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Dissolution and extraction of actinide oxides in supercritical carbon dioxide containing the complex of tri-*n*-butylphosphate with nitric acid

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Abstract

Dissolution of individual actinide oxides (Th, U, Pu, Np), or their mechanical mixtures, as well as of solid solutions U–Pu, U–Np, U–Am and U–Pu–Eu oxides in supercritical fluid carbon dioxide (SF-CO₂) containing the complex of tri-*n*-butyl phosphate (TBP) with nitric acid (TBP–HNO₃) has been investigated. The effect of the calcination temperature of solid solutions of dioxides on the separation of actinides during supercritical fluid extraction (SFE) has been studied as well. It was shown for the first time that milligram amounts of uranium dioxide could be quantitatively dissolved in (SF-CO₂) containing the TBP–HNO₃ complex and efficiently separated from Pu, Np, and Th during SFE of mechanical mixture of these oxides. On the contrary, both U and Pu are quantitatively dissolved in SF-CO₂–TBP–HNO₃ during SFE from solid solutions of U–Pu dioxide. An increase of the calcination temperature of the mixed U(IV)–Pu(IV) dioxide from 850 to 1200 °C has no influence on the relative extraction yield of these actinides during SFE. *To cite this article: T. Trofimov et al., C. R. Chimie 7 (2004).*
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Résumé

Dissolution d'oxydes d'actinides et extraction d'éléments dans le dioxyde de carbone supercritique contenant le complexe tri-*n*-butylphosphate–acide nitrique. La dissolution d'oxydes de Th, U, Pu et Np, de leurs mélanges et de solutions solides U–Pu, U–Np, U–Am et U–Pu–Eu dans le dioxyde de carbone supercritique (CO₂-SC) contenant le complexe tri-*n*-butyl phosphate–acide nitrique (TBP–HNO₃) a été étudiée, et notamment l'effet de la température de calcination des solutions solides. On montre que quelques milligrammes de UO₂ peuvent être dissous dans le système CO₂-SC–TBP–HNO₃ et être séparés de Pu, Np et Th en traitant un mélange d'oxydes. En revanche, U et Pu sont dissous dans la phase CO₂-SC–TBP–HNO₃ durant le traitement des solutions solides U(IV)–Pu(IV). Une augmentation de la température de calcination de 850 à 1200 °C de ces solutions solides n'a pas d'effet sur le rendement d'extraction des actinides. *Pour citer cet article : T. Trofimov et al., C. R. Chimie 7 (2004).*
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Keywords: Supercritical carbon dioxide; Actinides

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1. Introduction

Extraction and purification of U and Pu in spent nuclear fuel reprocessing (SNF) is a key chemical process in the nuclear industry. The most widely used commercial process to achieve this objective is the Plutonium Uranium Reduction EXtraction process (PUREX), which involves the dissolution of SNF in nitric acid followed by solvent extraction of U(VI) and Pu(IV) using tri-*n*-butyl phosphate (TBP) as extractant [1,2]. The PUREX process, though highly efficient, has the inherited drawbacks of liquid–liquid extraction, including generation of large volumes of aqueous and organic high-level radioactive wastes. So a search for new alternative techniques for reprocessing of SNF, which will allow minimizing waste generation, is a major task, challenging the future of the nuclear industry.

The possibility of using (SF-CO₂) as a solvent for reprocessing of SNF was suggested recently [3]. Of particular interest is the idea of direct dissolution of SNF in SF-CO₂ using a suitable complexing agent that should form a SF-CO₂ soluble complex with the main components of SNF, basically with uranium dioxide. SF-CO₂ is considered as a green solvent because it is non-toxic and environmentally benign. It is also cheap, readily available in relatively pure form, and has moderate critical constants ($T_c = 31.3$ °C, $P_c = 72.8$ atm, and $\rho_c = 0.47$ g cm⁻³) [4]. A major advantage of using supercritical CO₂ for reprocessing of SNF is the elimination of the use of acid and organic solvent required in the conventional PUREX process.

The hexavalent uranyl ion UO₂²⁺ is known to form SF-CO₂ soluble complexes with a number of complexing agents, including TBP and β -diketones [5]. It has been demonstrated that UO₃ can be dissolved in SF-CO₂ using thenoyltrifluoroacetone (HTTA) and TBP [6,7]. Recent studies have also demonstrated the possibility of lanthanide extraction from their oxides using SF-CO₂ containing the TBP–HNO₃ complex [8]. However, the extraction efficiency of all elements involved did not exceed 40%.

