

# Supercritical Carbon Dioxide Fluid Leaching (SFL) of Uranium from Solid Wastes Using HNO<sub>3</sub>-tributylphosphate (TBP) Complex as a Reactant

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**Abstract.** Supercritical carbon dioxide (CO<sub>2</sub>) leaching method (SFL), which is based on the efficient and selective dissolution of UO<sub>2</sub> and U<sub>3</sub>O<sub>8</sub> with supercritical CO<sub>2</sub> containing HNO<sub>3</sub>-tributylphosphate (TBP) complex at 333 K and 15 – 20 MPa, has been developed for the removal and recovery of uranium from the solid waste contaminated by uranium oxides. The decontamination factor of UO<sub>2</sub> or U<sub>3</sub>O<sub>8</sub> of higher than 500 were attained by the recommended procedure, which was demonstrated using synthetic solid waste samples of a mixture of the uranium oxides and sea sand.

## Introduction

Removal of radioactive contaminants from solid wastes such as various metallic, ceramic or organic materials and sludge or ash products from the nuclear waste treatment processes as well as mine tailings leads to safe and economical storage and disposal of the wastes. The decontamination treatment of the solid wastes, however, is not commonly conducted because of methodological limitations as follows; methods applicable to a large-scale treatment of the wastes are very limited and wet-chemical decontamination processes such as acid leaching process often generate large amount of the secondary wastes.

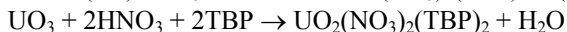
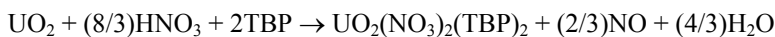
Recently, much attention has been paid to a novel technology for the separation of metals using the supercritical CO<sub>2</sub> fluid as a medium (Iso et al. 1995; Meguro et al. 1996; Lin et al. 1995; Toews et al. 1996; Erkey 2000). Supercritical CO<sub>2</sub> fluid extraction (SFE) with the supercritical CO<sub>2</sub> instead of an organic solvent has several advantages as follows. The extraction efficiency and rate are expected to be enhanced due to rapid mass transfer in the supercritical fluid phase. The rapid and complete recovery of the extracted substances from CO<sub>2</sub> is attained by gasification of CO<sub>2</sub>. The extraction efficiency or selectivity can be optimized by changing optionally the properties of the CO<sub>2</sub> medium by tuning pressure and temperature (Meguro et al. 1998; Lin et al. 1995). The application of the SFE technology in the nuclear field exhibits particular significance for minimizing the amount of the radioactive solvent waste. The most attractive method based on the SFE is “direct extraction (leaching)” of the metals from the solid samples. Neither organic solvent nor acid solution for the pretreatment of the samples are necessary to be used in this method, which leads to a total minimization of the secondary wastes from the separation process (Tomioka et al. 2000, 2001a; Murzin et al. 1998).

The present paper aims at presenting the recent results of the supercritical CO<sub>2</sub> fluid leaching (SFL) of uranium from the solid wastes containing uranium oxides. The HNO<sub>3</sub>-TBP complex was employed as a reactant to dissolve the uranium oxides efficiently and selectively into supercritical CO<sub>2</sub> phase.

