Study of Soil Decontamination Method Using Supercritical Carbon Dioxide and TBP

Jihye Park[a], Kwangheon Park[a*], Wonyoung Jung [a]
[a] *Department of Nuclear Engineering, Kyunghee University, Kyunggi-do, 446-701 ,Korea*
[*] *Corresponding author: khpark@khu.ac.kr*

1. Introduction

When severe accidents such as the incident at the Fukushima nuclear site occur, the soil near the power plant is contaminated with fission products or the activation metal structure of the power plant. The soil pollution form depends on the environment and soil characteristics of the contaminated areas. Thus, a-single-decontamination method is not effective for site cleanup. In addition, some soil decontamination methods are expensive and large amounts of secondary waste are generated. Therefore, we need new soil decontamination methods.

In this study, instead of using a conventional solvent method that generates secondary waste, supercritical carbon dioxide was used to remove metal ions from the soil. Supercritical carbon dioxide is known for good permeation characteristics. We expect that we will reduce the cost of soil pollution management.

2. Methods and Results

First, we selected the pollution source and ligand. Next, we extracted the metal ions from soil using the supercritical carbon dioxide. Finally, preprocess using the Microwave Acid Digestion System (MARS 5, CEM Corporation. Matthews, NC, USA) and doing the quantitative analysis using an Inductively Coupled Plasma Mass Spectrometer (ICP-MS).

2.1 Materials

2.1. 1 Selection of pollution source

We chose seasand (JUNSEL, chemical pure) as the contamination soil because the particle size is big and surface pore size is small. We selected several metal-ions (lithium, natrium, strontium, cesium) for contamination purposes.

2.1. 2 Selection of extractant

Decontaminated heavy metal in soil is metal ions or oxide form and it is polarity. On the other hand, carbon dioxide is a non-polar material. Therefore, for the metal ions present in the polar, it can't be extracted with supercritical carbon dioxide. If we want to extract metal using supercritical carbon dioxide, we have to use an extractant that combines well with metal, and dissolve in carbon dioxide well too.

In a previous paper, it was found that UO_2 and U_3O_8 powders could be dissolved in supercritical carbon dioxide containing a HNO_3–tri-*n*-butyl phosphate (TBP) complex. In this study, we use TBP as it is known as an extractant of actinium metal. TBP is usually used for uranium and strontium extraction. In uranium extraction, uranyl nitrate is not dissolved in supercritical carbon dioxide but uranyl nitrate. TBP complex is well dissolved in supercritical carbon dioxide. We use this mechanism in this study. Therefore, we select TBP-HNO_3 complex for extractant for this study.

2.2 Specimen

The specimen for supercritical carbon dioxide extraction was made in two steps.

2.2.1 Adsorption metal ions in soil

First, we mix 20g seasand and 10ml nitric acid. Then 5ml of each pollution source (lithium, natrium, strontium, cesium) is put in-to the mixture. The following Table 1 shows the material properties of the pollutant sources.

Table I: Material properties of pollutant sources

Materials	Atomic Weight (g/mol)	Concentration (ppb)
Lithium, Li	6.941	505570
Natrium, Na	22.99	502330
Strontium, Sr	87.62	502590
Cesium, Cs	132.91	505100

So that heavy metals are uniformly mixed in the soil, we use the ultrasonic cleaner for 1 hour. Since the evaporation of the nitrate from the soil and mixed with an aqueous solution, we dried for about 20 hours at 90 ℃ with the drying oven. Finally, we achieved a soil polluted only with only metal ions.

2.2.2 Specimen mock up

For the extraction experiment, we made a specimen using a contaminated soil. Fig. 1 shows the mocked up specimen.

