Extraction of Uranium(VI) from Nitric Acid Solution into Supercritical Carbon Dioxide Containing Tri-n-butylphosphate

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Uranium(VI) in the aqueous solution of (3 - 6) M (1 M = 1 mol dm^{-3}) HNO_3 + 3 M $LiNO_3$ was extracted into supercritical CO_2 fluid containing 3 vol% of tri-n-butylphosphate (TBP) at 60 °C and (1.5 - 3.5) x 10^7 Pa. Rapid and complete removal of CO_2 medium from the extract was attained by gasification of CO_2 at atmospheric temperature and pressure.

Large amount of liquid waste of used organic solvent is generated from conventional solvent-extraction processes such as tri-n-butylphosphate (TBP)-extraction process for reprocessing nuclear spent fuel, i. e., the so-called Purex process.[1] A supercritical CO_2 fluid is one of the promising substitute of extraction media because of a potential for minimization of the amount of the solvent waste, since CO_2 can be removed from the extracted substances by the evaporation. In addition, CO_2 has attractive properties such as being easily recyclable, non toxic, stable chemically and radiochemically, and less expensive. Despite these advantages particularly in the application to the field of nuclear technology, there have been only a few works on the supercritical fluid extraction (SFE) of metals from the aqueous solution. Pioneer studies have very recently been performed by Wai's group.[2-4] In the present letter, the authors will describe the extraction behavior of U(VI) from HNO_3 + $LiNO_3$ solution into supercritical CO_2 fluid containing TBP and discuss about a feasibility of the SFE to the separation process dealing with such highly radioactive materials as nuclear spent fuel.

Schematic diagram of the apparatus[5] employed for the SFE is illustrated in Figure 1. Main parts of an extraction vessel and a collection vessel are placed in an oven at a constant temperature above a critical temperature, Tc = 31 °C, e. g., 60 °C. Experimental procedure is as follows. Five ml of HNO_3 + $LiNO_3$ sample solution containing 240 µg U(VI), i. e., 2 x 10^{-4} M of U, was taken in the 10 ml extraction vessel of stainless steel SUS-316 (Jasco, Tokyo, Japan). The syringe pump (Isco, Model 260D) was filled with CO_2 from liquid-CO_2 cylinder of ca. 6 x 10^6 Pa and 99.99% pure (Shin Tokyo, Teisan, Japan), and then pressurized by means of the pump controller (Isco, Lincoln, NE). The CO_2 was allowed to flow through the system at a constant pressure higher than a critical pressure, Pc = ca. 7.3 x 10^6 Pa, e. g., (1.0 - 3.5) x 10^7 Pa. An appropriate portion of TBP was continuously added into the CO_2 stream using a plunger-type pump (Nihon Denshi, Model CAP-L02). After pre-warming up to 60 °C by passing the coil of stainless steel tubing of 100 cm in length and 1/16 inch o. d., the supercritical CO_2 - TBP mixture was introduced continuously into the extraction vessel with being bubbled into the sample solution at 60 °C. The effluent from the extraction vessel was depressurized down to atmospheric pressure by passing through a restrictor of a stainless steel tubing of ca. 33 cm in length and 50 µm i. d., and then bubbled into 1 M HNO_3 solution in the collection vessel. The flow rate of the supercritical CO_2 - TBP mixture was dependent both on a pressure of the fluid and a characteristic of the restrictor. In general procedure adopted in the present work, the flow rates of supercritical CO_2 and TBP were 1.1 and 0.033 ml min^{-1}, respectively, to prepare 3 vol% TBP mixture at 1.5 x 10^7 Pa. The time required for the completion of the continuous extraction using 33 ml of CO_2 initially taken in the syringe pump was, therefore, approximately 30 min. After the extraction procedure, the amounts of uranium remained in the sample solution in the extraction vessel as well as that in the collecting solution were determined by ICP-AES. The extraction efficiency and the recovery efficiency were calculated from these results.

The results of the SFE of U(VI) in HNO_3 + $LiNO_3$ solutions of various compositions with supercritical CO_2 - 3 vol% TBP mixture are summarized in Table 1. Percent extraction given in the last column of the table were calculated from the amount of uranium found in the extraction vessel after the extraction procedure. Uranium extracted into the supercritical fluid was not completely recovered in the collecting solution, and the recovery efficiencies calculated from the amount of uranium found in the collecting solution were in the range of 85 to 97%. The loss of a small portion of uranium is attributable to precipitation of uranium compound(s) inside the capillary of the restrictor at which CO_2 transforms from supercritical to gaseous phases. Further studies including technological improvement of the restrictor system are required to attain the complete recovery of the metals extracted.

