Actinide Speciation in Nuclear Fuel: From Aqueous Solution to Solid Solution

‘Degueldre C

‘Engineering Department, University of Lancaster, Lancaster LA1 4YW, UK

Abstract

Oxide fuels are currently used in the nuclear reactors. The study of the actinides atomic environment in homogeneous non-irradiated/irradiated fuel samples was performed employing x-ray fluorescence and x-ray absorption fine structure spectroscopy. This investigation is important from a safety view because the actinides can undergo various redox states going from III to VII contributing to specific chemical properties in the beginning of the family. Chemical bounds, valences and stoichiometries of the actinides (Th, U, Np, Pu, Am, Cm) are determined from the experimental data gained for the irradiated fuel material examined in its center location and peripheral zone of the fuel as well as when possible for the non-irradiated fuel. Their data are compared with those recorded for AnO₂ compounds. The speciation of these actinides in the oxide fuel samples have also been investigated by thermodynamic modeling taking into account recent chemical data. The actinides in nuclear fuels display redox states starting with IV for the lighter toward III for the heavier. Their state is buffered by uranium which undergoes slight oxidation toward its pentavalent state.

Keywords

Actinides; Redox State; Nuclear Fuel; X-ray Absorption Spectroscopy; Gibbs Energy Minimisation

1. Introduction

The light actinides (An) are well known to display a large range of redox state in aqueous or non-aqueous solutions. These correspond to solvated An⁺离子 which electronic structures range from 5f⁰ (empty shell) for Th³⁺ to 5f⁷ (half filled shell) for Cm³⁺ or Bk⁴⁺. These solvated species also develop consequently also a large range of colors (Table 1) corresponding to the complementary color of their main absorption bands [1, 2]. Starting from Ac³⁺, Th⁴⁺ PaO²⁺ as well as Cm³⁺ and Bk⁴⁺ that are colorless or pale (e.g. absorption band in UV) they can show most of the colors for the visible spectrum.

In solid state and specifically in the case of oxides they exhibit various darker colors according to their stoichiometries of mono-, sesqui-, bi-, hemipent-, tri-oxides. These colors are also function of their electronic structure in the oxide lattice. They range from 5f⁰ (Ac⁴⁺ in AcO₁.₅, Th⁴⁺ in ThO₂, Pa⁴⁺ in PaO₂.₅) to 5f⁷ (Am²⁺ in AmO, Cm³⁺ in CmO₁.₅ or (yellow) Bk⁴⁺ in BkO₂). Here again, ThO₂ is colorless white (absorbs in UV) and UO₃ is red (absorbing in blue), while most of the other oxides are dark along the series, absorbing through the visible domain.

*Corresponding author: Degueldre C, Engineering Department, University of Lancaster, Lancaster LA1 4YW, UK. E-mail: c.degueldre@lancaster.ac.uk

Received June 21, 2017; Accepted October 12, 2017; Published October 25, 2017


Copyright: © 2017 Degueldre C. This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original author and source are credited.
Since UO₂ is black, detection of actinide valence state using visible spectroscopy such as diffuse reflection spectroscopy is difficult. The X-ray absorption fine structure spectroscopy (XAFS) is however less sensitive to matrix interference. XAFS has been applied to characterize actinide compounds taking advantage of the analytical characteristics of their L₃ edge for determining their redox and coordination state.

In this frame several studies were performed by Nische and co-workers along the nuclear fuel cycle going from the mine environment to the repository environment [3, 4]. Even if Nische’s focus was targeting on uranium and plutonium [5, 6], he got a broad overview on environmental actinide science [7] among other thanks to his vision and action developing the Rossendorf beam line (ROBL) a dedicated experimental station for XAFS measurements of actinides and other radionuclides [8].

The purpose of this work is to complete what Nitsche could unfortunately not be able to perform (for regulatory reasons) on ROBL and to summarize the results recorded so far at the micro XAS, PSI for actinides in irradiated MOX along with results obtained from the analysis of Np in UO₂, to depict in a comprehensive way the actinide redox behavior in UO₂ fuel. The light actinides Th, U, Np, Pu, Am and Cm atom environments in non-irradiated and irradiated MOX picture are also confirmed by thermodynamic modeling of these actinides in the fuel.

