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# Dissolution of uranium, neptunium, plutonium and americium oxides in tri-*n*-butyl phosphate saturated with nitric acid

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**Uranium dioxide and its solid solutions with neptunium, plutonium and americium dioxides can be efficiently and quantitatively dissolved using tri-*n*-butyl phosphate (TBP) saturated with nitric acid. Individual $NpO_2$ and $PuO_2$ do not dissolve under these conditions. On the treatment of a mechanical mixture of $UO_2$ with $PuO_2$ and $NpO_2$ with TBP–$HNO_3$, a complex of uramiun completely dissolved, whereas Np and Pu remained in the residue.**

The extraction and purification of uranium and plutonium from spent nuclear fuel (SNF) is a key chemical process in nuclear industry. The PUREX (Plutonium Uranium Reduction Extraction) process is most widely used on a commercial scale for this purpose. Nevertheless, the generation of large volumes of aqueous and organic high-level radioactive wastes (HLW) is the main drawback of this process. A search for new alternative techniques for SNF reprocessing, which minimise waste generation, is a major challenge in nuclear industry.

The use of supercritical fluid carbon dioxide (SC-$CO_2$) as a solvent for SNF reprocessing was proposed.[1] Of particular interest is the direct dissolution of SNF in supercritical carbon dioxide with a suitable complexing agent forming SC-$CO_2$ soluble complexes with the main SNF components (U and Pu). Previously, we investigated the dissolution of actinide oxides and demonstrated that uranium dioxide is quantitatively dissolved in SC-$CO_2$ containing the TBP–$HNO_3$ complex and efficiently separated from plutonium, neptunium and thorium by supercritical fluid extraction (SFE) from a mechanical mixture of their oxides.[2,3] The interaction of actinide dioxides with SC-$CO_2$ presaturated with TBP–$HNO_3$ complex in the ligand cell was conducted in a special extraction cell.

This process in the actinide dioxide/TBP–$HNO_3$ complex heterogeneous system in the absence of SC-$CO_2$ was of particular interest. It is known that the interaction of TBP with an aqueous nitric acid solution results in the formation of the TBP–$HNO_3$ complex, whose composition depends on the initial $HNO_3$ concentration. A 8 M $HNO_3$ solution was experimentally found to be optimum. In this case, the TBP–$HNO_3$ (1:1) complex is formed.[4] Commercial $UO_2$, $NpO_2$ and $PuO_2$ samples, as well as their mechanical mixtures, were used. In addition, the solid solutions of U–Np, U–Pu, and U–Pu–Am–Eu were prepared by the calcination of their mixed oxalates at 850 °C for 8 h in an atmosphere of Ar + 10% $H_2$. The results of X-ray diffraction analysis of them showed that $UO_2$ (there are no reflexes of other uranium oxides, namely, $U_3O_8$ and $UO_3$) is the matrix of the solid solutions prepared, in the crystal lattice of which Np and Pu in the oxidation state 4+ are distributed.[5]

A known volume of the TBP–$HNO_3$ complex prepared according to the published procedure[6] was introduced into a centrifuge tube containing a known amount of the test sample. The tube was placed in a thermostat and heated at 60 °C for about 1.5 h, as in the case of SFE.[2] After mixing and centrifuging the solution, the liquid phase was analysed for radionuclides: Np, Pu and Am were determined by α-radiometry, and U was determined as described below. First, it was back extracted from the organic phase with 0.1 M $HNO_3$. The back extract was evaporated to a wet salt and then re-evaporated with 4 M HCl to dryness for the removal of $HNO_3$ traces. The residue was dissolved in 4 M HCl, and $U^{VI}$ was reduced to $U^{IV}$ using Zn amalgam. Uranium concentration was determined by spectrophotometry using an absorption band at 650 nm ($\varepsilon$ 63 $dm^3\,mol^{-1}\,cm^{-1}$). Europium concentration was determined by γ-radiometry. The composition of the oxide samples and data on the dissolution of individual actinide oxides, their mechanical mixtures and solid solutions of mixed actinide oxides are presented in Table 1.

