Development of Heavy Metal Ions Extraction Process from Soil in NPP Decommissioning Sites Using Supercritical Carbon Dioxide

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1. Introduction

Today, Korea is on the verge of decommissioning the nuclear power plant in Gori 1, and accordingly, the importance of the site remediation process after decommissioning is increasingly being highlighted. In the process of decommissioning and site remediation, the decontamination is essential, soil decontamination is quite difficult because radionuclides are adsorbed between pores. Therefore, various chemical decontamination technologies are used for contaminated soil decontamination, but the current technologies have a problem of generating a large amount of secondary waste. Accordingly, there is an urgent need for innovative methods to fundamentally suppress the generation of secondary waste during the decontamination process. In this study, soil decontamination technology using supercritical carbon dioxide is proposed, and a process environment with the highest efficiency is to be established.

2. Experimental Methods

2.1 Characteristics of Supercritical Carbon Dioxide

Supercritical CO_2 is harmless and is a very useful fluid with advantages such as high dissolution, high diffusion coefficient, and low surface tension. It also has the characteristic that physical properties change sensitively even with small changes in temperature and pressure. Using these characteristics, the volume of waste is minimized by separating the waste and the fluid through decompression after the process, and the separated CO_2 solvent is recycled to reduce process costs (Fig.1).[1]

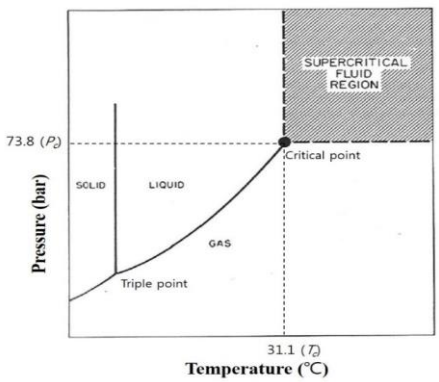

Fig. 1. Phase diagram of CO_2 [1]

2.2 Selection of Nuclides

Most radionuclides present in contaminated soil at the site of the decommissioning nuclear power plant are heavy metal elements, which are adsorbed into pores between soil particles and present as metal ions. Therefore, in this study, representative radioactive metal ions Cs, Sr, and Co were selected [2]. In addition, Cu and Pb were added to test the possibility of expansion to heavy metal contaminated soil decontamination in the future, and a total of five types of nuclides were finally selected.

2.3 Chelating Ligand and Concept of Decontamination Process

Since CO_2 is a non-polar material, it has a disadvantage in that there is a limitation in extraction of polar heavy metal ions. Therefore, a metal chelating ligand material was introduced as an additive for overcoming this and improving the decontamination efficiency. Metal chelating ligand is a polymer compound that helps extract metal ions into a non-polar solvent by forming a complex with metal ions in the soil. In this case, the chelating ligand used must be dissolved well in supercritical CO_2. Therefore, the chelating ligand that can be used in this study should have both a metal binding ligand region (the crab in Fig.2) capable of forming complexes with metal ions, and a CO_2-philic region (the wing in Fig.2) capable of dissolving in CO_2.[3]

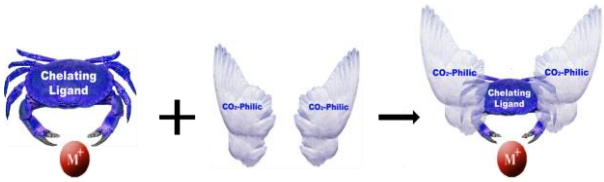

Fig. 2. Conditions of chelating ligands used in this study

In this study, a catechol amine was used as a chelating ligand material, and the composition of the material are as follows.

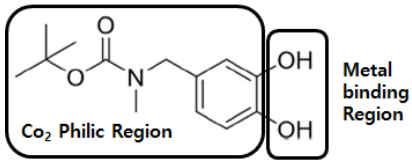

Fig. 3. Molecular structure of catechol amine (M.W.: 253.29 g/mol)

Through the characteristics of the additive, by dissolving and extracting pollutants in supercritical CO_2 and then lowering the pressure of supercritical CO_2, the pollutants and CO_2 can be separated. Therefore, it is possible to fundamentally prevent the generation of secondary waste. In addition, since the separated CO_2 can be reused, it is possible to build an economical and eco-friendly decontamination process.

