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Decontamination of Heavy metals in soil using supercritical CO_2

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1. Introduction

Nuclear energy becomes more important in Korea under the situation of high import prices of oil and coal. And within 20 years about 60% of electricity will come from nuclear power plants. As the number of nuclear power plants increases, the amount of waste continually increases. And the waste disposal cost is expected to rise up to about 6,000,000won/200L-drum. Volume reduction of radioactive wastes is essential nowadays.

The existing methods for soil decontamination may be divided in: "in-situ" and "out-situ" techniques. Among "out-situ" techniques, a generally used method is soil washing and flushing by extreme hydraulic pressure. The soil washing and flushing by extreme hydraulic pressure, however, has a problem to generate lots of secondary wastes. A supercritical fluid such as carbon dioxide has a very low surface tension with a very high permeability to the porous medium like soil. Due to their huge change of molar volume near the critical point, it is easy to change the solubility of a substance in the fluid by changing the pressure and the temperature at near the critical point. The good permeability and the ease of recovery of the fluid make the supercritical fluid a good solvent for decontamination. The most widely used supercritical fluid is carbon dioxide because of its good properties - nontoxic, nonflammable and inexpensive. The purpose of this work was to find the possibility for soil decontamination using the supercritical carbon dioxide.

2. Experiment

2.1 Making the mock-up specimens

We selected five environmentally-detrimental metal-ions (cobalt, lead, zinc, cadmium, and strontium) to make mock-up specimens. Of these, cobalt and strontium are the main nuclides found around nuclear facilities. The others are important heavy metal-ions detected in common soil. Each metal-ion was dissolved in 1 M HNO_3 up to the concentration of 1,000 ppm. So, the total concentrations of all five metal ions were 5,000 ppm. The solution was fully mixed by ultra-sonic for over 30 minutes.

To compare the effects of soil pore and sorts, we prepared four different types of soil depending on the size. The four types of soil for experiment are shown in Table Ⅰ. Mock-up specimens were made by putting the prepared soil (20g) in beaker and mixing the soil with 2,000 μL of the prepared metal-ions solution (i.e., metal-ion solution 100 μL per 1g soil). Fig. 1 shows the beaker containing 20g sample soil and 2,000 μL metal-ions solution. The beakers were placed in a heater (60℃) to fully evaporate 1 M HNO_3 for over 24 hours. Then the mock-up specimens are stored in a dry cell.

Table Ⅰ: Condition of Soil

Number	Type	Size (diameter, mm)
1	Sea-sand	0.5 – 1.0
2	Common soil	Over 1.0
3	Common soil	0.5 – 1.0
4	Common soil	Below 0.2

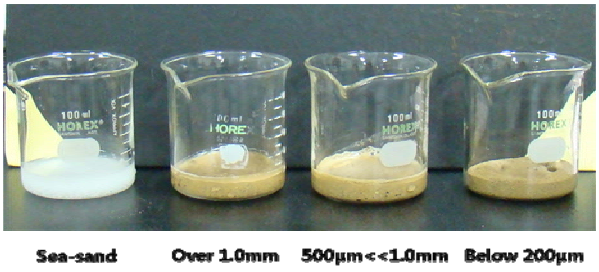


Fig. 1. The beaker containing sample soil (20g) and metal-ions solution (2,000 μL)

We put the mock-up contaminated soil into a glass tubing (5 cm in height, 0.7 cm in diameter) for decontamination experiments. The glass tubing was blocked by glass wool at both ends. Fig. 2 shows the glass tubing containing a sea sand (0.7 g) specimen.

