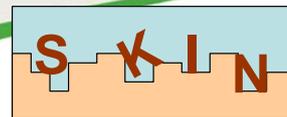




EUROPEAN  
COMMISSION

European  
Research Area



## Report on Thorium oxide Solubility behavior vs. the surface crystalline state

**SLOW PROCESSES IN CLOSE-TO-EQUILIBRIUM CONDITIONS FOR  
RADIONUCLIDES IN WATER/SOLID SYSTEMS OF RELEVANCE TO NUCLEAR  
WASTE MANAGEMENT**

**SKIN**

**DELIVERABLE D3.5**

**COLLABORATIVE PROJECT (CP)**

Grant agreement N°.: FP7-269688

Submitting organizations: ARMINES

Authors: Tomo Suzuki-Muresan, Johan Vandendorre, Katy Perrigaud, Bernd Grambow

Due date of deliverable: Project Month 34

Actual submission: Project Month 36

Start date of the project: 01 January 2011

Duration: 36 months

Project co-funded by the European Commission under the Seventh Framework Programme of the European Atomic Energy Community (Euratom) for nuclear research and training activities (2007 to 2011)

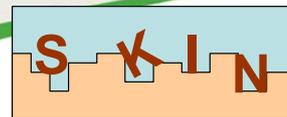
Dissemination Level

|           |  |   |
|-----------|--|---|
| <b>PU</b> | Public   | × |
| <b>RE</b> | Restricted to a group specified by the partners of the project |   |
| <b>CO</b> | Confidential, only for partners of the project                 |   |



EUROPEAN  
COMMISSION

European  
Research Area



## THORIUM OXIDE SOLUBILITY BEHAVIOR VS. THE SURFACE CRYSTALLINE STATE

Tomo Suzuki-Muresan<sup>1\*</sup>, Johan Vandendorre<sup>1</sup>, Katy Perrigaud<sup>1</sup>, Bernd Grambow<sup>1</sup>

<sup>1</sup> SUBATECH, Unité Mixte de Recherche 6457, Ecole des Mines de Nantes,  
CNRS/IN2P3, Université de Nantes, 4 rue Alfred Kastler, BP 20722, 44307 Nantes  
cedex 03, France.

\* Corresponding author: [tomo.suzuki@subatech.in2p3.fr](mailto:tomo.suzuki@subatech.in2p3.fr)

### Abstract

In literature, huge discrepancies are reported in solubility values and it is now accepted that the surface solid state may have influence on the determination of the solubility values. The aim of the work in SKIN-project was to re-assess the solubility of ThO<sub>2</sub>(s) in the pH range 3 to 7 as a function of the surface crystalline state.

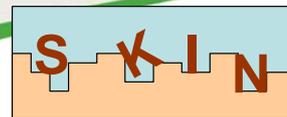
Previous studies indicated that thorium oxide solubility is very much dependent on the material at the grain boundary. With the use of powdered material, the cleaning of the surface is expected to be more effective, so that artefacts derived from pre-altered surface phases will be minimised. The attainment of apparent solubility equilibrium was followed by analysing <sup>232</sup>Th with time. In condition close to equilibrium, half of the solution was removed and kept for desorption experiment. In the remaining half solution in the experiments, <sup>229</sup>Th trace was added to the solution/solid system and the isotopic exchange was monitored by Q-ICP-MS. In all solution analyses, colloids were removed by ultra-filtration at 10kDa but Th analyses of colloidal material were included in the mass balance. Once <sup>229</sup>Th uptake on the surface has reached a steady state, desorption experiments was performed putting the solids with a <sup>229</sup>Th enriched surface into the previously conserved solution without <sup>229</sup>Th. Typical duration of experiments is longer than a year. Different analytical techniques will be used for solution and solid analyses: Q-ICP-MS, SEM, XRD and BET-method.

Synthesis of the solid oxide has been performed with different calcinations temperatures (RT, 700°, 900° and 1300°C) in order to obtain 4 crystalline states of oxide Thorium with different ratio of grains vs. grain boundaries. In addition, separation of ThO<sub>2</sub> crystallized kernel from the coating layers of HTR of ThO<sub>2</sub> has been conducted. These two methodologies have provided samples of the oxide with different crystallinity, i.e., grain size.



EUROPEAN  
COMMISSION

European  
Research Area



Dissolution,  $^{229}\text{Th}/^{232}\text{Th}$  isotopic exchange and desorption measurements have been conducted in the acidic pH range and the results compared with available data in the literature. Results show the relationship between the crystalline state of the  $\text{ThO}_2$  surface and the relative enrichment in  $^{229}\text{Th}$  at the solid/solution interface.

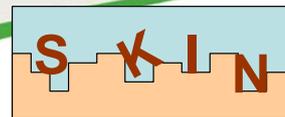
### Introduction

We study Th atom exchange between different thorium oxide surfaces and aqueous solution ( $0.01 \text{ mol.L}^{-1}$  NaCl for pH = 3.2, 5.0, 6.8) to address the Task 3.2. In a previous work (Vandenborre et al., 2010), we have determined by the solid-state characterization (XPS, SEM, AFM) that 80 % of the XPS accessible near surface region of sintered thorium oxide is represented by the less reactive  $\text{ThO}_2(\text{cr})$  grains. The remaining 20 % corresponds to  $\text{ThO}_x(\text{OH})_y(\text{H}_2\text{O})_z$  which is largely associated with grain boundaries. The empirical solubility data does not correspond to thermodynamic bulk phase/solution equilibrium, as measured solution concentrations are controlled by specific site exchange mechanisms at the solid/solution interface. Therefore for sparingly soluble solids, one needs to quantify the specific surface site involved in the attachment and detachment rates if one wants to assess solubility constraints. For this reason, the purpose of our work is to study different crystalline states of thorium oxide surfaces with different grains vs. grain boundaries ratios.

