

A study for uranium extraction from contaminated soil in supercritical carbon dioxide

Jinhyun Sung^a, Jeongsu Kim^a, Moonsung Koh^a, Kwangheon Park^{a*}, Gyeenam Kim^b, Jeikwon Moon^b

^{a)} Green Nuclear Research Laboratory, Kyung-Hee University, South Korea, sungjih@khu.ac.kr

^{b)} Decommissioning Technology Development Center, Korea Atomic Energy Research Institute, South Korea

1. Introduction

The extraction process of uranium is one of the most important fields from the uranium mining to the spent fuel reprocessing. However, conventional organic solvent extraction produces a lot of liquid waste. The SFE (Supercritical fluid extraction) is extraction by substances occurring at temperatures and pressures above critical. The agent most widely used for SFE is carbon dioxide, which is nontoxic, readily available, inexpensive and low critical parameters (temperature above 31 °C and pressure above 73 bar). The Sc-CO₂ (Supercritical carbon dioxide) may be a good extraction solvent due to the ease with which it can be recycled, and the fact it leaves negligible amounts of secondary wastes. But Sc-CO₂ do not extract metallic contaminants because it has the non-polar property. So, in order to extract the radioactive metal from radioactive wastes, Sc-CO₂ needs chelating ligands or surfactants such as organophosphorus[1,2], crown ethers[3], β-diketone[4-6], or dialkyldithiocarbamates[7]. In our previous works, TBOD (Tetrabutyl pentaaxadiazine) was effective chelating ligand than TBP for extraction of uranium ion from aqueous solution using Sc-CO₂[8]. The TBOD has some advantages: (i) high irradiation stability (ii) strong affinity to metallic ions (iii) completely incinerated without secondary solid waste. At this work, we have to extract the uranium metal from contaminated soil which adsorbed non-radioactive uranium using TBOD in Sc-CO₂.

2. Methods and Results

2.1 Chemicals, mock-up specimen

Carbon dioxide was purchased from Air Tech Co. The uranium metal ion which has AA standard solution, dibutylamine, triethylamine, diglycolyl amine, tributyl phosphate (TBP) were purchased from Aldrich Co. According to the known method[9-11], the TBOD was synthesized in a laboratory scale[8]. Chemical structure of TBOD was shown as Fig. 1.

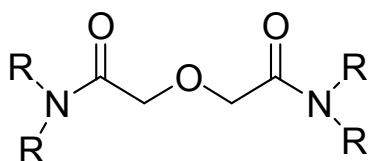


Fig. 1. Chemical structure of TBOD (R=(CH₂)₃CH₃)

The contaminated soil which adsorbed non-radioactive uranium was prepared shown as Fig. 2. The soil was separated below 2 mm size by sieve. The organic compound which adsorbed to soil was removed from soil by 30 % hydrogen peroxide. The metallic compound which adsorbed to soil was removed from soil by 6 M nitric acid. The uranium metal was adsorbed to soil by rotary evaporator under 60 torr at 70 °C.

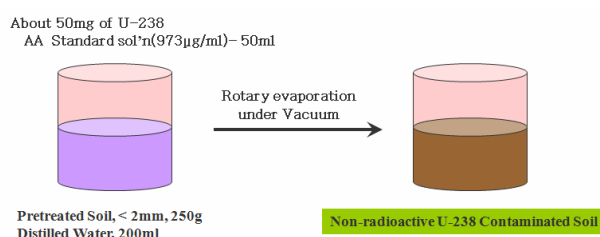


Fig. 2. Preparation of mock-up soil specimen

2.2 Equipments

The experimental equipments for this work manufactured shown as Fig. 3. It composed of a high pressure syringe pump, a premixing cell and an extraction cell in conventional oven with a thermo-controller and a separator. The ranges of pressure and temperature were up to 250 bar and 80 °C. The extraction column of ID 10 mm × IL 200 mm and the premixing cell of 10 mL which has sapphire window were used. The carbon dioxide was pressurized by syringe pump.

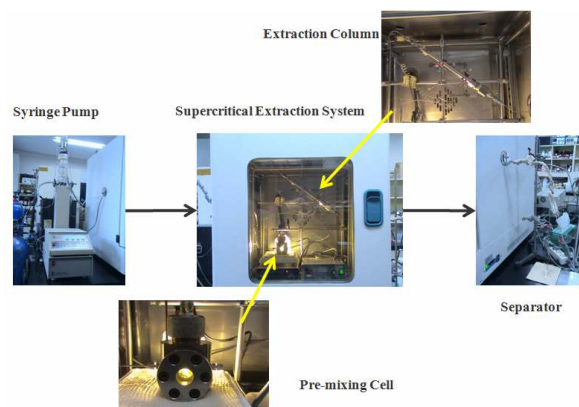


Fig. 3. The Sc-CO₂ extraction equipments

2.3 Experiments

In order to determine the SFE process temperature and pressure, the solubility of TBOD in Sc-CO₂ is important. This was measured in our previous works[8] and shows Fig. 4. The solubility of TBOD in Sc-CO₂ was found that :

- The lower the Sc-CO₂ temperature, the higher the TBOD solubility at same the Sc-CO₂ pressure.
- The higher the Sc-CO₂ pressure, the higher the TBOD solubility at same the Sc-CO₂ temperature.

According to this solubility, the uranium metal was extracted from mock-up soil at 40 °C and 200 bar.

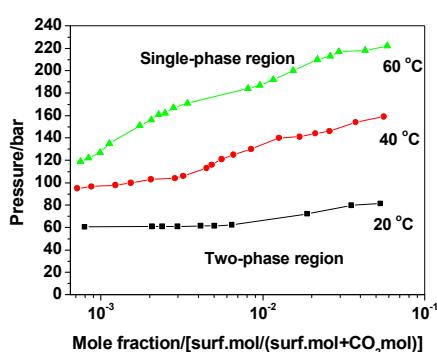


Fig. 4. The Solubility of TBOD in Sc-CO₂

The soil, 10 g, which adsorbed non-radioactive uranium metal (200 ppm) was replaced in extraction column. The chelating ligands (TBOD or TBP) and nitric acid were replaced in premixing cell with magnetic stirrer. The carbon dioxide was introduced to experimental pressure as 200 bar after increased to experimental temperature as 40 °C. After 20 min, the carbon dioxide was introduced continuously as 200 bar at 40 °C for 40 min. The uranium metal concentration in soil was analyzed by ICP-AES.

2.4 Results and discussion

The experimental results were summarized at Table 1. The extraction efficiencies using TBOD in Sc-CO₂ were lower than that using TBP in Sc-CO₂.

Table 1. Extraction efficiency of uranium from contaminated soil (40 °C, 200 bar)

Ligand	Ligand Amounts (mL)	HNO ₃ Concentration (M)	HNO ₃ Amounts (mL)	Extraction Efficiency (%)
TBP	0.25	6	0.20	92.5
TBOD	0.15	3	0.35	16.6
	0.30		3.30	15.2
	0.15	6	0.10	30.9
	0.30		0.20	29.2
	0.60		0.40	38.3
	0.90		1.50	57.5

3. Conclusions

The soil is a very complex system, made up of a heterogeneous mixture of solid, moisture, gaseous material. The solid phase is composed of a mineral portion, containing particles of varying sizes, shapes and chemical composition. The soil possesses a large surface area and porosity. These properties of soil have an effect on extraction of uranium from soil in Sc-CO₂.

In the further work, these properties of soil must be consider to increase the extraction efficiencies of uranium from soil.

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