In situ Raman spectroscopy on nuclear materials in hot cell

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Why Raman spectroscopy?

Raman spectroscopy is a powerful technique for analyzing the damage accumulation on nuclear materials (fuels, claddings and containment matrices), a non-contact and non-destructive technique and do not necessarily require special preparation.
DHA (High Activity Wastes) Atalante:

- 2 shielded lines compatible with very high-activity materials coming from industrial facilities (ex: fuel and fuel cladding from PWR) or produced in research laboratories.
- The aim of these shielded lines is to study the long-term behavior of high-level waste conditioning matrices (glass, ceramics, spent fuel).

**Shielded line C18**

- Solid sample preparation
- Physico-chemical measurements
- Vitrification
- Leaching behavior studies
- In situ Raman

**Shielded line C19**

- Physical measurement

Chemistry of spent fuel treatment/recycling, waste management, and fuel cycle processes.
Raman spectrometer coupled to a hot cell

In situ system

DHA Atalante Marcoule facility
DHA (Déchets de Haute Activité): High Activity Wastes
I. Oxidation of fuel cladding: zirconia
  - Zirconia irradiations with external ions beams
  - Fuel cladding coming from PWR

II. Nuclear fuels
  - Uox and Mox
    - Long-term interim storage

III. Simulated corium
  - Initial characterizations
  - Long-term interim storage

Conclusions
Oxidation of fuel cladding: Zirconia

**Industrial context**

The fuel cladding in Pressurized Water Reactor (PWR) is Zirconia (ZrO₂). The reaction between water and zirconium is given by:

\[
2H_2O + Zr \rightarrow ZrO_2 + 2H_2
\]

**Sources of radiation**

- Ionizing radiations: 99.7% of the dose induced by X, γ, and β-rays.
- Displacement cascades created by neutrons estimated to 3 dpa (displacements per atom) per year in the metal.

**Fuel rod**

- Water: 300 °C, 155 bars

**Fuel assembly**

- Rod cross-section
In this aggressive aqueous environment, a strong increase of the oxidation rate of Zircaloy-4 fuel cladding is observed for burnups above 35 GWd/MtU.

This oxidation acceleration is not reproduce in static autoclave or in corrosion loop.

Assumption: the acceleration of this oxidation rate will be induced by radiation damage. Necessity to quantify the effect of the oxide layer irradiation on the oxidation rate.
Oxidation of fuel cladding: Zirconia

**In situ Raman**

(M. Tupin and R. Verlet CEA/DMN)

**Model material: ZrO₂**

- Zircaloy-4 corroded in autoclave in PWR simulated conditions:
  - Liquid water at 360°C and a pressure of 187 bars with 2 ppm in mass of lithium from LiOH and 1000 ppm in mass of boron from H₃BO₄.
  - After 40 days a 1.5 µm thick oxide layer (ZrO₂) is formed on the metal.

- Irradiations at the JANNUS (Joint Accelerators for Nano-science and Nuclear Simulation) platform.

To induce ballistic collision

Follow the irradiation damage under ion beam irradiation.
Oxidation of fuel cladding: Zirconia

*In situ* Raman

(M. Tupin, R. Verlet and G. Gutierrez CEA/DMN)

S. Miro et al. J. Raman Spectrosc. 2015

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**ZrO₂ irradiated Au 12-MeV**

**Monoclinic** ➔ **Tetragonal**

**In situ Raman**

Defects band (oxygen vacancies)

Monoclinic reference

Monoclinic ➔ Tetragonal

Cross-section

Oxide

Metal

**Phase diagram**

**Disappearance of the monoclinic phase, in agreement with DRX.**
The irradiation increases the oxidation rate. After the kinetic transition, both samples have similar oxidation rates.

The defects bands disappear after 23 days of re-oxidation.

After re-oxidation, defects disappear and the oxidation rate of the irradiated sample comes back to that of the non-irradiated material.

Raman spectra of the oxide layer irradiated with 1.3 MeV-He at $10^{17}$ cm$^{-2}$ and re-oxidized in PWR conditions.

Slopes of the kinetic curves after re-oxidation obtained on the non-irradiated and the irradiated material.

Considering that there is a competition between the production and the annealing of irradiation defects, are the irradiation defects stable during the lifetime of the fuel cladding in reactor?

The same defects bands are present in PWR.
Oxidation of fuel cladding: Zirconia

External ZrO₂

(M. Tupin CEA/DMN)

The presence of defects seems to be responsible of the high burnup acceleration.

Oxidation occurs from the interface.

The presence of irradiation defects (oxygen vacancies) increases the oxidation rate.
Uox and Mox spent nuclear fuel  

- Industrial context

Fabrication

Uox and Mox

Lifetime in reactor

Interim storage

Geological disposal conditions

Radiation damage

Chemical effects

Radiolysis effect at the solid/water interface

Raman spectroscopy efficient to study these effects

\[ \text{UO}_2 \text{ Fluorite} \]

~445 cm\(^{-1}\)  

Defects band
MOX MIMAS (U, Pu)O₂ (7 wt. % Pu)

Comparison of the measured and calculated \( T_{2g} \) positions for the damaged MIMAS MOX disk.

