

UO₂ Contaminated Soil Clean-up Method Using Supercritical CO₂ and Reagent

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1. Introduction

Nuclear power generation has been recognized in many countries around the world as an environmentally friendly energy resource. However, there is a critical problem that radioactive waste generated behind it. Furthermore, the development of scientific and military industries using radioactive materials is accompanied by an increase in such waste. Among the many wastes, soil contamination by uranium, which is a fuel material mainly used in the nuclear power industry, is constantly occurring to meet the growing need for nuclear energy. In fact, uranium-contaminated soil, which was about 600 times the background level, had been found near the site where the uranium was mined [1]. Moreover, as the decommissioning time of domestic nuclear power plants is coming, decontamination of contaminated soil by uranium and other radioactive materials is indispensable for restoring the environment. However, conventional soil decontamination techniques have produced secondary wastes due to solvent by using a large amount of acids and organic solvents. Therefore, it is considered that the decontamination method using the supercritical fluid is suitable as an alternative to solve such a problem. Therefore, in this study, uranium extraction using supercritical carbon dioxide (scCO₂) decontamination technique was studied for artificially contaminated sea sand and actual soil. Furthermore, it has been confirmed that the decontamination efficiency is lowered as the contamination period increases in our previous research [2]. Therefore, in this study, the additional experiment was carried out to improve the extraction efficiency through the soil pretreatment process.

2. Materials and methods

2.1 Preparation of uranium artificially contaminated soil

Two types of specimens were used in this experiments. One is chemically pure sea sand (Junsei, Japan) used as received, without further purification. The other is real soil in a field. In case of soil, it is used after a series of treats to remove impurities. And then the soil classified into three groups according to the size of the soil. The details of the soil sample preparation had been described previous work [2]. Size of 4 samples are shown at Table. I. After this work, both samples were placed in a beaker with a nitric acid solution of uranium dissolved at a concentration appropriate to the target contamination level (50 µg-U per 1 g of sample). The beaker was then placed in an ultrasonic cleaner for 1 h to evenly mix the uranium ions in the sample. The beakers containing the sample and solution were placed in a vacuum oven and

dried at 90 °C for about 1 day for fully evaporating the solution. The dried sample was mixed with a spatula to ensure that the uranium was uniformly distributed in the sample. This procedure is illustrated in Fig. 1 as a simplified illustration.

Table. I. Classification of sand and soil samples

| Sample type | Size (mm) |
|-------------|-----------|
| Silica sand | 1.0~ |
| Coarse soil | 0.5~1.0 |
| Medium soil | 0.2~0.5 |
| Fine soil | 0.2~ |

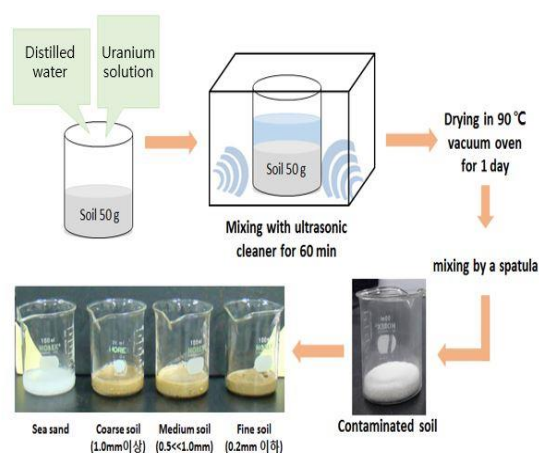


Fig. 1. Procedure for preparing contaminated sample

2.2 Preparation of the reagent

In order to extract uranium into scCO₂, which is a nonpolar solvent, reactants capable of forming a metal complex with uranium and also dissolving in scCO₂ are required. In this study, TBP-nitric acid complex was selected as reactants and the production procedure of it is shown in Fig. 2. And Fig. 3 shows the solubility of this reagent.

