THERMOPHYSICAL PROPERTIES OF LOW COST LITHIUM NITRATE SALTS PRODUCED IN NORTHERN CHILE FOR THERMAL ENERGY STORAGE

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Abstract

In recent years, lithium containing salts have been studied for thermal energy storage (TES) applications because of their excellent thermophysical properties. In solar power plants, lithium is seen as a way to improve the properties of state-of-the art molten salts used today. Lithium nitrate is a good candidate for sensible heat storage, because of its ability to increase the salt mixture's working temperature range. In the present research, thermophysical properties characterization of lithium nitrate containing salts, produced in Chile, have been carried out. Corrosion evaluations at 390° and 565°C for 1000 h were performed for low chromium steel T22 and stainless steels (AISI 430 and AISI 316), respectively. Chemical composition of the salts including identification of corrosion products and impurities was determined and an estimation of the Chilean production costs is reported. The study shows a loss of thermal properties after the corrosion tests. The heat capacity was reduced, possibly caused by the formation of oxides at high temperatures. The partial thermal decomposition of the salt was probably produced by the incorporation of corrosion products from the steel.

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

1. Introduction

In the Atacama Desert, located in the northern Chile, the solar conditions are excellent. The annual global radiation value is 2500 kWh/m² and the index of direct normal irradiance (DNI) is 3500 kWh/m². These conditions are among the best worldwide for capturing and storing solar energy. These features are of major interest when considering the extensive saline deposits that are present in this area. The raw minerals reservoirs are found as solid deposits (caliches) and brines in vast salt flats (Salares) with grades that are profitable when large extractions (30,000 tons/year) are targeted such as for solar thermal storage applications [1]. The North of Chile

contains the world's largest commercially exploited nitrate and iodine deposits, and it is the source of natural nitrates like caliche ore [2].

In recent years, lithium nitrate (LiNO_3) has been considered as a great additive to improve the thermal performance of molten salts [3]. These additions have shown to extend the temperature work range by lowering the melting point as well as increasing the thermal stability to higher temperatures. This effect can be profitable despite the higher cost of these salts. When comparing the production costs of lithium compounds from minerals and brines, Chile among other countries has been able to produce them in the most cost-effective way from the economical point of view.

LiNO_3 is an inorganic salt highly soluble in water that is usually obtained from lithium carbonate (Li_2CO_3) and nitric acid (HNO_3). The reaction for this process is the following:

The aqueous solution containing lithium nitrate obtained requires several evaporation steps to remove the water. D. Stern et al. [4] proposed a synthesis way to avoid these further processing steps by producing molten lithium nitrate ($T_m = 235^\circ\text{C}$):

The advantages of this method are:

- It uses available chemical raw materials in their industrially available form: Li_2CO_3 or NH_4NO_3 .
- Considerably less water evaporation is required because very little amount of water is formed and lithium carbonate has a low water solubility.
- Because no hydrated product is formed, vacuum or extreme drying times are avoided.

Using this process, the production of LiNO_3 at industrial scale could be viable in the Atacama Desert and it could be the key for a successful development of the next generation CSP plants.

Fernández et al. [5] studied nitrate molten salts with more than three components as a novel approach to achieve a synergic effect between the properties of LiNO_3 and $\text{Ca}(\text{NO}_3)_2$ as additives to Solar Salt (60wt.% NaNO_3 – 40wt.% KNO_3). The most notable property of the molten salts

using calcium and lithium nitrate is its energy density (based on heat capacity and density), which represents an important improvement over the currently used Solar Salt.

Based on this parameter, smaller volumes of the proposed salt could be used to store the same amount of energy as the current Solar Salt.

Different researchers have been focused on determining the eutectic compositions for ternary and quaternary molten salts. The first study documenting the eutectic point of ternary nitrate mixtures dates back to 1964 [6], in which it was determined that 17.3wt.% NaNO_3 + 59.4wt.% KNO_3 + 23.3wt.% LiNO_3 had the lowest melting point.

