

# DISSOLUTION OF ACTINIDE OXIDES IN SUPERCRITICAL CO<sub>2</sub> MEDIUM

Andrew SHADRIN\*, Andrew MURZIN, Valery ROMANOVSKY, Sergey PODOYNITZYN  
*Khlopin Radium Institute, St.-Petersburg, 194021, Russia*

*Tel. +7-812-247-5845, Fax. +7-812-247-8095, E-mail: [shadrin@atom.nw.ru](mailto:shadrin@atom.nw.ru)*

Tomozo KOYAMA, Yoshikazu KOMA  
*Japan Atomic Energy Agency, 319-1194, Japan*

## ABSTRACT

It is shown that the combined leaching of uranium and thorium may be carried out from the mixtures of actinide oxides simulating spent nuclear fuel (SNF) of fast breeder reactors (FBR) by the solution of 13-15% vol. TBP-HNO<sub>3</sub> in supercritical carbon dioxide (SC CO<sub>2</sub>) that it is possible to develop FBR SNF reprocessing technology meeting the requirements of nuclear materials non-proliferation. The data are given on the composition of residue arising from leaching of 95-98 % U from FBR SNF simulator. It is revealed that on leaching of more than 95 % U with its purification coefficients below 10 from fission products and with decrease of uranium leaching to 90%, the purification coefficients of uranium from main  $\gamma$ -emitters exceed 100.

## INTRODUCTION

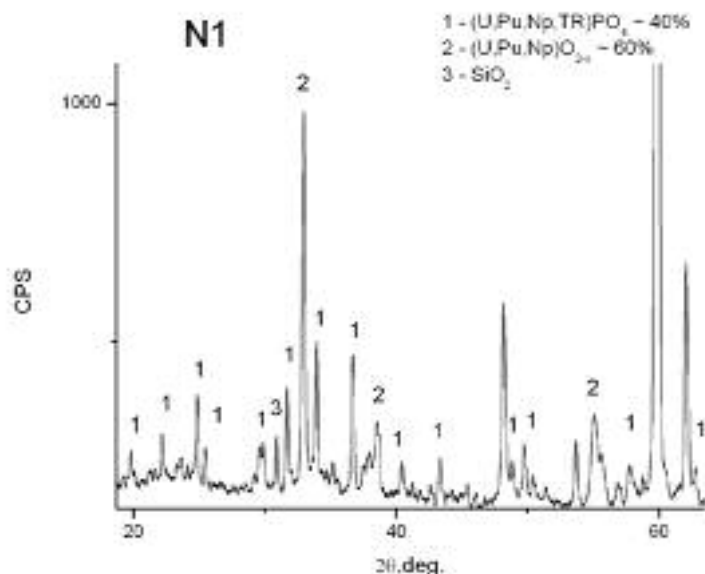
Extraction of metals by complexone solutions in supercritical carbon dioxide (supercritical fluid extraction - SFE) is new method for metal recovery which allows drastically to reduce volumes of secondary process liquid wastes. A series of papers have been recently published concerning SFE of metals, including U, Th and rare-earth elements (REE), by solutions of  $\beta$ -diketones, ntybutylphosphate (TBP) and its mixtures with  $\beta$ -diketones in SC CO<sub>2</sub>.

Investigations on applicability of CO<sub>2</sub> to SNF reprocessing are conducted in two main directions: (i) application of SC CO<sub>2</sub> as solvent for TBP at extraction of U and TRU from HNO<sub>3</sub> solutions and (ii) immediate dissolution of SNF in SC CO<sub>2</sub>, containing a complexone. In the first case SC CO<sub>2</sub> is diluent for TBP (analog of aliphatic hydrocarbons) and extraction proceeds from aqueous solution. On direct dissolving of SNF in SC CO<sub>2</sub>, containing TBP and HNO<sub>3</sub> one can really reduce the secondary liquid waste volume. Other advantage of using SFE for SNF reprocessing is joint recovery of uranium, plutonium and neptunium, in accordance with requirements of nuclear weapon non-proliferation. Besides, this "non-aqueous" technology permits to recover U-Pu-Np fraction with purification coefficient over 100 from REE and other fission products (FP), which may result in dramatic reduction of secondary waste volume to be conditioned.

