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Effects of irradiation on the thorium phosphate diphosphate ceramics and consequences on its dissolution

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Abstract

Thorium phosphate diphosphate samples (β-TPD), proposed as a ceramic for the long term immobilization of actinides, were externally irradiated with ions at several energies in order to simulate the self-irradiation as well as with γ-rays. The influence of the electronic energy loss was first investigated. XRD measurements showed a complete amorphization of the material at 10^{13} cm^{-2} of 840 MeV krypton while no significant structural change occurred at 5×10^{13} cm^{-2} of 410 MeV sulfur. The dissolution of raw and irradiated pellets was studied versus several parameters such as the amorphized fraction, the radiolytic species (as instance hydrogen peroxide) produced in situ in the leachate during irradiation, the temperature and the leachate acidity. The results obtained reveal a significant increase of the kinetics of dissolution for amorphized pellets compared to the raw ceramic.

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1. Introduction

In the field of the long-term storage of nuclear waste, several ceramics were often presented as good candidates for the nuclear waste immobilization. The β-thorium phosphate diphosphate, β-$Th_4(PO_4)_4$-P_2O_7, (β-TPD), appears as a potential actinide-bearing phase for nuclear waste storage in the field of a geological deposit. This material, which can be loaded with large amounts of tetravalent actinides [1,2], presents a high resistance to aqueous corrosion and exhibits a high thermal stability [3]. Nevertheless, due to the actinide loading, self-irradiation by α-decays could modify its performances. The released α-particles (~5 MeV) essentially disperse their energy by ionization and electronic excitations. Recoil nuclei (~100 keV) loss their energy mainly through ballistic process involving elastic collisions and causing direct atomic displacements [4,5]. These phenomena induce cascades of local defects (vacancies and interstitial atoms) and can lead to the amorphization of the material. Such radiation damages can affect the release of radionuclides from the waste matrix during the leaching tests by increasing the chemical reactivity and by modifying the thermodynamic stability of the material [6]. The leaching tests were preferentially realized on β-$Th_{3.6}U_{0.4}$-$(PO_4)_4P_2O_7$ (β-TUPD) solid solutions. Indeed, the

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substitution of thorium by uranium (IV) does not modify the structural properties of the ceramic and makes the determination of dissolution kinetics possible by using uranium as a tracer: contrary to thorium which quickly precipitates with phosphate anions in neoformed phases, uranium (IV) is oxidized to uranium (VI) which remains in solution [7].

Ion beams and γ-rays irradiations were performed on sintered pellets with the aim of determining the irradiation effects on the structure of the β-TPD (and β-TUPD) samples and on their dissolution. On the one hand, samples were irradiated then submitted to dissolution tests. These experiments, called ex-situ studies, aimed to underline the effect of the electronic linear energy transfer (LET) by using highly energetic ion beams (840 MeV krypton Kr^{32+}, 450 MeV xenon Xe^{17+} and 410 MeV sulfur S^{15+}) and the influence of the dose for γ-irradiation. On the other hand, the effect of the radiolytic species on the dissolution of β-TPD was also examined in situ by direct γ-irradiation of the mixture solid-solution.

2. Experimental

2.1. Synthesis

β-TPD can be synthesized through several chemical ways of syntheses [8]. The irradiation experiments require single phase and well homogeneous samples. Consequently the ceramic was prepared by wet chemistry processes, involving the precipitation of the thorium phosphate hydrogenphosphate hydrate (TPHPH): $Th_2(PO_4)_2(HPO_4) \cdot H_2O$, as a crystallized precursor [9]. A mixture of concentrated thorium nitrate and phosphoric acid solutions was heated at 423 K for 8–10 days in a closed PTFE container, considering a mole ratio $r = N_{Th}/N_P = 2/3$. After separation of the solid from the supernatant by centrifugation, the crystallized solid was washed several times with deionized water in order to eliminate the remaining acid and finally dried at 353 K. The solid solutions of β-$Th_{3.6}U_{0.4}(PO_4)_4P_2O_7$ (β-TUPD) were also synthesized by this way from $Th_{1.8}U_{0.2}(PO_4)_2(HPO_4) \cdot H_2O$. The powdered T(U)PHPH prepared was characterized by X-ray diffraction (XRD) and Brunauer Emmett Teller method (BET) (specific area of 15 $m^2\,g^{-1}$). After heating at 713 K to provide the elimination of volatile products [10], the powder was sintered via an uniaxial room temperature pressing (250 MPa) in a 10 mm diameter cylindric die [11]. The solid was then thermally heated in alumina crucibles. Both thermal treatments (713 K then 1513 K) were performed in air for β-TPD and under argon atmosphere for β-TUPD to prevent any oxidation of uranium (IV) into uranyl. The β-TPD and β-TUPD samples were characterized by XRD, electron probe microanalyses (EPMA) and scanning electron microscopy (SEM). The relative density was determined using water and helium pycnometries and the associated specific surface area was determined by N_2-BET.

