

The Effect of Long-term Corrosion on a Molten Salt Pump in Contact with a Ternary Mixture in a CSP Plant

Mauro Henriquez¹ [<https://orcid.org/0000-0002-0160-3394>], Carlos Soto¹ [<https://orcid.org/0009-0009-2420-0991>],
Carlos Duran¹ [<https://orcid.org/0009-0001-4343-1295>],, Sebastián Salazar¹ [<https://orcid.org/0000-0002-2010-2413>],
Felipe M. Galleguillos Madrid¹ [<https://orcid.org/0000-0002-1347-3726>], Luis Guerreiro² [<https://orcid.org/0000-0003-0594-2315>], Douglas Olivares¹ [<https://orcid.org/0000-0001-8260-5289>], Carlos Portillo¹ [<https://orcid.org/0000-0001-9301-5604>], Edward Fuentealba¹ [<https://orcid.org/0000-0002-8808-2615>], and Jose M. Cardemil³ [<https://orcid.org/0000-0002-9022-8150>]

¹ Centro de Desarrollo Energético Antofagasta (CDEA), Universidad de Antofagasta, Chile,

² ICT – Institute of Earth Sciences, University. Évora, Évora, Portugal

³ Department of Mechanical and Metallurgical Engineering, Pontificia Universidad Católica de Chile, Chile

Abstract. Solar thermal plants commonly plan their operation for a period of approximately 25 years. Therefore, it is key 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 molten salt pump in a low-melting-point ternary mixture composed of 30wt.%LiNO₃+57wt.%KNO₃+13wt.%NaNO₃ over a period of more than 5 years, corresponding to 30,000 hours of operation in a pilot experimental facility built at the University of Antofagasta (Chile).

Keywords: Thermal Energy Storage, Molten Salts, Lithium Nitrate, Corrosion

1. Introduction

The most common thermal energy storage 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 local solidification in the operation during standby periods, forcing solar thermal plants to work at a minimum operating temperature of 292°C [2]. In the last few years, different authors [3-5] have investigated the most important thermal properties related to the use of different mixtures containing LiNO₃ as thermal energy storage (TES) material. This preliminary study proposes to evaluate the effect of corrosion on the internal surface material of the pump in contact with a ternary mixture composed of 30%LiNO₃+57%KNO₃+13%NaNO₃ with a low melting point of 127±5°C [6-7].

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 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. 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 from the company Friatec that recirculates the fluid at a rate of 1 m³h⁻¹.



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

The molten salt pump of the pilot plant at the University of Antofagasta has been in contact with the ternary mixture for more than 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 effects because of the erosion-corrosion mechanism when the metal is in contact with the molten salt during movement of the molten salt (Figure 3). For the molten salt at high temperatures, erosion-corrosion is a significant concern due to the abrasive nature of the salt and its corrosive properties.

