

## Decontamination of Metal Ions in Soil by Supercritical CO<sub>2</sub> Extraction with Crown Ether

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### 1. Introduction

The largest drawback of nuclear power generation is probably the production of radioactive waste. As was shown in the Fukushima accident, radioactive materials such as Cs, Xe, I, Kr, etc. can be leaked outside in cases of severe accidents [1]. Moreover, these leaked radioactive materials can contaminate the ground of the nuclear plant site. Meanwhile, soil pollution has different types according to the contamination material or regional characteristics, which makes decontamination more difficult [2]. Moreover, previous decontamination methods have shortcomings in that they produce additional waste due to the usage of solutions with chemical toxicity. Hence, demand is strong for new decontamination methods that can guarantee effective decontamination while decreasing the chemical solution. In particular, methods using supercritical CO<sub>2</sub> as a means of decontamination are currently in progress [3]. This study examines the method of decontaminating metallic ions inside soil using supercritical CO<sub>2</sub>.

### 2. Material and Method

#### 2.1 Ligand

CO<sub>2</sub>, used in this study, is a non-polar ligand that can combine with metallic ions, which is necessary in order to decontaminate the polar substance of metallic ions [4]. In this study, a Crown Ether that was synthesized at the Department of Applied Chemistry at Kyunghee University was used as the ligand. Figure 1 shows the molecular structure of the Crown Ether used in this experiment.

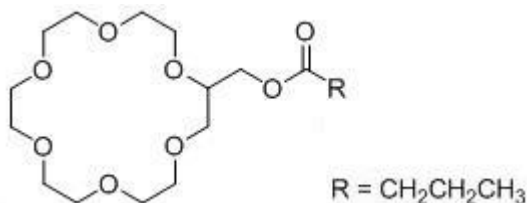


Fig. 1. Molecular structure of Crown Ether compound used as the ligand in this experiment

A co-ligand and additive were used along with the ligand for effective extraction. Net4pFOSA and H<sub>2</sub>O were used as the co-ligand and additive, respectively. In order to investigate the extraction effects, the extraction

experiment was performed by changing the amount of ligand, co-ligand, and additive. Table 1 summarizes the extraction experiment condition used in this study.

Table I: Condition of extraction experiment

Experiment number	Amount of reagent		
	Crown Ether (mg)	Net4pFOSA (mg)	H <sub>2</sub> O (ml)
E-1	1	1	10
E-2	5	5	10
E-3	10	10	10
E-4	15	10	10
E-5	10	5	10
E-6	15	10	5

#### 2.2 Specimen

Three types of metallic ion (Li, Cs, and Sr) were selected to be decontaminated and a mock-up specimen was fabricated by absorbing them on soil. Seasand (JUNSEL, chemical pure) was selected as a soil for the mock-up specimen. It has even-sized particles of around 1.0 mm and small surface pores. After pouring 10 ml of nitric acid and 5 ml each of Li, Cs, and Sr standard solutions on the Seasand, it was treated with ultrasonic cleaner for an hour so that the metallic ions inside the soil could be evenly mixed. After drying for some time at room temperature, it was dried in the 90°C vacuum oven for approximately 20 hours, until the nitric acid was vaporized so that only metallic ions were left. The final pollution level of the contaminated soil was 250 ug/1 g soil. This contaminated soil was put in a fabricated pipe-type container with a 7-cm length and 1/4 pipe diameter, and both ends of the pipe were sealed with glass wool in order to prevent soil from leaking during the extraction experiment.

#### 2.3 Experiment Method

Figure 2 shows the schematic diagram of the equipment that was used in this study for extracting metal ions from within soil using supercritical CO<sub>2</sub>.

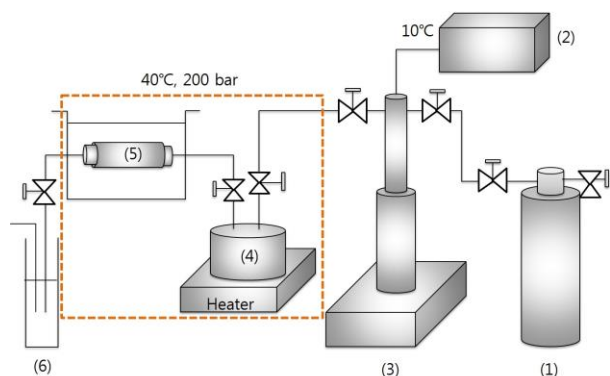


Fig. 2. Equipment for extraction test: (1) CO<sub>2</sub> cylinder (2) Temperature controller (3) Syringe pump (4) Mixing cell and heater (5) Preheating tube (6) Tubing cell (7) Water bath

