Effects of Zn(II) on hydrogen peroxide-induced corrosion of stainless steel

S Makjan¹, P Boonsri¹, J Channuie² and K Kanjana²

¹Department of Chemistry, Faculty of Science, Srinakharinwirot University, Bangkok, 10110, Thailand
²Thailand Institute of Nuclear Technology (Public Organization), Ongkharak, Nakhon Nayok 26120, Thailand

E-mail: kotchaphank@tint.or.th

Abstract. Zinc injection has been widely applied in nuclear industry for corrosion mitigation of nuclear materials. The corrosion resistance mechanism of zinc in the presence of the radiolytic oxidizing species is complex and has not been completely understood. Without such information it is not possible to improve the protocol. In the present study, zinc effects on corrosion of 304 SS exposed to H₂O₂ at 200-1000 ppb for 7 and 70 hrs were investigated at room temperature using a custom-made flow setup. XRF and SEM-EDX were used to examine the chemical composition and surface morphology of the specimens. The results indicated that pitting was the dominant form of corrosion found under the experimental conditions. Zinc ions tend to help mitigate corrosion of the material via playing a significant role in oxide formation on the steel surface.

1. Introduction

The 300 series Stainless Steels (SSs) are one of the most commonly used structural materials in nuclear power reactors. Despite their excellent corrosion resistance, corrosion failures of the SS components in nuclear reactors are still frequently reported. Irradiation-Assisted Stress Corrosion Cracking (IASCC) was found to be the main corrosion problem in the SS components of nuclear reactors. This form of corrosion originates from the combination of high applied stresses and harsh environments, i.e., corrosive coolant chemistry, strong radiation filed, high temperature, and in some cases high pressure [1-3]. Among those, water chemistry seems to be the factor that can be possibly modified to mitigate IASCC of the materials.

Generally, corrosive environment of a nuclear reactor cooling system stems from the generation of radiolytic oxidizers, e.g., *OH and H₂O₂, in the water coolant [4-5]. The presence of these highly reactive chemical species leads to an increase of the Electrochemical Corrosion Potential (ECP, Ecorr) at the metal/solution interface. Once the ECP increases, the stability of the oxides on the alloy surface will decrease, hence making the materials more susceptible to corrosion [6-7]. The effects of the radiolytic primary species H₂O₂ on corrosion of metal alloys were investigated intensively. Unlike *OH- a short-lived oxidizing species affecting corrosion of the surface in contact- H₂O₂ can potentially contribute to corrosion even at a distance away from the metal surface. The first way this molecule induces corrosion is interacting directly with the metal surface via a redox reaction. Another way is inducing corrosion of the metal surface through catalytic decomposition, the process in which O₂ and...
water are formed. In addition, in the case of stainless steels, it was claimed that \( \text{H}_2\text{O}_2 \) could induce a breakdown of the iron-rich outer layer of the protective film leading to exposure of the chromium-rich inner layer of the film to the environments. Consequently, chromium depletion and a loss of metals in the material would be unavoidable [6-13].

To cope with this problem, zinc injection has been implemented in nuclear industry for several decades. The protocol has been proven to be highly effective for corrosion prevention and mitigation of the nuclear materials. It is generally accepted that when zinc at a very low concentration (~20 ppb) is added into the cooling system of a nuclear reactor, the zinc atom will incorporate into the protective oxide layers of the material. This transition metal will substitute some of the iron, nickel and cobalt atoms in the oxides as zinc oxide has the lowest energy of formation comparing to those of the other elements. Such process helps reduce both corrosion rate and deposition of the radioactive corrosion products on the material surface [14-17]. All this information seems to be well-established. However, the important information regarding the effects of zinc on material corrosion in the presence of the radiolytic oxidizing species is still missing. Therefore, the present research was aimed to investigate the role of zinc ions in mitigating corrosion in 304 SS exposed to \( \text{H}_2\text{O}_2 \). A flow setup simulating the nuclear reactor cooling system was designed and assembled. The chemical composition and surface morphology of the SS specimens before and after the treatment were studied using X-ray Fluorescence (XRF) and Scanning Electron Microscopy – Energy Dispersive X-ray (SEM-EDX).

