

# CORROSION BEHAVIOR OF STAINLESS STEELS IN MOLTEN SALTS USED FOR CONCENTRATED SOLAR POWER

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## Abstract

The current demand for energy to produce electricity from non-sustainable fuels such as oil and natural gas, is becoming a huge problem for the country, as they are likely to become depleted in the near future. However, solar energy is a major renewable energy source and concentrated solar power (CSP) technology is the most suitable candidate for storing energy due to its low cost and relatively high efficiency. The thermal energy received from CSP is transferred via a heat transfer fluid (HTF), one of which is molten nitrate salts. However, the major degradation of materials are concerned with high temperature corrosion in the hot molten salts. The purpose of this study is to study the corrosion behavior of ferritic AISI430 and austenitic AISI304 stainless steels samples immersed in conventional (60 wt% sodium nitrate ( $\text{NaNO}_3$ )/40 wt% potassium nitrate ( $\text{KNO}_3$ )) and modified (57 wt% sodium nitrate ( $\text{NaNO}_3$ )/38 wt% potassium nitrate ( $\text{KNO}_3$ )/5 wt% sodium chloride ( $\text{NaCl}$ )) molten nitrate salt mixtures at 600°C for 2 h to simulate the working conditions in a CSP plant. Corrosion products of materials were primarily Fe and Fe oxide. Corrosion testing determined with a potentiostat analyzer, electrochemical characterizations were then investigated. It was found that there was the effect of NaCl on the corrosion rate, showing higher corrosion rate. According to the surface morphology and electrochemical results, the mechanism of hot corrosion of stainless steels was further discussed in this research.

**Keywords:** High temperature corrosion, Molten salts, Stainless steel

## Introduction

The current demand for energy to produce electricity from non-sustainable fuels such as oil, natural gas and coal is becoming a major issue as they are likely to become depleted in the near future. However, renewable energy sources have been

developed over the past few decades to mitigate this problem. Solar energy is a major renewable energy source that is environmentally-friendly, cost-effective, and infinite, and concentrated solar power (CSP) technology is the most suitable candidate

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for harnessing this alternative energy source in the future (Mueller and Trieb, 2004).

CSP plants, which are operated at high temperatures ( $>250^{\circ}\text{C}$ ) consist of two parts: part one to collect the solar energy and convert it into heat and the other to convert the heat energy into electricity (Mueller and Trieb, 2004). Stainless steel is widely used in CSP plants. Thermal energy storage (TES), performance and material stability are limited by the high operating temperature, especially the corrosion behavior of the steel used depending on the temperature, molten salt composition, and nature of the steel. In general, TES commercial designs are two-tank systems with molten salts as the heat transfer fluids (HTF) (Figure 1) (Bauer *et al.*, 2012) and for energy storage, and is thus one of the most important components for overall performance and efficiency of CSP systems.

It is to be noted that, not much of work is reported on corrosion behavior of stainless steels in molten salts for concentrating solar power. However, there are some literatures were conducted to study on corrosion of 321H, 304, 316L, P91 metal materials in modified solar two molten salts. For example, reported that 304, 321H corroded at a rate of 40% less than P91. Corrosion rates of 304, 321H, and 316L slowly increased with changed temperature. Corrosion products of metal materials observed at  $450^{\circ}\text{C}$  and  $500^{\circ}\text{C}$  were primarily Fe oxide and Fe, Cr oxide, respectively. Slusser *et al.*, (1985) evaluated the corrosion behavior of a variety of alloys in solar salts (60wt%  $\text{NaNO}_3$ /40wt%  $\text{KNO}_3$ ). Nickel-based alloys were generally much more resistant than iron-based alloys. Increasing nickel content improved alloy corrosion resistance to molten nitrate. However, pure nickel suffered rapid corrosion attack. Lai *et al.*, (1985) evaluated various iron, nickel, and cobalt based alloys in a  $\text{NaCl-KCl-BaCl}_2$  salt bath two high nickel alloys (alloys 600 and 601) suffered

more corrosion attack than stainless steels such as Types 304 and 310.

