

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

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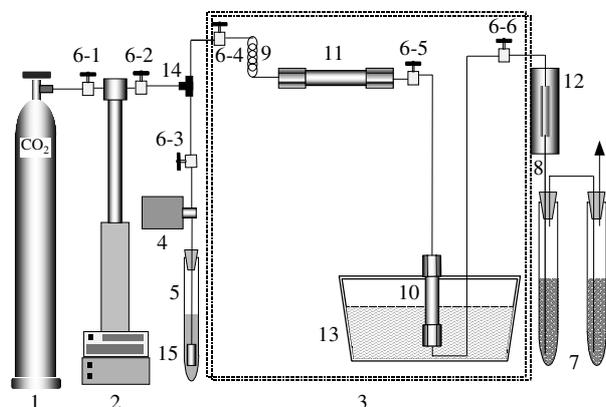
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10.1070/MC2001v011n04ABEH001468

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.<sup>1,2</sup> SFE provides several advantages over conventional solvent extraction, including minimisation of hazardous liquid wastes. Since Laintz *et al.*<sup>3</sup> demonstrated the possibility of copper chelate extraction with supercritical CO<sub>2</sub>, this method was applied to the extraction of actinides,<sup>4–7</sup> caesium<sup>8</sup> and strontium.<sup>9</sup> Uranium and lanthanides can be directly extracted from their solid oxides using such ligands as TTA and TBP.<sup>4,10</sup> Recent studies also demonstrated the possibility of lanthanide extraction from their oxides using supercritical CO<sub>2</sub> containing the TBP–HNO<sub>3</sub> complex.<sup>11</sup> 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<sub>2</sub> 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<sub>3</sub>, UO<sub>2</sub>, U<sub>3</sub>O<sub>8</sub>, CeO<sub>2</sub>, La<sub>2</sub>O<sub>3</sub> and ThO<sub>2</sub>) were placed in a 3.5 ml extraction cell. The saturation of supercritical CO<sub>2</sub> with ligands (TTA or the TBP–HNO<sub>3</sub> 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<sup>-1</sup>, which corresponded to its concentration in supercritical CO<sub>2</sub> 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.

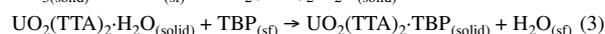
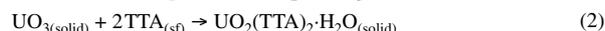


**Figure 1** Schematic diagram of the experimental system for the dissolution of uranium oxides in supercritical carbon dioxide: (1) CO<sub>2</sub> cylinder; (2) syringe pump; (3) oven; (4) HPLC pump; (5) test-tube with TBP; (6-1)–(6-6) valves; (7) collection system; (8) restrictor; (9) fluid preheating 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<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> in the case of the TBP–HNO<sub>3</sub> complex. Uranium was determined by spectrophotometry with Arsenazo I.<sup>12</sup> 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<sup>10</sup> to be optimal for the UO<sub>3</sub>–TTA–TBP system.

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

Mass transport of TTA and TBP dissolved in supercritical CO<sub>2</sub> to UO<sub>3</sub> reaction site (1)



Mass transport of UO<sub>2</sub>(TTA)<sub>2</sub>·TBP(sf) in supercritical CO<sub>2</sub> from the extraction cell (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<sub>2</sub> containing TTA and TBP using ultrasonication.

| Oxide                         | U added/mg | U trapped/mg (%)             |
|-------------------------------|------------|------------------------------|
| UO <sub>3</sub>               | 22.9       | 8.5±0.3 (37.0 <sup>a</sup> ) |
| UO <sub>3</sub>               | 25.2       | 24.0±0.6 (96.5)              |
| U <sub>3</sub> O <sub>8</sub> | 30.9       | 0.7±0.1 (2.3)                |
| UO <sub>2</sub>               | 23.9       | 1.2±0.2 (5.0)                |

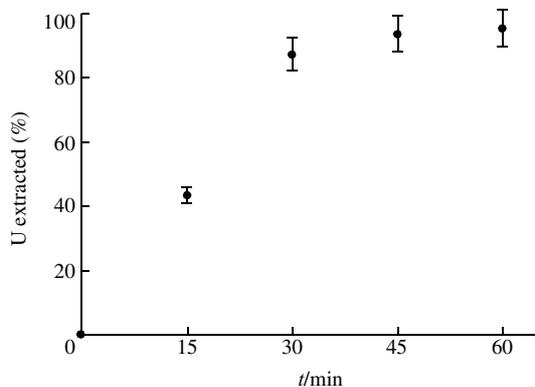
<sup>a</sup>Without ultrasonication.

