

Article

Decontamination of Uranium-Contaminated Soil Sand Using Supercritical CO₂ with a TBP–HNO₃ Complex

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Abstract: An environmentally friendly decontamination process for uranium-contaminated soil sand is proposed. The process uses supercritical CO₂ as the cleaning solvent and a TBP–HNO₃ complex as the reagent. Four types of samples (sea sand and coarse, medium, and fine soil sand) were artificially contaminated with uranium. The effects of the amount of the reagent, sand type, and elapsed time after the preparation of the samples on decontamination were examined. The extraction ratios of uranium in all of the four types of sand samples were very high when the time that elapsed after preparation was less than a few days. The extraction ratio of uranium decreased in the soil sand with a higher surface area as the elapsed time increased, indicating the possible formation of chemisorbed uranium on the surface of the samples. The solvent of supercritical CO₂ seemed to be very effective in the decontamination of soil sand. However, the extraction of chemisorbed uranium in soil sand may need additional processes, such as the application of mechanical vibration and the addition of bond-breaking reagents.

Keywords: supercritical CO₂; decontamination; uranium; soil sand; TBP–HNO₃ complex

1. Introduction

Nuclear energy is environmentally friendly because of its high energy density, with no release of greenhouse gases. However, nuclear energy by fission generates radioactive fission products, such as Cs-137, Xe-133, I-131, and Sr-90. Worldwide, there have been two major nuclear accidents: Chernobyl in 1986 and Fukushima in 2011. These major nuclear accidents showed that radioactive products that leak from a plant could contaminate the soil in a large area near the nuclear power plant [1,2]. Soil can also be contaminated by natural radioactive isotopes, such as uranium. Uranium-contaminated soil is common around uranium production, ore, and nuclear fuel production facilities. The pollution of these sites by radioactive isotopes is directly harmful to human health and disrupts soil functions that support terrestrial ecosystems [3]. Cleaning the soil contaminated by radioactive materials requires huge efforts, as the amount of soil needed for decontamination is generally immense due to the large contaminated area that has to be cleaned. Moreover, a large amount of secondary aqueous waste is generated during decontamination, and this waste has to be decontaminated again later. Hence, conventional soil-cleaning methods do not seem to be effective for cleaning soil because they generate secondary wastes [4,5].

Plutonium uranium redox extraction (PUREX), a solvent-extraction process, can be used for the extraction of uranium and plutonium from spent nuclear fuels [6]. Tributylphosphate (TBP) is a key extractant for uranium and plutonium in the PUREX process, and it dissolves well in organic solvents, such as kerosene. According to a recent report, TBP dissolved easily in supercritical carbon dioxide (CO₂) [7]. Supercritical CO₂ has good qualities as a solvent, combining the high solubility of a liquid with the fast reaction speed of a gas. CO₂ has great potential as a supercritical solvent because it becomes supercritical relatively easily at 31 °C and 73.8 bar. It is easy to recycle CO₂ because the phase, in addition to the temperature, can be easily controlled by a depressurization/compression process [8]. CO₂ is a nonpolar organic solvent, which shows low solubility in polar substances, such as inorganic matter, and in ionic substances, such as metal ions. To develop an effective uranium decontamination process using supercritical CO₂, an extraction reagent (e.g., TBP) that combines with uranium metal must be used [9]. TBP and nitric acid form a complex that dissolves well in supercritical CO₂ [10]. A technology to directly reprocess spent fuels using a TBP-nitric acid compound has been proposed [11], and a reprocessing method based on CO₂, referred to as Super-Direx, has been developed. The potential of supercritical CO₂ technology in the extraction of actinide-based metal ions has also been studied [12,13].

In this study, an environmentally friendly decontamination method to clean uranium-contaminated soil is proposed. The method uses a complex of TBP and nitric acid as the extracting agent in supercritical CO₂. CO₂, the solvent in the cleaning process, can be easily recycled by changing its pressure. In addition, the TBP and nitric acid are reusable after the removal of the uranium from the TBP-nitric acid complex using conventional technology applied in the PUREX process. Hence, no secondary waste is generated. The experimental decontamination method is explained, and the results are discussed to the conclusion to see the feasibility of the supercritical CO₂ decontamination method.