2. Experimental Section
The 304 SS specimens of dimensions: 2 cm x 2 cm x 0.2 cm with a hole (0.7 cm of diameter) at the center were prepared. Subsequently the specimens were wet polished using a Buehler MetaServ 250 Twin polisher with abrasive paper up to 1200 grit. After polishing the specimens were then cleaned in an ultrasonic bath for 5 mins using acetone, methanol and ethanol, respectively. The cleaned specimens were air-dried and stored in a desiccator at room temperature before weighing. X-ray Fluorescence (XRF) (Bruker, S8 TIGER) was used to determine the chemical composition of the prepared samples.

The solutions of \( \text{Zn(ClO}_4\text{)}_2 \) (Sigma Aldrich) at the concentration of 20 ppb and \( \text{H}_2\text{O}_2 \) (30% Merck Millipore) at the concentration of 200, 500 and 1000 ppb were prepared. The concentration of Zn(II) was fixed at 20 ppb based on the concentration implemented in nuclear reactors[14]. Deionized water from Thermo Scientific (18.2 M\( \Omega \)-cm resistivity) with total organic carbon < 1 ppb was used throughout the experiment. Prior to starting experiment the solutions were deaerated for 2 hours by 99.999% \( \text{N}_2 \) to minimize the level of oxygen. Following that using an HPLC pump, the \( \text{N}_2 \)-saturated solutions were flowed into a glass cell where the SS specimens were hung inside with the flow rate of 2 ml/min. After passing the glass cell, the solutions were finally flowed into a collecting reservoir. The details of the custom-made flow system were published previously[18].

Immediately after experiment, the dried SS specimens were weighed. The morphology of the post-treatment specimens and their chemical compositions were characterized using SEM-EDX (TESCAN VEGA 3) at 20 keV. The EDX characterization was focused on the 4 major elements: Fe, Cr, Ni and O. The EDX spectra were acquired using point analysis. For each surface feather of interest, the EDX data reported were the average chemical composition taken from 5 locations.

3. Results and Discussion
Prior to performing experiment, the chemical composition of the SS samples was first examined using XRF. Table 1. shows the chemical composition from XRF in comparison with those from the American Society Testing and Materials (ASTM) standard and the manufacturer certificate.

As indicated in table 1. the chemical composition of the SS received falls in the range of the ASTM standard and the manufacturer values. This is to ensure that the SS sample was 304 SS. The difference between the weights of the specimens before and after experiment was found to be not statistically significant.
Table 1. Chemical composition of the 304 SS samples examined by XRF in comparison with those of the 304 SS ASTM standard and the manufacturer certificate.

| Element (%) | Cr   | Ni   | Mn   | Si  | C   | P   | S   | Cu  | Mo  | Co  | Fe  |
|-------------|------|------|------|-----|-----|-----|-----|-----|-----|-----|-----|
| ASTM Standard | 17.5-19.50 | 8-10.5 | 2.00 | 0.75 | 0.08 | 0.05 | 0.03 | -   | -   | -   | Balance |
| Certificate  | 18.54 | 8.09  | 1.85 | 0.46 | 0.04 | -   | 0.58 | 0.13 | -   | 70.30 | -   |
| XRF         | 18.75 | 7.75  | 1.80 | 0.44 | 0.04 | -   | 0.57 | 0.13 | 0.11 | 70.20 | -   |

3.1 Surface morphology

The surface morphology of the samples exposed to H₂O₂ at different concentrations and 20 ppb of Zn(II) at 25°C for 7 and 70 hrs is demonstrated in figure 1 and figure 2, respectively.

![Figure 1](image)

*Figure 1. SEM images of the 304 SS surface exposed to different concentrations of H₂O₂ and 20 ppb Zn(II) for 7 hrs: (a) de-ionized water, (b) 200 ppb H₂O₂, (c) 500 ppb H₂O₂, (d) 1000 ppb H₂O₂, (e) 200 ppb H₂O₂/20 ppb Zn(II), (f) 500 ppb H₂O₂/20 ppb Zn(II) and (g) 1000 ppb H₂O₂/20 ppb Zn(II).*

It can be clearly seen that for the 7-hr experiment, there are 3 distinct feathers found on the specimen surface: smooth area, corrosion product and pit, whereas in the case of 70-hr experiment, an additional trench-like feather is observed (see figure 1 and figure 2). The trench density seems to increase with H₂O₂ concentration. The highest trench density is observed in the 1000 ppb H₂O₂ case (figure 2(d)). It was reported previously that trenches developed on SS surface were actually propagated pits which was related to inclusion[19]. This mysterious trench feature, however, will be left for our future study and will not be further discussed in this paper. The corrosion products are found to deposit all over the surface (figures 1(c), 1(d), 2(c) and 2(d)) with ununiform distribution. The maximum size, ca. 40 µm wide (figure 3), is observed on the specimen surface exposed to 1000 ppb H₂O₂ for 70 hrs.