### Material and Methods

#### *Samples*

In this aim, we synthesized thorium oxides from thorium oxalate  $\text{Th}(\text{C}_2\text{O}_4)_2 \cdot 4 \text{H}_2\text{O}$  as precursor in order to control the grain size of  $\text{ThO}_2$  crystallized with different heating temperatures ( $T = 700^\circ\text{C}$ ,  $900^\circ\text{C}$ ,  $1300^\circ\text{C}$ ) (Heisbourg, 2003; Oktay and Yayli, 2001; Rand et al., 2008). The second solid used in this study is provided by J. Fachinger from Forschungszentrum Jülich (Germany). The particles are spherical and synthesized at a high calcination temperature ( $1600^\circ\text{C}$ ). A part of the spheres used for solubility experiments are crushed in order to remove all the grain boundaries even into the core of the sphere by the pre-washing experiments. The synthesis method and the physical properties of the solid are described in (Müller, 2006; Vandenborre et al., 2010), respectively. **Table 1** presents the 4 sets of solid sample: (I) Crushed  $\text{ThO}_2$  spheres, (II) Initial  $\text{ThO}_2$  spheres, (III)  $\text{ThO}_2$  powder synthesized at  $1300^\circ\text{C}$ , (IV)  $\text{ThO}_2$  powder synthesized at  $700^\circ\text{C}$ .

**Table 1:** Sets of solid samples

| Samples | Solid description                             |
|---------|---|
| I       | Crushed ThO <sub>2</sub> spheres              |
| II      | Initial ThO <sub>2</sub> spheres              |
| III     | ThO <sub>2</sub> powder synthesized at 1300°C |
| IV      | ThO <sub>2</sub> powder synthesized at 700°C  |

#### *Solid characterization*

Solid surface pictures are performed by SEM (scanning electron microscopy, JEOL 5800 SV with a 15 kV voltage). The SEM samples were covered by a Pt layer in order to improve electron conduction and increase the picture resolution. XRD patterns are recorded with the diffractometer BRUKER-AXS D5000 (Bragg-Brentano geometry, copper anticathode Cu at  $\lambda = 1.5406 \text{ \AA}$ ). Moreover N<sub>2</sub>-gas adsorption by B.E.T. method, using a COULTER SA3100 apparatus, is carried out in order to determine the specific surface area for each solid sample, in particular versus the heating temperature during the synthesis process.

#### *Dissolution and <sup>229</sup>Th Addition experiments*

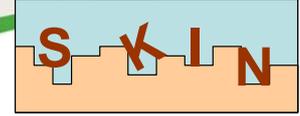
The pre-washing and dissolution batch experiments were performed exposing 150 mg of solids ThO<sub>2</sub>(cr) (synthesized powder with different heating temperature, spheres crushed or intact) to an aqueous solution in undersaturated conditions. A HDPE (High Density poly-ethylene) reaction vessel is used, containing 15 mL 0.1 mol.L<sup>-1</sup> HCl solution under continuous stirring during 15 days.

We have started the dissolution experiments by the contact between each pre-washed solid with the NaCl 0.01 mol.L<sup>-1</sup> aqueous solution at different pH values (3.2, 5.0, 6.8). For the experiments at pH = 3.2, solutions were spiked with a <sup>229</sup>Th ( $t_{1/2} = 7340$  years) carrier-free solution to achieve a final  $[^{229}\text{Th}]_{\text{aq}} = 4.9 \cdot 10^{-10} \text{ mol.L}^{-1}$ . The addition date of 200 days corresponds to the time necessary to reach a constant <sup>232</sup>Th concentration (“steady state”). Immediately after the addition of the acid <sup>229</sup>Th aliquot, the acid perturbation of the solution pH was compensated for by the addition of small aliquots of 0.01 mol.L<sup>-1</sup> NaOH until the target pH value of 3.2 was reached again. The objective of adding the spike is to test the reversibility and to allow one to follow the potentially ongoing solution/surface isotopic exchange on the ThO<sub>2</sub>(cr) surface at “steady state”. The dissolution process of <sup>232</sup>ThO<sub>2</sub>(cr) and the uptake of <sup>229</sup>Th from solution are monitored by sampling aliquots of 0.5 mL over a period of 220 days. After, the solution samples were ultrafiltered, using 1.8 nm cutoff membranes (5 kDa) in order to exclude colloidal particles commonly described in the literature. The ultrafiltered solutions were then acidified with 2% distilled nitric acid and analyzed by inductively coupled plasma mass



EUROPEAN  
COMMISSION

European  
Research Area



spectrometry (THERMOELECTRON) for determination of the  $^{232/229}\text{Th}$  concentration in solution ( $[\text{}^{232/229}\text{Th}]_{\text{aq}}$ ) with an estimated error of 10%.

#### *Desorption experiments*

For the last part of the dissolution experiment, we have performed desorption experiment. At 470 days from the initial contact time, solutions are totally removed from each batch sample. Moreover, initial solutions (15 mL NaCl 0.01 mol.L<sup>-1</sup> with pH = 3.0) are added to each batch sample in order to carry out the desorption experiments. Solutions measurements are performed with the same protocol as the previous dissolution experiments. The total contact time is about 500 days for the experiment.

#### *Normalization of solution concentrations and rate values*

The measured solution concentrations in experiments are normalized to solid composition and surface area and expressed as normalized mass loss NL using the equation

$$\text{NL} = \frac{[\text{Th}] \times \text{MW}_{\text{ThO}_2}}{S/V} \quad (1)$$

where [Th] signifies the measured  $^{232}\text{Th}$  or  $^{229}\text{Th}$  concentrations in mol.m<sup>-3</sup><sub>H<sub>2</sub>O</sub>, MW<sub>ThO<sub>2</sub></sub> is the molecular weight of ThO<sub>2</sub> (g.mol<sup>-1</sup>), S is the surface area (m<sup>2</sup>) of the solid, and V the solution volume (m<sup>3</sup>). The normalized mass loss rate (in g.m<sup>-2</sup>.d<sup>-1</sup>) is then calculated with the following equation:

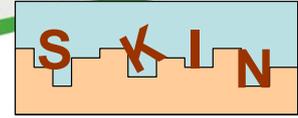
$$\text{NLR} = \frac{\Delta\text{NL}}{\Delta t} \quad (2)$$

where  $\Delta t$  signifies an interval in contact time (d) and  $\Delta\text{NL}$  the variation of normalized mass loss in this interval.

