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# Oxidation of plutonium dioxide: an X-ray absorption spectroscopy study [☆]

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## Abstract

X-ray absorption spectroscopy experiments were conducted in order to characterise plutonium dioxide oxidation. It is shown that the sample preparation adopted does not enable elaboration of hyperstoichiometric plutonium dioxide. These results could mean that plutonium dioxide oxidation only occurs under very specific conditions.

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## 1. Introduction

X-ray absorption spectroscopy (XAS) allows to probe both the oxidation state and the atomic local environment of the absorbing atom. To our knowledge, very few studies using synchrotron radiation have been reported with respect to nuclear fuels. Jones et al. [1 and references therein] showed that the presence of defects in non-stoichiometric uranium oxides is easily demonstrated by this technique. Recently, Martin et al. [2] confirmed that uranium and cerium mixed oxide form an ideal solid solution for cerium concentrations ranging between 0 and 50 at.%. The chemical state of molybdenum in uranium dioxide has also been studied using this technique [3]. An experimental programme based on the study of xenon and krypton atoms implanted in unirradiated uranium dioxide samples is currently underway. This programme should generate the data necessary to ascertain calculation hypotheses made in the parallel theoretical approach [4].

In the present paper, we propose to highlight the benefits of XAS to characterize plutonium dioxide oxidation revealed by Haschke et al. [5]. This potential oxidation has to be taken into account for transmutation experiments especially for once-through targets containing plutonium dioxide. Indeed, during final storage of such targets in a geological repository this potential effect must be taken into account. After a description of the sample preparation and fitting procedures, the results obtained are presented and discussed.

## 2. Sample preparation

$PuO_{2.00\pm0,02}$ was prepared from a pure Pu(IV) nitrate solution by a conventional oxalate conversion. The precipitation stage was carried out using similar chemical

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[☆] In the intervening time between the acceptance of the paper and its publication the department has been struck by the tragic loss of Thierry Petit at the age of 33. He was at the head of the LLCC, the laboratory which he had founded four years ago, and was unanimously recognised by his friends and colleagues as a brilliant scientist whose competence, knowledge and enthusiasm were inspiring. Thierry was a very kind hearted person, perpetually attentive to his colleagues' personal situations. He was also a husband and father of two young children and his friends and colleagues extend their deepest sympathies to his grieving family. He will be sorely missed by all.

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conditions (acidity, oxalate concentration) to those used in the Plutonium Facilities at the La Hague plant in France. This precipitate was then converted into $PuO_2$ by firing at 923 K for 1 h in argon to obtain:

- a powder with a specific surface ranging from 10 to 20 $m^2\,g^{-1}$ which enhances the expected reaction rate with water,
- a crystal lattice order suitable for structural investigations (X-ray diffraction (XRD) and XAS).

This product was then transferred in a 2 l tubular furnace fitted with seals, internal thermocouples, an attachment to a moisturised argon delivery system (argon saturated with water at 323 K) and a filter-protected gas evacuation.

The reaction of the oxide with water was investigated by exposing the $PuO_2$ powder to a flow of moisturised argon (around 5 $ml\,min^{-1}$) at 613 ± 10 K for 900 and 1800 h.

The expected chemical reaction, according to Haschke et al. [5], is:

$$PuO_{2,00} + xH_2O \rightarrow PuO_{2+x} + xH_2$$

According to the kinetic data taken from their experiments, a reaction rate of about 750 nmol $O\,m^{-2}\,h^{-1}$ was assumed at 613 K.

After a 900 h exposure to water vapour at this temperature and with a specific area of the oxide ranging from 10 to 20 $m^2\,g^{-1}$, $x$ was expected to reach the maximum value of 0.27 obtained by Haschke et al. [5] (assuming neither surface chemistry nor unknown catalytic effects significantly affect the reaction rate).

