

RESEARCH ARTICLE | MAY 31 2016

Thermophysical properties and corrosion characterization of low cost lithium containing nitrate salts produced in northern Chile for thermal energy storage **FREE**

Ángel G. Fernández; Judith C. Gomez; Hector Galleguillos; Edward Fuentealba



AIP Conf. Proc. 1734, 050014 (2016)

<https://doi.org/10.1063/1.4949112>



CrossMark

Articles You May Be Interested In

Economic and strategic analysis of the current situation of Chilean copper smelters

AIP Conference Proceedings (October 2020)

Tests of the HYDAD-D Landmine Detector on Dry Soil in Northern Chile

AIP Conference Proceedings (August 2010)

A thermo-economic assessment of CSP+TES in the north of Chile for current and future grid scenarios

AIP Conference Proceedings (July 2019)

500 kHz or 8.5 GHz?
And all the ranges in between.

Lock-in Amplifiers for your periodic signal measurements



Find out more



Thermophysical Properties and Corrosion Characterization of Low Cost Lithium Containing Nitrate Salts Produced in Northern Chile for Thermal Energy Storage

Ángel G. Fernández^{1, 2, a)}, Judith C. Gomez², Hector Galleguillos³,
Edward Fuentealba¹

¹Energy Development Center, University of Antofagasta, Av. Universidad de Antofagasta 02800, Antofagasta, Chile.

²National Renewable Energy Laboratory, 15013 Denver West Parkway 80401, Golden, Colorado. USA

³Chemical Engineering Department, University of Antofagasta, Av. Universidad de Antofagasta 02800, Antofagasta, Chile.

^{a)}Corresponding author: angel.fernandez@uantof.cl

Abstract. In recent years, lithium containing salts have been studied for thermal energy storage (TES) systems applications, because of their optimal thermophysical properties. In solar power plants, lithium is seen as a way to improve the properties of molten salts used today. Lithium nitrate is a good candidate for sensible heat storage, due to 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 of carbon and low chromium steels were performed at 390°C for 1000 hours. Thermophysical properties of the salt mixtures, such as thermal stability and heat capacity, were measured before and after corrosion tests. Chemical composition of the salts was also determined and an estimation of Chilean production costs is reported. Results showed that purity, thermal stability and heat capacity of the salts were reduced, caused by partial thermal decomposition and incorporation of corrosion products from the steel.

INTRODUCTION

In the northern Chile, in particular the Atacama Desert, 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 founded as solid deposits (caliches) and brines in vast salt flats, called 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 is the source of natural nitrates like caliche ore [2].

In recent years, lithium nitrate 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 operating plants with these fluids. In this direction, when comparing the production costs of lithium compounds from minerals and brines, Chile among other countries, can produce lithium compounds from brines in a most effective way from the economical point of view.

Fernández et al. [4] proposed the study of molten salts of more than three components as a novel approach to achieve a synergic effect between the properties of LiNO₃ and Ca(NO₃)₂ additives and the solar salt's components.

The most notable property of the molten salts using calcium and lithium nitrate is its energy density (based on the heat capacity), which represents an important improvement over the solar salt currently used. Note that based on this parameter, a smaller amount of salt could be used to store the same amount of energy.

It is accepted that impurity levels tend to drive corrosion [5]. Kruizenga et al. [6] postulated that chlorine initially grows at surface 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]. Due to these properties, salt purification is critical for materials and for their corrosion properties. In the literature, purification was performed using the following approaches: a chlorinating process (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 of Chilean nitrates with 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 compounds, which are frequently found in molten salts. The formation of these solid compounds can clog vessels, thus reducing the flowability of the mixtures through the pipes of the solar centrals. 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, note the integration of magnesium in the structure of hematite (Fe_2O_3 , and other corrosion products present in steels) that leads to the development of magnesium ferrites (MgFe_2O_4).
- Cl^- appears as a corrosion enhancing agent and is found in the form of perchlorates. Therefore, the study of the distribution and content of Cl^- , as well as its evolution in the salt, is important.

This paper aims to evaluate the main parameters that affect the thermal storage ability of LiNO_3 molten salts. To achieve this goal, we compared the variation of the most important parameters (heat capacity and thermal stability) after a corrosion process performed in a low-Cr steel (T22) and AISI 430 and 316 stainless steels, immersed in the molten salts during 1000 hours at 390°C , in an air atmosphere.

