Effect of Chemical Reagents in Foam Decontamination

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1. Introduction

Nuclear industry will have to meet the challenge of dismantling nuclear facilities the first-generation nuclear power plants. In the frame of the future dismantling of nuclear facilities, the foam decontamination process has been assessed as an alternative technique to liquid decontamination. Because decontamination foam is a unstable two phase fluid with the aqueous phase representing not more than 10% of the total volume, it decrease the amount of chemicals used during the decontamination processes and the secondary nuclear waste volume [1]. Moreover using foams allows the decommissioning of complex shaped facilities. The decontamination foam comprises at least one surfactant to generate the foam and one or more chemical reactants to achieve the dissolution of the contaminants at the solid surface. In order to improve the efficiency of decontamination foam, the present study attempts to find the optimum condition of chemical reagents to the foaming solution.

This paper deals with understanding the effects of chemical reagents involved in foam decontamination efficiency, evaluation of side effect on foam stability and finally the improvement brought by formulation science.

2. Materials and Methods

In this section some of the experimental reagents, instrument, methods, procedures and results are described.

2.1 Reagents and Instruments

Non-ionic surfactant, Elotant[TM] Milcoside 100 is a C8-10 alkyl polyglucoside supplied by LG Household & Health Care in the Republic of Korea. Fumed silica (M-5, Cabosil) was used as a nanoparticle and M-5 is stable in an acidic medium. The specimen size were normally 20mm x 20mm x 1.5mm plate type of carbon steel, aluminum, stainless steel 304, inconel 600 and cupper material specimen were used for the metal corrosion test in nitric and/or phosphoric acid solution.

Dynamic Foam Analyzer, KRUSS Co. (Model: DFA100, Germany), Electric Balance (Mettler Co, Model: TOLEDQ) and Radiation Survey Meter LB 123 Umo (Berthold Co. Germany, β-γ contamination monitor) were used for analysis.

2.2 Metal Corrosion Test in Acid Solution

Laboratory specimen immersion tests were conducted simple procedure in our laboratory. The weight of specimen was measured within 0.0001g. The specimens were immersed in 0.5M, 1.0M, 1.5M, 2.0M, 3.0M nitric acid or phosphoric acid and the mixture solution of nitric and phosphoric acid. The specimens were weighed after water cleaning to determine the general corrosion weight loss measurements in each solution. The tests were conducted in 100 mL glass bottles with screw caps.

Weight loss percent = (initial weight - final weight)/ (initial weight) x100

Nitric acid is strongly oxidizing and attacks most metals but due to its powerful oxidizing nature, it promotes the resistance of stainless steel to corrosion. Generally stainless steels are resistant to corrosion in nitric acid over a wide range of concentration and temperature. The helpful oxidizing properties of nitric acid are used in the chemical "passivation" of stainless steels. Stainless steel is resistant to corrosion, difficult to treat, needs a strong decontamination process to remove several *μ*m. Carbon steel is quite porous and low resistance to corrosion, needs a soft process but the contamination depth reaches several thousand *μ*m.

There are some consideration parameters for the selection of a decontamination process [2]. The parameters are type of plant and plant process, operating history of the plant, type of components (pipe, tank), type of material (steel, Zr, concrete), type of surface (rough, porous, coated), type of contaminants (oxide, crud, sludge), composition of the contaminant (actinides, lanthanides), ease of access to area/plant (internal or external contaminated surface), decontamination factor required, destination of the components after decontamination, time required for application, capability of treatment and conditioning of the secondary waste generated.