#### *Relative Enrichment in $^{229}\text{Th}$ calculations*

The relative enrichment in  $^{229}\text{Th}$  is a parameter linked to the solubility of a solid surface and is calculated by the ratio between two ratios of  $^{229}\text{Th}$  onto  $^{232}\text{Th}$  at the surface and at the solution as described by:

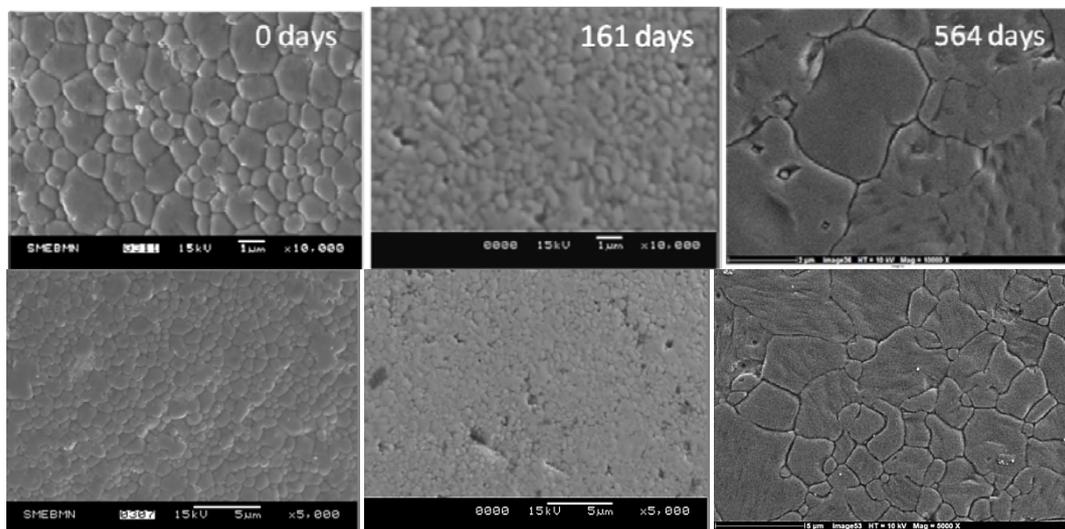
$$\text{RE} = \frac{\left( \frac{^{229}\text{Th}}{^{232}\text{Th}} \right)_{\text{surface}}}{\left( \frac{^{229}\text{Th}}{^{232}\text{Th}} \right)_{\text{solution}}}$$



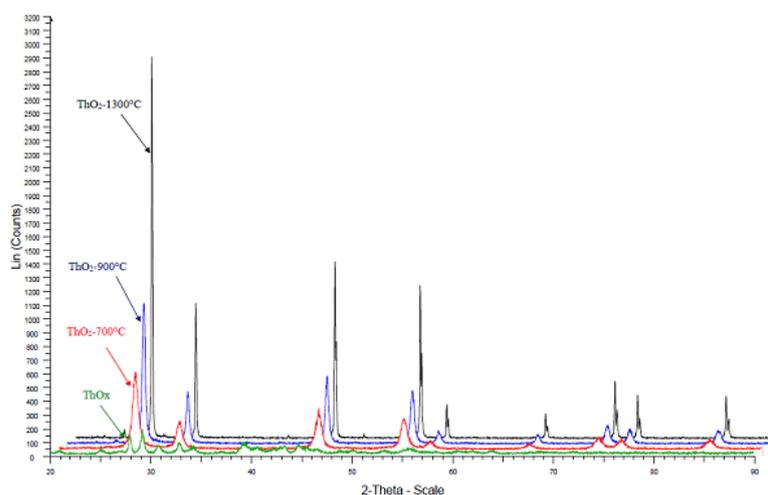
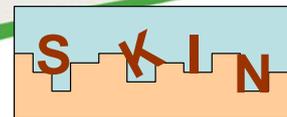
## Results

### 1. Solid characterization

SEM picture of HTR sphere surface shows grains of thorium oxide coated by grain boundaries (**Figure 1**) which control the solubility without pre-washing. The solids characterization by X-Rays Diffraction is performed onto the  $\text{ThO}_2$  spheres in order to check the high crystalline state of this sample. From the results, we confirm the different crystallization states by the decrease of Full Width Half Middle observed onto the XRD peaks when the heating temperature increases (**Figure 2**). Hence, the ratio between grains and grain boundaries is different for all these samples. The B.E.T. method give us the specific surface area values between  $17.8 \text{ m}^2/\text{g}$  for the lower crystallized sample (synthesized at  $700^\circ\text{C}$ ) and  $1.9 \text{ m}^2/\text{g}$  for the higher crystallized (synthesized at  $1300^\circ\text{C}$ ) in **Table 2**. The specific area value for initial  $\text{ThO}_2$  sphere can be estimated from the geometric structure at  $1.2 \cdot 10^{-3} \text{ m}^2/\text{g}$ . However, it seems not realistic because the pre-washing must be implying a non negligible effect onto the surface of the spheres which increase the specific surface area. Moreover, as shown by **Figure 1**, the specific surface evolves during the different dissolution, isotopic exchange and desorption experiments.