Fig. 2. 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 chelating ligands, Cyanex-272(diisooctylphosphinic acid, 290.43 g/mole) mixed with DEA(diethylamine, 73 g/mole). Cyanex-272 and DEA have shown a good extraction ability in removing cobalt, zinc, lead and cadmium [1,2] under supercritical CO_2. Experimental setup consists of a CO_2 cylinder, syringe pump, a mixing cell, preheating tube, a tube cell, stirrer and a water bath, which are presented in Fig. 2. Firstly, chelating ligands were placed in the mixing cell (Cyanex-272 1860 μL and DEA 20 μL). Secondly, the prepared mock-up specimen was inserted into the tube cell. The mixing cell was stirred by a magnetic bar. Pressure was maintained at 200 bar by using the syringe pump and the temperature was maintained at 60℃ using a water bath. Static extraction was performed under 200 bar, at 60 ℃ for 30 minutes and then dynamic extraction was performed for 30 minutes under the same condition. The analysis for sample was conducted by ICP (Inductively Coupled Plasma Emission Spectroscopy, Perkin-Elmer, US/OPTIMA 4300DV).

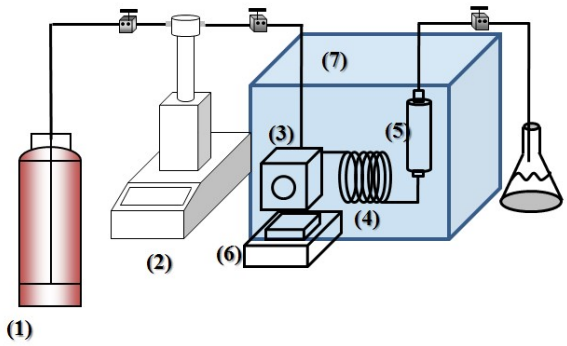
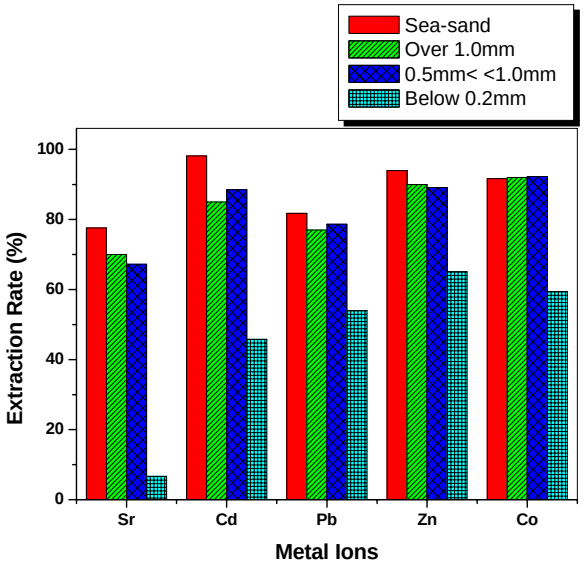


Fig. 2. Experimental setup for extraction experiments; (1) CO_2 Cylinder (2) Syringe pump (3) Mixing cell (4) Preheating tube (5) Tubing cell (6) Stirrer and (7) Water bath.

3. Results and Discussion

Fig. 3. shows the extraction rate of each metal-ion (strontium, cadmium, lead, zinc, and cobalt) depending on the type of soil. The extraction rate was somewhat dependent on the soil type. And the extraction rates of Cd, Zn, and Co are slightly better than the other ions. The surface condition and the specific surface area of the soil definitely affect the extraction rate. When the size of the soil is larger than 0.5mm, the extraction rates were not different much. However, in the case of the soil size less than 0.2mm, the extraction rates were quite reduced. Sr ions looked mostly affected (lower than 10%). The increased specific surface area and the smaller gap size among the soil particles seem to be the reason.



4. Conclusions

By using the Cyanex-272 and DEA, more than 80% of metal ions were extracted from the soil in the case that the size of soil was larger than 0.5mm. When the soil size was lower than 0.2mm, the extraction rate was reduced down. The mostly affected ion was Sr. Sr ion seems to be adsorbed more strongly to the soil surface than other metal ions used in this study. Through this experiment, we found that the extraction of metal ions in the soil were feasible. However, we need more effective chelating ligands to gain high extraction rate.

Fig. 3. The Extraction rate of metal-ions (Sr, Cd, Pb, Zn, Co) according to four different types of soil: when adsorption amount of metal-ions is 100 μL per 1g soil

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