2.2. Irradiation experiments

The structural stability of the matrix under irradiation was first studied using highly energetic heavy ions which, like γ-rays, interact with the material by ionization effects only (electronic contribution) except at the end of the path of the ion where the nuclear contribution predominates. Such experiments enabled to study the influence of the electronic energy loss. The amorphization experiments were performed on the SME line in GANIL (Caen, France). One experiment (with 840 MeV Kr) was performed on the CHEXPIR line: this installation enables to follow in situ the structural evolution of the irradiated material thanks to a static XRD apparatus from 10 to 120°.

Other irradiations with medium energy heavy ions (Au^{3+} of 4 MeV) were performed on ARAMIS installation in CSNSM (Orsay, France) to study the influence of the contribution of the nuclear stopping power, which is not negligible at this energy.

γ-irradiations were performed at room temperature with a ^{137}Cs source in an IBL-637 irradiator in the Institut Curie (Orsay, France).

2.3. Leaching tests

The leaching tests were performed in high density polyethylene containers for the experiments at room temperature and in PTFE vessels for experiments above 333 K. The concentrations of cations were determined by inductively coupled plasma-mass spectroscopy (ICP-MS) for Th and U and by laser induced fluorescence for U [7]. The normalized dissolution rate R_L ($g\,m^{-2}\,d^{-1}$) represents the mass loss of the dissolved solid per time unit. It was calculated from the following equation:

$$R_L(i) = \frac{dN_L(i)}{dt} = \frac{d}{dt}\left(\frac{C_i \times V \times M_i}{x_i \times S}\right), \qquad (1)$$

where C_i represents the concentration of the measured element (Th, U), V the volume of the leachate, x_i the mass ratio of the element i in the solid, M_i the molar mass of i and S the effective surface area of the pellet.

3. Results and discussion

3.1. Ion beam irradiations

A sintered pellet of β-TPD was irradiated with 10.8 MeV/u $^{78}Kr^{32+}$ ($(dE/dx)_{elect} = 10$ MeV μm^{-1}) on the CHEXPIR line of GANIL. This experiment revealed a complete amorphization of β-TPD for a threshold fluence of 10^{13} cm^{-2}. According to SRIM (stopping and range of ions in matter) calculations [12], the electronic LET of 10 MeV μm^{-1} is effective and constant on a projected range larger than the thickness sensed by the XRD analysis which is about 10 μm (Fig. 1).

For each fluence, the ratio between the net area of the diffraction lines of the irradiated sample and that of the raw material was evaluated. The amorphous fraction f_a was defined as the average of the obtained ratios for the main diffraction lines of β-TPD in the XRD diagram. f_a increases depending on the fluence Φ. This dependence is perfectly described by the direct impact model [13], which enables to calculate the cross section of damage of the projectile σ:

$$f_a = 1 - \exp(-\sigma\Phi). \quad (2)$$

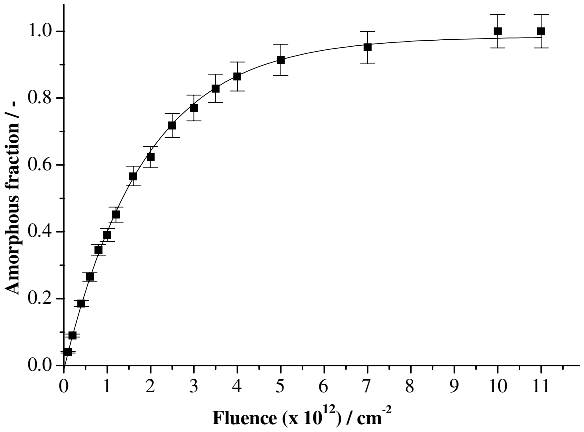

Fig. 1. Amorphous fraction versus the fluence of β-TPD irradiated sample (840 MeV Kr^{32+}, at 298 K). The solid line is a fit to experimental data based on a direct impact model.