The objective of the present work is to investigate the leaching of actinide oxides into solutions of TBP - HNO<sub>3</sub> complex in SC CO<sub>2</sub>.

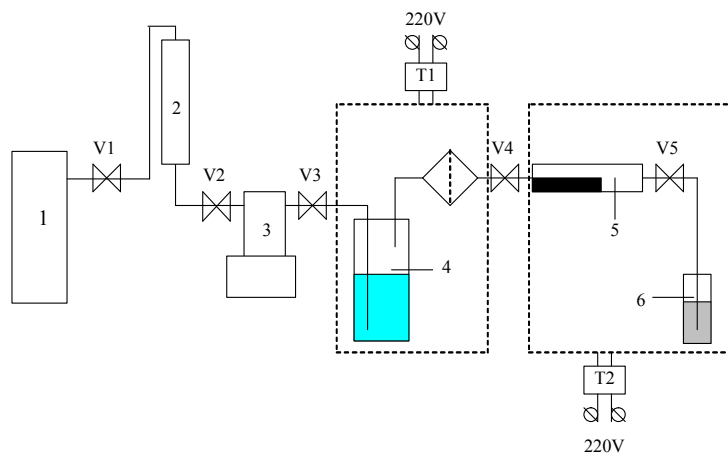
## EXPERIMENTAL PROCEDURE

FR SNF simulator was synthesized wherein the sum of Pu + Np was replaced by the same amount of Th. X-ray phase analysis of the simulator indicated that this is a solid solution of element oxides in uranium dioxide (**Figure 1**). Monophasicity of the simulator was confirmed by dissolution of its weighed portion in 6M HNO<sub>3</sub> at 60°C without any residue.



**Figure 1:** Diffractogram of FR SNF simulator containing U, Pu, Np, Zr, Mo, REE, Cs, Sr, Ba. Cubic solid solution based on uranium dioxide.

Nitric acid, TBP, and analytical reagents were received from “Vekton” Ltd (Russia). TBP was purified by traditional technique [1]. Block-diagram of experimental setup is shown in **Figure 2**. Experiments on dissolving of actinides were performed by the following procedure. A weighed simulator portion of mass ~1 g was placed into cell 5, 30 ml TPB were poured into bubbler 3, 20 ml of 12,2 mole/L HNO<sub>3</sub> were poured into bubbler 4, the setup was thermostatically controlled during 2 hours at 60<sup>0</sup>C; then it was filled with CO<sub>2</sub>, pressure of 300 atm was built up in pump, the first 10 ml CO<sub>2</sub>, were pumped, scouring fluid through filter into thermostat vessel; valves V3, V4 were opened and TBP-HNO<sub>3</sub> complex solution was pumped into CO<sub>2</sub> through cell 5, collecting extract into CCl<sub>4</sub> by fractions and changing receiver after pumping 20 ml CO<sub>2</sub> (the first three fractions) and next after pumping 10 ml (the fourth fraction). The overall volume of pumped CO<sub>2</sub> was equal to 70 ml. Upon completing the test, the resultant residue was washed-out by water from the cell for X-ray phase analysis or by 2 mole/L HNO<sub>3</sub> for subsequent dissolution and chemical and radiochemical analyses.



