

# MECHANOCHEMICALLY INDUCED PHASE TRANSFORMATION AND LEACHING OF DECAY PRODUCTS FROM U(IV, VI) OXIDE

## МЕХАНОХИМИЧНО-ИНДУЦИРАНИ ФАЗОВО ПРЕВРЪЩАНЕ И ИЗВЛИЧАНЕ НА ПРОДУКТИТЕ НА РАДИОАКТИВНО РАЗПАДАНЕ ОТ U(IV, VI) ОКСИД

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**Abstract:** Depleted  $U_3O_8$  was mechanically activated in suspension with tributyl phosphate (TBP), trioctylamine (TOA) and ethylenglycolmonomethylether (EGME) in planetary ball mill with stainless steel vessels and balls. X-ray diffractograms and IR spectra of the activated solid samples were taken. The radioactivities of  $^{238}U$  and  $^{234}Th$  in the leaching solutions were determined by  $\alpha/\beta$  liquid scintillation spectrometry. The reduction degree of the oxide, the mean crystallite size of  $U_3O_8$  and  $U_3O_7$  and the leaching of  $^{238}U$  and  $^{234}Th$  as a result of the mechanoactivation were determined. Higher degree of  $^{238}U$  and  $^{234}Th$  leaching was achieved when mechanoactivation with TBP was performed. No leaching of  $^{238}U$  daughter product ( $^{234}Th$ ) proceeded at mechanoactivation with TOA and EGME. The role of the solvents complexation ability, milling induced increase of crystal defect concentration and  $UO_2 - ThO_2$  solid solution formation is discussed. Further studies have to be made to elucidate the potential of the applied approach as a step in spent nuclear fuel processing.

**Keywords:** URANIUM OXIDES, THORIUM, MECHANOACTIVATION, EXTRACTION, XRD, IR-SPECTROSCOPY, LIQUID SCINTILLATION SPECTROMETRY

### 1. Introduction

The application of solvent extraction is recognized for a long time to play important role in actinides recovery and purification, radionuclide production, preparation of the reactor materials and other aspects of the nuclear technology [1]. Plenty of scientific efforts are spent to develop solvent extraction processes that display selectivity, simplicity and speed.

The effects of the mechanoactivation on the compounds of 5f-elements were reported in series of papers [2-9]. It was shown that uranium oxides and salts are comparatively stable upon mechanical treatment. The main effect of the mechanoactivation on the  $U_3O_8$  and  $UO_3$  is the reduction of U(VI) with the formation of  $UO_2$ ,  $U_3O_7$  and  $U_2O_5$ ; the degree of reduction is found to depend on the treatment conditions [2-4]. Mechanochemical synthesis of  $NO[UO_2(NO_3)_3]$  is proven in the course of  $UO_2(NO_3)_2 \cdot 6H_2O$  milling [5]. Mixed U-Th [6] and U-Ce [7] oxides are prepared by sol-gel method followed by mechanoactivation and a solid (U,Pu) $O_2$  solution is obtained by co-milling of  $UO_2$  and  $PuO_2$  [8].

U-leaching from  $UO_2(CH_3COO)_2 \cdot 2H_2O$ , due to transformation of bidentate bonding of the  $CH_3COO^-$  in monodentate one in the course of mechanical activation with toluene and benzene was registered [9]. Of special interest are the results for the influence of the high-energy ball milling of  $U_3O_8$  in air and in suspension (with thionyltrifluoroacetone, TTA) on the migration of  $^{238}U$  and its daughter product  $^{234}Th$  [2].

Taking into account the wide and successful application of tributyl phosphate (TBP) [10], trioctylamine (TOA) [11, 12] and ethers and ketones [1, 13] in the radionuclide extraction for the reactor technology, TBP, TOA and ethylenglycolmonomethylether (EGME) were used in the present paper as media to investigate the degree of leaching of  $^{238}U$  and its daughter product  $^{234}Th$  from U(IV, VI) oxide by mechanochemical activation in suspension. The structural changes and the degree of reduction of the initial oxide were also studied.

### 2. Experimental

Approx. 2 g of  $U_3O_8$  (Koch-Light, depleted,  $^{235}U$  content 0.375%; it was shown that the product is a mixture of  $\alpha$ - $U_3O_8$  and  $U_3O_7$  [3] and has to be described as  $U_3O_{8-x}$ ) were mechanically activated in stainless steel vessels in suspension with 5 ml TBP or TOA or EGME in planetary ball mill (Pulverisette 5, Fritch).

Stainless steel vessels of 80 cm<sup>3</sup> volume and balls from the same material (7-15 mm in diameter) were used. The activation was performed for 5 h at mechanical load of 12g.