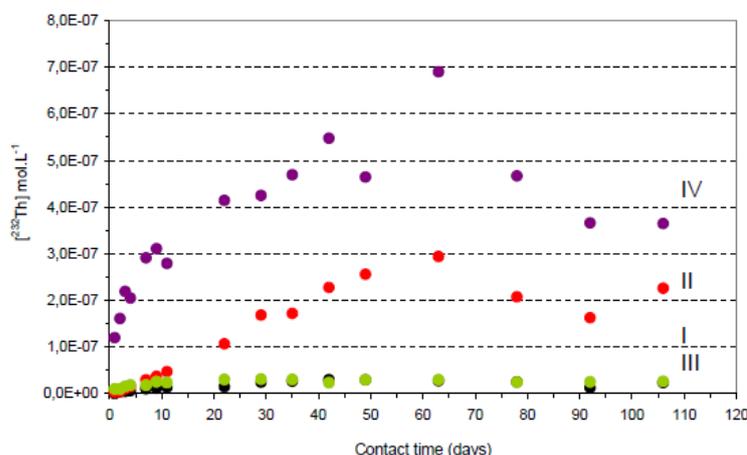
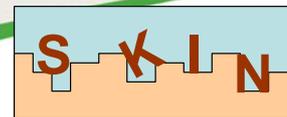
**Figure 1:** SEM pictures of  $\text{ThO}_2(\text{cr})$  HTR sphere at different contact times with the  $\times 10000$  and  $\times 5000$  zoom



**Figure 2:** XRD diagrams of  $\text{ThO}_2$  synthesized samples crystallized at  $700^\circ\text{C}$ ,  $900^\circ\text{C}$  or  $1300^\circ\text{C}$

## 2. Dissolution experiments

The **Figure 3** presents the results for a contact time of about 100 days. During the dissolution step corresponding to the period between 0 and 10 days, the slopes are different between the 4 sets of sample: (I), (II), (III), (IV) (cf. **Table 1**). From the results (**Table 2**), the slope values, which describe the kinetic state of the system, are higher for the powder samples than for the spheres ones and they are similar between the powder synthesized at  $1300^\circ\text{C}$  (III) and the crushed sphere (I). After about 50 days, the pseudo steady-state equilibrium is reached for all samples with different [Th] measurements presented in **Table 2**. Again, the values are close between the powder synthesized at  $1300^\circ\text{C}$  and the crushed sphere. It seems that the global and the kinetic dissolution behaviours are similar for these two samples. These results indicate the similar behaviour and the close crystalline degree between the powder synthesized at  $1300^\circ\text{C}$  (III) and the crushed sphere (I). We can notice that the NLR value for the sample (II) has been not calculated depending on the value of the specific surface area which has changed during the Dissolution experiments (cf. SEM pictures in **Figure 1**).



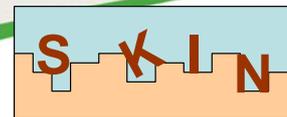
**Figure 3:**  $[^{232}\text{Th}] = f(\text{contact time})$  for each sample at  $\text{pH} = 3.2$ , monitored by ICP-MS, (I) Crushed  $\text{ThO}_2$  spheres, (II) Initial  $\text{ThO}_2$  spheres, (III)  $\text{ThO}_2$  powder synthesized at  $1300^\circ\text{C}$ , (IV)  $\text{ThO}_2$  powder synthesized at  $700^\circ\text{C}$ .

**Table 2:** Experimental data from the dissolution experiments for Samples (I), (II), (III), (IV) with a contact time of 110 days.

| Samples | [Th]10d<br>mol/L     | Slope (1-10d)<br>mol/L/d | Specific Area<br>$\text{m}^2/\text{g}$ | NLR(1-10d)<br>$\text{g}/\text{m}^2/\text{d}$ | [Th]50d<br>mol/L     |
|---------|----------------------|--------------------------|--|--|----------------------|
| I       | $1.35 \cdot 10^{-8}$ | $1.35 \cdot 10^{-9}$     | 1.9                                    | $1.88 \cdot 10^{-5}$                         | $2.95 \cdot 10^{-8}$ |
| II      | $4.71 \cdot 10^{-8}$ | $4.38 \cdot 10^{-9}$     | ?                                      | ?  | $2.56 \cdot 10^{-7}$ |
| III     | $2.37 \cdot 10^{-8}$ | $1.33 \cdot 10^{-9}$     | 1.9                                    | $1.85 \cdot 10^{-5}$                         | $2.98 \cdot 10^{-8}$ |
| IV      | $3.11 \cdot 10^{-7}$ | $1.91 \cdot 10^{-8}$     | 17.8                                   | $2.83 \cdot 10^{-5}$                         | $4.64 \cdot 10^{-7}$ |

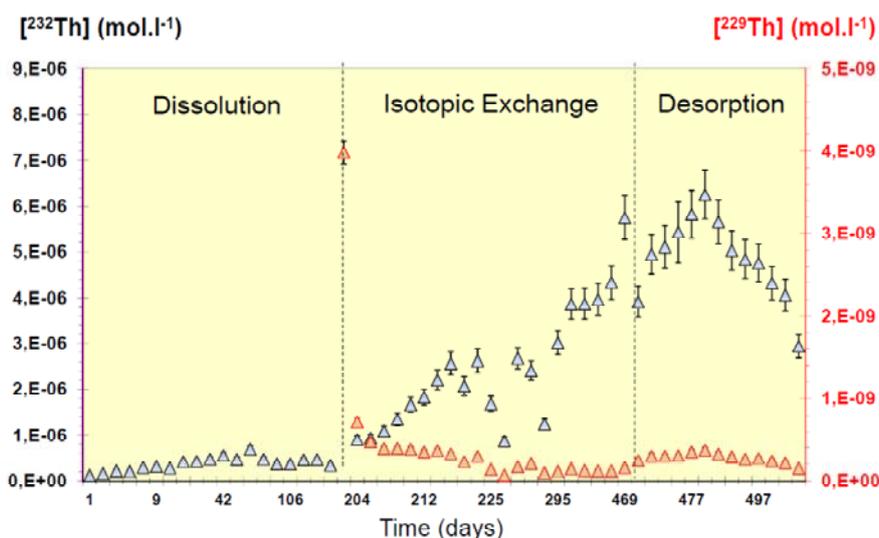
From the results, we made the evidence that the crystalline state of the samples is involved in the dissolution mechanism during the initial kinetic leaching and the reaching of the pseudo steady-state equilibrium. The normalized mass loss rates (NLR) depending on the specific surface area show again the similar behaviour between the powder synthesized at  $1300^\circ\text{C}$  (III) and the crushed sphere (I).