The exact eutectic point has not yet been determined because the measurement is influenced by the quality of the salt used and the types of impurities in it. In a recent study, T. Wang et al. [7] stated the eutectic composition as 25.9wt.% LiNO_3 + 20.6wt.% NaNO_3 + 54.1wt.% KNO_3 but Olivares et al. [8] using FactSage software appointed the eutectic composition as 30wt.% LiNO_3 + 18wt.% NaNO_3 + 52wt.% KNO_3 .

One of the main scopes of this research is to evaluate the influence of the corrosion processes on these molten salts containing lithium nitrate. It is accepted that impurity levels tend to drive corrosion [9]. Kruizenga et al. [10, 11] postulated that chlorine initially grows on top of the oxide-metal interface. As the metal chloride diffuses toward the external surface, it is oxidized to form a non-protective oxide layer [7]. Because of this, salt purification is critical to control corrosion of containment materials and salt's thermal properties. Purification of salts has been performed using the following approaches: chlorinating processes (CCl_4 , HCl , or another chlorinating compound); reduction of the salt using active metals, such as Mg; saturation of a salt with a liquid metal (i.e., LiCl with Li metal) such that redox potential of the melt is lowered.

The impurities found in the Chilean nitrates, that can have an influence on the thermal behavior at elevated temperatures, are the following:

- SO_4^{2-} and CO_3^{2-} : easily form calcium, magnesium, sodium and potassium solid compounds, which are frequently found in molten salts. The formation of these compounds can clog vessels, thus reducing the flowability of the mixtures through pipes. Corrosion-erosion problems arise in the connections, vessels as well as in propulsion pumps and heat exchangers.

- Mg: present in the form of magnesium nitrate, easily forms magnesium oxides, which can be found attached to the steel surface during the initial hours of exposure to the salt. In addition, the incorporation of Mg in the structure of hematite (Fe_2O_3) and other corrosion products can lead to the formation of magnesium ferrites (MgFe_2O_4).
- Cl^- : a corrosion enhancing agent, is found in the form of perchlorates [15]. Therefore, it is important to determine the distribution and content of Cl^- , as well as its evolution in the salt.

Impurities not only change the corrosion ability of the molten salts but also affect their thermal storage properties due to the corrosion products and insoluble salt's impurities that are formed during operation of the solar plant.

This paper aims to evaluate the main parameters that affect the thermal storage ability of LiNO_3 containing molten salts. To achieve this goal, we compared the variation of the most important parameters (heat capacity, viscosity and thermal stability) before and after the corrosion process of low-Cr steel T22 and stainless steels AISI 430, and AISI 316. The corrosion was performed by immersing the alloys in LiNO_3 containing molten salts and Solar Salt during 1000 h at 390 and 565°C in an air atmosphere.

2. Experimental section

The saline nitrates used in the research were NaNO_3 and KNO_3 (SQM-SSR grade), $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and LiNO_3 (Merk 98%). The pre-melted and solidified mixtures were analyzed (before and after corrosion test) to determine their melting point, heat capacity and thermal stability. A simultaneous thermogravimetric analyzer (TGA) with a differential scanning calorimeter (DSC) from Mettler-Toledo was used. The instrument was responsible for providing a TGA/DSC signal and a differential thermal analysis (DTA) signal, from which thermal decomposition curves were obtained for the tested salt mixtures. A thermal treatment was performed in the salt mixture before test consisting in a two stages heating: at 140°C for at least 4h and at 250°C for 8h. Once the thermal purification treatment was performed, the salts were carefully handled to avoid water absorption. After that, the mixed formulations were sealed inside a dry box with desiccants.

Different crucibles were used for the thermal properties tests. The crucibles that were used in the thermal analysis varied and were made of platinum in the case of the TGA equipment and aluminium for the DSC; the crucibles were not hermetically sealed in the latter case.