After the mechanoactivation 70-80 cm<sup>3</sup> benzene (p.a.) was added to each suspension and the latter was filtered (fine porous filter). The solid phase was rinsed with benzene (5 times with total volume of 20 cm<sup>3</sup>) and filtered again. The joint filtrates were analyzed by IR- and liquid scintillation spectrometry.

The X-ray diffractograms of the activated solid samples were taken by a powder diffractometer Siemens D500 using  $CuK_{\alpha}$  radiation filtered by a secondary monochromator (40 kV, 30 mA, 0.05° 2 $\theta$ /2 s for the interval 5–45° 2 $\theta$ ). Relative content and mean crystallite size of  $U_3O_8$  and  $U_3O_7$  were determined from XRD pattern using the program POWDER CELL for Windows, version 2.4 [14].

The IR spectra in the range 2500-400 cm<sup>-1</sup> were recorded by a Bruker spectrometer in capillary layer.

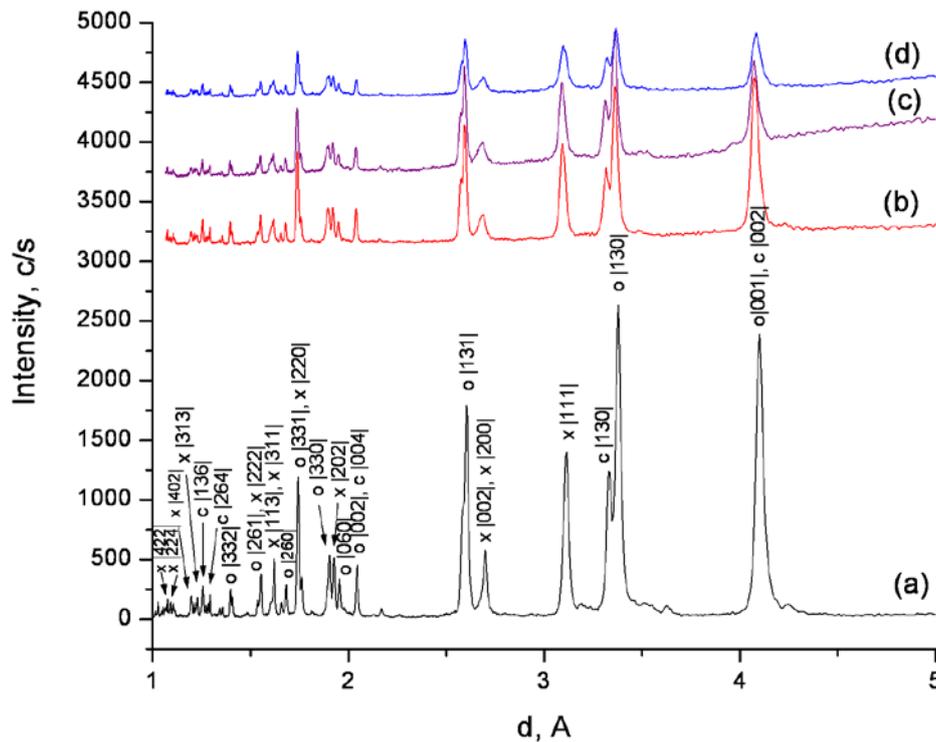
The radioactivity of  $^{238}U$  and  $^{234}Th$  in the leaching solutions were determined by  $\alpha/\beta$  liquid scintillation spectrometry (LSC) measuring the alpha-activity of U-isotopes and beta-activity of  $^{234}Th$  via  $^{234m}Pa$  in optimized regions of interest. The radiometric procedure was performed by  $\alpha/\beta$  liquid scintillation spectrometer Tricarb-2550 TR/LL, using scintillation cocktail Packard Ultima Gold AB. The quench level of each sample was determined by the  $^{135}Ba$  external standard of the spectrometer before each counting. All measured activities were recalculated to the moment of separation of leaching solution from the residue.

### 3. Results and Discussion

#### 3.1. Phase transformation, crystallites size

The mechanoactivation of  $U_3O_{8-x}$  in suspension with the three abovementioned organic reagents leads to the clearly expressed reduction process, already observed in different degree in all the experiments including mechanochemical stress of  $U_3O_{8-x}$  [2-4].

The X-ray powder diffractograms of the initial product and of the mechanoactivated samples are presented in Fig. 1a-d. The quantitative changes, occurred as a result of the mechanoactivation process, are shown in Table 1.



