,

$M_2O_{\ (s)} + CO_{2\ (g)} = M_2CO_{3\ (s)}$ (4)

These reactions are undesirable and shall be avoided, for several reasons, namely: (a) firstly, because can cause a substantial change in the melt composition, affecting their thermal and physical properties; (b) also because the release of gases is irreversible phenomena causing loss of material and harmful emissions; (c) finally because the formation of solid products, even at small scale, can have deleterious effects on the storing and transporting equipment in a TES plant.

For mixtures containing nitrites, some additional decomposition reactions can also be found, as expressed by the following equations,

$2\ MNO_{2\ (l)} = M_2O_{\ (s)} + 3/2\ O_{2\ (g)} + N_{2\ (g)}$ (5)

$2\ MNO_{2\ (l)} = M_2O_{\ (s)} + NO_{2\ (g)} + NO_{\ (g)}$ (6)

$5\ MNO_{2\ (l)} = 3\ MNO_{3\ (l)} + M_2O_{\ (s)} + N_{2\ (g)}$ (7)

The last reactions were proposed in a study involving a Hitec-type salt mixture [17], were the evolved gases were analyzed. Under air or oxygen atmosphere, nitrite oxidation to nitrate was found at temperatures of 370 and 392 ºC, respectively, although at small scale. The bulk decomposition of the salt was only found at higher temperatures.

The extension of the previous reactions depends essentially from thermodynamic criteria and from working conditions (temperature, partial/total pressure, concentrations/activities of species), but also from kinetic factors.

Decomposition of nitrate/nitrite molten salt mixtures occurs normally within the range 400-550 ºC. So, the working temperature interval is derived from the difference between the melting point and the decomposition point (applying a safety value of 20-30 ºC above and below, respectively).

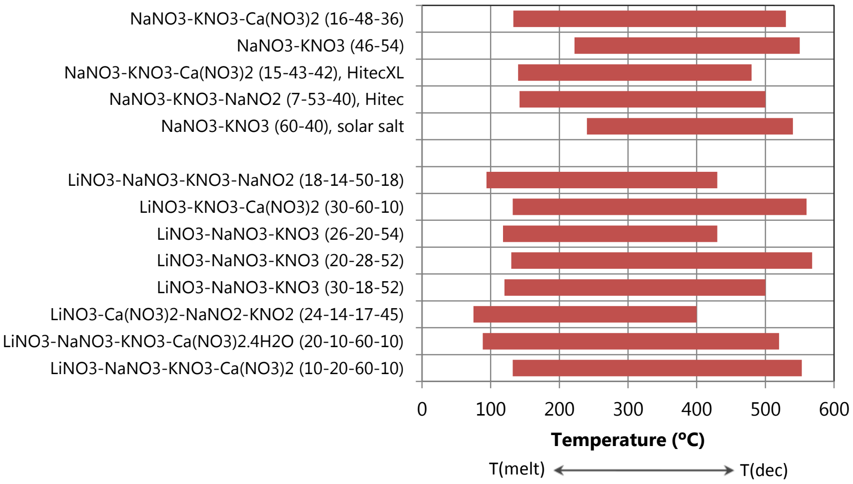

Fig. 3. Temperature intervals defining working ranges, from melting to decomposition, for selected nitrate-nitrite salt mixtures (values in brackets are wt% concentrations of each component).

Figure 3 shows temperature working intervals for a set of selected salt mixtures. The values presented were taken from the bibliography survey, the same presented in Table 1. Intervals of 300-430 ºC are commonly found. It is observed that some ternary and quaternary mixtures containing lithium can provide higher temperature intervals when compared with the most common commercial salts (presented in the upper part of the figure). However, it must be stressed out that the published data does not always correspond exactly to the same experimental conditions. Different furnace types, different atmospheres and pressures, are some of the factors that can affect results. Difficulties in obtaining accurate data are frequently reported, attributed to dehydration inefficiency, mixing/homogenizing and to sample instability during measurements due to salt creeping and overflow through crucibles. This can have impacts on the exact determination of transformation temperatures and heat flows. Moreover, the stability criteria shall be defined based on long-term/large scale stability tests, rather than by simple TG experiments or short-term tests. In this domain, investigations are scarce (at least, not widely published) and many challenging research work is still required.