The characteristics needed by an HTF are low melting point, low viscosity, high thermal conductivity, high heat capacity for energy storage, low cost, high boiling point and thermal stability, low vapor pressure, and low corrosion of metal alloys (Vignarooban *et al.*, 2015). A molten salt mixture comprising commercial grade sodium nitrate ( $\text{NaNO}_3$ ) and potassium nitrate ( $\text{KNO}_3$ ), also known as solar salts (60wt%  $\text{NaNO}_3$ /40wt%  $\text{KNO}_3$ ), is a suitable HTF candidate due to its advantage of a high working temperature (more than  $500^{\circ}\text{C}$ ). Furthermore, in order to develop salt mixtures in a country such as NaCl based on nitrate molten salts with adding 5% NaCl in solar salt with preliminary test (Chen *et al.*, 2014), it was found that a low melting point temperature, high specific heat capacity which is the desired characteristic of a Heat Transfer Fluid (HTF). Thus, the study of materials used in CSP plants is necessary because of the high working temperature and the presence of molten salts used as HTFs. However, their thermal stability at high temperatures is not satisfactory and especially, they can corrode steel alloys, which can lead to serious operational safety issues.

For such green energy application, robust, reliable and durable materials for CSP constructions are required. The corrosion resistance is among many parameters to consider in these thermal-electrical plants such as for storage tanks and pipes in CSP. Consequently, an investigation into the corrosion behavior of steel alloys in various molten salt mixtures is of great interest. The results for storage tanks, pipelines and related equipment of solar thermal energy storage for service life estimation to provide technical support and theoretical guidance.

Based on the importance and previous studies about corrosion behavior of stainless steels at high temperature, the corrosion behavior of ferritic and austenitic stainless steels such as AISI430 and AISI304 with a similar content in Cr was intensively studied. Although ferritic stainless steels are not as resistant to corrosion as austenitic steels, their corrosion and oxidation resistance are satisfied. In addition, ferritic stainless steels are often used due to less expensive than other stainless steel types. The objective of this research is to study the corrosion behavior of AISI 430 ferritic and AISI 304 austenitic stainless steel samples in conventional and modified molten nitrate salt (solar salts and 57 wt% sodium nitrate ( $\text{NaNO}_3$ )/38 wt% potassium nitrate ( $\text{KNO}_3$ )/5 wt% sodium chloride ( $\text{NaCl}$ )) at  $600^{\circ}\text{C}$  for 2 h.

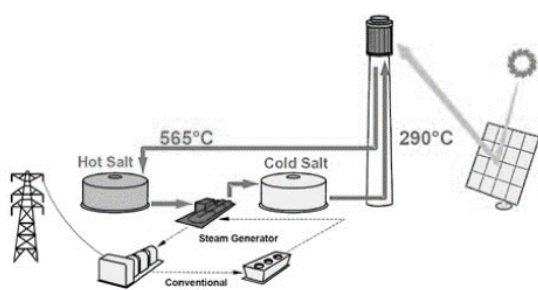


Figure 1. Diagram with two-tank direct storage system (Bauer *et al.*, 2012).

## Materials and Methods

Sheets of AISI 430 (18% Cr-Fe) and AISI 304 (18% Cr-8%Ni) were cut into  $10 \times 10 \times 50 \text{ mm}^3$  sizes. The AISI 430 and AISI 304 pieces were ground with silicon carbide (SiC) paper number until 1000 grit. The surface was then cleaned with acetone and an ultrasonic cleaner and finally dried with air.

Corrosion testing of samples of AISI 430 and AISI 304 was performed using a potentiostat analyzer. Conditions for potentiodynamic measurement are detailed as follows: determination with open circuit potential (OCP), the maximum time is 900 second, the scan rate is 0.001 V/s. After setting open circuit potential (OCP), start input potential at -0.15 V and end potential at 0.15 V. The corrosion rate can be calculated with Equation (1):

$$r = 0.00327 \frac{ai}{nD} \quad (1)$$

where  $i$ , defined as current density ( $\mu\text{A}/\text{cm}^2$ ),  $a/n$  is equivalent weight and  $D$  is density. The density of the AISI 304 and AISI 430 were 7.9 and 7.7  $\text{g}/\text{cm}^3$ , respectively. The equivalent weight of the AISI 304 and AISI 430 were 25.12 and 25.3 g/equivalent, consequently. The salt mixture used in this experiment were solar salts and 57 wt%  $\text{NaNO}_3$ /38 wt%  $\text{KNO}_3$ /5 wt% NaCl. The samples were immersed in the molten salt mixtures at  $600^\circ\text{C}$  for 2 h in argon gas to create an inert atmosphere for protecting oxidation with air during the experiment.