## Principle of the SFL of UO<sub>2</sub> and U<sub>3</sub>O<sub>8</sub>

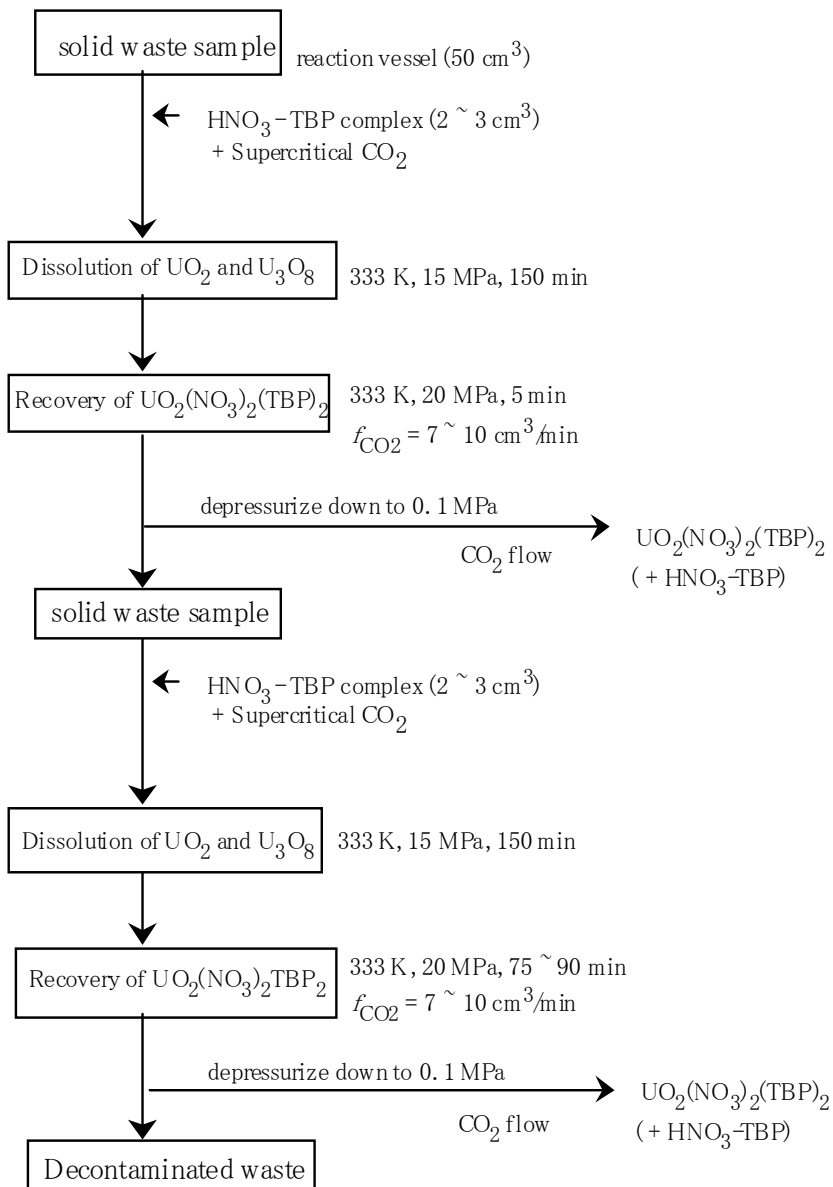
The SFL method for removal and recovery of uranium from solid samples consists of two elementary processes, one of which is the dissolution of the uranium oxide with the HNO<sub>3</sub>-TBP complex in the supercritical CO<sub>2</sub> and the other is the recovery of supercritical CO<sub>2</sub>-soluble substances, which are UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(TBP)<sub>2</sub> formed and the HNO<sub>3</sub>-TBP complex unreacted in the collector. The solutes, UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(TBP)<sub>2</sub> and the HNO<sub>3</sub>-TBP complex, are transported with the supercritical CO<sub>2</sub> flow to the collector kept at an atmospheric pressure where the solutes are deposited completely by gasification of CO<sub>2</sub>.

The oxides, UO<sub>2</sub> and U<sub>3</sub>O<sub>8</sub>, react with the HNO<sub>3</sub>-TBP complex and the overall dissolution reactions are expressed by the following equations:



Tetravalent uranium U(IV) once dissolved in the supercritical CO<sub>2</sub> containing the HNO<sub>3</sub>-TBP complex is liable to be oxidized to U(VI). It was found (Tomioka et al. 2001b) that dissolution rate increased with increasing the HNO<sub>3</sub>/TBP ratio and the concentration of the reactant in the supercritical CO<sub>2</sub>. The dissolution rate was practically independent on the temperature in the range of 313 to 333 K, and decreased slightly with an increase of the pressure in the range of 12 to 25 MPa. The HNO<sub>3</sub>-TBP complex has multi-functions in promoting such elementary reaction

steps involved in the dissolution reaction as protonation of the oxides, oxidation of U(IV) to U(VI) and solubilization of U(VI) in the supercritical CO<sub>2</sub> through a formation of UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub>(TBP)<sub>2</sub>.