We have reported earlier [9] about the quantitative dissolution of milligram amounts of UO₃ in SF-CO₂ containing HTTA and TBP, which was performed using ultrasonication. Also, it was reported that uranium can be quantitatively extracted and efficiently separated from Pu, Np and Th in the process of SFE of the

mechanical mixture of their dioxides using SF-CO₂ modified with TBP–HNO₃ complex [10].

The study of dissolution of solid solutions of actinide dioxides in UO₂ using the system SF-CO₂–TBP–HNO₃ is the purpose of this work. Preliminary results obtained are presented below in comparison with previous results.

2. Experimental

Commercial oxides were used in the above-mentioned research about the dissolution of individual actinide oxides in SF-CO₂ containing the TBP–HNO₃ complex [9,10]. In the present work, we used the synthesized samples of solid solutions of actinide dioxides and Eu₂O₃ in UO₂. Their preparation was carried out in accordance with the scheme presented in Fig. 1. According to [1,11] Np and Pu dioxides are formed in the process of air calcination of many Np and Pu compounds, such as hydroxide, acetate, nitrate and oxalate. Though Np and Pu may have any oxidation state in these compounds, the product of their calcinations is always NpO₂ and PuO₂. Since UO₂ was the basis of all samples of the solid solutions of actinide dioxides prepared, it should be obtained in the form of pure UO₂. For this purpose, drying, decomposition, and calcinations of mixed actinide oxalates up to the solid solution of their oxides were conducted under argon–hydrogen atmosphere. These operations were performed in glass–graphite crucibles, increasing the temperature from 20 to 850 °C for 5 h. Further calcination

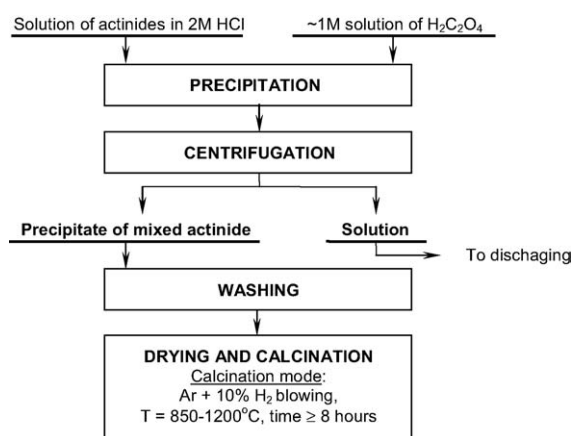


Fig. 1. Preparation of the solid solutions of mixed actinide and Eu oxides.

was continued for 8 h at 850 °C. In the case of U–Pu–Eu, about a half of the mixed oxide sample prepared was additionally calcined at 1200 °C for 8 h in order to simulate samples that may be obtained from real SNF, since the temperature in the fuel elements in the nuclear reactor can reach 1200 °C. A schematic diagram of the experimental set-up for SFE of actinide oxides, the preparation technique of the TBP–HNO₃ complex and experimental procedures were described earlier [9,10]. Types and composition of the solid solutions of the corresponding actinides and Eu are presented in Table 1.

3. Result and discussion

The results of X-ray structure analysis (Table 2) of the prepared U–Pu oxides carried out by the method of the X-ray powder diffraction pattern have shown that, in all cases, UO₂ was the matrix of the mixed oxides.

Table 1
Samples of the solid solutions of actinide and Eu oxides

Composition of the solid solutions	Weight %
AmO ₂	10.7
UO ₂	89.3
NpO ₂	5.0
UO ₂	95.0
PuO ₂	5.0
UO ₂	95.0
PuO ₂	25.0
Eu ₂ O ₃	5.0
AmO ₂	0.05
UO ₂	69.95

Table 2
Interplanar spacing $d(\text{Å})$ and relative intensities (Int) for solid solutions of U–Pu oxides prepared and reference data for UO₂