EXPERIMENTAL PROCEDURE

The saline nitrates that were 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 (Panreac 98%). The pre-melted and solidified mixtures were analysed (before and after the corrosion test) to determine their melting point, heat capacity and thermal stability. A simultaneous thermogravimetric analyzer (TGA) and 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 designed salt mixtures. Once thermal purification treatment was arranged, the salts were carefully handled in order 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. Both tests were conducted in an inert atmosphere of ultra-high purity (UHP) nitrogen (50 ml/min). Specific liquid heat capacity was calculated following the standard test method ASTM E 1269-05.

The corrosion produced by these LiNO_3 based molten salts was studied in a low-Cr steel (T22) and AISI 430 and 316 stainless steels. The chemical composition of the steel is shown in Table 1.

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

The corrosion of the steel was carried out at 390°C during 1000 hours. After the test, the salt was analysed via x-ray diffraction (XRD) to evaluate the corrosion and insoluble products formed. These last products were formed from the impurities present into the salt.

RESULTS

Thermophysical and chemical characterizations have been performed to Chilean lithium nitrate containing salts (results are shown in Table 2). Results were compared to baseline Solar Salt (60wt.% NaNO₃ – 40wt.% KNO₃) properties found in the literature [8,9].

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

Molten salt mixture (wt.%)	Work temp. range (°C)	Viscosity at 250°C (cP)	Corrosion rate of A516 Steel at 390°C (mm/year)	Electrical conductivity at 390°C ($\Omega^{-1}\text{m}^{-1}$)	Energy density (MJ/m³)	Salt Price (US\$/Ton)	Two-tanks system cost/stored energy (US\$/kWh_{th})
Solar Salt	221–589	5.51	0.97	0.37	550	893	11.67
20 LiNO₃ – 52 KNO₃ – 28 NaNO₃	130–600	6.3	0.31	0.67	513	1161	16.35
30 LiNO₃ – 10 Ca(NO₃)₂ – 60 KNO₃	134–567	5.72	0.027	0.56	607	1274	15.07
10 LiNO₃ – 10 Ca(NO₃)₂ – 60 KNO₃ – 20 NaNO₃	132–580	5.78	0.013	0.45	680	1038	10.98

Using lithium and calcium nitrate, in small quantities (10wt.%), the salt mixture energy density increased by 19%. It is important to note that based on this parameter, a smaller amounts of this salt could be used to store the same amount of energy as the Solar Salt. An estimation of industrial production costs of LiNO₃ in Chile has been included.

The production of LiNO₃ at industrial scale is the current challenge in northern Chile and could be the key for a successful development of the new generation of CSP plants. The economic evaluation was obtained through the thermal parameters and is focused only in the material costs in the storage block.

Thermal stability of the salts, before and after corrosion test, was also determined. Results are shown in Figure 1.

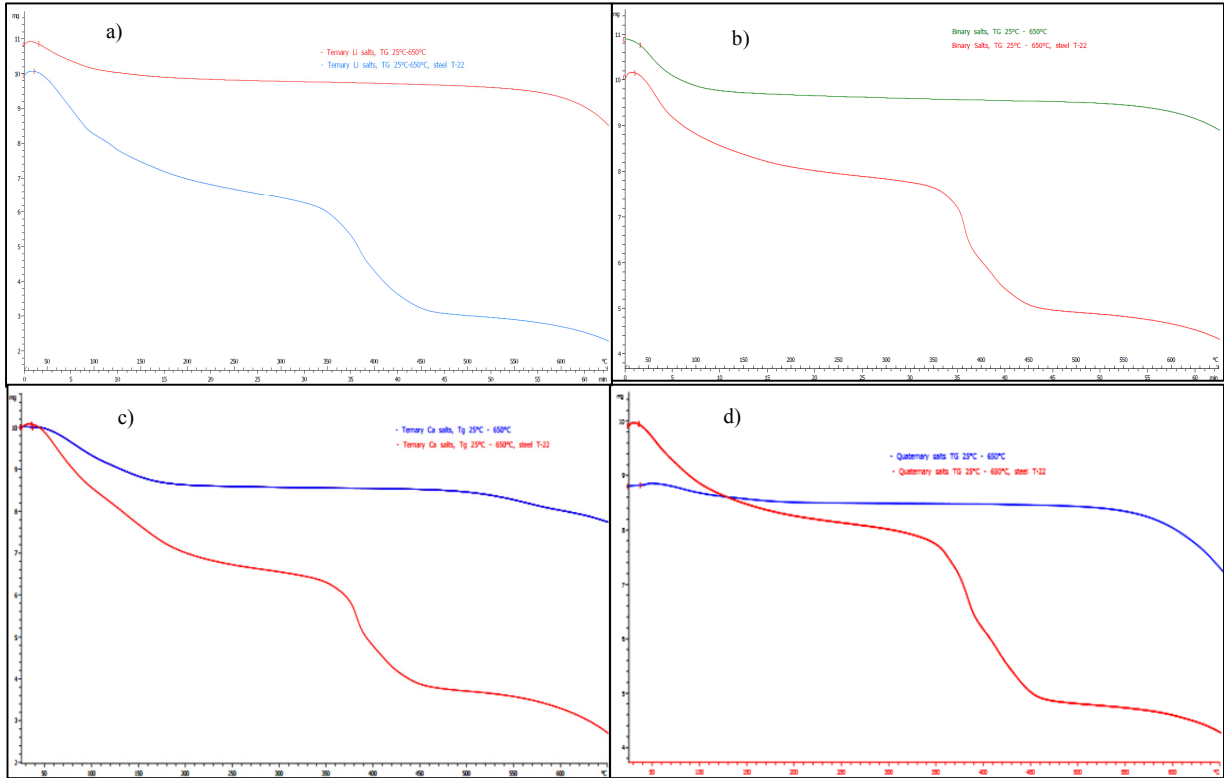
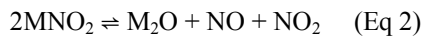
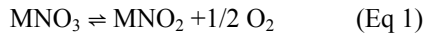