**Fig. 1.** SFLe procedure for the decontamination of UO<sub>2</sub> and U<sub>3</sub>O<sub>8</sub> from solid wastes.

## Recommended procedure

The flowsheet of the recommended procedure for the SFL of  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$  from the solid waste sample which consists of two cycles of dissolution-recovery processes is shown in Fig. 1. The highest dissolution efficiency of  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$  was observed at the pressure in the range of 12.5 to 17.5 MPa at 333 K, and the highest recovery efficiency was observed at 17.5 to 20 MPa (Meguro et al. 2002). The pressure in the recommended procedure was thus chosen to be 15 MPa for the dissolution process and 20 MPa for the recovery process.

In this flowsheet the flow rate of  $\text{CO}_2$ ,  $f_{\text{CO}_2}$ , is expressed as that inside the reaction vessel at 333 K and 20 MPa.

## Experimental

Apparatus for the SFL was essentially identical to that reported previously (Tomioka et al. 2002). The main part of the apparatus consisted of a stainless steel reaction vessel ( 50 ml ), which was installed in a thermostat oven ( 333 K ), a reactant mixing vessel and a collector. Stainless steel balls of 3.2 mm in diameter were packed in the collector which was made of Pyrex glass cylinder of 300 mm in height and 10 mm in diameter with water jacket to keep temperature at 333 K. A syringe pump was used to flow  $\text{CO}_2$ .

The  $\text{HNO}_3$ -TBP complex was prepared by mixing vigorously 100 ml of 70%  $\text{HNO}_3$  with 100 ml of TBP in a conventional extraction tube for 30 min. The  $\text{HNO}_3$ -TBP complex liquid thus obtained contained  $\text{HNO}_3$  and TBP at mole ratio of 1.4 ~ 1.5 : 1 as the mixture of  $(\text{HNO}_3)_2(\text{TBP})$  and  $\text{HNO}_3(\text{TBP})$  complexes. The water content of the  $\text{HNO}_3$ -TBP complex was approximately 1.3 mol/l (Tomioka et al. 2001b).

Synthetic solid waste samples were mixture of ca. 100 ~ 200 mg of  $\text{UO}_2$  or  $\text{U}_3\text{O}_8$  powers and 20 ~ 50 g of matrix. The matrices employed were the standard sea sand (20 ~ 30 mesh), ash, and polyvinyl chloride (PVC) materials of various types such as powder, film and plate.

## Results

Decontamination factors of uranium from the synthetic waste samples were determined according to the recommended procedure.

The decontamination factors obtained for the sample of the mixture of 100 mg  $\text{UO}_2$  or  $\text{U}_3\text{O}_8$  powders and 50 g sea sand were enough high and approximately 500. Most of uranium, *i. e.*, 95 to 99%, contained in the sample was recovered in the collector.

The mixture of 25 g of PVC powders (Wako Pure Chemical Ind. Ltd, reagent grade PVC of about 0.2 mm in diameter) and 120 to 135 mg  $\text{UO}_2$  or  $\text{U}_3\text{O}_8$  powders was treated by the SFL. In this experiment, single cycle dissolution-recovery

process consisting of the dissolution at 333 K and 15 MPa for 150 min and the recovery at 333 K and 20 MPa with  $\text{CO}_2$  flow at  $f_{\text{CO}_2} = 8 \text{ cm}^3/\text{min}$  for 75 min was employed. The amount of uranium, which was present as a form of oxide and  $\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$  complex, remaining in the reaction vessel after the SFL was determined distinguishing the chemical form. It was found that 25 - 27% and 3 - 5% of uranium of the total uranium taken initially remained in the reaction vessel with the PVC powders as a form of uranium oxide and  $\text{UO}_2(\text{NO}_3)_2(\text{TBP})_2$  complex, respectively. The inhibition of the dissolution of the uranium oxides by the presence of the PVC was observed, which is attributable to the lowering of the oxidation potential or the proton activity arising from the  $\text{HNO}_3$ -TBP complex when the PVC coexists in the supercritical  $\text{CO}_2$  phase. Further investigation is required to optimize the SFL condition for the decontamination of solid wastes of the PVC matrix.

The mixture of ash and uranium oxide powders was tested. In this experiment the synthetic ash sample was treated by the SFL after packed in an inner container made of porous alumina cylinder to prevent discharge of the fine ash particles from the reaction vessel to the down stream of the SFL system. Only 10 - 20% of uranium of the total uranium initially taken was removed from the ash sample. An appropriate procedure to enhance the mass transport between inside and outside of the alumina container during the dissolution and recovery processes is necessary to be developed by adopting such techniques as a "pressure-swing" method, which is now in progress.

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