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Dry Decontamination of Surrogate Specimens by PFC

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Abstract: Decontamination of metal specimens loosely contaminated with Eu2O3 particles was performed in a mixed solution of PFC (Perfluorocarbon) and anionic surfactant by applying ultrasonic waves. The remaining portion of particles decreased with the increase of the surfactant concentration. The decontamination behavior was explained by electrostatic interaction between the carboxylic group of the surfactant and the surface charge of the contaminant particles. Eu2O3 particles on metal specimens were contaminated with Cs-137 and Co-60, and the specimens were decontaminated with PFC solution. Decontamination factors were in a range from 9.6 to 62.4. Spent PFC solutions were recycled through distillation and filtration. The PFC solution showed good decontamination performance irrespective of the number of distillations. 97 % of the PFC was recycled without loss of decontamination efficiency.

Introduction

Chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs) having potential to deplete the ozone layer should be replaced with alternative compounds that do not deplete the ozone layer or affect global warming [1]. PFCs are extremely stable compounds with unique physical and chemical properties that make them usefully suited for certain specialized applications. The major applications of PFCs are: (1) semiconductor manufacturing processes [2], (2) fire suppression agents [3], (3) precision cleaning solvents [4], (4) heat transfer fluids or coolants [5], and (5) atmospheric tracers [6]. It is also noted that the aluminum–smelting process is a major generation source of CF_4 and C_2F_6 in industrial applications [7].

The Sonatol process was developed under a contract with DOE [8]. The Sonatol process uses ultrasonic agitation in fluorinated surfactant solutions to remove radioactive particles from surfaces. Filtering the suspended particles allows the solutions to be reused indefinitely. The Sonatol process was applied to the decontamination of heterogeneous legacy Pu-238 waste which exhibits excessive hydrogen gas generation, that prevents transportation of the waste to the Waste Isolation Pilot Plant.

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The Korea Atomic Energy Research Institute is developing dry decontamination technologies applicable to the decontamination of highly radioactive surfaces loosely contaminated with radioactive particles. The developed technologies are foam decontamination, laser decontamination, clay covering decontamination, sand blasting and dry ice blasting decontamination. As a part of the project, PFC ultrasonic decontamination technology development has been performed.

The main objective of the present study is to evaluate the ultrasonic decontamination efficiency of surrogate type 304 stainless steel specimens in PFC solution as an ultrasonic medium. Feasibility study on the reuse of PFC solution by distillation and filtration was also performed.

Experimental

Reagents

The PFC solution used in this study was perfluoroheptane (PF-5070, 3M). Table 1 shows the physical properties of perfluoroheptane and water. Anionic fluorinated surfactant (Krytox, DuPont Co.) containing the carboxylic group on the terminal fluoromethylene group of poly(hexafluoropropylene oxide) was mixed with perfluoroheptane solution and mixture was used as ultrasonic medium. Eu_2O_3 powders (99.9 % purity, Merck Co.) were used as received.

Table 1. Physical Properties of PFC and Water.

	Water	PFC- 5070
Molecular Formula	H_2O	C_7F_{16}
Molecular Weight	18	388
Boiling Point, !	100	80
Dynamic Viscosity, 10^{-6} m^2/s	1.06	0.55
Surface Tension, dyne/cm	73	13
Latent Heat, kJ/kg	539	80
Specific Heat, kJ/kg.K	4.2	1.1
Density, g/cm^3	1.0	1.7

Diameter of ceramic membrane (Sterilite Co.) was 47 mm and pore size was 0.2 mm. For filtration tests, 0.3 mm a-Al_2O_3 powders were used.

