

Solar Collector Systems

Placeholder TIB Open Publishing)

© Authors. This work is licensed under a [Creative Commons Attribution 4.0 International License](https://creativecommons.org/licenses/by/4.0/)

Published:

The effect of long-term corrosion on a molten salt pump in contact with a ternary mixture in a CSP plant

Mauro Henriquez¹, Carlos Soto¹, Carlos Duran¹, Abdiel Mallco^{1,3}, Sebastián Salazar¹, Felipe M. Galleguillos Madrid¹, Jose M. Cardemil⁴, Douglas Olivares¹, Carlos Portillo¹, and Luis Guerreiro²

¹ Centro de Desarrollo Energético Antofagasta (CDEA), Universidad de Antofagasta, Av. Universidad de Antofagasta 02800, +56552513545, Antofagasta, Chile, mauro.henriquez@uantof.cl

² ICT Institute of Earth Sciences, Univ. Évora, Rua Romão Ramalho, 59, 7002 – 554 Évora, Portugal

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

⁴ Department of Mechanical and Metallurgical Engineering, Pontificia Universidad Católica de Chile, Vicuña Makenna 4860, Macul, Santiago, Chile

Abstract. Solar thermal plants commonly plan their operation for a 25 years period, therefore, it is important to accurately predict and evaluate the damage and faults occurring for that long period. Among all components, we find that choosing the heat storage medium (molten salt) and the material (steel) used in the equipment and piping plays a crucial role in the plant's design. We tested the long-term corrosion effect of the stainless steel used in the molten salt pump (AISI 316L) having a low melting point ternary mixture composed of 30wt.%LiNO₃ + 57wt.%KNO₃ + 13 wt.%NaNO₃ tested over a period of more than 6 years, corresponding to 30,000 hours of operation in a pilot experimental facility at the University of Antofagasta (Chile).

Keywords: Thermal Energy Storage; Molten Salts; lithium Nitrate; Corrosion, AISI 316L, stainless steel

1. Introduction

The most common thermal energy storage system used in CSP (Concentrated Solar Power) plants consists of two tanks that store sensible heat using Solar Salt (60wt% NaNO₃ + 40wt% KNO₃). The first solar project to use this binary mixture was the "Solar Two" plant, whose facilities were built in the Mojave Desert just east of Barstow, California, United States [1], which set the basis for the current CSP plants with tower technology. However, this mixture's relatively high melting point (222 °C) represents a significant risk of solidification in the operation during stand-by periods, forcing solar thermal plants to work at a minimum operating temperature of 292°C [2]. Recently, several authors [3-5] have investigated and characterized the most important thermal properties concerning the usage of LiNO₃ as thermal energy storage (TES) medium. This study proposes to evaluate the effect of corrosion on the internal surface material of a pump immersed in a tank with a ternary mixture composed of 30%LiNO₃ + 57%KNO₃ + 13%NaNO₃ with a low melting point of 127°C.

2. Procedure

The tests performed in Antofagasta, Chile in the pilot-scale plant used a ternary mixture (30 wt%LiNO₃+57 wt%KNO₃+13 wt%NaNO₃) that was prepared with nitrate salts NaNO₃ (purity level of 99.5%) and KNO₃ (purity level of 99.5%) both provided by the company SQM from Antofagasta, Chile, and LiNO₃ (purity level of 99%) which was provided by Todini Chemical company from Italy. The tests for the ternary mixture were carried out in a stainless steel grade 316L tank with a total net volume of 0.83 m³ and 203 kg weight. The tank was equipped with commercial components (Figure 1), where four electric resistances of 1200 Watt each provided the heat to melt the salt and to keep it above a well defined temperature. The system contains 15 PT100 class B 3-wire temperature sensors with AISI316L sheaths inside and outside the tank. A high-temperature vertical pump GVSO40 / 160A recirculated the fluid at a rate of 1 m³/h.



