REMOVAL AND RECOVERY OF URANIUM FROM SOLID WASTES BY SUPERCRITICAL CARBON DIOXIDE FLUID LEACHING METHOD

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ABSTRACT

Supercritical CO_2 fluid leaching (SFL) method using supercritical CO_2 fluid containing a complex of HNO_3 - tri-n-butyl phosphate (TBP) was applied to removal of uranium from radioactive solid wastes. Sea sands, incineration ashes and porous alumina bricks were employed as matrixes of simulated solid wastes. Real radioactive incineration ash wastes and firebrick wastes were also subjected to the SFL treatment. It was found that uranium could be efficiently removed from both of the simulated wastes and the real wastes by the SFL method. The removal efficiency of uranium from the real waste was lower than that from the corresponding simulated waste. About 1 g and 35 mg of uranium were recovered from 10 g of the real ash waste and 37 g of the real firebrick waste, respectively.

INTRODUCTION

Various solid wastes such as metals, papers, bricks, ashes and sludge products contaminated by uranium are generated from nuclear fuel fabrication facilities. Radioactivity of the uranium-contaminated waste increases by daughter nuclides of ^{238}U during storage of the waste for a long time. Removal of uranium from the wastes leads to safe and economical storage and disposal of the wastes. Decontamination treatment of the uranium-contaminated solid wastes, however, has not been commonly conducted because of the following methodological limitations. A method feasible for a large-scale treatment of the wastes is very limited, a large amount of secondary wastes is often generated from the decontamination process and an appreciable quantity of a solvent and reactants

remains in the solid wastes after the treatment. A method that can be applied to a large amount of the wastes and generates less secondary wastes is required to be developed.

Recently, much attention has been paid to a separation technology of metals using supercritical CO_2 as a medium [1, 2]. Several methods of supercritical CO_2 extraction (SFE) were developed for separation of metal ions from an aqueous solution using the supercritical CO_2 instead of an organic solvent [3-8]. It is particularly worth noting that an alternative and more attractive method of supercritical CO_2 technology is "direct leaching" of metals from solid samples [9-19]. Neither organic solvent nor acid solution for the leaching of the metals are necessary to be used in this method, which leads to a total minimization of the secondary wastes from the process.

In order to remove uranium from the radioactive wastes, the authors have developed the supercritical CO_2 fluid leaching (SFL) method [9, 11], in which the supercritical CO_2 medium containing a reactant is used as a medium to dissolve metal compounds involved in a solid matrix. The SFL is a method for direct removal and recovery of metals from a solid sample without using any acid leaching and shows several attractive properties as follows: (i) extraction efficiency and rate are enhanced due to the large penetration force and rapid diffusion of supercritical CO_2, (ii) rapid and complete recovery of the extracted substances from the CO_2 medium is attained by gasification of CO_2, (iii) a large amount of the wastes is treated, (iv) generation of secondary wastes from a process is totally minimized and (v) the solid sample after the SFL treatment is in a form of dried solid that does not contain an appreciable quantity of an organic reactant and acid. Previously the authors have demonstrated that the SFL method using a nitric acid - tri-n-butyl phosphate (TBP) complex as a reactant is applicable to the removal of uranium from solid samples using a simulated sea sand sample contaminated by uranium oxides [9, 11]. In these studies a recommended procedure was proposed and optimum experimental conditions were determined for the removal of uranium from the solid sample.

The radioactive wastes generated from nuclear fuel fabrication facilities show a variety of chemical and physical properties. In order to remove uranium efficiently from these wastes, therefore, it is essential that effects of matrix structures and chemical properties of the wastes on the removal efficiency of uranium is understood in detail. In the present study, the SFL method using the supercritical CO_2 medium containing the HNO_3-TBP complex as a reactant was applied to the removal of uranium from simulated radioactive solid wastes. The sea sand, incineration ashes and porous alumina bricks were employed as matrixes of the simulated wastes containing uranium oxides and the removal efficiencies of uranium from these wastes were determined. In addition the SFL method was also applied to the removal and recovery of uranium from real uranium contaminated wastes generated from the nuclear fuel fabrication processes.