Pitting corrosion which appears to be the major corrosion type found under the experimental conditions could be seen even in the specimen exposed to only de-ionized water, figure 1(a). When
comparing the results from the two sets, it is shown that pit density is affected slightly by exposure time. Even though in both sets of experiment the pit size on the specimen surface remains unchanged with different concentrations of H$_2$O$_2$; However, the effects of H$_2$O$_2$ on pitting corrosion of the specimen can be indicated by the increase of pit and corrosion products densities with H$_2$O$_2$ concentration. Precisely, H$_2$O$_2$ plays a role in pitting initiation by increasing $E_{corr}$ at the metal/solution interface resulting in a breakdown of the protective film. Zhang et al. demonstrated that exposing metal alloy surface to H$_2$O$_2$ could induce a local breakdown of the outer oxide layer, and consequently the inner oxide layer would be exposed to the environments [7]. This would potentially increase the possibility of the inner oxide layer damage which can lead to dissolution of the metal ions from the bulk material into the solution. In this case pitting corrosion is worsen unavoidably.

Figure 2. SEM images of the 304 SS surface exposed to different concentrations of H$_2$O$_2$ and 20 ppb Zn(II) for 70 hrs: (a) de-ionized water, (b) 200 ppb H$_2$O$_2$, (c) 500 ppb H$_2$O$_2$, (d) 1000 ppb H$_2$O$_2$, (e) 200 ppb H$_2$O$_2$/20 ppb Zn(II), (f) 500 ppb H$_2$O$_2$/20 ppb Zn(II) and (g) 1000 ppb H$_2$O$_2$/20 ppb Zn(II).

When 20 ppb Zn(II) was added, it was obvious that deposition of the corrosion products decreased dramatically, figures 1(e)-1(g) and figures 2(e)-2(g). The effects of Zn(II) on pit density, however, is not clear. This suggests that Zn(II) ions at this concentration hardly interfere with the pit nucleation, but in fact they resist corrosion by mitigating the pit propagation process. To confirm this assumption, EDX was later used to further characterize the chemical composition of the specimen surface.

Figure 3. Corrosion product(s) deposited on the 304 SS surface exposed to 1000 ppb of H$_2$O$_2$ for 70 hrs.
3.2. Chemical composition

The EDX analysis was focused on the chemical composition of the 3 distinct feathers: smooth area, white product and pit (figures 4-6).

![Figure 4](image)

**Figure 4.** Chemical composition of the smooth area on the 304 SS surface exposed to different concentrations of H$_2$O$_2$ and 20 ppb Zn(II) for 7 and 70 hrs.

According to the EDX results obtained from the smooth area (figure 4), exposing to 200 ppb H$_2$O$_2$ leads to a small decrease in Fe and Ni percentages with a large increase in Cr percentage. However, changing the concentration of H$_2$O$_2$ from 200 ppb to 500 ppb and 1000 ppb in all cases has no apparent effects on the atomic percentages of Fe, Ni and Cr in this area. The decrease in Fe and Ni contents can be explained by the fact that as H$_2$O$_2$ is added into the chemical system, $E_{corr}$ between the metal/solution interface increases causing some of the unstable iron and nickel oxides to be removed from the surface. The more stable chromite-based oxide which was claimed to position in the inner layer of the M$_3$O$_4$-MCr$_2$O$_4$ binary system of SS passivation[15], therefore, exposes to the environments resulting in the higher Cr content detected. In addition, there is no effects of Zn(II) and exposure time seen in this area. It should be also noted that there was no O content detected on this smooth surface. As a result, it can be mentioned that this smooth area is nearly safe from corrosion due to still being covered by the thin inner layer of chromite-based oxide film and its all properties should stay closed to those of untreated 304 SS.