On the basis of these results, the damage track diameter was found to be about 8 nm for 840 MeV krypton.

As shown in Fig. 2, the amorphization of the matrix with 450 MeV xenon ($(dE/dx)_{elect} = 20$ MeV μm^{-1}) for a fluence of 10^{13} cm^{-2} led to an obvious modification of the pellet surface: the pores disappeared to give a 'vitreous' aspect.

For the same fluence, a weaker electronic LET (410 MeV sulfur, $(dE/dx)_{elect} = 3$ MeV μm^{-1}) induces a partial amorphization. This observation reveals the existence of a critical electronic LET for full amorphization: the complete amorphization occurs easily for electronic LET greater than 10 MeV μm^{-1}. But if the electronic stopping power of the ion is lower than this threshold (about 4 MeV μm^{-1}), the complete amorphization could not be reached with experimental fluences obtained by the facilities used (Fig. 3).

EPMA experiments revealed that the elementary composition of the pellet was slightly modified by 410 MeV sulfur irradiation (Table 1). Indeed a slight uranium depletion is observed in the first micrometers. According to SRIM calculations, the irradiation zone of β-TUPD with 410 MeV sulfur reached a depth of 110 μm.

Furthermore, μ-Raman studies confirm that the main vibrations bands associated to the P–O and P–O–P edge were not modified in the irradiated zone: except for luminescence due to defects induced by irradiation, the μ-Raman spectra are quite similar for the raw and the irradiated material.

The annealing of the amorphous phase was also studied. Under α-irradiation at a fluence of 2×10^{16} cm^{-2} performed with 1.6 MeV He (ARAMIS facilities), no significant annealing was observed for samples previously amorphized by ion beam irradiation. On the contrary, thermal annealing allowed the recrystallization of the material: with isothermal steps of 10 h each, XRD experiments showed that the material was completely repaired at 963 K (Fig. 4).

The kinetics of annealing was also studied by XRD for several heating temperatures (893 K, 1013 K and 1163 K) (Fig. 5). In all the cases, the kinetics of recrystallization of the different plans of the crystal lattice was followed through the evolution of the XRD lines. It appeared that there was no preferential repairing of the crystal plans: the lattice recrystallization is isotropic, whatever the temperature considered. The activation energy of thermal annealing was estimated by the ratio of

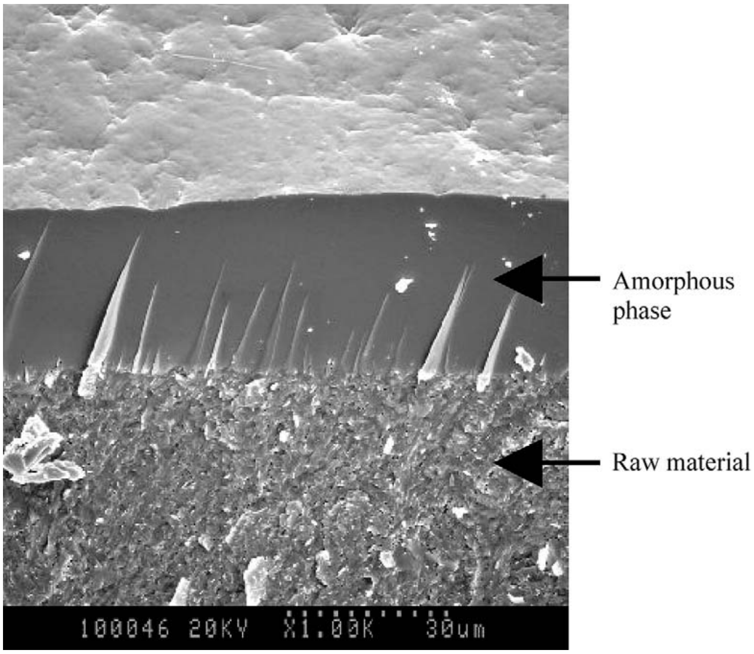

Fig. 2. SEM micrograph of a section of β-TPD irradiated pellet (450 MeV Xe^{17+}, 10^{13} cm^{-2}, at 298 K).