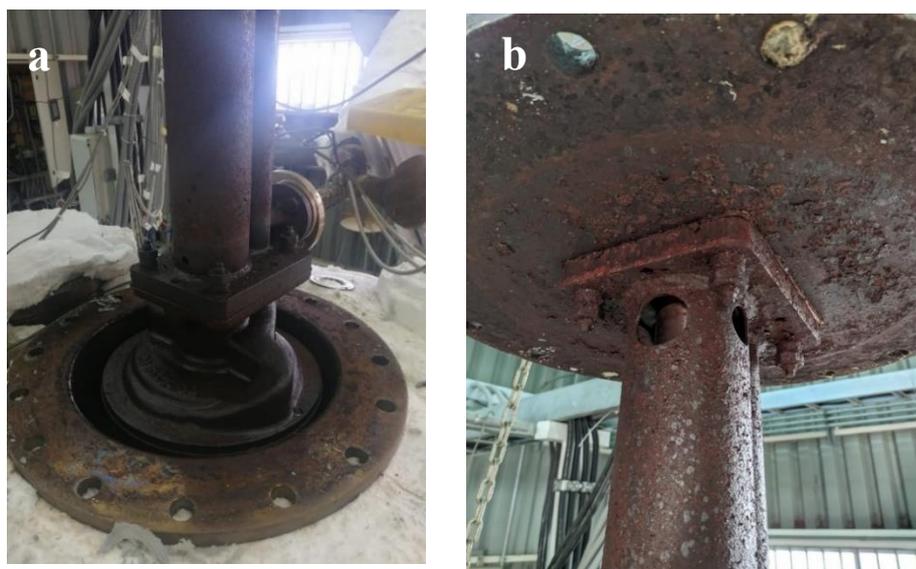


Figure 2. Centrifugal pump with evident corrosion products a) and b).

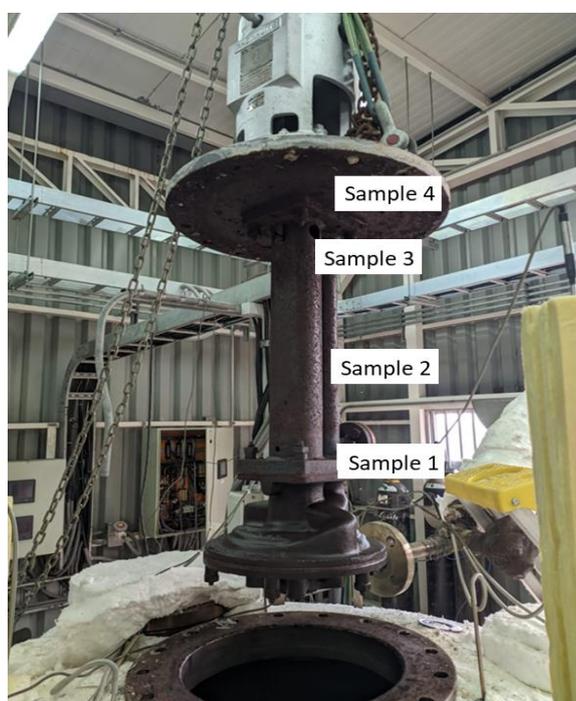


Figure 3. Molten salt pump removed from the molten salt tank.

To evaluate and analyse the corrosion of the pump generated by the ternary mixture during a long period of exposure, three samples were taken from different sectors of the salt pump, which can be identified in Figure 4.

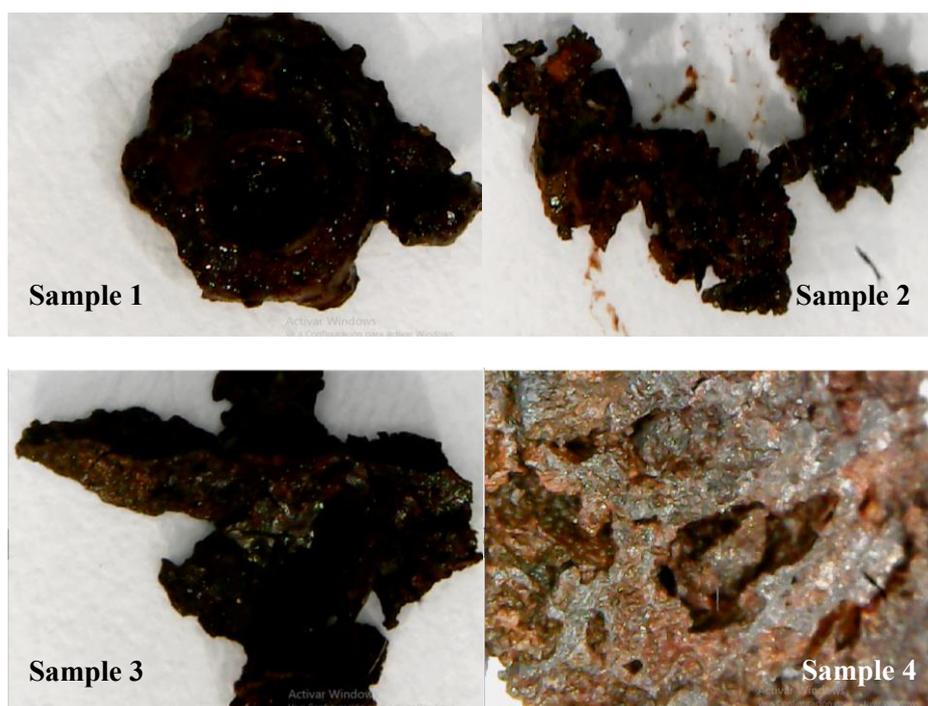


Figure 4. Samples from different sectors of the molten salt pump.

