

## Research Article

# Effect of Oxidizing Decontamination Process on Corrosion Property of 304L Stainless Steel

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Corrosion behaviors of 304L stainless steel (SS) and 304L SS with oxides film (preoxidation 304L SS) in 1 g/L potassium permanganate solution of various pH values were investigated by using mass loss, electrochemical measurement and scanning electron microscope (SEM) observation. The results showed that mass loss of 304L SS increases with the increase of sodium hydroxide or nitric acid concentration in 1 g/L potassium permanganate solution. The polarization curves of 304L SS in potassium permanganate solution show that passive zones are destroyed more easily in acid potassium permanganate solution than alkaline potassium permanganate solution. The corrosion ability of acid potassium permanganate (NP) decontamination solution used for 304L SS is more aggressive than alkaline potassium permanganate (AP) solution. The oxide film on the surface of preoxidation 304L SS can be removed completely in two oxidation reduction decontamination cycles, oxidizing solution of which comprised 0.4g/L sodium hydroxide and 1g/L potassium permanganate. The 304L SS and preoxidation 304L SS performed alkaline oxidation reduction decontamination of 3 cycles were reoxidation. The micromorphology of reoxidation specimens was similar to preoxidation 304L SS. Therefore the chemical decontamination of alkaline oxidizing and acid reducing steps had no negative effect on corrosion of 304L SS and reoxidation of 304L SS carried out decontamination.

## 1. Introduction

Corrosion products are generated in the steam generators, loop piping, and other reactor internal surfaces during reactor operation [1–3]. These corrosion products eventually comprise the source term of the crud in the reactor. Radioactive isotopes of the transition metals ( $\text{Co}^{60}$ ,  $\text{Mn}^{54}$ ,  $\text{Cr}^{51}$ , etc.) also participate in oxides and contribute greatly to increasing the dose rate in circuit [4–6]. Chemical decontamination is an effective method to reduce occupational radiation exposure during large-scale maintenance tasks such as the overhaul of primary recirculation pumps and shroud replacement in in-service nuclear power plants (NPPs) [7]. Therefore, many different chemical decontamination methods have been developed [8–15], such as HP/CORD (Chemical Oxidation Reduction Decontamination), AP/CITROX (Citric plus Oxalic acids), and LOMI (Low Oxidation state Metal Ion). Each has its own merits and demerits. In most cases, the most crucial step for chemical decontamination to be

successful is the removal of the Cr enriched layer of oxide. Especially in Pressurized Water Reactor (PWR) conditions, the decontamination process calls for oxidation of these Cr ions from trivalent to hexavalent, which form more easily soluble species. Among the various known pretreatment chemicals, the permanganate-based reagents are known to be the most efficient [13–15]. Resulting from a decontamination procedure performed, the corrosion rate of the metals may eventually be increased; therefore, to minimize the corrosion damage, the preparation of perfectly clean and passive surfaces in addition to a chemical decontamination is strongly recommended.

Austenitic stainless steels are widely used as construction material in PWRs all over the world. In this paper, the effect of oxidation decontamination steps on corrosion performance of 304L stainless steels (SS) was investigated. The pH of potassium permanganate solution is evaluated for the optimum removal of oxides and generating minimum corrosion of 304L SS.

TABLE 1: Chemical compositions of tested 304L SS (mass. %).

C	Si	Mn	S	P	Ni	Cr	Fe
0.024	0.33	1.30	0.001	0.015	8.19	18.22	71.92

TABLE 2: Oxidizing decontamination solution.

Process decontamination cycles		NaOH (g/L)	HNO <sub>3</sub> (g/L)	KMnO <sub>4</sub> (g/L)	pH
Acid oxidizing step	1	0	0.05	1	3
	2	0	0.2	1	2.5
	3	0	0.65	1	2
	4	0	2	1	1.5
	5	0	6.5	1	1
Alkaline oxidizing step	1	0.1	0	1	11.4
	2	0.4	0	1	12
	3	1	0	1	12.5
	4	4	0	1	13
	5	10	0	1	13.5

## 2. Experimental Details

The chemical compositions of 304L SS used in this work are shown in Table 1. The dimension of sample used is 20 mm × 3 mm × 2 mm. The surfaces of samples were polished with a series of silicon carbide abrasive papers to a finish grit of 1200#. After that, samples were placed in an ultrasonic acetone bath for about five minutes and then air-dried.