**Table 1** Direct dissolution of actinide oxides using the TBP–$HNO_3$ complex. $V_{complex}$ = 1 ml.

| Oxide type | Oxide | Oxide content (%) | Metal added/ mg | Metal found in liquid phase (%) |
|---|---|---|---|---|
| Individual | $UO_2$ | 100 | 9.6 | 98.4 |
| Individual | $NpO_2$ | 100 | 6.4 | < 0.01 |
| Individual | $PuO_2$ | 100 | 1.5 | < 0.01 |
| Mechanical mixture | $PuO_2$<br>$UO_2$ | 39.8<br>60.2 | 3.7<br>5.6 | < 0.01<br>98.9 |
| Mechanical mixture | $NpO_2$<br>$UO_2$ | 46.3<br>53.7 | 5.7<br>6.6 | < 0.1<br>96.9 |
| Solid solution | $AmO_2$<br>$UO_2$ | 10.7<br>89.3 | 0.55<br>4.56 | 92.0<br>98.2 |
| Solid solution | $NpO_2$<br>$UO_2$ | 5.0<br>95.0 | 0.25<br>4.70 | 84.0<br>93.6 |
| Solid solution | $PuO_2$<br>$UO_2$ | 5.0<br>95.0 | 0.67<br>14.60 | 89.0<br>93,3 |
| Solid solution | $PuO_2$<br>$UO_2$<br>$Eu_2O_3$<br>$AmO_2$ | 25.0<br>69.95<br>5.0<br>0.05 | 2.15<br>6.14<br>0.43<br>0.004 | 86.1<br>94.4<br>93.6<br>86.0 |

$UO_2$ is practically (93.3–98.4%) quantitatively dissolved in the phase of the TBP–$HNO_3$ complex. Its dissolution proceeds owing to the oxidation of $U^{IV}$ to $U^{VI}$ (Figure 1, spectrum *1*) with the formation of the complex $UO_2(NO_3)_2(TBP)_2$, which is highly soluble in a SC-$CO_2$ phase.[7]

The data obtained suggest that in the case of SFE the TBP–$HNO_3$ complex should be introduced into the extraction cell along with the solid sample for the full dissolution of the sample and effective consumption of a complex. Then, the solute may be removed from the cell using SC-$CO_2$ and trapped in a suitable collection system.

As can be seen in Table 1, contrary to $UO_2$, both $NpO_2$ and $PuO_2$ are insoluble in the phase of the TBP–$HNO_3$ complex. These oxides are also insoluble while they are in the mechani-

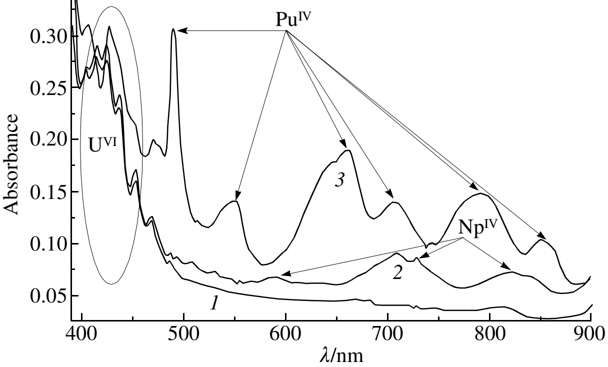

**Figure 1** Absorption spectra of the liquid phase resulted from the dissolution of actinide oxides in the TBP–$HNO_3$ complex: (*1*) $UO_2$, (*2*) solid solutions of $UO_2$ (5% $NpO_2$) and (*3*) $UO_2$ (25% $PuO_2$).

cal mixture with $UO_2$, which quantitatively dissolves in the test system and can be separated from $NpO_2$ and $PuO_2$.

Unlike mechanical mixtures of actinide oxides, solid solutions of neptunium, plutonium, americium and europium oxides with $UO_2$ practically quantitatively dissolve in the TBP–$HNO_3$ complex. Spectra *2* and *3* in Figure 1 indicate that Pu and Np in the phase of the TBP–$HNO_3$ complex are in the oxidation state 4+, whereas U is in the oxidation state 6+. Most likely, the difference in the behaviours of mechanical mixtures and solid solutions of actinide oxides is that, on the contact of the TBP–$HNO_3$ complex with the phase of U–Pu and U–Np, solid solutions of $U^{IV}$ are easily oxidised to $U^{VI}$. As this takes place, the crystal lattice of the solid solution collapses and the formation of $Pu^{IV}$ and $Np^{IV}$ complexes with TBP–$HNO_3$ is initiated.

Thus, we found for the first time that TBP saturated with $HNO_3$ can dissolve solid $UO_2$, which provides the basis of nuclear fuel. In so doing, the new possibilities are opened up for the replacement of the stages of SNF dissolution in $HNO_3$ followed by solvent extraction of the main fuel components with the stage of the direct dissolution of SNF in TBP–$HNO_3$ complex. It may result in minimising environmentally hazardous aqueous and organic HLW generation. Further management of the TBP–$HNO_3$ complex containing dissolved SNF components may be performed using supercritical or liquid $CO_2$, which, however, do not preclude other alternative approaches.

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