Decontamination of surrogate specimens

After weighing of the specimen, it was contaminated with alcohol containing Eu_2O_3 powder and fluorescent material, dried in a shaded place, and photographed. Sample was weighed again and dipped into the PFC ultrasonic decontamination chamber. Schematic diagram of the PFC ultrasonic decontamination test equipment is shown in Fig. 1. PFC ultrasonic decontamination medium was a mixture of perfluoroheptane and anionic surfactant. The frequency of the transducer was 28 KHz and the power was 30 W. Decontamination was performed in dual mode, one static and the other rotation mode. After 5 mins' ultrasonic application, the specimen was pulled out dried

and weighed again. To investigate the decontaminated surface, it was photographed again. In separate tests, the specimens loosely contaminated with Eu_2O_3 were radioactively contaminated with a radioactive solution containings Co-60 and Cs-137 radio-isotopes. These were then decontaminated in the PFC ultrasonic decontamination chamber. Before and after decontamination, the radioactivity of specimens was measured by MCA (Multichannel analyzer, Canberra Co.). The FT-IR spectra of the PFC solution containing anionic surfactant were obtained by FT-IR spectrometer (Model MB-102, Bomem Co.). The UV spectra on the PFC solution containing anionic surfactant were obtained by UV spectrometer (Model: DR 5000, Hach Co.).

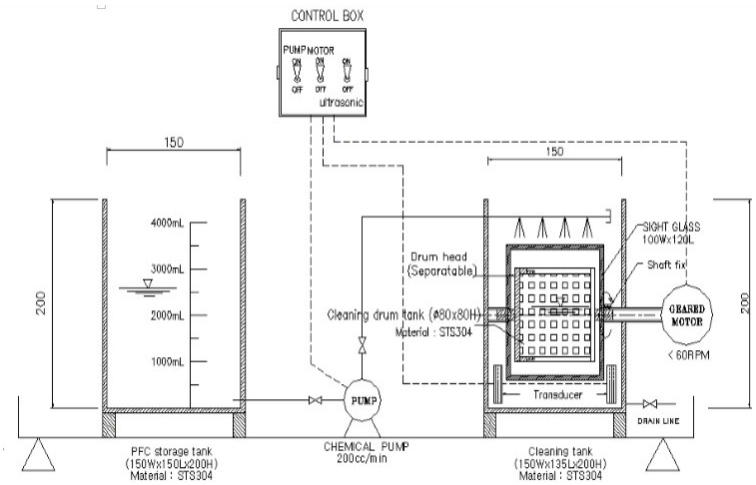

Figure 1: Schematic Diagram of Ultrasonic Decontamination Equipment.

Recycling of decontamination agent and filtration characteristics

After multiple applications of PFC solution, the solution containing Eu_2O_3 powders and fluorescent material was distilled. Before and after distillation, the turbidity of the solution was measured (Model, DRT 15-CE HF Scientific, Inc.). For the filtration tests, a stirred cell (Model 8050) was used. Disc type membrane filters were positioned on the bottom of the cell. The maximum endurance pressure of the cell was 75 psi and the maximum volume was 50 ml. For effective filtration tests, the flow rate of PFC solution through the membrane in the cell was controlled using N_2 gas.

Results and Discussion

Decontamination of surrogate specimens

Decontamination efficiency according to variation of ultrasonic media was investigated. A rectangular type metal specimen (4 cm X 1.5 cm X 0.1 cm) was used as a surrogate contaminated specimen. Fig. 2 shows a plot of the remaining portion of contaminants against the application time. For all three solutions, most contaminants were removed in an early stage of ultrasonic application. The portion of contaminants remaining after

5 mins' application decreased from 5 % and 2 % to 0.5 % as the ultrasonic media changed from water and PFC to PFC + 0.1 vol% surfactant solution.

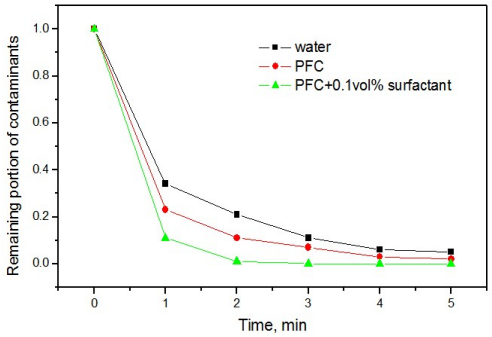

Figure 2: Remaining Portion of Contaminants According to Application Time for Three Kinds of Solutions.