The ligand and co-ligand in the experiment condition were made liquid inside the stirring container (4) by maintaining the temperature of CO<sub>2</sub> that entered syringe pump (3) at 10°C using the temperature controller (2). The temperature of the stirring container (4) and mock-up specimen container (5) was maintained at 40°C using the temperature controller (5) and heater (4). Finally, the pressure of CO<sub>2</sub> entering the stirring container (4) and mock-up specimen container (5) was maintained at 120 bar using the syringe pump (3). The extraction experiment proceeded following two steps. First, supercritical CO<sub>2</sub> was created through a static extraction procedure to be mixed with the ligand. Next, the ligand was mixed with supercritical CO<sub>2</sub>-extracted metallic ions from the soil by directly reacting to the contaminated soil through the dynamic extraction procedure. Each procedure was performed for 30 minutes, with a total extraction experiment time of one hour.

#### 2.4 Analysis

In order to examine the extraction effectiveness, a quantitative analysis was conducted on the metallic elements left in the soil after the experiment. After the pretreatment using the Microwave Acid Digestion System (MARS 5, CEM Corporation, Matthews, NC, USA), quantitative analysis was conducted using an inductively coupled plasma mass spectrometer (ICP-MS, Leeman Labs, Inc., USA). After placing 1g of soil in a vial along with 5ml of distilled water and 5ml of nitric acid, MARS 5 was used for 15 minutes to achieve 300 psi at 180°C. The condition was maintained for another 15 minutes for acid hydrolysis. The electronic power was set according to the number of vials loaded inside MARS 5. That is, if the number of vials was less than three, the power was set at 300W; if it was between three and five, the power was 600W; and in cases of more than six, the power was 1200W. The specimen that was preprocessed using MARS 5 received quantitative analysis by ICP-MS to measure the decontamination effectiveness.

### 3. Result and Discussion

Prior to regular extraction experiment, solubility experiment were performed to verify that the ligand in Figure 1 is how well dissolved in supercritical CO<sub>2</sub>. The solubility experiment results that Crown Ether is dissolved in supercritical CO<sub>2</sub> at 40°C, 90bar condition and at 60°C, 112bar condition. In this study, the experiment proceeded under the 40°C, 120bar condition, in which Crown Ether is known to be sufficiently dissolved in supercritical CO<sub>2</sub>.

First, the experiment was performed by increasing the amount of ligand and co-ligand while fixing the amount of H<sub>2</sub>O. Specific extraction conditions are summarized in Table 1. Figure 3 shows the change of extraction effectiveness according to the amount of extract. As shown in Figure 3, the extraction ratio was less than 10% on average in the E-1 and E-2 experiments, which used small amounts of ligand and co-ligand. However, the extraction ratio drastically increased in the E-3 and E-4 experiments, which used increased amounts of extracts. Specifically, in the E-4 experiment, the extraction ratio increased up to almost 100%.

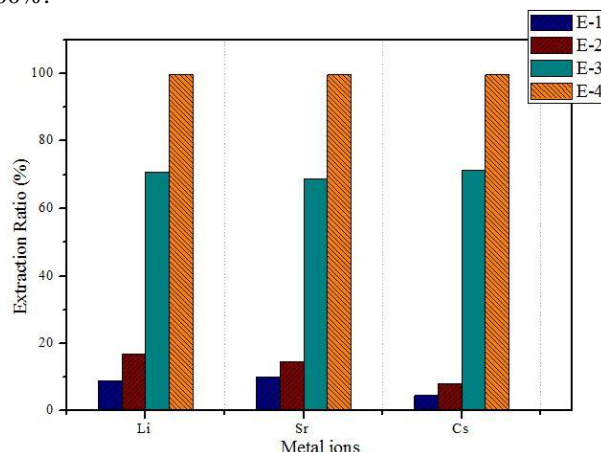


Fig. 3. Extraction ratio change according to amount of reagent

Next, the experiment was performed with decreased amounts of co-ligand in order to investigate its effect. While maintaining all other conditions to be the same as in the E-3 experiment, this experiment was performed with half the amount of co-ligand (Experiment number: E-5). Figure 4 shows the changes in the extraction ratio according to the amount of co-ligand. In Figure 4, the extraction ratio was nearly 70% in the E-3 experiment, while it decreased to approximately 20% in the E-4 experiment, which used half the amount of co-ligand.

