Dissolution of uranium oxides in supercritical carbon dioxide containing tri-*n*-butyl phosphate and thenoyltrifluoroacetone

Trofim I. Trofimov,*[a] **Maksim D. Samsonov,**[a] **Su C. Lee,**[b] **Boris F. Myasoedov**[a] **and Chien M. Wai**[b]

[a] *V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, 117975 Moscow, Russian Federation. Fax: +7 095 938 2054*
[b] *Department of Chemistry, University of Idaho, Moscow, ID 83844, USA. Fax: +1 208 885 6173*

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Milligram amounts of uranium dioxide can be quantitatively dissolved in supercritical carbon dioxide containing a complex of tri-*n*-butyl phosphate (TBP) with nitric acid and separated from thorium(IV). The quantitative dissolution of milligram amounts of solid uranium trioxide in supercritical carbon dioxide containing thenoyltrifluoroacetone (TTA) and TBP was performed using ultrasonication. The separation of uranium(VI) and cerium(IV) in the test system was demonstrated.

Supercritical fluid extraction (SFE) of metals from liquid and solid materials using environmentally friendly supercritical carbon dioxide containing a suitable ligand is a very promising method for chemical processes.[1,2] SFE provides several advantages over conventional solvent extraction, including minimisation of hazardous liquid wastes. Since Laintz *et al.*[3] demonstrated the possibility of copper chelate extraction with supercritical CO_2, this method was applied to the extraction of actinides,[4–7] caesium[8] and strontium.[9] Uranium and lanthanides can be directly extracted from their solid oxides using such ligands as TTA and TBP.[4,10] Recent studies also demonstrated the possibility of lanthanide extraction from their oxides using supercritical CO_2 containing the TBP–HNO_3 complex.[11] However, the extraction efficiency of all elements did not exceed 50%. Thus, it was of interest to develop a procedure for the quantitative extraction of uranium from its oxides simultaneously with its separation from other metals. Such a procedure can be used in a nuclear fuel cycle.

Figure 1 shows a schematic diagram of the set-up employed for SFE. A syringe pump was used to deliver liquid CO_2 through a pre-heating coil to the extraction system placed in a chromatographic oven for heating the system to a required temperature. Metal oxides (UO_3, UO_2, U_3O_8, CeO_2, La_2O_3 and ThO_2) were placed in a 3.5 ml extraction cell. The saturation of supercritical CO_2 with ligands (TTA or the TBP–HNO_3 complex) was performed in a 10.4 ml ligand cell connected upstream of the extraction cell. Pure TBP was injected into the system through a T-end joint using an HPLC pump. A flow rate of TBP injected into the system was about 0.02 ml min^{-1}, which corresponded to its concentration in supercritical CO_2 of about 5 vol.%. Extracted metal complexes were collected in a trap solution (chloroform) through the restrictors made of a capillary tube of deactivated fused-silica 25 cm in length and 50 μm in internal diameter.

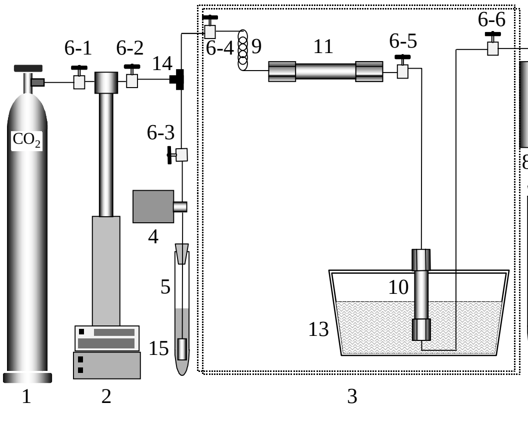

Figure 1 Schematic diagram of the experimental system for the dissolution of uranium oxides in supercritical carbon doxide: (1) CO_2 cylinder; (2) syringe pump; (3) oven; (4) HPLC pump; (5) test-tube with TBP; (6-1)–(6-6) valves; (7) collection system; (8) restrictor; (9) fluid preheating coil; (10) extraction vessel; (11) ligand cell; (12) restrictor heater; (13) ultrasonic cleaner; (14) T-joint and (15) filter.