2. Actinide XAS Analysis Background

Even if the actinides display one K and three L edges, the work is generally carried out on the L₃ edges that provide more sensitivity for analytical purpose.
Consequently in (non-)irradiated fuel the accessible An XAFS edges are the L3 edges recorded in transmission or reflection mode within the 16200 to 19000 eV range. Prior analysis it is relevant to track the elements that could interfere. These interfering elements would exhibit K lines in this energy domain. Sr at 16105 eV, Y at 17038 eV, Zr at 17998 eV and Nb at 18986 eV do not interfere because their concentration as fission product is not larger that the actinide to study and because the fluorescence line can be well discriminated.

The evaluation of the redox state \( X \) of An(\( X \)) or of AnO\(_{X/2}\) is based on the XAFS data gained from the XAFS spectra: \( I = f(E) \) with \( I \) the normalized intensity recorded as a function of the photon incident energy \( E \).

The comparison of An XAFS in their pure dioxides (AnO\(_2\)) show that the first absorption peak (white line) decreases when their atomic number increases. This may be ascribed to the well known actinide radius contraction [9], its reduction of distance absorbent – next neighbor (R(An-O)) and its direct effect on the first wave (absorption peak or first maximum intensity: IM). Clearly from the analysis of the spectra three parameters connected to the redox and coordination state of the actinide may be easily gained:

\[
E_0 \text{ may be determined} \quad \frac{dI}{dE} = 0 \quad (1)
\]

R(An-O):

\[
\frac{d}{dR} | FT k^n | = 0 \quad (2)
\]

Finally, \( I_M \) is defined as

\[
\frac{dI}{dE} = 0 \quad (3)
\]

With \( x \) the normalized absorption and \( kn \) the n pondered wave vector.

Actinide XAFS data are however limited in their exploitation by the precision they can be recorded. \( E_0 \): precision and accuracy are of the order \( \pm 1 \) eV; R(An-O): a precision of \( \pm 0.02 \) Å, and \( I_M \): a precision of \( \pm 5 \% \).

The quality of the data is linked to signal noise, smoothing, damping, \( k \) window filtering, phase correction and calibration. The calculated fraction of An(\( X \)) can then reach a 10 % precision.

3. Experimental

Mixed oxide (MOX) fuels have been irradiated since more than 35 years in Europe. MOX fuel has been used since 35 years in Switzerland. MOX reached high burn-up in Swiss PWR’s during the late 80ies.

The fuel material examined here is a homogeneous MOX prepared at PSI by internal solgel method followed by calcinations and sintering. The final (4.7 wt% Pu at beginning of live (BOL)) PuUO\(_2\) product was irradiated for 6 years up to a burn-up of 60 MW d kg\(^{-1}\) in the Pressurized Water Reactor of Beznau, Switzerland. Plutonium underwent production of americium and curium as well as of fission products while trace amount of thorium were also found at BOL and end of live (EOL). All \( \beta \) decays or neutron captures of actinide did not induce atom displacement in the UO\(_2\) fuel matrix. Actinide, fission products and other trace components are given in.

Figure 1: Composition (weight fraction) of the Non Irradiated Sample as Analyzed at BOL Composition of Irradiated Fuel as Calculated by ORIGEN at EOL.
4. Actinide XAS Analysis Results

Actinides may form a priori a solid solution in the fuel. The fuel matrix of UO₂ crystallizes in a cubic structure as depicted in UO₂ fluorite super cell with 295 ions (78 uranium, 8 plutonium, 1 actinide and 208 oxygen ions). This super cell is used to model the XAFS data and to derive the actinide – oxygen distances and next neighbor number in case of vacancies.

Figure 2: UO, Fluorite Super cell with 295 Ions (78 Uranium, 8 Plutonium, 1 Absorber Actinide and 208 oxide Ions).

The actinide spectra recorded in the fuel are given in for comparison.

Figure 3: Actinide Spectra Recorded in the Fuel. Note the Reduction of the White Line Along the Actinide Series. Conditions: in MOX: Th, Pu, Am, Cm (all in Fluorescence Mode) and U (in Fluorescence & Transmission), and in UO₂, Np (in Fluorescence Mode).

The XAFS data gained from Fig 3 spectra are reported in Table 2.

Table 2: Comparing for Th, U, Pu, Np, Am, Cm in Fuel the L3 edge Energy (E₀ and Eₘ), Actinide – Oxygen Distances and White Line Intensity. Note: the Underlined X Value is Estimated from the XAFS Data.