Figure 1. The molten salt pilot plant at the University of Antofagasta

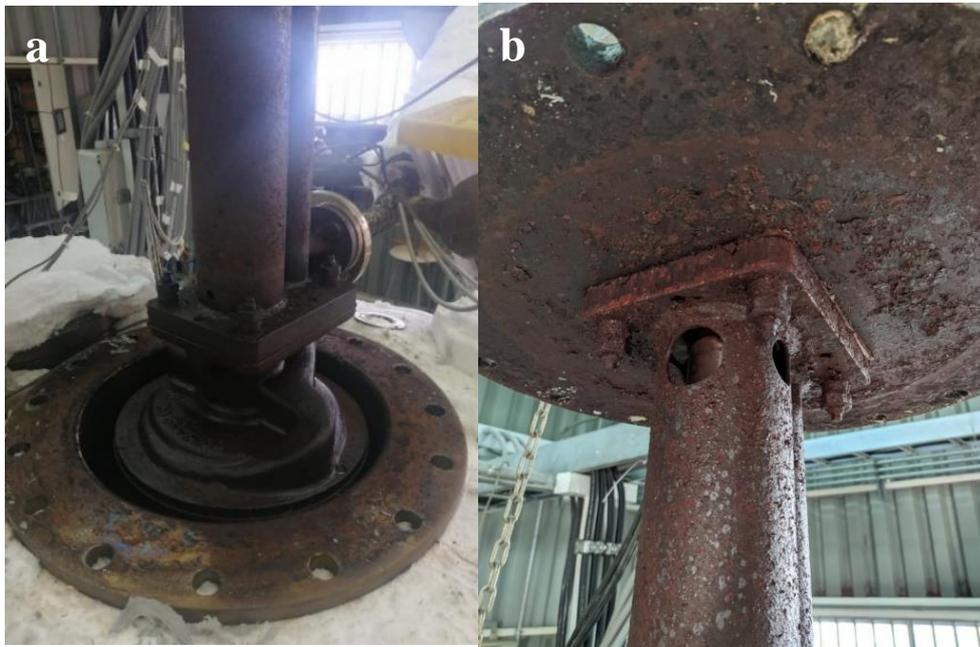


Figure 2. Centrifugal pump with evident corrosion products a) and b)

The molten salt pump of the pilot plant at the University of Antofagasta has been in contact with

the ternary mixture for more than 6 years corresponding to 30,000 h (Figure 2). After this period, the pump was removed (Figure 3) to assess the mechanical conditions and the degradation that it has suffered due to the effects of the corrosion product by being in contact with the molten salt.

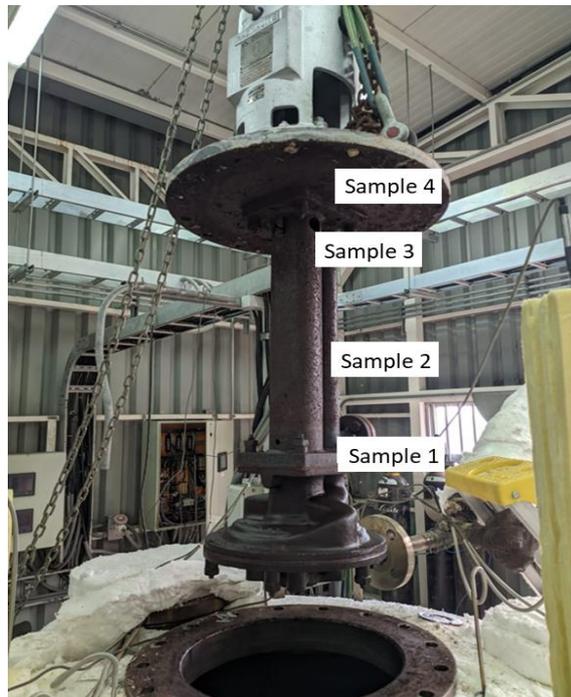


Figure 3. Molten salt pump removed from the molten salt tank

To evaluate the degradation and analyze the products of corrosion of the stainless steel that was in direct contact with the ternary mixture during a long period of exposure, three samples were taken from different sectors of the salt pump, as presented in Figure 4.