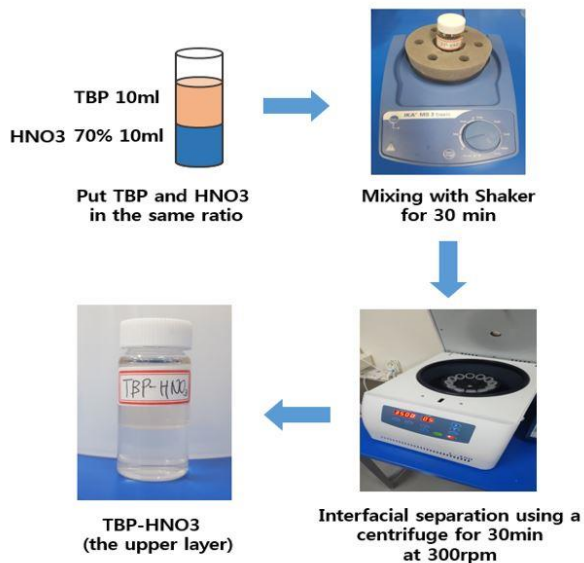


Fig. 2. Procedure of preparing TBP-HNO₃ complex

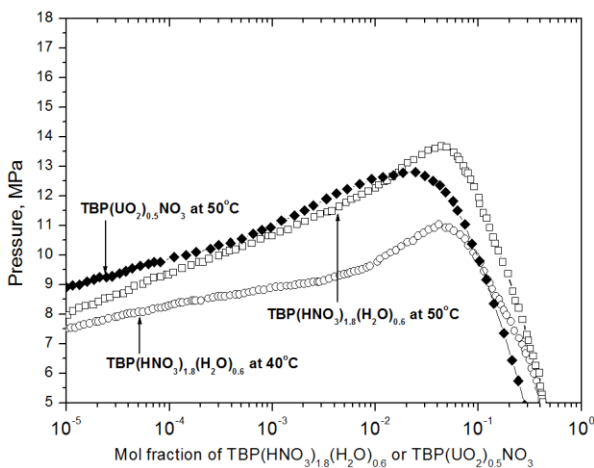


Fig. 3. Solubility curves for the transition pressures from two-phase to single-phase TBP·(UO₂)_{0.5}·NO₃ and TBP·(HNO₃)_{1.8}·(H₂O)_{0.6} in scCO₂ [3]

2.3 Experiment for uranium extraction

The experimental apparatus for extracting uranium from soil using scCO₂ is shown in Fig. 4. The mixing cell contains a magnetic bar, which mixed the TBP-HNO₃ complex with the scCO₂. The specimen container is a stainless tube, which contain a 1g of soil sample. The experiment was carried out with 30 minutes of static extraction to dissolve TBP-HNO₃ in the mixing cell and then dynamic extraction with TBP-HNO₃-dissolved scCO₂ to the specimen container for 30 minutes.

After the experiment, the sample was collected from the container and the residual uranium extracted from the soil through MARS5 (CEM Co., Matthews, NC, USA). And the extracted solution were quantitatively analyzed by ICP-MS (Leeman Labs, Lowell, MA, USA). The Extracted fraction of uranium (f_U) is determined by

difference between the before and after concentration of the solution following Eq. 1; where C_B and C_A are the concentration of uranium in the solution before and after the experiment, respectively.

$$f_U = \frac{C_B - C_A}{C_B} \quad (1)$$

All experiments were conducted under the following conditions; Pressure 200 bar, temperature 40 °C, flow rate about 3 ml / min.

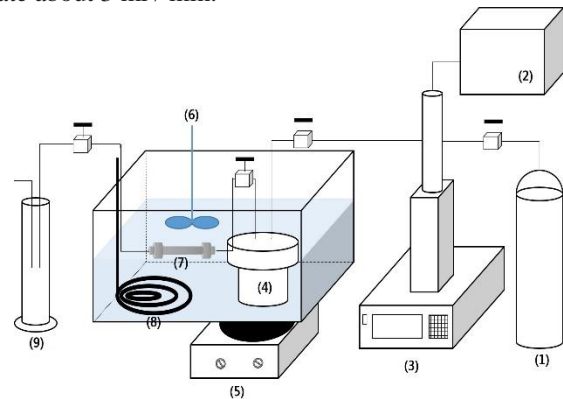


Fig. 4. Experimental apparatus for Uranium extraction experiment using scCO₂ (1) CO₂ cylinder; (2) chiller; (3) syringe pump; (4) mixing cell; (5) agitator; (6) immersion heater; (6) mixer; (7) specimen container; and (9) collector