2.4 Types of Soil and Soil Adsorption

In this study, soil specimens to be used as decontamination targets were collected directly within Kyunghee University, and after removing organic materials through pretreatment, they were classified into three types: Coarse (0.5 to 1.0 mm), Medium (0.2 to 0.5 mm), and Fine (below 0.2 mm) according to particle size (by U.S. Department of Agriculture, USDA). In addition, Sea Sand (JUNSEL, chemical pure, purity: 99.7%), which was chemically produced for comparison with actual soil, was used as another specimen. Sea Sand has fewer pores and a larger particle diameter than an actual soil, and is composed of pure SiO_2, so it is considered that it can serve as a standard specimen. The classified soil specimens were adsorbed using a non-radioactive standard solution (Kanto, JCSS, 1000 ppm) and a rotary evaporator with the aim of 200 ug-nuclide/g-soil contamination per nuclide.

2.5 Experimental Apparatus and Methods

The decontamination experiment was conducted to find an optimal process environment while maintaining the principle of this decontamination technology, and to confirm the difference in efficiency according to the type of soil specimen. In all experiments, the conditions of temperature 40 ℃, pressure 200 bar and reaction time of 90 minutes were maintained. Also the amount of soil specimen was commonly 1 g, and the amount of ligand corresponding to ligand mole : nuclide mole = 5 : 1 was commonly injected. First, the blank test was performed as shown in Fig.4 below to determine the effect of the chelating ligand. After that, in order to improve the process efficiency, a new process in which a flow extraction process was added in the existing static extraction process was designed (see Fig.5) and the results were compared. In the static extraction process, soil specimen and chelating ligand were put together inside the reaction cell and reacted in a closed state. However, in the new flow extraction process, the chelating ligand is dissolved in supercritical CO_2 in the separated mixing cell and reacted with the soil in the reaction cell at a flow rate of 10 ml/min in an open state. Finally, the difference according to the type of soil specimen was tested.

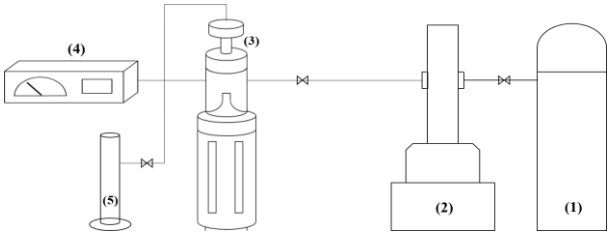

Fig. 4. Experimental apparatus of static extraction process
(1) CO_2 Tank (2) 260D Syringe Pump (3) Reaction Cell
(4) Temperature Controller (5) Bubbler

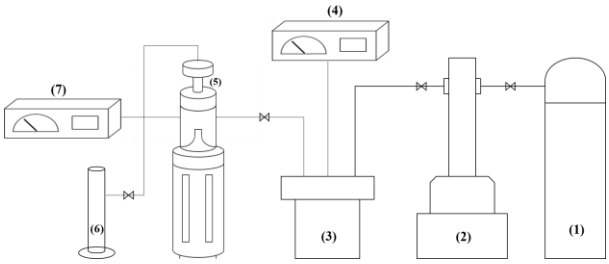

Fig. 5. Experimental apparatus of flow extraction process
(1) CO_2 Tank (2) 260D Syringe Pump (3) Mixing Cell
(4) Temperature Controller (5) Reaction Cell
(6) Bubbler (7) Temperature Controller

2.6 Decontamination Efficiency

The concentrations of nuclides in the soil before and after decontamination were measured using ICP-MS (Inductively Coupled Plasma Mass Spectrometer, Agilent 7500cx, Agilent Technologies Inc., Santa Clara, CA, USA) within center for research facilities in Kyunghee University. However, since ICP-MS measure liquid concentrations, an additional pretreatment process is needed to turn soil specimens into aqueous solutions. So nitric acid and water were added to 1 g of a soil specimen at a ratio of 1:1, and then mixed for 100 minutes using an ultrasonic cleaner. After that, the pretreatment process was performed in a vacuum oven at 90 ℃ for 12 hours and at room temperature for 6 hours. The decontamination efficiency was derived by the following equation using the measured concentration of nuclides in the soil before and after decontamination.

$$\text{D.E.} = \frac{C_b - C_a}{C_b} \times 100\ (\%)$$

C_b = Concentration of nuclides before decontamination
C_a = Concentration of nuclides after decontamination