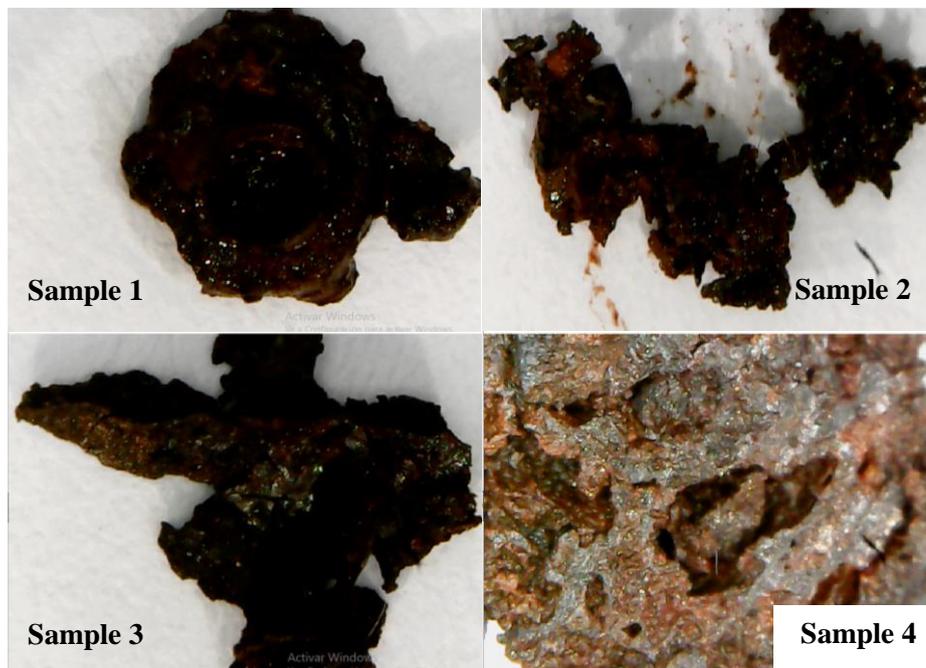


Figure 4. Samples from different sectors of the molten salt pump

3. Results

Due to the corrosion process by the ternary lithium mixture, a characterization by scanning electron microscopy (SEM) and using X-ray diffraction (XRD) has been performed, it shows the morphological damage of the AISI 316L microstructure that has occurred during corrosion at high temperature. Knowing the changes produced over time as the formation of different corrosion products and the effects it causes in the material of the pump, it is possible to define a preventive maintenance plan as well as to elaborate a list of recommendations to be carried out when designing the mechanical components used in the concentrated solar thermal industry.

Figure 5, shows the SEM images captured from samples of a different part of the shaft pump according to figure 3. Figure 6, shows the EDS mapping of corrosion products corresponding to sample 1.