Finally the same evolution of the ratios grain/grains boundaries and global/kinetic leaching behaviour can be described as following: (IV) > (II) > (I) = (III) with (I) Crushed  $\text{ThO}_2$  spheres, (II) Initial  $\text{ThO}_2$  spheres, (III)  $\text{ThO}_2$  powder synthesized at  $1300^\circ\text{C}$ , (IV)  $\text{ThO}_2$  powder synthesized at  $700^\circ\text{C}$ .

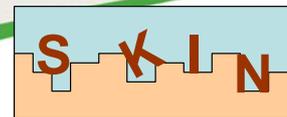


### 2.1 $\text{ThO}_2$ powder synthesized at $700^\circ\text{C}$ (Sample IV)

The **Figure 4** presents the concentrations of  $[\text{}^{232}\text{Th}]$  and  $[\text{}^{229}\text{Th}]$  as a function of the contact time for sample (IV)  $\text{ThO}_2$  powder synthesized at  $700^\circ\text{C}$  at  $\text{pH} = 3.2$  and monitored by ICP-MS for a contact time of 500 days. The **Table 3** presents the experimental data from the dissolution experiments of sample (IV). When the NLR is determined as a negative value, we can assume that a precipitation process occurs onto the solid surface after the  $^{229}\text{Th}$  spike experiments. Then, after the  $^{229}\text{Th}$  addition, a quick precipitation of the  $\text{ThO}_x(\text{OH})_y(\text{H}_2\text{O})_z$  phase occurs at the surface of the  $\text{ThO}_2$  powder synthesized at  $700^\circ\text{C}$  (I) and the slow leaching of this phase is following by the  $^{229}\text{Th}$  and  $^{232}\text{Th}$  isotopes measurements. Then, we assume that the Thorium Oxide at the surface is not completely crystallized and/or is nano-crystallized. That is the reason why we propose  $\text{ThO}_x(\text{OH})_y(\text{H}_2\text{O})_z$  as possible phase at the surface as described elsewhere (Vandenborre et al., 2010). Moreover we can observe a dynamic exchange between the  $^{232}\text{Th}$  onto the surface with the  $^{229}\text{Th}$  in the solution. This dynamic exchange process is based on the increasing concentration values of  $^{232}\text{Th}$  and on the decreasing concentration values of  $^{229}\text{Th}$ . So, we can conclude that the  $\text{ThO}_x(\text{OH})_y(\text{H}_2\text{O})_z$  phase with the low crystallinity of the surface and then the high kinetic of leaching is reactive versus the isotopic Th exchange. During the Desorption experiment, the same behaviour of the surface/solution system is displayed. Then, the dynamic exchange between the surface and the solution is quickly reached, less than one day. So we can conclude that the thermodynamic solubility has been reached for this sample due to the secondary phase  $\text{ThO}_x(\text{OH})_y(\text{H}_2\text{O})_z$  which control the solubility.



**Figure 4:**  $[\text{}^{232}\text{Th}]$  and  $[\text{}^{229}\text{Th}] = f(\text{contact time})$  for Sample (IV)  $\text{ThO}_2$  powder synthesized at  $700^\circ\text{C}$  at  $\text{pH} = 3.2$ , monitored by ICP-MS.

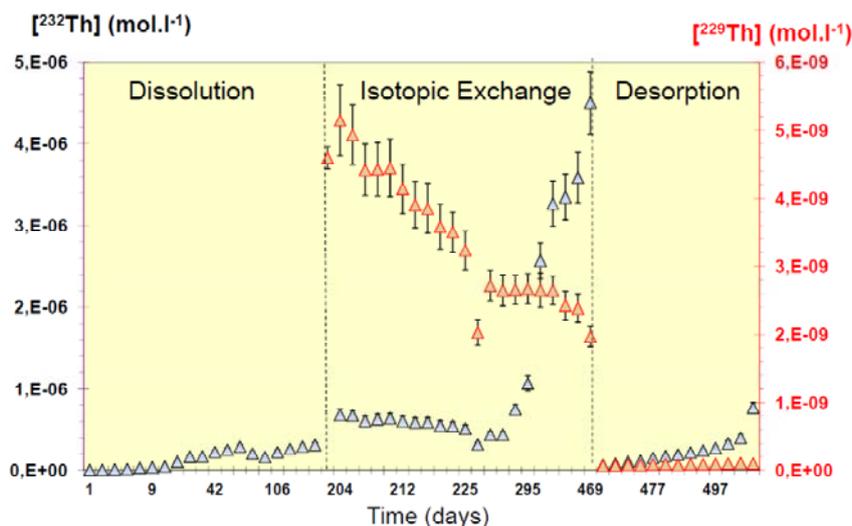
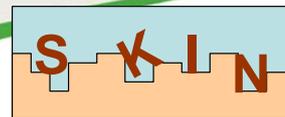


**Table 3:** Experimental data from the Dissolution experiments for Sample (IV) with a contact time of 220 days.

| Th isotope        | [Th]50d<br>mol/L     | Slope (1-10d)<br>mol/L/d | NLR(1-10d)<br>g/m <sup>2</sup> /d | Slope (200-220d)<br>mol/L/d | NLR(200-220d)<br>g/m <sup>2</sup> /d |
|-------------------|----------------------|--------------------------|-----------------------------------|-----------------------------|--------------------------------------|
| <sup>232</sup> Th | $4.64 \cdot 10^{-7}$ | $1.91 \cdot 10^{-8}$     | $2.83 \cdot 10^{-5}$              | $1.01 \cdot 10^{-7}$        | $1.50 \cdot 10^{-4}$                 |
| <sup>229</sup> Th | ×                    | ×                        | ×                                 | $-2.86 \cdot 10^{-11}$      | $-4.25 \cdot 10^{-8}$                |