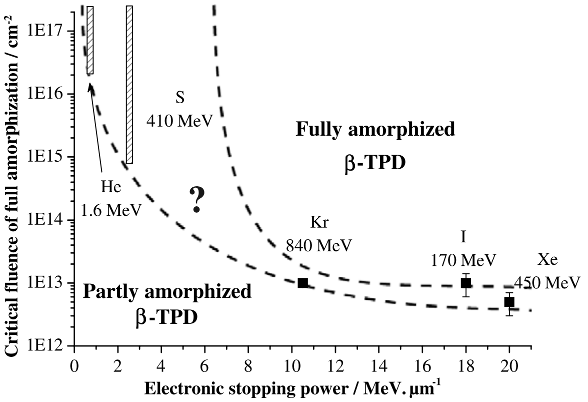

Fig. 3. Variation of the critical fluence for full amorphization versus the electronic LET for β-TPD irradiated with various ions. β-TPD is not fully amorphized under the curve. The behavior above the curve is not determined for the irradiation under 410 MeV sulfur and 1.6 MeV helium beams.

the slopes of the annealing curves. It is equal to about 2 eV, which is similar to that determined for other ceramics [14]. Previous studies [15] revealed that paramagnetic defects in the phosphate sublattice appear under irradiation and can disappear by annealing. RPE studies, performed to follow the thermal annealing of these paramagnetic defects, showed that it begins at 463 K with 10 h steps while that of the crystal lattice followed by XRD occurs at 963 K.

3.2. Leaching tests on irradiated samples

Partly and fully amorphized pellets were submitted to leaching tests in nitric acid media at various temperatures and pH values. These experiments revealed an increase of the kinetics of dissolution versus the amorphous fraction (Fig. 6 and Table 2). The normalized leaching rates as determined from the uranium release ($R_L(U)$) of fully amorphized β-TUPD is one order of magnitude higher than that to the raw material. This is observed for all the investigated leaching conditions. The normalized leaching rate R_L seems to depend on the amorphous fraction f_a with the empirical law:

$$R_L = R_L^0 \times \left(\frac{R_L^*}{R_L^0}\right)^{f_a} \tag{3}$$

where R_L^0 is the normalized leaching rate of the raw material ($f_a = 0$) and R_L^* is the normalized leaching rate of the fully amorphous material ($f_a = 1$).

The release of thorium was also followed, showing the incongruence of the dissolution at 353 K. The thorium concentration in the leachate gets quickly lower than uranium: for example, in 10^{-1} M HNO_3 at 363 K, the normalized leaching of thorium and uranium were respectively about 0.01 and 0.3 $g\,m^{-2}$ after 100 days of leaching. Indeed, a congruent dissolution would have implied

Table 1
Profile of elementary composition from EPMA in a 410 MeV sulfur irradiated β-TUPD pellet

	Raw phase	Average depth in the irradiated phase (μm)		
		6	29	47
U (wt%)	4.9 ± 0.3	3.3 ± 0.5	4.7 ± 0.6	4.7 ± 0.5
Th (wt%)	56.2 ± 0.2	59.8 ± 1.3	56.8 ± 1.2	56.4 ± 1.4
P (wt%)	12.5 ± 0.3	12.4 ± 0.5	12.3 ± 0.2	12.4 ± 0.2
U/Th (at.%)	0.08 ± 0.01	0.05 ± 0.01	0.08 ± 0.02	0.08 ± 0.02
(U + Th)/P (at.%)	0.66 ± 0.01	0.67 ± 0.02	0.66 ± 0.02	0.66 ± 0.02

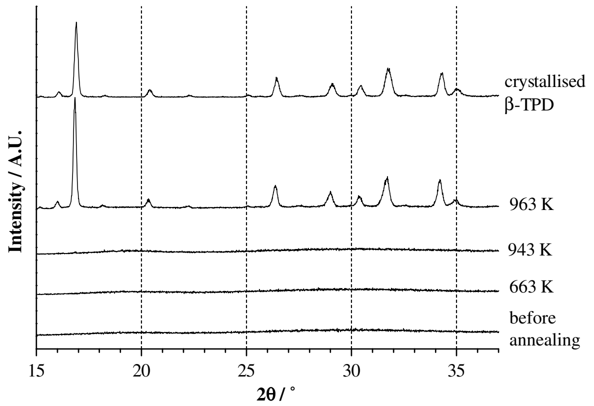

Fig. 4. XRD diagrams obtained during the thermal annealing of amorphous β-TPD (steps of 10 h).

