# Proposal for the development of Chilean $LiNO_3$ as thermal energy storage material for CSP plants

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**Abstract**

The addition of lithium nitrate could be a replacement alternative to the current molten salts used in CSP technology. The results are promising respect to the melting point where it was found that it is around 124 ° C (reduction of 96 ° C compared to solar salt) and a maximum temperature of thermal stability around 596 ° C. In addition, the proposed ternary mixture would mean an improvement of approximately 16% respect to the heat capacity, and the viscosity has a very similar behavior. Finally, the results of the molten salt pilot plant built at the University of Antofagasta, which consists of a tank with a capacity of one ton, was determined to be possible to work without any inconvenience at a new minimum operating temperature of 190 ° C, these results were obtained after conducting controlled cooling tests from 400 ° C to 190 ° C, and flow tests at 190 ° C for a period of 200 hours.

*Keywords: Thermal Energy Storage; Molten Salts; Lithium Nitrate; Concentrated Solar Power.*

## 1. Introduction

In latest years, Chile has been one of the most attractive solar markets due to its excellent solar conditions, in particular the Atacama Desert, which presents an annual global radiation value of 2571 kWh $m^{-2}$ and an index of direct normal irradiance (DNI) of 3389 kWh $m^{-2}$. This location is among the best worldwide for capturing and storing solar energy (Escobar et al. 2015) and thus Concentrated Solar Power (CSP) rises as a promising solution. These features are of major interest when considering the extensive saline deposits that are present in this north region of Chile with a great potential to be used as energy storage material (SQM 2019). One of the technological limitations in the use of solar energy is their intermittent generation during the night or cloudy days but the integration of thermal energy storage (TES) systems can help to solve this problem. The thermal storage allows a more stable generation of electrical energy and improves the variability of the solar resource to solar thermal power plants. The most common storage system is to use two tanks storing sensible heat using solar salt (60% $NaNO_3$ + 40% $KNO_3$) as storage media. This mixture has a melting point of 222 ° C (Kuravi et al. 2013; Medrano et al. 2010), and It was used for the first time in the Solar Two project. This project operated from 1995 to 1999 and consisted of two tanks, one cold (290ºC) and another hot (565 ºC) with a capacity of 105 MWt through which the salts circulated passing through the solar field and storing energy for 3 hours. This project was the basis of the current CSP plants with tower technology using molten salts. The molten salt widely used in the concentrating solar plants as an intermediate fluid or storage medium to convey or store the thermal energy. Many different mixtures of molten salt have been introduced as energy storage medium in recent years in order to improve the thermal properties and the working temperature range Lithium nitrate in different proportions added to the current solar salt is one of the most promising elements to improve the properties and working ranges of the molten salts currently used in Concentrated Solar Power (CSP) ). One of the first authors to report the advantages of using lithium nitrate was N. Siegel et al. (Robert W. Bradshaw and Siegel 2009). However, this author reported that lithium nitrate is more expensive than potassium, calcium and sodium nitrate, so cost is one of the main reasons why lithium-based salts have not been used in any commercial application, as well as the nitrates of AgNO3 and $CsNO_3$, which are even more expensive. Mantha et al. (Reddy, Wang, and Mantha 2012) determined the melting temperature using a model based on


Selection and/or peer review under responsibility of Scientific Committee
doi:10.18086/swc.2019.24.05 Available at http://proceedings.ises.org

thermodynamic principles to predict the temperature and composition of the eutectic of the ternary salt. This calculation was validated experimentally with the DSC technique, obtaining in a precise way the theoretically reported value. Bradshaw and Meeker (R. W. Bradshaw and Meeker 1990) evaluated four ternary mixtures with 12%, 20%, 27% and 30% $LiNO_3$, where they determined their respective melting points and the maximum decomposition temperature for the different amounts of Li. One of the mixtures that offered a very low melting point and an excellent thermal stability is composed by 25.92% $LiNO_3$ + 20% $NaNO_3$ + 54.07% $KNO_3$, where it was reached to obtain 118 º C of temperature eutectic according to the studies carried out by Wang and colleagues (Wang, Mantha, and Reddy 2012b). Mehedi et al. (Mohammad 2016) performed experimental tests with the mixture 29.63-13.23-57.14% where it was determined that the experimental melting point was 122.8 ° C, and included simulations with the FactSage software, where a value of 120.84 ° was obtained. Different authors (Robert W. Bradshaw 2008; Robert W. Bradshaw and Siegel 2009; Robert W Bradshaw 2010; Nissen 1982) have analyzed the behavior of the viscosity of different mixtures to be used in the solar concentration industry. Table 3 provides a bibliographic compilation of viscosity values for the ternary nitrate mixtures of Li/K/Na, measured in different temperature ranges.