## 3. Results and discussion

The XAS experiment took place at the Laboratoire pour l'Utilisation du Rayonnement Électromagnétique (LURE) in France on beam line D44. For each sample, both extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge spectroscopy (XANES) spectra were recorded in transmission mode at the plutonium $L_3$ edge ($E = 18\,057$ eV). Energy calibration of the XANES data was achieved using a Zr foil ($E = 17\,998$ eV) positioned after the second ionization chamber.

We used Newville's IFEFFIT program [6] for both extracting EXAFS oscillations from the raw absorption spectra and for data analysis. To extract metric parameters (neighbouring atomic distances ($R$), mean squared radial displacements or EXAFS Debye–Waller factors ($\sigma^2$), coordination numbers ($N$)) from the EXAFS, backscattering amplitudes and phase shift functions are calculated using FEFF8.10 [7]. They are then optimised using the IFEFFIT code. Fourier transforms of the $k^3$-weighted data were calculated for $k$ values in the range 24–140 $nm^{-1}$. Curve fitting was performed for $R$-values in the range 0.13–0.43 nm. The amplitude reduction factor ($So^2$) [8] is fixed to 0.9. This value reproduces the theoretical coordination number of 8 for the first oxygen neighbours in the $PuO_2$ fluorite structure.

The space group of plutonium dioxide is $Fm\bar{3}m$ with a cell parameter $a$ of 0.5394 ± 0.004 nm (measured by XRD on our $PuO_2$ reference). In our calculations, plutonium and oxygen atoms are placed in (0,0,0) and (0.25,0.25,0.25) positions respectively. Each XAS spectrum is compared with the $PuO_2$ standard.

The two samples presented here were thermally treated for 900 and 1800 h respectively. Irrespective of

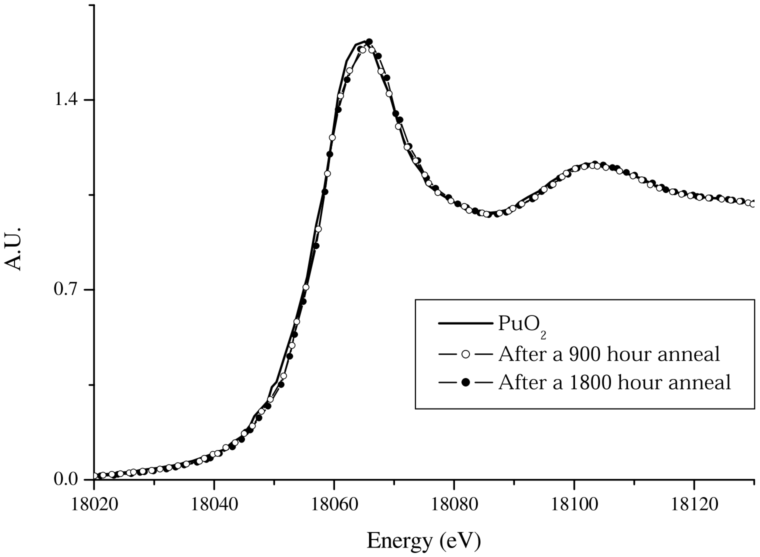

Fig. 1. XANES Pu $L_3$ edge spectra of $PuO_2$ standard and samples thermally treated over 900 and 1800 h periods at 613 K.

