Transactions of the Korean Nuclear Society Autumn Meeting
Goyang, Korea, October 24-25, 2019

Composition of Foaming Agents Containing Nanoparticles for Decontamination of Chromium-rich Oxides

Chong Hun Jung[a*], I. H. Yoon[a], W. K. Choi[a], S. B. Kim[a], B. K. Seo[a]

[a]*Korea Atomic Energy Research Institute,*
Decommissioning Technology Research Dept.
[*]*Corresponding author:nchjung@kaeri.re.kr*

1. Introduction

Decontamination foam is a non-stable, two-phase fluid with aqueous and gas phases representing 10% and 90% of the total volume, respectively. This can significantly decrease the amounts of the chemical reagents and secondary waste compared to chemical decontamination technology. It can be easily applied to facilities and equipment that are difficult for workers to access, due to its high structural complexity. However, in order to increase the relatively low decontamination coefficient, the contact time of the foam decontamination agent on the contaminated surface must increase [1]. The decontamination efficiency can be enhanced by improving the contact time between the chemical reagents and a contaminated surface through adding surfactants and silica nanoparticles into the decontamination foam [2].

In this study, the composition of foaming agents containing nanoparticles suitable for Ce-HNO_3 chemical reagents to decontaminate of chromium-rich radioactive oxide was investigated.

2. Methods and Results

2.1 Experimental Methods

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 [3]. Because the 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 Cr^{6+}. Therefore, it is necessary to derive a foaming agent that contains nanoparticles suitable for Ce-HNO_3 chemical reagents, in order to develop foam decontamination agents that are effective in removing corrosive oxides containing cerium.

The oxidizing decontamination agent should have a high oxidation state that is stable in acidic solution, has a fast dissolution rate for the metal to be decontaminated, and is easily regenerated. Therefore, a Ce^{4+} / Ce^{3+} system with a high dissolution rate and regeneration efficiency for SUS metals was selected. In addition, the medium was selected based on the medium's dissolution behavior of the due to the different stability in the Ce (IV) solution.

Since the solubility of cerium nitrate is much higher than that of cerium sulfate, and cerium precipitates at low H_2SO_4 concentration, the HNO_3 medium was chosen.

The formulation of 0.5M Ce (IV)-2M HNO_3 was chosen as the appropriate oxidizing agent composition, based on the HNO_3 concentration with the largest cerium redox potential and the differential pulse voltammetry results.

Nonionic surfactants (EM100), cationic surfactants (CTABr), and anionic surfactants (TBS, SDS) were used to investigate surfactants that are one of the components of foaming agents suitable for Ce-HNO_3 based decontamination agents (Table 1). After mixing and preparing the decontamination agents, foam stability experiments were performed using a Dynamic Foam Analyzer (DFA-100, KRUSS, Germany).

In addition, 1% of commercial silica SiO_2 (Sigma-Aldrich), M5 (Carbosil) and KAERI-produced silica nanoparticles (KAERI-1, KAERI-S, KAERI-Cal, KAERI-S-SE) was dispersed in Ce-HNO_3 decontamination agents to select nanoparticles suitable for foam stability.

Table 1. Types of chemical decontaminating agents

Name	Type	pH (1wt%)
EM-100 (LG Household & Health Care)	Non-ionic	10.5
TBS (Dupont)	Anionic	1.84
SDS (Sigma Aldrich)	Anionic	5.92
CTABr (Sigma Aldrich)	Cationic	3.79

2.2 Results & Discussion

Four types of surfactants were dispersed in 1M HNO_3 medium at a concentration of 1wt%, respectively, and the bubble stability was tested for about 2 hours.

The foam stability was shown in the order of TBS> M100> CTABr> SDS. Surfactants other than TBS tended to decay rapidly at approximately 1500 seconds.

The foam stability of the surfactant alone was relatively low in 1M HNO_3 media. Four types of surfactants were dispersed in 1M HNO_3 media with 1wt% silica nanoparticles (Sigma-Aldrich SiO_2), and the foam stability was measured for about 3 hours.