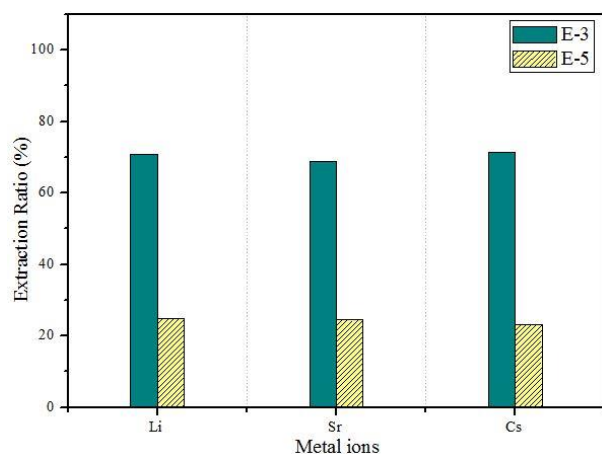


Fig. 4. Extraction ratio change according to amount of co-ligand.

Finally, we conducted an experiment by decreasing the amount of H<sub>2</sub>O in order to investigate its effect. While maintaining all other conditions to be the same as in the E-4 experiment, this experiment was performed with half the amount of H<sub>2</sub>O (Experiment number: E-6). Figure 5 shows the changes in the extraction ratio according to the amount of H<sub>2</sub>O. In Figure 5, the extraction ratio was nearly 100% in the E-4 experiment, while it decreased to approximately 40% in the E-6 experiment, which used half the amount of H<sub>2</sub>O.

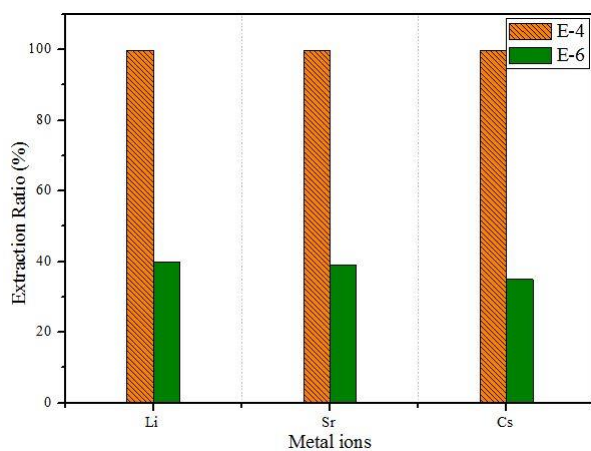


Fig. 5. Extraction ratio change according to amount H<sub>2</sub>O.

### 3. Conclusions

This paper examined the effects of extracting metallic ions inside soil using supercritical CO<sub>2</sub> and crown ether as the ligand. It was confirmed that extraction effectiveness increases following greater usage of ligand and co-ligand, with a drastic increase in extraction effectiveness when using extracts over a certain dose. Moreover, it was shown that if the usage of ligand and additive decreases, the extraction ratio also decreases. However, the purpose of this study was to decrease the generation of the secondary waste that induces additional environmental pollution, and ligand and H<sub>2</sub>O left over after the decontamination can also be

additional waste. Moreover, as metallic ions tend to be washed well by water, it is surmised that the H<sub>2</sub>O effect was notable. Hence, searching for more effective ways of decontamination using smaller amounts of the extract and H<sub>2</sub>O will give us a direction for future research.

### REFERENCES

- [1] P. Thakur, S. Ballard, and R. Nelson, An overview of Fukushima radionuclides measured in the northern hemisphere, *The Science of the total environment*, Vol.458-460, p.577-613, 2013.
- [2] K. H. Park, J. K. Lee, and J. H. Sung, Metal extraction from the artificially contaminated soil using supercritical CO<sub>2</sub> with mixed ligands, *Chemosphere*, Vol.91, No.5, p.616-622, 2013.
- [3] K. H. Park, H. W. Kim, H. D. Kim, M. S. Koh, J. D. Ryu, Y. E. Kim, B. S. Lee, and H. T. Park, Application of CO<sub>2</sub> Technology in Nuclear Decontamination, *Journal of the Korean Institute of Surface Engineering*, Vol. 34, No. 1, Feb, 2001.
- [4] J. McHardy, P. S. Samuel, *Supercritical fluid cleaning: fundamentals, technology, and applications*, Materials science and process technology series, William Andrew, 2008.