3. Results and discussion

3.1 Extraction efficiency depending on the amount of reagent

In order to estimate the amount of extraction agent suitable for the extraction experiment, the uranium extracted fraction was confirmed in sand specimens by increasing the amount of the extractant. The results are shown in Fig. 5.

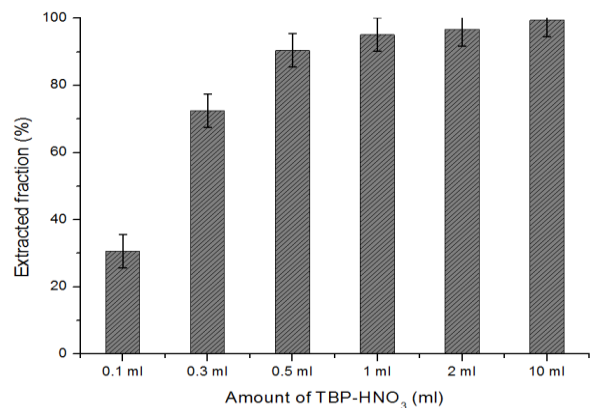


Fig. 5. Uranium extracted fraction depending on the amount of reagent

The results show that most of the uranium is extracted from about 0.5 ml considering the $\pm 5\%$ analysis error of ICP-MS. According to this result, the amount of extractant used in this extraction experiment was selected as 0.5 ml.

3.2 Extraction efficiency depending on the type of soil and contamination period

The classification of soil samples was described above more detail, and the extraction efficiency according to the pollution period was tested under various conditions from 1 day to 7 years. The results are shown in Fig. 6 below.

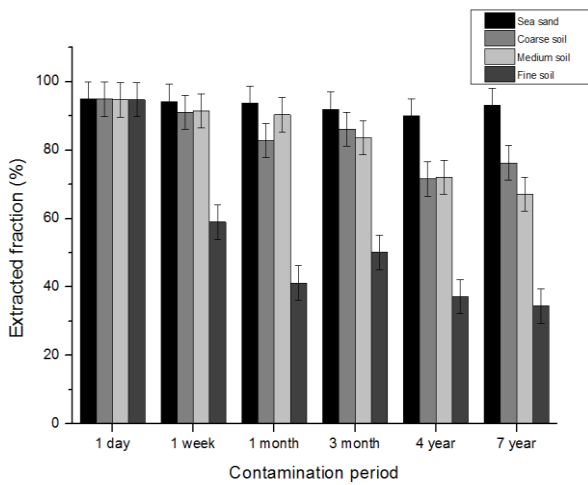


Fig. 6. Uranium extracted fraction depending on the type, size and period of contamination

According to the results, it was confirmed that the sea sand showed almost consistent high extraction efficiency regardless of the contamination period. On the other hand, in case of actual soil, the longer the period of contamination, the lower the extraction efficiency. This tendency became more apparent as the soil size was smaller. The reason for this could be found through analysis using SEM-EDX. Fig. 7 is the images of the surface of sea sand (silica sand) and actual soil, respectively.

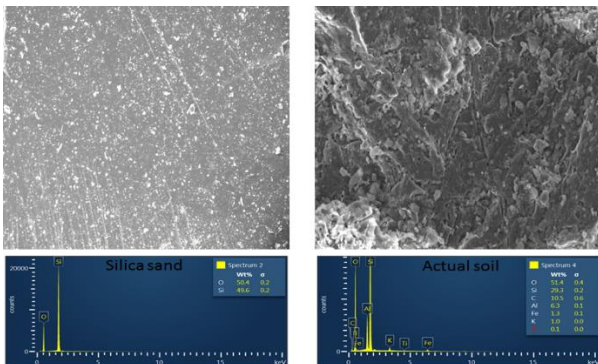


Fig. 7. SEM-EDX images of sea sand (left) and real soil (right)

The surface of the sea sand is smooth and flat, whereas the actual soil has large and small pores and cracks on the surface. It was considered that the metal had adsorbed on such a tiny region was difficult to react with the extracting agent.