<table>
<thead>
<tr>
<th>An</th>
<th>E₀ ±1(eV)</th>
<th>Eₘ ±1(eV)</th>
<th>ΔE (eV)</th>
<th>R(An-O) ±0.01(Å)</th>
<th>AnO₂ IM ±0.05(-)</th>
<th>Fuel IM ±0.05(-)</th>
<th>Redox state An(X)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Th</td>
<td>16299</td>
<td>16304</td>
<td>5±1</td>
<td>2.41</td>
<td>2.33-1.93</td>
<td>2.10-1.97</td>
<td>Th(IV)</td>
</tr>
<tr>
<td>U</td>
<td>17171</td>
<td>17177</td>
<td>6±1</td>
<td>2.37</td>
<td>1.70</td>
<td>1.71-1.54</td>
<td>U(IV-V)</td>
</tr>
<tr>
<td>Np</td>
<td>17615</td>
<td>17619</td>
<td>4±1</td>
<td>2.366</td>
<td>1.74</td>
<td>1.68</td>
<td>Np(IV)</td>
</tr>
<tr>
<td>Pu</td>
<td>18057</td>
<td>18061</td>
<td>4±1</td>
<td>2.34-2.39</td>
<td>1.59</td>
<td>1.68-1.62</td>
<td>Pu(III-IV)</td>
</tr>
<tr>
<td>Am</td>
<td>18513</td>
<td>18515</td>
<td>2±1</td>
<td>2.33-2.38</td>
<td>1.60</td>
<td>1.67</td>
<td>Am(III)</td>
</tr>
<tr>
<td>Cm</td>
<td>18972</td>
<td>18978</td>
<td>6±2</td>
<td>2.32-2.37</td>
<td>1.40</td>
<td>1.65</td>
<td>Cm(III)</td>
</tr>
</tbody>
</table>

For thorium in U₀.₉₆Pu₀.₀₄O₂ (non-)irradiated MOX samples spectra show similar [11]. With E₀ = 16299 eV, R(Th-O) = 0.241 nm and I_m values ranging from 2.33 to 1.93, thorium is definitely Th⁴⁺ in the fuel.

Uranium in U₀.₉₆Pu₀.₀₄O₂ irradiated MOX samples show similar spectra because XAFS is not sensitive enough to record any small redox change due to burn-up. For U the data are: E₀ = 17171 eV, R(U-O) = 0.237 nm and I_m = 1.70 – 1.55, consequently uranium is mainly U⁴⁺.

For neptunium, data [12] were obtained from Np in U₀.₉Np₀.₁O₂ fuel and were: E₀ = 17615 eV, R(Np-O) = 2.366 Å and I_m = 1.68. Neptunium is consequently Np⁴⁺.

Plutonium redox in MOX fuel is likely to remain unchanged during burn-up [10]. The data for Pu are: E₀ = 18057±2 eV, R(Pu-O) = 0.234 nm and I_m = 1.62-1.68. Consequently plutonium is mostly Pu⁴⁺.

Americium in the investigated U₀.₉₆Pu₀.₀₄O₂
irradiated MOX sample [13] shows data from the spectra: 
\[ E_0 = 18513 \text{ eV}, \quad R(\text{Am-O}) = 0.238 \text{ nm} \quad \text{and} \quad I_M = 1.67, \]

consequently americium is Am\(^{3+}\).

Curium in U\(_{0.96}\)Pu\(_{0.04}\)O\(_2\) irradiated MOX shows similar spectra [13] as Am. The data are: \[ E_0 = 18972 \text{ eV}, \quad R(\text{Cm-O}) = 0.237 \text{ nm} \quad \text{and} \quad I_M = 1.65. \] Similarly Cm is Cm\(^{3+}\).

Clearly from Table 2 it can be seen that,

- \( \Delta E = E_M - E_0 \)
- Both \( R(\text{An}^{4+}-\text{O}) \) and \( R(\text{An}^{3+}-\text{O}) \) values follow the actinide ionic radius compression along the actinide series [15].
- \( R(\text{An}^{4+}-\text{O}) < R(\text{An}^{3+}-\text{O}) \) as expected.
- \( I_M \) reduces subsequently along the actinide series.

The analysis of the actinides in fuel as well as in their dioxide is carried out on the basis of the \( I_M \) vs. \( R(\text{An-O}) \).

**Figure 4:** Comparing White Line Intensity and Actinide – Oxygen Distance for Th, U, Pu, Np, Am, Cm in AnO\(_2\) and Nuclear Fuel.