Scanning electron microscopy (SEM) was used to examine the corroded samples for surface morphology. The chemical composition of the oxide layer formation was determined by X-ray diffraction (XRD) analysis.

## Results and Discussion

### Electrochemical testing

In order to evaluate the corrosion behavior of the AISI 430 and AISI 304 samples immersed in the conventional and modified molten nitrate salt mixtures, the results of electrochemical testing by potentiodynamic measurements was shown in Figure 2. The corrosion current density ( $I_{\text{corr}}$ ) of AISI 430 increased with adding 5% NaCl to the solar salt and its electrochemical corrosion potential ( $E_{\text{corr}}$ ), indicating the possibility of a thermodynamically stable reaction, decreased compared to AISI 304. Furthermore the corrosion rate of AISI 430 was higher than that of AISI 304, especially in the molten salt mixture containing 5 wt% NaCl. In Figure 3, the corrosion rates

in 5%NaCl-solar salt were 0.5035 and 0.3184 mm/year for AISI 430 and AISI 304 respectively. In the other hands, the corrosion rates in conventional solar salt were 5.0895 and 1.2516 mm/year for AISI 430 and AISI 304 respectively.

According to the electrochemical results, the corrosion rate of AISI 304 austenitic stainless steel was lower than that of AISI 430 in the same solar salt mixture. Due to the chemical composition of AISI 304 (18 wt% Cr and 8 wt% Ni), chromium makes the iron surface “passive” by forming a surface oxide film which protects the underlying metal from corrosion. In order to produce this protective film, the stainless steel surface must be in contact with oxidizing agents. The nickel is appreciable amounts of austenite stabilizers. The additions of nickel are needed to produce austenitic stainless steel because iron based alloys have a BCC crystal structure at room temperature due to the allotropic transformation of iron below  $738^\circ\text{C}$  (Callister, 2007). The Ni and Cr in AISI 304 improve the passive layer property and its resistance to oxidation and corrosion due to the formation of spinel  $\text{NiCr}_2\text{O}_4$  protective oxide scales. Thus, AISI 304 (18% Cr-8%Ni) austenitic stainless steel is a good choice for use in CSP plants.

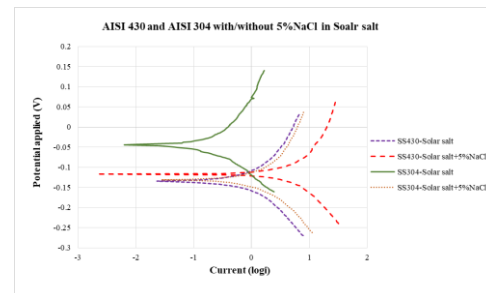


Figure 2. Potentiodynamic polarization curve of AISI 430 ferritic stainless steel and AISI 304 austenitic stainless steel in molten salt with and without 5% NaCl at  $600^\circ\text{C}$  for 2 h.

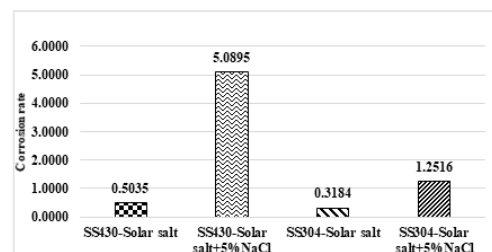


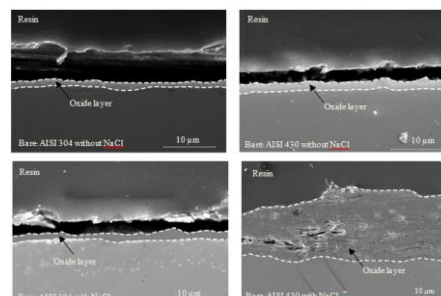
Figure 3. Corrosion rate of AISI 430 and AISI 304 in molten salt with and without 5% NaCl at  $600^\circ\text{C}$  for 2 h.