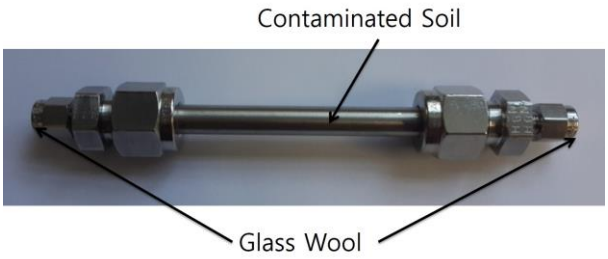

Fig. 1 Mocked up specimen

The mocked up specimen length was 7cm and diameter is 1/4 in. We put 1.0359g contaminated soil into a pipe and closed the inlet and outlet of the pipe with glass wool. When the supercritical carbon dioxide passed through the pipe, the glass wool prevented soil from escaping.

2.3 Experiment

Fig 2 shows a schematic diagram of the equipment for extracting heavy metals in soil using supercritical carbon dioxide.

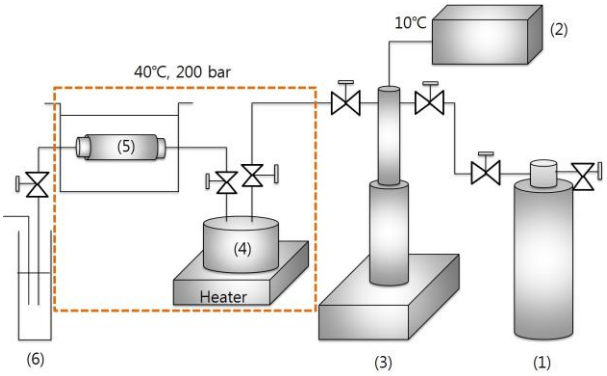

Fig. 2 Equipment for extraction test : (1) CO_2 Cylinder (2) Temperature controller (3) Syringe pump (4) Mixing cell (5) Specimen and temperature controller (6) bubbler

The temperature of the inlet carbon dioxide gas was maintained at 10 ℃ and the temperature of the mixing cell and specimen was maintained at 40℃ using the temperature controller and heater. TBP-HNO_3 complex was put in the mixing cell. - The carbon dioxide became a liquid at 10℃. After achieving and maintaining a temperature of 40℃, we pressurized to 200bar using a syringe pump. The carbon dioxide became a supercritical state at 40℃, 200bar.

The experiment process was two steps. One is the static extraction process (1 hour 30 minutes) and the other is the dynamic extraction process (1 hour 30 minutes). The total experiment time was 3 hours. The first process was the step to raise the carbon dioxide temperature up to 40°C and to mix with TBP-HNO_3 complex. The second process was the step to remove heavy metal ions using supercritical carbon dioxide with the TBP-HNO_3 complex.

2.4 Analysis

After the experiment, we did the pre-processing using the Microwave Acid Digestion System (MARS 5) for a quantitative analysis of metal ions remaining in the soil. We put the soil in a vial, and mixed 5ml distilled water and 5ml nitric acid. We set an experimental condition of power (300W), pressure (300psi), and temperature (180℃). - The heating rate was 15 minutes and hold for 15 minutes.

After a pre-processed through the MARS 5, and a quantitative analysis using the ICP-MS.

2.5 Result

The following Fig. 3 shows the soil of before extraction and after extraction using supercritical carbon dioxide.

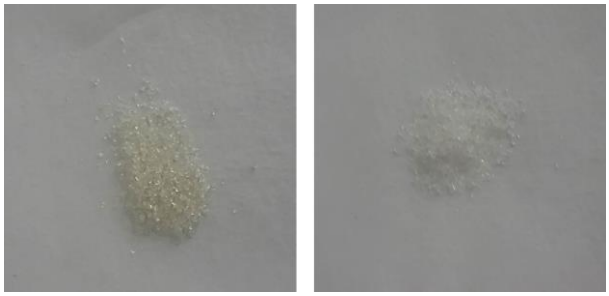

Fig. 3 Soil of before and after extraction (left: before, right: after)

The soil before extraction looked yellow, which indicated that the soil was contaminated by metal ions. The soil after extraction using supercritical carbon dioxide and TBP-HNO_3 complex looked like the white color that is the original seasand color.

Figs. 4 and 5 show the concentration and extraction rates for the metal ions in soil using ICP-MS.