### 5. Thermodynamic Modelling Results

In the fuel the actinides interact together according to reactions that can be modeled on the basis of their thermodynamic properties. The reactions are:

\[ 2\text{AnO}_{1.5} + 4\text{UO}_2 \Leftrightarrow 2\text{AnO}_2 + 4\text{UO}_{2.25} \quad (1) \]

and/or

\[ 4\text{UO}_2 + 2\text{AnO}_2 \Leftrightarrow 4\text{UO}_{2.25} + 2\text{AnO}_{1.5} \quad (2) \]

The thermodynamic approach is based on the calculation of the free energy of reaction \( G^0_r \). The approach discriminates the actinide oxide behavior with regards to their solubility within the matrix UO\(_2\) as well as with all actinide oxide phases accounting their segregation or the formation of ideal or non ideal solid solution.

If the reaction takes place in separate phases then the free energy of reaction becomes:

\[ G^0_r = \sum G^0_j(\text{products}) - \sum G^0_j(\text{reactants}) \quad (4) \]

With \( G^0_j \) the free energy of formation of the individual products or reactants.

If the reaction takes place in ideal solid solution the free energy is corrected:

\[ \Delta G_{\text{total}} = G^0_r + \Delta G^0_{\text{mix}} \quad \text{with} \quad \Delta G^0_{\text{mix}} = RT \sum_{i=1}^{n} X_i \ln X_i \quad (5) \]

With \( X_i \) the molar fraction of the solid solution components.

In reality, the reaction takes place in non-ideal solid solution and the free energy becomes:

\[ \Delta G^0_{\text{mix}} = G^0_r + \Delta G^0_{\text{ex}} + \Delta G^0_{\text{id}} \quad \text{with} \quad \Delta G^0_{\text{ex}} = X_A X_B (w_{AB} X_A + X_B) \quad (6) \]

Where \( G^0_{\text{ex}} \) depends upon the interactions among the end-members (A&B) and with \( X_A \) and \( X_B \) are the molar fractions of the end-members and \( w_{AB} \) and \( w_{BA} \) are the Margules interaction parameters, with \( w_{AB} \neq w_{BA} \).

All possible reaction of actinide oxides with the fuel matrix may be evaluated on the basis of the thermodynamic data of these oxides [14]. The Gibbs energy of reaction (kJ mol\(^{-1}\) of the actinide oxides with UO\(_2\) at 300 – 1300 K were calculated. The initial actinide concentrations used in the calculations are the composition in spent fuel after burn-up given in [4].

The results obtained so far are depicted in Figure 5 for the separated phases the ideal and non-ideal solid solution as well as for the fuel at low temperature e.g. periphery of the fuel, and high temperature i.e. center of the fuel.
Clearly because of its oxidative properties, Am$^{4+}$ (AmO$_2$) reduce to Am$^{3+}$ or AmO$_{1.5}$ for all cases treated confirming the XAFS result. On the other side, plutonium may slightly (<5%) reduce and that is mainly the case in solid solution at higher temperature which cannot be assessed by XAFS. Curium is definitely trivalent in the fuel and it can be anticipated that both Bk and Cf shall also be trivalent.

6. Conclusion

The speciation of actinides in the oxide fuel samples has also been investigated successfully by x-ray absorption spectroscopy. The provided data ($E_0$, R(An-O) and $I_0$) for the actinides in the fuel were analyzed with emphasis on their redox properties. The reference remains thorium with Th$^{4+}$ and its $5f^0$ electronic structure. For the other actinides UO$_2$ may act as a reducer buffering the fuel. Neptunium keeps its tetravalent state. Plutonium also while minor fractions of Pu(III) are derived from the thermodynamic model. Both americium and curium reduce to Am$^{3+}$ and Cm$^{3+}$.

The actinides in nuclear fuels display redox states starting with IV for the lighter toward III for the heavier. Their state is buffered by uranium which undergoes slight oxidation toward its pentavalent state. The actinide redox states in the fuel are summarized in Table 3.

Table 3: Actinide Oxide XAFS Speciation for UOX and MOX fuel. Note for UO$_{2.5}$, PuO$_{1.5}$ and AmO$_2$ Fractions see Figure 5.