In the present work, experimental tests of the ternary mixture 30wt% $LiNO_3$ + 57wt% $KNO_3$ + 13wt% $NaNO_3$ were performed at the laboratory level and at the pilot scale inside the tank of molten sales of the University of Antofagasta. These tests served to know different thermal properties and the process of crystallization, solidification, as well as the distribution of temperatures.

**Tab. 1: Viscosity of molten nitrate salt mixtures**

| % 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) | Ref. |
|---|---|---|---|---|---|---|
| | 50 | 50 | - | - | 1.5 | (Nissen 1982) |
| 29.1 | 22.6 | 48.3 | 25 | 10 | 6 | (Robert W. Bradshaw 2008) |
| 20 | 40 | 40 | 25 | 10.2 | 5.8 | (Robert W. Bradshaw 2008) |
| 15 | 42 | 42.5 | 24.5 | 8.5 | 4.7 | (Robert W. Bradshaw 2008) |
| 37 | 18 | 45 | 19 | 7.5 | - | (Robert W Bradshaw 2010) |
| 33 | 33 | 34 | 19 | 7.5 | - | (Robert W Bradshaw 2010) |
| 30 | 18 | 52 | 19 | 8 | - | (Robert W Bradshaw 2010) |
| 23.4 | 17.3 | 59.3 | 13.3 | 6.4 | 2.8 | (Jin et al. 2016) |
| 30 | 21 | 49 | 20 | 10 | 4 | (Coscia 2013) |

## 2. Experimental procedure

The mixtures used for laboratory tests were prepared with $LiNO_3$ from Atacama Desert (99.7%). The $NaNO_3$ (99.5%), $KNO_3$ (99.5%) was provided by SQM. The mixtures used in the pilot scale plant tests were prepared with $LiNO_3$ from Todini (99%). The $NaNO_3$ (99.5%), $KNO_3$ (99.5%) was provided by SQM.

The pre-melted and solidification of the mixtures were analyzed to determine their heat capacity and for the differential scanning calorimetry (DSC) analysis. The viscosities of molten salt mixtures were measured using a Brookfield DV-III viscometer (Brookfield Engineering, Middleboro, MA), taking measurements at 150, 175, 200 and 300 °C. The molten salt mixtures were contained in a stainless steel crucible that was heated in a furnace maintained at constant temperature by a Brookfield Thermosel controller until 300ºC. A Brookfield 21S stainless steel spindle SC4-31 was appropriate for the range of viscosity of the molten salt mixtures. Thermogravimetric analysis (TGA) was performed using a Mettler Toledo TGA-DSC 1 LF/894 STARe in the temperature range 25°C to 600 °C at a heating rate of 10 K $min^{-1}$. A mass of approximately 10 mg to 18 mg was also sealed in a 40-ml aluminum pan. Finally the tests of the new $LiNO_3$ ternary mixture were carried out in a stainless steel tank with 1 Ton of salt capacity and are equipped with commercial components. The molten salt is heated by four electric resistances of a power of 1200 W each and to evaluate the temperature, 15 temperature sensors are integrated.

## 3. Results

The use of the ternary molten salt incorporating lithium nitrate proposed in this research would reduce the lowest temperature point by almost 96ºC when comparing with Solar Salt. Tab. 2 shows a summary of the main thermal properties obtained for $LiNO_3$ ternary mixture compared with solar salt. $LiNO_3$ codified as Atacama Desert, was obtained, using Salar de Atacama brines. The results of the thermal analysis of this mixture with a composition of 30wt% $LiNO_3$ + 57wt% $KNO_3$+13wt% $NaNO_3$ (Tab. 2) showed a melting point of 124.14°C and the energy required to melt the mixture was 118.5 J/g. The heat capacity measured was 1.740 J/g °C at 390ºC. In the case of the thermal results obtained for the Li based salt with a composition of 30wt% $LiNO_3$ + 57wt% $KNO_3$+13wt% $NaNO_3$ using $LiNO_3$ with 99% of Todini, showed a melting point of 124 °C and the heat capacity was 1,824 J/g °C at 390ºC . The energy required to melt the mixture was 121.5 J/g. It is observed that the heat capacity of the different ternary mixtures of lithium nitrate has an increase between 16 to 21% compared to the conventional binary solar salt, which increases the storage capacity of the lithium mixture for a similar volume using solar salt. In the thermal stability analyzes of the ternary Li/K/Na nitrate mixtures $LiNO_3$, The maximum temperatures was 596 ° C. In this zone the decomposition could be given by the formation of lithium oxides (Wang, Mantha, and Reddy 2012b), due to the instability of LiNO3, and the evolution at high temperature of such gases $N_2$, NO, $O_2$, $N_2O$, and $NO_2$ (Olivares 2012).

