

## Dissolution of Chemical Decontaminating Agent for a Foam Decontamination

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### 1. Introduction

Prior to confirming the decontamination performance of a foam decontaminating agent mixed with a chemical decontaminating agent as part of the development of a foam decontaminating agent having characteristics capable of significantly reducing the waste liquid generated during decontamination, a study was conducted to optimize the composition of the chemical decontaminating agent available for the foam decontaminating agent.

Radioactive corrosion oxides in pressurized light water reactors consist of an inner layer formed of crystals of Fe, Ni and Cr ions formed through the oxidation of a metal element at the interface between the oxide film and metal, and an outer layer formed by being diffused to the boundary between the coolant and oxide film through the pores of the oxide film and precipitated. Because the  $\text{Cr}^{3+}$  component present in the inner layer of the corrosion oxide film has insoluble characteristics, an oxidizing agent has to be added to oxidize to soluble  $\text{Cr}^{6+}$  [1].

To confirm the decontamination performance of three kinds of chemical decontaminators varying in terms of the concentration of Ce (IV) and  $\text{HNO}_3$ , which are the main components of an oxidizing chemical decontamination agent, decontamination specimens were prepared to form  $\text{FeCr}_2\text{O}_4$  on SUS 304 metal in an autoclave. The weight loss and SEM / EDX of the specimens was measured before and after decontamination, and the concentration of Fe and Cr ions in the solution after decontamination was analyzed using AA spectroscopy.

### 2. Methods and Results

#### 2.1 Experimental Methods

304 stainless steel specimens (20 mm x 20 mm x 2 mm) were prepared through corrosion for 7 days at 230 °C using 0.05M  $\text{Na}_2\text{H}_4 \cdot \text{EDTA}$  and 5 ppm  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  in an autoclave (SUS-316, capacity: 4.5 L, temperature deviation within  $\pm 1$  °C). The dissolved oxygen concentration was controlled to 800 ppb by  $\text{N}_2$  gas.

Three types of chemical decontaminating agents were prepared as shown in Table 1 by varying the concentrations of  $\text{HNO}_3$  and Ce (IV), which are components of the chemical decontamination agent.

75 mL of three kinds of chemical decontamination solutions were prepared by mixing appropriate amounts of chemicals in accordance with the concentrations of Ce (IV) and  $\text{HNO}_3$ . The weight loss of the specimens was measured every 2 hours after decontamination. SEM (SNE-4000M, Korea) and EDX (BRUKER, XFLASH DETECTOR, 410-M, Germany) were measured before and after the decontamination experiment, and the concentrations of Fe and Cr ions in the solution after decontamination were analyzed using an atomic absorption spectrometer (AAAnalyst 400, PerkinElmer).

Table 1. Types of chemical decontaminating agents

Solution type	Composition
solution-1	1M $\text{HNO}_3$ & 0.1M Ce(IV)
solution-2	2M $\text{HNO}_3$ & 0.1M Ce(IV)
solution-3	2M $\text{HNO}_3$ & 0.5M Ce(IV)

#### 2.2 Results & Discussion

The decontamination metal ions should have a high oxidation potential for stability in an acidic solution, have a fast dissolution rate to the SUS metal, and be readily regenerable through electrolysis. A  $\text{Ce}^{4+} - \text{Ce}^{3+}$  system with a high dissolution rate and electrolytic regeneration efficiency for SUS metal was selected. The selection of the medium was based on its dissolution behavior owing to the stability difference of Ce (IV) in a medium solution. A  $\text{HNO}_3$  medium was selected because the solubility of cerous nitrate is much larger than the solubility of cerous sulphate and the formation of Ce hydroxide / oxide precipitate even at a low  $\text{H}_2\text{SO}_4$  concentration. In addition, the experimental range for the concentration of nitric acid was selected to be 2-3 M, taking into consideration the criterion that the redox potential of  $\text{Ce}^{4+} - \text{Ce}^{3+}$  couple is the highest (Ce solubility = 710 g / L in 2-3 M  $\text{HNO}_3$ ).

The dissolution of the oxide was continued for up to 8 h regardless of the  $\text{HNO}_3$  concentration at a 0.1 M Ce (IV) concentration, as shown in Fig. 1. On the other hand, at a 0.5 M Ce (IV) concentration, it is considered that the dissolution of the base metal started at this time from the result of the abrupt weight loss after 6 h of decontamination.