<table>
<thead>
<tr>
<th>redox</th>
<th>89</th>
<th>90</th>
<th>91</th>
<th>92</th>
<th>93</th>
<th>94</th>
<th>95</th>
<th>96</th>
<th>97</th>
<th>98</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AcO$_{1.5}$</td>
<td>AcO$_{1.5}$</td>
<td>AcO$_{1.5}$</td>
<td>AcO$_{1.5}$</td>
<td>AcO$_{1.5}$</td>
<td>AcO$_{1.5}$</td>
<td>AcO$_{1.5}$</td>
<td>AcO$_{1.5}$</td>
<td>AcO$_{1.5}$</td>
<td>AcO$_{1.5}$</td>
</tr>
<tr>
<td>+2</td>
<td>ThO$_2$</td>
<td>ThO$_2$</td>
<td>ThO$_2$</td>
<td>ThO$_2$</td>
<td>ThO$_2$</td>
<td>ThO$_2$</td>
<td>ThO$_2$</td>
<td>ThO$_2$</td>
<td>ThO$_2$</td>
<td>ThO$_2$</td>
</tr>
<tr>
<td>+3</td>
<td>PaO$_{2.5}$</td>
<td>PaO$_{2.5}$</td>
<td>PaO$_{2.5}$</td>
<td>PaO$_{2.5}$</td>
<td>PaO$_{2.5}$</td>
<td>PaO$_{2.5}$</td>
<td>PaO$_{2.5}$</td>
<td>PaO$_{2.5}$</td>
<td>PaO$_{2.5}$</td>
<td>PaO$_{2.5}$</td>
</tr>
<tr>
<td>+4</td>
<td>UO$_2$</td>
<td>UO$_2$</td>
<td>UO$_2$</td>
<td>UO$_2$</td>
<td>UO$_2$</td>
<td>UO$_2$</td>
<td>UO$_2$</td>
<td>UO$_2$</td>
<td>UO$_2$</td>
<td>UO$_2$</td>
</tr>
<tr>
<td>+6</td>
<td>PuO$_2$</td>
<td>PuO$_2$</td>
<td>PuO$_2$</td>
<td>PuO$_2$</td>
<td>PuO$_2$</td>
<td>PuO$_2$</td>
<td>PuO$_2$</td>
<td>PuO$_2$</td>
<td>PuO$_2$</td>
<td>PuO$_2$</td>
</tr>
<tr>
<td>+7</td>
<td>AmO$_{1.5}$</td>
<td>AmO$_{1.5}$</td>
<td>AmO$_{1.5}$</td>
<td>AmO$_{1.5}$</td>
<td>AmO$_{1.5}$</td>
<td>AmO$_{1.5}$</td>
<td>AmO$_{1.5}$</td>
<td>AmO$_{1.5}$</td>
<td>AmO$_{1.5}$</td>
<td>AmO$_{1.5}$</td>
</tr>
<tr>
<td>+8</td>
<td>CmO$_{1.5}$</td>
<td>CmO$_{1.5}$</td>
<td>CmO$_{1.5}$</td>
<td>CmO$_{1.5}$</td>
<td>CmO$_{1.5}$</td>
<td>CmO$_{1.5}$</td>
<td>CmO$_{1.5}$</td>
<td>CmO$_{1.5}$</td>
<td>CmO$_{1.5}$</td>
<td>CmO$_{1.5}$</td>
</tr>
<tr>
<td>+9</td>
<td>BkO$_{1.5}$</td>
<td>BkO$_{1.5}$</td>
<td>BkO$_{1.5}$</td>
<td>BkO$_{1.5}$</td>
<td>BkO$_{1.5}$</td>
<td>BkO$_{1.5}$</td>
<td>BkO$_{1.5}$</td>
<td>BkO$_{1.5}$</td>
<td>BkO$_{1.5}$</td>
<td>BkO$_{1.5}$</td>
</tr>
<tr>
<td>+10</td>
<td>CfO$_{1.5}$</td>
<td>CfO$_{1.5}$</td>
<td>CfO$_{1.5}$</td>
<td>CfO$_{1.5}$</td>
<td>CfO$_{1.5}$</td>
<td>CfO$_{1.5}$</td>
<td>CfO$_{1.5}$</td>
<td>CfO$_{1.5}$</td>
<td>CfO$_{1.5}$</td>
<td>CfO$_{1.5}$</td>
</tr>
<tr>
<td>e structure</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$\kappa$</td>
<td>$5f^0$</td>
<td>$5f^1$</td>
<td>$5f^2$</td>
<td>$5f^3$</td>
<td>$5f^4$</td>
<td>$5f^5$</td>
<td>$5f^6$</td>
<td>$5f^7$</td>
<td>$5f^8$</td>
<td>$5f^9$</td>
</tr>
</tbody>
</table>

In memory of Professor Doctor Heino Nitsche

He did promote the use of X-ray absorption spectroscopy for the characterisation of actinide compounds. We shall never forget his loyalty and his clear vision in Science.

References


