Development of Nuclear Decontamination Technology Using Supercritical Fluid

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1. Introduction

In the 21st century, most industries cannot but consider environmental problems. In particular, environmental problems are an important part of decontamination in the area of nuclear power. New environment-friendly technologies are necessary for safely and efficiently treating the wastes and various kinds of contaminants generated by nuclear power plants.

Although many kinds of radioactive decontamination are needed because of nuclear power use, soil in particular is problematic. Soil cannot be effectively decontaminated using a single decontamination method because soils in different areas vary greatly in their characteristics, and therefore in the forms of contamination that occur in them.

In addition, soil cleaning technologies that have been developed thus far increase treatment costs in contaminated soil recovery processes because they generate large amounts of secondary wastes.

In this respect, this study is intended to develop soil decontamination methods using CO_2, which is a nontoxic, environmentally friendly substance, in order to fundamentally suppress the generation of secondary wastes from the decontamination process and to create high added values.

2. Methods and Results

In this section, the principle of decontaminating uranium-contaminated soil by adding supercritical CO_2 with a TBP-HNO3 complex is explained in detail.

2.1 Experimental Apparatus

An experimental device for conducting experiments to remove uranium from soil using supercritical CO_2 is shown in Fig. 1.

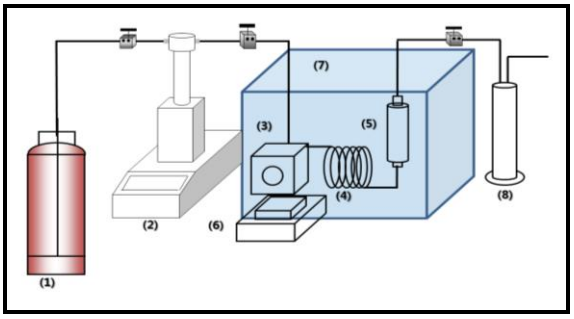

Fig. 1. Block diagram of an experimental device for experiments to extract uranium from soil. (1) CO_2 cylinder, (2) syringe pump, (3) agitating container, (4) preheating container, (5) cylindrical experimental container, (6) agitator, (7) thermostat, (8) collector.

As shown in Fig. 1, the experimental device largely consists of seven parts. The CO_2 contained in the CO_2 cylinder is pressurized to the experimental condition, 200 bar, by the syringe pump. The TBP-HNO3 complex, which is an extraction agent, is put into the agitating container, and the uranium-contaminated soil is put into the cylindrical experimental container. Then, the water temperature in the thermostat is fixed at 40 ℃ so that the same temperature is always maintained during the experiment.

The experiment consists of *static extraction* and *dynamic extraction*. Static extraction is a process for putting CO_2 into a supercritical state so the extraction agent and supercritical CO_2 can be sufficiently mixed. Even when CO_2 has been injected into the experimental device, the CO_2's temperature does not immediately increase to 40 ℃, the same temperature as the water tank. Time is necessary for the CO_2 and water in the water tank to reach the same temperature as static extraction proceeds. Once the CO_2 injected into the experimental device has been put into the supercritical state, it is sufficiently mixed with the extraction agent, the TBP-HNO3 complex. The dynamic extraction process is an experimental process in which supercritical CO_2 and the TBP-HNO3 complex remove heavy metals such as uranium.

2.2 Experimental Procedures

As we mentioned earlier, we have used supercritical CO_2 because of its high speed of diffusion, its powerful penetration, and its easy property, which can be changed only by changing the pressure and temperature. It is also harmless to humans and has a weak effect on the environment. Table I shows the representative properties that accord with the CO_2's state. When it is supercritical, CO_2 has both the penetration force of gases and the solubility of liquids so that it becomes an excellent solvent that can extract solutes quickly in large quantities. In particular, since dissolved contaminants can be easily extracted and pure CO_2 can be collected and reused by reducing the pressure to evaporate it, CO_2

has the big advantage of being able to fundamentally eliminate the generation of secondary wastes.

Uranium (U) exists as UO2 2+, which is a hexavalent ion in nitric acid solutions. It can be dissolved in kerosene that contains tributyl phosphate (TBP) and extracted as kerosene, which is an organic solvent in the form of a U-containing chelate.

Expression (1) shows that U^{6+} ions contained in nitric acid solutions can be extracted as organic solvents.

$$UO_2^{2+} + 2NO_3^- + 2TBP = UO_2(NO_3)_2\ 2TBP \quad (1)$$

To substitute CO_2 for the organic solvent kerosene currently in use, we used the results measured by Enokida.