Fig. 3 shows a plot of the remaining portion of contaminants against the surfactant concentration. For all three kinds of specimens, the portion of contaminants remaining after 5 mins' application decreased with increase of the surfactant concentration.

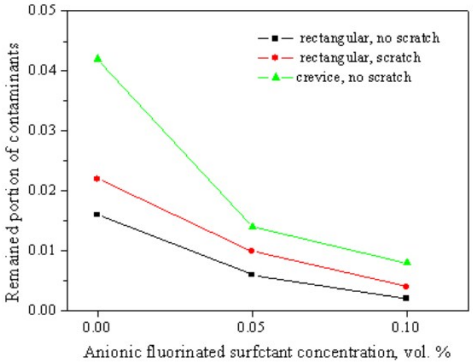

Figure 3: Remaining Portion of Contaminants according to Surfactant Concentration.

Fig. 4 shows the FT-IR spectra of PFC and PFC+ surfactant mixed solutions. In the spectrum in (b), we can see the carboxyl groups at wave numbers of 3000 and 1750 cm-

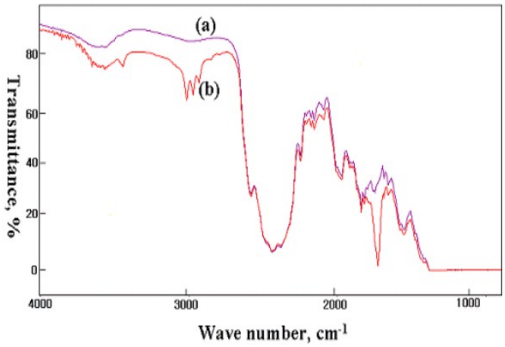

Figure 4: FT-IR Spectra, (a) Pure PFC, (b) PFC + 2 vol% Surfactant.

Fig. 5 shows a plot of surface potential against pH in aqueous solution of KCl. Surface potential of metal oxide varies with change of solution pH [9]. From the measurement of the zeta potential of Eu_2O_3 in an aqueous solution, we found that the surface potential of Eu_2O_3 powder has a positive value in the decontamination condition.

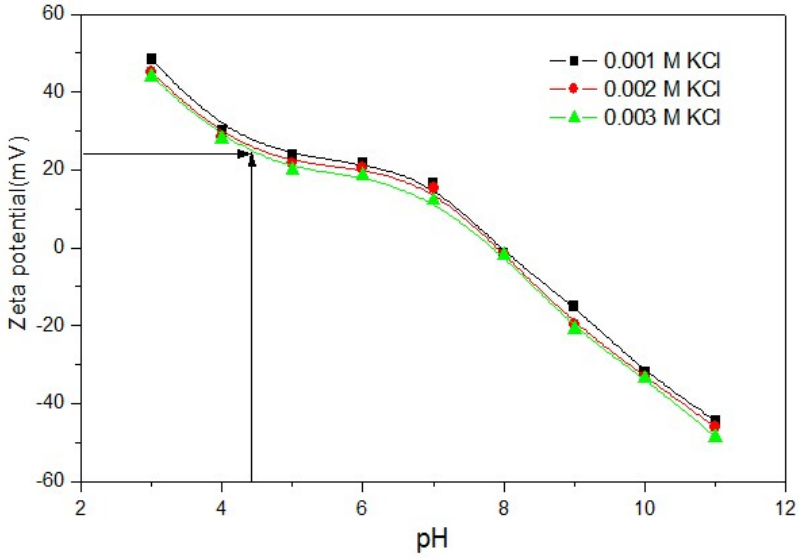

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Figure 5: Variation of Zeta Potential of Eu_2O_3 with pH in Aqueous Solutions of KCl, 0.15g Eu_2O_3/L (PFC Solution pH = 4.5).

