Decontamination experiments of Soil from the Decommission of NPP Using Supercritical CO_2 with Ultrasonic horn

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1. Introduction

Recently, in Korea, decommissioning of Nuclear Power Plants (NPP) comes to be an effective and important issue, due to decommission about KORI unit 1. Korea has not experienced about decommissioning of commercial NPP. Therefore, variety field of technology development is demanded. Decontamination of soil, which is expected to produce a large amount of radioactive waste, is also one of the technologies that must be developed in remediation the site after decommissioning. The current methods used in soil decontamination generate large amounts of secondary waste. In terms of reducing secondary waste, it is effective to use supercritical carbon dioxide ($SCCO_2$) as a solvent. In decontamination using $SCCO_2$, the amount of secondary waste can be reduced by lowering the pressure after termination of the decontamination process. In this study, metal ion extraction from soil using $SCCO_2$ decontamination technique with ultrasonic horn was studied for artificially contaminated sea sand.

2. Material and Method

2.1 Preparation of Soil specimen

This study was conducted in a stage prior to application to the actual soil, treated marine sand (Chemical pure, JUNSEI, Chuo-ku, Tokyo, Japan) was used. For the selection of adsorption elements, examples of the decommission cases of commercial NPPs such as Maine Yankee power plant and Rancho-seco power plant in the US were referenced. Radioactive isotopes Co-60 and Cs-137 were found in the soil at the decommissioning site of each power plant. [1, 2] Therefore, in this experiment, stable isotopes Co and Cs were adsorbed to the soil to describe references condition. The adsorption process was shown in Fig. 1. In this study, Co and Cs standard solution (Kanto chemical CO. INC, Tokyo, Japan) was used for adsorption to sea sand. The standard solution were placed in the beakers containing the sea sand. The beaker was then placed in an ultrasonic cleaner for 1 hour to evenly mix the Co and Cs ions with the sea sand. To adsorb Co and Cs to sea sand evenly, dry step was separated 2 steps. The beakers containing the solution and sea sand were placed in a desiccator and dried room temperature with 20% humidity for about 24 hour. And the beakers containing the solution and sea sand were placed in vacuum oven and dried at 90 ℃ for 24 hour.

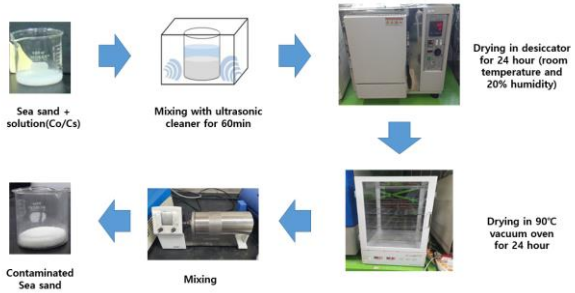

Fig. 1. Procedure for preparing contaminated sea sand

2.2 Selection of surfactant

$SCCO_2$ 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 $SCCO_2$. 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 $SCCO_2$ decreases. Therefore, to prevent this phenomenon, a counter anion soluble in $SCCO_2$ to replace an anion insoluble in $SCCO_2$ was added. Net4pFOSA, purchased from Sigma-Aldrich, was used to counter anion in the experiment.

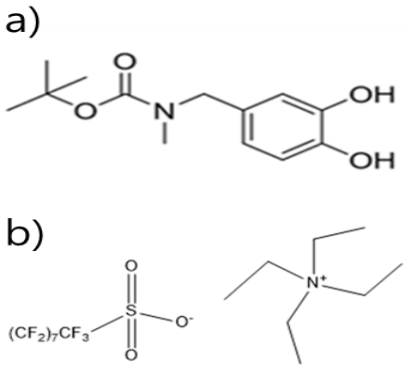

Fig. 2. a) Catechol ligand (tert-butyl 3,4-dihydroxybenzyl (methyl) carbamate), 253.3 g/mol)
b) Net4pFOSA (Heptadecafluorooctanesulfonic acid tetraethylammonium salt, 629.37 g/mol)

Through previous experiments in the laboratory, it was

confirmed that the conditions of 200bar and 40℃ are necessary for dissolution of these substances [3]. For this reason, this condition was applied as an experimental condition in this study.

