High Temperature Sensible Storage—Molten Salts

Luis Guerreiro[a] and Mauro Henriquez[b], [a]Institute for Earth Sciences (ICT), University of Evora, Evora, Portugal; [b]Centro de Desarrollo Energético Antofagasta (CDEA), Universidad de Antofagasta, Av. Universidad de Antofagasta, Antofagasta, Chile

Introduction

The technological limitation in the use of solar energy is intermittent generation due to the lack of storage capacity. The impediment that plants do not generate at night and cloudy days makes their massive participation in the energy matrix complex. For this reason, storage systems allow solar thermal power plants a more stable generation of electrical energy independent of the variability of the solar resource. These systems increase the performance and competitiveness of CSP technologies in terms of LCOE (Levelized Cost of Energy) (Stepper, 2014).

The main types of thermal energy storage are classified into thermochemical storage, latent heat storage, and sensible heat storage. In the first case, this type of storage involves a reversible chemical reaction where the used medium must have the ability to completely dissociate in the temperature range of the solar field heat. The amount of heat stored will depend on the heat of reaction and the degree of conversion that is achieved in the exothermic and endothermic process. In the case of latent heat storage, the materials used undergo a phase change at a temperature within the upper and lower range of the solar field. The typical phase used is solid-liquid. These systems are governed by the specific heat of the material and by the enthalpy of the phase change, which allows a large amount of energy to be stored in a smaller volume, and thus at a lower cost if compared to sensible heat storage systems (González-Roubaud et al., 2017).

The most common storage system utilizes two tanks that store sensible heat. Solar Two project used this mixture for the first time (Gil et al., 2010), operating from 1995 to 1999 and comprising two storage tanks, one cold (290 °C) and one hot (565 °C) with a capacity of 105 MWt of circulating salt, which stored energy for 3 h. The project was the basis of the current CSP plants with tower technology. The sensible heat method consists of raising the temperature of a medium (generally solid or liquid), without changing phase. It depends on the heat capacity, density, thermal diffusivity, vapor pressure and thermal conductivity. The amount of stored energy Q is given by Eq. (1) (Kuravi et al., 2013).

$$Q = m \cdot Cp \cdot \triangle T \tag{1}$$

Where m is the mass of the storage medium (kg), Cp is the specific heat of the material (kj/kgK), and $\triangle T$ is the process temperature range in (°C).

Molten Salt mixtures

Molten salts have been the current choice to store energy with the method above mentioned, acting as an intermediate fluid and thermal storage medium, with multiple mixtures introduced in recent years that improve the thermal properties and the working temperature range. Solar Salts are one of the most widely used materials in CSP plants, because they have a low average cost compared to other materials, also exhibit many desirable heat transfer characteristics at temperatures up to 600 °C, presents high density, high heat capacity, high thermal stability, are non-toxic or flammable and have very low vapor pressure at high temperatures. The low viscosity of solar salt allows it to be pumped over a wide temperature range (220–580 °C) and it are also compatible with stainless steel, which is the material employed to transport and store the salt. However, the biggest limitation of the salts currently used is the high melting point, which means that the current design of plants with tower and parabolic trough must operate at a minimum temperature of 290 °C.

Different proportions of lithium nitrate to the solar salt in order to improve the thermophysical properties and the working ranges of CSPs. Bradshaw and Siegel (2009) published one of the first works on the advantages of using lithium nitrate; however, they reported that lithium nitrate is more expensive than potassium, calcium, and sodium nitrate.

Wang et al. (2013), Trujillo (2013) and Wang et al. (2012) determined the melting temperature and of the eutectic composition in 25.9 wt%,$LiNO_3$ + 20.06wt%$NaNO_3$ + 54.1wt%KNO_3 ternary system using a thermodynamic-based model reaching 118 °C of eutectic temperature. This calculation was experimentally validated using the DSC technique, obtaining the theoretically reported value with high accuracy. Wang et al. (2012) evaluated four ternary mixtures with 12%, 20%, 27%, and 30% $LiNO_3$, determining their respective melting points and the maximum decomposition temperature for the different concentrations of Li.

Table 1 Viscosity of molten nitrate salt mixtures (Henríquez et al., 2019).