3.3 Developments in lithium molten salt mixtures

Several publications have been made in recent years regarding ternary and quaternary mixtures of nitrates, some of them also containing nitrites (usually called ternary and quaternary reciprocal NO_3-NO_2 mixtures). As referred in the literature [18] lithium-containing salt mixtures have comparable heat capacities and lower melting points, thus allowing to attain higher energy densities (~1000 MJ m^{-3}), but normally higher prices (1.4-2.2 USD/kg) when compared, for example, to solar salt (0.72-1.0 USD/kg) [18,19].

The ternary mixture Li-Na-K/NO_3, near the eutectic point, has been proposed and studied by several authors [9,10,20]. However, the exact composition of the eutectic was not always agreed (composition range of 25-30wt% $LiNO_3$, 17-20wt% $NaNO_3$, 52-54wt% KNO_3). Reasons of discrepancies are attributed to the presence of impurities in the raw materials. The quaternary salt with low Li content (10wt% $LiNO_3$ + 20wt% $NaNO_3$ + 60wt% KNO_3 + 10wt% $Ca(NO_3)_2$) was proposed [7], with a relatively low melting point (132 ºC) and a decomposition point at 580 ºC (although incipient decomposition was already observed at 470 ºC). It is also referred that much lower melting points were obtained by other authors (e.g. 70 ºC using cesium nitrate additive or even 60 ºC with KCl addition), but problems related with high cost or corrosion make the application prohibitive. Another quaternary mixture (18 wt% $LiNO_3$ + 15 wt% $NaNO_3$ + 36 wt% KNO_3 + 31wt% $2KNO_3.Mg(NO_3)_2$) was proposed [12] with a melting point of 102 ºC.

Developments of mixtures with nitrate/nitrite anions are also found. The mixture 18wt% $LiNO_3$ + 14 wt% $NaNO_3$ + 50 wt% KNO_3 + 18wt% $NaNO_2$ was studied [13], with a good heat capacity (up to 1.57 J g^{-1} K^{-1} at 350 ºC) and a melting point of just 94 ºC. A very similar formulation was the eutectic mixture 17.5wt% $LiNO_3$ + 14.2wt% $NaNO_3$ + 50.5wt% KNO_3 + 17.8wt% KNO_2 , with a melting point of 98.6 ºC [14]. Finally, another Li-Na-K salt mixture with a NO_3^-/NO_2^- molar ratio of 0.56 was proposed [21] with a melting point as lower as 80 ºC. The same authors refer that even lower melting points are possible to achieve with calcium addition.

4. Other physical properties

Viscosity and density of molten salts are also important parameters in the design of a TES facility. Data collected from literature is presented in Fig. 4, where plots of viscosity and density as a function of temperature are depicted. Original data (experimental and correlated) was taken from the work published by Bradshaw (2009 and 2010) [22,8], and such data was fitted in order to obtain the trends here presented. Essentially, an attempt is made to evaluate the effect of the content of lithium and calcium in mixtures. The comparison of different salt mixtures is not always absolutely precise since the compositions always vary. However, the Figure shows very clear trends that can be useful for discussion.

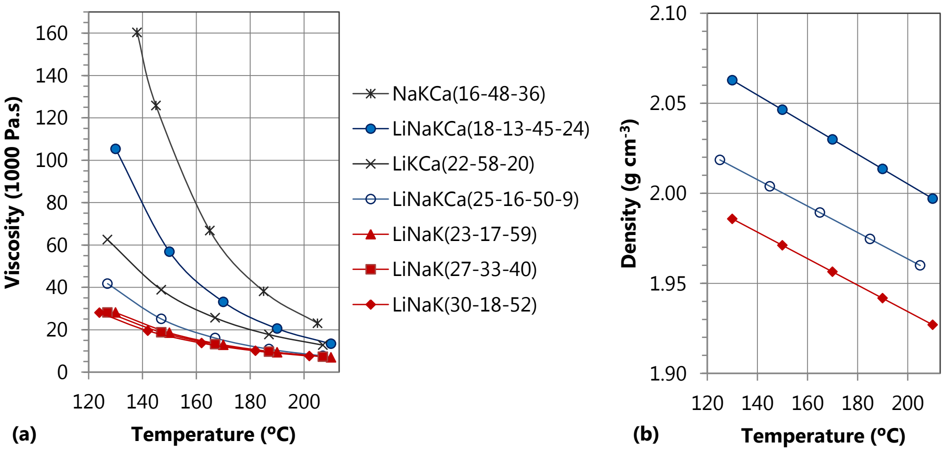

Fig. 4. Variation of (a) viscosity and (b) density of nitrate molten salts with temperature, for selected ternary/quaternary mixtures. Values in brackets of legend are metal nitrate content (wt%).