Nitric Acid Corrosion Mechanism

The nitric acid corrosion mechanism has been studied for many years. Although the anodic reaction is fairly simple, iron being oxidized to ferrous cation (Fe^{2+}), there are a number of cathodic reactions that occur in process. The cathodic reduction of nitric acid likely proceeds in five steps [3]:

$$H_+ + e^- = H \qquad (1)$$
$$HNO_3 + H + e^- = NO_2 + H_2O \qquad (2)$$
$$NO_2 + e^- = NO_2- \qquad (3)$$
$$H_+ + NO_2^- = HNO_2 \qquad (4)$$

$$HNO_2 + H = NO + H_2O \qquad (5)$$

The nitrous acid (HNO_2) that was formed in step (4) regenerates NO_2 by an interaction with the nitric acid:

$$HNO_2 + HNO_3 = 2NO_2 + H_2O \quad (6)$$
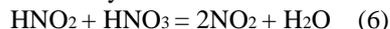
Thus the reaction becomes autocatalytic. Ammonia salts are also formed during the cathodic reaction. The ammonia salts decompose to form N_2 and NOx compounds by the following reactions.

$$NH_4NO_2 = N_2 + 2H_2O \qquad (7)$$
$$NH_4NO_3 = N_2O + 2\ H_2O \qquad (8)$$

Thus formation of NO_2, NO, N_2O and N_2 (i.e., a brown gas should be emitted) due to the cathodic reaction is expected. Iron differs from many metals in that the corrosion rate increases with acid concentration, up to approximately 6 M, and then decreases dramatically. The corrosion rate in 1 M nitric acid at 25 C is approximately 2 inches per year. The corrosion rate increases to a maximum of approximately 13 inches per year at 6 M nitric acid. However, at higher concentrations a passive ferric oxide film forms on the surface and corrosion rate is reduced significantly. At 15 M nitric acid the corrosion rate is 0.02 inches per year. Unless the ferric oxide film is disturbed, (i.e., mechanically ruptured or reduced), the carbon steel surface will remain passivized.

2.3 The Effect of Chemical Reagents on Foam Ability and Foam Stability

Two of the most important factors in foaming a liquid are how easily it foams (its foam ability) and its stability[4~5]. Foamability is the foam generating power of a liquid and foam ability is directly linked to physical factors such as viscosity, surface tension, and others within the liquid. As a result of coexistence of chemical reagent (in this case, 1.5M HNO_3 solution), foam ability increases with increasing the concentration of surfactant concentration from 1% to 10%. Once a liquid has foamed, its stability involves the factors that lead to its breakdown and collapse. The rate of deterioration of liquid foam depends on the relative activities of three interactive physical phenomena, gravitational separation (drainage), flocculation and coalescence, and Ostwald ripening (disproportionation). Foam stability also increases with increasing the concentration of surfactant concentration from 1% to 10%. Chemical factors that affect foam stability generally are classified into two categories, those that are hydrophobic and foam a viscoelastic adsorbed layer at the gas/liquid interface, imparting both resistance to rupture and retardation of disproportionation, and those (generally high molecular weight materials) that are hydrophilic, do not have a strong capacity to adsorb at surfaces, but that increase the viscosity of the continuous phase and strongly retard gravitational separation.

2.4 Carbon Steel Corrosion Test

Fig. 1 is the Photographs of metal corrosion test in (A) carbon steel - HNO_3 system and (B) carbon steel -

H_3PO_4 system at room temperature. This figure shows the carbon steel specimens that were immersed in various different acid concentrations.

| 0.5M | 1.0M | 1.5M | 2.0M | 3.0M |

(A): Corrosion test in carbon steel - HNO_3 system

| 0.5M | 1.0M | 1.5M | 2.0M | 3.0M |

(B): Corrosion test in carbon steel - H_3PO_4 system
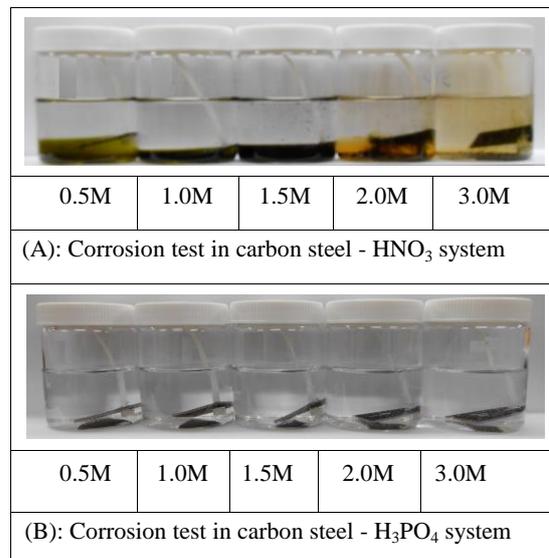
Fig. 1. Photographs of metal corrosion test.
(A) Carbon steel - HNO_3 system
(B) Carbon steel - H_3PO_4 system