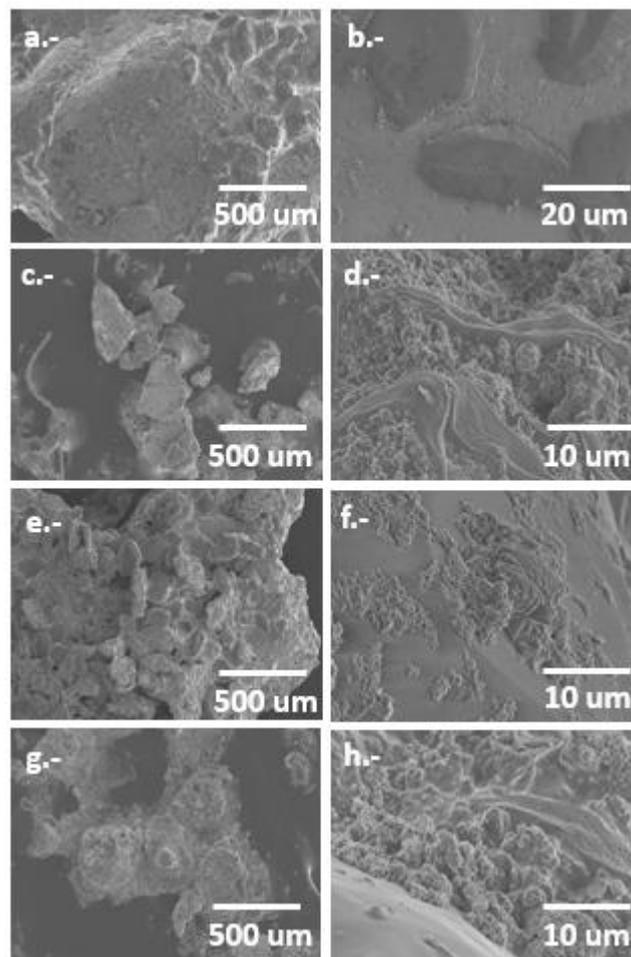


Figure 5. Corrosion products from the shaft of the molten salt pump. Sample 1 (a-b), sample 2 (c-d), sample 3 (e-f), sample 4 (g-h).

The AISI 316L material (Table 1) under analysis was exposed to a ternary mixture of salts with a low melting point for 30.000h, the ternary salt has generated morphological changes over the surface of AISI 316L.

Table 1: Composition of stainless steel AISI 316L

AISI 316L	%C	%Si	%Mn	%P	%S	%Ni	%Cr	%Mo	%N
	0.020	0.506	0.852	<0.150	0.003	10.11	16.43	1.896	0.221

Fig. 6 shows the formation of a continuous and adherent oxide on the AISI 316L material surface product in contact with ternary molten solar salt at a minimum temperature of 127°C. Localized as well as general corrosion attack was detected on the equipment but the shaft has suffered only minor damage that enabled the operational continuity of the pumping system [6], [7]. In addition, the AISI 316L presents a good corrosion resistance, and no excessive degradation (descaled metal losses) considering this long-term exposure to molten solar salts operating at “low temperatures”. The time dependence of metal loss can often be used to infer its corrosion mechanism. The metal losses increase in proportion to the square root of time implying that the surface scales grow by a self-limiting process which is controlled by diffusion of one of the chemical species that constitute the scale, with the temperature directly affecting the material causing stress corrosion cracking (SCC). The AISI 316L samples investigated showed that the oxide scales were generally adherent, regardless of the temperature or the impurities in the molten salt mixtures. Similarly, the average thickness of the oxide layers observed is based on the descaled metal losses.