Regarding viscosity (Fig. 4a), the presence of calcium always involves a substantial rise, more pronounced as the temperature decreases and approaches the melting point. This behavior is due to the exponential dependence from temperature, usually expressed by an Arrhenius-type expression [8]. One of the first calcium-containing salt proposed was the mixture 44wt% $Ca(NO_3)_2$ + 44wt% KNO_3 + 12wt% $NaNO_3$, which was rejected due to viscosity problems [10], although its good thermal behavior. Another mixture proposed later was 60wt% KNO_3 + 22wt% $LiNO_3$ + 18wt% $Ca(NO_3)_2$, with lower viscosity and a melting point of 112 ºC [10]. By the contrary, the Li presence seems to decrease the viscosity, as the Figure shows. The ternary mixture Na-K-Ca/NO_3 attains values near 0.160 Pa.s at the lower temperature (138 ºC), when compared with the other ternary nitrate mixtures Li-K-Ca and Li-Na-K (maximum values of 0.062 and 0.028 Pa.s, respectively, at 125-130 ºC). The two quaternary salts, essentially differing in the calcium nitrate contents (9 and 24 wt%), show quite different viscosities, as higher as the calcium concentration. The several Li-Na-K/NO_3 salt mixtures evaluated have similar viscosities. To be noted that Hitec salt has a viscosity of 0.007 Pa.s at 200 ºC (internal report).

The dependence of density from temperature is linear (Fig. 4b), thus variations with temperature are clearly less pronounced. Nevertheless, the salt mixtures containing calcium also reveal higher densities than the other combinations. The non-containing lithium mixtures Hitec and Solar Salt reveal densities of 1.93 g cm^{-3} at 200 ºC and 1.84 g cm^{-3} at 400 ºC, respectively.

5. Corrosion

Use of molten nitrate salts as heat transfer fluid as well as thermal energy storage material is well documented in CSP plants. The salt mixtures already in use or potentially to be used in commercial applications are the Solar salt, the Hitec and the Hitec XL [23].

Due to the high operating temperature, austenitic stainless steels have been identified as especially suitable materials in the storage system [24]. Low alloy steel often reveals insufficient corrosion resistance [25]. From the literature, the Solar salt is compatible with 316, 304, 321 and 347 austenitic stainless steels, with metal losses varying between 4-15 μm/year [26,27]. Combined studies of Spanish and Chilean researchers demonstrated a detailed comparison of materials corrosion behaviour in molten Solar salt and Hitec XL, concluding that Hitec XL salt decreases the corrosiveness of the energy storage salts, which increases the operational life cycle of current solar technology [25,28].

However, compatibility of molten salts with the structural alloys as well as materials corrosion have been of real concern mainly because of the high operating temperatures. Hence, the material development and corrosion studies turn out to be an essential part of research [29]. Corrosion resistance of alloys depends on the content of elements, generally Cr, Ni and Mo, which influence the development of passivating oxide layers. Accordingly, the formation of Ni and/or Cr oxides layers in alloyed steels and stainless steels produce a better corrosion resistance than the only formation of iron oxides in carbon steels. Moreover, the presence of Mo significantly increases the resistance to both uniform and localized corrosion. The corrosion that takes place on metallic materials in contact with HTF and TES medium is largely affected by the chemical reaction that occurs on the molten salts [30].

So, efforts have been made to understand the selective removal of elemental constituents from the alloys in order to propose corrosion mechanisms. This makes analysis of corrosion products or oxide scales significantly important [31].

To achieve this, large number of analytical methods has been used. Molten salt corrosion has been predominantly studied by gravimetric, electrochemical techniques and, morphology and chemical analysis of corrosion products by means of XRD, SEM/ EDS, Raman spectroscopy etc, after long exposures at high temperatures. In general, iron oxides are identified at corrosion scales. Results suggested that magnetite (Fe_3O_4) was mainly located close to base metal while hematite (Fe_2O_3) was in higher proportion in the outermost oxide layers. The formation of Fe_2O_3 in preference to other compounds is strongly linked to the values of pO_2 in the salt [32].