The method is a multistage chemical decontamination composed of an oxidizing decontamination step and a reducing decontamination step. The alkaline potassium permanganate oxidizing and acid reducing steps are defined as AP-N, and acid potassium permanganate oxidizing and acid reducing steps are defined as NP-N. The compositions in oxidizing decontamination solution are shown in Table 2. Potassium permanganate solution is used as oxidizing agent, controlled to pH of 1~3 by addition of acidifying agent or 11.4~13.5 by addition of alkalizing agent. Ascorbic acid solution (1 g/L C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>) is used as reducing agent, controlled to pH by addition of 1 g/L nitric acid.

Decontamination of the 304LSS specimens was performed by the oxidizing step and the reducing step. The 304L SS specimens were immersed into oxidizing decontamination solution for 8 h. Then specimens were washed by using deionized water and air-dried. After that, these specimens were immersed into reducing solutions for 5 h. The temperature of oxidizing solutions and reducing solutions was maintained at 80°C and the rotating speed of samples was 30r·min<sup>-1</sup>. This multicycle chemical decontamination of 5 cycles had been carried out. The mass was measured by an XS105DU electric balance with an accuracy of 0.1 mg.

High-temperature high-pressure water immersion test was conducted in a 2.5 L autoclave made by Alloy 625. Corrosion tests were conducted at 300°C under a pressure of 15.5 MPa for time periods up to 1000 h. The tested solution is 800 mg/L B as well as 2.2 mg/L Li water solution which was prepared by H<sub>3</sub>BO<sub>3</sub>, LiOH, and deionized water. The purities of all chemicals were of analytical grade. The preoxidation

304L SS undergoing three AP-N (0.4 g/L NaOH + 1 g/L KMnO<sub>4</sub>) decontamination cycles was placed into autoclave again for reoxidation.

The surface morphologies were observed using Quanta 400FEG SEM. Electrochemical tests were carried out using a Reference 600+ electrochemical workstation. The working electrode was the 304L SS alloy with a 1 cm<sup>2</sup> exposed area. All working electrodes were ground by emery papers down to 1200#. A saturated calomel electrode (SCE) and a platinum electrode were used as reference electrode and auxiliary electrode, respectively. The testing medium, at a temperature of 40 ± 1°C, was the deionization water with KMnO<sub>4</sub> and NaOH or HNO<sub>3</sub>. The potentials range of polarization test was -0.2~1V (vs. OCP), with a scanning rate of 0.333 mV/s.

## 3. Results

**3.1. Mass Loss of 304L SS.** The mass loss of 304L SS after NP-N and AP-N is shown in Figures 1 and 2, respectively. It is obvious that the mass loss of 304L SS after NP-N and AP-N decontamination increases in both cases with decontamination cycles. Figure 1 shows the highest mass loss of 304L SS occurring in 1 g/L KMnO<sub>4</sub> + 6.5 g/L HNO<sub>3</sub> solution (pH=1). As may be seen from Figure 1, excessive HNO<sub>3</sub> gives rise to serious corrosion of 304L SS, which is consistent with literatures [16, 17]. Therefore, the alkaline oxidizing solution is more beneficial to reduce corrosion of 304L SS than acid oxidizing solution.

**3.2. Mass Loss of Preoxidation 304L SS.** Figure 3 shows the relationship of mass loss for preoxidation 304L SS and AP-N decontamination cycles. The mass loss of preoxidation 304L SS gradually decreases with the increase of decontamination cycles. The mass loss of preoxidation 304L SS in AP-N chemical decontamination of 1~5 cycles is 0.161 mg/cm<sup>2</sup>, 0.256 mg/cm<sup>2</sup>, 0.351 mg/cm<sup>2</sup>, 0.354 mg/cm<sup>2</sup>, and 0.358 mg/cm<sup>2</sup>, respectively. The mass loss of preoxidation 304L