Extraction efficiency increases with an increase of the concentration of HNO_3 and is enhanced by the presence of such nitrate salts as $LiNO_3$ as shown in Table 1. Such

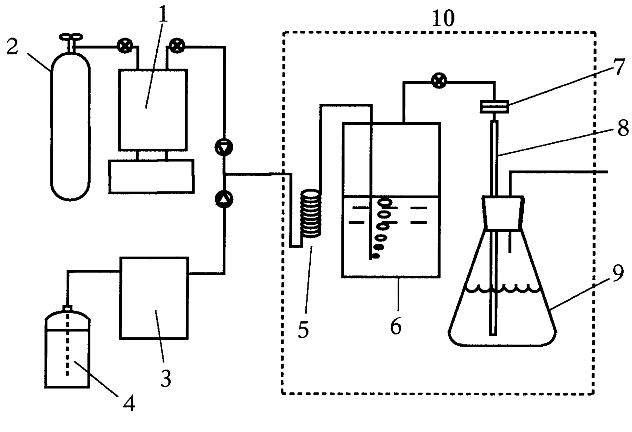

Figure 1. Apparatus for the extraction with supercritical CO_2 - TBP mixture fluid.
1; syringe pump and controller, 2; liquid CO_2 cylinder,
3; plunger-type pump, 4; TBP-container,
5; pre-warming coil, 6; extraction vessel, 7; filter,
8; restrictor, 9; collection vessel, 10; oven (60 °C)

characteristics are identical to those observed in the extraction of U(VI) with TBP-containing n-dodecane or kerosene conventionally employed.[6] With increasing the concentration of TBP in the supercritical CO_2 mixture, the higher extraction efficiency could be achieved.

It is valuable for the evaluation of a feasibility of SFE to compare characteristics of supercritical CO_2 as an extraction medium with those of such organic solvents as n-dodecane. For comparison, the extraction efficiency of U(VI) into continuous flow of n-dodecane containing TBP was determined according to the identical procedure as given in Table 1, where n-dodecane - 3 vol% TBP mixture (ca. 1×10^5 Pa, 60 °C) was used instead of supercritical CO_2 - 3 vol% TBP (1.5×10^7 Pa , 60 °C). From aqueous sample solutions of 9 M HNO_3, 6 M HNO_3 + 3 M $LiNO_3$, 6 M HNO_3, and 3 M HNO_3 +3 M $LiNO_3$, the extraction efficiencies found were 48, 68, 50, and 69%, respectively. It is not easy to make quantitative and strict comparison of these two extraction media on the basis of these data and results in Table 1 , because the extraction efficiency in the present experiment was measured under the kinetically controlled condition using continuous flow of the extraction medium through the aqueous sample solution at a given flow rate. Nevertheless, it is noteworthy that supercritical CO_2 medium is superior to n-dodecane for achieving the higher extraction efficiency.

Table 1. Extraction of U(VI) from HNO_3 + $LiNO_3$ solution with supercritical CO_2 - 3 vol% TBP mixture at 60 °C and 1.5×10^7 Pa

Sample Media	U_{found} / µg (1) Extraction Vessel	(2) Collection Vessel	U_{loss} [a] / µg	% Extraction[b]
9 M HNO_3	43	186	11	82
6 M HNO_3 + 3 M $LiNO_3$	5	190	45	98
6 M HNO_3	26	205	9	89
3 M HNO_3 + 3 M $LiNO_3$	7	227	6	97
3 M HNO_3	53	171	16	78
1 M HNO_3	130	101	9	46
0.1 M HNO_3	220	<2	<20	9

Sample ; 5 ml of 2×10^{-4} M U(VI), amount of U taken ; 240µg

[a] $U_{loss} = U_{taken} - U_{found}\{(1) + (2)\}$

[b] Calculated from the amount of U remained in the extraction vessel.

Under the extraction condition as given in Table 1, lanthanide elements which are some of the main fission products involved in the nuclear spent fuel, were not extracted into supercritical CO_2 phase; the extraction efficiencies of ca. 350 µg La^{3+}, Eu^{3+}, and Lu^{3+} were determined to be less than 1%. Uranium can, therefore, be recovered separately from lanthanide elements by the proposed SFE method. Referring to the extraction behavior of trivalent ions of lanthanide elements studied in the previous work,[5] the lanthanide elements can be successively recovered after the separation of uranium by the SFE with supercritical CO_2 - 30 vol% TBP mixture, by means of the same apparatus and procedure presently employed.

The SFE is a very promising method for the application to the separation process in the field of nuclear technology handling a large quantity of radioactive materials, because of the following advantages. (1) Medium can be removed from the extracted substances rapidly and completely, and treatment of CO_2 is simple, which may lead to minimization and simplification of the process. (2) The amount of the radioactive organic waste can be minimized. (3) The extraction kinetics can be improved by the use of supercritical fluid instead of the conventional organic solvents. The detailed studies on the effect of temperature, pressure, TBP-concentration, etc. on the extraction efficiency are now in progress.

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References and Notes

1 E. R. Irish and W. H. Reas, *USAEC Report* **TID-7534**, 83 (1957).

2 Y. Lin, R. D. Brauer, K. E. Laintz, and C. M. Wai, *Anal. Chem.*, **65**, 2549 (1993).

3 Y. Lin and C. M. Wai, *Anal. Chem.*, **66**, 1971 (1994).

4 Y. Lin, C. M. Wai, F. M. Jean, and R. D. Brauer, *Environ. Sci. Technol.*, **28**, 1190 (1994).

5 K. E. Laintz and E. Tachikawa, *Anal. Chem.*, **66**, 2190 (1994).

6 Z. Kolarik, "Gmelin Handbook of Inorganic Chemistry U D2." ed by R. Keim, Y. Marcus, and C. Keller, Springer-Verlag(1982), Ch 2-4, pp. 77.