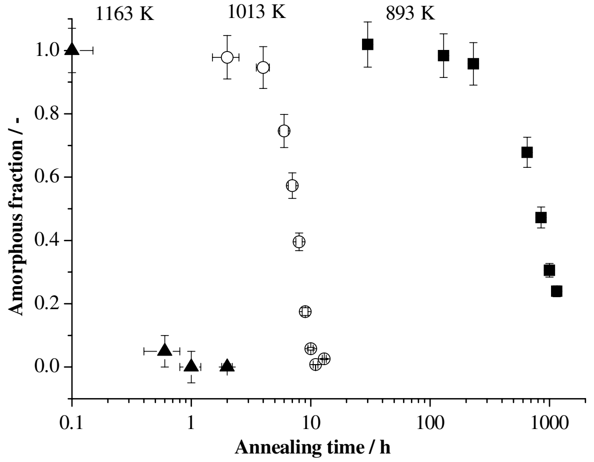

Fig. 5. Kinetics of thermal annealing of amorphous β-TPD at 1013 K.

a thorium normalized leaching rate equal to that of uranium. In the presence of phosphate ions, the saturation in thorium occurs rapidly and leads to the precipitation of a neoformed phase onto the surface of the β-TUPD pellets. This phase was found to be significantly depleted in uranium since uranium (IV) was oxidized to the uranyl (VI) species which remains in solution, while thorium was quantitatively precipitated. The identification of the neoformed phase was performed by EPMA and SEM studies: this precipitate corresponds to the hydrated crystallized precursor TPHPH used for the synthesis. The neoformed phase limits the release of uranium thanks to diffusion processes: the normalized leaching of uranium presents a linear trend versus the square root of time. The neoformed layer onto the surface of the sample consists of the passivation of the material towards the dissolution. In this regard, the leaching behavior of irradiated β-TUPD is quite similar to that of the raw β-TUPD: the presence of the amorphous phase does not modify the nature of the neoformed phase and its conditions of precipitation.

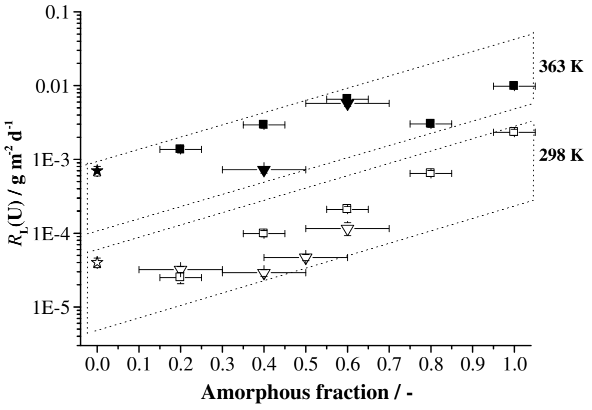

Fig. 6. Variation of the normalized dissolution rates in 10^{-1} M HNO_3 versus the amorphous fraction for irradiated β-TUPD. (★/☆ : raw sample ; ▼/▽: samples irradiated with 410 MeV S; ■/□: samples irradiated with 840 MeV Kr-open symbols: leaching at 298 K; full symbols: leaching at 353 K).

Some pellets were irradiated with γ-rays for doses between 310 kGy and 1.14 MGy with a ^{137}Cs source. No alteration of the crystal lattice was

Table 2
Normalized leaching rate $R_L(U)$ of partly and fully amorphized samples under irradiation in 10^{-1} M HNO_3 for different temperatures

Ion irradiation	Amorphous fraction	$R_L(U)$ ($g\,m^{-2}\,d^{-1}$)			
		298 K	326 K	343 K	363 K
No irradiation	0	$(4.0 \pm 0.5) \times 10^{-5}$	$(1.2 \pm 0.1) \times 10^{-4}$	$(2.8 \pm 0.3) \times 10^{-4}$	$(7.0 \pm 0.2) \times 10^{-4}$
Kr^{32+} 840 MeV	0.2	$(1.4 \pm 0.2) \times 10^{-4}$	—	$(2.8 \pm 0.3) \times 10^{-4}$	$(1.4 \pm 0.2) \times 10^{-3}$
	0.4	$(9.9 \pm 1.0) \times 10^{-5}$	—	$(6.5 \pm 0.7) \times 10^{-4}$	$(2.9 \pm 0.3) \times 10^{-3}$
	0.6	$(2.1 \pm 0.2) \times 10^{-4}$	$(1.5 \pm 0.2) \times 10^{-3}$	$(5.9 \pm 0.5) \times 10^{-3}$	$(6.6 \pm 1.0) \times 10^{-3}$
	0.8	$(6.5 \pm 0.6) \times 10^{-4}$	$(1.5 \pm 0.2) \times 10^{-3}$	$(1.5 \pm 0.2) \times 10^{-3}$	$(3.0 \pm 0.3) \times 10^{-3}$
	1	$(2.0 \pm 0.2) \times 10^{-3}$	$(3.1 \pm 0.3) \times 10^{-3}$	$(4.0 \pm 0.3) \times 10^{-3}$	$(9.9 \pm 1.0) \times 10^{-3}$
S^{15+}410 MeV	0.2	$(3.2 \pm 0.3) \times 10^{-5}$	—	—	—
	0.4	$(3.0 \pm 0.3) \times 10^{-5}$	$(1.6 \pm 0.2) \times 10^{-4}$	—	$(7.3 \pm 0.8) \times 10^{-4}$
	0.5	$(4.7 \pm 0.5) \times 10^{-5}$	—	—	—
	0.6	$(1.2 \pm 0.3) \times 10^{-4}$	$(4.1 \pm 0.4) \times 10^{-4}$	—	$(5.8 \pm 0.6) \times 10^{-3}$