EXPERIMENTAL

Apparatus

An apparatus for the SFL, which was essentially identical to that used for the supercritical CO_2 fluid extraction of the metal from the aqueous solution [4], is shown in Fig. 1. The main part of the apparatus consisted of a stainless steel reaction vessel (50 cm^3) installed in a thermostat water bath, a reactant mixing vessel, a collector vessel and a restrictor. Glass balls of 3.2 mm in diameter were packed in the collector vessel and the restrictor was inserted into a gap between the balls. A syringe pump was used to flow CO_2 at given pressure.
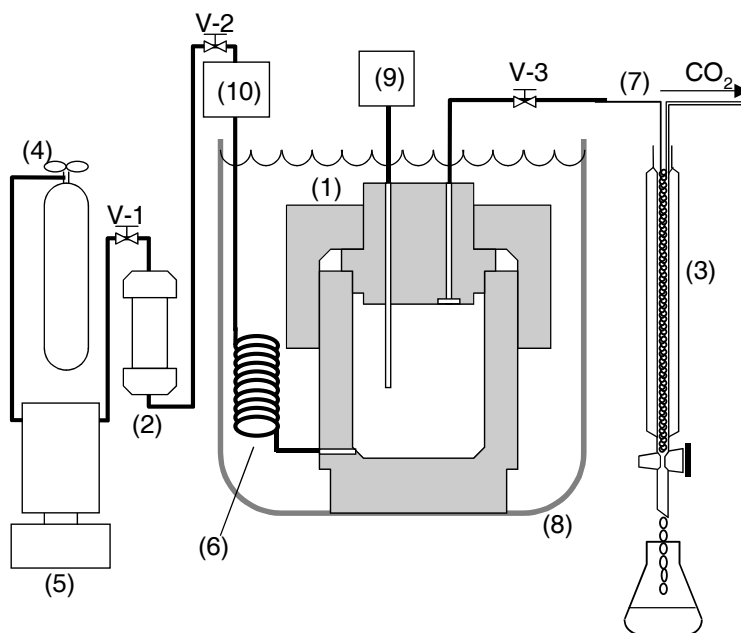
Fig. 1 Apparatus for the SFL for the removal of uranium from radioactive solid waste.
(1) reaction vessel, (2) reactant mixing vessel, (3) collector, (4) liquid CO_2 cylinder, (5) syringe pump, (6) pre-heating coil, (7) restrictor, (8) thermostat water bath, (9) thermometer, (10) pressure gauge.

Chemicals

Uranium dioxide powder was obtained by grinding mechanically a UO_2 nuclear fuel pellet using a vibrating sample mill (Heiko, TI-100). The grain size of the UO_2 powder was 1-5 μm. Three types of the simulated solid waste samples were prepared. The sea sand was employed as a matrix of the simulated waste sample. The simulated sea sand sample was prepared by mixing 100 mg of the UO_2 powder with 50 g of the sea sand (particle size; 0.425 - 0.850 mm). Incineration ashes obtained from an incinerator of general burnable garbage were employed as a matrix material to simulate a real waste.

The ash was fractionated using a sieve of 8.6 mesh. Simulated ash waste A was a mixture of 100 mg of the UO_2 powder with 5 g of the incineration ash. Simulated ash waste B was a mixture of 100 mg of the UO_2 powder with 5 g of the ash that had been neutralized with a nitric acid solution, filtrated, washed with water and dried at 150 °C. A porous alumina (Al_2O_3) brick of 40% porosity and *ca.* 1 μm pore size was employed as a matrix material. A nitric acid solution containing 100 mg U(VI) was impregnated into the brick of 35x15x7 mm and then the brick was heated at 950 °C for 6 h, in which the uranyl nitrate in the brick became U_3O_8. The real wastes of incineration ashes and firebricks contaminated by uranium were obtained. A stock solution of the HNO_3-TBP complex solution was prepared by mixing 100 cm^3 of an anhydrous TBP (Koso) and 100 cm^3 of 70 % HNO_3 (Wako), and shaking the mixture vigorously using a conventional extraction tube for 30 min. The HNO_3-TBP complex thus obtained was a mixture of HNO_3, TBP and H_2O. The contents of HNO_3, TBP and H_2O in the stock solution of the HNO_3-TBP complex were determined to be 4.5 M, 3 M and 1 M, respectively.