<table>
<thead>
<tr>
<th>EPMA (Electron Probe MicroAnalysis)</th>
<th>RAMAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pu content (%)</td>
<td>( T_{2g} )</td>
</tr>
<tr>
<td>0.24</td>
<td>454</td>
</tr>
<tr>
<td>0.18</td>
<td>452</td>
</tr>
<tr>
<td>0.16</td>
<td>452</td>
</tr>
<tr>
<td>0.12</td>
<td>447</td>
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<td>0.11</td>
<td>447</td>
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<td>0.1</td>
<td>447</td>
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<td>0.07</td>
<td>447</td>
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<tr>
<td>0.05</td>
<td>447</td>
</tr>
<tr>
<td>0.04</td>
<td>446</td>
</tr>
<tr>
<td>0.03</td>
<td>445</td>
</tr>
<tr>
<td>0.02</td>
<td>445</td>
</tr>
<tr>
<td>0.01</td>
<td>444</td>
</tr>
</tbody>
</table>

© M. Gennisson, Z. Talip, M. Magnin, S. Peuget CEA/DE2D

Nuclear fuel ➤ Mox

Comparison of the optical microscope image and EPMA results of \( \text{UO}_2 \) matrix, coating phase and Pu agglomerate

\( T_{2g} \) position in Pu agglomerate and disappearance of the 2LO band.

\( T_{2g} \) position versus Pu content in agreement with the lattice parameter.
While awaiting reprocessing or direct geological disposal, MOX fuel assemblies may be stored underwater in special storage pools for several decades. One incident scenario is to consider that a defect in the fuel cladding could mean direct contact between the water and the fuel matrix. The storage pool conditions favor the precipitation of possible secondary phases U (VI), such as studtite (UO₄.4H₂O).
Segment of failed fuel rod stored during 15 years in storage pool.

Water interaction

Secondary phases U(VI) not identified with possible incorporation of cladding elements or fission products from the fuel.

Where is the main failure and have secondary phases been formed?

Perforated zone 400 μm x 150 μm

Secondary phases U(VI) with Zr or FP?
Simulated Corium

Context

(CEA/DE2D and JAEA)

In the case of severe accident, the materials of the nuclear reactor (nuclear fuel, cladding, metallic alloys, structural materials, concrete, etc…) could melt to form complex and aggressive mixtures called corium.

Fukushima Daiichi nuclear accident 2011

After a removal, medium or long term storages of corium, are one of possible options. This option may include a step of transport and a step of storage in deionized water.

Consequently, leaching data of corium in deionized water are needed before a removal.
Simulated Corium Storage

(CEA/DE2D and JAEA)

Samples of simulated corium: Loading composition of COLIMA CA-U4

- Fuel
- Claddings
- Metallic alloys
- Concrete

Ex vessel sample:
- Temperature ~ 2000°C
- Nitrogen atmosphere

Colima facility

SEM (Scanning Electron Microprobe) analyzes:
- Matrix (U, Zr)O₂ with different ratio of U/Zr
- Fe, Cr inclusions

Raman analyzes:
- Matrix (U, Zr)O₂ crystallizes in the fluorite structure
- The position of the T2g depends of the U/Zr ratio

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO₂</td>
<td>1178</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>498</td>
</tr>
<tr>
<td>Cr</td>
<td>60</td>
</tr>
<tr>
<td>Fe</td>
<td>65</td>
</tr>
<tr>
<td>CaO</td>
<td>73</td>
</tr>
<tr>
<td>SiO₂</td>
<td>80</td>
</tr>
<tr>
<td>MgO</td>
<td>27</td>
</tr>
</tbody>
</table>

Raman analyzes:
- T2g (465-470 cm⁻¹)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Mass (g)</th>
</tr>
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<tbody>
<tr>
<td>SrO</td>
<td>1.3</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>0.7</td>
</tr>
<tr>
<td>MoO₂</td>
<td>4.2</td>
</tr>
<tr>
<td>Ru₂O₃</td>
<td>3.1</td>
</tr>
<tr>
<td>Rh₂O₃</td>
<td>0.6</td>
</tr>
<tr>
<td>TeO₂</td>
<td>0.6</td>
</tr>
<tr>
<td>I₂O₅</td>
<td>0.3</td>
</tr>
<tr>
<td>CsOH (hydrated)</td>
<td>3.9</td>
</tr>
<tr>
<td>BaO</td>
<td>1.8</td>
</tr>
<tr>
<td>CeO₂.ZrO₂</td>
<td>6.5</td>
</tr>
<tr>
<td>Pr₂O₃</td>
<td>1.3</td>
</tr>
<tr>
<td>Nd₂O₃</td>
<td>4.0</td>
</tr>
</tbody>
</table>

| Samples of simulated corium: | Loading composition of COLIMA CA-U4 |

Simulated Fission Products

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</tr>
<tr>
<td>Nd₂O₃</td>
<td>4.0</td>
</tr>
</tbody>
</table>
Simulated Corium ➤ Storage

(CEA/DE2D and JAEA)

Leaching conditions:

- Leaching experiments
  - deionized water
  - at 25°C
  - in air
  - under irradiation.