From these results, the decontamination condition for dissolving only the oxide requires a Ce (IV) concentration of 0.5M or more, and a decontamination time of about 6 h in the decontamination composition of 1-2 M HNO<sub>3</sub> and 0.5M Ce (IV).

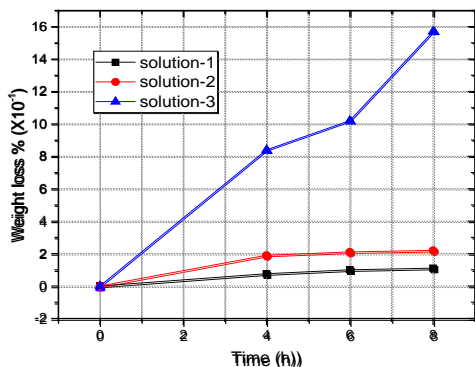


Fig. 1. Weight loss % for the FeCr<sub>2</sub>O<sub>4</sub> specimens in the decontamination solution of (1) 1M HNO<sub>3</sub> & 0.1M Ce(IV), (2) 2M HNO<sub>3</sub> & 0.1M Ce(IV), (3) 2M HNO<sub>3</sub> & 0.5M Ce(IV).

This decontamination behavior can be clearly confirmed from the photograph of the surface of the specimen shown in Fig. 2. It shows the results of observing the surface morphology after decontamination at various HNO<sub>3</sub> and Ce (IV) concentrations for corrosion-oxidized specimens having the above chemical composition. The oxide film appeared black before decontamination, but turned greenish as the decontamination time elapsed. From the results, the oxide outer layer was composed of Fe<sub>3</sub>O<sub>4</sub> and the inner layer was mainly composed of Cr<sub>2</sub>O<sub>3</sub>. According to Carter et al., the corrosion oxide film formed on the surface of SUS 304 in EDTA solution is reported to form Fe<sub>3</sub>O<sub>4</sub> and Cr<sub>2</sub>O<sub>3</sub> [2].

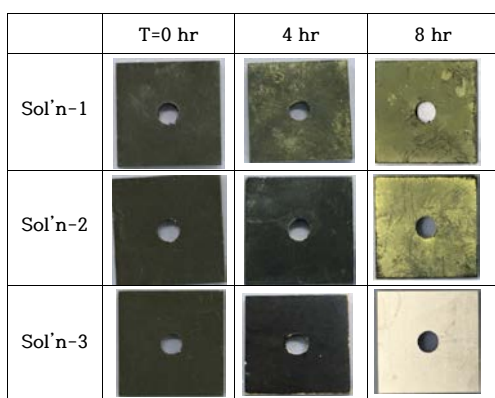


Fig. 2. Optical results on FeCr<sub>2</sub>O<sub>4</sub> in the decontamination solution of (1) 1M HNO<sub>3</sub> & 0.1M Ce(IV), (2) 2M HNO<sub>3</sub> & 0.1M Ce(IV), (3) 2M HNO<sub>3</sub> & 0.5M Ce(IV).

### 3. Conclusions

Prior to confirming the decontamination performance of a foam decontaminating agent, a study was conducted to optimize the composition of the chemical decontaminating agent available for foam decontaminating agent. The following conclusions were obtained.

At lower concentrations of 0.1 M Ce (IV), the amounts of Fe and Cr dissolved increased by 25% and 67%, respectively, as the HNO<sub>3</sub> concentration was doubled, whereas the amounts of Fe and Cr dissolved were increased at higher concentrations of Ce (IV) by 2.6- and 1.3-fold, respectively.

Therefore, it seems to be possible to use it as a chemical decontamination agent necessary for optimizing foam decontamination composition which is effective in reducing liquid waste.

### ACKNOWLEDGEMENTS

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### REFERENCES

- [1] I. Penfold, R. K. Tucker, and J. Zhang, *Langmuir* 21 10061 (2005).
- [2] J.H. Carter, "Corrosion and passivation studies on PWR primary materials to reduce corrosion product activity", *Nucl. Energy* 24 (1985).