

## Dissolution of Iron Chromium Oxide Using Foam Decontaminating Agent

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### 1. Introduction

As part of the development of a foam decontaminating agent having characteristics capable of significantly reducing the waste liquid generated during decontamination, and after optimizing the composition of the chemical decontaminating agent available for the foam decontaminating agent, the decontamination performance of a foam decontaminating agent mixed with a chemical decontaminating agent has been investigated [1].

Radioactive corrosion oxides in pressurized light water reactors consist of an inner layer formed of crystals of Fe, Ni and Cr ions developed through the oxidation of a metal element at the interface between the oxide film and metal, and an outer layer formed through diffusion into 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 into soluble  $\text{Cr}^{6+}$  [2].

To confirm the decontamination performance of three kinds of foam decontaminating agents varying in terms of the concentration of Ce (IV) and  $\text{HNO}_3$  which are the main components of an oxidizing chemical decontamination agent, and fixing the formulation of the foaming 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 at 800 ppb using  $\text{N}_2$  gas.

Three types of foam decontaminating agent 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 and

the fixing formulation of the foaming agent (1% v/v TBS surfactant + 1wt% M-5 silica nanoparticles).

75 ml of foam decontaminating agent using 25 mL of chemical decontamination solutions and 50 mL of  $\text{N}_2$  gas were prepared by mixing appropriate amounts of chemicals in accordance with the concentrations of Ce (IV) and  $\text{HNO}_3$  in the fixed foaming agent. For a comparison of the decontamination performance, 75 ml of chemical decontaminating agent was prepared. 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) measurements were taken 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 (AAnalyst 400, PerkinElmer).

Table 1. 3 types of foam decontaminating agents and solution decontaminating agent

Type	Foaming agent	Chemical decontaminating agent
Solution decontamination	1% v/v TBS & 1wt% M5	2M $\text{HNO}_3$ & 0.5M Ce(IV)
Foam -1	1% v/v TBS & 1wt% M5	2M $\text{HNO}_3$ & 0.5M Ce(IV)
Foam -2	1% v/v TBS & 1wt% M5	1M $\text{HNO}_3$ & 0.5M Ce(IV)
Foam -3	1% v/v TBS & 1wt% M5	2M $\text{HNO}_3$ & 0.2M 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 2-3M, taking into consideration the criterion in which the redox potential of the  $Ce^{4+} - Ce^{3+}$  couple is the highest (Ce solubility = 710 g / L in 2-3 M  $HNO_3$ ).

Based on the analysis results of weight loss over time, as shown in Fig. 1, it can be seen that Ce concentration has more influence on the decontamination behavior than  $HNO_3$  concentration, and a Ce(IV) concentration above 0.5M is needed. Comparing the decontamination behavior of the solution decontamination method with the foam decontamination method for 8 h using the same chemical agent, the removal efficiency of the foam decontamination represents about 85% of the solution decontamination, showing a more effective decontamination performance than expected.

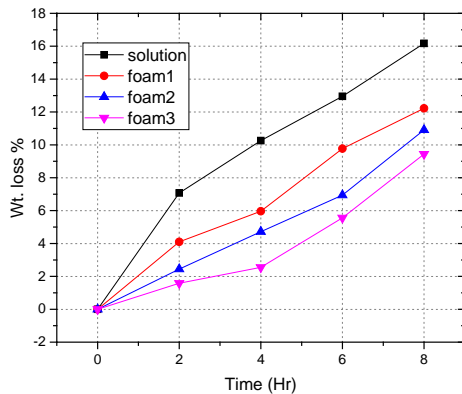


Fig. 1. Weight loss % for the  $FeCr_2O_4$  specimens in the decontamination solution of 2M  $HNO_3$  & 0.5M Ce(IV), decontamination foam-1 of 2M  $HNO_3$  & 0.5M Ce(IV), decontamination foam-2 of 1M  $HNO_3$  & 0.5M Ce(IV), and decontamination foam-3 of 2M  $HNO_3$  & 0.2M Ce(IV).

This decontamination behavior can be clearly confirmed from the optical observation of the surface of the oxide specimen shown in Fig. 2. As a result of the analysis, it was confirmed that after the decontamination for 8 h, the oxide film formed on the specimen by the solution decontamination method and the foam decontamination method was all removed and the corrosion of the base metal started.

In the case of decontamination using the chemical solution, most of the contaminated oxide film was removed for 2 h after decontamination, and the weight loss was 7%. Based on this value, the time required for most of the contaminated oxide film to be removed in the foam decontamination process is about 4.5, 6.0, and 7.0 h for foam decontamination-1, foam decontamination-2, and foam decontamination-3, respectively.

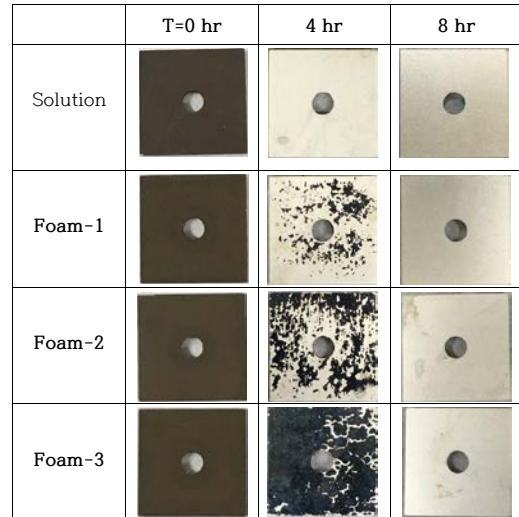


Fig. 2. Optical results on  $FeCr_2O_4$  in the decontamination solution of 2M  $HNO_3$  & 0.5M Ce(IV), decontamination foam-1 of 2M  $HNO_3$  & 0.5M Ce(IV), decontamination foam-2 of 1M  $HNO_3$  & 0.5M Ce(IV), and decontamination foam-3 of 2M  $HNO_3$  & 0.2M Ce(IV).

### 3. Conclusions

The decontamination performance of a foam decontaminating agent mixed with a chemical decontaminating agent was investigated as a part of the development of a foam decontaminating agent. The following conclusions were obtained.

At lower concentrations of 0.1M Ce (IV), the amounts of Fe and Cr dissolved increased by 25% and 67%, respectively, as the  $HNO_3$  concentration was doubled, whereas the amounts of Fe and Cr dissolved were increased at higher concentrations of 0.5M Ce (IV) by 2.6- and 1.3-fold, respectively. It can be seen that the Ce (IV) concentration, rather than the nitric acid concentration, plays an important role in the dissolution behavior. At a Ce (IV) concentration of 0.5M, high decontamination performance was obtained even at a relatively low concentration of 1M of nitric acid during the 6 h dissolution time.

### ACKNOWLEDGEMENTS

This work has been carried out under the Nuclear R&D Program (2012M2A8A5025655) funded by Ministry of Science, ICT & Future planning.

### REFERENCES

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- [2] I. Penfold, R. K. Tucker, and J. Zhang, *Langmuir* 21 10061 (2005).