Uranium was back extracted from the trap solutions with 50% nitric acid in the case of TTA and TBP as the ligands or with 0.1 M $(NH_4)_2CO_3$ in the case of the TBP–HNO_3 complex. Uranium was determined by spectrophotometry with Arsenazo I.[12] The data obtained were consistent with the ICP-MS data to within 10%. Cerium and thorium were determined by only ICP-MS. The mass balance on uranium in all runs was close to 100±7%. The extraction was performed in static, dynamic and combined modes (a static mode followed by a dynamic mode). The time of the static mode was about 10 min in all runs, and that of the dynamic one was changed from 15 to 60 min. The majority of the extractions were carried out at 60 °C and 150 atm. The above SFE conditions were found previously[10] to be optimal for the UO_3–TTA–TBP system.

The mechanism of processes in the test system is given below:

$$\text{Mass transport of TTA and TBP dissolved in supercritical } CO_2 \text{ to } UO_3 \text{ reaction site} \qquad (1)$$

$$UO_{3(\text{solid})} + 2\,TTA_{(\text{sf})} \rightarrow UO_2(TTA)_2{\cdot}H_2O_{(\text{solid})} \qquad (2)$$

$$UO_2(TTA)_2{\cdot}H_2O_{(\text{solid})} + TBP_{(\text{sf})} \rightarrow UO_2(TTA)_2{\cdot}TBP_{(\text{solid})} + H_2O_{(\text{sf})} \qquad (3)$$

$$UO_2(TTA)_2{\cdot}TBP_{(\text{solid})} + \text{supercritical } CO_2 \rightarrow UO_2(TTA)_2{\cdot}TBP_{(\text{sf})} \qquad (4)$$

$$\text{Mass transport of } UO_2(TTA)_2{\cdot}TBP_{(\text{sf})} \text{ in supercritical } CO_2 \text{ from the extraction cell} \qquad (5)$$

It is well known that ultrasonication can accelerate heterogeneous processes. We used an ultrasonic cleaner with a heater (model FS30, Fisher Scientific, USA) with a working frequency of 44–48 kHz (Figure 1). Table 1 shows the effect of ultrasonication on the SFE of uranium from its oxides with supercritical

Table 1 Dissolution of uranium oxides in supercritical CO_2 containing TTA and TBP using ultrasonication.

Oxide	U added/mg	U trapped/mg (%)
UO_3	22.9	8.5±0.3 (37.0[a])
UO_3	25.2	24.0±0.6 (96.5)
U_3O_8	30.9	0.7±0.1 (2.3)
UO_2	23.9	1.2±0.2 (5.0)

[a]Without ultrasonication.

Table 2 Separation of U^{VI} and Ce^{IV} using supercritical CO_2 containing TTA and TBP under ultrasonication.

Oxide	Metal added/mg	Metal trapped/mg (%)
UO_3	23.0	21.3±0.4 (92.7)
CeO_2	13.6	0.4±0.1 (3.1)

Table 3 Extraction of U, Th and La from the their oxides using supercritical CO_2 containing the TBP–HNO_3 complex.

Oxide	Metal added	Metal trapped/mg (%)
UO_2	22.6	21.7±0.4 (96)
UO_2	51.6	51.6±0.6 (100)
ThO_2	25.1	0.2±0.1 (<0.1)
La_2O_3	25.1	25.1±0.5 (100)

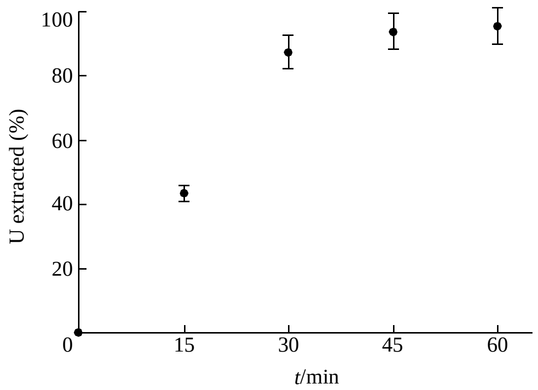

Figure 2 SFE of uranium from UO_2 with supercritical CO_2 containing the $TBP–HNO_3$ complex.