The carbon steels corrosion test in nitric acid solutions, the concentration of nitric acid increasing leads to a violent dissolution of carbon steel in room temperature. The corrosion solubility percent of carbon steel in nitric acid solution is higher than in phosphoric acid solution (Fig. 2~Fig. 3).
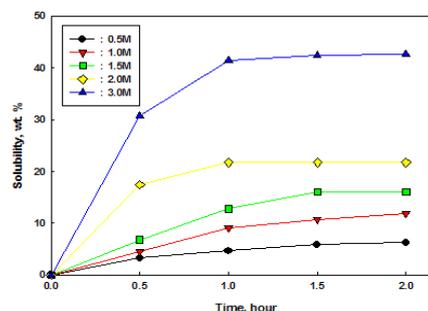
Fig.2. Corrosion test of carbon steel in HNO_3 solution.
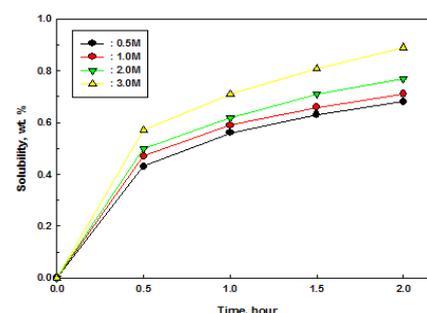
Fig. 3. Corrosion test of carbon steel in H_3PO_4 solution.

2.5 Foam Decontamination Application in Radio-
logically Contaminated Surface

Bench-scale testing was used to evaluate the efficacy of three decontamination formulations on contaminant carbon steel component of dry oven. Fig. 4 shows radioactivity measurement result three times successive decontamination test. Fig. 5 shows decontamination factor was in the range of 6.1~13.4. Results suggest that our foam formulations have a feasibility potential to removal of about 83~93% total radioactivity in contaminant.
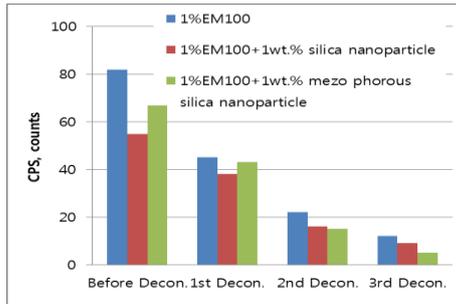
Fig. 4. Decontamination test of carbon steel surface of the dry oven component contaminated with radioisotope (Co-60) using different several foam formulations
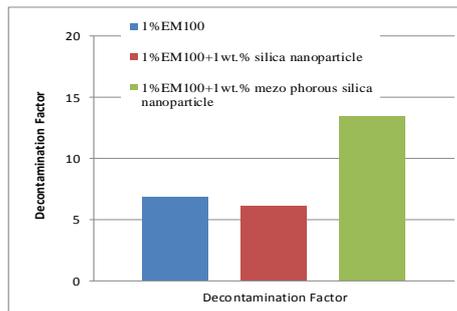
Fig. 5. Decontamination factors of carbon steel surface of the dry oven component contaminated with radio-isotope using different several foam formulations.

3. Conclusions

Basic experiments using the nanoparticle-based complex fluid decontamination foam have been performed in order to development of decontamination foam technology. Results show that in the case of co-existence of chemical reagents, for the purpose of the good foam ability and foam stability, it is necessary to increase the concentration of surfactant. In corrosion test, metal materials including carbon steel, stainless steel 304, aluminum, inconel 600 and cupper, generally corrosion solubility percent in nitric acid solution were higher than in phosphoric acid solution. Bench-scale testing was used to evaluate the efficacy of three decontamination formulations on contaminant carbon steel component of dry oven. The results shows decontamination factor was in the range of 6.1~13.4. Results suggest that our foam formulations have a

feasibility potential to removal of about 83~93% total radioactivity in contaminant.

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