

DISSOLUTION OF MIXED ACTINIDE OXIDES IN SOLUTIONS OF COMPLEXONES IN CARBON DIOXIDE

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SUMMARY

It has been shown with the use of simulators that the dissolution of mixed oxides of actinides with low content of actinides (IV) can be conducted in medium of liquid or supercritical carbon dioxide in the presence of mixtures of tributylphosphate (TBP) - hexafluoroacetylacetone (HFA) or TBP - nitric acid. It is also found that the efficient dissolution mixed actinide oxides with high content of actinides (IV) may be attained only by using TBP - HNO₃ mixture in dense CO₂. The possibility for practically complete dissolution of mixed actinide oxides and efficient combined extraction of all actinides (IV, V and VI) has been demonstrated.

INTRODUCTION

It is known that the mixed actinide oxides can be dissolved in "dense" carbon dioxide containing TBP and HFA mixtures [1,2] or TBP complex with nitric acid [3-6]. Previously this was shown as applied to the mixtures of actinide oxides with low content (~ 1%) of other actinide oxides in uranium dioxide. In this case the dissolution of oxides and the extraction of all actinides proceed similar to uranium.

The objective of the present work was studying the dissolution of mixed actinide oxides with high plutonium content (up to 25%).

EXPERIMENTAL PROCEDURE

Hexafluoroacetylacetone (Fluorochem Limited, UK) and tributylphosphate ("Vekton Ltd, Russia) were used. HFA was used without any additional purification, TBP was purified by traditional technique [7]. Plutonium and neptunium isotopes were received from "Isotop" Co (Russia).

Two mixtures of actinide oxides were prepared. Composition of actinide oxides mixtures is given in Table 1. To prepare the mixtures, the solutions of uranyl, Pu and Np nitrates were mixed, the resultant solution was heated to boiling point and the metal hydroxides were precipitated with hydrazine nitrate excess. The hydroxide precipitate was filtered and calcined for two hours in argon in the presence of 5% hydrogen at 600⁰C and for three hours at 1000⁰C. To produce uranium trioxide powders, the prepared simulators were oxidized in NO₂ current at 320-350⁰C.

Table 1 Composition of mixed actinide oxides

Oxide	Oxide content in simulated SNF, %	
	Mixture 1	Mixture 2
UO ₂	98,7	79,5
PuO ₂	0,8	18,9
Np ₃ O ₈	0,5	1,6

Experiments on dissolving the actinide oxide mixtures were carried out by using a laboratory setup consisting of syringe pump with control board, extraction cell with 3.47 ml volume and 9.48 ml bubbler. Block diagram of the setup is presented in Fig. 1. Work on mixture 1 was done in a light box (Fig. 2), experiments on mixture 2 were performed in a heavy box (Fig. 3).