Procedure

Place the solid waste sample in the reaction vessel of *ca.* 50 cm^3 in inner volume and keep the temperature of the vessel at 60 °C using the thermostat water bath. Close valves V-1 - V-3. Take 2 cm^3 of the HNO_3-TBP complex solution in the reactant-mixing vessel of *ca.* 5 cm^3 in inner volume that is kept at 25 °C. Open valve V-1 and introduce CO_2 into the reactant-mixing vessel with the syringe pump until the pressure inside the vessel becomes 15 MPa. Open V-2 to introduce a mixture of CO_2 and the HNO_3-TBP complex into the reaction vessel through the pre-heating coil using the syringe pump until the pressure becomes 15 MPa. Close V-2 and allow the system to stand for sufficiently long time to react the uranium oxide in the solid sample with the HNO_3-TBP complex to form a U(VI)-TBP complex (complexation process). After the complexation, open V-2 and V-3 and then allow to flow CO_2 at 20 MPa to transport and recover CO_2-soluble components such as the U(VI)-TBP complex and the HNO_3-TBP complex in the collection vessel at an ambient pressure (dissolution process). Flow the supercritical CO_2 at a relatively low flow rate, *e. g.*, 8 cm^3/min, for 75 min. Here the flow rate is expressed as that inside the reaction vessel at 60 °C and 20 MPa. The removal efficiency was determined from the amount of uranium initially taken in the sample and that remained in the sample after the SFL. In the case of the simulated sea sand waste, the uranium remained in the sample after the SFL was dissolved with ethanol and then a hot HNO_3 solution (7 M). The amounts of uranium in these solutions were determined by ICP-AES. In the case of the simulated ash and brick wastes and the real wastes, the activities of γ-ray at 186 keV of [235]U in the sample was measured before and after the SFL treatment.

RESULTS AND DISCUSSION

The SFL method for removal of the uranium oxide from solid wastes consists of two elementary processes. In the first-process the uranium oxide is allowed to react with the HNO_3-TBP complex in the supercritical CO_2 to form the U(VI)-TBP complex, $UO_2(NO_3)_2(TBP)_2$, (the complexation process). In the second-process the U(VI)-TBP complex is dissolved in the supercritical CO_2 flow and is recovered in the collection

vessel by gasification of CO_2 (the dissolution process). In the complexation process the U(VI)-TBP complex is formed passing through several elemental reactions such as dissociation of U-O bonds, oxidation of U(IV) to U(VI), combination of UO_2^{2+} ion with nitrate anions and coordination of TBP molecules [10]. Previously the experimental conditions such as temperature, pressure and reaction time, which influenced the removal efficiency of uranium, were optimized using a standard sample of a mixture of the sea sand and the uranium oxide [11]. Here the sea sand was chosen as a standard matrix because the sea sand provides a simple physical structure and is made of SiO_2. SiO_2 does not have any specific interaction with the uranium oxide and does not react with the HNO_3-TBP complex as well as CO_2.

The removal efficiencies of uranium from the simulated solid wastes and the real wastes were determined and the results are summarized in Table I. In these experiments the complexation process was conducted at 60 °C and 15 MPa for 150 min and the dissolution process was preceded using CO_2 flow of 8 cm^3/min at 60 °C and 20 MPa for 75 min unless otherwise noted.

Table I   Removal efficiency of uranium from simulated and real wastes by single SFL procedure

Sample	Decontamination Factor	Removal efficiency(%)
Sea sand	91	98.9
Simulated ash A	~1	<1
Simulated ash B	25	96
Real ash	1.7	40
Simulated porous Al_2O_3 brick	10	90
Real firebrick	1.8	45

Removal efficiency(%)= (1 -1 / [Decontamination Factor])*100
Complexation procedure; 60 °C, 15 MPa, 60 min,
Dissolution procedure; 60 °C, 20 MPa, 8 cm^3/min, 75 min.

Almost 99% of UO_2 was removed from the sea sand sample. The removal efficiency increased to 99.8% by repetition of the SFL procedure. The uranium remained in the sample was determined fractionally as the uranium oxide that did not react with the HNO_3-TBP complex and as the U(VI)-complex formed by the reaction with the reactant. The uranium oxide remained in the sample was 0.05 mg and the uranium complex was 0.16 mg. Flowing more CO_2 during the dissolution process, therefore, will lead to the enhancement of the removal efficiency.

