

Selective Decontamination Effect of Metal Ions in Soil Using Supercritical CO₂ and TBP Complex

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1. Introduction

Despite continuing concern regarding nuclear power, it remains an ongoing area of research and development. As a result, there has been a continuing increase in radioactive waste and the cost of processing such waste.

Fission products contain various heavy metals, including uranium. If such fission products start to leak from a nuclear plant, the soil in the surrounding vegetation is at risk of contamination. Decontamination of soil pollution is difficult because the type of contamination largely depends on the characteristics of the pollutant and the area [1]. Also, existing soil decontamination methods generate large quantities of secondary waste and additional process costs. For this reason, new decontamination methods are always under active investigation. A method involving the use of supercritical carbon dioxide with excellent permeability in place of chemical solvents is currently being studied [2].

Unlike other heavy metals in fission products, uranium is used as fuel, and must be handled carefully. Therefore, in this paper, we studied a supercritical carbon dioxide method for decontaminating heavy metal ions in soil using tri-*n*-butyl phosphate(TBP), which is well known as a ligand for the extraction of metal ions of actinium.

2. Methods and Results

In this study, we experimented with a decontamination test in order to confirm the selective decontamination effect of metal ions in soil, after contaminating the soil sample with metal ions (lithium, strontium, and cesium). We then compared the results of these tests with the results from soil decontaminated with uranium. Information regarding the decontaminating effect of uranium is contained in a study by W. Y. Jung [3].

After mocking up the polluted soil specimen with three metal ions, we experimented with the extraction test using TBP and supercritical carbon dioxide. For quantitative analysis, we carried out preprocessing using the Microwave Acid Digestion System (MARS 5, CEM Corporation, Matthews, NC, USA); for quantitative analysis, we used the Inductively Coupled Plasma Mass Spectrometer (ICP-MS).

2.1 TBP-HNO₃ Complex

Supercritical carbon dioxide has been studied in many fields because of its high solubility, prompt reaction rate, and the ease with which it can be combined with other organic materials [4]. Most of the heavy metals in soil are polar and form ions or an oxidation state. But carbon dioxide is non-polar. It cannot be used to extract polar and non-polar materials, so as an extractant, it is necessary to use an additive that combines well with metal ions and will also dissolve in carbon dioxide. In this study, we used TBP-HNO₃ complex as an extractant.

TBP is known as a ligand for the extraction of the metal ions of actinium. It is especially known for its high solubility in supercritical carbon dioxide [5]. It forms a complex with nitride easily, and this complex is also highly soluble with supercritical carbon dioxide [6].

Therefore, in this study, we used the mechanism uranyl nitrate-TBP complex generated from uranyl nitrate, which is insoluble in supercritical carbon dioxide. The TBP reagent is easily soluble in supercritical carbon dioxide.

2.2 Mock up the specimen

We mixed 10ml nitric acid with sea sand (JUNSEL, chemical pure), which has a large particle size and a small surface pore size. We then placed the mixture into a 5ml standard solution of three pollution sources (lithium, strontium, and cesium). In order to mix the metal ions well in the soil, we used an ultrasonic cleaner for one hour. The contaminated soil dried in the drying oven for about 20 hours at 90°C until only the metal ions remained and the nitric acid had evaporated in the mixture of soil and aqueous solution.

We then made a mock-up specimen using the contaminated soil in readiness for the experiment. We put the specimen into polluted soil in a pipe (length 7cm, diameter 1/4in) and blocked the outlet hole with glass wool in order to prevent soil leakage. Figure 1 below shows the mocked-up specimen used in the extraction test.

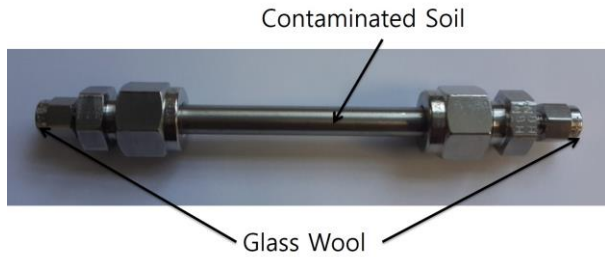


Fig 1: Mocked-up specimen

2.3 Experiment method

Figure 2 below shows the equipment used for the heavy metals in the soil extraction test using supercritical carbon dioxide.

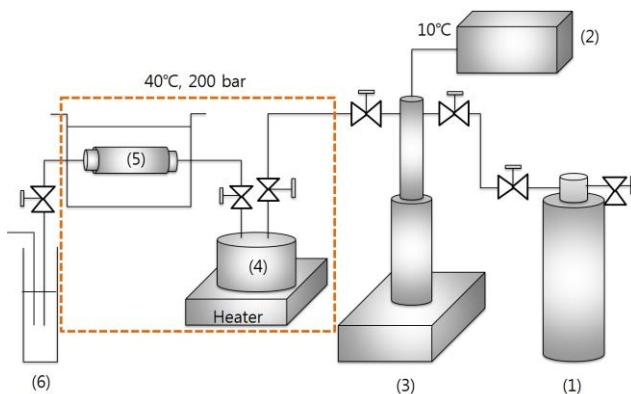


Fig. 2: Equipment for Extraction Test: (1) CO₂ cylinder; (2) temperature controller; (3) syringe pump; (4) mixing cell and heater; (5) specimen and temperature controller; (6) bubbler.

