

Sea sand decontamination using a supercritical CO₂

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1. Introduction

Nuclear power plants are environmentally-friendly energy producers that generate tremendous electrical powers with very little waste. However, in further developing such facilities, the amount of waste is continually increasing. In particular, the soil around nuclear facilities can be contaminated with radionuclides in the long-term. Existing soil decontamination methods include washing and flushing soil using extreme hydraulic pressure. A main problem, however, is the resultant secondary waste such methods spawn. Therefore, a decontamination method is needed to reduce secondary waste. This research involved experiments using supercritical CO₂ as a decontaminant because supercritical CO₂ is non toxic and produces little secondary waste. The purpose of this research was to confirm the possibility of decontaminating real soil by decontaminating mock-up specimens.

2. Experiments

2.1 Making the mock-up specimens

To create mock-up specimens, we selected several main metal-ions (cobalt, lead, zinc, cadmium, strontium). Of these, cobalt and strontium are the main nuclides found around nuclear facilities. The others are important heavy metal-ions used in nuclear power plants. Each metal-ion was dissolved in 1 M HNO₃ and its concentration was around 1,000 ppm. To achieve a uniform metal-ion solution, a 5 mL sample was taken using a micro pipette. This was then placed in a vial (the total amount of metal-ion solution in the vial was 25 mL). The solution was mixed by ultra-sonic. To create the mock-up specimens, sea sand (JUNSEI, 20-30 mesh, chemical pure) was prepared. Glass tubing (5 cm in height, 0.7 cm in diameter) was filled with glass wool on one-side to stop leakage of the sea sand. The sea sand (1.0 g) then filled the glass tubing. 100 µL of metal-ion solution was selected from the 25 mL metal-ion solution and inserted into the sea sand in the glass tubing. The sea sand containing the 100 µL metal-ion solution was placed in a vacuum pump for about one hour (80 °C, 40 Torr). After any HNO₃ in the sea sand evaporated, the sea sand contained 0.02 µg of each metal-ion (total metal-ions were 0.1 µg).



Fig. 1. Mock-up specimen; in which the surface of the sea sand was impregnated with metal-ions

2.2 Extraction experiments

For the extraction experiments, we selected several chelating ligands [Cyanex-272(Diisooctylphosphinic acid, 290.43 g/mole), DEA(Di Ethyl Amine, 73 g/mole), B18C6(Benzo-18-crown-6, 312.37 g/mole), Net4 pFOSA(Perfluoro-1-Octanesulfonic acid, 629.38 g/mole)]. Of these chelating ligands, Cyanex-272 and DEA have generally a good extraction rate in removing cobalt, lead, zinc and cadmium [1,2]. B18C6 and Net4 PFOSA have a good extraction rate in removing strontium [4]. Equipment for the experiment consisted of a CO₂ Cylinder, syringe pump, mixing cell, preheating tube, tubing cell, stirrer and water vessel. Firstly, chelating ligands were placed in the mixing cell under experimental condition, shown in Table I. Secondly, the prepared mock-up specimen was inserted into the tubing cell. The mixing cell was stirred by the stirrer. Pressure was kept at 200 bar by using the syringe pump and the temperature was maintained at 60 °C using a water bath. Static extraction was performed under 200 bar, at 60 °C for 30 minutes and then dynamic extraction was performed for 30 minutes under 200 bar, at 60 °C.

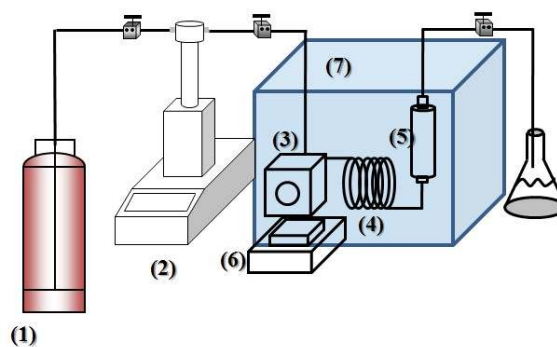


Fig. 2. Equipment for Extraction; (1) CO₂ Cylinder (2) Syringe pump (3) Mixing cell (4) Preheating tube (5) Tubing cell (6) Stirrer and (7) Water bath.