### 2.2 Initial ThO<sub>2</sub> spheres (Sample II)

The **Figure 5** presents the concentrations of [<sup>232</sup>Th] and [<sup>229</sup>Th] as a function of the contact time for Sample (II) Initial ThO<sub>2</sub> spheres at pH = 3.2 and monitored by ICP-MS for a contact time of 500 days. The **Table 4** presents the experimental data from the Dissolution experiments of Sample (II). The “×” indicate that <sup>229</sup>Th has not been spiked into the solution before a contact time of 200 days. From the results, we can conclude that, in the case of the Initial ThO<sub>2</sub> spheres (II), leaching phenomena did not occur after the <sup>229</sup>Th addition. However, for this case (at contact time of 160 days) the SEM picture in **Figure 1** shows the dissolution process of the grain boundaries. On the contrary, in the first part (between 200 and 225 days), the slow precipitation of one phase mixing <sup>229</sup>Th and <sup>232</sup>Th is shown with a low kinetic explained by its slow diffusion into the grain boundaries of the solid surface. The second part (between 225 and 470 days) shows a dissolution process of the fresh precipitate phase, maybe the same ThO<sub>x</sub>(OH)<sub>y</sub>(H<sub>2</sub>O)<sub>z</sub> phase with the same dynamic exchange observed in the sample IV (see below). In the final range of time (564 days) the SEM picture (**Figure 1**) displays the reprecipitation process into the grain boundaries (grain size increase). This change of the surface behaviour during the Isotopic Exchange implies a difference in the accessibility of the grains boundaries for the Th into the solution. The gap displayed at 470 days of contact time makes the evidence that this dissolution mechanism is a kinetic process. In the desorption experiment, the redissolution process of this phase goes on to occur at the solid/solution interface. The thermodynamic solubility of this solid has not been reached in this experiment. Nevertheless, the results, presented here for the Initial ThO<sub>2</sub> spheres (II), are not quite determined because the Specific Surface Area can not be measured the classical N<sub>2</sub> adsorption method. Moreover, as seen in the SEM pictures (see **Figure 1**), the specific surface area has changed during the Dissolution, isotopic exchange and desorption experiments with an evolution of the grains vs. grain boundaries ratio. So, we cannot measure or calculate the specific surface area for this solid sample.



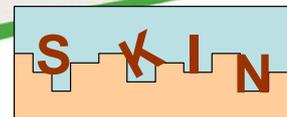
**Figure 5:**  $[^{232}\text{Th}]$  and  $[^{229}\text{Th}] = f(\text{contact time})$  for Sample (II) Initial  $\text{ThO}_2$  spheres at  $\text{pH} = 3.2$ , monitored by ICP-MS.

**Table 4:** Experimental data from the Dissolution experiments for Sample (II) with a contact time of 220 days.

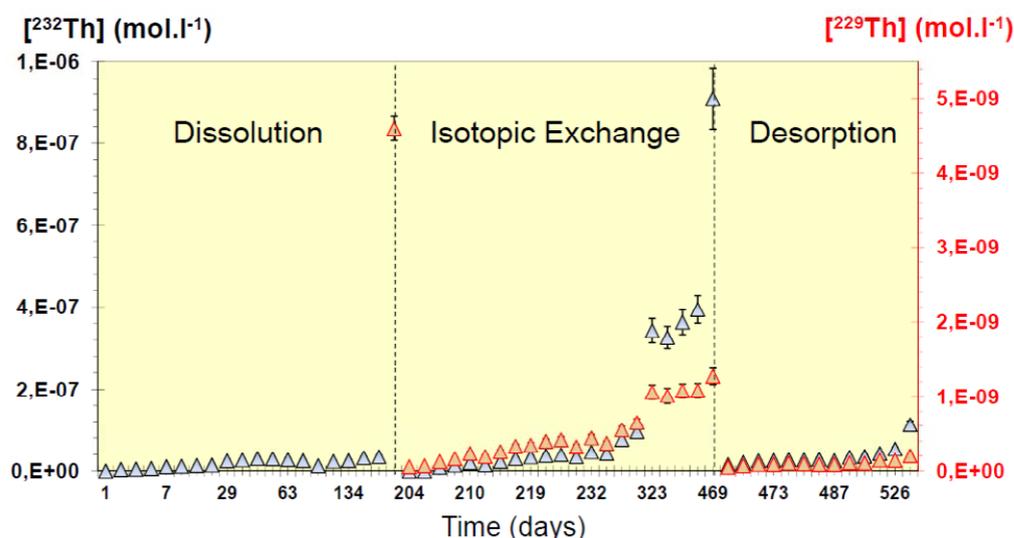
| Th isotope        | $[\text{Th}]_{50\text{d}}$<br>mol/L | Slope (1-10d)<br>mol/L/d | NLR(1-10d)<br>g/m <sup>2</sup> /d | Slope (200-220d)<br>mol/L/d | NLR(200-220d)<br>g/m <sup>2</sup> /d |
|-------------------|-------------------------------------|--------------------------|-----------------------------------|-----------------------------|--------------------------------------|
| <sup>232</sup> Th | $2.56 \cdot 10^{-7}$                | $4.38 \cdot 10^{-9}$     | ?                                 | $-7.76 \cdot 10^{-9}$       | ?                                    |
| <sup>229</sup> Th | ×                                   | ×                        | ×                                 | $-9.65 \cdot 10^{-11}$      | ?                                    |

### 2.3 Crushed $\text{ThO}_2$ sphere and $\text{ThO}_2$ powder synthesized at $1300^\circ\text{C}$ (Samples I and III)

The **Figure 6** presents the concentrations of  $[^{232}\text{Th}]$  and  $[^{229}\text{Th}]$  as a function of the contact time for sample (I) Crushed  $\text{ThO}_2$  sphere and sample (III)  $\text{ThO}_2$  powder synthesized at  $1300^\circ\text{C}$  at  $\text{pH} = 3.2$ , monitored by ICP-MS for a contact time up to 500 days. The **Table 5** presents the experimental data from the dissolution experiments of Samples (I) and (III). The “×” indicate that <sup>229</sup>Th has not been spiked into the solution before a contact time of 200 days. As shown in the previous Dissolution experiments, before the <sup>229</sup>Th addition, the behavior versus the leaching phenomena of the surface of the Crushed  $\text{ThO}_2$  spheres (I) and of the  $\text{ThO}_2$  powder synthesized at  $1300^\circ\text{C}$  (III) is very close. Moreover, the same results are been observed after the <sup>229</sup>Th addition: there is no exchange between the two isotopes of the Th (229 and 232) and we observed a slower leaching process of the solid surface. Moreover, we can conclude that the leaching rate values for the samples (I) and (III), respectively  $2.22 \cdot 10^{-5}$  g/m<sup>2</sup>/d and 1.62