### Surface Morphology Results

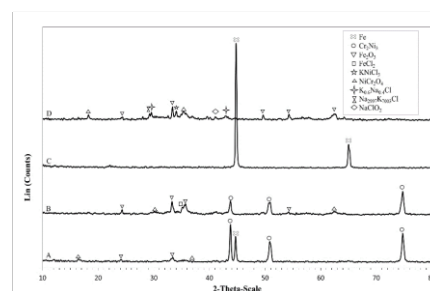
Observation of the cross-sectional morphologies of the samples before and after immersion in the solar salt mixtures using SEM is presented in Figure 4. In the samples in contact with the standard solar salt mixture without 5 wt% NaCl, AISI 304 better corrosion resistance than AISI 430 ferritic stainless steel because its oxide layer was thinner, as shown in Figure 4(a) and Figure 4(b). This was also the case after the samples had come into contact with the solar salt mixture with 5 wt% NaCl, as shown in Figures 4(c) and Figures 4(d). Referred to the SEM images in Figure 4(a), 4(d), 4(c) and 4(d) the change of thicknesses of oxide scales was analyzed using the ImageJ Software. It were found that the thickness of oxide scales of AISI 304 in conventional (Solar salt) and modified molten nitrate salt mixtures as 1.08  $\mu\text{m}$  and 1.63  $\mu\text{m}$ , respectively. And AISI 430 in conventional (Solar salt) and modified molten nitrate salt mixtures as 1.85  $\mu\text{m}$  and 11.79  $\mu\text{m}$ . Thus, austenitic stainless steel AISI 304 had better corrosion resistance than ferritic stainless steel AISI 430. Moreover, both types of stainless steel showed increased corrosion after contact with the solar salt mixture containing 5 wt% NaCl.

Furthermore, in the images, EDS was utilized to analyze the elemental composition of the corrosion scale. The results of EDX were collected and shown in the Table 1 which showed the intense oxygen content at the surface and emphasized the oxidation reaction. Oxygen was present throughout the corrosion scale, as was Fe in the form of iron (III) oxide ( $\text{Fe}_2\text{O}_3$ ). The Ni and Cr in the AISI 304 corrosion scale than in AISI 430. Moreover, more Oxygen was present in the corrosion scale of both steels alloys after exposure to the solar salt mixture containing 5 wt% NaCl due to a thicker oxide layer. In both types of stainless steel, the high amounts of Cr and Fe in the corrosion scale can be explained

by the presence of various corrosion products such as iron oxide (Fernandez *et al.*, 2012). Moreover, in this work corrosion products of materials were



**Figure 4.** Cross sectional micrograph of the bulk corrosion scale after exposure to molten salt for 2 h at 600°C under Argon atmosphere; (a) AISI 304 with solar salt; (b) AISI 430 with solar salt; (c) AISI 304 with solar salt adding 5%NaCl; (d) AISI 430 with solar salt adding 5%NaCl.



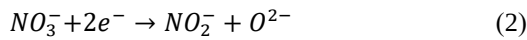
**Figure 5.** X-ray Powder Diffraction (XRD) after exposure to molten salt for 2 h at 600°C under Argon atmosphere; (A) AISI 304 with solar salt; (B) AISI 304 with solar salt adding 5%NaCl; (C) AISI 430 with solar salt; (D) AISI 430 with solar salt adding 5%NaCl.

**Table 1.** EDX results after immersion in molten salt for 2 h at 600°C.

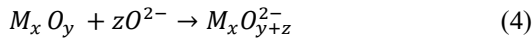
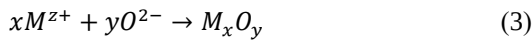
| Material and solution        | Element | Weight % | Atomic % |
|------------------------------|---------|----------|----------|
| AISI 304 solar salts         | Fe      | 53.46    | 30.51    |
|                              | O       | 3.3      | 6.58     |
|                              | Cr      | 15.39    | 9.43     |
|                              | Ni      | 4.89     | 2.65     |
| AISI 304 solar salts +5%NaCl | Fe      | 30.61    | 12.45    |
|                              | O       | 8.77     | 12.44    |
|                              | Cr      | 14.13    | 6.17     |
|                              | Ni      | 4.47     | 1.73     |
| AISI 430 solar salts         | Fe      | 45.21    | 19.09    |
|                              | O       | 4.14     | 6.10     |
|                              | Cr      | 10.45    | 4.74     |
|                              | Ni      | 0.42     | 0.17     |
| AISI 430 solar salts +5%NaCl | Fe      | 38.42    | 16.86    |
|                              | O       | 25.93    | 39.72    |
|                              | Cr      | 10.06    | 4.74     |
|                              | Ni      | 0.26     | 0.11     |