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 microstructure that has occurred during corrosion at high temperature (400°C). Knowing the changes produced over time as the formation of different corrosion products and the effects it causes in the material shows us the necessary procedures to be carried out in maintenance plans or redesign of mechanical elements used in the solar thermal industry.

Figure 5, shows the SEM images captured from samples of a different part of the shaft pump according to Figure 3.

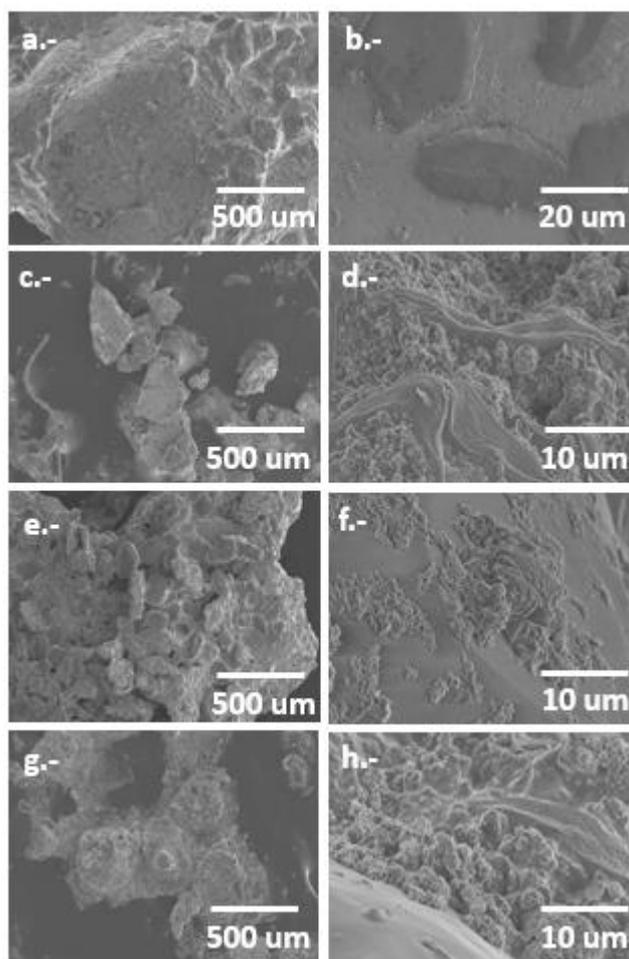


Figure 5. Corrosion product from the shaft of the molten salt pump. Sample 1 (a-b), sample 2 (c-d), sample 3 (e-f), sample 4 (g-h).

The material under analysis was exposed to a ternary mixture of salts with a low melting point for 30.000h (see Fig.1). The ternary salt 30%LiNO₃+57%KNO₃+13%NaNO₃ generates morphological change over the surface of the steel pump.

Fig. 5 shows the formation of a continuous and adherent oxide on the material surface product the contact with ternary molten salts. Molten salts can be highly corrosive, and their elevated temperatures and aggressive chemical nature can accelerate the degradation of pump components. In the case of a continuous oxide layer, its effectiveness in protecting against corrosion. Localized and general corrosion attack is detectable on the equipment but is not appreciable destruction of the shaft that does not impede the operational continuity of the pumping system [8-9]. The corrosive nature of molten salts can eventually compromise or penetrate the oxide layer, leading to corrosion erosion. Molten salts can attack and dissolve the protective oxide layer, exposing the underlying metal to direct corrosion. In addition, the cast steel presents a good corrosion resistance, and no excessive degradation (descaled metal losses) considering a long-term isothermal exposure to molten salts at low temperatures operating. The time dependence of metal loss can often be used to infer a 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 that is controlled by diffusion of one of the chemical species that constitute the scale, but the temperature directly affects the material causing stress corrosion cracking (SCC). The square root of time relationship implies that the growth of the protective scale is limited by the diffusion of ions or molecules involved in the corrosion process. As these species diffuse through the scale, they participate in the dissolution and redeposition reactions, influencing