As shown in Fig. 1, the foams remained stable for EM-100 and TBS, while CTABr and SDS showed low foam stability that started to collapse within 2000 seconds.

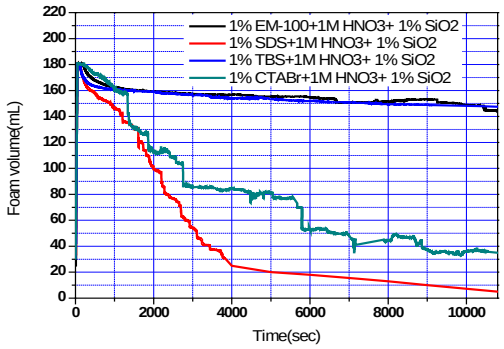

Fig. 1. Foam stability of various surfactants containing silica nanoparticles.

The decomposition property of the surfactant by Ce (IV) was investigated by adding a 1% surfactant to a 1M Ce / 1M HNO_3 solution using an absorbance meter. As a result, only SDS and TBS satisfied the degradation rate condition of less than 10% during the 6-hour contact time in which the surfactant can be reused twice.

However, since SDS has low foaming and foam stability, TBS was finally selected as a suitable surfactant for the Ce (IV) decontamination agent.

1 wt% of TBS, an excellent foam stability surfactant, was added to the Ce-HNO_3 decontamination agent and commercially available silica (Sigma-Aldrich SiO_2, Carbosil M5). In addition, silica nanoparticles prepared by KAERI's method (KAERI-1, KAERI-S, KAERI-Cal, KAERI-S-SE) were dispersed at a concentration of 1wt%, and foam stability experiments were performed.

As shown in Figure 2, the addition of Sigma SiO_2 and KAERI-1 remained very stable for 3 hours. On the other hand, when the synthesized silica nanoparticles KAERI-S-Cal and KAERI-S-SE were added, the foams collapsed after 5000 seconds and after 2000 seconds, respectively.

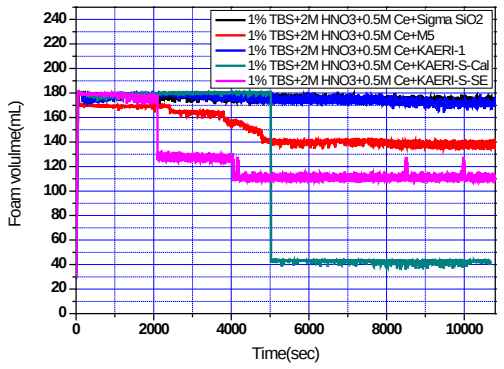

Fig. 2. Foam stability of the TBS surfactant in the foam of various nanoparticles.

Sigma SiO_2 and KAERI-1 showed very stable foaming behavior. However, KAERI-1 had a long synthesis time and a low yield, and Sigma SiO_2 had a high price as a commercial silica with high purity. Although foam stability is about 85% of Sigma SiO_2 and KAERI-1, it is inexpensive and considered more effective in improving foam stability by modifying M5. A modification of the commercial silica M5 surface was performed.

3. Conclusions

In this study, we formulated foam decontamination agent to remove Cr-rich corrosion oxide.

A foaming agent composition containing a surfactant and nanoparticles with excellent chemical stability and foam stability suitable for the Ce-HNO_3 decontamination agent was obtained.

ACKNOWLEDGEMENTS

The authors would like to express their appreciation to the National Research Foundation of Korea (NRF) for the award of a grant funded by the Ministry of Science and ICT of the Republic of Korea, in support of the authors' work through the Nuclear Research and Development Program (NRF-2017M2A8A5015144).

REFERENCES

[1] C. Dame, et al., Colloids Surface A, 263 210-218 (2005).
[2] L. Nunez, and M. Kaminski, US Patent 7,166,758 B2 (2007).
[3] R. S. Rodliffe, et al., Modelling the behavior of corrosion products in the primary heat transfer circuits of pressurized water reactors, IAEA Report TECDOC-429, Vienna, (1987).