2. Experiments

2.1. Preparation of the Reagent for Extraction and the Extraction Conditions

Uranium dioxide in its solid state can be dissolved directly in supercritical CO₂ with a TBP–HNO₃ complex [14–16]. To prepare the reagent (*i.e.*, TBP–HNO₃ complex) for extraction, anhydrous TBP and 70% HNO₃ were fully mixed in a 1:1 ratio in a beaker using a rotating magnetic stirring bar. The mixture was then separated by centrifuging for 40 min. The ratio of HNO₃:TBP:H₂O in the TBP–HNO₃ complex obtained after separation was 1:1.8:0.4 [13]. The solubility of the TBP–HNO₃ and TBP–U–NO₃ complexes in the supercritical CO₂ was observed through a view cell. The solubility of TBP–HNO₃ was measured at 40–60 °C, and the solubility of TBP–U–NO₃ was determined at 50 °C, as illustrated in Figure 1 [13]. As shown in the figure, these complexes can form a single phase with supercritical CO₂ in a wide range of concentrations. At 50 °C, both complexes fully dissolved in supercritical CO₂ when the applied pressure was higher than 17 MPa. In this study, the following conditions were used for the extraction of uranium from contaminated soil sand: a pressure of 20 MPa and temperature of 40 °C.

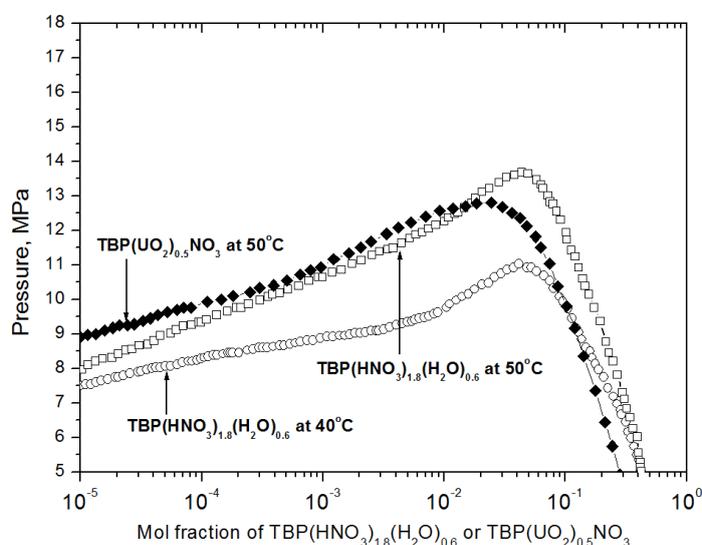


Figure 1. Solubility curves for the transition pressures from two-phase to single-phase TBP (UO₂)_{0.5} NO₃ and TBP (HNO₃)_{1.8} (H₂O)_{0.6} in supercritical CO₂ [13].

2.2. Specimen Preparation

Soil is made up of many components, such as minerals, organic matter, gases, liquids, and countless organisms [17]. In this study, we focused only on the effect of the soil grains (*i.e.*, sand). Two types of sand were prepared: sea sand and soil sand collected from a hill in the campus of Kyung Hee University (located south of Seoul, Korea). The sea sand was pure grade and purchased from JUNSEI Chemical Co., Tokyo, Japan. The soil sand for the experiment was collected at a depth of 50 cm from the ground surface. The soil was immersed in a 30% peroxide solution for about 3 h to remove organic matter. The soil was then cleaned in 6 M nitric acid for 3 h to remove metallic impurities on the surface. After rinsing the soil in hot water (about 80 °C), it was dried in a vacuum glass container for one week. The dried soil

was then screened to obtain soil sand. The soil sand was grouped into four sizes according to the diameter of the grains: larger than 1, 0.5–1.0, 0.2–0.5, and less than 0.2 mm. Particles in the sand larger than 1 mm were not considered. In the experiments, the sand was classified as follows: (1) sea sand (0.5–1.0 mm); (2) coarse soil sand (0.5–1.0 mm); (3) medium soil sand (0.2–0.5 mm); and (4) fine soil sand (less than 0.2 mm). The details of the soil sample preparation have been described previously [4].

A nitric acid solution containing uranium was prepared by dissolving a small amount of uranium oxide in the solution. The sand samples (50 µg-U per 1 g of sample) were placed in beakers containing the solution. The beaker was then placed in an ultrasonic cleaner for 1 h to evenly mix the uranium ions in the sand. The beakers containing the sand and solution were placed in a vacuum oven and dried at 90 °C for about 24 h. After full evaporation of the solution, the dried sand was mixed again with a spatula to ensure that the uranium was uniformly distributed in the sand. The sand samples artificially contaminated by uranium are shown in Figure 2. In each experiment, 1 g of the contaminated sand specimen was used.

