

Comparison Extraction Rates by Supercritical CO₂ Decontamination According to Elapsed Time after Heavy Metal Ions were Adsorbed

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1. Introduction

Due to the increasing price of oil and coal and the tightening of regulations on greenhouse gases, nuclear power plants will become a more important source of electricity. Therefore, the number of nuclear power plants will constantly increase over the world. However, nuclear power plants have a disadvantage: they generate radioactive waste. Among radioactive waste, heavy metals in soil have a special feature: they change the form of contamination depending on the types and sizes of the soil. Therefore, diverse methods have to be used for decontamination. The current methods used for decontaminating heavy metals in soil are the electrokinetic method, the biodegradation method, and soil washing. Since soil washing in particular creates many secondary wastes, the cost of decontaminating soil has increased. In this case supercritical carbon dioxide (scCO₂) was used to reduce the secondary waste, and is expected to lower the cost as well.

2. Experiments

2.1 Selection of heavy metal ions and extractants for experiments

Soil pollutants are defined by law in Korea. Of these soil pollutants, heavy metals are Cd, Cu, As, Hg, Pb, Cr, Zn and Ni. Among these heavy metals, Cd, Pd and Zn were selected for the present study because these heavy metals have not been studied by many researchers. And ⁶⁰Co and ⁹⁰Sr were selected for this study because they can remain in the soil because these metals are used for nuclear power plants. Diisooctyl phosphinic acid (Cyanex-272), diethylamine (DEA), benzo-18-crown-6 (B18C6), and perfluoro-1-octanesulfonic acid (Net4 pFOSA) were selected as extractants for these extraction experiments. In general, Cyanex-272 and DEA have shown good extraction abilities in removing Co, Cd and Zn and B18C6 and Net4 pFOSA are good extractants for extracting Sr and Pb [1,2].

2.2 Making the mock-up specimens

For the extraction experiments, two types of soil were prepared. One was sea-sand (JUNSEI, chemical pure) and the other was common soil. Because common soil was composed of various sizes, common soil was classified according to size. The common soil used in these experiments was coarse sand (classification

standards by United States department of Agriculture [USDA], diameter: from 0.50 mm to 1.00 mm). Every heavy metal ion was dissolved with a concentration of 1,000 ppm in 1 M HNO₃. To mix uniformly heavy metal ions, each heavy metal ion solution 5 mL was inserted vial by micro pipette. Therefore, there were 25 mL in the vial, and the solution was fully mixed by ultra-sonic apparatus for more than 30 minutes. This solution of the heavy metal ions was mixed with soil in a beaker based on the experimental conditions (see the Table I). The beakers were placed in a heater (60 °C, 40 torr) to completely evaporate 1 M HNO₃ for 24 hours.

2.3 Experiments

The experimental setups were composed of seven parts, as shown in Fig. 1. CO₂ was pressurized and heated by syringe pump (2) and water bath (7) up to 200 bar and 60 °C, and then, CO₂ became a supercritical state. Based on the extraction experimental conditions, the completed mock-up specimens were inserted into the mixing cell (3), and extractants to remove heavy metal-ions were inserted into the tubing cell (5). The processes of the experiment consisted of two steps. One was the static extraction process (30 minutes) and the other was the dynamic extraction process (30 minutes). The static extraction process was the step to raise the CO₂ temperature up to 60 °C and to mix extractants with scCO₂. The dynamic extraction process was the step to remove heavy metal-ions by scCO₂ with the extractants. To analyze the specimens conducted in the experiments, a micro-wave was used for pre-handling (MARS 5, CEM Corporation, Matthews, NC, USA) and an inductively coupled plasma spectrometer (ICP, LEEMAN ABS. INC., U.S.A) was used for analysis.

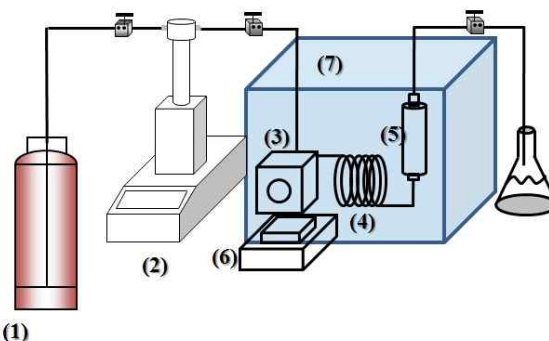


Fig. 1. Equipment for Extraction; (1) CO₂ Cylinder (2) Syringe pump (3) Mixing cell (4) Preheating tube (5) Tubing cell (6) Stirrer and (7) Water bath.