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. For the safety of the equipment, the maximum output ultrasonic was performed for 30 minutes and other experiments were performed for 1 hour.

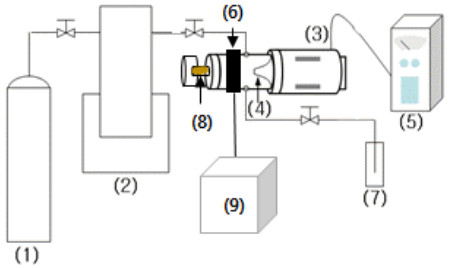

Fig. 3. Experimental apparatus for Soil decontamination experiment using $SCCO_2$ (1) CO2 cylinder (2) syringe pump (3) ultrasonic generator (4) ultrasonic horn (5) ultrasonic horn controller (6) heating line (7) collector (8) specimen container (9) heat controller

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 Co, Cs ion in the solution extracted from the sea sand specimen was analyzed with Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Leeman Labs, Lowell, MA, USA).

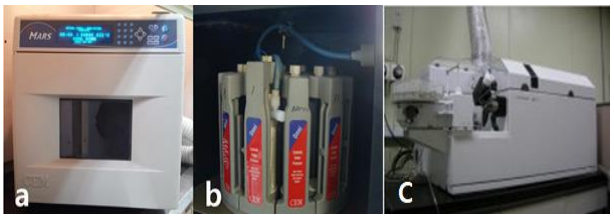

Fig. 4. Measurement apparatus for analysis the experiment sample a) MARS 5 b) reaction vessel c) ICP-MS

3. Results

The decontamination efficiency of Co and Cs was 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 Co and Cs in the solution before and after the experiment, respectively.

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

In order to estimate suitable ultrasonic horn energy for the decontamination experiments, the Co and Cs decontamination efficiency increase was confirmed in sea sand specimens by increasing the ultrasonic horn. Experimental results through the contaminated soil specimens are shown in Fig. 5. Overall, Co showed lower decontamination efficiency than Cs. Co has a higher sensitivity to ultrasonic energy. It showed 72% and 87% decontamination efficiency at each of Co and Cs, and 84% and 91% at 1/3 energy. At maximum energy, they have decontamination efficiencies of 93% and 94%, despite half of the reaction time.

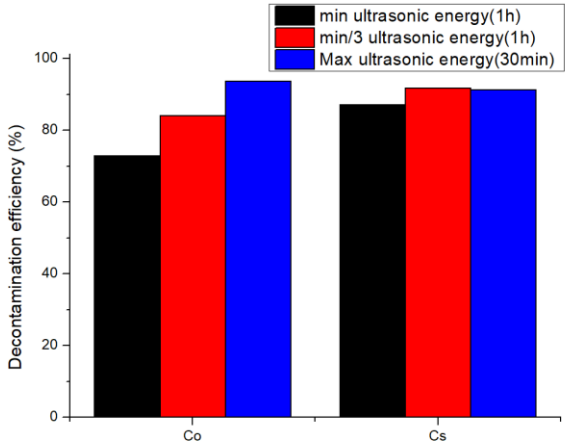

Fig. 5. Co, Cs decontamination efficiency depending on the ultrasonic energy

4. Conclusions

In this study, the feasibility of the supercritical decontamination technology was evaluated as one of the decontamination techniques for extracting Co and Cs from the soil. Through experiment results, decontamination efficiency change for ultrasonic energy was measured. Experiment results showed that the decontamination efficiency increase is proportion with ultrasonic energy increase. In particular, cobalt shows very low decontamination efficiency when the ultrasonic energy is low, but it indicates high decontamination efficiency when the maximum ultrasonic energy is used. Cesium also changed little, but the decontamination efficiency increased with the increase of ultrasonic energy. Based on these results, it is confirmed that one of the dominant factors in this $SCCO_2$ soil decontamination technique is the ultrasonic horn energy.

REFERENCES

[1] Maine Yankee License Termination Plan, Revision 3, dated October 15, 2002.

[2] Rancho Seco License Termination Plan, Chapter 6, Revision 0 dated April 2006.
[3] Kwangheon Park, Taehun Kim, Jihey Park, Xinhao Yan, Hakwon Kim,
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