Fig. 6 shows a plot of the adhesive force between Eu_2O_3 and the Si wafer under three different conditions. The difference of decontamination efficiency between pure PFC and PFC + surfactant solution is explained by interaction between the positively charged Eu_2O_3 powders and the carboxylic group of anionic surfactant in PFC solution. The adhesive force between the positively charged Eu_2O_3 powders decreases significantly with the addition of surfactant. From the test results, the addition of surfactant to PFC solution is necessary for the effective removal of contaminant particles.

Table 2 lists the decontamination factors and radioactivity of the surrogate specimens before and after PFC decontamination (PFC + 0.1 vol % surfactant). Decontamination factor (DF) is described in the following equation;

$$\mathrm{DF} = \frac{Radioactivity\ before\ decontamination}{Radioactivity\ after\ decontamoination} \quad (1)$$

For the test specimens, the order of DF is no scratch > linear scratch > cross line scratch. Decontamination factors are in the range of 9.6 to 62.4. Decontamination efficiency becomes low when the surface is rough. It was considered that the radioisotopes were removed with the Eu_2O_3 particles.

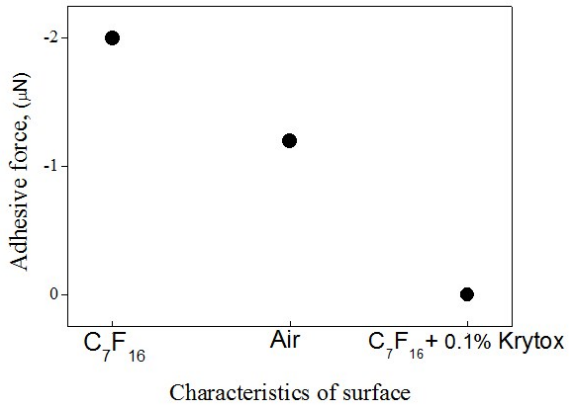

Figure 6: Adhesive Force, Measured on Si Wafer in PFC, Air and PFC + Surfactant.

Table 2. Radioactivity and Decontamination Factors.

Specimen		Radioactivity,Bq/1000cm^2 Before	After	D.F.
Disc, No Scratch	Co-60	872.4	20.3	43.1
	Cs-137	832.5	10.1	62.4
Disc, Linear Scratch, Depth: 0.1 mm	Co-60	732.4	49.6	14.8
	Cs-137	942.2	53.4	17.6
Disc, Cross line Scratch, Depth: 0.1 mm	Co-60	931.5	69.6	15.4
	Cs-137	821.3	85.6	9.6

Recycling of decontamination agent and filtration characteristics

Figure 7 shows the variation of turbidity of PFC solution under various particle sizes of Al_2O_3 (0.05g/L). As a result of multiple applications, PFC solution becomes dirty. The contaminants were satisfactorily removed from the decontamination solution irrespective of the particle size. The contaminants in the solution are removed by distillation and the solution can be recycled. After seven distillations, the turbidity of the PFC solution was almost the same as that of the original solution. It was found that more than 97 % of the PFC had been recovered by distillation.

Figure 8 shows UV spectra on the PFC decontamination solution. When the surfactant is in the PFC solution, the absorption peak near 210 nm directly increases with the increase of the surfactant concentration. It was found that the surfactant is also not in the distilled PFC solution.

Figure 9 shows the permeate volume of surrogate particulate solution through the ceramic filter against time. The flux increases with the increase of applied pressure. The flux, however, does not reach the maximum value. This characteristic is explained by the formation of cake on the surface of the ceramic filter [10,11]. The cake increases the filtration resistance. Ceramic filters show higher filtration efficiency with low permeate volume, however, ceramic filters can break during testing and their cost is high. In comparison with polymeric filters, ceramic filters are highly stable against radioactivity, which generates H_2 gas in alpha radioactive environment.