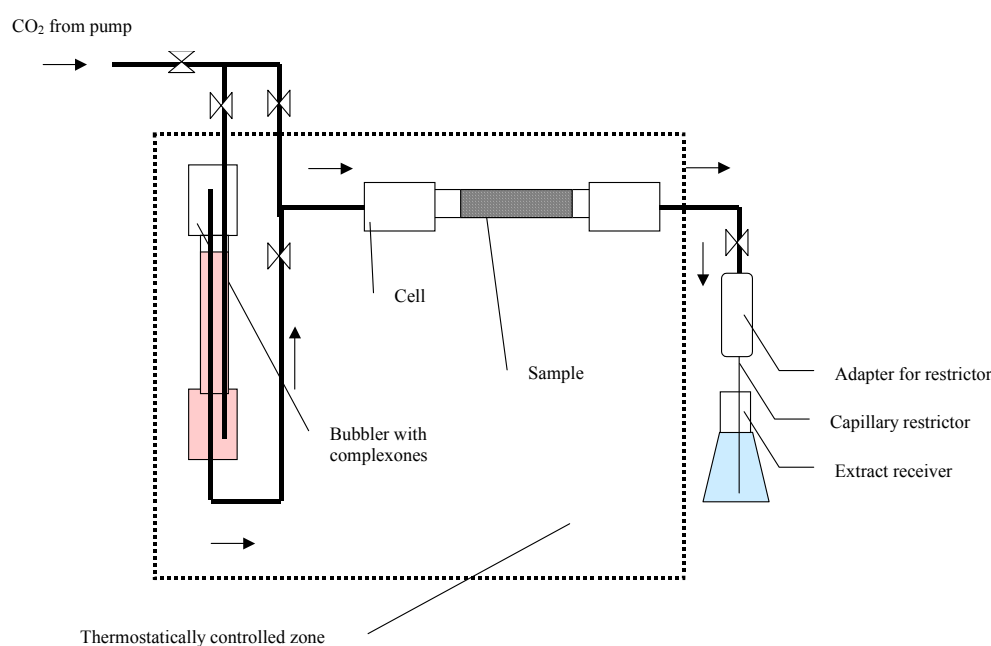


Fig. 1 Block diagram of setup for studying the dissolution process of actinide oxides

Experiments on supercritical fluid extraction (SFE) of actinides from mixed oxides were conducted by the following procedure. A weighed portion of mixed oxide (50÷200 mg) was placed into 3.4 ml extraction cell; the needed reagents were placed into bubbler; then the cell was sealed and thermostatically controlled for 10 min. Thereafter, carbon dioxide was pumped into the cell up to the pressure of 70 or 200 atm. The cell was kept at the preset pressure for 40 min (at 70 atm.) or 20 min (at 200 atm.) to attain equilibrium in the system. Next 35÷40 ml CO₂ were pumped through the cell at flowrate no more than 1 ml/min. Extracts were collected through a capillary into ethyl alcohol or acetone.



Fig. 2 Light glove box



Fig. 3 Laboratory SFE setup in heavy box

Upon the completion of the experiment the cell was depressurized; then a fresh portion of complexones was introduced and the experiment was repeated, or, alternatively, acetone was added and the resultant suspension was withdrawn by a pipette into conical flask. The operation for withdrawal of insoluble residue was conducted 3-4 times, in order to achieve the complete transfer of the powder into the flask. The obtained products were analyzed for U, Pu and Np content.

RESULTS AND DISCUSSION

Experiments on actinide oxides dissolution in CO_2 containing HFA, TBP and H_2O were conducted with mixtures oxidized to UO_3 , as it is known that the individual oxides of uranium (IV) and plutonium (IV) do not dissolve in HFA-containing systems [6]. The data on dissolving the actinide oxide mixtures with low content of Pu testify that in this system the dissolution degrees of uranium trioxide in liquid and supercritical carbon dioxide are practically the same, and 91-93% of uranium can be extracted by three operations (Fig.4). At the same time the differences in dissolution and extraction efficiency of plutonium and neptunium by liquid and supercritical CO_2 are rather significant. On dissolving the this mixture in supercritical carbon dioxide containing HFA, TBP and water, plutonium and neptunium oxides dissolve to the same degree as uranium trioxide. Under these conditions 92-96% of all actinides are recovered by three operations. Under the same conditions in liquid carbon dioxide it is possible to dissolve about 70-80% of plutonium and neptunium. It has been established that in the case of the actinide oxide mixtures with high content of Pu the HFA-TBP solutions inadequately dissolve plutonium oxides even under supercritical conditions.

Furthermore, the investigation was carried out on dissolution of the actinide oxide mixtures with low and high content of Pu, both non additionally oxidized (main form - UO_2) and fully oxidized ones in nitrogen dioxide current (main form - UO_3). The obtained data have revealed that the solutions of TBP- HNO_3 complex in liquid CO_2 efficiently dissolve the actinide oxide mixtures with low content of Pu and recover actinides. No considerable differences in dissolution of non-oxidized and fully oxidized actinide oxide mixtures are observed (Fig. 5). As a result of three

dissolving operations of the fully oxidized PWR SNF simulator the residue contains 1-3% of uranium, plutonium and neptunium.