the overall rate of metal loss. The diffusion process acts as a rate-limiting step, determining the growth rate of the scale. While diffusion-controlled processes can contribute to the erosion-corrosion mechanism, it's important to note that the temperature of the molten salt also plays a critical role. Elevated temperatures can promote stress corrosion cracking (SCC) in certain materials [10-11]. The cast steel revealed that the oxide scales exhibited good adhesion, irrespective of temperature or the presence of impurities in the molten salt mixtures. Additionally, the average thickness of the observed oxide layers can be attributed to the corresponding descaled metal losses. The oxide scales in molten salt environments typically form through a process known as selective oxidation. This process involves the preferential oxidation of certain elements in the metal, leading to the formation of a protective oxide layer. The initial formation mechanism of the oxide scales contributes to their inherent adherence [12].

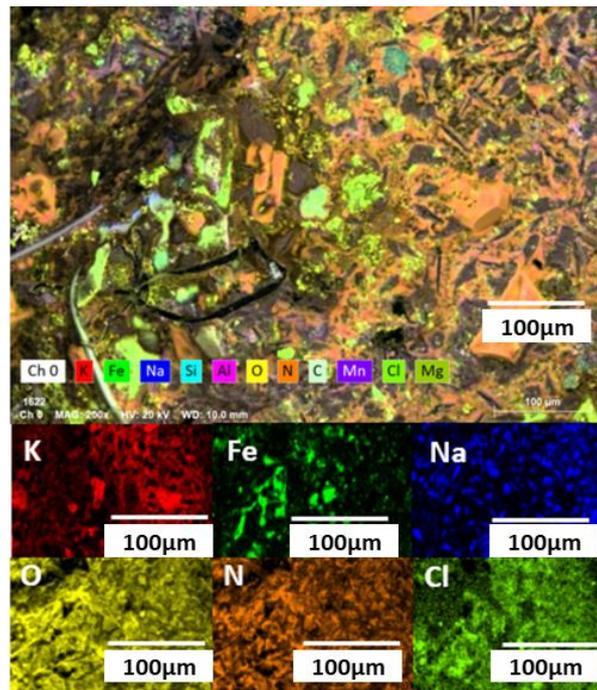


Figure 6. EDS mapping of corrosion product from sample 4.

Figure 6 shows the EDS mapping from corrosion products using sample 4. This sector of the shaft pump was in contact with mixed molten salt during a 30.000 h operation where is possible to identify different deposits of 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 %) over surface. The presence of Si (0.34 w/w%) and Mn (0.18 w/w %) are part of composition of the cast steel. The components Al (0.34 w/w %), and Mg (0.07 w/w %) are consider impurities from the solar salts. The presence of Cl (0.01 w/w %) could be the product of the marine environment, but this ion at the high temperature promotes considerably the corrosion considering the high dispersion over the surface.

The X-ray diffraction technique shown in figure 7 was carried out to study the decomposition of the ternary mixture at times 0 h and after 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). We initially observe 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 later stage ($t = 30,000$ h) we identified new compounds: LiO , LiO_2 , Fe_2O_3 , Na_2O , CaCO_3 and MgCO_3 .

The presence of CaCO_3 and MgCO_3 in Figure 7 b) demonstrates 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 CO₂, 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 [13], [14]. Lithium oxides are also identified as LiO and LiO₂, which means that LiNO₃ is the unstable species and it is the component that leads to the ternary mixture's weight loss; Wang et al. [15] also reported this behaviour. The presence of small peaks of Na₂O corresponds to the decomposition of NaNO₃, as the salt starts its partial decomposition around 450 °C [16]. The low intensity of the Na₂O peaks demonstrates substantial thermal stability of the sodium nitrate during this long-term period (30,000 h) [12].