Melting Point °C	*Wt% $LiNO_3$*	*Wt% $NaNO_3$*	*Wt% KNO_3*	*Viscosity from 133 °C to 150 °C (cP)*	*Viscosity from 190 °C to 200 °C (cP)*	*Viscosity from 300 °C to 450 °C (cP)*	*References*
128	30 $_{(99,995)}$	13	57	20.4 $_{(150°C)}$	10.01 $_{(200°C)}$	8.71 $_{(300°C)}$	Henríquez et al. (2019)
125	30 $_{(99,9)}$	13	57	20.4 $_{(150°C)}$	9.78 $_{(200°C)}$	7.13 $_{(300°C)}$	Henríquez et al. (2019)
128	30 $_{(98)}$	13	57	20.8 $_{(150°C)}$	9.75 $_{(200°C)}$	6.75 $_{(300°C)}$	Henríquez et al. (2019)
80	29.1	22.6	48.3	25$_{(133°C)}$	10$_{(197°C)}$	6 $_{(450°C)}$	Bradshaw (2008)
95	20	40	40	25$_{(133°C)}$	10.2$_{(197°C)}$	5.8 $_{(450°C)}$	Bradshaw (2008)
105	15	42	42.5	24.5$_{(133°C)}$	8.5$_{(197°C)}$	4.7 $_{(450°C)}$	Bradshaw (2008)
120	37	18	45	19$_{(150°C)}$	7.5$_{(200°C)}$	–	Bradshaw (2010)
170	33	33	34	19$_{(150°C)}$	7.5$_{(200°C)}$	–	Bradshaw (2010)
140	30	18	52	19$_{(150°C)}$	8$_{(200°C)}$	–	Bradshaw (2010)
140	23.4	17.3	59.3	13.3$_{(133°C)}$	6.4$_{(197°C)}$	2.8 $_{(300°C)}$	Jin et al. (2016)
127	30	21	49	20 $_{(150°C)}$	10 $_{(200°C)}$	4 $_{(300°C)}$	Coscia (2013)

Bin Mohammad et al. (2017) performed experimental tests with the mixture 29.63%$LiNO_3$ + −13.23%$NaNO_3$ + 57.14%KNO_3, achieving an experimental melting point of 122.8 °C, and included simulations with the FactSage software, obtaining a value of 120.84 °C. Olivares (2012) studied the thermal behavior of the mixture composed by 30wt%$LiNO_3$ + 18 wt% $NaNO_3$ + 52wt% KNO_3, using the DSC/TGA, determining that the melting points obtained using different cover atmospheres of argon, nitrogen, and oxygen were, 121 °C, 122 °C and 120 °C, respectively.

Several studies (Nissen, 1982; Bradshaw, 2008, 2010; Jin et al., 2016; Coscia, 2013). Analyzed the behavior of the viscosity for different mixtures of Li/K/Na, measured at various temperature ranges for their utilization in the CSP industry. Among those studies, they identified the mixture comprised of 23.4wt%$LiNO_3$+ 59.3wt%KNO_3 + 17.3 wt% $NaNO_3$, which offered viscosities close to those of the solar salt: 3.3 cP at 150 °C y 2.8 cP at 300 °C. Table 1 shows viscosity values for ternary nitrate mixtures, measured in different temperature ranges.

Innovative Molten Salt

Molten Salts has been a promising research field in the last 20 years due to the potential usage of using molten salts both as a heat transfer fluid and also as a heat storage media in a broad range of applications.

Henríquez et al. (2019) conducted a thermophysical study of the mixture of 30wt%$LiNO_3$ + 13wt%$NaNO_3$ + 57wt%KNO_3 for different purities of $LiNO_3$ obtaining melting points between 124 °C and 128 °C (Fig. 1). Heat capacity measurement for the ternary mixture with $LiNO_3$ (98%) were conducted through modulated differential scanning calorimetry, MDSC study showed that heat capacity of the salt at 390 °C was 1.718 J/g °C (Fig. 2).