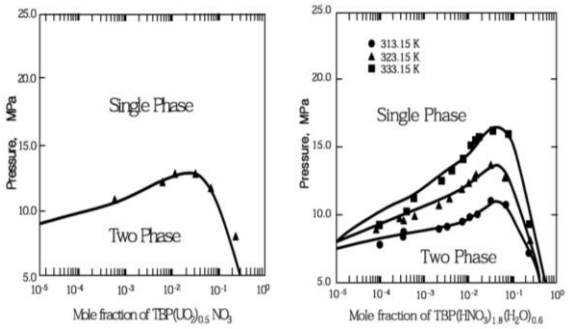

Fig. 2. Solubility curves of U-nitrate-TBP chelate (left) and TBP-nitrate chelate (right).

The first result in Fig. 2 shows that although the solubility curves change according to the concentration of chelate formed, the chelate formed can be completely dissolved in CO_2 at a pressure exceeding approximately 130 MPa.

On reviewing the second result in Fig. 2, it can be seen that the solubility curve changes according to the concentration of chelate and temperatures. This result indicates that under the experimental conditions in this study, the chelate compound formed can be completely dissolved in CO_2.

Based on these two results, experiments to decontaminate soil contaminated by uranium were conducted using a TBP-HNO3 complex as an extraction agent.

First, the contaminated soil was put into the cylindrical experimental container (5) illustrated in Fig. 1, and both ends of the container were plugged using glass wool so that the soil would not come out during the process of extraction. The extraction experiments were conducted with this container using supercritical CO_2 and the TBP-HNO3 complex.

A microwave method was used to analyze the decontaminated soil. Analyzing samples with a view to clarifying the kinds and quantities of elements that constitute the samples is called *coulometric analysis*. Since accurate coulometric analysis can be conducted only after removing all organic matter contained in the soil, the soil was pretreated using a microwave system under the following conditions: 300 W, 300 psi, and 30 min.

2.3 Experimental Results

The results were analyzed using an inductively coupled plasma mass spectrometer (ICP-MS).

Table I: Experimental Results

	Sand weight (g)	TBP-HNO3 complex (ml)	Result (ppb)
Before	1.0494	–	2.224×10^4
Result 1	1.0507	10	115.6
Result 2	1.0498	15	35.08

3. Conclusions

In this study, to develop decontamination methods for uranium-contaminated soil using supercritical CO_2, a soil decontamination system using supercritical CO_2 was constructed. In addition, the basic principle of supercritical CO_2 decontamination using a TBP-HNO3 complex was explained.

According to the results of the study, sea-sand samples having the same degree of contamination showed different results of decontamination according to the quantities of the TBP-HNO3 complex used as an extraction agent, which resulted in high extraction rates.

Thus far, a most widely used method of extracting uranium has been the dissolving of uranium in acids. However, this method has the large adverse effect of generating strong acidic wastes that cannot be easily treated. On the other hand, supercritical CO_2 requires critical conditions that are no more difficult to meet than those of other supercritical fluids, since its density can be changed from a very low state close to that of an ideal gas to a high state close to that of liquids. The critical gas conditions are a pressure of 71 bar and a temperature of 31 ℃, both of which are inexpensive to achieve. Moreover, CO_2 is a solvent that is not harmful to the human body and few effects on environmental pollution. Therefore, nontoxic and environment friendly processes can be developed using supercritical CO_2.

Supercritical CO_2's advantages over prevailing methods suggest its potential for developing innovative decontamination methods, as demonstrated by the results of this study .

REFERENCES

[1] M. J. Carrott, B. E. Waller, N. G. Smart and C. M. Wai, Commun. 1998.
[2] O. Tomioka, Y. Meguro, Y. Enokida, I. Yamamoto, Z. Yosida, J. Nucl. Sci. Tech. 38. 2001.
[3] O. Tomioka, Y. Meguro, S. Iso, Z. Yosida, Y. Enokida, I. Yamamoto, J. Nucl. Sci. Tech. 38. 2001.

[4] M. Shamsipur, A. R. Ghiasvand, Y. Yamini, J. Supercrit. Fluid 20. 2001
[5] Y. Meguro, S. Iso, T. Sasaki, Z. Yoshida. Anal. Chem 70. 1998
[6] Y. Enokida and I. Yamamoto, J. Nucl. Sci, Tech. sup. 3. 2002
[7] T.shimada, S.Ogumo, N. Ishihara, Bull. Korean Chem. Soc. 23. 2002