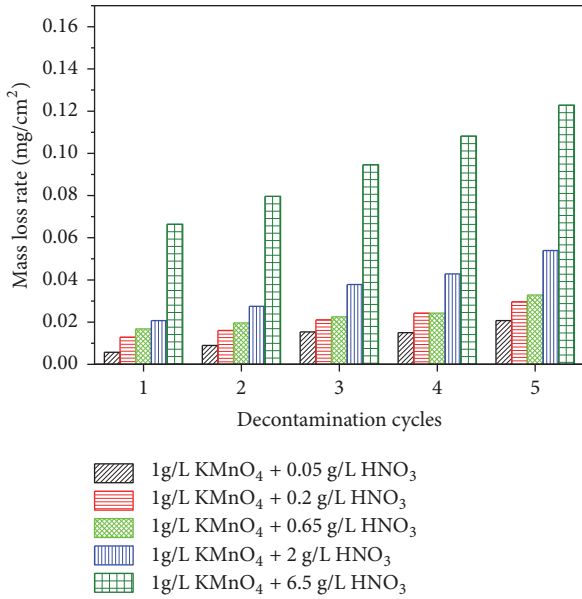


FIGURE 1: The mass loss of 304L SS carrying out NP-N decontamination.

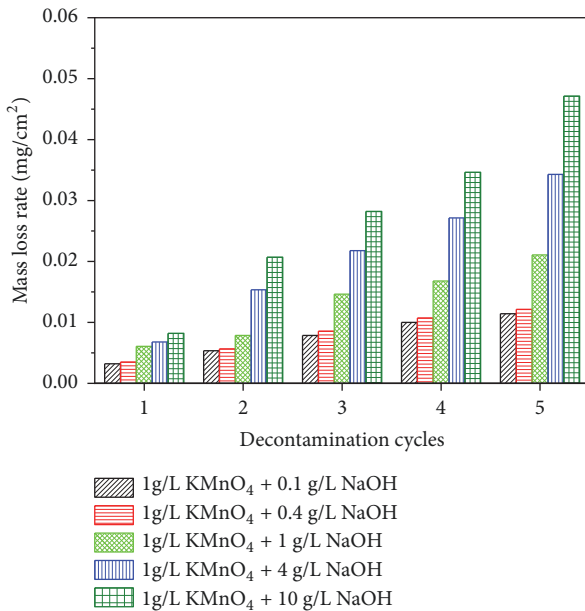


FIGURE 2: The mass loss of 304L SS carrying out AP-N decontamination.

SS in 3~5 chemical decontamination cycles has no obvious increase. The result shows that the oxides on the surface of 304L SS that had been completely removed only carried out AP-N chemical decontamination of 2 cycles.

3.3. *Electrochemical Behavior.* The potentiodynamic polarization curves of 304L SS in 1 g/L KMnO<sub>4</sub> + X g/L HNO<sub>3</sub> (X = 0.05, 0.2, 0.6, 2, and 6.5) solution are shown in Figure 4. It can be seen from Figure 4 that the corrosion potential of 304L SS increases with increasing of HNO<sub>3</sub> concentration. There are no obvious passivation zones, when HNO<sub>3</sub> concentration

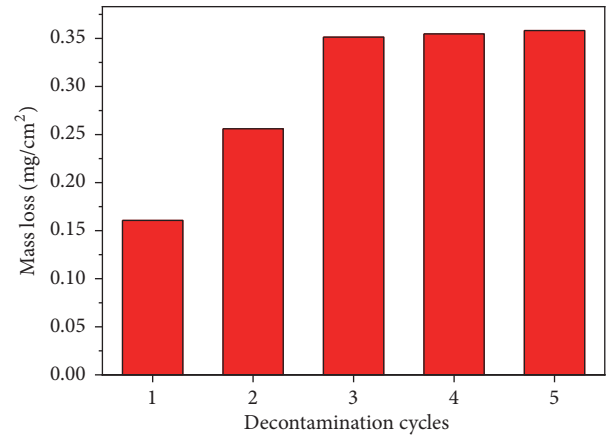


FIGURE 3: Mass loss of preoxidation 304L SS carrying out AP-N chemical decontamination.