3. Results

3.1 Effect of Chelating Ligand

Blank Test was conducted to find out the effect of chelating ligands on the decontamination efficiency. The soil specimens used in the experiment were

conducted with Sea Sand. As a result, when only supercritical CO_2 was used, decontamination efficiency was about 20 to 30 % for each nuclide. However, the addition of chelating ligands resulted in decontamination efficiency of about 45 to 65 % for each nuclide. (see Fig.6)

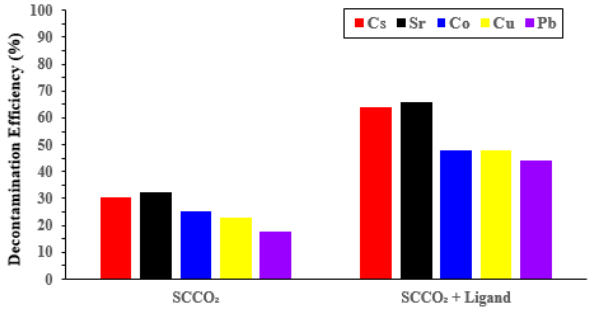

Fig. 6. Effect of chelating ligands on decontamination efficiency (using Sea Sand in the static extraction process)

3.2 Difference in Extraction Methods

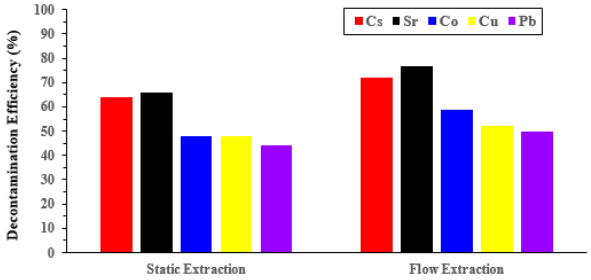

Fig. 7. Effect of different extraction processes on decontamination efficiency (using Sea Sand)

Experiments were conducted using Sea Sand in the static and flow extraction processes to confirm the effect of the difference in the extraction process on the decontamination efficiency (see Fig.7). As a result of the experiment, the flow extraction process was about 51 to 77 % per each nuclide, slightly higher than the static extraction process of 45 to 65%. This result seems to be because the mixing cell separated in the flow extraction process increases the volume of the system and further increases the solubility. In addition, unlike the static extraction process in a closed state, it is considered that it is not necessary to consider re-adsorption of metal ions, which may contribute to an increase in decontamination efficiency.

3.3 Difference in Type of Soil

Through the previous two experiments, a flow extraction process with chelating ligand as an additive was constructed, and an experiment was conducted to confirm the difference in decontamination efficiency according to the particle size of the soil. As shown in Fig. 8, it was confirmed that the decontamination efficiency tends to decrease as the particle size of the soil decreases. This phenomenon is shown that the extraction efficiency of metal ions decreases because the number of pores increases as the particle size of the soil decreases.

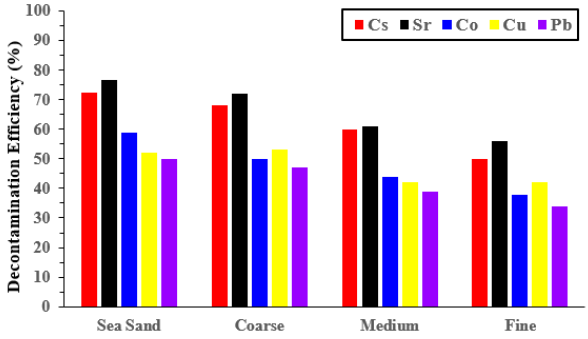

Fig. 8. Effect of different types of soil on decontamination efficiency (in the flow extraction process)

4. Conclusions

In this study, the importance of chelating ligands as additives in the decontamination technology using supercritical CO_2 was shown, and an extraction method for a better process environment was developed and applied. In addition, the difference in the decontamination efficiency according to the particle size of the soil was confirmed, and it is considered that the decontamination efficiency can be increased while adjusting the type and amount of additives. As a result of this study, it was shown that the decontamination process using supercritical CO_2 can be applied to radioactive contaminated soil, and if the process continues to develop in the future, there is a possibility of entering other industries such as remediation of heavy metal contaminated soil.

REFERENCES

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