These tests were conducted in ultra-high purity (UHP) nitrogen (50 ml/min) and specific liquid heat capacity (C_{pL}) was calculated following the standard test method ASTM E 1269-05. Corrosion studies were performed in about 30g of salt and a statistical sampling method has been carried out in order to analyse the entire salt sample. In this direction five thermal tests were analysed with the scope to reduce the uncertainty.

We also studied the viscosity of the ternary salts taking measurements at 200°, 250° and 300°C. The equipment used was a rheometer coupled with parallel plates in an environmental furnace using nitrogen gas (TA instruments). The plates with the salt were heated to the working temperature and the shear rate of $100s^{-1}$ was used to calculate the viscosity.

The chemical composition of the steels tested in this investigation is shown in Table 1. The corrosion of the steels was carried out at 390°C (T22) and 565°C (AISI 430 and AISI 316) during 1000 h but steel corrosion evaluations are not the aim of this research. After the test, the salts were analyzed via x-ray diffraction (XRD) to determine the presence of the insoluble and crystalline corrosion products formed.

Table 1. Chemical composition of tested steels.

Steel	Weight %							
	Si	Mn	Cr	P	Mo	C	Ni	S
430	0.4	0.2	16.21	0.018	0.01	0.12	0.18	0.002
316	0.36	1.2	16.88	0.025	2.14	0.03	10.55	0.002
T-22	0.3	0.4	2.25	0.3	1	0.12	-	0.3

3. Results and discussion

Thermophysical and chemical characterizations have been performed to Chilean lithium nitrate containing salts (results are shown in Table 2 [5, 12, 14]). The results were compared to baseline Solar Salt properties found in the literature [12, 13].

It is important to highlight that lithium nitrate containing salts could be used as thermal storage material in CSP plants because of the lower melting point, and extended working temperature range $\sim 128^{\circ} - 600^{\circ}C$, depending on the salt composition.

The most notable thermal property improvement of the lithium nitrate mixtures is the energy density, compared to the currently used Solar Salt. Because at temperatures above 170°C, the viscosity of these salts is very similar to the salts commercially available in the market, these salts can be used as they will have the proper flow throughout the plant.

Table 2. Thermophysical properties of Chilean lithium nitrate containing molten salts.

Molten salt mixture (wt.%)	Work temp. range (°C)	Viscosity at 250°C (cP)	Energy density (MJ/m ³)	Salt Price (US\$/Ton)	Two-tanks system cost/stored energy (US\$/kWh _{th})	Reference
Solar Salt	221–589	5.51	550	893	11.67	[12]
20 LiNO ₃ – 52 KNO ₃ – 28 NaNO ₃	128–600	6.3	513	1161	16.35	[5]
30 LiNO ₃ – 10 Ca(NO ₃) ₂ – 60 KNO ₃	134–567	5.72	607	1274	15.07	[5]
10 LiNO ₃ – 10 Ca(NO ₃) ₂ – 60 KNO ₃ – 20 NaNO ₃	131–580	5.78	680	1038	10.98	[14]

In the Atacama Desert are present the most important lithium reservoirs and an industrial production of this product extracted from the brines present in the north of Chile could be the key for obtain an inexpensive lithium nitrate [16,17]. The production of LiNO₃ at industrial scale could be the key for a successful development of the next generation CSP plants. The economic evaluation was obtained using the thermal parameters and it is focused only on the material costs of the storage block. An estimation of this industrial production costs in Chile was performed.

The corrosiveness of these salts, with different LiNO₃ additions, was evaluated at the common storage temperatures for solar plants with parabolic cylindrical collectors (T22 at 390°C) and central tower (AISI 430 and AISI 316 at 565°C). The corrosion rates of the steels in the molten salts were determined for 1000h of immersion. Results are shown in Table 3, including corrosion products and insoluble salt's impurities resolved in XRD. The corrosion rate using LiNO₃ containing salts is lower than in the binary Solar Salt.