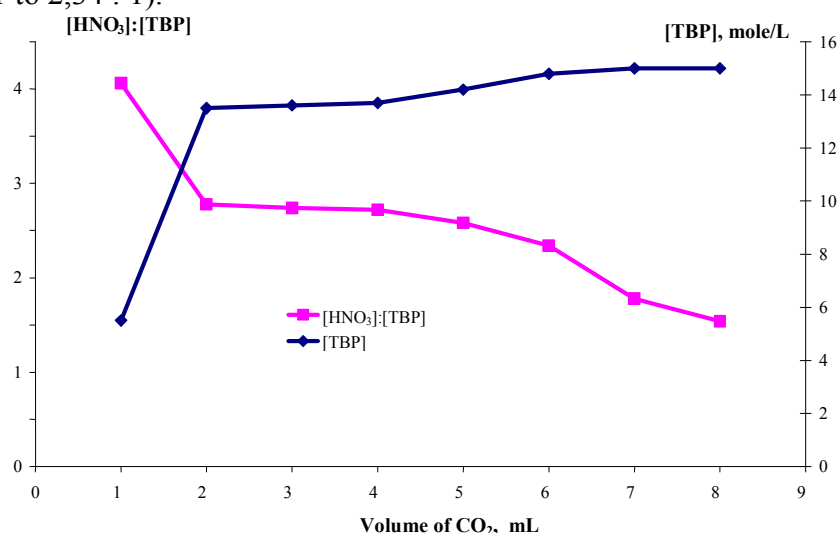
**Figure 2:** Setup for leaching of actinide oxides

Laser-luminescent, spectrophotometric (Arsenazo III) and volumetric vanadatometric methods were used for determination of uranium in taken samples [2,3]. Concentration of other elements in extract and residue was determined by ICP mass-spectrometry (VG Plasma Quad PQ2 Turbo+).

X-ray phase analysis of powders was conducted in conventional aluminum holders. Analysis was carried out on diffractometer of «Ridaku» Co by using Co K $\alpha$  emission with current 40 mA and voltage on tube 30 kV at scanning rate of 2 degrees/min with spacing of 0,01 degree.

## RESULTS AND DISCUSSION

Preliminary experiments disclosed that under certain conditions the constant concentration of TBP in CO<sub>2</sub>, (13,5-14.8 % vol.) may be attained at constant molar ratio of [HNO<sub>3</sub>]:[TBP] (from 2,78 : 1 to 2,34 : 1).