primarily Fe and Fe oxide were confirmed in the XRD analysis (Figure 5). Therefore, the samples after exposure in conventional (Solar salt) and modified molten nitrate salt mixtures (adding 5% NaCl in Solar salt). The main oxide layer found in materials at temperatures at 600°C were hematite (Fe<sub>2</sub>O<sub>3</sub>) for AISI 430 in modified molten nitrate salt and Fe present in AISI 430 in conventional molten salt (Solar salt), hematite (Fe<sub>2</sub>O<sub>3</sub>) and a spinel-like phase (NiCr<sub>2</sub>O<sub>4</sub>) for AISI 304 exposure in both of molten salt. The activation energy for oxidation is smaller for AISI 430 steel in relation to AISI 304 steel in the range of studied temperatures, and therefore the AISI 430 steel is less resistant towards oxidation at high temperatures.

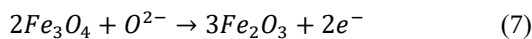
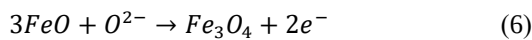
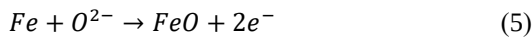
The increase of oxide scale thickness was also related to the oxidation reaction. In case of immersion of metal (M) in the molten nitrate salt, the sample was experienced in the basic environment that had high amount of alkaline oxide or oxygen ion (O<sup>2-</sup>) which decomposed from nitrate ion (NO<sub>3</sub><sup>-</sup>) as shown in the reaction (2), the corrosive effect is based on the following reduction reaction (Fernandez *et al.*, 2012):



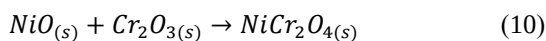
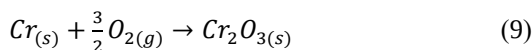
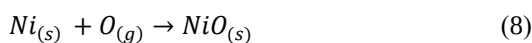
This typical oxidation reaction of Fe atoms which diffuse from the material:



However, this corrosion mechanism occurred in the sample which oxide scales was Fe<sub>2</sub>O<sub>3</sub> as the following reactions:

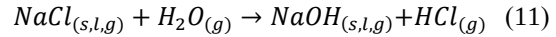


The mechanism of spinel NiCr<sub>2</sub>O<sub>4</sub> oxide scales formation as the following reactions Equations (8)-(10):

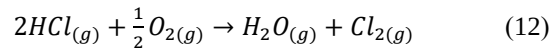


Corrosion is driven by oxidants like H<sub>2</sub>O, O<sub>2</sub>, OH<sup>-</sup>, H<sup>+</sup>, and other impurities in molten chloride

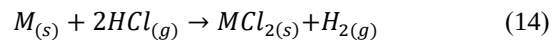
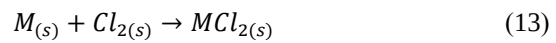
(NaCl). Therefore, any moisture content in the system could lead to the formation of HCl as follows (Sarvghad *et al.*, 2017):



The process could then progress by the oxidation of hydrochloric acid, and resulting in the formation of chlorine gas (Sarvghad *et al.*, 2017):



In addition, other Cl containing can also lead to the corrosion of the alloy (Sarvghad *et al.*, 2017):



Therefore, the production of chlorine and its reaction with metal oxides on the surface becomes the predominant corrosion mechanism in molten chloride (NaCl).

## Conclusions

In this research into the corrosion behavior of stainless steel alloys exposed to solar salts with and without 5 wt% NaCl used as storage materials in CSP plants, following conclusions can be drawn.

1. AISI 430 ferritic stainless steel showed a very high corrosion rate with a lot of corrosion products on its surface.

2. AISI 304 austenitic stainless steel can be used at the temperature applied in the study due to its composition. Especially, the presence of Ni and Cr element constituents in oxide can improve oxidation resistance property and corrosion due to the presence of species such as spinel NiCr<sub>2</sub>O<sub>4</sub>. Moreover, high Cr content leads to the formation of a semi-protective film on the surface in contact with the solar salts.

3. The corrosion rate of AISI 304 austenitic stainless steel was lower than AISI 430 ferritic stainless steel. Thus, AISI 304 is a good choice for use in CSP components.

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