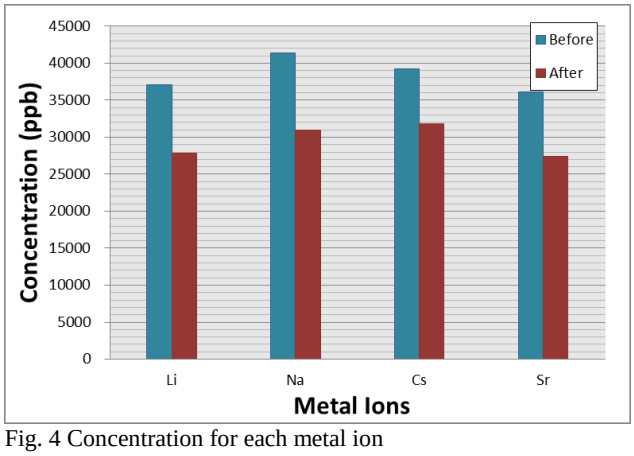

Fig. 4 Concentration for each metal ion

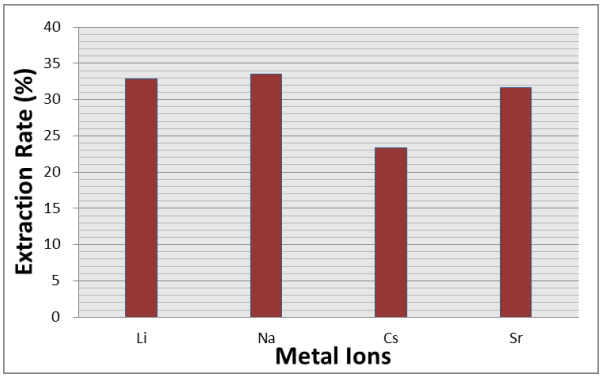

Fig. 5 Extraction rate for each metal ions

As in Fig. 4, the concentration of metal ions was reduced after extraction. In Fig. 5, the extraction rate for metal ions was about 30%.

3. Conclusions

Supercritical carbon dioxide can decontaminate soil easily, as it has the ability to penetrate even narrow gaps with very good moisture permeability. We used TBP, which is a known for extractant of actinium metal. TBP is usually used for uranium and strontium extraction. Using TBP-HNO_3 complex and supercritical carbon dioxide, we did extraction experiments for several heavy metals in contaminated soil. As a Fig.3 shows, decontamination observed with the unaided eye. Also, the extraction rate of metal ions differed for each metal, but most of them were about 30%. The result of this study means that we have a possible new method for cheap and less wasteful nuclear waste decontamination.

REFERENCES

[1] K. H. Park, Fiber Technology and Industry, Vol. 5, No. 34, p 185-193, 2001.
[2] M. A. McHugh and V. J. Krukonis, "Supercritical Fluid Extraction-principles and Practice", 2nd Ed., Butterworh-Keinemann, 1994.
[3] K. H. Park, H. W. Kim, H. D. Kim, M. S. Koh, J. D. Ryu, Y. E. Kim, B. S. Lee, H. T. Park, Journal of the Korea Institue of Surface Engineering, Vol. 34, N0. 1, p 62-67, 2001.
[4] Tessy Vincenta, Mamata Mukhopadhayb, P.K. Wattala, Supercritical direct extraction of neodymium using TTA and TBP, T. Vincent et al. / Desalination 232, 91-101, 2008.
[5] Chien M. Wai, Yurii Kulyako, Hwa-Kwang Yak,a Xiaoyuan Chena, Suh-Jane Lee, Selective extraction of strontium with supercritical fluid carbon dioxide, Chem. Commun., 2533–2534, 1999.
[6] O. Tomioka, Y. Meguro, Y. Enokida, I. Yamamoto, Z. Yoshida, Dissolution behavior of uranium oxides with supercritical CO2 using HNO3–TBP complex as a reactant, J. Nucl. Sci. Technol. 38, 1097, 2001.