Samples were measured from 150°C to 300 °C and tests were performed with controlled shear rates from 2.94 rpm to 191 rpm and the reported viscosities were obtained at a shear rate of 149 rpm (Tab. 3). Binary solar salt mixture shows lower viscosities than the ternary mixtures; however viscosity results for different lithium mixtures showed a drops from 20 cP, at 150 °C until 9 to 8 cP at 200°C. Above 200°C the viscosity values showed a slight reduction until 300ºC. These results are in agreement with publications by other authors (Robert W Bradshaw and Brosseau 2009; Jin et al. 2016) . It was observed that for all mixtures the viscosity decreases as the temperature increases.

**Tab. 2:Thermal results obtained in ternary 30wt% LiNO3 + 13wt% NaNO3 + 57wt% KNO3 and Solar salt.**

| Mixture | Melting point (°C) | Descomposition temperature (°C) | Solidification point (°C) | Heat Capacity (J $g^{-1}°C^{-1}$)) | (% wt ) Heat Capacity/ Heat Capacity solar salt |
|---|---|---|---|---|---|
| 30wt% $LiNO_3$ + 13wt% $NaNO_3$ + 57wt% $KNO_3$ Todini (99% Li) | 125 | 596 | 76.05 | 1.824 | +21.6 |
| 30wt% $LiNO_3$ + 13wt% $NaNO_3$ + 57wt% $KNO_3$ Atacama Desert | 124 | 596 | 76.48 | 1.74 | +16.0 |
| Solar Salt | 223 | 565 | - | 1.50 | 0 |

**Tab. 3: Viscosity results of ternary molten nitrate salt mixtures composed by 30% $LiNO_3$ 57% $KNO_3$, and 13% $NaNO_3$.**

| T ( °C) | Viscosity (cP) $LiNO_3$ 99 % | Viscosity (cP) $LiNO_3$ 99.7 Atacama Desert | Viscosity (cP) Solar salt |
|---|---|---|---|
| 150 | 20.4 | 19.3 | - |
| 170 | 13.81 | 13.5 | - |
| 200 | 9.78 | 8.6 | 6.7 |
| 230 | 8.74 | 7.2 | 5.51 |
| 260 | 8.55 | 5.7 | 4.83 |
| 300 | 7.13 | 5.4 | 4.68 |

The tests of the new $LiNO_3$ ternary mixture were carried out in a stainless steel tank with 1 Ton of salt capacity (Figure 1) and are equipped with commercial components. The molten salt is heated by four electric resistances of a power of 1200 W each and to evaluate the temperature, 15 sensors are integrated at different positions. Prior to the evaluation of the liquid phase cooling process of the ternary mixture of $LiNO_3$ + $KNO_3$ + $NaNO_3$, the salts were heated by all electrical resistances from 190 °C to 400 °C at the maximum power. Once a temperature of 400 °C was reached, all electrical resistances were turned off to begin with the evaluation of the cooling process until reaching 190 °C (Fig. 2). This is the minimum operating temperature proposed for this mixture, maintaining a safety temperature range of 60 °C with respect to the temperature at which the salt begins to crystallize inside the tank. After stabilizing the ternary salt mixture at 400 ° C, and switched off the electrical resistances, the time elapsed until reaching the proposed operating temperature for this ternary mixture of 190 ° C was 70 hr.

**Fig. 1: Photo of pilot plant of molten salts of the University of Antofagasta**

In Fig. 3, the physical aspect of the salts is observed when maintaining the temperature at 190 °C during a period of 24 hours without recirculation. It can be seen that the salt is completely in liquid phase.