**Fig. 1** X-ray diffractogrammes of  $U_3O_8$  before (a) and after 5 h milling in stainless steel vessel in TBP (b), TOA (c) and EGME (d). Miller indices are shown: o -  $\alpha$ - $U_3O_8$ , c -  $\beta$ - $U_3O_8$ , x -  $U_3O_7$ .

The data, presented in Table 1 show that the highest degree of reduction is reached when mechanoactivation in suspension with EGME is performed.

**Table 1:** Relative content of  $U_3O_8$  and  $U_3O_7$ , crystallites sizes of the  $U_3O_{8-x}$  and  $^{238}U$  and  $^{234}Th$  leaching

Sample	$U_3O_{8-x}$ (fresh)	Mechanoactivation		
		$U_3O_{8-x}+$ TBP	$U_3O_{8-x}+$ TOA	$U_3O_{8-x}+$ EGME
<b>Content, %:</b>				
$U_3O_8$	81.4	72.8	67.3	63.3
$U_3O_7$	18.6	27.1	32.7	36.7
$U_3O_8/U_3O_7$	4.4	2.7	2.1	1.7
<b>Crystallite size, nm</b>				
$U_3O_8$	51	46	41	34
$U_3O_7$	83	35	59	18
<b>Leached, g/g <math>U_3O_8</math></b>				
$^{238}U$		$7.0 \times 10^{-2}$	$1.9 \times 10^{-3}$	$< 1.6 \times 10^{-5}$
$^{234}Th$		$5.5 \times 10^{-14}$	$< 3.5 \times 10^{-17}$	$< 3.5 \times 10^{-17}$

The reduction process can be explained by the triboemission of electrons, taking place during the high-energy ball milling. The low specific electroconductivity of the reaction media prevents their dissemination within its volume. They stay in close proximity of the solid substance and can be easily accepted by the oxidized form [4]. This hypothesis is supported by the data for the dielectric constant of the studied media. Their values for  $C_6H_5CH_3$  and  $CCl_4$  are rather close (2.328 and 2.238) and the reduction degrees are similar (100%, 93.4%, respectively [4]). The constant of TTA is higher ( $\approx 7$  [15]) and the reduction degree is lower.

It is worth to mention that the order of increase of the reduction degree in the different media is opposite to the order of increase of the degree of  $^{238}U$  and  $^{234}Th$  leaching from the matrix. However compared to the result for the treatment of  $U_3O_8$  at the same conditions in air,  $CCl_4$  and  $C_6H_5CH_3$  (in these media  $U_3O_8/U_3O_7$  is 0.35, 0.07 and 0, respectively [4]), the reduction resulted in the

milling in suspension in the investigated complexing agents is, in fact, suppressed as far as the above mentioned ratio in the present study is significantly higher (1.7 - 2.7, Table 1) for all the samples.

Decrease of the particle size of both  $U_3O_8$  and  $U_3O_7$ , provoked by the mechanochemical treatment is observed for all the samples. The effect is stronger revealed for the  $U_3O_7$  phase - the new formed particles, result of reduction and the respective phase transformation, have smaller crystallites. As a tendency, the decrease of the crystallites size follows the increase of the reduction degree. These observations are in agreement with the data for the samples milled in  $CCl_4$  and  $C_6H_5CH_3$  [4].

### 3.2. Uranium and thorium leaching

The quantities of U and Th in the liquid phase were calculated on the basis of their radioactivity in the organic solutions, measured by LSC. The obtained results are presented in Tables 1, 2.