FIGURE 1. Thermal stability of the salts before and after corrosion tests on a) Li ternary salt, b) Solar salt, c) Ca ternary salt and d) Quaternary salt

An important reduction in thermal stability was detected due to the incorporation of corrosion products into the salt. A steep reduction in weight % was observed around 350°C in the salts after the corrosion tests. Olivares et al. [10] reported the evolution of nitrous oxide (NO) at 325°C in Ar atmosphere (via TG-MS) for Li-Na-K-NO₃ salts. The partial decomposition observed at 350°C, probably because of the following reactions:



with M= Li or Na

In this study, the presence of Li₂O and Na₂O after the corrosion process was confirmed (see Table 3). Those oxides are probably dispersed into the salt matrix, producing a catalytic phenomenon related with the thermal decomposition that happens after the corrosion process. Thermal studies using TGA-MS will be done in the future in order to analyze the volatile products formed with the corrosion product as well as a study of this behavior in a molten salt loop to avoid interferences that could be present due the small amount of salts used in the TGA tests (around 10 mg).

The variation in the liquid heat capacity was also studied (Figure 2). The reduction in this parameter was between 8% to 20% for the corrosion tests performed in 30wt%LiNO₃ + 60wt%KNO₃ + 10wt%Ca(NO₃)₂ and 10%LiNO₃ + 10%Ca(NO₃)₂ + 20%NaNO₃ + 60%KNO₃, after the immersion in AISI 430 and 316 stainless steels.

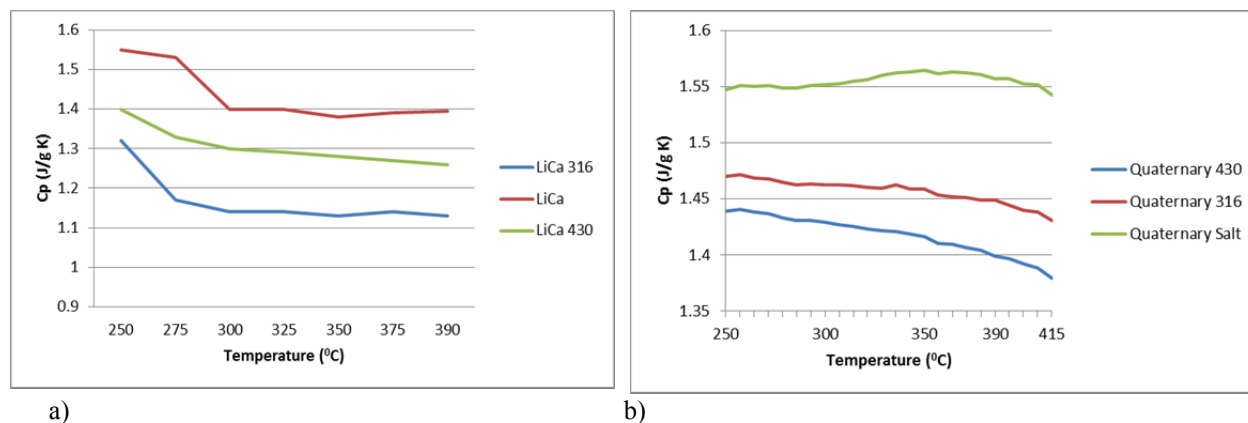


FIGURE 2. Liquid heat capacity before and after corrosion test in a) 30wt%LiNO₃+60wt%KNO₃+10wt%Ca(NO₃)₂ and b) 10%LiNO₃ + 10%Ca(NO₃)₂ + 20%NaNO₃+60%KNO₃ after the immersion in AISI 430 and 316 stainless steels.