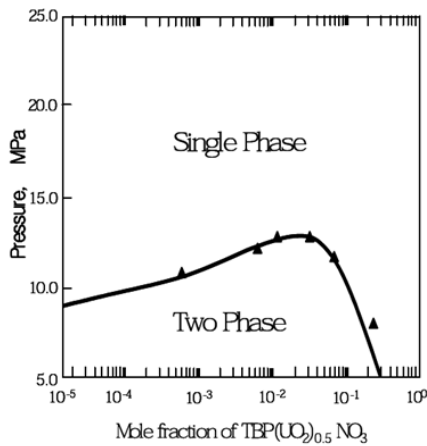


Fig. 3: TBP solubility of carbon dioxide at 40°C using Enikida's test [7]

Carbon dioxide becomes a supercritical fluid when it reaches 30°C and 70 bar [4]. Figure 3 shows the TBP solubility of carbon dioxide at 40°C. As shown in Figure 3, at a temperature of 40°C, carbon dioxide completely dissolves when the TBP is 130 bar or more. Therefore, we maintained experimental conditions of about 40°C and 200 bar [7].

The temperature of the inlet gas into the syringe pump (3) is maintained at 10°C by the temperature controller (2). In this area, the carbon dioxide is in a liquid state. Next, using the temperature controller (5) and heater (4), the temperature of the mixing cell (4) and specimen (5) is maintained at 40°C. Subsequently, using the syringe pump (3), the pressure of the carbon dioxide let into the mixing cell (4) and the specimen (5) is maintained at 200 bar. Finally, the carbon dioxide enters a supercritical state.

In the experiment procedure, the static extraction produces supercritical carbon dioxide which then mixes with the extractant; dynamic extraction involves extracting a real sample of soil using supercritical carbon dioxide. Each procedure takes about an hour and 30 minutes and the total experiment time is three hours.

To check the effect of the extractant amount, we experimented with different amounts of extractant: 15ml, 5ml, and 1ml.

2.4 Analysis

For analysis purposes, we used ICP-MS. The decontaminated soil preprocessed using the Microwave Acid Digestion System (MARS 5) for quantitative analysis of the metal ions remained in the soil after extraction. We placed 1g decontaminated soil into a vial, along with 5ml distilled water and 5ml nitric acid. We increased the temperature and pressure to 180°C, 300 psi at 300W for 15 minutes using MARS 5. The same temperature and pressure were maintained for 15 minutes. After preprocessing, we carried out a quantitative analysis using the ICP-MS.

3. Result and Discussion

Figure 4 below shows the extraction rate of each metal ion, as well as the amount of extractant used.

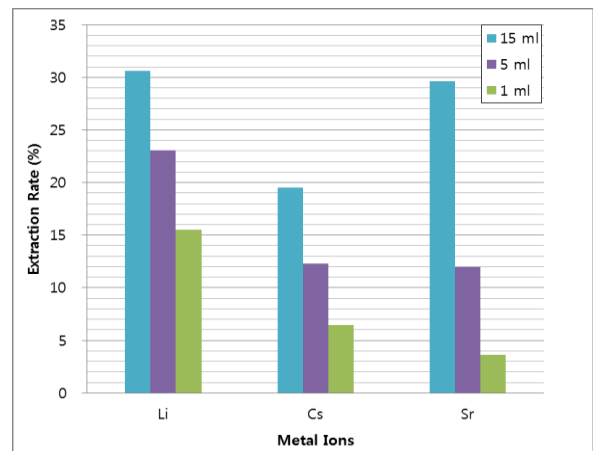


Fig. 4: Extraction rate and quantity of extractant

As we can see in Figure 4, in the case of 15ml of extractant, the extraction rate of Li and Sr is about 30% and the extraction rate of Cs is about 20%. If the

quantity of extractant is reduced to 5ml and 1ml, the extraction rate rapidly decreases. In particular, the extraction rate of Sr dropped sharply to about 3% when 1ml of extractant was used. This result shows that the extraction rate of Sr is hardly effective in the case of very small amounts of extractant.

W. Y. Jung [3] extracted uranium using TBP-HNO₃ Complex when the supercritical carbon dioxide was at 40°C and 200 bar. Table 1 below shows the changes to the uranium extraction rate according to the extractant amount.

Table 1: Change to uranium extraction rate according to extractant amount [3]

Amount of extractant (ml)	Extraction rate (%)
15	99.84
10	99.48
5	98.96
4	98.52
2	96.69
1	95.14
0.8	94.78
0.5	90.42
0.4	91.38
0.3	72.49
0.2	59.44
0.1	30.57

It can be seen from Table 1 that when over 0.4ml of extractant is used, the extraction rate is visibly high, at over 90%. This result proves that an effective decontamination method for extracting uranium is to use supercritical carbon dioxide and TBP-HNO₃ Complex.

The combined results of Figure 4 and Table 1 show a very high extraction rate of uranium, despite the use of a small amount of extractant; on the other hand, Li, Cs, and Sr show a significantly lower extraction rate than uranium in the case of a relatively large amount of extractant.

4. Conclusions

We investigated the decontamination effect of heavy metal ions in the soil using TBP-HNO₃ Complex and supercritical carbon dioxide. The study results showed that when heavy metals in soil are extracted using supercritical carbon dioxide, the extraction efficiency is different according to the type of pollutant metal ions in the soil. When TBP-HNO₃ Complex is used with an extractant, uranium extraction is very effective, but lithium, strontium, and cesium extraction is not effective. Therefore, in the case of a mixture of uranium and other metals such as lithium, strontium, cesium, and so on in soil contaminated by fission product leaks from nuclear

power plants, we can selectively decontaminate uranium with supercritical carbon dioxide and TBP-HNO₃ Complex. Also, because the amount of TBP-HNO₃ Complex used in selective decontamination is very small, it can be said that this is an environmentally friendly method which generates almost no secondary waste.

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