Experimental Results of Oxidation / Reduction Process Based on Permanganic-Oxalic Acid

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1. Introduction

The primary goal of the Chemical Decontamination is to achieve a dose rate reduction for the decommissioning worker. The oxide film layer formed on the surface of the structural material of the Light-Water-Reactor is composed of metal oxides of iron, nickel and chromium[1]. The chromium oxide is dissolved by the oxidation reaction, and iron and nickel in metal oxides are dissolved by the reduction reaction.

In this study, the oxidation/reduction process experiments were conducted using System Decontamination Process Development Equipment of Lab scale. The removal rate of the oxides film in the specimen was evaluated and the decontamination process time was confirmed.

2. Methods

In this experiment, oxidation / reduction process experiments were conducted using a System Decontamination Process Development Equipment of Lab scale (Fig. 1). The experiment was carried out under the following conditions.

- Specimen Type: SUS304, SUS316, SUS410, Alloy600, SA508
- Oxidation / reduction process conditions

	Agent	Concentration	Time	Temperature
Oxidation	$HMnO_4$	300 ppm	48hr	95℃
Reduction	$C_2H_2O_4$	2000 ppm	24hr	

The oxide film thickness of each pre-decontamination specimen was analyzed using Glow Discharge Spectrometer (GDS) and the surface of the specimens was carried out using Videoscope.

The weight of the specimens before and after decontamination was measured to evaluate the oxide removal rate. The concentration of Fe, Cr and Ni ions was analyzed using inductively coupled plasma-optical emission spectrometry (ICP-OES).

Fig. 1. System Decontamination Process Development Equipment.

3. Results and Discussion

3.1 Characterization of the oxide film

As a result of the Glow Discharge Spectrometer (GDS) analysis of the pre-decontamination specimen, the thickness of the oxide film was found to be 15 μm for SUS304, 1.6 μm for SUS316, 7.11 μm for SUS410, 2.52 μm for SA508, 6.2 μm for Alloy 600.

For analyzing the surface of the specimen before and after decontamination, the specimen surface was observed using Videoscope. The pre-decontamination specimens were confirmed that black oxide layer was formed. Videoscope analysis of the specimens after decontamination showed that all of the oxide films were removed in SUS304 and SUS316. In particular, a large amount of pitting was occurred in the surface of SUS304. In the case of SUS410 and SA508, iron oxide was formed on the surface and serious localized corrosion was observed. In the case of Alloy 600, all of the oxide film was not removed and chromium oxide of green color was observed[2,3].

3.2 Experimental results of oxidation / reduction process

The removal rate of the oxide film was evaluated through an oxidation / reduction process experiment based on permanganic-oxalic acid. The weight of the specimens was shown in Table 1. As a result, in the case of SUS 304 and Alloy 600, the oxide film was removed by 75%.

Table 1. The weight of the specimens before and after decontamination

Type	Decontamination Process		Removed Weight(g)
	Before(g)	After(g)	
SUS304	10.12081	10.05679	0.06402
SUS316	10.18898	10.12936	0.05962
SUS410	9.86923	9.76737	0.10186
Alloy600	10.74154	10.71774	0.02380
SA508	9.97664	9.72351	0.25313

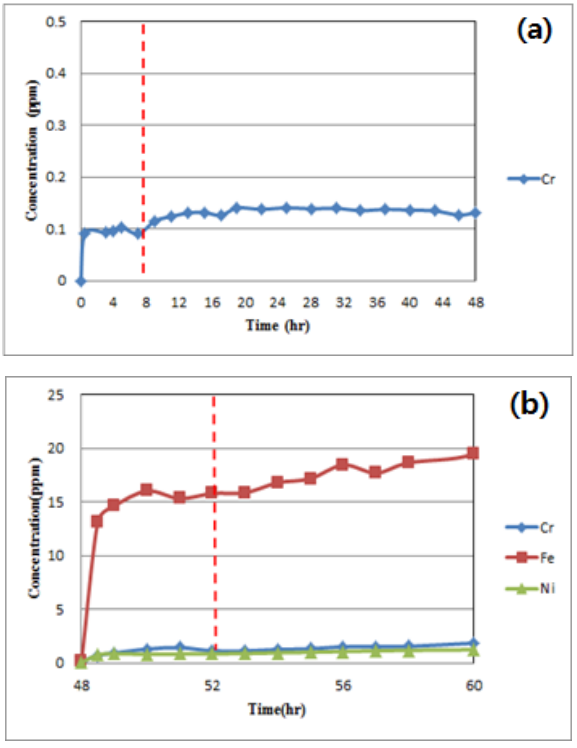

Fig. 2. The concentration of dissolved metal ions in the decontamination agent ((a) oxidation process, (b) reduction process).

The concentration of metal ions dissolved in decontamination agent was shown in Fig. 2. During oxidation, Cr ions were dissolved in 0.1132 ppm and Fe and Ni ions were not dissolved. It is considered that the Cr^{3+} in the oxide film is oxidized to Cr^{6+} by the permanganic acid. After the reduction process, Cr ions were dissolved at 2.057 ppm, Fe ions were dissolved at 22 ppm, and Ni ions were dissolved at 1.5 ppm. Through the analysis of the dissolved metal ions concentration with time, it can be confirmed that the oxidation and reduction processes are completed within 5 hours.

4. Conclusions

In this study, the removal rate of oxide film in the simulated specimen was evaluated and decontamination process time was determined through oxidation ($HMnO_4$) / reduction ($C_2H_2O_4$) process experiment.

SUS304 and Alloy 600 showed that the oxide film was removed by 75%. The decontamination process time was 5 hours for the oxidation process and 4 hours for the reduction process.

Based on these experimental results, an oxidation / reduction continuous process (more than 2 cycles) will be carried and determine the number of consecutive cycles of systematic decontamination.

Acknowledgments

This work was supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP), granted financial resources from the Ministry of Trade, Industry & Energy, Republic of Korea (Number 20141510300310)

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