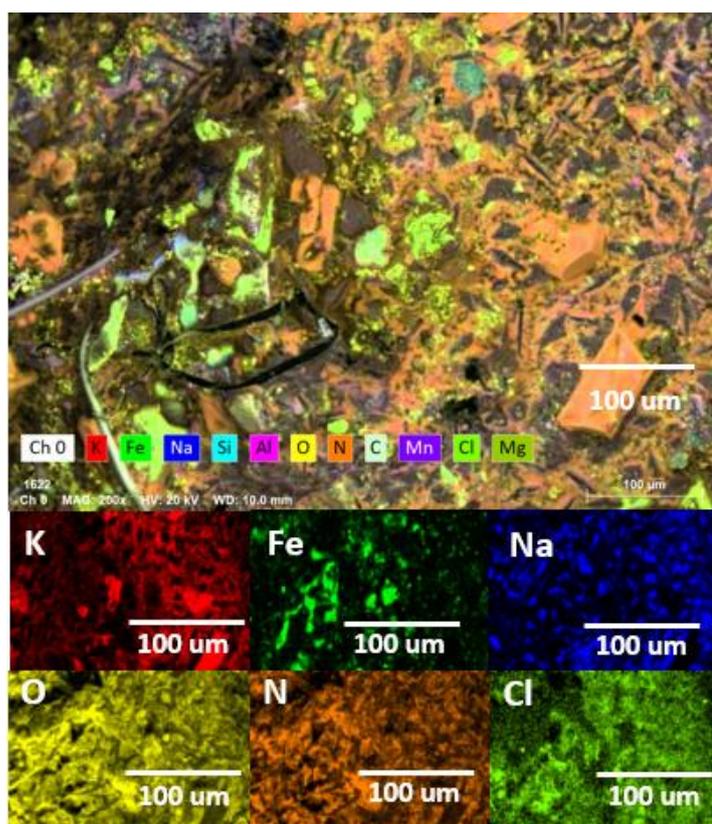


Figure 6: EDS mapping of corrosion product from (sample 1)

Figure 6 shows the EDS mapping from corrosion products (sample 1). This part of the shaft pump was in contact with mixed molten salt during 30.000 h operation, following deposits over the AISI 316L surface have been observed: K (12.81 w/w%), Fe (6.44 w/w %), Na (7.66 w/w %), O (60.67 w/w %), N (19.98 w/w %). The presence of Si (0.34 w/w%) and Mn (0.18 w/w %) are part of the composition of AISI 316L. The components Al (0.34 w/w %), and Mg (0.07 w/w %) are considered

to be impurities from the solar salts. The presence of Cl (0.01 w/w %) could be the product of a marine environment, knowing that this ion at high temperature promotes considerably the corrosion considering the high dispersion over the AISI 316L surface.

The X-ray diffraction technique shown in figure 7 was carried out to study the decomposition of the ternary mixture at initial time (0 h) and at final stage (30,000 h). The compounds identified correspond to (a) KNO_3 , (b) LiNO_3 , (c) NaNO_3 , (d) LiO , (e) LiO_2 , (f) Fe_2O_3 , (g) Na_2O , (h) CaCO_3 , and (i) MgCO_3 (Fig. 6). Initially it was also observed the presence of KNO_3 , LiNO_3 , and NaNO_3 , corresponding to the initial components of the ternary mixture that were loaded and melted inside the tank. At the final stage ($t = 30,000$ h) it were also identified new compounds: LiO , LiO_2 , Fe_2O_3 , Na_2O , CaCO_3 and MgCO_3 .

The presence of CaCO_3 and MgCO_3 (Figure 7 b) is an evidence of the decomposition of the salt mixture. It is well known that the presence of these carbonates occurs mainly due to the interaction of salts with atmospheric gases such as CO_2 , and they can lead to the formation of insoluble materials that generate obstruction or erosion in the heating circuit pipes hindering the salt's fluidity [8], [9]. Lithium oxides are also identified as LiO and LiO_2 , which means that LiNO_3 is the unstable species and it is the component that leads to the ternary mixture's weight loss, Wang et al. [10] also reported this behavior. The presence of small peaks of Na_2O corresponds to the decomposition of NaNO_3 , as the salt starts its partial decomposition around 450°C [11]. The low intensity of the Na_2O peaks demonstrates substantial thermal stability of the sodium nitrate during this long term period (30,000 h) [12].