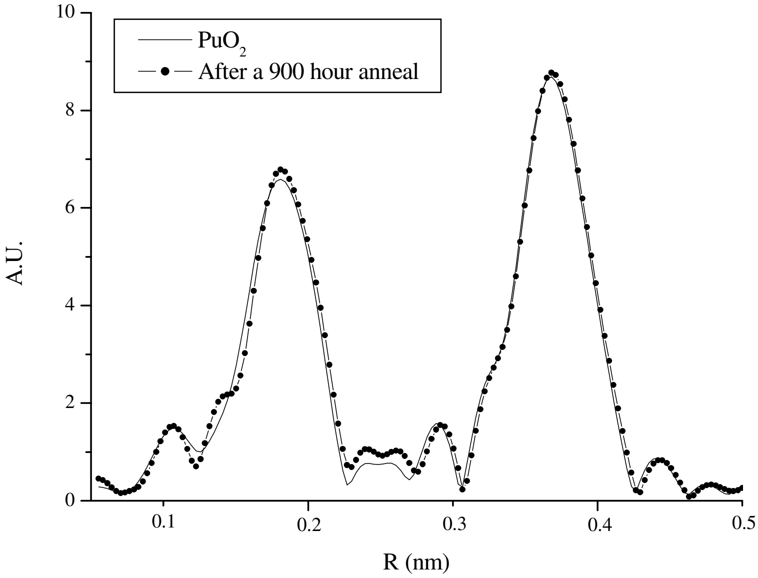

Fig. 2. Comparison of Fourier transform data for PuO$_2$ standard and sample thermally treated over a 900 h period at 613 K.

Table 1
Coordination results obtained from Pu L$_3$ EXAFS analysis

| Sample | Atom pair | $R$ (nm) | $R$ (nm) XRD | $N$ | $\sigma^2$ ($\times 10^{-2}$nm$^2$) | $R_f$-factor |
|---|---|---|---|---|---|---|
| PuO$_2$ | Pu–O | $0.2330 \pm 0.0005$ | 0.2336 | 8 | $0.0065 \pm 0.0004$ | 0.011 |
| | Pu–Pu | $0.381 \pm 0.001$ | 0.3814 | 12 | $0.0049 \pm 0.0001$ | |
| | Pu–O | $0.446 \pm 0.002$ | 0.4472 | 24 | $0.008 \pm 0.001$ | |
| PuO$_2$ 900 h | Pu–O | $0.2333 \pm 0.0005$ | 0.2336 | $8.0 \pm 0.5$ | $0.0065 \pm 0.0004$ | 0.0099 |
| | Pu–Pu | $0.381 \pm 0.001$ | 0.3814 | $12.0 \pm 0.5$ | $0.0048 \pm 0.0001$ | |
| | Pu–O | $0.445 \pm 0.002$ | 0.4472 | $24 \pm 2$ | $0.008 \pm 0.001$ | |
| PuO$_2$ 1800 h | Pu–O | $0.2329 \pm 0.0005$ | 0.2336 | $8.0 \pm 0.5$ | $0.0065 \pm 0.0004$ | 0.0145 |
| | Pu–Pu | $0.381 \pm 0.0005$ | 0.3814 | $12.0 \pm 0.5$ | $0.0049 \pm 0.0001$ | |
| | Pu–O | $0.445 \pm 0.002$ | 0.4472 | $24 \pm 2$ | $0.008 \pm 0.001$ | |

the thermal anneal time, the intensity and position of the white lines in the XANES spectra are identical to those of the PuO$_2$ reference sample as shown in Fig. 1. As a consequence, we can say that the oxidation state of a majority of plutonium ions remains equal to +IV and the local symmetry around plutonium atoms does not appear to vary.

The Fourier transforms of the EXAFS spectra are presented in Fig. 2. The numerical values obtained from the fitting procedure are given in Table 1. The overall quality of the fit evaluated by IFEFFIT is given as the '$R_f$-factor' in the last column of the Table 1 ($R_f = 0.01$ signifies that theory and data agree within 1%). As we can see in Fig. 2, the two spectra are almost identical and the numerical values confirm that the thermally treated samples remain strictly stoichiometric under these oxidising conditions.

## 4. Conclusion

XAS experiments were conducted in order to characterise plutonium dioxide oxidation but they showed that the sample preparation adopted does not enable elaboration of hyperstoichiometric plutonium dioxide. These results could mean that plutonium dioxide oxidation only occurs under very specific conditions. Another study using different oxidising conditions is in progress.

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