observed. Indeed, the linear attenuation coefficient of the γ-rays was found to be very low ($\mu = 0.0183\ mm^{-1}$). Consequently, it is logical to not observe any significant influence of the irradiation dose on the normalized leaching rate in 10^{-1} M HNO_3 and in deionized water at room temperature.

3.3. Radiolytic study

It is well known that irradiation in pure water causes radiolysis reactions which lead to the formation of molecular species (H_2O_2, H_2, O_2) and radicals ($OH^\bullet$, $H^\bullet$). Some of them are strongly reactive and can highly influence the kinetics of dissolution [16].

γ-irradiations were performed on β-TPD in nitric media at room temperature: the flasks containing the sample and the leachate are exposed to γ-rays at different fluences (between 30 kGy and 1.14 MGy) for 50 h or 14 days. These experiments revealed (Fig. 7) that the exposure time is the only parameter which influences the kinetics of dissolution during irradiation and during the first following days. This may be the influence of the formation of very short life-time radical species produced during irradiation. In 10^{-1} M HNO_3 and at room temperature, there is one order of magnitude between the $R_L(U)$ value for leaching during irradiation ($2.1 \times 10^{-4}\ g\,m^{-2}\,d^{-1}$) and that determined on samples irradiated before leaching ($3.2 \times 10^{-5}\ g\,m^{-2}\,d^{-1}$). But a few days after irradiation, whatever the dose considered, the dissolution rate is similar to that of the raw ceramic.

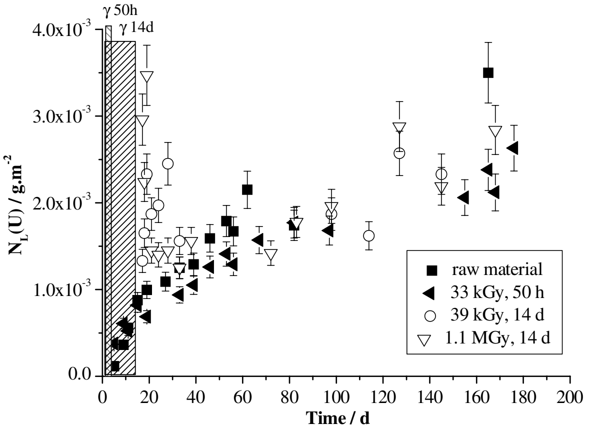

Fig. 7. Evolution of the normalized leaching $N_L(U)$ in 10^{-1} M HNO_3 and at 298 K, after γ-irradiation for the immerged samples at several doses for 50 h or 14 days.

4. Conclusions

A critical threshold of amorphization of β-TPD for ionization process was determined: for 840 MeV krypton with $(dE/dx)_{elect} = 10\ MeV\ \mu m^{-1}$, the complete amorphization was observed above $10^{13}\ cm^{-2}$ in an isotropic way : all the crystal plans are altered with the same kinetics. The track diameter was found to be about 8 nm. The amorphization increased the normalized dissolution rate of about one order of magnitude for the fully amorphized material compared to the raw material. A neoformed phase was observed: it was identified to the thorium phosphate hydrogenphosphate hydrate.

No significant structural modification was induced by γ-irradiation even with a dose of 1.14 MGy and no modification of the kinetics of dissolution was observed for the pellets irradiated by this way. However, radiolytic species produced by γ-rays in leachate increased the uranium release during the few days following the irradiation.

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