Localized phenomena such as pitting, intergranular corrosion, selective leaching, among others could be found after characterizing corrosion coupons transversal sections. Evaluation performed by SEM/EDS over the surface and cross section of metallic specimens could show the delaminated morphology of corrosion products as well as the enrichment of the outermost oxides layers with cation species coming from nitrate salt mixtures [33].

In recent years, lithium nitrate has been considered as a great additive to improve the thermal performance of molten salts [15] as aforementioned. However, there are a reduced number of publications in the literature reporting the corrosion ability in these promising molten salts.

Fernandez et al. [34], have examined the behaviour of ternary molten salts containing $LiNO_3$ and $Ca(NO_3)_2$ in contrast with the obtained results in the binary Solar salt currently used in CSP plants. The main results that were obtained are indicated in Table 2.

Under these experimental conditions, it is clearly observed that the corrosion rate of steels is lower in Li ternary mixtures than in Solar salt.

Based on results related to weight gain, descaled weight loss and the microstructure of the corrosion scales, Cheng et al. [35] proposed a possible corrosion mechanism of steel in $LiNaKNO_3$ mixture at 550 °C for 1000 h, Fig. 5. According to chemical composition profiles obtained from the corrosion scales, the accumulation of chromium was primarily in the inner portion of the $(Fe,Cr)_3O_4$ layer, immediately adjacent to the steel substrate. The accumulation of chromium in the scales can be attributed to the corrosion of Cr–Mo steel leading to the formation of $FeLiO_2$ and $(Fe,Cr)_3O_4$, followed by the predominant outward diffusion of Fe^{2+} and Fe^{3+} ions, leaving the inert chromium distributed in the scale next to the steel substrate. It follows therefore that steel with higher chromium content would be less susceptible to corrosion.

Table 2. Corrosion rate and corrosion products obtained at 390 ℃ with A1 steel [34].

Molten salt	Corrosion products		Corrosion rate (μm/h)
	Steel	Salt	
Solar Salt	$MgFe_2O_4$, Fe_2O_3, MgO	Fe_2O_3, Na_2O, $MgFe_2O_4$	0.1108
Lithium ternary salt	$MgFe_2O_4$, K_2FeO_4, Fe_3O_4	$MgFe_2O_4$, Na_2O, $LiFeO_2$, Li_2O_2	0.0359
Li/Ca ternary salt	$MgFe_2O_4$, Fe_3O_4	$MgFe_2O_4$, $LiFeO_2$	0.0031

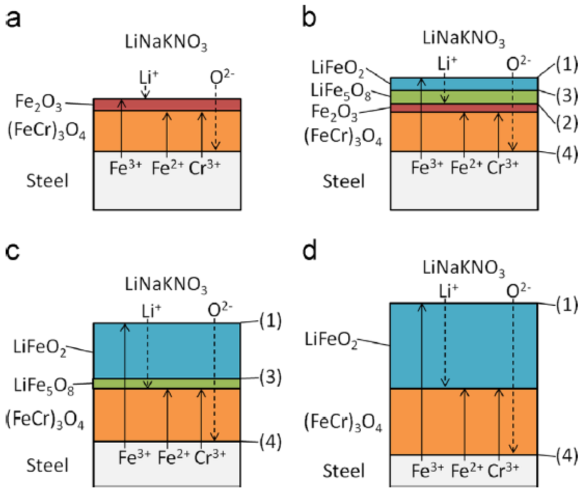

Fig. 5. Schematic illustration of the growth stages involved in the formation of corrosion scales on steel following exposure to $LiNaKNO_3$ at 550 ºC [35].

6. Conclusions

Research and development on molten salts for sensible heat thermal energy storage has been driven by the search for high energy density mixtures. Several ternary and quaternary salt formulations have been proposed and studied, containing lithium and calcium in the formulations, and also NO_3^- /NO_2^- as anions, in order to decrease the melting points and therefore allowing higher operating temperature intervals. Questions regarding the stability and decomposition of the salts have been considered, as well as the control of important physical properties such as viscosity. Degradability of materials in contact with the salts, namely corrosion studies are other crucial aspects that shall be carefully examined. Regarding stability and corrosion, long-term accurate experiments are mandatory in further investigations.

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