$10^{-5}$  g/m<sup>2</sup>/d, are lower to its of the ThO<sub>2</sub> powder synthesized at 700°C (I),  $2.83 \cdot 10^{-5}$  g/m<sup>2</sup>/d, which has been described as an ThO<sub>x</sub>(OH)<sub>y</sub>(H<sub>2</sub>O)<sub>z</sub> phase. Similar as the Desorption experiment for the Initial ThO<sub>2</sub> sphere (sample II), a gap in Th concentrations is measured in solution. However, in this desorption experiment the curve slope calculated ( $6 \cdot 10^{-10}$  mol/L/d) is ten-fold lower than the value calculated in the Initial HTR sphere ( $6.0 \cdot 10^{-9}$  mol/L/d). We can conclude that there is no ThO<sub>x</sub>(OH)<sub>y</sub>(H<sub>2</sub>O)<sub>z</sub> phase precipitation/dissolution in this case and no grain boundaries at the solid surface. Thus, the dissolution mechanism is a kinetic process for this sample and thermodynamic solubility is not yet reached in this experiment and need a longer duration time (more than 500 days in this experiment).



**Figure 6:**  $[^{232}\text{Th}]$  and  $[^{229}\text{Th}] = f(\text{contact time})$  for Sample (I) Crushed ThO<sub>2</sub> sphere and Sample (III) ThO<sub>2</sub> powder synthesized at 1300°C at pH = 3.2, monitored by ICP-MS.

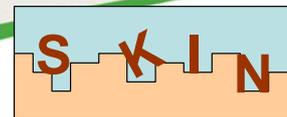
**Table 5:** Experimental data from the Dissolution experiments for Samples (I) and (III) with a contact time of 220 days.

| Th isotope                  | [Th]50d<br>mol/L     | Slope (1-10d)<br>mol/L/d | NLR(1-10d)<br>g/m <sup>2</sup> /d | Slope (200-220d)<br>mol/L/d | NLR(200-220d)<br>g/m <sup>2</sup> /d |
|-----------------------------|----------------------|--------------------------|-----------------------------------|-----------------------------|--------------------------------------|
| <sup>232</sup> Th / Ech I   | $2.95 \cdot 10^{-8}$ | $1.35 \cdot 10^{-9}$     | $1.88 \cdot 10^{-5}$              | $1.60 \cdot 10^{-9}$        | $2.22 \cdot 10^{-5}$                 |
| <sup>232</sup> Th / Ech III | $2.98 \cdot 10^{-8}$ | $1.33 \cdot 10^{-9}$     | $1.85 \cdot 10^{-5}$              | $1.17 \cdot 10^{-9}$        | $1.62 \cdot 10^{-5}$                 |
| <sup>229</sup> Th / Ech I   | ×                    | ×                        | ×                                 | $1.98 \cdot 10^{-11}$       | $2.75 \cdot 10^{-7}$                 |
| <sup>229</sup> Th / Ech III | ×                    | ×                        | ×                                 | $2.01 \cdot 10^{-11}$       | $2.79 \cdot 10^{-7}$                 |



