

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

Jihye Park<sup>a</sup>, Hakwon Kim<sup>b</sup>, Kwangheon Park<sup>a\*</sup>

<sup>a</sup> Department of Nuclear Engineering, Kyunghee University, Kyunggi-do, 446-701, Korea

<sup>b</sup> Department of Applied Chemistry, Kyunghee University, Kyunggi-do, 446-701, Korea

\*Corresponding author: khpark@khu.ac.kr

### 1. Introduction

The role of fuel cladding and reactor vessels is to help prevent the leakage of radioactive materials, including the fission products. However, if these shielding materials are damaged by a severe disaster such as the Fukushima Accident, radioactive materials could leak outside of a power plant site. Indeed, after the Fukushima Accident, radioactive materials have been detected in air and water samples [1]. The air and water pollution lead to soil pollution, which is particularly difficult to decontaminate, as soil pollution has several types that vary according to the characteristics of a pollutant or its area [2]. The existing decontamination methods generate a secondary waste owing to use of chemical toxicity solvents. It is also disadvantageous due to the additional cost of handling them. Therefore, new effective decontamination methods that reduce the use of toxicity solvents are necessary. For example, using supercritical CO<sub>2</sub> has been studied as a new decontamination method [3]. This study examines the method of decontaminating metallic ions inside of the soil using supercritical CO<sub>2</sub> and a catecholamine compound.

### 2. Material and Method

#### 2.1 Ligand

The known catechol did not dissolve in supercritical CO<sub>2</sub>. However, an advanced catecholamine compound was synthesized at the Department of Applied Chemistry at Kyunghee University. The new ligand dissolved in supercritical CO<sub>2</sub>, and has the ability of chelate ligand. A solubility test was performed using this new ligand. Among the several synthetic ligands, the compound shown in Fig. 1 was selected for this study. This catecholamine compound showed a high extraction ratio for Cs<sup>+</sup> ions. Supercritical CO<sub>2</sub> is a non-polar state that can't combine with metallic ions, but only in case with polar co-ligand [4]. For this reason, Net4pFOSA (perfluoro-1-octanesulfonic acid tetraethylammonium salt) was used as a co-ligand. Additionally, H<sub>2</sub>O was used as an additive in order to obtain a high extraction ratio. Fig. 1 and Fig. 2 show the molecular structure of the ligand and co-ligand, respectively.

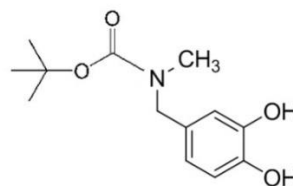


Fig. 1. Molecular structure of catecholamine (molecular weight: 390.42 g/mol)

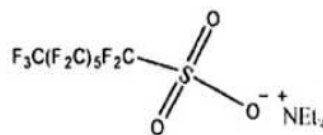


Fig. 2. Molecular structure of Net4pFOSA (molecular weight: 629.38 g/mol)

#### 2.2 Specimen

Li, Sr, and Cs were selected and absorbed on seasand (JUNSEL, chemical pure). The particle size of seasand is around 1.0 mm, and it has small surface pores. 15 ml of distilled water and 5 ml of each standard solution was poured into 20 g of seasand. To mix all of the components evenly, they were blended with ultrasonic cleaner for one hour. After drying for another hour at room temperature, it was then dried in the drying oven for approximately 20 hours at 90°C. Finally, only metallic ions remained on the seasand, and the pollution level of the soil was 250ug/g of soil. 1 g of contaminated soil was selected for each experiment. This soil specimen was put in a cylindrical container (length: 7 cm, diameter: 0.7 cm) and both ends were sealed with glass wool to prevent a leakage during the experiment.

#### 2.3 Experiment Method

Fig. 3 shows the schematic diagram of the extraction experiment. The reagents and a magnetic bar were put into a mixing cell. The magnetic bar mixed the CO<sub>2</sub> and reagents uniformly during the experiment. The specimen and the mixing cell were both placed in a water bath. The temperature of water bath was maintained at 40°C by an immersion heater and stirrer. The experiment was performed by flushing (gas CO<sub>2</sub>, flow rate: 15 ml/min) first. After cooling the syringe pump at 10°C using a

chiller, a syringe pump supplied CO<sub>2</sub> at a pressure of 210 bar. Two processes performed the extraction experiment. The first process was static extraction. The CO<sub>2</sub> underwent a phase change into supercritical and mixed with ligand. The second process was dynamic extraction. Both the CO<sub>2</sub> and the ligand mixture were directly extracted with metallic ions in the soil. Each process lasted for 30 min.

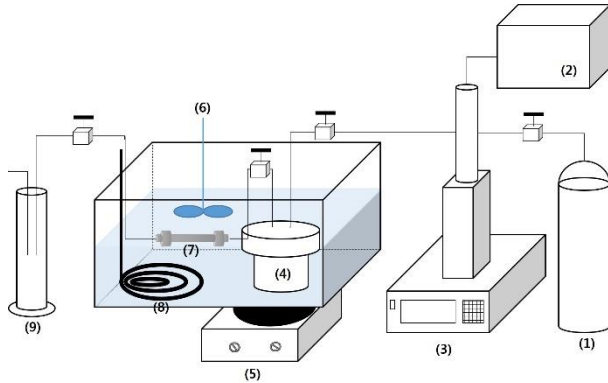


Fig. 3. Equipment for Extraction Test: (1) CO<sub>2</sub> cylinder (2) chiller (3) syringe pump (4) mixing cell (5) magnetic stirrer (6) stirrer (7) specimen (8) immersion heater and (9) bubbler

The extraction experiment was performed by changing the amount of reagent in each of the following: ligand, co-ligand, and H<sub>2</sub>O. Table 1 shows the condition of the extraction experiment in this study.