The thermal stability analysis of the ternary Li/K/Na nitrate mixture results can be observed: from Figs. 3 four zones were defined where zone 1 and 2 correspond to the loss of supramolecular and intramolecular water mass respectively, zone 3 is a stable zone

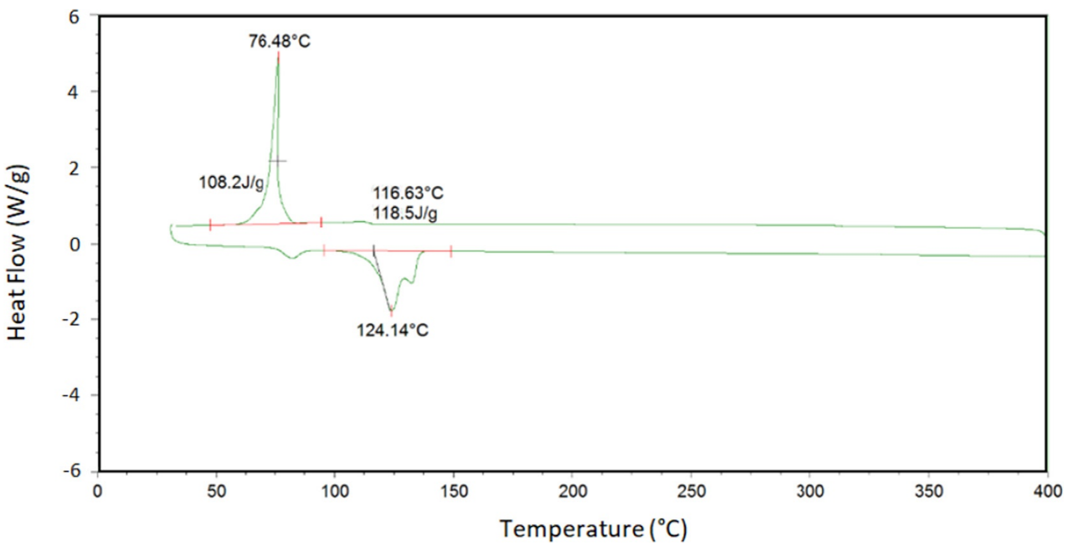

Fig. 1 DSC test of ternary 30wt%$LiNO_3$ + 13wt%$NaNO_3$ + 57wt%KNO_3.

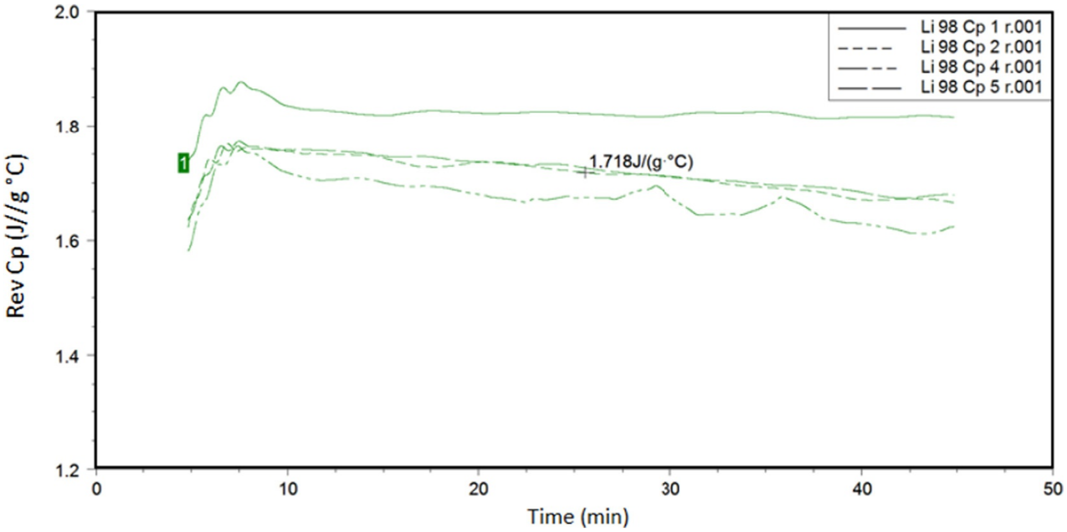

Fig. 2 MDSC test of ternary 30wt%$LiNO_3$ (98%) + 13wt%$NaNO_3$ + 57wt%KNO_3 at 390 °C.