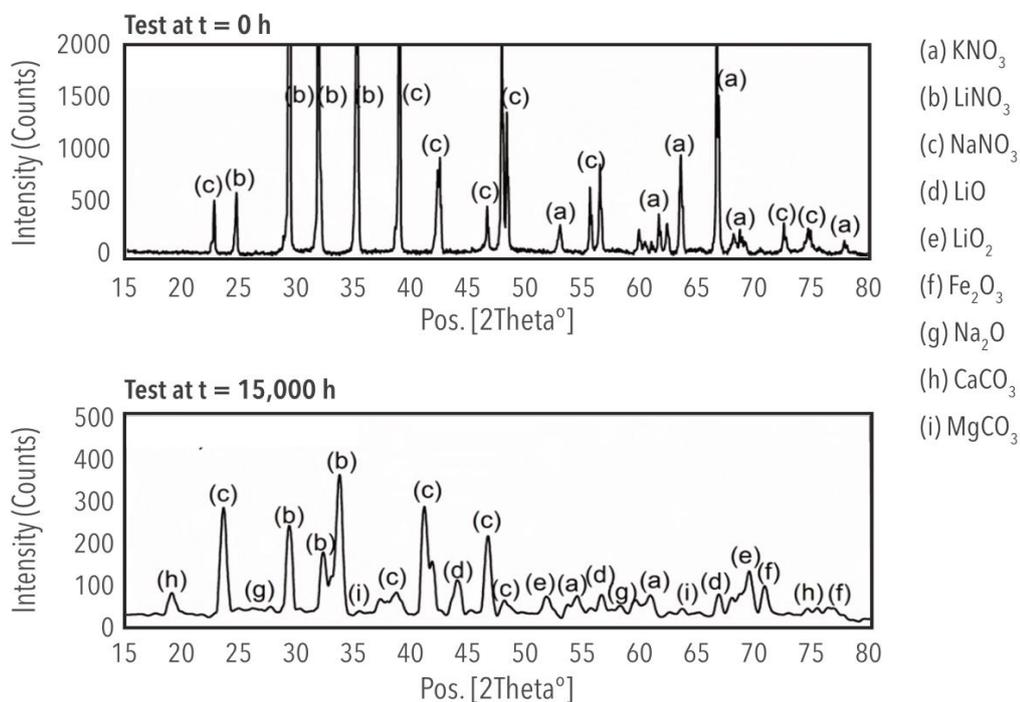


Figure 7: Diffractogram of 30%wt. LiNO_3 +13%wt. NaNO_3 +57%wt. KNO_3 mixture
a) at the initial stage ($t = 0$) and (b) final stage ($t = 30,000$ hours)

The analysis to the corrosion products of the pump and tank made of stainless steel AISI 316L indicates the presence of different products such as hematite (Fe_2O_3) [13], [14], [15]. This corrosion effect relates to the concentration of oxides produced by ionic reactions in the electrolyte

and different atmospheric conditions in the medium. Therefore, the molten salts at high temperatures eliminate the oxide layers in the container materials, which in some instances could act as a protective layer [16], a topic that deserves further investigation.

Conclusions

In this research, it was investigated the long-term corrosion of a molten salt pump made of stainless steel AISI 316L in contact with a low-melting-point ternary mixture composed of 30wt.%LiNO₃ + 57wt.%KNO₃ + 13 wt.%NaNO₃. The main conclusions of this work performed in a test facility located in Antofagasta, Chile are the following:

- 1) The results obtained provide an insight of the problems that occur in such a rotating equipment, an essential part of all commercial CSP plants. It is an important information since real plant operation conditions are not easy to be evaluated, in fact very few data exists about this topic
- 2) The effect of corrosion in the AISI 316L steel (pump and tank) generated the presence of hematite (Fe₂O₃) in the molten salt mixture after 30,000 h of exposure, however it was not possible to determine the weigh loss of the equipment
- 3) The corrossion did not prevented the operation of the pump, which was fully operational for more than 6 years
- 4) Future investigations will be oriented to the examination of the elemental composition of the corrosion products to determine the correlation that existed between the corrosion products and corrosion kinetics at high temperatures for the ternary mixture used

Acknowledgment

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. Scaling-UP Engineering 2030 UA-OTL Funds. VIU21P0051 Project National Research and Development Agency, Government of Chile.