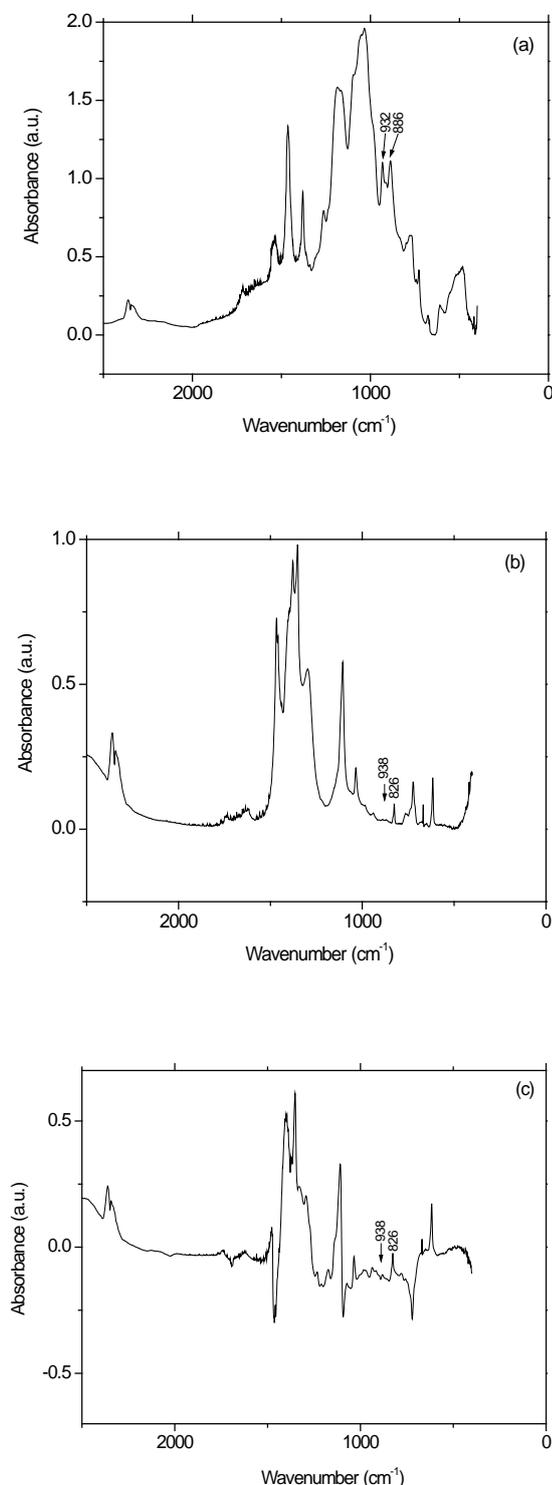
**Table 2:** Leaching of  $^{238}U$  and  $^{234}Th$

Activation medium	Mass ratio $^{238}U/^{234}Th$ , $n \times 10^{11}$	Leached nuclide/nuclide in the sample, %		Enrichment in Th of the extract
		$^{238}U$	$^{234}Th$	
TTA-stirring [2]	19±9	6.0	10.4	1.7
TTA [2]	4.4±1.2	9.8	74.1	7.6
TBP	12.7	8.3	21.6	2.6
TOA		0.22	$< 1.4 \times 10^{-2}$	
EGME		$< 0.002$	$< 1.4 \times 10^{-2}$	

Significant leaching of  $^{238}U$  (8.3% from the  $^{238}U$  and almost 22% of  $^{234}Th$  present in the solid matrix) is achieved as a result of the mechanochemical activation in suspension with TBP. Much smaller is the quantity of uranium, leached from  $U_3O_{8-x}$  by TOA and practically no  $^{234}Th$  is found in the organic extract. Only traces

of uranium and no  $^{234}\text{Th}$  are registered in EGME phase (Tables 1, 2).

The presence of  $\text{UO}_2^{2+}$  in the solutions of the activated media (TBP and TOA) in benzene can be observed on the IR spectra (Fig. 2a,b) with the appearance of the bands for  $\nu_s(\text{U-O})$  at  $886\text{ cm}^{-1}$  (TBP) and  $826\text{ cm}^{-1}$  (TOA) and for  $\nu_{as}(\text{U-O})$  at  $932\text{ cm}^{-1}$  (TBP) and  $938\text{ cm}^{-1}$  (TOA).



**Fig. 2** IR-spectra ( $2500 - 400\text{ cm}^{-1}$ ) of the product obtained after milling of  $\text{U}_3\text{O}_{8-x}$  in stainless steel vessel in TBP (a) or TOA (b), dissolved in benzene, the spectrum (b) after subtraction of IR bands of TOA (c).

Because of the lower uranium concentration in the TOA extract the abovementioned bands are very weak and better observable on the differential IR spectrum (Fig. 2c), where the IR bands of TOA are subtracted from the IR spectrum of the  $\text{UO}_2^{2+}$  - TOA phase.

Table 2 gives the possibility to compare the results obtained in the present work with those reported in [2] concerning  $\text{U}_3\text{O}_8$  treatment with 0.25 M benzene solution of TTA.

### 3.2.1. Leaching of uranium

The leaching of a component is due to desorption of its particles from the crystal surface. The increase of the specific surface, due to mechanoactivation, will enhance the leaching of uranium which is readily available on the sample surface. Furthermore, the formation of insoluble U-TTA-complexes suppresses the extraction [15] and the continuous formation of new, fresh surface (result in the milling) partially overcomes this effect (for both uranium and thorium). These expectations are confirmed (for the TTA-system) by the data in Table 2.

