

## Self irradiation effects on the Thorium Phosphate Diphosphate dissolution (TPD): simulation by external irradiations

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**Abstract** – *The Thorium Phosphate Diphosphate (TPD), proposed as a ceramic for the long term immobilization of actinides, was externally irradiated with several ions and energies (but also with gamma rays) in order to simulate the self-irradiation. The influence of the electronic energy loss was first investigated. Thus, the XRD measurements have shown a complete amorphization of the material under  $10^{13}$  ions of  $\text{Kr}\cdot\text{cm}^{-2}$ , while no significant structural change occurred after  $5\cdot 10^{13}$   $\text{S}\cdot\text{cm}^{-2}$ ,  $2\cdot 10^{16}$   $\text{He}\cdot\text{cm}^{-2}$  or 320 kGy of dose of gamma rays. The dissolution of the raw and irradiated pellets was studied versus several parameters such as amorphized fraction, energy loss of incident ions, radiolytic species produced in situ in the leachate during irradiation (such as  $\text{H}_2\text{O}_2$ ), temperature and acidity. The results reveal an important increase of the dissolution kinetics for amorphized pellets compared to raw ceramic.*

## INTRODUCTION

In the field of the long-term storage of nuclear waste, ceramics were clearly presented as good candidates for nuclear waste immobilization. The Thorium Phosphate Diphosphate (TPD),  $\text{Th}_4(\text{PO}_4)_4\text{P}_2\text{O}_7$ , has been selected as an actinide-bearing phase for nuclear waste storage. This material, which can be loaded *in situ* with large amounts of tetravalent actinides [1-2], presents a high resistance to aqueous corrosion and exhibits a high thermal stability [3]. But it must also be resistant to irradiation. Nuclear waste storage ceramics are submitted to internal alpha-irradiation which is likely to damage crystal structure. The released  $\alpha$ -particles ( $\sim 5$  MeV) disperse their energy by ionization and electronic excitations. Recoil nuclei ( $\sim 100$  keV) lose their energy through ballistic process involving elastic collisions and causing direct atomic displacement [4-5]. This induces cascades of local defects (vacancies and interstitial atoms) which can lead to amorphization of the material. Such radiation damages can affect the release of radionuclides from waste matrix during leaching tests by increasing the surface area and by modifying the thermodynamic stability of the material [6]. The dissolution tests were preferentially realized on solid solutions 10mol% TUPD,  $\text{Th}_{3,6}\text{U}_{0,4}(\text{PO}_4)_4\text{P}_2\text{O}_7$ . Thorium substitution by uranium does not modify the chemical properties of the ceramic and makes the determination of dissolution kinetics possible by using uranium as a tracer: contrary to Th which

precipitates with phosphate anions, U(IV) oxidizes in U(VI) which remains in solution and can be measured.

With the aim of determining the irradiation effects on the structure of the T(U)PD and then on its dissolution, ion beams and gamma-rays irradiations were performed on sintered pellets. The first realized experiments aimed to underline the effect of the electronic stopping power ( $dE/dx_e$ ) by using high energetic ion beams (810 MeV Krypton, 450 MeV Xenon and 410 MeV Sulphur). The effect of the radiolytic species on the dissolution of the TPD was also studied by gamma and alpha irradiation of immersed pellets.

## EXPERIMENTAL

### Synthesis

TPD and associated TUPD solid solutions can be synthesized through different ways [7]. For performing the irradiation experiments, the samples are prepared by a wet chemical method [8], which leads to the precipitation of a precursor, the Thorium Phosphate HydrogenPhosphate monohydrate (THPH):  $\text{Th}_2(\text{PO}_4)_2\text{HPO}_4\cdot\text{H}_2\text{O}$ . A mixture of concentrated thorium nitrate and phosphoric acid solutions, considering a mole ratio  $r = \text{PO}_4/\text{Th} = 3/2$ , is slowly heated at  $150^\circ\text{C}$  for 8-10 days in a closed PTFE container. The crystallized solids are separated from the supernatant by centrifugation, washed several times with deionized water in