Reference data for UO ₂		Measured data for the samples prepared					
$d(\text{Å})$	Int. (%)	U–Pu(5%) (Sample 1)		U–Pu(25%)–Eu (Sample 2)		U–Pu(25%)–Eu (Sample 3)	
		$T_{\text{cal}} = 850\text{ °C}$	$T_{\text{cal}} = 850\text{ °C}$	$T_{\text{cal}} = 850\text{ °C}$	$T_{\text{cal}} = 850\text{ °C}$	$T_{\text{cal}} = 1200\text{ °C}$	$T_{\text{cal}} = 1200\text{ °C}$
3.156	100.0	3.154	100.0	3.135	100.0	3.147	100.0
2.733	34.7	2.729	44.4	2.716	50.0	2.725	50.0
1.932	40.9	1.934	56.4	1.920	70.0	1.927	70.0
1.648	35.0	1.649	63.6	1.636	70.0	1.642	70.0
1.578	7.6	1.579	18.4	1.570	10.0	1.572	20.0
1.366	5.0	1.368	14.2	1.359	10.0	1.361	10.0
1.254	11.5	1.255	29.9	1.245	30.0	1.249	30.0
1.222	8.5	1.224	23.4	1.214	20.0	1.217	20.0

Unit cell parameters for the samples #1, #2, and #3 are equal to 5.4703 Å, 5.4232 Å, and 5.4421 Å, respectively. Reference data for UO₂ are taken from the database PDF-2 (JCPDS-ICDD, 1999). According to it, $a(\text{Å}) = 5.4704 - 0.0935 x$, for UO_{2+x} at 25 °C. An increase of Pu content in sample #2 in comparison with #1 results in a considerable decrease in the unit-cell parameter of UO₂. At the same time, additional calcination of the sample #3 at 1200 °C results in its increase. Potentially, these changes in the unit-cell parameter value may influence the processes of dissolution of actinide dioxides in the course of SFE.

We present in Tables 3 and 4 the results obtained earlier [9,10] of SFE of actinides from their individual and mixed oxides using SF–CO₂ modified with the TBP–HNO₃ complex. The new results on SFE of U, Np, Pu, Am and Eu from the solid solutions of their oxide are presented in Table 5. As seen from the data presented (Tables 3 and 4), uranium can be quantitatively extracted from all the oxides investigated. It was shown by spectrophotometry that uranium is present in the oxidation state +6 only in the trap solution (Fig. 2). Therefore, the interaction of TBP–HNO₃ complex with UO₂ results in the oxidation of the tetravalent uranium to the hexavalent one. This leads to the formation of highly soluble UO₂(NO₃)₂·2 TBP complex in the SF–CO₂ phase. Oxidation of Np and Pu up to the oxidation state +6 under the conditions investigated does not occur. So, the extraction efficiencies of Pu, Np, and Th from both individual oxides and their mixtures with uranium dioxide are extremely poor.

At the same time, it can be seen from the data presented in Table 5 that during SFE of the solid solution of U–Np, U–Am, U–Pu, U–Pu–Eu oxides,

Table 3
SFE of actinides from their individual oxides using SF-CO₂ with the TBP-HNO₃ complex. $T = 65\text{ }^{\circ}\text{C}$, $P = 250\text{ atm}$

Oxide	Actinide added (mg)	Molar ratio An:complex	Extraction efficiency (%)
UO ₂	61,5	1:50	> 99
	334.4	1:10	90 ± 5
	367.9 ^a	1:10	65 ± 3
UO ₃	175.1	1:20	92 ± 5
U ₃ O ₈	177.3	1:20	85 ± 3
PuO ₂	8.1	1:250	< 0.1
	50.1	1:50	< 0.1
NpO ₂	5.6	1:250	< 0.1
	55.0	1:50	< 0.1
ThO ₂	52.9	1:50	< 0.1

^a Non-milled uranium fuel pellet.

Table 4
Separation of U from Pu, Np, and Th using SF-CO₂ with the TBP-HNO₃ complex $T = 65\text{ }^{\circ}\text{C}$, $P = 250\text{ atm}$, molar ratio An:complex ~ 1:20

Mixture of oxides	Actinide added (mg)	Extraction efficiency (%)	Separation factor ($S_{U/An}$)
UO ₂	150.5	87 ± 4	~1200
PuO ₂	37.4	< 0.1	
UO ₂	120.6	91 ± 5	~1400
NpO ₂	11.5	< 0.1	
UO ₂	133.5	89 ± 4	~1100
ThO ₂	58.5	< 0.1	