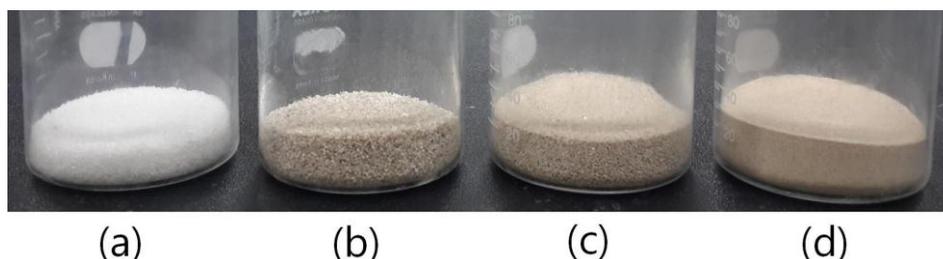


Figure 2. Sand samples artificially contaminated with uranium. (a) Sea sand; (b) coarse soil sand; (c) medium soil sand; and (d) fine soil sand.

2.3. Experimental Process

The experimental setup for the uranium extraction from sand using supercritical CO₂ is shown in Figure 3. The experimental apparatus was composed of a syringe pump, mixing cell, and reaction cell. The mixing cell contained a magnetic bar, which mixed both the TBP–HNO₃ complex and the CO₂ inside. The reaction cell was a stainless tube, inside which the contaminated sand sample was located. The syringe pump supplied CO₂ at a pressure of 20 MPa from the tank to the system. The CO₂ was pumped into the mixing cell and combined with the TBP–HNO₃ complex inside the cell for 30 min. The mixture was then transferred to the reaction cell containing the sand sample. Uranium was extracted from the sand sample in the reaction cell. This dynamic extraction process lasted for more than 30 min. The flow rate of the CO₂ from the syringe pump was about 3 mL (liquid CO₂) per min. The reacted TBP–HNO₃ complex that dissolved in the CO₂ was collected in a beaker after depressurization outside the system. Both the mixing cell and the reaction cell were inside a water bath (*i.e.*, a reaction zone), the temperature of which was maintained at 40 °C. The effects of each of three variables on the extraction of uranium were determined: the amount of the reagent, sand type (or size), and duration of the postcontamination period (one hour, one day, one week, one month, three months, and four years). Table 1 shows the experimental conditions in the uranium-extraction experiments.

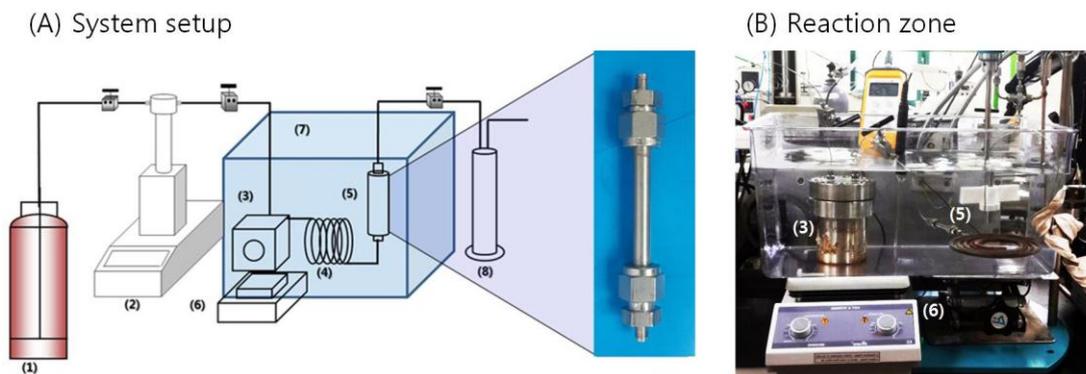


Figure 3. Experiment setup and the reaction zone for uranium extraction from the contaminated sand: (1) CO₂ cylinder; (2) syringe pump; (3) mixing cell; (4) preheating cell; (5) specimen; (6) mixer; (7) thermostat; and (8) collector.

Table 1. Conditions for the extraction experiments.