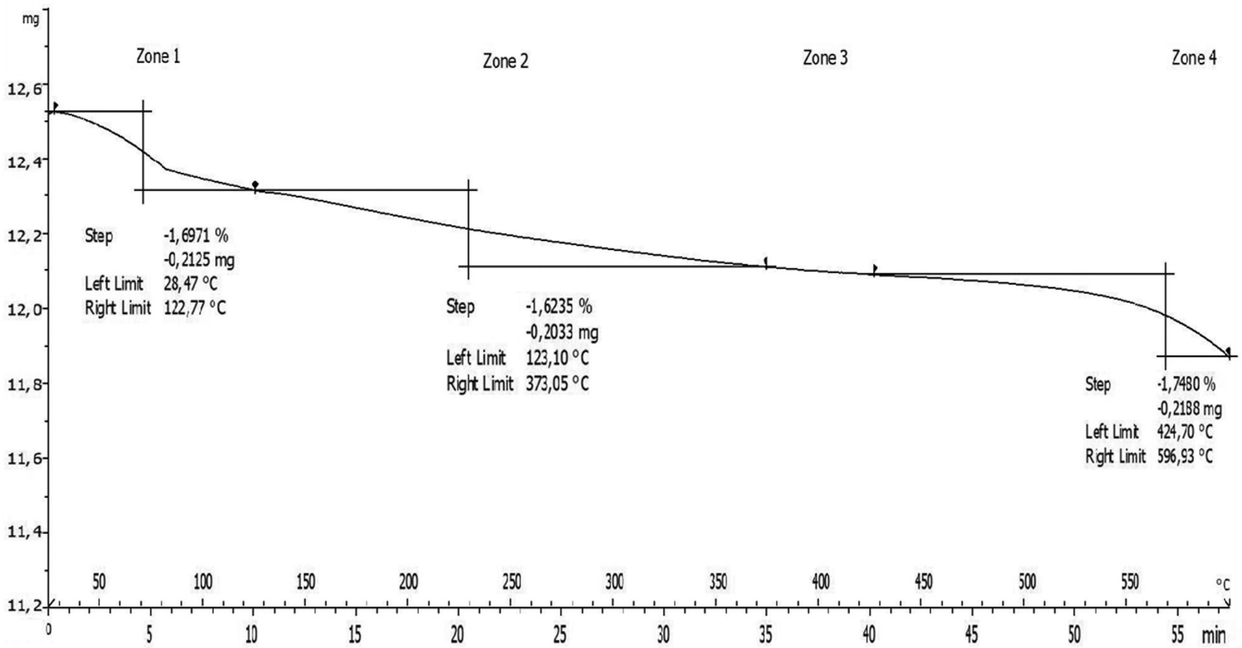

Fig. 3 Thermal ternary salt decomposition curve of 30% $LiNO_3$ + 13% $NaNO_3$ + 57% KNO_3 mixture with 98% $LiNO_3$ purity.

where there is no mass loss and zone 4 that corresponds to the loss of mass by decomposition of nitrate salts. Which is in accordance with results reported by other authors (Bin Mohammad et al., 2017; Olivares, 2012).

The use of the ternary molten salts incorporating lithium nitrate proposed in this research, would reduce the lowest temperature point by almost 100 °C when comparing with Solar Salt.

Table 2 shows a summary of the main thermal properties obtained for $LiNO_3$ ternary mixture, compared with solar salt (Zavoico, 2001).

Table 3 shows the viscosity results of the ternary mixtures of molten nitrate salts composed of 30% $LiNO_3$ + 57% KNO_3 + 13% $NaNO_3$ and it is compared with the solar salt. Lithium nitrate salts presents reasonable viscosity with values below 10 cP at 200 °C, which are in agreement with publications by other authors (Jin et al., 2016; Bradshaw and Brosseau, 2009).

This author carried out tests of the new ternary mixture of $LiNO_3$ on a pilot scale, in a stainless-steel tank with 1 Ton of salt capacity (Fig. 4) equipped with commercial components and determine that after 200 h of recirculation of the ternary mixture into

Table 2 Thermal results obtained in ternary 30 wt% $LiNO_3$ + 13 wt% $NaNO_3$ + 57 wt% KNO_3 using different $LiNO_3$ purity grades.

Mixture	*Melting point (°C)*	*Decomposition temperature (°C)*	*Heat Capacity (J/(g°C))*
Li 98	128	596	1.718
Solar Salt	223	565	1.50

Table 3 Viscosity of ternary mixtures composed by 30% $LiNO_3$ + 57% KNO_3 + 13% $NaNO_3$.