In addition, the cause of the deterioration of the extraction efficiency according to the contamination period is expected to be different binding mechanism between soil and uranium. At the beginning of the contamination, uranium would be expected to be simply physically adsorbed on the soil surface, but as the contamination period elapsed, it would be interact with the soil and be strongly adsorbed physicochemically.

3.3 Extraction efficiency depending on the type of soil and contamination period

'Soil wet pretreatment' was performed to increase the extraction efficiency of long-term (7 years) contaminated specimens [4]. This pretreatment method was carried out by injecting a certain amount of water together with the soil into the specimen container. The results were shown in Fig. 8.

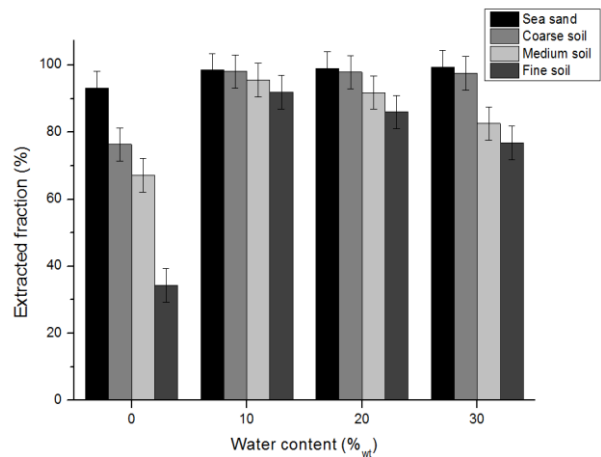


Fig. 8. Uranium extracted fraction depending on water content

The results showed that the extraction efficiency was improved in all types of samples as the moisture was supplied. This improved extraction efficiency was the most evident when the amount of water about 10% of the soil weight was added. Following these results, in the case of long-term contaminated soils, it was confirmed that a small amount of water is required to promote the reaction of metal and reagent. However, the amount of water exceeding 10% caused a decline in the improved decontamination efficiency. This is probably due to the formation of a water layer that prevents metal from reacting with the extractant [5]. A schematic illustration of this phenomenon is given in Fig. 9.

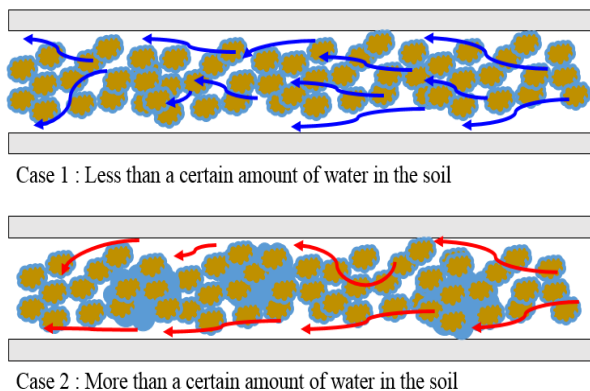


Fig.9. Schematic illustration of scCO₂ flow predicted by the amount of water content in specimen container

4. Conclusion

In this study, the feasibility of the supercritical extraction technology as one of the decontamination techniques for extracting uranium from the soil was evaluated positively. In addition, some results of supercritical extraction technology have been obtained for several factors for evaluating soil decontamination technology. Through our experimental results, it is confirmed that the results of the extraction efficiency of the decontamination technique using sea sand as a specimen are needed to be evaluated from a more conservative standpoint. Decontamination technic using supercritical fluids has also been found to require a certain amount of water for effectively extracting the metal ions from long-period contaminated soil. In order to maximize the advantages of supercritical fluid extraction technology, it is most important to find an optimum ratio of the amount of extractant and added water.

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