Variables	Specimen	Description
Amount of the reagent used	Sea sand	0.1–15 mL
Sand size (or type)	Sea sand	1.0 mm (reagent amount: 0.5 mL)
	Soil sand	Coarse (0.5–1.0 mm), medium (0.2–0.5 mm), fine (less than 0.2 mm) (reagent amount: 0.5 mL)
Elapsed time after sample preparation	Sea sand	1 h, 1 day, 1 week, 1 month, 4 years (reagent amount: 0.5 mL)

2.4. Analysis of the Extracted Fraction of Uranium

The extracted fraction of uranium from the sand samples was obtained by comparing the amount of uranium in the sample before and after the experiment using microwave digestion and Inductively Coupled Plasma (ICP) measurements. After the experiment, 1 g of each sand sample was placed in a Teflon XP-1500 container (MARS5 Digestion Microwave System, CEM Co., Matthews, NC, USA) with 20 mL of 35% nitric acid. A reference specimen (*i.e.*, a sample not exposed to the cleaning process) containing the same amount of nitric acid was placed in another XP-1500 container. Both containers were heated slowly by microwaves from room temperature to 180 °C for 15 min. The maximum pressure inside the XP-1500 container was set as 2 MPa. The temperature was maintained at 180 °C for another 15 min. After cooling the containers, the nitric acid was extracted from each container, and the amount of uranium in each solution was analyzed using ICP (Leeman Labs, Lowell, MA, USA). The fraction of uranium extracted after the experiment was obtained by comparing the uranium concentration between the two nitric acids. The extracted fraction of uranium or the extraction ratio, f_U , was estimated as:

$$f_U = \frac{C_{\text{bef}} - C_{\text{aft}}}{C_{\text{bef}}} \tag{1}$$

where C_{bef} and C_{aft} are the concentration of uranium in the solution before and after the experiment, respectively.

The concentration measured from the ICP analysis is known to have an uncertainty of 5%–10%. Based on this uncertainty, the uncertainty of the extraction ratio may be 5%–20%.

3. Results and Discussion

3.1. The Effect of the Amount of Extraction Reagent Used

Sea sand was used in these experiments, and the amount of the extraction reagent used was 0.1–15 mL. Figure 4 shows the results. The extraction ratio of uranium increased with the amount of extraction reagent used. The extraction ratio of uranium exceeded 90% when the amount of reagent was 0.4 mL or higher. As the weight of the sample was 1 g in the experiment, the total amount of uranium in the reaction cell was about 50 µg. The extraction reaction of the uranium by the reagent, the TBP–HNO₃ complex, can be expressed as follows:

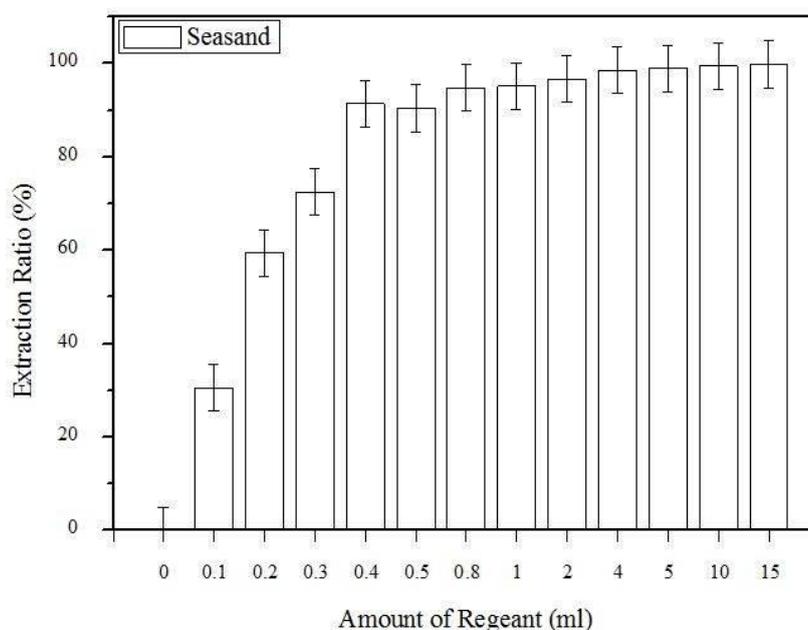
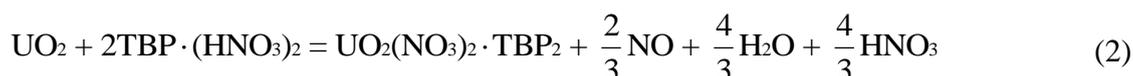


Figure 4. Extracted fraction of uranium as a function of the amount of extraction reagent used (specimen: sea sand with 50 µg-U/g, uncertainty applied: 5%).