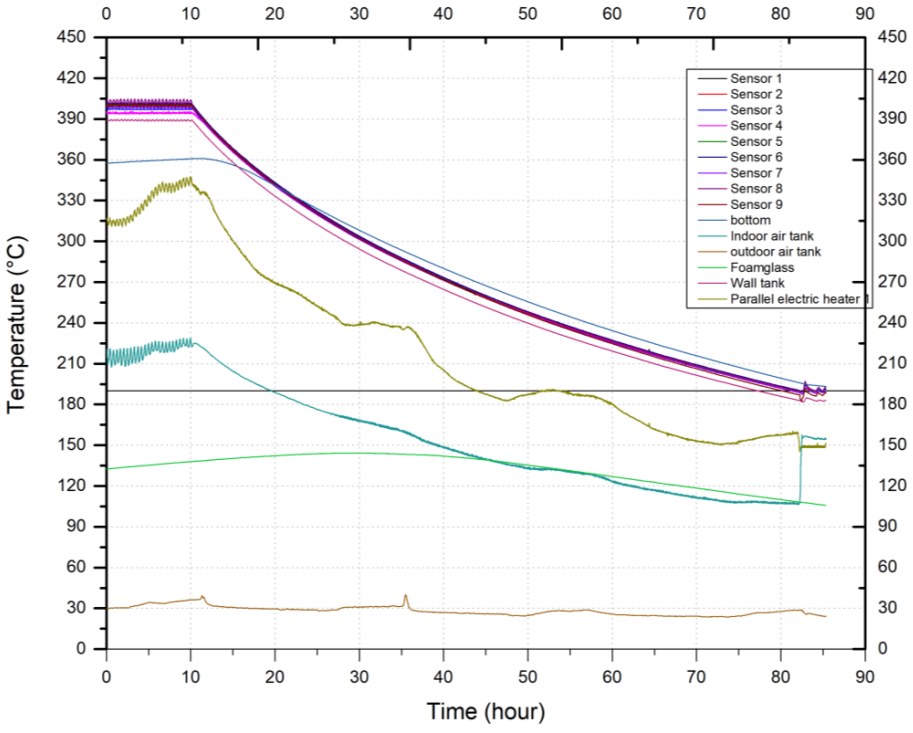


**Fig. 2: Cooling of the Ternary Lithium Mixture in the Pilot Plant from 400 to 190°C.**

**Fig. 3: Ternary mixture composed by 30% LiNO3 +57% KNO3 + 13%NaNO3 inside the tank at 190 ° C during 24 hours without recirculation.**

Figure 4 shows the ternary mixture of lithium nitrate at a temperature of 190 ° C, recirculating for a period of 200 hr in the closed circuit of the pilot plant. From this test, in which the behavior of the ternary mixture with Todini lithium is evaluated at this temperature, it can be observed that before, during and after the test there was no problem regarding the fluidity of the salt. Nor was any cold zone identified in which any crystallization process could be generated.

**Fig. 4: Recirculation of the ternary mixture in liquid phase inside the sales tank of the pilot plant at 190 ° C after 200 h.**

## 4. Conclusions

The ternary mixtures obtained at laboratory scale through mineral Chilean sources and Todini shows a heat capacity of 1.740 J/g °C and 1.824 J/g °C at 390°C, and a melting point of 124°C y 125°C respectively, improving the thermal behavior of the binary solar salt.

Binary solar salt mixture shows lower viscosities than the ternary mixtures, however, both ternary mixtures showed reasonable viscosity results from 200 °C, with a value below 10 cp.

The present work carried out at laboratory scale and in the pilot plant confirms the excellent thermophysical properties that would allow Chilean lithium nitrate to be an option to replace the current solar salt, with a stable minimum operation temperature around 190 ºC.

The elapsed time of the ternary mixture cooling process from 400 to 190 ° C was 70 h. To evaluate the results with respect to solar salt, this same process is expected to be carried out experimentally or through simulation.

It is confirmed that the ternary mixture does not have any inconvenience when the ternary mixture is recirculated in a closed circuit at 190 ° C for a period of 200 hours. No problem was observed regarding the fluidity of the salt. Nor was any cold zone identified in which some crystallization process could be generated. This generates a 100 ° C operating gradient with respect to solar salt.

## 5. Acknowledgments

The authors would like to acknowledge the financial support provided by CONICYT / FONDAP 15110019 “Solar Energy Research Center” SERC-Chile. FIC-R 30413089 – 30488809 funded by Antofagasta Government.

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