Effect of Cerium(IV) – Surfactant Reaction in Foam Decontamination

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1. Introduction

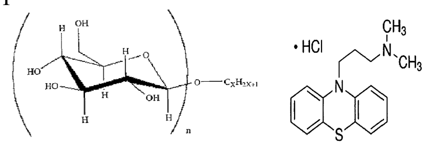
Nuclear industry will have to meet the challenge of dismantling nuclear facilities the first-generation nuclear power plants. In the frame of the future dismantling of nuclear facilities, the foam decontamination process has been assessed as an alternative technique to liquid decontamination. Because 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 in the decontamination process and the secondary nuclear waste volume [1-2]. 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. The corrosion rate of radioactive nuclides contaminated stainless steel metal is very important factor for the foam decontamination process.

The goal of this study is to develop the decontamination process for contaminated stainless steel in medium of nitric acid – Ce(IV) ion solution. Stainless steel needs a strong oxidizing agent such as Ce(IV) ion and the effects of cerium(IV) – surfactant interaction involved in foam decontamination and finally the improvement brought by formulation science.

2. Methods and Results

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 and sodium dodecyl sulfate (SDS, Sigma-Aldrich co.) surfactant was used as an anionic surfactant compound [Fig 1]. Fumed silica (M-5, Cabosil) was used as a nanoparticle and M-5 is stable in an acidic medium. Sulfuric acid, ammonium cerium(IV) nitrate($(NH_4)_2Ce(NO_3)_6$), promazine hydrochloride (PMH, 10-(3-dimethylaminopropyl) phenothiazine hydro chloride) were Sigma-Aldrich reagents. All solutions were prepared using deionized water obtained with a Milli-Q water system. The coupons size of stainless steel 304 coupons were normally 20mm x 20mm x 1.5mm plate type and it was used for the metal corrosion test in nitric acid solution. Uv-vis scanning spectrophotometer (HACH, model: DR 5000) was used for Ce(IV) ion concentration analysis and Electric Balance (Mettler Co, model: Topedq) was used for measurement of stainless steel 304 coupons in corrosion test .



(A) (B)

Fig. 1. The structure of (A) Alkyl polyglucoside and (B) Promazine hydrochloride (PMH)

2.2 Determination of Cerium(IV) Concentration

An aliquot of the stock solution containing 12.5-525 µg of Cerium(IV), 5ml of 5M sulfuric or phosphoric acid, and 2.5ml of 0.2% PMH solution were taken in a 25ml volumetric flask, and the solution was diluted to the mark with distilled water. The flask was shaken and the absorbance was measured at 505 nm against a corresponding reagent blank prepared in the same manner. The amount of cerium was then deduced from the calibration curve [3].

2.3 *Dissolution test of stainless steel 304 coupons in Ce(IV)-nitric acid mixture and in HNO_3 solution.*

Decontamination of stainless steel-304(SUS-304) contaminated with radionuclides by nitric acid is very difficult to meet the requirement of regulations in the room temperature condition [4-7].

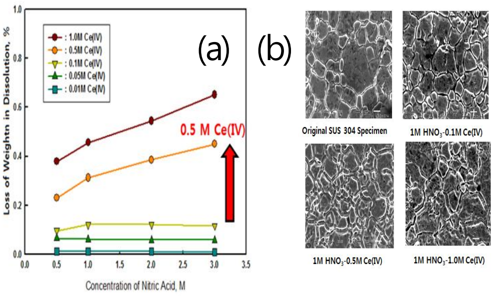


Fig. 2. (a) Dissolution test of SUS-304 in Ce(IV)-nitric acid mixture and in HNO_3 solution. (b) SEM Photographs of SUS 304 coupon after corrosion test.

To increase the dissolution rate of oxide formed on the stainless steel in nitric acid solution and addition of Ce(IV) in nitric acid are necessary to enhance the dissolution rate of stainless steel. Fig. 2 shows the Ce(IV) in nitric acid is an effective chemical decontamination material, since it is possible to get the higher decontamination factors within a few hours.

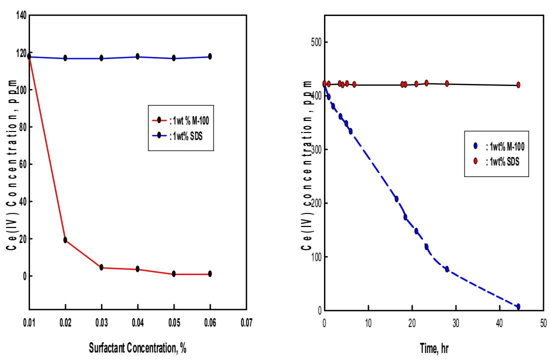
Cerium(IV) is a strong oxidizing agent (E_0 = 1.6 volts in 4M HNO_3) and can efficiently oxidise the constituent of stainless steel as following redox chemical reactions[1]:

$$3Ce^{4+} + Fe = Fe^{3+} + 3Ce^{3+}$$
$$2Ce^{4+} + Ni = Ni^{2+} + 2Ce^{3+}$$
$$6Ce^{4+} + Cr = Cr^{6+} + 6Ce^{3+}$$

In general contamination gets extended up to depth of 10 to 12 micron from surface. Removal of this thickness of layer can result in overall effective decontamination. The rate of metallic corrosion depends on the concentration of ceric ion, nitric acid as well as temperature. To maintain a uniform corrosion rate, it is required to regenerate the reduced Ce^{3+} into the Ce^{4+} state during the decontamination. Ce^{4+} can be easily regenerated either by electro oxidation or by chemical oxidation employing ozone. The process of oxidation by ozone gas is relatively simpler and amenable to online conversion.

2.4. Chemistry of Redox reaction between Ce(IV) and Surfactants

The nitric acid - Ce(IV) decontamination process could be applied into nuclear facilities. Unfortunately, we found the redox interaction reaction between Ce(IV) ions and M-100 surfactant. Competitive reaction between Ce(IV) – surfactant and Ce(IV) - stainless steel material reduces the effectiveness of the foam decontamination [Fig 3].



(A) (B)

Fig. 3. Redox interaction reaction between Ce(IV) - surfactant M-100 and Ce(IV) – surfactant SDS.
: (A) Variation of surfactant concentration.
: (B) Variation of time.

But, Ce(IV)- SDS has no effects on the degradation of anionic surfactant.

3. Conclusions

Foam decontamination process technique is available to decontamination large internally contaminated component with complex shapes nuclear facilities. The formulation of foams loaded with strong oxidizing reagents such as Ce(IV) is an important factor. The enhanced decontamina- tion properties of nitric acid with Ce(IV) additive on stainless steel is well known in liquid mediums. stainless steel metal is an important aspect in the foam decontamination process. Unfortunately, Ce(IV) ion is transformed into Ce(III) by reaction with not only the M-100 surfactant but also stainless steel in our case. To solve this problem, we recommend SDS surfactant instead of M-100 surfactant for the stainless steel decontamination.

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