It was difficult to remove uranium from simulated ash waste A by the single SFL procedure because HNO_3 in the reactant was consumed in a reaction with such basic components as CaO in the ash. It was determined by an acid-base titration method that 13 mmol of HNO_3 was required to neutralize 1 g of the ash. First a mixture of the supercritical CO_2 flow of 8 cm^3/min and the HNO_3-TBP complex flow of 0.3 cm^3/min was flowed through the reaction vessel, in which simulated ash waste A was placed, for

50 min, and then the single SFL procedure was performed to the waste A. An excess quantity of HNO_3 over the amount of HNO_3 required to neutralize the ash was included in the mixed fluid. By this procedure 90% of uranium was removed from waste A. This result suggests that uranium can be removed as neutralizing the ash in situ by the SFL procedure. Removal of 96% of UO_2 was attained from simulated ash waste B by the single SFL procedure. This fact indicates that the pretreatment for the neutralization of the ash leads rapid and efficient removal of uranium from the incineration ash wastes. The removal efficiency increased to be more than 99% from ash waste B by repetition of the SFL procedure.

The real incineration ash waste is generated by simultaneous incineration of a mixture of combustible wastes and uranium compounds. The real ash examined in this study included the basic components of *ca*. 1/10 as much as those in the simulated one. Removal of 40% uranium from 10 g of the real ash waste was attained by the single SFL procedure. This result indicates that the SFL method is applicable to the removal of uranium from the real radioactive solid waste. However eight repetitions of the SFL procedure were required to remove 99% uranium from the real waste. By the SFL method 988 mg of uranium was recovered from 10 g of the real ash waste.

The removal efficiency of uranium was determined in the SFL of uranium in the sample having a complex structure such as porous alumina brick. In this experiment the complexation process in the SFL method was subjected for 15 and 150 min. The removal efficiency of uranium from the simulated alumina brick was *ca*. 90% by the single SFL procedure despite the time for the complexation process. It suggests that the complex formation equilibrium under the experimental conditions examined was attained within 15 min. The removal efficiency increased by repetition of the SFL procedure. For comparison the simulated waste was kept in 50 cm^3 of 7 M HNO_3 solution at 90 °C for 15 or 150 min. It was hard to remove uranium by the acid leaching for 15 min, however, ca. 90% of uranium was removed by the acid leaching for 150 min. It was concluded that the removal rate of uranium in the porous matrix by the SFL is faster than that by the acid leaching. It was attributed to a difference in mass transfer of substances in the medium.

The real firebrick waste is generated from a sintering furnace of nuclear fuel pellets and has been kept under reduction atmosphere at high temperature for a long time. The firebrick waste was broken and a column-shaped chunk among the broken bricks (*ca*. 30 mm in diameter, *ca*. 35 mm in height and 37 g) was subjected to the SFL treatment. From the real firebrick waste 45% of uranium was removed by the single SFL method. It was found that the removal efficiency did not exceed 90% even after several repetitions of the SFL treatment. Thirty-five mg of uranium was recovered from 37 g of the brick.

CONCLUSION

Uranium could be successfully removed by the SFL method from not only the sea sand sample having the simple component and structure but also the simulated ash sample consisting of several chemical components and the brick sample of complex structure. Uranium could be removed even from the real radioactive solid wastes as well as the

simulated wastes by the SFL method. It is concluded that the SFL method can be applied to the removal of uranium from the various wastes generated in the field of nuclear technology. In the next step for the practical application of the SFL method to the removal of uranium from the real wastes, the removal behavior of uranium from other wastes having different chemical and physical properties should be investigated.

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REFERENCES

1   Y. Lin, N. G. Smart, C. M. Wai, "Supercritical fluid extraction and chromatography of metal chelates and organometallic compounds," Trends Anal. Chem., 14 (1995) 123.

2   C. Erkey, "Supercritical carbon dioxide extraction of metals from aqueous solutions: a review," J. Supercrit. Fluids, 17 (2000) 259.

3   S. Iso, Y. Meguro, Z. Yoshida, "Extraction of uranium(VI) from nitric acid solution into supercritical carbon dioxide containing tri-n-butylphosphate," Chem. Lett., 1995 (1995) 365.