It is important to note that in 30wt.%LiNO₃ + 60wt.%KNO₃ + 10wt.%Ca(NO₃)₂, the protective spinel MgCr₂O₄ was identified. The formation of this spinel indicates Cr diffusion to the outer zone of the corrosion zone and further reaction with the salt's impurity MgO. The corrosion rate using the Li-containing salts was small probably because of the formation of this protective spinel. The protective chromium spinel layers were identified as FeCr₂O₄ and MgCr₂O₄. The insoluble impurities resolved in the salt contained sulfates and carbonates. This corrosion evaluation has been focused in different oxides, spinels and insoluble products detected in the salt after corrosion to understand the variations in the thermophysical storage properties.

Table 3. Corrosion rates in mm/year and secondary phases resolved by XRD in the salts after 1000 h of immersion.

Molten salts, wt. %	Corrosion products	Insoluble products	Corrosion rate (mm/year)		
			T22 (390°C)	AISI 430 (565°C)	AISI 316 (565°C)
Solar Salt	Fe ₂ O ₃ , Na ₂ O, MgFe ₂ O ₄	CaCO ₃ , Na ₂ CO ₃	0.071	1.157	0.023
20 LiNO₃ – 52 KNO₃ – 28 NaNO₃	Fe ₂ O ₃ , FeCr ₂ O ₄ , Na ₂ O	Na ₂ CO ₃ , CaCO ₃ , MgCO ₃	0.03	0.24	0.017
30 LiNO₃ – 10 Ca(NO₃)₂ – 60 KNO₃	MgCr ₂ O ₄ , Fe ₂ O ₃ , Li ₂ O, FeSO ₄	MgSO ₄ , MgCO ₃	0.027	0.103	0.009
10 LiNO₃ – 10 Ca(NO₃)₂ – 60 KNO₃ – 20 NaNO₃	MgCr ₂ O ₄	Na ₂ CO ₃ , CaCO ₃ , Na ₂ SO ₄	0.007	0.054	0.019

The thermal stability plots of the molten salts before and after corrosion tests of T22 steel are shown in Figure 1. The reduction in thermal stability for the salts evaluated including Solar Salt (Figure 1b) could be related with the incorporation of corrosion products into the salt. This behavior was also obtained in ternary and quaternary molten salts (Fig 1a), c) and d) containing LiNO₃ and/or Ca(NO₃)₂ (composition shown in table 3). A steep reduction in the salts weight % after corrosion was observed around 350°C. Olivares et al. [10] reported the evolution of nitrous oxide (NO) at 325°C in Ar atmosphere (via TGA-MS) for (Li-Na-K)NO₃ salts. The partial decomposition observed at 350°C is probably because of the following reactions:

with M = Li or Na

In this study, the presence of Li_2O and Na_2O after corrosion was confirmed by XRD. These secondary phases are also present in Solar Salt (see Table 3). Those oxides are probably dispersed into the salt matrix, producing a catalytic thermal decomposition phenomenon. Thermal studies using TGA-MS will be performed in the future to analyze the volatile products formed during corrosion to confirm possible decomposition following reactions (3) and/or (4). Because TGA tests use small amounts of sample (~ 10 mg), the thermal decomposition due to corrosion product will need to be verified at larger scale using a molten salt loop.

Figure 1. Thermal stability of the salts before and after corrosion tests on a) Li ternary, b) Solar Salt, c) Ca ternary and d) Quaternary.

The Energy Development Center at Antofagasta University is equipped with a molten salts loop able to work in a temperature range from 130° to 500°C. This loop is intended to test the

performance of new fluids potentially suitable for the existing solar technologies using molten salt storage. In addition, the current facilities also include systems for testing dynamic corrosion produced by molten salts on different carbon steels, stainless steels and other coated steels, under different flow rates. The pilot plant has a capacity of about 600 kg, so the influence of corrosion products can be analysed in a semi-industrial scale in a future work.