order to eliminate the remaining acid and finally dried at 100-120°C. The powdered T(U)PHP prepared is characterized by X-Rays analysis and its surface area is estimated at about  $15 \text{ m}^2 \cdot \text{g}^{-1}$ . After heating at 450°C in air to eliminate volatile products, the powder [9] is sintered via a uniaxial room temperature pressing at 250 MPa in a 10mm diameter cylindrical matrix [10]. The solid is then thermally heated in alumina crucibles under inert atmosphere for TUPD to prevent any oxidation of uranium (IV). First series are treated at 1200°C for 15 hours but it appeared afterwards that the sintering was much effective at 1250°C for 10 hours of treatment. The  $\beta$ -T(U)PD samples were characterized by Xray diffraction; density is determined by water pycnometry and the specific surface area by  $\text{N}_2$  BET (Tab.1).

TABLE 1: Some characteristics of sintered pellets.

sintering	Density (relative density)	Surface area ( $\text{m}^2 \cdot \text{g}^{-1}$ )
1200°C ; 15 h	4.7 (90%)	0.4
1250°C ; 10 h	5.0 (95%)	0.05

### Leaching tests

The leaching tests were performed in HDPE containers for experiments at room temperature and in PTFE vessels for experiments above 70°C. Concentrations of cations were determined by ICP-MS (Inductively Coupled Plasma Mass Spectroscopy) for Th and U and by TRLIFS (Time Resolved Laser Induced Fluorescence Spectroscopy) for U after dilution and centrifugation at 13000 rpm [11]. The normalized dissolution rate  $R_L$  ( $\text{g} \cdot \text{m}^2 \cdot \text{day}^{-1}$ ) that represents the mass loss of the dissolved solid in the solution, is determined from the following equation :

$$R_L(M_i) = \frac{dN_L(M_i)}{dt} = \frac{d}{dt} \left( \frac{C_{M_i} \times V \times M_{M_i}}{x_{M_i} \times S} \right)$$

where  $C_{M_i}$  represents the concentration of the measured element (Th, U),  $V$  the volume of the leachate,  $x_{M_i}$  the mass ratio of  $M_i$  in the solid and  $S$  the effective surface area of the pellet.

### Irradiation experiments

Ion beam irradiations are performed on the SME line in GANIL (Caen, France) for irradiation with high energy ions. One experiment was performed on the CHEXPIR line: this installation enables to follow *in situ* the structural evolution of the irradiated material

thanks to an X-ray diffractometer with an angular field from 10 to 120°. The irradiation with low energy ions are realized on ARAMIS installation in CSNSM (Orsay, France).

Gamma-irradiations are performed with a  $^{137}\text{Cs}$  source. Alpha-radiolysis studies are carried out in CERI (Orléans, France) [12]. One face of a thin pellet is in contact with ultra-pure water leachate and the other one is irradiated by helions. The emergent beam of 8 MeV  $\text{He}^{2+}$  simulates the effect of the  $\alpha$ -decay of the actinides: radiolytic species are created near the face in contact with the leachate.

## RESULTS

### Ion beam irradiations

A sintered pellet of TPD was irradiated with 10.8 MeV/u  $^{78}\text{Kr}^{32+}$  on the CHEXPIR line of GANIL. The acquisition was realised on the angular field from 10 to 60°. The ion beam irradiated the sample with a uniform flux estimated to  $5.2 \cdot 10^8 \text{ cm}^{-2} \cdot \text{s}^{-1}$ . XRD acquisitions were performed for several fluences between  $10^{11}$  and  $1.1 \cdot 10^{13} \text{ cm}^{-2}$ . According to SRIM 2000 calculations [13], the projected range of the ions in the sample is about 70  $\mu\text{m}$ . The diffraction analysis reveals a total amorphization of TPD from  $10^{13} \text{ cm}^{-2}$  with 840 MeV  $\text{Kr}^{32+}$  ( $dE/dx_e = 10 \text{ MeV} / \mu\text{m}$ ) (Fig.1).