**Table 2** Separation of U<sup>VI</sup> and Ce<sup>IV</sup> using supercritical CO<sub>2</sub> containing TTA and TBP under ultrasonication.

| Oxide            | Metal added/mg | Metal trapped/mg (%) |
|------------------|----------------|----------------------|
| UO <sub>3</sub>  | 23.0           | 21.3±0.4 (92.7)      |
| CeO <sub>2</sub> | 13.6           | 0.4±0.1 (3.1)        |

**Table 3** Extraction of U, Th and La from their oxides using supercritical CO<sub>2</sub> containing the TBP–HNO<sub>3</sub> complex.

| Oxide                          | Metal added | Metal trapped/mg (%) |
|--------------------------------|-------------|----------------------|
| UO <sub>2</sub>                | 22.6        | 21.7±0.4 (96)        |
| UO <sub>2</sub>                | 51.6        | 51.6±0.6 (100)       |
| ThO <sub>2</sub>               | 25.1        | 0.2±0.1 (<0.1)       |
| La <sub>2</sub> O <sub>3</sub> | 25.1        | 25.1±0.5 (100)       |



**Figure 2** SFE of uranium from  $\text{UO}_2$  with supercritical  $\text{CO}_2$  containing the TBP- $\text{HNO}_3$  complex.

$\text{CO}_2$  containing TTA and TBP. As can be seen, ultrasound allows uranium to be quantitatively extracted from  $\text{UO}_3$  with the above system. Unfortunately, ultrasonication did not improve the dissolution of both  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$  in supercritical  $\text{CO}_2$  containing TTA and TBP. This fact may be explained by structural differences between  $\text{UO}_2$ ,  $\text{U}_3\text{O}_8$  and  $\text{UO}_3$  ( $\text{UO}_2$ , face-centered;  $\text{U}_3\text{O}_8$ , orthorhombic;  $\text{UO}_3$ , octahedral), as well as by steric hindrances in the  $\text{U}^{\text{IV}}$  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  $\text{UO}_3$  and  $\text{CeO}_2$ . The molar ratio  $[\text{U}]:[\text{Ce}]$  in the trap solution is about 30 times higher than that in the starting mixture.

The effect of ultrasound was maximum in  $\text{UO}_3$ , where uranium is in an oxidation state of 6+. We attempted to dissolve  $\text{UO}_2$  and  $\text{U}_3\text{O}_8$  after a preliminary treatment with  $\text{H}_2\text{O}_2$  directly in the extraction cell. For this purpose, 0.2 ml of 30%  $\text{H}_2\text{O}_2$  was introduced into the extraction vessel containing either  $\text{UO}_2$  or  $\text{U}_3\text{O}_8$ . The mixture was heated at 90 °C for 2 h and evacuated to oxidise uranium to  $\text{U}^{\text{VI}}$  and to evaporate the aqueous phase before SFE. About 50%  $\text{UO}_2$  was dissolved under the above conditions. However, we failed to obtain a positive result for  $\text{U}_3\text{O}_8$ . Apparently, conditions for the quantitative dissolution of  $\text{UO}_2$  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  $\text{UO}_2$ .

The system based on supercritical  $\text{CO}_2$  containing the TBP- $\text{HNO}_3$  complex was successfully applied to the quantitative extraction of uranium from  $\text{UO}_2$ . This system was recently used for Nd and Gd extraction from  $\text{Nd}_2\text{O}_3$  and  $\text{Gd}_2\text{O}_3$ .<sup>11</sup> To obtain the TBP- $\text{HNO}_3$  complex, a 100% TBP solution was treated with concentrated  $\text{HNO}_3$ . After separating phases by centrifuging, 2 ml of the complex obtained were placed in the ligand cell, where supercritical  $\text{CO}_2$  was saturated with the TBP- $\text{HNO}_3$  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- $\text{HNO}_3$  complex was used in all runs.

As can be seen in Figure 2, uranium was quantitatively extracted from  $\text{UO}_2$ . Table 3 shows the SFE of uranium, lanthanum and thorium from their oxides with supercritical  $\text{CO}_2$  containing TBP- $\text{HNO}_3$  complex. The order of metal extraction from their oxides is  $\text{UO}_2 \approx \text{La}_2\text{O}_3 \gg \text{ThO}_2$ ; hence, uranium and thorium, as well as lanthanum and thorium, may be easily separated in the extraction from a mixture of their oxides ( $\text{UO}_2$  and  $\text{ThO}_2$ ,  $\text{La}_2\text{O}_3$  and  $\text{ThO}_2$ ) with supercritical  $\text{CO}_2$  containing the TBP- $\text{HNO}_3$  complex.

Thus, milligram amounts of uranium can be quantitatively extracted from  $\text{UO}_2$  with supercritical  $\text{CO}_2$  containing the TBP- $\text{HNO}_3$  complex, as well as from  $\text{UO}_3$  with supercritical  $\text{CO}_2$  containing TTA and TBP under ultrasonication. The enhanced dissolution of  $\text{UO}_3$  by means of ultrasound is, probably, caused by removing the  $\text{UO}_2(\text{TTA})_2 \cdot \text{H}_2\text{O}$  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.

This work was supported by British Nuclear Fuel Ltd. (BNFL), contract no. A80153.

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Received: 27th April 2001; Com. 01/1794