The degrees of the uranium leaching (as percent from the uranium content in the milled sample) in the course of the mechanoactivation in suspensions in TTA and in TBP are rather similar. Much less U is leached as a result of the milling the oxide in TOA or EGME medium. The difference in the stability constants of the respective extractable forms could be a reason (or one of the reasons) for the difference in the leaching capability of the studied solvents. Indeed, regarding uranium, oxygen-containing solvents and especially ethers have high selectivity but rather low extraction ability; amines are effective extracting reagents for metals when they exist as anions and anionic complexes [15]. The leaching of the impurities (Th in the studied system) is closely connected with their migration from the bulk of the crystal to its surface as a result of diffusion, mainly via crystal defects. Producing a new surface and a wide spectrum of crystal defects, the mechanoactivation will enhance the diffusion and, respectively, the leaching of the Th. The results for TTA-system confirm this expectation.

### 3.2.2. Leaching of thorium

The most interesting result is the prevailing leaching of Th (in comparison with U) observed in non-activated and activated TTA- and activated TBP- systems. Factors that could be responsible for the easier leaching of Th are discussed in [2]: the higher energy of U-O bonds in  $\text{U}_3\text{O}_8$  than of Th-O in  $\text{ThO}_2$ ; the relaxation of Th recoil atoms as  $\text{Th}^{4+}$  in a highly disturbed zone; the higher value of the stability constant of Th complex with the studied reagent. These factors could explain the enrichment (comparatively low) of the TTA-extract obtained from non-activated  $\text{U}_3\text{O}_8$  (Table 2).

It can be expected that the mechanoactivation will enhance preferable leaching of Th: (i) the disintegration of the solids during the milling goes preferably along the places with higher impurities concentration due to their weaker bonding with the matrix; (ii) the crystal defects (point defects and dislocations) are thermodynamically favourable places for the impurities, their concentration in these places increases and they diffuse through them to the crystal surface. The later effect was confirmed for a system, similar to the one studied in this paper in relation to the amount of the impurity (ultramicro amount of radi sulphur in ionic single crystal) [16]. The increase of the crystal defect concentration as a result of the mechanoactivation will make this mechanism rather important. The effect is already used in practice to enhance the extraction of valuable components from ores and other materials.

The significant difference in the Th leaching in the course of milling in TTA and in TBP (Table 2) is not surprising - the chelating agent TTA will be much more effective extracting agent than TBP, the later most probably forming less stable adducts with the extractable forms. Such an advantage of TTA will be more significant when extraction of the much less available impurity (Th) is concerned.

The two other studied complexing agents practically do not extract Th at conditions applied in the present work. In the same time they manifest highest (for the systems studied in this work) degree of reduction of uranium (Table 1). In [2] it was discussed and grounded a potential role of the mechanochemically induced solid solution formation=destruction processes taking place in the course of the mechanoactivation [17]. These processes are stronger expressed at milling in air but they can proceed in suspension, also. New-formed  $\text{UO}_2$  can form solid solution  $\text{UO}_2\text{-ThO}_2$ . In the presence of strong complexing agents (TTA, TBP) the  $\text{ThO}_2$  can be removed from the equilibrium and formation of solid solution will be less probable. TOA and EGME have not such ability, solid solution can be formed and  $\text{Th}^{4+}$  (stronger bonded in it, comparing to the bonding in  $\text{U}_3\text{O}_8$  -  $\text{ThO}_2$  system) will remain in the matrix.

#### 4. Conclusion

The mechanical activation of  $\text{U}_3\text{O}_{8-x}$  in planetary ball mill in suspensions with TBP, TOA and EGME leads to:

- clearly pronounced reduction; the content of  $\text{U}_3\text{O}_7$  increasing in the above mentioned order of media with, respectively, 46%, 76% and 97%, compared to the fresh product,
- decrease of the crystallite sizes of both the  $\text{U}_3\text{O}_8$  (with 10%, 20% and 30% for the studied media) and the  $\text{U}_3\text{O}_7$ , (with 58%, 29% and 78%), compared to the fresh product,
- leaching of  $^{238}\text{U}$  and its daughter product  $^{234}\text{Th}$ ; the degree of leaching strongly depending on the nature of the used liquid reagents,
- prevailing leaching of  $^{234}\text{Th}$ , achieved when mechanoactivation in TBP (and in TTA [2]) is performed; the later effect is ascribed to the increase of  $^{234}\text{Th}$  concentration at defect places and the preferable disintegration of the samples along these places as result of the mechanical loading,
- practically no leaching of  $^{234}\text{Th}$  is observed at activation in TOA and in EGME, possibly due to the formation of  $\text{UO}_2$  -  $\text{ThO}_2$  solid solution.

Further studies have to be made to elucidate the potential of the applied approach as a step in spent nuclear fuel processing aiming separation or stronger bonding of uranium fission products.

#### 5. Acknowledgment

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#### 6. Literature

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