Table 3 shows the corrosion and insoluble products detected via XRD in the salts after the corrosion tests in contact with AISI 430 and 316 stainless steels.

TABLE 3. Impurities present in the molten salts after the corrosion process in contact with AISI 430 and 316 stainless steels

Molten Salts, wt%	Corrosion Products	Insoluble Products
Solar Salt	Fe ₂ O ₃ , Na ₂ O, MgFe ₂ O ₄	CaCO ₃ , Na ₂ CO ₃
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
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
10 LiNO₃ – 10 Ca(NO₃)₂ – 60 KNO₃ – 20 NaNO₃	MgCr ₂ O ₄	Na ₂ CO ₃ , CaCO ₃ , Na ₂ SO ₄

Table 3 shows a comparison of the corrosion and insoluble compounds detected in the salt that was in contact with AISI 430 and 316 stainless steels. It is important to note that in 30wt%LiNO₃+60wt%KNO₃+10wt%Ca(NO₃)₂ salt, MgCr₂O₄, a protective spinel, was identified. The formation of this spinel indicates a good Cr diffusion into the outer zone of the corrosion layer because Mg is a salt's impurity. In all the cases, using LiNO₃, the corrosion rate is lower than that of the currently used binary Solar Salt.

The viscosity of these salts at temperatures above 170°C was similar to those currently available in the market. This opens the opportunity for these salts to be used in solar energy plants because they can properly flow throughout the pipes. Furthermore, the proposed fluids exhibit higher electrical conductivity compared with the binary Solar Salt, which is another important factor for improving the thermal conversion ratio of solar plant heat exchangers.

The study shows an important loss of thermal properties after the corrosion tests. Purity and heat capacity of the salt was reduced, partly 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.

CONCLUSION

Nitrate chemistry and their storage conditions produce corrosion. This corrosion affects not only the durability of the stainless steels of commercial plants but also the purity of the molten salts. As corrosion products slowly become integrated into the storage salt mix, the composition of the molten salt is altered and consequently affects the physiochemical properties including the storage capacity.

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.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the financial support provided by CONICYT / FONDAPE 15110019 “Solar Energy Research Center” SERC-Chile, Fondecyt Postdoctoral grant n°3140014 and the Education Ministry of Chile Grant PMI ANT 1201. The work at NREL was financially supported by the U.S. Department of Energy under Contract No. DE-AC36-08-GO28308.

REFERENCES

1. Ortega, A., Escobar, R., Colle, S., de Abreu, S.L., *The state of solar energy resource assessment in Chile*. [Renewable Energy](#), 2010. 35: p. 2514-2524.
2. Ushak, S., *Development of Thermal Energy Storage Materials from Waste-process Salts*. *Energy Procedia*. 57(0): p. 627-632.
3. Cabeza, L.F., *Lithium in thermal energy storage: A state-of-the-art review*. [Renewable and Sustainable Energy Reviews](#). 2015. 42(0): p. 1106-1112.
4. Fernandez, A.G. *Development of new molten salts with LiNO₃ and Ca(NO₃)₂ for energy storage in CSP plants*. [Applied Energy](#). 2014, 119(0): p. 131-140.
5. Medrano, M., et al., *State of the art on high-temperature thermal energy storage for power generation. Part 2-- Case studies*. [Renewable and Sustainable Energy Reviews](#). 14(1): p. 56-72.
6. Kruienza, A.M., *Corrosion Mechanisms in Chloride and Carbonate Salts*. Sandia Report, 2012. SAND2012-7594.
7. Wang, T., D. Mantha, and R.G. Reddy, *Thermal stability of the eutectic composition in LiNO₃-NaNO₃-KNO₃ ternary system used for thermal energy storage*. *Solar Energy Materials and Solar Cells*. 100(0): p. 162-168.
8. Gil, A., *State of the art on high temperature thermal energy storage for power generation. Part 1: Concepts, materials and modellization*. [Renewable and Sustainable Energy Reviews](#). 14(1): p. 31-55
9. Fernández, A., M. Lasanta, and F. Pérez, *Molten Salt Corrosion of Stainless Steels and Low-Cr Steel in CSP Plants*. [Oxidation of Metals](#). 2012; 78(5-6) p. 329-398.
10. Olivares, R.I., *The thermal stability of molten nitrite/nitrates salt for solar thermal energy storage in different atmospheres*. [Solar Energy](#). 86(9): p. 2576-2583