The change of the heat capacity before and after corrosion is shown in Figures 2 and 3. The Li- and Ca-containing salts (in wt.%: $30\text{LiNO}_3 + 60\text{KNO}_3 + 10\text{Ca(NO}_3)_2$; and $10\text{LiNO}_3 - 10\text{Ca(NO}_3)_2 - 20\text{NaNO}_3 - 60\text{KNO}_3$) showed a reduction of 8 to 20 % in the heat capacity after corrosion of AISI 316 and AISI 430 at 565°C , respectively. The lower heat capacity was obtained for AISI 430 which also showed a larger corrosion rate.

The heat capacity of each component identified in XRD was calculated using HSC thermochemical software (Table 4). The highest heat capacity is for lithium oxide.

Figure 2. Liquid heat capacities before and after corrosion in: a) LiCa: 30wt.%LiNO₃ + 60wt.%KNO₃ + 10wt.%Ca(NO₃)₂ and b) Quaternary: 10wt.%LiNO₃ + 10wt.%Ca(NO₃)₂ + 20wt.%NaNO₃ + 60wt.%KNO₃ after the immersion in AISI 430 and 316 stainless steels.

Figure 3. Liquid heat capacities before and after corrosion in: 20wt.%% LiNO_3 + 52wt.%% KNO_3 + 28wt.%% NaNO_3 (Li) after the immersion in AISI 430 and 316 stainless steels.

The salt without Ca-nitrate (in wt %: 20 LiNO_3 + 52 KNO_3 + 28 NaNO_3) showed an increase in the heat capacity after corrosion (Figure 3). This effect could be explained by the presence of higher LiO_2 content.

The viscosity of the LiCa- and Li-ternary salts (Figure 4) at temperatures between 200°–300°C, increased after corrosion. The trend of decreasing values with temperature is similar for all the salts before and after corrosion. The larger viscosity was obtained for the salts exposed to AISI 430. This alloy reported the highest corrosion rates, so it is expected that more insoluble corrosion products were formed. The more particles are dispersed in a fluid the higher the viscosity will be. The effects observed in the heat capacity and the viscosity of the salts after corrosion could be influenced by the amount of corrosion products formed. Because the ratio salt-volume to exposed alloy-surface was very small compared to the expected values during plant operation, these results could be affected in a way that does not represent the CSP plant operation. To confirm the effect on these important thermal properties, we are planning on performing the corrosion tests and salts evaluations at a pilot scale using a molten salt loop that is currently under construction.

Table 4. Liquid heat capacity for detected insoluble products, using HSC thermochemical software

Compounds	Liquid heat capacity, J/g*K
Na ₂ O	1.69
Li ₂ O	3.48
CaCO ₃	1.60
Na ₂ SO ₄	1.44
MgCO ₃	1.78
Na ₂ CO ₃	1.79

Figure 4. Viscosity before and after corrosion in: a) LiCa: 30wt.%LiNO₃ + 60wt.%KNO₃ + 10wt.%Ca(NO₃)₂ and b) Li: 20% LiNO₃ + 52% KNO₃ + 28% NaNO₃ after immersion in AISI 430 and 316 stainless steels.

4. Conclusions:

Nitrate chemistry at high temperature storage conditions produce corrosion that affects not only the durability of the stainless steels of commercial plants, but also the molten salt's purity. As corrosion products are incorporated into the molten salt mixture, the composition of the salt is altered and consequently the thermal stability as well as the storage capacity are affected.

In this study, the presence of Li₂O and Na₂O after the corrosion process was confirmed and those oxides are probably dispersed into the salt matrix, producing a catalytic phenomenon related with the thermal decomposition that happens after the corrosion process. The change of the heat capacity before and after corrosion showed a reduction of 8 to 20 %.

A large viscosity was obtained for the salt exposed to AISI 430 involving the reduction in the thermophysical properties with higher corrosion behavior.

The search of new molten salts, including lithium nitrate with a reasonable economic cost, is the key for novel TES materials. New fluids are required for the advanced solar power technology development. Higher energy density is needed in future TES applications. In this direction, using small quantities (10wt.%) of lithium and calcium nitrate, the salt mixture energy density increased by 19%.

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