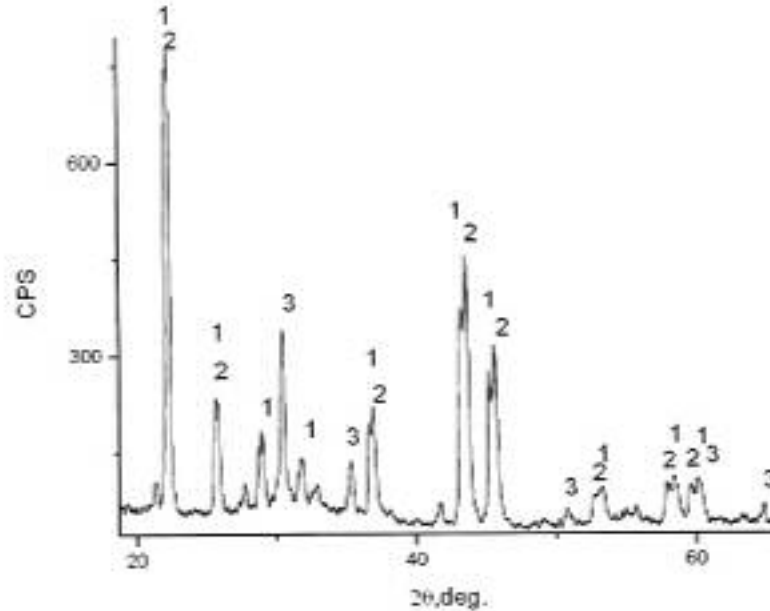


**Figure 3:** Extraction of HNO<sub>3</sub> from its 12,2 mole/L aqueous by TBP solution in SC CO<sub>2</sub>

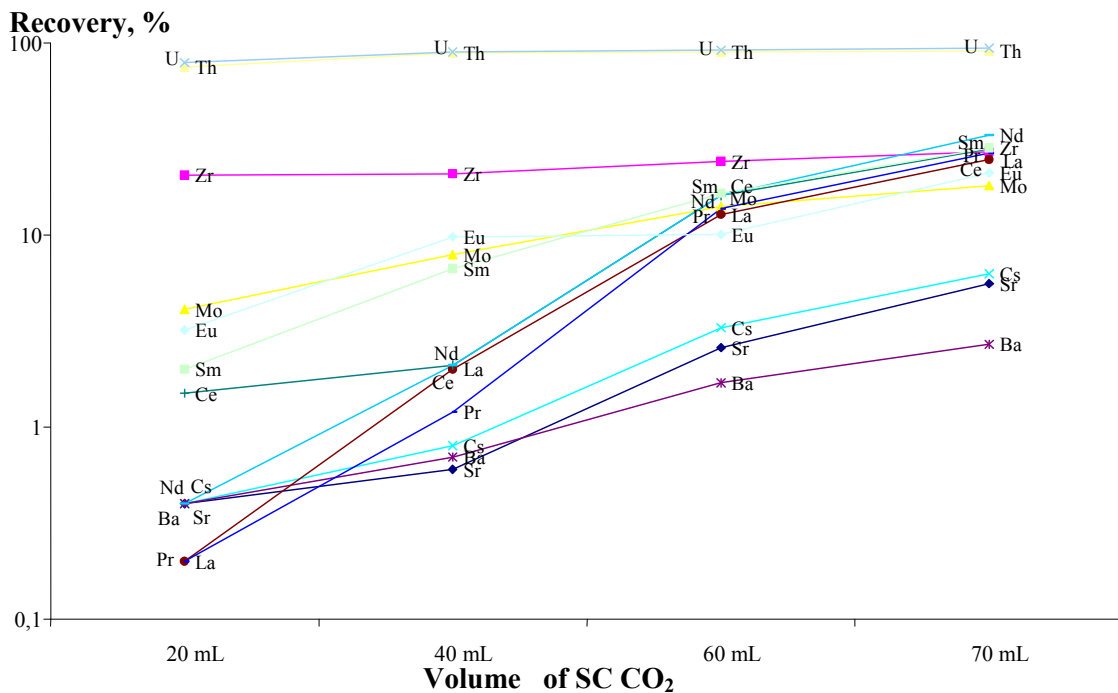
The performed experiments have revealed that solid and aqueous phases remain in cell after leaching. The ratio between them in residue may be estimated as 1:1. Crystals of Cs, Ba, Sr, and Ln nitrates with water-insoluble inclusions may be distinguished in the residue. In preparing the residue to analysis it is found that, as distinct from the initial simulators easily dissolving in 6 mole/L HNO<sub>3</sub> on heating, the residues arising from leaching are dissolved only on prolonged boiling with 12 mole/L HNO<sub>3</sub> and added H<sub>2</sub>O<sub>2</sub>. On evidence derived from X-ray phase analysis (Fig. 4), the residue washed from the bulk of water-soluble nitrates remaining after leaching of FR SNF (U(Th)O<sub>2</sub>) simulator constitutes a mixture of complicated molybdate of cesium, barium, lanthanum and, perhaps, zirconium with a phase of probable composition U(Th,Zr,Mo)O<sub>x</sub>(OH)<sub>y</sub>. Leaching 1g of simulator produces around 50 mg of water-insoluble solid residue. Analysis of the data obtained shows that the leaching of all elements under investigation increases with increasing the amount of the passed TBP-HNO<sub>3</sub> solution in SC CO<sub>2</sub> (Figure 5).

It should be noted that actinides are separated into the first fractions much more effectively than other elements. However, the overall recovery of other elements, especially Zr and REE, considerably increases even in the third fraction. Analysis for recovery of elements into each fraction makes it apparent that the recovery degree of actinides decreases with decreasing the total amount of actinides in the mixture. It is clear that the recovery of other elements