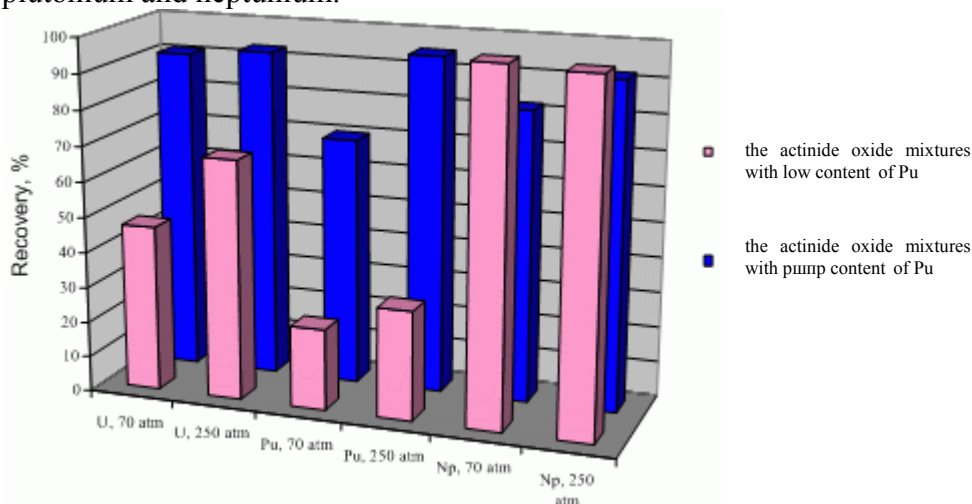


Fig. 4 Recovery of actinides on dissolving of mixed actinide oxides in carbon dioxide medium in the presence of HFA, TBP and water. (100-200 mg mixture, 10 μ l H₂O, [U]:[HFA]:[TBP] = 1:2:1).

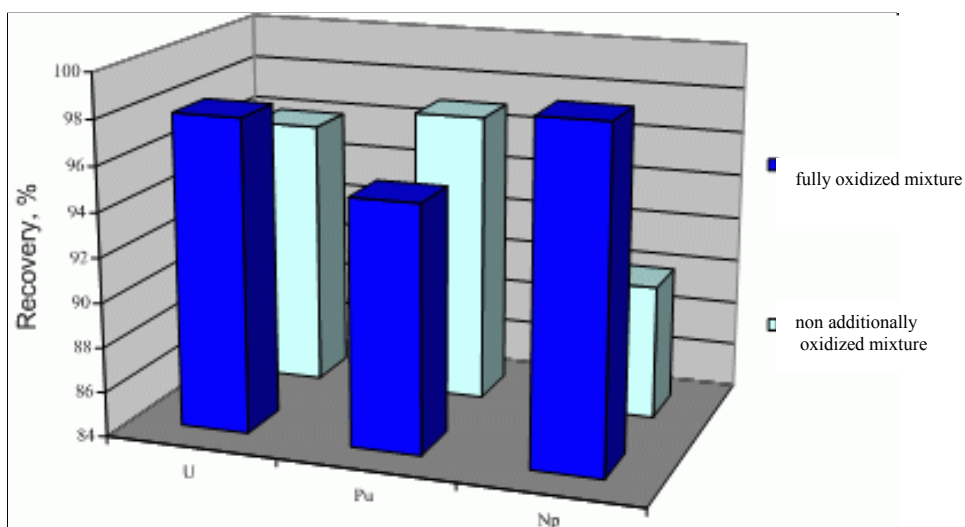


Fig. 5. Recovery of actinides on dissolving the actinide oxide mixtures with low content of Pu in liquid carbon dioxide in the presence of TBP and nitric acid (200 mg mixture, 0.5 ml TBP-HNO₃, [U]:[TBP] = 1:2, 70 atm., 25 °C).

The data obtained with the use of the actinide oxide mixtures with high content of Pu indicate that the dissolving degrees of non additionally oxidized and oxidized the actinide oxide mixtures with high content of Pu by solutions of TBP-HNO₃ complex in liquid carbon dioxide are similar, but lower than the dissolving efficiency of the actinide oxide mixtures with low content of Pu (Fig. 6).

By using the solutions of TBP-nitric acid complex in liquid CO₂ it has been possible to dissolve and extract only 70-80% of actinides from the actinide oxide mixtures with high content of Pu in three operations, while from the actinide oxide mixtures with low content of Pu one can extract 90-

99% of actinides under the similar conditions. Pressure and temperature are found to have no effect dissolution of the actinide oxide mixtures with high content of Pu (Table 2), because the dissolving ability of TBP-HNO₃ complex little depends on pressure and temperature.