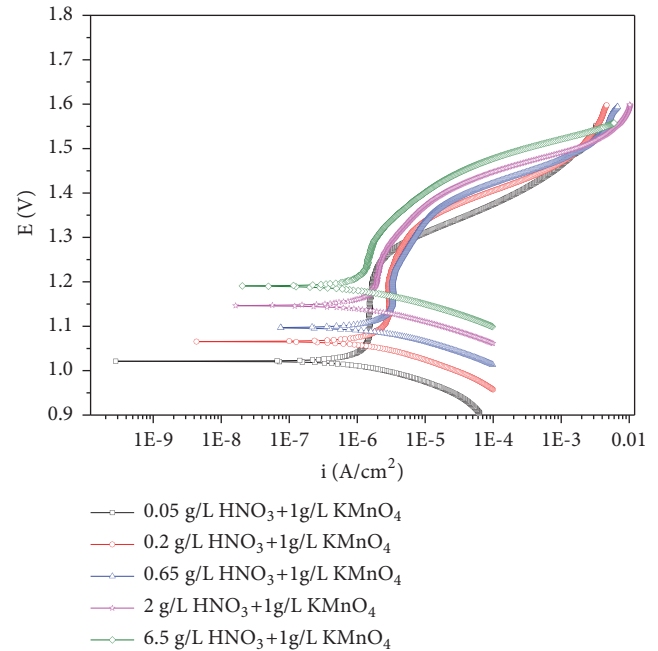


FIGURE 4: The potentiodynamic polarization curves of 304L SS in acid KMnO<sub>4</sub> solution.

reaches 2 ~ 6.5g/L (pH=1.5~1). The lower pH in acid oxidizing decontamination solution increases the corrosion of 304L SS.

The potentiodynamic polarization curves of 304L SS in 1 g/L KMnO<sub>4</sub> + X g/L NaOH (X = 0.1, 0.4, 1, 4, and 10) solution are shown in Figure 5. It can be seen from Figure 5 that the range of passivation potential gradually reduces with the increase of NaOH concentration. The stable passivation zones of 304L SS in alkaline KMnO<sub>4</sub> solution are destroyed, when the NaOH concentration reaches 10g/L (pH=13.5). The cathodic polarization of 304L SS in alkaline KMnO<sub>4</sub> solution change and corrosion potential greatly increase, when the NaOH concentration reaches 4g/L (pH=13) and 10/L (pH=13.5). The corrosion potential of 304L SS in acid KMnO<sub>4</sub> solution is greater than alkaline KMnO<sub>4</sub> solution.

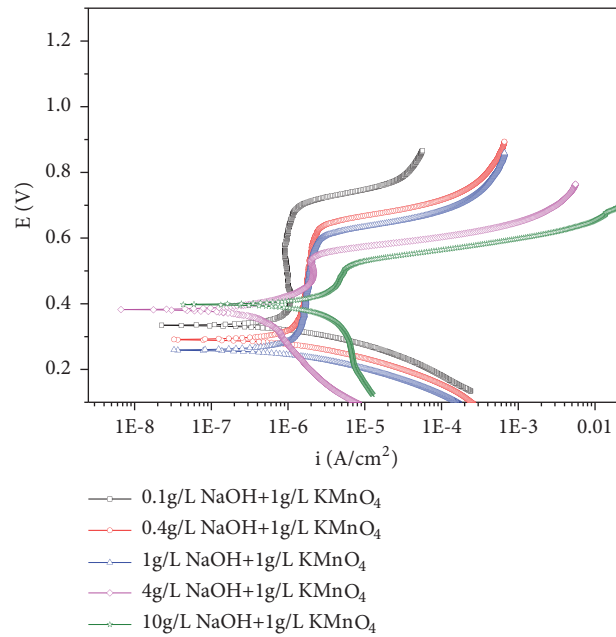


FIGURE 5: The potentiodynamic polarization curve of 304L SS in alkaline  $\text{KMnO}_4$  solution.