T (°C)	*Viscosity (cP) $LiNO_3$ 98%*	*Viscosity (cP) Solar salt*
150	20.8	–
170	12.62	–
200	9.75	6.7
230	9.61	5.51
260	8.59	4.83
300	6.75	4.68

Fig. 4 Photo of pilot plant of molten salts of the University of Antofagasta.

the tank, it is observed that: At a temperature of 190 °C, the salt flows without presenting any inconvenience, nor is any cold zone that could generate crystallization identified. Therefore, considering this ternary mixture, it is concluded that it is possible to work at a minimum operating temperature of 190 °C in CSP plants (Henríquez et al., 2020).

References

Bin Mohammad M, Brooks GA, and Rhamdhani MA (2017) Thermal analysis of molten ternary lithium-sodium-potassium nitrates. *Renewable Energy* 104: 76–87.

Bradshaw RW (2008) Low Melting Point Heat Transfer Fluid-Patent No US 7,828,990 B1.

Bradshaw RW (2010) Viscosity of Multi-component Molten Nitrate Salts—Liquidus to 200 °C, p. 21.

Bradshaw RW and Brosseau DA (2009) Low-Melting Point Inorganic Nitrate Salt Heat Transfer Fluid, United States Pat. US 7,588,694 B1, vol. 1, no. 12, pp. 1–9.

Bradshaw RW and Siegel NP (2009) Molten Nitrate Salt Development For Thermal Energy Storage In Parabolic Trough Solar Power Systems. *Es2008 Proceeding of the 2nd International Conference on Energy Sustainability* vol. 2, 631–637.

Coscia K (2013) Thermophysical Properties of $LiNO_3$-$NaNO_3$- KNO_3 Mixtures for Use in Concentrated Solar Thermophysical Properties of for Use in Concentrated Solar Power.

A. Gil et al., “State of the art on high temperature thermal energy storage for power generation. Part 1—Concepts, materials and modellization,” Renewable and Sustainable Energy Reviews, vol. 14, no. 1, pp. 31–55, Jan. 2010.

González-Roubaud E, Pérez-Osorio D, and Prieto C (2017) Review of commercial thermal energy storage in concentrated solar power plants: Steam vs. molten salts. *Renewable and Sustainable Energy Reviews* 80: 133–148.

Henríquez M, Guerreiro L, Fernández ÁG, and Fuentealba E (2019) Lithium nitrate purity influence assessment in ternary molten salts as thermal energy storage material for CSP plants. *Renewable Energy* 149: 940–950.

Henríquez M, Fernández ÁG, Soto C, and Fuentealba E (2020) Proposal for the development of Chilean $LiNO_3$ as thermal energy storage material for CSP plants. In: *Proceeding of the ISES Solar World Congress 2019 IEA SHC Int. Conf. Sol. Heat. Cool. Build. Ind. 2019*, pp. 1373–1380.
Jin Y, Cheng J, An X, Su T, Zhang P, and Li Z (2016) Accurate viscosity measurement of nitrates / nitrites salts for concentrated solar power. *Solar Energy* 137: 385–392.
Kuravi S, Trahan J, Goswami DY, Rahman MM, and Stefanakos EK (2013) Thermal energy storage technologies and systems for concentrating solar power plants. *Progress in Energy and Combustion Science* 39(4): 285–319.
Nissen DA (1982) Thermophysical properties of the equimolar mixture NaN0,-KNO, from 300 to 600°C. *Journal of Chemical & Engineering Data*, pp. 269–273.
Olivares RI (2012) The thermal stability of molten nitrite/nitrates salt for solar thermal energy storage in different atmospheres. *Solar Energy* 86(9): 2576–2583.
Stepper R (2014) Tecnología de Almacenamiento de CSP—Ultimos Desarrollos.
Trujillo U (2013) Novel Molten Salts Thermal Energy Storage for Concentrating Solar Power Generation.
Wang T, Mantha D, and Reddy RG (2012) Thermal stability of the eutectic composition in $LiNO_3$–$NaNO_3$–KNO_3 ternary system used for thermal energy storage. *Solar Energy Materials & Solar Cells* 100: 162–168.
Wang T, Mantha D, and Reddy RG (2013) Thermodynamic properties of $LiNO_3$–$NaNO_3$–KNO_3–$2KNO_3 \cdot Mg(NO_3)_2$ system. *Thermochimica Acta* 551: 92–98.
Zavoico AB (2001) *Solar Power Tower—Design Basis Document*. Tech. Rep. SAND2001-2100, p. 148.