Table 5
Dissolution of solid solutions of mixed radionuclide oxides in SF-CO₂ with the TBP-HNO₃ complex $V_{\text{complex}} = 3\text{ ml}$ (0.01 mol), $T = 65\text{ }^{\circ}\text{C}$, $P = 200\text{ atm}$

Calcination temperature (°C)	Solid solution of mixed oxides	Wt %	Actinide content in oxide (mg)	Extraction efficiency (%)
850	AmO ₂	10.7	0.55	92.0
	UO ₂	89.3	4.56	98.2
850	NpO ₂	5.0	0.25	84.0
	UO ₂	95.0	4.70	93.6
850	PuO ₂	5.0	0.67	89.0
	UO ₂	95.0	14.60	93.3
850	PuO ₂	25.0	2.15	86.1
	UO ₂	69.95	6.14	94.4
	Eu ₂ O ₃	5.0	0.43	93.6
	AmO ₂	0.05	0.0037	86.0
	PuO ₂	25.0	3.91	89.6
1200	UO ₂	69.95	11.17	93.1
	Eu ₂ O ₃	5.0	0.78	91.0
	AmO ₂	0.05	0.0066	88.0

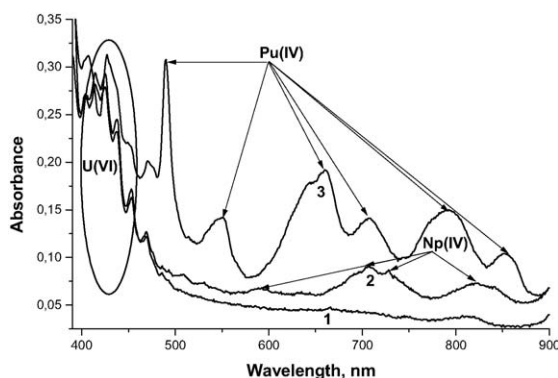


Fig. 2. Absorption spectra of the trap solutions obtained from SFE of UO₂ (1) and of solid solutions of mixed U-Np (2) and U-Pu (3) dioxides.

practically quantitative extraction of Np, Pu, Am and Eu occurs. It turned out that the Np and Pu passing into the trap solution exists in the oxidation state +4 (see Fig. 2). Other oxidation states of Np and Pu in absorption spectrum of this solution are not seen on the spectra. It means that during the contact of the TBP-HNO₃ complex with the solid phase of U-Pu or U-Np oxides U(IV) easily oxidizes to U(VI), resulting in breaking the structure of the actinide solid solutions and in initiating the formation of the SF-CO₂-soluble complexes of Pu(IV) and Np(IV) with the TBP-HNO₃ complex. The results obtained show that trivalent europium and americium pass quantitatively into the trap solution as well. Increase in the Pu content in the matrix of UO₂ from 5 to 25% has practically no effect

on the relative yield of U and Pu on SFE for solid solution or their mixed dioxides under the conditions investigated. An increase of the calcination temperature of the mixed U–Pu–Eu oxide from 850 to 1200 °C has no influence on the relative yield of radionuclides involved.

4. Conclusion

Uranium can be quantitatively extracted from UO_2 , UO_3 and U_3O_8 with SF-CO_2 containing the TBP– HNO_3 complex. On dissolution of UO_2 in the system, the oxidation of U(IV) to U(VI) proceeds with the formation of the SF-CO_2 -soluble complex $\text{UO}_2(\text{NO}_3)_2 \cdot 2 \text{TBP}$. Uranium can be efficiently separated from Pu, Np and Th in the course of SFE from mechanical mixtures of their oxides. Contrary to the mechanical mixtures of actinide oxides, solid solutions of mixed actinide oxides are quantitatively dissolved in SF-CO_2 containing the TBP– HNO_3 complex. Pu and Np trapped during SFE of solid solutions of mixed oxides turn out in the trap solution in the oxidation state +4, whereas U is in the oxidation state +6. An increase in the Pu content in the matrix of UO_2 from 5 to 25% has practically no effect on the relative yields of U and Pu on the SFE of the solid solution of their mixed dioxide under the conditions investigated. An increase in the calcination temperature of the mixed U–Pu–Eu oxide from 850 to 1200 °C has no influence on the relative yield of radionuclides involved during

SFE as well. Application of SFE technique may be very promising for SNF reprocessing

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