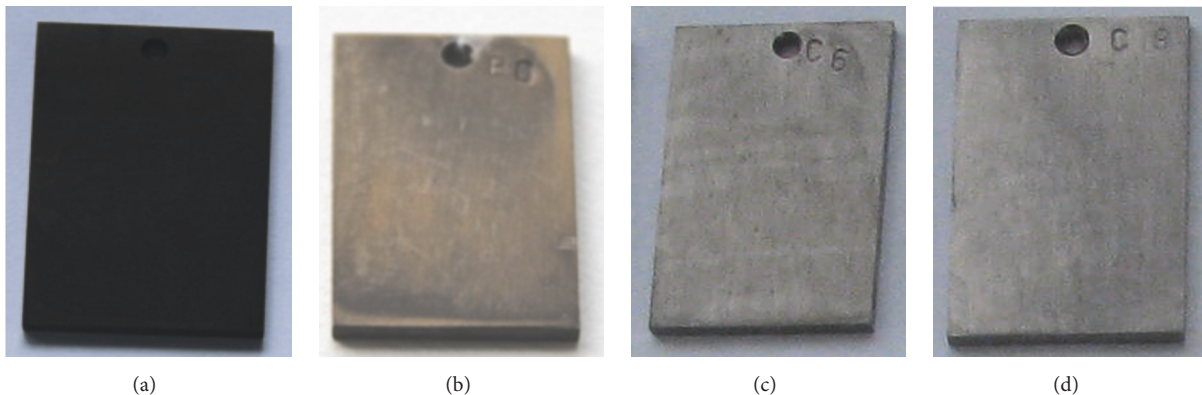


FIGURE 6: The morphologies of (a) preoxidation 304L SS and ((b), (c), and (d)) preoxidation 304L SS carrying out AP-N decontamination of 1~3 cycles.

The acid  $\text{KMnO}_4$  solution is more harmful on corrosion of 304L SS than alkaline  $\text{KMnO}_4$  solution.

**3.4. Surface Morphology.** Figure 6 shows the morphologies of (a) preoxidation 304L SS and ((b), (c), and (d)) preoxidation 304L SS carrying out AP-N decontamination of 1~3 cycles. It can be seen that preoxidation 304L SS is covered with a layer of black oxide film, as shown in Figure 6(a). After the decontamination of 1 cycle, the surface of sample is brown. With the increase of decontamination cycles, the surface of preoxidation 304L SS turns into metal gray gradually. And the macromorphologies of preoxidation 304L SS carrying out decontamination of 2 and 3 cycles are similar.

There are many large particles on the outer surface and small particles on the inside surface of preoxidation 304L SS shown in Figure 7(a). It can be seen from Figure 7(b1) that there are no oxides particles on the surface of preoxidation

304L SS carrying out decontamination of 1 cycle. Figure 7(b2) shows that there was much porous structure on the surface of preoxidation 304L SS carrying out decontamination of 2 cycles. The micromorphology of preoxidation 304L SS carrying out decontamination of 3 cycles is similar to 2 cycles. It is indicated that surface oxidation films were almost removed through AP-N decontamination of 2 cycles. Figure 7(c) shows a lot of oxide particles on the surface preoxidation 304L SS specimens carrying out AP-N decontamination of 3 cycles. And the micromorphology of reoxidation specimens is similar to preoxidation 304L SS.

#### 4. Conclusions

The mass loss of 304L SS carrying out oxidation reduction decontamination gradually increases with the increase of nitric acid or NaOH concentration. In the oxidizing decontamination solution, the acid  $\text{KMnO}_4$  solution was more

