Actual Soil Decontamination Using Supercritical CO_2 with Ultrasonic horn

Jaebin Shin [a], Kwangheon Park [a*], Seungil Ha [a], Hyokyung Son [a]
[a] *Department of nuclear engineering, Kyunghee University, Kyunggi-do, 446-701, Republic of Korea*
[*] *kpark@khu.ac.kr*

1. Introduction

Nuclear power is the greenest power resource in Korea, but there are several problems. One of the important problems is the radioactive waste. Korea is facing to decommissioning Gori unit-1. In the cases of decommissioning nuclear power plants overseas, unexpected soil waste resulted in increasing radioactive waste amount to be disposed. [1] Acid or organic solvents are generally used for conventional radioactive soil waste decontamination. However, conventional technology generates large amounts of secondary waste. To solve the problem, in this study, supercritical carbon dioxide was used for soil decontamination. Supercritical carbon dioxide is excellent as a solvent and does not produce secondary waste. Also, Ultrasonic horns are used to increase decontamination efficiency. In the case of soil contamination, decontamination efficiency was depended on particle size. Therefore, in this study, the actual soil is classified by size and the experiment was carried out. For comparison with previous experimental results, the difference in decontamination efficiency with Sea sand is compared.

2. Material and Method

2.1 Preparation of Soil specimen

This study was conducted in a stage to application to the actual soil. In previous study, treated marine sand (Chemical pure, JUNSEI, Chuo-ku, Tokyo, Japan) was used. In case of actual soil, it was collected in Yongin-shi. After nitric acid treatment to remove impurities, soil was classified into 3 groups according to the size of the soil. Size of 4 samples are shown at Table. I. The largest size soil was excluded in this study.

Table I: Classification of sand and soil samples

Sample type	Size(mm)
Silica sand	1.0~
Coarse soil	0.5~1.0
Medium soil	0.2~0.5
Fine soil	0.2~

For the selection of adsorption elements, examples of the decommissioning cases of the Haddam Neck Plant, Maine Yankee power plant and Rancho-seco nuclear generation station in the US, which were commercial power plants, were referenced. Radioactive isotope Cs-137 was found in the soil at the decommissioning site of each power plant. [1] Therefore, in this experiment, stable isotopes, Cs, were adsorbed to the soil to describe this. The adsorption process is shown in Fig. 1. In this study, Cs standard solution (Kanto chemical CO. INC, Tokyo, Japan) was used for adsorption to samples (sea sand and classified actual soils). The standard solution were placed in the beakers containing the samples. The beaker was then placed in an ultrasonic cleaner for 1 hour to evenly mix the Cs ions with the samples. To adsorb Cs to samples evenly, dry step was separated 2 steps. The beakers containing the solution and samples were placed in a desiccator and dried room temperature with 20% humidity for about 24 hour. And the beakers containing the solution and samples were placed in vacuum oven and dried at 90 ℃ for about 24 hour.

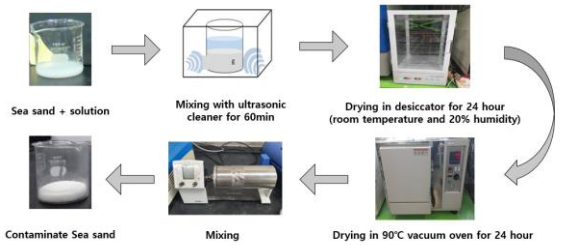

Fig. 1. Procedure for preparing contaminated sea sand

2.2 Selection of surfactant

Supercritical carbon dioxide is a non-polar material and cannot directly dissolve the metal adsorbed on the soil. Therefore, a Catechol Amine ligand, which has excellent binding strength with metal, was used to dissolve the metal and supercritical carbon dioxide. Catechol Amine ligand combines with metal cations to form metal complexes. However, in order to maintain the electrical neutrality of the metal complex, the counter anions of the metal ions follow together. Since the counter anion does not dissolve in supercritical carbon dioxide, it plays a role of preventing metal extraction, and as a result, the solubility of metal complexes in supercritical carbon dioxide decreases. Therefore, in order to prevent this, a counter anion soluble in $SCCO_2$ to replace an anion insoluble in $SCCO_2$ was added. Net4pFOSA was used to counter anion in the experiment and purchased from Sigma-Aldrich.

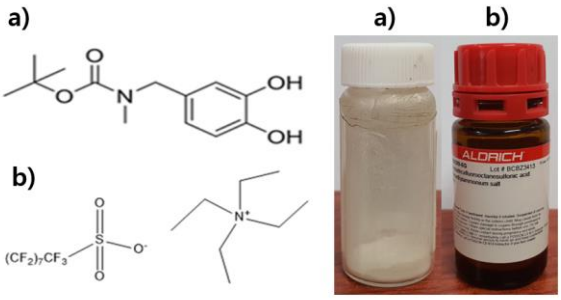

Fig. 2. a) Catechol ligand (tert-butyl 3,4-dihydroxybenzyl (methyl) carbamate), 253.3 g/mol)
b) Net4pFOSA (Heptadecafluorooctanesulfonic acid tetraethylammonium salt, 629.37 g/mol)

Through previous experiments in the lab, it was confirmed that the conditions of 200bar and 40℃ are necessary for dissolution of these substances [2]. In this study, this condition was applied as an experimental condition.