The formation of corrosion products around the pits is indicated by the appearance of white component at the pit edge. The corrosion products are also observed to distribute ununiformly on the specimen surface. The EDX results of the corrosion product and pit areas are illustrated in figure 5 and figure 6. It can be seen that the trends of Fe, Cr, Ni and O %at. in the area with corrosion products and the pit area are similar. As the concentration of H$_2$O$_2$ increased, Fe and Ni are seen to decrease with an increase of Cr and O. More importantly, a large production of O confirms the formation of oxides in all cases. The decrease of Fe and Ni contents in the corrosion product and the pit areas with H$_2$O$_2$ concentration implies that the presence of H$_2$O$_2$ results in the reduction of the iron and nickel oxide stability. In this case, Fe and Ni should be released into the solution in the form of Fe$^{3+}$ and Ni$^{2+}$. The less effects of H$_2$O$_2$ to the stability of chromium oxide are pronounced since the Cr content in the corrosion products stays constant even with higher H$_2$O$_2$ concentration. The O content in the area
covered by corrosion products is found to increase significantly as a function of H$_2$O$_2$ concentration. This observation can be explained by the fact that with higher concentration of H$_2$O$_2$, more oxides are generated with greater dissolution of Fe and Ni. The ratios of O to Fe and O to Ni, therefore increase. When comparing the results between the 7-hr and 70-hr experiments, it is obvious that all this phenomenon is worsen by time.

![Figure 5](image)

**Figure 5.** Chemical composition of the corrosion product area generated on the 304 SS surface exposed to different concentrations of H$_2$O$_2$ and 20 ppb Zn(II) for 7 and 70 hrs: (a) Fe, (b) Cr, (c) Ni and (d) O.

The contents of Fe and Ni in the corrosion product area are seen to increase with Zn(II) addition. On the other hand, Cr and O contents are seen to decrease in the presence of Zn(II). This suggests that Zn(II) helps prevent dissolution of Fe and Ni into the solution, meaning the outer oxide layer is more stable. In turn, the exposure of the inner chromite-based layer to the environment is reduced. Less corrosion oxides are formed. A number of studies reported that Zn(II) ions played an important role in corrosion resistance by incorporating into the oxide structures. Due to having low energy of formation, Zn had ability to substitute the Fe and Ni atoms in the oxides forming more stable zinc oxides[14-16]. Surprisingly, in the present research, Zn was undetectable in all cases. However, under the experimental conditions, we believe that the substitution took place with a fairly small amount. This suggests that performing experiment up to 70 hrs is not enough to generate a detectable substitution; nevertheless, it is sufficient to show the impact of Zn(II) in corrosion mitigation.

Based on the information obtained in this study, it can be proposed that in the presence of H$_2$O$_2$ Zn(II) ions hardly interfere with pitting nucleation, but it is rather involved in pit propagation. The effects can be clearly seen in both corrosion product and pit areas. In the presence of a radiolytic
oxidizing species, the mechanism of corrosion resistance by Zn(II) is related to atom substitution with Fe and Ni in the oxides, corresponding to the information available in the literature.

Figure 6. Chemical composition in the pit area on the 304 SS surface exposed to different concentrations of H2O2 and 20 ppb Zn(II) for 7 and 70 hrs: (a) Fe, (b) Cr, (c) Ni and (d) O.

4. Conclusion
The effects of Zn(II) on the corrosion of SS 304 exposed to different concentrations of H2O2 was investigated. The surface morphology of the SS surface after experiment was revealed by SEM showing the formation of pitting corrosion and its corrosion products. Further chemical composition analysis was performed using EDX. The effects of H2O2 and Zn(II) on the chemical composition of the SS surface could be clearly seen by this technique. H2O2 triggers pitting corrosion of SS surface by inducing the formation of unstable iron and nickel oxides which eventually dissolve into the solution leaving pits behind. Zn(II) helps mitigate this pitting corrosion by substituting some of the Fe and Ni atoms in the oxide structures forming stable zinc oxide layer on the surface. The results obtained from this study therefore can fulfill the understanding of the process in which Zn resists corrosion in the presence of a radiolytic oxidizer.

Acknowledgements
The research described herein was jointly supported by Thailand Institute of Nuclear Technology (TINT) and the Budget Bureau of Thailand. The authors also would like to acknowledge the Office of Atoms for Peace for SEM-EDX service and Dr. Pantip Ampornrat at the Office of Atoms for Peace for her assistance in the sample preparation process.
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