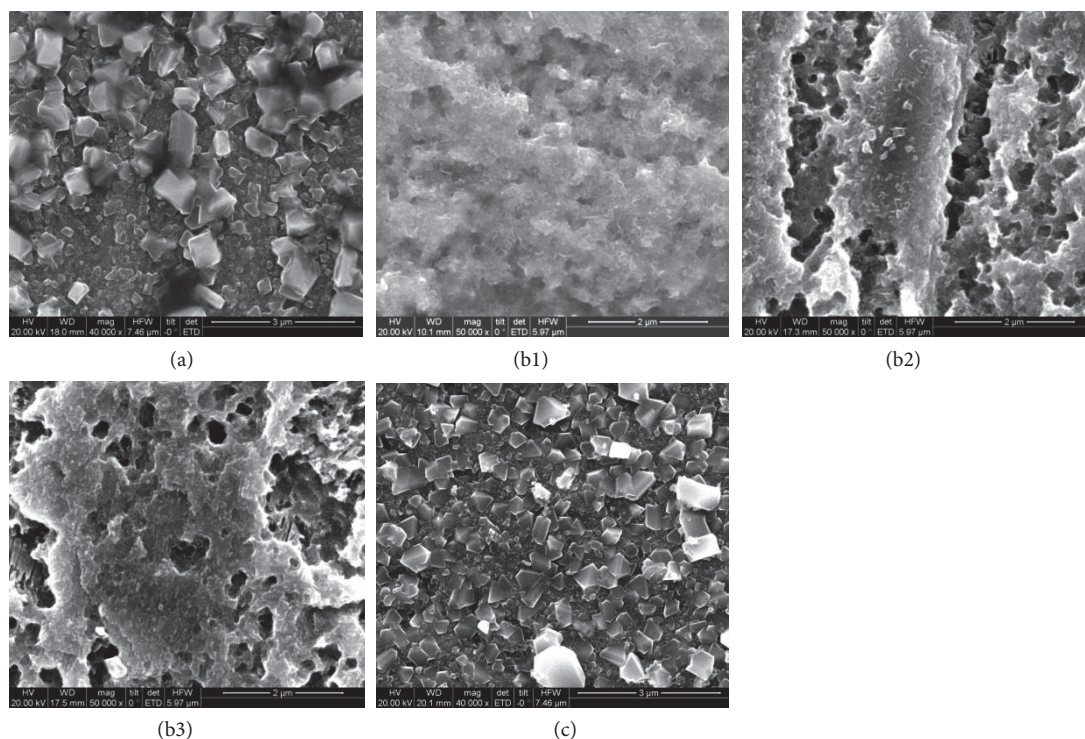


FIGURE 7: The micromorphology of (a) preoxidation 304L SS, ((b1) (b2) and (b3)) preoxidation 304L SS carrying out AP-N decontamination of 1~3 cycles, respectively, and (c) reoxidation 304L SS carrying out AP-N decontamination of 3 cycles.

corrosive to the 304L SS than alkaline  $\text{KMnO}_4$  solution. The passive zones of 304L SS were destroyed easily when acid or alkaline concentration in  $\text{KMnO}_4$  solution is enough. The oxide films on the surface of preoxidation 304L SS have been totally removed after AP-N (0.4 g/L NaOH + 1 g/L  $\text{KMnO}_4$ ) decontamination of 2 cycles and left lots of microspores on the surface. The macromorphology and micromorphology of preoxidation 304L SS were similar to reoxidation samples.

### Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

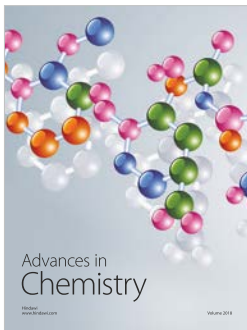
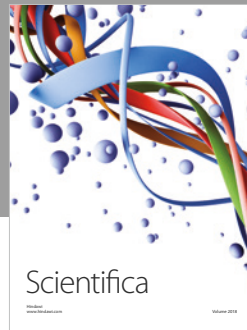
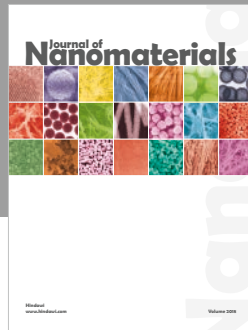
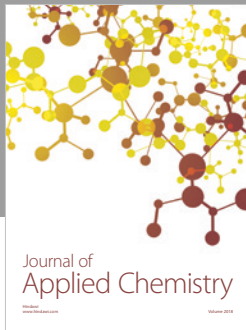
### Conflicts of Interest

The authors declare that there are no conflicts of interest.

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