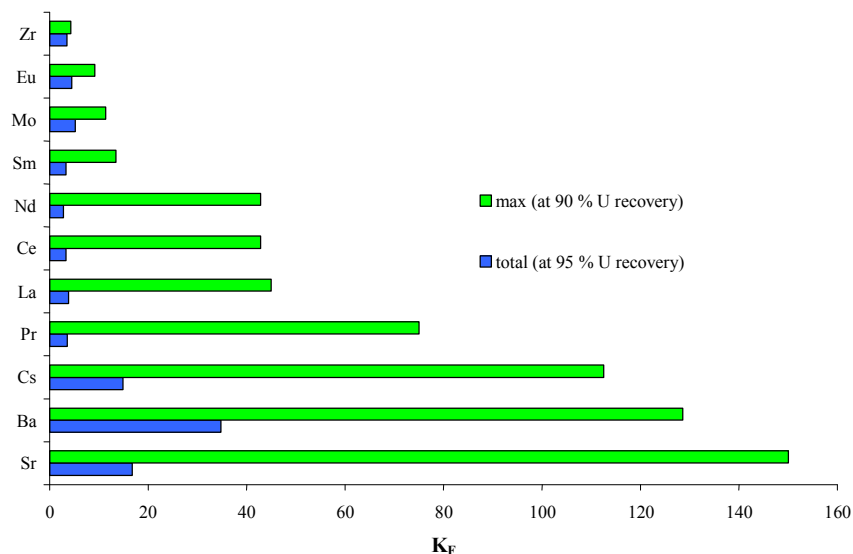
increases after removing 90 % of main matrix (uranium). However, despite the sharp decrease of purification coefficients with increasing volume of passed TBP-HNO<sub>3</sub> solution in SC CO<sub>2</sub> for individual fractions, the overall purification coefficients remain rather high. The high coefficients of uranium purification from fission products may be attained at recovery of uranium from oxide at a level of 90% (**Figure 6**).



**Figure 4:** Diffractogram of residue resulting from leaching of (U,Th)O<sub>2</sub> simulator  
*The residue is washed from bulk of water-soluble nitrates;  
 main phases in residue - Ba(Sr)(NO<sub>3</sub>)<sub>2</sub>, 2-CsBaLaMoO<sub>6</sub>, 3- U(Th, Zr, Mo)O<sub>x</sub>(OH)<sub>y</sub>*



**Figure 5:** Recovery of elements (as recovery is built up) on leaching by TBP-HNO<sub>3</sub> solution in SC CO<sub>2</sub> from (U,Th)O<sub>2</sub> simulator as a function of pumped CO<sub>2</sub> volume



**Figure 6:** Overall coefficients of uranium purification from elements on leaching by TBP-HNO<sub>3</sub> solution in SC CO<sub>2</sub> from (U(Th)O<sub>2</sub>) simulator as a function of pumped CO<sub>2</sub> volume

## CONCLUSION

1. It is shown that the combined leaching of uranium and thorium from the mixture of actinide oxides simulating FR SNF may be conducted by the solution of 13-15% vol. TBP - HNO<sub>3</sub> in supercritical carbon dioxide.
2. It is revealed that the residue remaining after leaching represents a mixture of aqueous and solid phases (Solid : Liquid ~ 1 : 1) consisting of solution and crystals of Cs, Ba, Sr and Ln nitrates with water-insoluble inclusions which constitute a complicated molybdate of cesium, barium, lanthanum and, possibly, zirconium with a phase of probable composition U(Th,Zr,Mo)O<sub>x</sub>(OH)<sub>y</sub> at the ratio of U:Th:Zr:Mo:Sr:Ba:Cs:Ln= 1:1,6:0,2:3:0,2:0,3:0,3:0,5.
3. It is established that 95-98 % U may be removed from the simulated FR MOX SNF by passing 50-70 ml of the solution of 13-15% vol. TBP-HNO<sub>3</sub> ([HNO<sub>3</sub>]:[TBP]≈2,7:1) in supercritical carbon dioxide.
4. It is indicated that in the case of uranium leaching by 90% the coefficients of its purification from the main  $\gamma$ -emitting radionuclides (Cs and Sr) are more than 100 and those from REE are ~ 10-20.

The work was carried out under the financial support of ISTC (Project 3181).

## REFERENCES

- [1] MCDOWELL, W., PERDUE, P., JINC, Vol. 31, **1969**, p. 2587
- [2] NIKITINA, S., STEPANOV, A., Radiochemistry, Vol.26, N 5, **1986**, pp.606 – 610 (In Russian)
- [3] MARKOV, V., VINOGRADOV, A., ELINSON, A., et al., Uranium. Methods of its determination. M., Atomizdat, **1960**, p.263 (In Russian)