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A Study on the Pre-treatment and Adsorption Methodology of Soil Specimens for the Development of Radioactive Contaminated Soil Decontamination Process

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1. Introduction

Nuclear power plants emit little carbon dioxide, one of the Greenhouse gases (GHGs), and are called clean energy sources. Currently, more and more power plants are approaching the expiration of their design life. Therefore, among the Nuclear Backend Cycle fields, decommissioning areas are being discussed worldwide. According to Article 2 (24) of the 'Nuclear Safety Act' in Republic of Korea, the term "decommissioning" means 'all activities to be exempt from the application of this act by decommissioning facilities and sites, or by removing radioactive contamination after permanently suspending the operation of facilities licensed or designated under this act'. Therefore, the site of the nuclear power plant must undergo the site remediation as the final decommissioning stage before the license for the nuclear power plant project is completed. To reduce secondary waste generated during soil decontamination, in this study, it was described the methodology of making soil samples by selecting target nuclides and adsorbing soil samples with target contamination as a preliminary step for metal extraction using ecofriendly supercritical carbon dioxide.

2. Material Preparation and Method

2.1. Soil specimen

The soil to be used in the experiment was collected from the site of the engineering college of Kyunghee University Global Campus. The 5 cm top Soil was removed and a 30 cm deep plow layer soil was collected. 30 % of hydrogen peroxide was used to decompose the remaining organic matter in the soil, and the remaining impurities were removed with 6 M nitric acid (HNO_3). After that, the soil was washed with flowing water and dried at room temperature. The dried soil was sieved based on USDA (United States Department of Agriculture) Soil Classification, the standard for classifying soil particles used in Korea. Coarse size (0.5 to 1.0 mm) and medium size (0.2 to 0.5 mm) were classified with reference to the USDA System. However, unlike USDA's classification of soil below fine sand into 'Very fine soil', 'Silt', and 'Clay', in this experiment, all particle sizes below 0.2 mm were considered as fine sand. (following Table I)

Table I: USDA Soil Classification [1]

USDA System		Particle number per 1 g	SSA (cm^2/g)
Name	D (mm)		
Coarse	1.0~0.5	722	23
Medium	0.5~0.25	5,777	45
Fine	0.25~0.1	46,213	91
Very fine	0.1~0.05	722,074	227
Silt	0.05~0.002	5,776,674	454
Clay	< 0.002	90,260,853,860	11,343

2.2. Target nuclide

Various nuclides exist in radioactive contaminated soil, which is the subject of site remediation. Since there are no cases of decommissioning for commercial reactors in Korea, radionuclides were selected by referring to the distribution of site contamination at 'Maine Yankee' and 'Rancho Seco' Nuclear Power Plants in the United States. (see Table II)

Table II: Distribution of nuclides,
Decommissioned Nuclear power plants in U.S.
Maine Yankee (left), Rancho Seco (right) [2]

Radionuclide Fraction in Soil at Maine Yankee		Rancho Seco Soil Characterization Results	
Radio nuclide	Avg. Fraction of Total Activity (%)	Radio nuclide	Soil con-centration range (pCi/g)
H-3	0.053	H-3	4.0~10.2
		C-14	1.7~10.0
Ni-63	0.048	Co-60	0.3~6.5
		Ni-63	37~170
Co-60	0.009	Sr-90	1.3
		Tc-99	4.5~5
Cs-137	0.890	Cs-134	0.21
		Cs-137	8.0~942

Since the Fukushima Nuclear Accident in March 2011, it has been reported that the site has been contaminated with Cs and Sr. [3] In particular, in the case of Cs, the concentration deposited in the soil on the site was large. In addition, the half-life of Cs is 30.17 years, and Sr is 28.8 years, which is very long, so both nuclides are valuable as targets of decontamination. Nuclides were adsorbed to the soil using standard solutions (Kanto, JCSS, 1000 ppm) of Cs and Sr. The concentration of target nuclides was set at 200 ug-nuclide/g-soil.