4   Y. Meguro, S. Iso, H. Takeishi, Z. Yoshida, "Extraction of uranium (VI) in nitric acid solution with supercritical carbon dioxide fluid containing tributylphosphate," Radiochim. Acta, 75 (1996) 185.

5   Y. Meguro, S. Iso, Z. Yoshida, "Correlation between extraction equilibrium of uranium(VI) and density of CO_2 medium in a HNO_3/spercritical CO_2-tributylphosphate system," Anal. Chem., 70 (1998) 1262.

6   S. Iso, S. Uno, Y. Meguro, T. Sasaki, Z. Yoshida, "Pressure dependence of extraction behavior of plutonium(IV) and uranium(VI) from nitric acid solution to supercritical carbon dioxide containing tributylphosphate," Prog. Nucl. Energ., 37 (2000) 423.

7   J. Ougiyanagi, Y. Meguro, Z. Yoshida, K. Ohashi, "Extraction equilibrium of palladium(II) with 2-methyl-8-quinolinol into supercritical carbon dioxide fluid," Talanta, 57 (2002) 213.

8   J. Ougiyanagi, Y. Meguro, Z. Yoshida, H. Imura, K. Ohashi, "Solvent effect on distribution ratio of Pd(II) in supercritical carbon dioxide extraction and solvent extraction using 2-methyl-8-qunolinol," Talanta, 59 (2003) 1189.

9   O. Tomioka, Y. Meguro, S. Iso, Z. Yoshida, Y. Enokida, I. Yamamoto, "New method for the removal of uranium from solid wastes with supercritical CO_2 medium containing HNO_3-TBP complex," J. Nucl. Sci. Technol., 38 (2001) 461.

10   O. Tomioka, Y. Meguro, Y. Enokida, I. Yamamoto, Z. Yoshida, "Dissolution behavior of uranium oxides with supercritical CO_2 using HNO_3-TBP complex as a reactant," J. Nucl. Sci. Technol., 38 (2001) 1097.

11   Y. Meguro, S. Iso, Z. Yoshida, O. Tomioka, Y. Enokida, I. Yamamoto, "Decontamination of uranium oxides from solid wastes by supercritical CO_2 fluid leaching method using HNO_3-TBP complex as a reactant," J. Supercrit. Fluids, in press.

12   M. A. Khorassani, L. T. Taylor, "SFE Of Mercury(II) Ion Via In Situ Chelation And pre-formed mercury complexes from different matrices," Anal. Chim. Acta, 1 (1999) 379.

13   Z. J. Cui, J. C. Liu, L. C. Gao, Y. Q. Wei, "Extraction Of Copper Ions By Supercritical carbon dioxide," J. Environ. Sci., 12 (2000) 444.

14   N. G. Smart, T. E. Carleson, S. Elshani, S. Wang, C. M. Wai, "Extraction of toxic heavy metals using supercritical fluid carbon dioxide containing organophosphorus reagents," Ind. Eng. Chem. Res., 36 (1997) 1819.

15   A. A. Murzin, V. A. Babain, A. Yu. Shadrin, I. V. Smirnov, V. N. Romanovskii, M. Z. Muradymov, "Supercritical fluid extraction of uranium, transuranium and rare earth elements from the solid surfaces," Radiochemistry, 40 (1998) 47.

16   M. D. Burford, M. Z. Ozel, A. A. Clifford, K. D. Bartle, Y. Lin, C. M. Wai, N. G. Smart, "Extraction and recovery of metals using a supercritical fluid with chelating agents," Analyst, 124 (1999) 609.

17   A. Shadrin, A. Murzin, V. Romanovsky, V. Starchenko, "Study on supercritical fluid extraction of uranium and transuranium complexes with β-diketones and other complexones, as Applied to decontamination," JAERI-Conf, 2002-004 (2002) 557.

18   M. Shamsipur, A. R. Ghiasvand, Y. Yamini, "Extraction of uranium from solid matrices using modified supercritical fluid CO_2," J. Supercrit. Fluids, 20 (2001) 163.

19   R. Kumar, N. Sivaraman, E. Senthil Vadivu, T. G. Srinivasa, P. R. Vasudeva Rao, "Complete removal of uranium nitrate from tissue matrix using supercritical fluid extraction," Radiochim. Acta, 91 (2003) 19