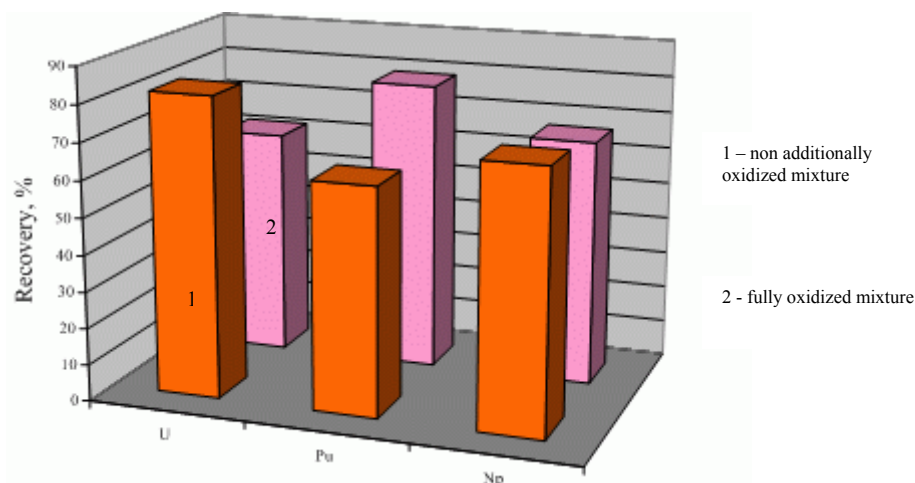


Fig. 6 Recovery of actinides on dissolving of the actinide oxide mixtures with high content of Pu in liquid carbon dioxide in the presence of TBP and nitric acid (200 mg SNF, 0.5 ml TBP-HNO₃, [U]:[TBP] = 1:2, 70 atm., 25 °C).

Table 2 Dissolution of fully oxidized the actinide oxide mixtures with high content of Pu and extraction of actinides by solutions of TBP-nitric acid complex in liquid and supercritical CO₂ (200 mg mixture, 0.5 ml TBP-HNO₃, [U]:[TBP] = 1:2)

Element	Pressure, temperature	Building up recovery over stages, %					Solid residue, %
		1-st	2-nd	3-rd	4-th	5-th	
U	70 atm., 25 °C	24 \pm 10	45 \pm 8	62 \pm 8	79 \pm 11	88 \pm 13	11 \pm 8
	250 atm, 70 °C	47 \pm 6	73 \pm 7	83 \pm 6	99 \pm 6	99 \pm 8	2 \pm 8
Pu	70 atm., 25 °C	21 \pm 8	47 \pm 13	79 \pm 11	82 \pm 10	87 \pm 12	13 \pm 11
	250 atm, 70 °C	52 \pm 7	68 \pm 10	84 \pm 9	90 \pm 11	91 \pm 8	10 \pm 7
Np	70 atm., 25 °C	18 \pm 7	42 \pm 6	67 \pm 6	82 \pm 8	89 \pm 8	10 \pm 7
	250 atm, 70°C	25 \pm 9	37 \pm 11	55 \pm 10	77 \pm 9	85 \pm 8	10 \pm 6

It has been found that the solutions of TBP-nitric acid complex in both liquid and supercritical carbon dioxide may be applied to dissolving of the actinide oxide mixtures with high content of Pu as well as to the actinide oxide mixtures with low content of Pu.

CONCLUSION

The conducted study has shown that the dissolving efficiency of the actinide oxide mixtures with low content of Pu oxidized in nitrogen dioxide current containing HFA, TBP and water is rather high (91-93% U and 70-80% Pu and Np are extracted into liquid CO₂ and 92-96% of all actinides are recovered into supercritical CO₂ by means of three operations). However the

dissolving ability of this mixture is insufficient to dissolve the actinide oxide mixtures with high content of Pu.

It is found that the solutions of TBP-nitric acid complex in liquid CO₂ efficiently dissolve the simulators of the actinide oxide mixtures with low content of Pu and the actinide oxide mixtures with high content of Pu. By using the solutions of TBP-HNO₃ complex in liquid CO₂ it has been possible to dissolve and extract 70-80% of actinides from the actinide oxide mixtures with high content of Pu and 90-99% of actinides from the actinide oxide mixtures with low content of Pu by means of three operations.

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