2.3. Soil adsorption

Among the soil specimens classified according to the USDA system, adsorption was performed on coarse soil. With the aim of 200ug-nuclide/g-soil of concentration, specimen was concentrated under reduced pressure with rotary evaporator (Buchi Rotavapor R-124, Buchi Waterbath B-480). Cs standard solution and Sr standard solution were added to 200 g of coarse sand in receiving flasks. Deionized water (DIW) was added to adsorb the soil evenly immersed in the standard solution. The pressure of 700 mmHg was maintained with the vacuum pump to operate the rotary evaporator, and the temperature of the coolant injected into the main condenser through the chiller was maintained at 15 °C. The receiving flask was rotated at 60 rpm while maintaining the double boiling temperature of the flask in the water bath at 60 to 65 °C. The adsorption process was carried out for a total of 4 hours per specimen. After the standard solution was evaporated, the soil was poured into a glass tray and dried at room temperature for 12 hours to completely dry the soil attached to the wall in the receiving flasks. Control group specimens were additionally made to analyze the concentration with the dried specimen. Sea sand (SiO_2, JUNSEL, 99.7 % purity) was selected as the control group. Sea sand was adsorbed at a concentration of 200 ug-nuclide/g-soil in the same method as the actual soil adsorption in 2.3.

2.4. Pretreatment for ICP-MS

ICP-MS (Inductively Coupled Plasma Mass Spectrometer, Agilent 7500cx, Agilent Technologies Inc.) in Kyunghee University CRF (Center for Research Facilities) was used to analyze whether the target nuclides were well adsorbed to dry soil specimens. Radionuclides in the soil, namely metal ions, were pretreated to extracted and measure concentration. Based on 1 g of soil, 65 % of HNO_3 was made into a total of 10 ml nitric acid solution. It was placed in a teflon (PTFE) container that resistant to acid and heat, and was reacted in a vacuum oven for 12 hours at 90°C. Then it was taken out of the oven and the sample was stabilized at room temperature for 6 hours. Soil residues that were not dissolved in acid were filtered using a syringe filter (Advantec Disposable Membrane Filter, 0.20 um), and then ICP-MS sample preparation was completed.

3. Analysis method: Development method for adsorption reliability evaluation

Prior to confirming the result of adsorption, reliability evaluation was conducted to reduce concentration errors that may appear during the adsorption process by using a rotary evaporator. During the adsorption process, it was found that a part of the soil was attached to the receiving flasks wall. Additionally, during the adsorption process, soil particles were agglomerated or coarse particles were pulverized by friction and reduced to fine soil size.

Fig. 1 Mud covered wall inside the receiving flask(left), The appearance of being Scraped soil off from the muddy wall (right)

Since the specimen characteristics have been physically subdivided, it is necessary to introduce subdivided classifications to consider the chemical properties accordingly. The concentration was determined by dividing the sample into a total of eight. Therefore, the sample was subdivided as shown in the table below to improve adsorption accuracy. (Shown in Table III below)

Table III: Classification of subdivided coarse soil

[Side Wall] Chunk	[Side Wall] Soil	[Bulk] Chunk	[Bulk] Fine
Bulk 1	Bulk 2	Bulk 3	Bulk 4

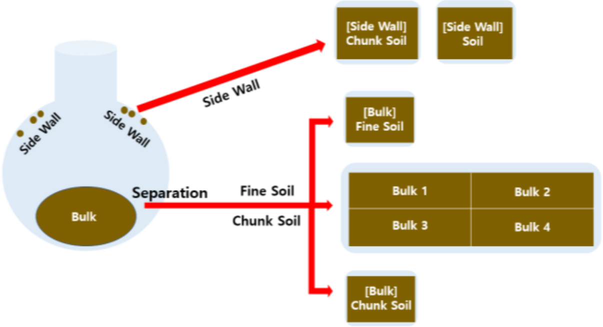

Fig. 2 Sampling diagram for soil adsorption distribution evaluation

The location of each sample according to soil classification is shown in Fig. 2 above. The soil sample corresponding to the 'bulk' was placed in glass tray and divided into quadrants. After that, samples were taken from 4 spots on the each of quadrant in a random zig zag manner. The soil except for the bulk was collected by conical quartering, a method used to obtain an average sample of composition when sampling solid samples.