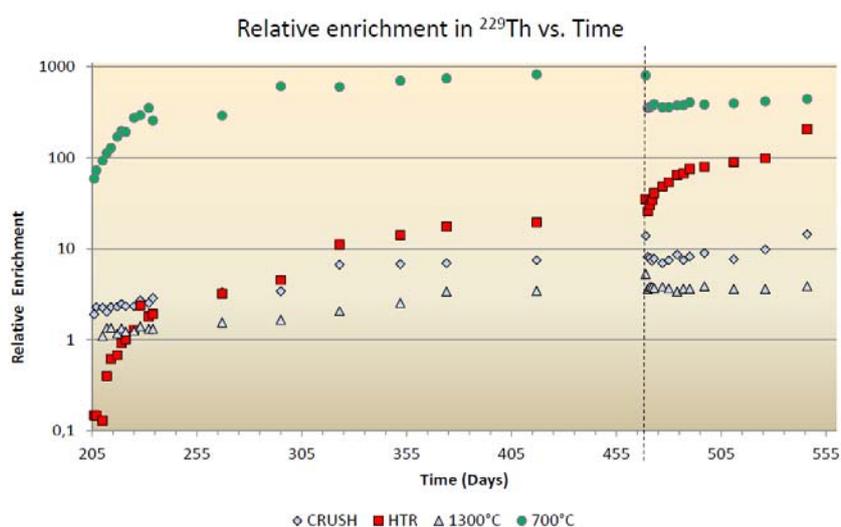
EUROPEAN  
COMMISSION

European  
Research Area

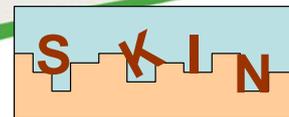


### 2.3 Relative Enrichment for the samples I, II, III and IV

Relative enrichment (RE) values in  $^{229}\text{Th}$  have been calculated for each sample, as described in experimental section. Results are shown in **Figure 7** with logarithmic scale for y-axis. These calculations check that all sample surfaces are more and more rich in  $^{229}\text{Th}$  isotope because RE increases with contact time and is high than 1. The RE values of samples IV, 700°C powder, and II, initial sphere, quickly increase for the first days of contact time after  $^{229}\text{Th}$  addition (between 200 and 250 days) which correspond to the precipitation process of the  $\text{ThO}_x(\text{OH})_y(\text{H}_2\text{O})_z$  phase in grain boundaries (GB) for the Initial sphere case. For the second part of contact time (between 300 and 450 days) a steady-state is measured for all the samples with for higher than 10 RE values (samples IV and II with GB) a dynamic isotopic exchange between the surface and the solution; and for the other samples (I and III without GB) with RE values lower than 10 a pseudo equilibrium state with no Th isotopes exchange between the surface and the solution. For the last part (between 450 and 550 days of contact time) no change in RE values occurs for the samples (I and III) without GB because of the slow dissolution process of the  $\text{ThO}_2$  crystallized grains ( $5 < \text{RE} < 10$ ). Moreover, no change occurs too for the samples IV (700°C powder) due to the thermodynamic solubility equilibrium reached for this system by the main  $\text{ThO}_x(\text{OH})_y(\text{H}_2\text{O})_z$  phase control with an high RE value ( $300 < \text{RE} < 400$ ). However, for the Initial sphere (sample II) the same behaviour than for the first part is observed but it is relied on the redissolution process of the  $\text{ThO}_x(\text{OH})_y(\text{H}_2\text{O})_z$  phase into the GB with RE value close to the sample IV ( $\sim 100$ ).



**Figure 7:** Relative Enrichment in  $^{229}\text{Th}$  in Log scale =  $f(\text{contact time})$  for Samples (I) Crushed  $\text{ThO}_2$  sphere, (II) Initial  $\text{ThO}_2$  spheres, (III)  $\text{ThO}_2$  powder synthesized at 1300°C and (IV)  $\text{ThO}_2$  powder synthesized at 700°C at pH = 3.2.



### Conclusions and Future work

We have described the different behaviour of the surfaces of ThO<sub>2</sub> versus the surface crystalline state. The use of the isotopic <sup>229</sup>Th/<sup>232</sup>Th exchange assesses the key issue of this Workpackage: the realistic solubility behaviour of the ThO<sub>2</sub> surface. We have classified the 4 sets of solid samples versus the leaching behaviour: (IV) > (II) > (I) = (III) with (I) Crushed ThO<sub>2</sub> spheres, (II) Initial ThO<sub>2</sub> spheres, (III) ThO<sub>2</sub> powder synthesized at 1300°C, (IV) ThO<sub>2</sub> powder synthesized at 700°C. Moreover, the behavior of the solid versus the <sup>229</sup>Th/<sup>232</sup>Th exchange occurs if the ThO<sub>x</sub>(OH)<sub>y</sub>(H<sub>2</sub>O)<sub>z</sub> phase is implied into the solid surface leaching. Moreover, three kinds of surfaces of the ThO<sub>2</sub> have been studied:

1) Powder synthesized at low temperature (700°C): this surface displays a low crystallinity with a strong control of the thermodynamic solubility by the ThO<sub>x</sub>(OH)<sub>y</sub>(H<sub>2</sub>O)<sub>z</sub> phase. The curve of relative enrichment in <sup>229</sup>Th isotope vs. the contact time gives the high exchange between the surface and the solution in order to reach this thermodynamic equilibrium.

2) Initial HTR sphere of ThO<sub>2</sub>: this surface presents a high crystallinity but with grain boundaries (GB). In this case it is the accessibility of the GB phase, probably the same phase that ThO<sub>x</sub>(OH)<sub>y</sub>(H<sub>2</sub>O)<sub>z</sub>, which control the dissolution/precipitation/redissolution mechanisms. These processes have been checked by SEM analysis where the grain size of ThO<sub>2</sub> clearly evolves during the contact time. The curve of relative enrichment in <sup>229</sup>Th isotope vs. the contact time makes the evidence that the high slope value of the RE corresponds to the precipitation process and for the second one the redissolution process of the GB phase.

3) Powder synthesized at high temperature (1300°C) and the crushed HTR sphere: these both samples present exactly the same behavior for all the 500 days of solid/solution contact experiment. These surfaces present a high crystallinity without GB. The main process is the slow dissolution of the ThO<sub>2</sub> crystallized grains which is validated by the slow evolution of the RE curve slope. In this case, the thermodynamic solubility cannot be reached before a higher contact time than in our study (500 days).

The future and complementary work which can be performed is the modelisation of our experimental data in order to propose dissolution/precipitation mechanisms of the ThO<sub>2</sub> in solution, in particular by taking into account the ThO<sub>x</sub>(OH)<sub>y</sub>(H<sub>2</sub>O)<sub>z</sub> phase which can be described as a solution-solid at the solid surface.

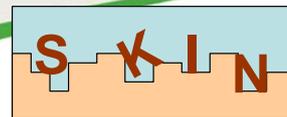
### Acknowledgement

We acknowledge N.Stephant for SEM measurements from the “Institut des Matériaux Jean Rouxel” laboratory.



EUROPEAN  
COMMISSION

European  
Research Area



*The research leading to these results has received funding from the European Union's European Atomic Energy Community's (Euratom) Seventh Framework Programme FP7-Fission-2010 under grant agreement n° 269688 (SKIN project).*

## References

Heisbourg, G., 2003. Synthèse, caractérisation et études cinétique et thermodynamique de la dissolution de  $\text{ThO}_2$  et des solutions solides  $\text{Th}_{1-x}\text{M}_x\text{O}_2$  ( $\text{M} = \text{U}, \text{Pu}$ ), Ph.D. Université Paris XI, Orsay.

Müller, A., 2006. Establishment of the technology to manufacture uranium dioxide kernels for PBMR fuel. Proceedings HTR2006 : 3rd International Topical Meeting on High Temperature Reactor Technology B00000070.

Oktay, E., Yayli, A., 2001. Physical properties of thorium oxalate powders and their influence on the thermal decomposition. Journal of Nuclear Materials 288, 76-82.

Rand, M., Fuger, J., Neck, V., Grenthe, I., Rai, D., 2008. Chemical Thermodynamics of Thorium. North Holland Elsevier Science Publishers B. V., Amsterdam, The Netherlands.

Vandenborre, J., Grambow, B., Abdelouas, A., 2010. Discrepancies in Thorium Oxide Solubility Values: Study of Attachment/Detachment Processes at the Solid/Solution Interface. Inorganic Chemistry 49, 8736-8748.