CO_2 containing TTA and TBP. As can be seen, ultrasound allows uranium to be quantitatively extracted from UO_3 with the above system. Unfortunately, ultrasonication did not improve the dissolution of both UO_2 and U_3O_8 in supercritical CO_2 containing TTA and TBP. This fact may be explained by structural differences between UO_2, U_3O_8 and UO_3 (UO_2, face-centered; U_3O_8, orthorhombic; UO_3, octahedral), as well as by steric hindrances in the U^{IV} complexation with TTA and TBP. The effect of ultrasound can be attributed to the cleaning of the oxide surface by removing the complex formed. As a result, the reaction with TTA takes place more effectively.

Table 2 shows that the suggested system can be successfully applied to the separation of uranium and cerium in the SFE from a mixture of UO_3 and CeO_2. The molar ratio [U]:[Ce] in the trap solution is about 30 times higher than that in the starting mixture.

The effect of ultrasound was maximum in UO_3, where uranium is in an oxidation state of 6+. We attempted to dissolve UO_2 and U_3O_8 after a preliminary treatment with H_2O_2 directly in the extraction cell. For this purpose, 0.2 ml of 30% H_2O_2 was introduced into the extraction vessel containing either UO_2 or U_3O_8. The mixture was heated at 90 °C for 2 h and evacuated to oxidise uranium to U^{VI} and to evaporate the aqueous phase before SFE. About 50% UO_2 was dissolved under the above conditions. However, we failed to obtain a positive result for U_3O_8. Apparently, conditions for the quantitative dissolution of UO_2 may be found in the further investigation of the system, which may be used for uranium extraction from spent nuclear fuel, which is known to consist mainly of UO_2.

The system based on supercritical CO_2 containing the $TBP–HNO_3$ complex was successfully applied to the quantitative extraction of uranium from UO_2. This system was recently used for Nd and Gd extraction from Nd_2O_3 and Gd_2O_3.[11] To obtain the $TBP–HNO_3$ complex, a 100% TBP solution was treated with concentrated HNO_3. After separating phases by centrifuging, 2 ml of the complex obtained were placed in the ligand cell, where supercritical CO_2 was saturated with the $TBP–HNO_3$ complex for 20 min. Then, it was introduced into the extraction cell containing the oxides. SFE was conducted using the combined mode as described above for the TTA–TBP system. The freshly prepared $TBP–HNO_3$ complex was used in all runs.

As can be seen in Figure 2, uranium was quantitatively extracted from UO_2. Table 3 shows the SFE of uranium, lanthanum and thorium from their oxides with supercritical CO_2 containing $TBP–HNO_3$ complex. The order of metal extraction from their oxides is $UO_2 \approx La_2O_3 >> ThO_2$; hence, uranium and thorium, as well as lanthanum and thorium, may be easily separated in the extraction from a mixture of their oxides (UO_2 and ThO_2, La_2O_3 and ThO_2) with supercritical CO_2 containing the $TBP–HNO_3$ complex.

Thus, milligram amounts of uranium can be quantitatively extracted from UO_2 with supercritical CO_2 containing the $TBP–HNO_3$ complex, as well as from UO_3 with supercritical CO_2 containing TTA and TBP under ultrasonication. The enhanced dissolution of UO_3 by means of ultrasound is, probably, caused by removing the $UO_2(TTA)_2 \cdot H_2O$ complex from the oxide surface, hence facilitating the complexation process. The results demonstrate that SFE is very promising for the reprocessing of spent nuclear fuel.

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