4. Result

4.1. ICP-MS analysis of soil specimen

Table IV: Cs, Sr concentration for specimens

Soil		Concentration (ug-nuclide/g-soil)		Mass (g)
		Cs	Sr	
Sea sand		224.9	189.9	500
Soil (Coarse)	1	203.0	198.5	158.4
	2	202.0	194.4	158.4

The concentration of the specimen using ICP-MS was confirmed as above table. However, a single sample was collected twice through a conical quadrant method, not a random zig zag method performed in the reliability evaluation of 3.1. The concentration was evaluated in the same way for the sea sand specimen to compare with the actual soil specimen. The concentrations of samples in the control group and the experimental group appear to be almost same. Consequently, the final concentration of soil specimens corresponding to Table IV above was obtained. Considering the error ±10 % of the ICP-MS system, it was confirmed that the measured value was within the target range of 200 ug-nuclide/g-soil.

4.2. Adsorption specimen reliability evaluation: Evaluation of mass balance

As a result of analyzing 8 soil samples with different spots through ICP-MS for reliability evaluation, the concentration corresponding to table V below was obtained. In addition, the mass balance was checked by measuring the mass of each sample.

Table V: Concentration and mass by soil spot

Spot	Concentration (ug-nuclide/g-soil)		Mass (g)
	Cs	Sr	
[Side Wall]	263.4	342.4	17.9
[Side Wall] Chunk	229.5	285.1	3.7
[Bulk] Chunk	260.3	207.1	14.4
[Bulk] Fine	744.2	739.7	1.7
Bulk 1	186.9	185.2	158.4
Bulk 2	189.7	183.6	
Bulk 3	184.3	174.9	
Bulk 4	207.8	205.9	

The amount of radionuclide adsorbed in each sample was shown in Table 5, and the concentration of the total soil was finally derived to confirm mass balance. (Shown in table 6 below) It can be seen that fine particles generated by the crushing of bulk soil showed a greater concentration than the target concentration. However, since the amount of sample is small compared to the concentration, the total amount of nuclide is shown to be negligible.

Table VI: Total amount of nuclides to confirm mass balance

Coarse soil classification	Total Amount (ug)	
	Cs	Sr
[Side Wall]	4713.3	6126.9
[Side Wall] Chunk	852.1	1058.6
[Bulk] Chunk	3754.3	2987.0
[Bulk] Fine	1274.8	1267.1
Bulk 1	30435.5	29679.3
Bulk 2		
Bulk 3		
Bulk 4		

Table VII: Nuclide contamination calculated considering mass balance

Total mass (g)	
196.1	
Total Cs concentration (ug)	Total Sr concentration (ug)
41030.1	41118.9
Cs concentration per mass (ug-nuclide/g-soil)	Sr concentration per mass (ug-nuclide/g-soil)
209.2	209.7

The final sample mass was 196.1 g. Compared to the existing sample mass of 200 g, mass loss in the existing adsorption process may be considered within an error range, and based on this, it is expected that the total concentration may also be ensured reliability of the adsorption result.

5. Conclusion

In this study, a methodology for adsorbing nuclides to the soil specimen during the soil decontamination experiment process using supercritical carbon dioxide was presented and reliability was evaluated. Through the results of this study, it is expected that high accuracy can be maintained if the methodology introduced in this study is applied during the adsorption process for soil decontamination experiments in the future.

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