Based on the above reaction, the required amount of TBP–HNO₃ complex to extract 1 mol of uranium (238.029 g) would be 2 mol (284.66 g). Hence, the weight of the extraction reagent required to extract 50 µg uranium would be 165 µg. Assuming that the density of the extraction reagent was 0.98, about 0.17 mL of the reagent would be needed theoretically to achieve uranium extraction. In this experimental setup, the process turns out to need the extraction reagent about three times more than the theoretical amount for full extraction of uranium. We selected 0.5 mL of the extraction reagent as a reference, which was the minimum amount for full extraction of uranium from the sea sand specimen in this experiment system.

3.2. The Effects of the Sand Type and Elapsed Time after Sample Preparation

Four types of samples (sea sand and coarse, medium, and fine soil sand) were used for the experiment. Some of the samples were four years old. The sample preparation process of these four-year-old samples

was almost identical to that of the current samples, except that the soil was collected in fields surrounding Daejun City, which is located in the central part of the Republic of Korea (specifically, the Korea Atomic Energy Research Institute) [4]. The amount of the reagent used in the experiment was 0.5 mL. The results, extraction ratios with respect to sand type, and elapsed time after the sample preparation are shown in Figure 5. In all four types of samples, when the samples had been prepared only a few days earlier, the extraction ratios of uranium were more than 94%. As the elapsed time increased, the extraction ratios of the four sand types decreased, but the level of decrease differed according to the sample type. The uranium extraction ratios of the sea sand samples were high (higher than 90%), even those of the four-year-old samples. The extraction ratios of the coarse and medium soil sand that were several months old were also good. After four years, the extraction ratio dropped to 70%. However, in the case of the fine soil sand, the reduction in the extraction ratio of uranium started as early as one week later after the sample preparation, and the extraction ratio dropped to less than 50%. In summary, the extraction ratio of the sea sand was good, regardless of the time that had elapsed after the sample preparation, and the extraction ratios of the coarse and medium soil sand were reasonably good (approximately 90% after a few months and 70% after four years). However, the extraction ratio of the fine soil sand decreased rapidly (below 60%) after one week.

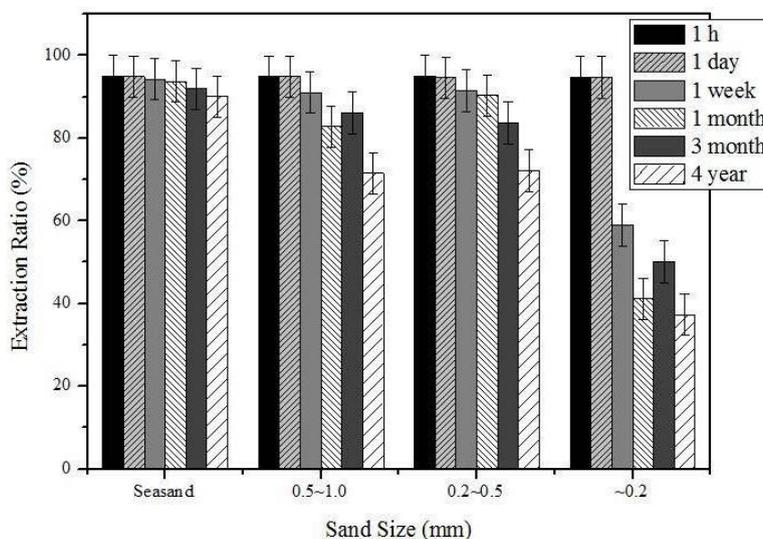


Figure 5. Extracted ratio changes according to soil type and the elapsed time after sample preparation (uncertainty applied: 5%).