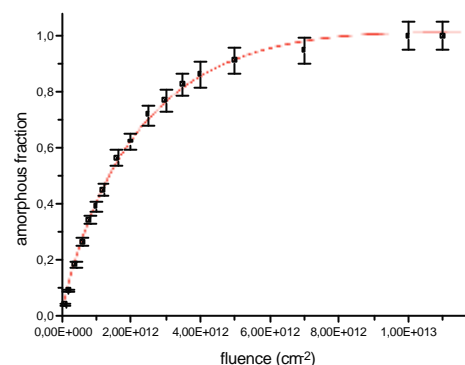


Figure 1 : Fitting of amorphous fraction vs fluence according to the direct impact model (840 MeV Kr).

For each fluence, the average of the diffraction lines net area is determined (Fig.1). According to the direct impact model [14], the amorphous fraction  $f$  is a function of fluence  $\Phi$ :  $f = 1 - \exp(-\sigma\Phi)$  where  $\sigma$  is the electronic interaction cross section of the projectile. Experimental results are well fitted for a damage track diameter of 8 nm.

As seen on Figure 2, the impact of 450 MeV Xe ( $dE/dx = 20 \text{ MeV}/\mu\text{m}$ ) with a fluence of  $10^{13} \text{ cm}^{-2}$  led to a “vitrification” of the pellet surface: the pores disappear in the amorphous phase. For the same fluence, a beam of 410 MeV S ( $dE/dx = 3 \text{ MeV}/\mu\text{m}$ ) induces a partial amorphization.

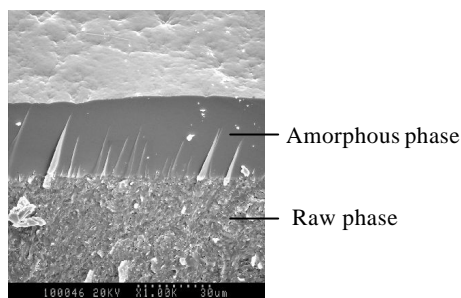


Figure 2: SEM micrography<sup>1</sup> of a section of irradiated TPD pellet (Xe 450MeV  $10^{13} \text{ cm}^{-2}$ ).

Electron Probe Microanalysis (EPMA) experiments<sup>2</sup> revealed that the elementary composition of the pellet is modified by 410 MeV S irradiation. In the first micrometers of thickness U depletion is observed; but this phenomenon is not explicated yet.

TABLE 2: Elementary profile in a 410 MeV S irradiated TUPD pellet obtained by EPMA.

	Non irradiated phase	Analysis depth in the irradiated phase ( $\mu\text{m}$ )		
		6	29	47
U (wt %)	$4.9 \pm 0.3$	$3.3 \pm 0.5$	$4.7 \pm 0.6$	$4.7 \pm 0.5$
Th (wt %)	$56.2 \pm 0.2$	$59.8 \pm 1.3$	$56.8 \pm 1.2$	$56.4 \pm 1.4$
P (wt %)	$12.5 \pm 0.3$	$12.4 \pm 0.5$	$12.3 \pm 0.2$	$12.4 \pm 0.2$
U/Th	0.08	0.05	0.08	0.08
M/PQ <sub>4</sub>	0.66	0.67	0.66	0.66

Based on the CHEXPIR experiments (Fig.1), other pellets were irradiated with a 840 MeV Kr at several fluences: they were afterwards submitted to leaching tests in nitric acid media at two temperatures and two pH values. It reveals an enhance of the dissolution kinetics for the amorphous phase (Fig 3). In all studied leaching conditions, the normalized leaching rate  $R_L(U)$

<sup>1</sup> performed with a Hitachi S2500 scanning electron microscope.

<sup>2</sup> performed with a Cameca SX 50 apparatus and using  $\text{ThO}_2$ ,  $\text{UO}_2$  and  $\text{SmPO}_4$  as monitors.

for amorphous TUPD is multiplied by a factor 100 in comparison to the raw material. A neoformed phase (precipitation) is observed on the TUPD. Complementary analyses are in progress.

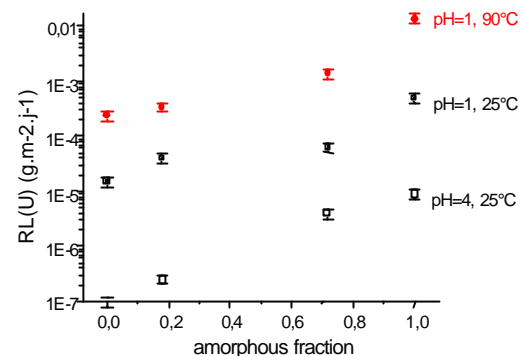


Figure 3: Normalized leaching rates in nitric acid media for amorphized TUPD (840 MeV Kr).