References

- [1] M. Medrano, A. Gil, I. Martorell, X. Potau, and L. F. Cabeza, "State of the art on high-temperature thermal energy storage for power generation. Part 2—Case studies," *Renew. Sustain. Energy Rev.*, vol. 14, no. 1, pp. 56–72, Jan. 2010.
- [2] J. A. Gil *et al.*, "State of the art on high-temperature thermal energy storage for power generation. Part 1-Concepts, materials, and modelization," *Renew. Sustain. Energy Rev.*, vol. 14, no. 1, pp. 31–55, 2010, DOI: 10.1016/j.rser.2009.07.035.
- [3] A. G. Fernández, S. Ushak, H. Galleguillos, and F. J. Pérez, "Development of new molten salts with LiNO₃ and Ca(NO₃)₂ for energy storage in CSP plants," *Appl. Energy*, vol. 119, no. 3, pp. 131–140, 2014, DOI: 10.1016/j.apenergy.2013.12.061.
- [4] S. Ushak, A. G. Fernández, and M. Grageda Using molten salts and other liquid sensible storage media in thermal energy storage (TES) systems. Woodhead Publishing Limited, 2015.
- [5] L. F. Cabeza *et al.*, "Lithium in thermal energy storage: A state-of-the-art review," *Renew. Sustain. Energy Rev.*, vol. 42, pp. 1106–1112, 2015, DOI: 10.1016/j.rser.2014.10.096.
- [6] M. Sarvghad, G. Will, and T. A. Steinberg, "Corrosion of Inconel 601 in molten salts for thermal energy storage," *Sol. Energy Mater. Sol. Cells*, vol. 172, pp. 220–229, 2017.

- [7] M. Sarvghad, G. Will, and T. A. Steinberg, "Corrosion of steel alloys in molten NaCl + Na₂SO₄ at 700 °C for thermal energy storage," *Sol. Energy Mater. Sol. Cells*, vol. 179, no. March, pp. 207–216, 2018.
- [8] A. G. Fernández, J. Gomez-Vidal, E. Oró, A. Kruizenga, A. Solé, and L. F. Cabeza, "Mainstreaming commercial CSP systems: A technology review," *Renew. Energy*, vol. 140, pp. 152–176, 2019.
- [9] C. M. Kramer, Z. A. Munir, and J. V. Volponi, "Screening tests of sodium nitrate decomposition," *Sol. Energy Mater.*, vol. 6, no. 1, pp. 85–95, 1981.
- [10] T. Wang, D. Mantha, and R. G. Reddy, "Thermal stability of the eutectic composition in LiNO₃–NaNO₃–KNO₃ ternary system used for thermal energy storage," *Sol. Energy Mater. Sol. Cells*, vol. 100, pp. 162–168, 2012.
- [11] A. O. Hoshino Yoshio, Utsunomiya Taizo, "The Thermal Decomposition of Sodium Nitrate and the effects of Several Oxides on the Decomposition," *Chem. Soc. Japan*, 1981.
- [12] T. Wang, D. Mantha, and R. G. Reddy, "Thermal stability of the eutectic composition in LiNO₃–NaNO₃–KNO₃ ternary system used for thermal energy storage," *Sol. Energy Mater. Sol. Cells*, vol. 100, pp. 162–168, May 2012.
- [13] A. G. Fernández, H. Galleguillos, and F. J. Pérez, "Corrosion Ability of a Novel Heat Transfer Fluid for Energy Storage in CSP Plants," *Oxid. Met.*, vol. 82, no. 5–6, pp. 331–345, 2014.
- [14] A. G. Fernández and F. J. Pérez, "Improvement of the corrosion properties in ternary molten nitrate salts for direct energy storage in CSP plants," *Sol. Energy*, vol. 134, no. 3, pp. 468–478, 2016.
- [15] A. G. Fernández, M. I. Lasanta, and F. J. Pérez, "Molten salt corrosion of stainless steels and low-Cr steel in CSP plants," *Oxid. Met.*, vol. 78, no. 5–6, pp. 329–348, 2012.
- [16] A. Mallco, C. Portillo, M. J. Kogan, F. Galleguillos, and A. G. Fernández, "A materials screening test of corrosion monitoring in LiNO₃ containing molten salts as a thermal energy storage material for CSP plants," *Appl. Sci.*, vol. 10, no. 9, 2020.