Table I: Experiment conditions for comparing extraction yields with elapsed time after heavy metal-ions are adsorbed

experiment number	elapsed time	soil type (soil size, diameter)	amounts of metal-ions solution (μL)	Extractants				additive (μL)
				Cyanex-272 (μL)	DEA (μL)	B18C6 (μg)	Net4 pFOSA (μg)	
1	1 hour	sea-sand (1.0 mm) or common soil (0.5 mm < < 1.0 mm)	200	1860	40	104.5	47	0.1 M HNO_3 50
2	2 hours							
3	6 hours							
4	12 hours							
5	1 day							
6	3 days							
7	7 days							
8	30 days							
9	60 days							

3. Results and Discussion

As shown in Fig. 2, the extraction yields of sea-sand and those of common soil within 7 days (experiment number is 1, 2, 3, 4, 5, 6 and 7) did not change according to elapsed time. However, the common soil extraction yields after 7 days (experiment number is 8 and 9) were sharply decreased. In this study, it is assumed that sudden decreases occurred because of changes in chemical bonds. To confirm this assumption, x-ray photoelectron spectroscopy (XPS, Thermo Electron, K-Alpha, UK) was used for analysis. The Fig. 3 shows the XPS results for Cd. As shown in Fig. 3, Cd had one chemical bond when the elapsed time that heavy metal-ions were adsorbed in soil was 3 days. However, if the adsorbed elapsed time became 60 days, Cd had three chemical bonds. This showed that the chemical bonds of Cd are changed according to elapsed time.

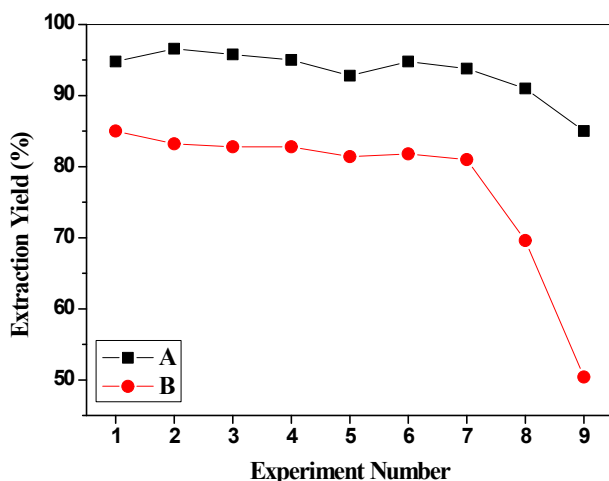


Fig. 2. Comparison of the extraction yield of the sea-sand and common soil (the conditions for the experiments are listed in Table I.): (A) sea-sand and (B) common soil

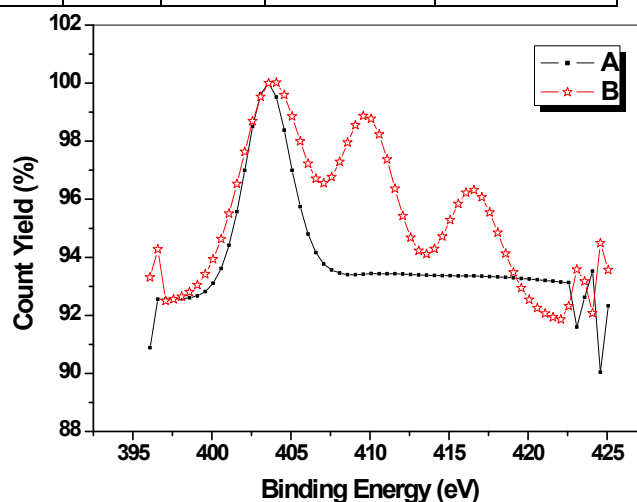


Fig. 3. Analysis output of Cd by XPS: (A) 3 days and (B) 60 days elapse after heavy-metal ions are adsorbed

4. Conclusions

In this study, heavy metal ions in soil were decontaminated by scCO_2 . scCO_2 was selected due to being non-toxic and producing little secondary waste and Cyanex-272, DEA, Net4 pFOSA and B18C6 were used as extractants because those had good extraction rates under scCO_2 . From the experiments in this study, we knew that extraction yield in the sea-sand was constant and that of the common soil was decreased depending on elapsed time. It is assumed that these results were caused by physicochemical combination. The analysis output by XPS shows that this assumption may be valid. However, diverse analysis will be conducted for demonstrating definitely this assumption.

REFERENCES

- [1] Moonsung Koh, Kwangheon Park, Doohyun Yang, Kakwon Kim, Hongdoo Kim, "The Synergistic Effect of Organophosphorus and Dithiocarbamate Ligands on Metal Extraction in Supercritical CO_2 ", Bull Korean Chem.Soc., 2005
- [2] Joanna Shaofen Wang, Moonsung Koh, Chien M. Wai, Nuclear Laundry Using Supercritical Fluid Solutions, Ind. Eng. Chem. Res. 43, 1580-1585, 2004