At the same time, some pellets were exposed to different doses of gamma-rays (between 310 kGy and 1,14 MGy with a  $^{137}\text{Cs}$  source). Previous studies [15] have revealed the existence of different paramagnetic defects which could disappear by thermal annealing. Crystalline structure is not altered by  $\gamma$ -rays which deposit too low energy (attenuation factor  $\mu=0.0183 \text{ mm}^{-1}$ ). Consequently, it is not surprising to observe an insignificant influence of the irradiation dose on the normalized leaching rate in 0.1M  $\text{HNO}_3$  and in deionized water at room temperature (RT): kinetics is quite similar to that of raw TPD.

### Radiolytic study

So far presented studies were realized on pellets which were irradiated before leaching tests. But it is well known that irradiation in water causes radiolysis reactions and leads to the formation of molecular species ( $\text{H}_2\text{O}_2$ ,  $\text{H}_2$ ,  $\text{O}_2$ ) and also free radical ones ( $\text{OH}^\bullet$ ,  $\text{H}^\bullet$ ). Some of them are very reactive and can highly influence the kinetics of dissolution.

Gamma-irradiations are performed at different fluences (between 30 kGy and 1.14 MGy) on TPD in aqueous and nitric media at RT. It reveals that the only parameter which influences kinetics is the exposure time. It may be the influence of the formation of very short life-time radical species: they exist only during irradiation.  $R_L(U)$  in  $\text{HNO}_3$  0,1M at RT is about 10 times greater during irradiation ( $2.1 \cdot 10^{-4} \text{ g.m}^{-2}.\text{d}^{-1}$ ) than

out irradiation ( $0.3 \cdot 10^4 \text{ g}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ ). But after irradiation, whatever the dose may have been, the rate is similar to that of the raw ceramic.

In order to distinguish the effects of hydrogen peroxide (major molecular radiolytic species produced in pure water) from the other radiolytic species, leaching tests have been realized by additional  $\text{H}_2\text{O}_2$ . According to the first results, radiolytic peroxide exhibited a low influence under leaching kinetics. Actually, for  $\alpha$ -radiolysis,  $\text{H}_2\text{O}_2$  production concentration in ultra pure water irradiated for 1 hour is about  $10^{-4} \text{ M}$ . The ratio between the  $R_L(\text{U})$  under 1 hour-irradiation and the  $R_L(\text{U})$  in  $10^{-4} \text{ M}$  added  $\text{H}_2\text{O}_2$  solution is approximately 40. The results of these two kinds of radiolysis experiments ( $\gamma$  and  $\alpha$ ) show that radical species are the main actors of the dissolution of TPD under irradiation. Determination of these species is now under progress.

## CONCLUSION

Amorphization threshold of the TPD ceramic for the electronic contribution has been determined by XRD for 810 MeV Kr ( $dE/dx_e = 10 \text{ MeV}/\mu\text{m}$ ): the complete amorphization is observed from  $10^{13} \text{ cm}^{-2}$ . The amorphization fraction evolves according to a direct impact phenomenon (one track diameter = 8nm). This amorphization goes with an U depletion in the first micrometers of thickness of irradiated material. The amorphized material show an increase of the dissolution rate of two order of magnitude. No significant structural modification is induced by high dose of  $\gamma$ -rays, and the dissolution kinetics of  $\gamma$ -irradiated pellets is similar to the raw ones. Further irradiations have just been realized with low energetic ions (4 MeV Au  $dE/dx_e = 2.8 \text{ MeV}/\mu\text{m}$ ,  $dE/dx_n = 2.7 \text{ MeV}/\mu\text{m}$ ) to study the nuclear contribution.

The radiolytic studies revealed the weak influence of the hydrogen peroxide (major radiolytic molecular species) on the dissolution kinetics and highlighted the effective contribution of short live-time free radicals (the identifications are in progress).

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