In the present study, the reduction in the extraction ratio of uranium ions in the soil sand may have originated from two mechanisms: the trapping of uranium ions in cracks and pores and chemisorption of uranium ions on the surface. The microstructures of the sea sand and soil sand were observed by SEM (Figure 6) (Stereoscan 440, Leica, Cambridge, UK). The surface of the sea sand was relatively smooth and glassy, whereas that of the soil sand was rough and contained cracks and small pores. If uranium ions are adsorbed to the surfaces inside cracks or pores, they may not be easy to remove or extract. In the case of chemisorption, the extraction of uranium may also be difficult. Chemically pure sea sand is mainly silica, which rarely reacts chemically with uranium ions. An SEM-EDX analysis of the sand indicated the existence of various impurities, including Fe, Mg, K, and Al (Figure 7). These impurities may take different structures on the surface, and they can provide sites for chemical reactions with

uranium ions. Initially, uranium ions in soil are mainly physically adsorbed on the surface of the soil. Over time, the uranium ions and impurities on the surface of the soil start to chemically react with each other (chemisorption). Once the uranium ions are chemically bonded with the impurities on the soil surface, it becomes more difficult to extract uranium from the surface, and a stronger extraction process is required.

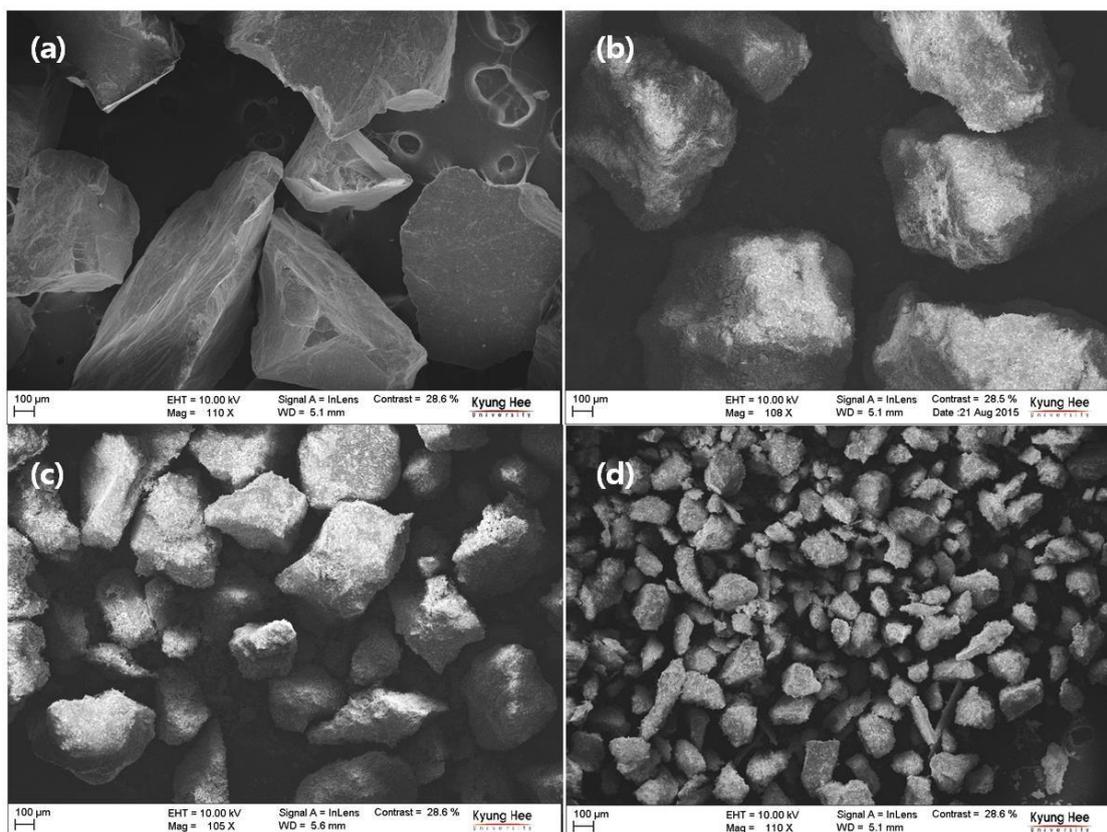


Figure 6. SEM images of the four types of soil samples before the cleaning process (four-year-old samples). (a) Sea sand; (b) coarse soil sand; (c) medium soil sand; (d) fine soil sand.