2.3 Procedure of decontamination experiment

The experiment was conducted using 5 g of adsorbed soil and additives (ligand/co-ligand/water). For the stability of the pressure vessel, the cycle was performed using 3 minutes of ultrasonic waves and 3 minutes without ultrasonic waves. Total time condition was fixed on 1 hour.

Experiment was conducted 3 case of apparatus setting. Case 1 and Case 2 was consist of closed cycle that fluid was restricted in system. Case 3 was consist of open cycle. Case 1 and case 2 has differences in ultrasonic energy. Case 1 and case 3 were conducted on minimum ultrasonic power. Case 2 was conducted 30% power of Maximum power. Closed cycle system and Open cycle system were shown at Fig 3 and Fig 4.

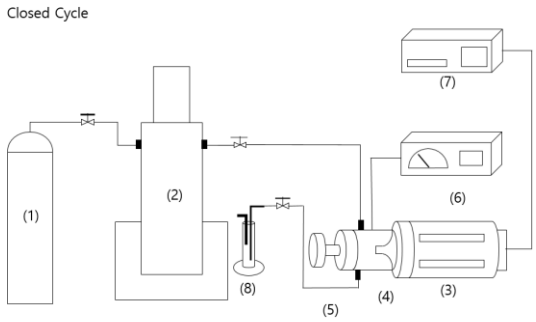

Fig. 3. Closed cycle system for Soil decontamination experiment using $SCCO_2$ (1) CO2 cylinder (2) syringe pump (3) ultrasonic generator (4) ultrasonic horn (5) specimen container (6) heating controller (7) ultrasonic controller (8) collector

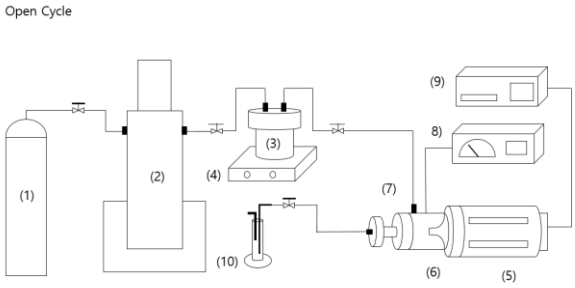

Fig. 4. Open cycle system for Soil decontamination experiment using $SCCO_2$ (1) CO2 cylinder (2) syringe pump (3) Reaction cell (4) Stirrer (5) ultrasonic generator (6) ultrasonic horn (7) specimen container (8) heat controller (9) ultrasonic controller (10) collector

2.4 Procedure of Measurement

After the experiment, the collected sea sand specimen was placed in a reaction vessel with 10 ml nitric acid. And heated up to 180℃ in a microwave accelerated reaction system (MARS 5, CEM Co., Matthews, NC, USA). The amount of Cs ion in the solution containing the specimen was analyzed with Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Leeman Labs, Lowell, MA, USA).

3. Results

The decontamination efficiency of Cs is determined by difference between the before and after concentration of the solution following Eq. 1; where C_B and C_A are the concentration of Cs in the solution before and after the experiment, respectively.

$$Decontamination\ efficiency = \frac{C_B - C_A}{C_B} \times 100\ (\%) \quad (1)$$

Sea sand had a high decontamination efficiency of over 85% in all cases. On the other hand, Coarse, Medium and Fine showed overall low decontamination efficiency. In Case 1, all three types of Actual Soil showed low decontamination efficiency of less than 50%. In case 2 with the same closed system but high energy, Coarse and Medium saw an increase in efficiency of about 20%. In the case of Fine, the overall low decontamination efficiency was confirmed. Case 3, an Open cycle, showed higher decontamination efficiency than the other two cases.

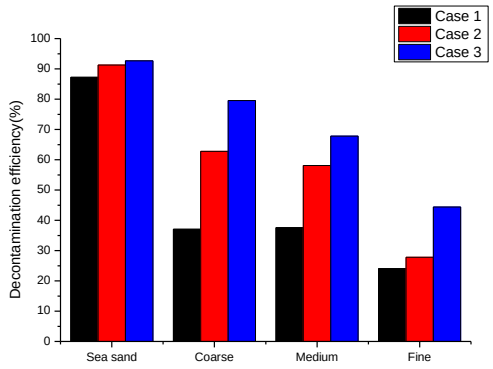

Fig. 5. Cs decontamination efficiency depending on the ultrasonic energy

4. Conclusions

In this study, the feasibility of the supercritical decontamination technology as one of the decontamination techniques for extracting Cs from the soil was evaluated. This study was conducted by dividing the actual soil by size. In addition, the decontamination efficiency changes were identified according to the three experimental conditions. It was confirmed that the energy of the ultrasonic horn resulted in an increase in decontamination efficiency of the actual soil. The difference in decontamination efficiency between closed and open systems was identified. The decontamination efficiency of the open system was excellent.

REFERENCES

[1] Hyoung-Woo Lee, Ju-Youl Kim, and Chang-Lak Kim, Study on the Experiences of Subsurface Soil Remediation at Commercial Nuclear Power Plants in the United States, JNFCWT Vol.17 No.2 pp.213-226, June 2019

[2] Kwangheon Park, Taehun Kim, Jihey Park, Xinhao Yan, Hakwon Kim, Development of a carbamate-conjugated catechol ligand and its application to Cs extraction from contaminated soil by using supercritical CO2, Chemosphere, Volume 242, 2020.