Table 1 : Condition of Experiments

	Metal-ions solution (μL)	Cyanex-272 (μL)	DEA (μL)	B18C6 (μg)	Net4 PFOSA (μg)	Additive (μL)
Experiment 1	100	1860	20	0	0	H ₂ O 50
Experiment 2	100	1860	40	0	0	MeOH 50
Experiment 3	100	1860	40	0	0	0.1M HNO ₃ 50
Experiment 4	100	1860	40	209	0	H ₂ O 50
Experiment 5	100	1860	40	104.5	47	0.1M HNO ₃ 50

2.3 Analysis

To compare the experimental results, a standard solution was needed. A mass cylinder was filled with 15 mL of 1 M HNO₃ and a mock-up specimen not subjected to extraction was inserted into the mass cylinder. By using the ultra-sonic, metal-ion in the mock-up specimen was mixed with 1 M HNO₃ 15 mL in the mass cylinder. After the ultra sonic process was completed, the mixture of HNO₃ and metal-ions was filtered and 10 mL of HNO₃ was diluted in 90 mL of distilled water. This solution (10 mL HNO₃ + 90 mL distilled water) was analyzed using an ICP (Inductively Coupled Plasma Spectrometer, LEEMAN ABS. INC., U.S.A). To achieve the experimental results, the mock-up specimen was removed from the tubing cell after being flushed with supercritical CO₂ for 30 minutes. The mock-up specimen was inserted into the cylinder, which was filled with 15mL of 1 M HNO₃. After HNO₃ was mixed with metal-ions by using the ultra-sonic for 30 minutes, 10mL of HNO₃ was mixed with 90mL of distilled water. This solution (10mL HNO₃ + 90mL distilled water) was analyzed using the ICP.

3. Results and Discussion

Figure 3 shows the extraction rate of the metal-ions strontium, cadmium, lead, zinc, and cobalt. When only cyanex-272 and DEA were placed in the mixing cell, the extraction rate of cadmium and zinc was almost 90%, but that of strontium and lead was about 70%. Because of the low extraction rate of strontium and lead, in this study, B18C6 and Net4 PFOSA were added. As a result, the extraction rate of strontium reached 93% and that of lead reached 97%.

4. Conclusions

Supercritical CO₂ was applied to extract metal-ions and to reduce secondary waste. By using the cyanex-272 and DEA, more than 90% of cadmium and zinc were extracted. To extract strontium and lead, B18C6 and Net4 PFOSA were added, so extraction rate of strontium and lead became 93% and 97% respectively.

Through extraction of metal-ions from mock-up specimens, we can confirm the possibility of extracting metal-ions (cobalt, strontium, cadmium, lead, zinc) from real specimens. To apply this method to real specimens, the amount of chelating ligands needs to be was

optimized. Our next study will determine the amount of chelating ligands.

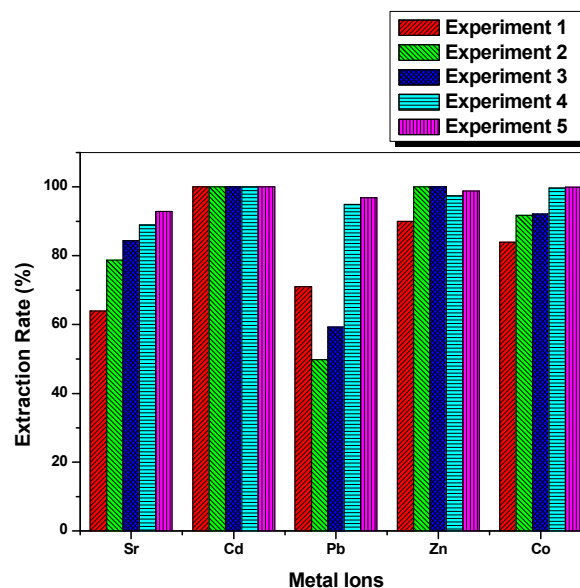


Fig. 3. The extraction rate of metal-ions, Sr, Cd, Pb, Zn, Co. Four different extraction cases are shown in Table 1 : Condition of Experiments

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