Table 1: Condition of extraction experiment

Experiment Number	Amount of reagent		
	Catechol-amine (mg)	Net4pFOSA (mg)	H <sub>2</sub> O (ml)
(1) The effect of the single reagent			
E-1	15.19	0	0
E-2	0	37.76	0
E-3	0	0	0.55
(2) The effect of the amount of H <sub>2</sub> O			
E-4	15.19	37.76	0.10
E-5	15.19	37.76	0.30
E-6	15.19	37.76	0.55
(3) The effect of the amount of co-ligand			
E-7	15.19	18.88	0.30
E-5	15.19	37.76	0.30
E-9	15.19	75.52	0.30

#### 2.4 Analysis

The extraction ratio of metallic ions was obtained by comparing the amount of metallic ions in the soil before and after extraction. A Microwave Acid Digestion System (MARS 5, CEM Corporation, Matthews, NC, USA) was used in pretreatment and then quantitative

analysis was conducted by an Inductively Coupled Plasma Mass Spectrometer (ICP-MS, Leeman Labs, Inc., USA). 1 g of soil specimen, 5 ml of 60% nitric acid, and 5 ml of distilled water were put into a vessel. This vessel was heated by microwave from room temperature to 180°C for 15 min and maintained at this temperature for 30 min. The pressure of the vessel was 300 psi during pretreatment.

### 3. Result and Discussion

#### 3.1 The effect of the single reagent

An extraction experiment was conducted using a ligand, a co-ligand, and H<sub>2</sub>O, merely to examine a reagent's exclusive extraction effects. According to these results, E-1 and E-2 both exhibited extraction rates below 5 %, and E-3 exhibited an extraction ratio below 10 %. These results verify that no exclusive reagent extraction occurs.

#### 3.2 The effect of the amount of H<sub>2</sub>O

Subsequently, an extraction experiment was conducted using a ligand, a co-ligand, and H<sub>2</sub>O simultaneously. After fixing the amounts of ligand and co-ligand, the experiment proceeded while the amount of H<sub>2</sub>O was adjusted. When more than 0.55 ml of H<sub>2</sub>O were added the extraction ratio increased to nearly 100 %. Figure 4 shows the changes to extraction efficiency for the various amounts of H<sub>2</sub>O.

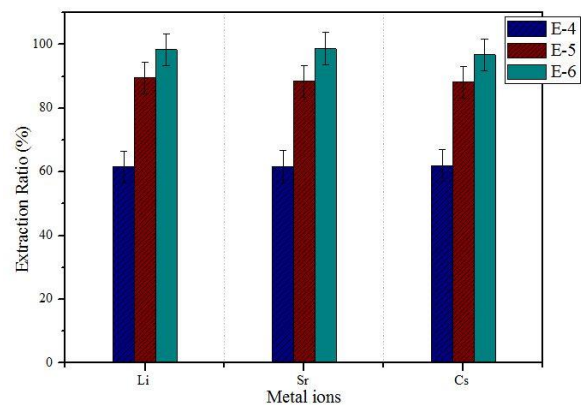


Fig. 4. Extraction ratio change according to amount of H<sub>2</sub>O.

#### 3.3 The effect of the amount of co-ligand

An effective extraction rate was evident with 0.3 ml of H<sub>2</sub>O in E-5, and when a large amount of H<sub>2</sub>O was used the amount of secondary waste also increased. Therefore the amount of H<sub>2</sub>O was reduced and fixed at 0.3 ml, and the amount of co-ligand was also changed. The experiment was conducted with ligand and co-ligand mole numbers at 1:0.5, 1:1, and 1:2. Figure 5 shows changes in extraction efficiency according to the amount of co-ligand present. When the amount of H<sub>2</sub>O decreased and the amount of co-ligand was twice that of the ligand, an extraction ratio close to 100 % was evident.

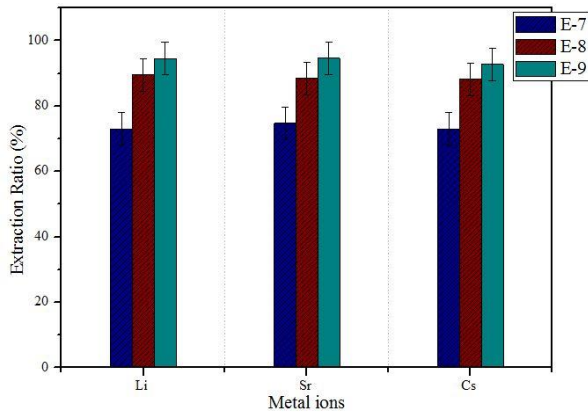


Fig. 4. Extraction ratio change according to amount of co-ligand.

#### 4. Conclusions

This study examined the effects of extracting metallic ions inside the soil using supercritical CO<sub>2</sub> and catecholamine as the ligand. Based on these results, it is evident that when only the extraction agent was used, there was no extraction effect and that only when the ligand, co-ligand, and additive were used together was there an extraction effect. Following this, the optimal extraction-agent ratio was confirmed using varying amounts of extraction agents. The most effective extraction ratio of ligand to co-ligand was 1:2 in E-9 when 0.3 ml of H<sub>2</sub>O were added. However, effective extraction efficiencies should be expected even if the amounts of ligand and co-ligand are increased after decreasing the amount of H<sub>2</sub>O. Hence, searching for more effective ways of decontamination using smaller amounts of H<sub>2</sub>O will give us a direction for future research.

#### REFERENCES

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