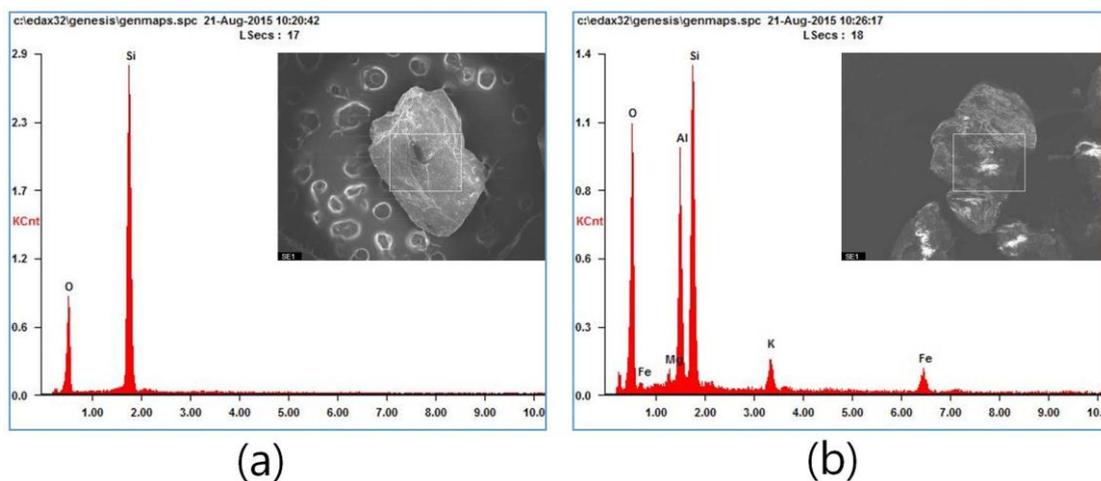


Figure 7. EDX analyses of the sea sand and fine soil sand before the cleaning process (four-year-old samples). (a) Sea sand and (b) fine soil sand.

The results shown in Figure 5 indicate that the extraction ratios of all the four types of soil sand were very high when the elapsed time was less than one day. Based on these results, it seems more difficult to extract chemisorbed uranium ions on the surface than trapped uranium ions in cracks and pores. Supercritical CO₂ has a very good ability to penetrate solid gaps, such as cracks and open pores. Although soil sand has a large surface area, with cracks and pores, supercritical CO₂ can carry the extraction reagent to cracks and pores by penetrating fine gaps in the sample. However, as time progresses, physically adsorbed uranium ions transform to a chemically bonded state, with impurities on the surface. Once uranium ions enter a chemisorbed state, they are not easy to extract. Some soil, such as fine soil sand, which has a greater higher surface area, has more chemical bonding sites for uranium ions. In such soil samples, the extraction ratio decreases with the elapsed time since the preparation of the samples. The extraction of chemisorbed uranium may require mechanical energy, such as ultrasonic vibrations, and additional chemical reagents that prevent chemical bonding.

4. Conclusions

Sand fractions sorted from soil contaminated with uranium were cleaned by supercritical CO₂ with a TBP–HNO₃ complex. Four types of sand (sea sand, and coarse, medium, and fine soil sand) were used, and experiments were performed to examine the effects of the amount of reagent, sand type, and elapsed time after sample preparation on the uranium extraction.

In this experimental setup, about three times more extraction reagent was needed than the theoretical amount for full extraction of uranium from the sea sand specimens. Only if the elapsed time after the sample preparation was less than a day were the extraction ratios of uranium very high in all the four types of sand. This indicates that supercritical CO₂ can easily pump the extraction reagent into cracks and pores by penetrating through the fine gaps in the sample. Over time, physically adsorbed uranium ions transform to a chemically bonded state, with impurities on the surface. Once uranium ions enter a chemisorbed state, they are not easy to extract. Thus, the extraction ratio of the fine soil sand, which has the largest surface area of the samples, decreased the most in the present study as the elapsed time since the sample preparation increased.

The process suggested in this study is environmentally friendly. CO₂, the solvent in the cleaning process, can be easily recycled, and TBP and nitric acid can be reused. Thus, no secondary waste is generated during the uranium-decontamination process. The solvent of supercritical CO₂ seems very effective in the decontamination of soil. However, the extraction of chemisorbed uranium in soil may require additional processes, such as the application of mechanical vibration and the addition of bond-breaking reagents.

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Author Contributions

Kwangheon Park interpreted the results and drafted the paper. Wonyoung Jung built the experimental setup, prepared the specimens and produced the results. Jihye Park analyzed the specimens.

Conflicts of interest

The authors declare no conflict of interest.

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