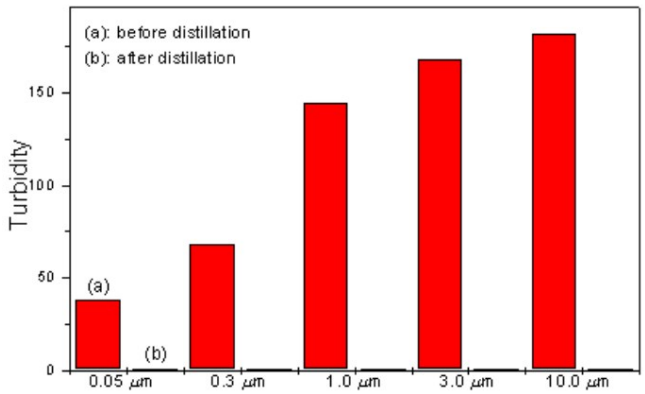

Figure 7: Turbidity of PFC Solution and Particle Size of Al_2O_3.

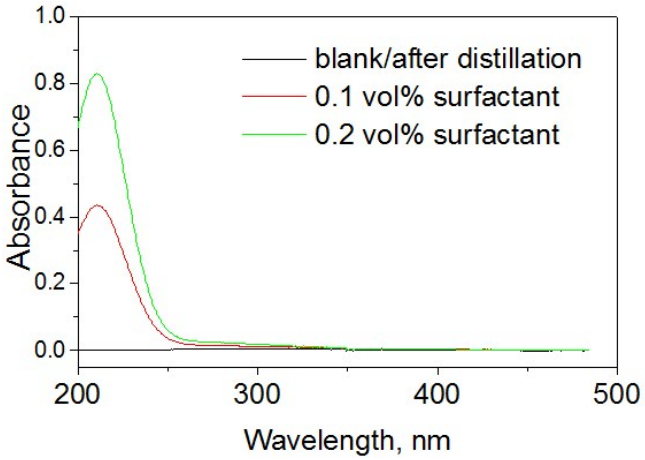

Figure 8: UV Spectra of PFC + Surfactant Solution.

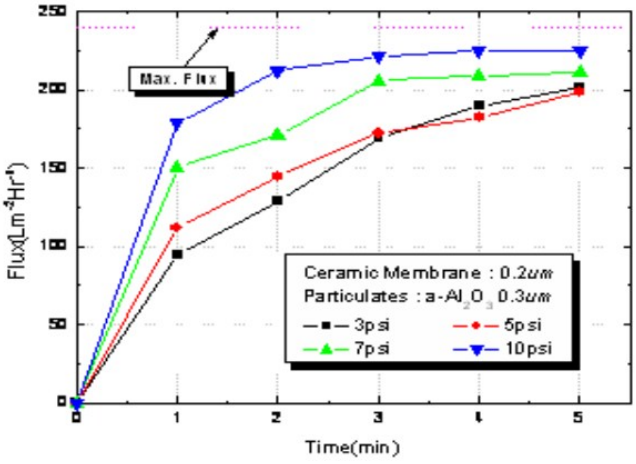

Figure 9: Permeate Volume of Surrogate Particulate Solution.

Conclusion

A study of PFC solution for decontamination of surrogate metal specimens using ultrasonic waves was performed. For all test specimens, we found that ultrasonic decontamination is satisfactorily applicable. The recycling of PFC solution by distillation makes the process more reliable. Also, oxide particles were easily removed by a ceramic filter. Decontamination work is performed with little loss of main decontamination agents. As the PFC solution is a non-conducting substance and easily separated from the contaminants, the PFC ultrasonic decontamination process is a promising method to decontaminate metal specimens loosely contaminated with radioactive particles. Based on the test results, we are developing the decontamination process using PFC emulsion. The process will be used to decontaminate the internals of highly contaminated nuclear facilities.

Acknowledgement

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