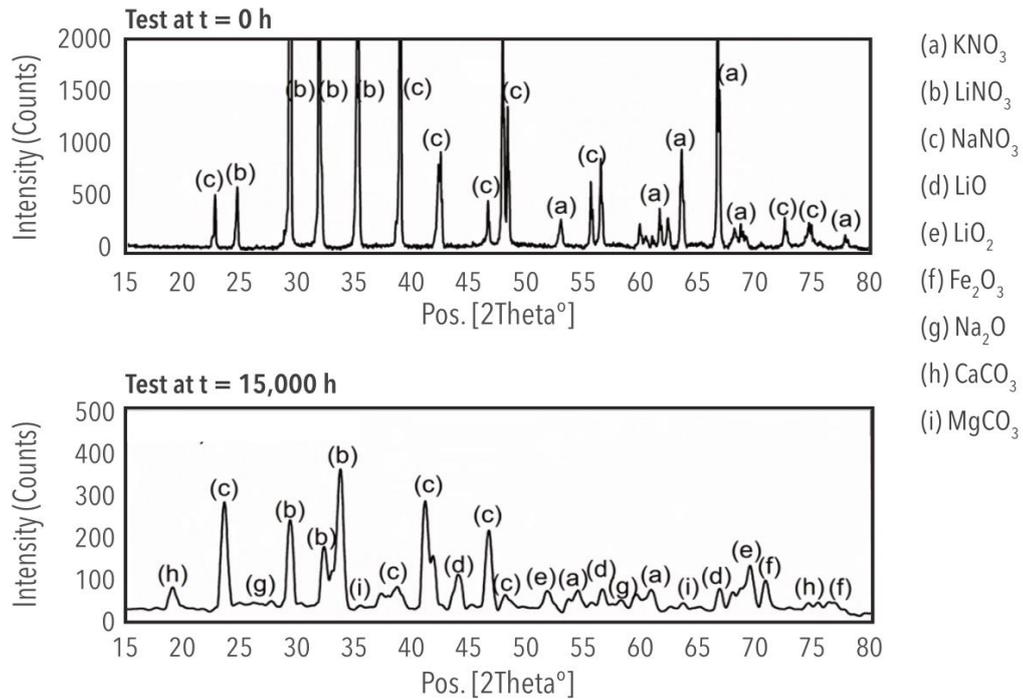


Figure 7. Diffractogram of 30wt.%LiNO₃+13wt.%NaNO₃+57wt.%KNO₃ mixture a) at the initial stage ($t = 0$) and (b) final stage ($t = 30,000$ hours).

The analysis to the corrosion products of the pump and tank, indicates the presence of different corrosion products such as hematite (Fe₂O₃) [17], [18], [19]. 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 [20], a topic that deserves further investigation.

4. Conclusions

In this manuscript, we investigated the long-term corrosion on a molten salt pump 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 exist about this topic.

2. The effect of corrosion in the 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 weight loss of the equipment.
3. The corrosion did not prevent the operation of the pump, which was fully operational for more than 5 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.

Data availability statement

This article refers to information that includes strategic knowledge generated by the Universidad de Antofagasta through research results. This information allows generating new strategic lines of research and or projects that can be susceptible to be protected either as intellectual or industrial property, with the potential to be transferred, according to national legislation (Chile), so that this information acquires the character of confidential.

Author contributions

Methodology, Validation, Analysis, and Writing: Mauro Henriquez, Felipe M. Galleguillos.

Methodology, Validation: Carlos Soto, Carlos Duran, Luis Guerreiro.

Analysis, and Writing: Jose M. Cardemil 4, Douglas Olivares, Sebastian Salazar.

Resources Analysis and Writing.: Edward Fuentealba, Carlos Portillo.

Competing interests

The authors declare that they have no competing interests

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