Fragments of simulated corium

Scheme of the leaching device and photo of the leaching reactor

Raman analyzes after leaching:

- Uranyl phase with Zr and additional elements?

Leaching tests induce precipitation of secondary phases on a few part of the sample.
These analyzes show the interest of using micro-Raman spectroscopy:

- To understand the behavior during usage conditions: in zirconia, the presence of defects seems to be responsible of the high burnup acceleration.

- In fuel: to separate the Pu agglomerate to the UO$_2$ matrix and in long-term storage to study their interaction with storage pool.

- To study corium formed during severe accident and the secondary phases formed after interaction with the surrounding environment.
CONCLUSIONS

The complementarity of these both approaches allows understanding the damage mechanisms of these nuclear materials.

Oxidation of fuel cladding

Nuclear fuels

Nuclear glasses

These analyzes show the interest to continue studies on models materials irradiated by ion beams, to separate different parameters ($S_e$ and $S_n$), but also to observe highly radioactive materials having experienced the actual usage conditions.
Oxidation of fuel cladding: Zirconia

External and internal ZrO₂

- Oxidation occurs from the interface.
- The presence of irradiation defects (oxygen vacancies) increases the oxidation rate.

The presence of defects seems to be responsible of the high burnup acceleration.

- External ZrO₂
- Internal ZrO₂

Monoclinic

Tetragonal
Simulation of the damage accumulation process induced by neutrons in nuclear materials

Study their main consequences on both microstructure and mechanical properties.

- Chemistry of spent fuel treatment/recycling, waste management and fuel cycle processes.
  - 17 laboratories ⇒ radioactive materials in 250 glove boxes
  - 9 shielded lines ⇒ very high activity materials
Simulation of the damage accumulation process induced by neutrons in nuclear materials
Study their main consequences on both microstructure and mechanical properties.
JANNUS Saclay facility

JANNUS: Joint Accelerators for Nano-science and Nuclear Simulation

Experimental techniques:

- Ion Beam Analysis
- Raman spectroscopy

ECR (Electronic Cyclotron Resonance)
⇒ Multi-charged ions

SNICS (Source of Negative Ions by Cesium Sputtering)
⇒ Multi-charged ions

RF (Radio Frequency)
⇒ Singly charged ions

200 keV < E < 60 MeV

Dissociate (de/dx)\(_e\) and (de/dx)\(_n\)

JAPET 2 MV

PANDORE 2.5 MV

EPIMÉTHÉE 3 MV
Raman spectrometer coupled to the triple beam chamber

*In situ* configuration
CEA IN SITU RAMAN FACILITIES ON NUCLEAR MATERIALS

- Simulation of the damage accumulation process induced by neutrons in nuclear materials
- Study their main consequences on both microstructure and mechanical properties.

- Chemistry of spent fuel treatment/recycling, waste management and fuel cycle processes.
  - 17 laboratories => radioactive materials in 250 glove boxes
  - 9 shielded lines => very high activity materials

Saclay

Marcoule
Model materials irradiated by external ions beams

Highly radioactive materials
The French high-level waste are immobilized in the reference “R7T7” glass matrix.

The main source of radiation damage in these glasses is $\alpha$ decays.

Confinement of radioactive elements over the long term requires evaluating the potential impact of this self-irradiation on the glass properties.

- Curium doped glasses
- External irradiation with light and heavy ions
Nuclear glasses

Experimental simulation of the irradiation damage

(S. Peuget and C. Mendoza, LMPA)

6 oxides (SiO₂-B₂O₃-Na₂O-CaO-Al₂O₃-ZrO₂) glass, ISG (International Standard Glass)

<table>
<thead>
<tr>
<th>(dE/dx)ₑ/(dE/dx)ₙ</th>
<th>Recoil : 0.65</th>
<th>α particle : 500</th>
<th>3.4</th>
<th>526</th>
</tr>
</thead>
</table>

1-7 MeV Au irradiations

CSNSM, Orsay

74 MeV Kr irradiations

GANIL, Caen

- Increase of the Q₃ band (tetrahedron with three bridging oxygen atoms) ⇒ depolymerisation of the network.
- Emergence of the D₂ band that corresponds to three-membered Si rings.
- Shift of the R band towards the higher wave numbers, attributed to a decrease of the Si-O-Si mean angle.

Same structural state in the case of a tracks or ballistic regime.
Damage weaker in doped glasses: role of the α particle?
Nuclear glasses

- Dissociation of \((dE/dx)_e\) and \((dE/dx)_n\) effects

\((S.\ Peuget\ and\ A.\ H.\ Mir,\ LMPA)\)

- Heavy ions induce the higher changes
- The \(\alpha\) particles induce annealing effects which may explain the variations between the doped and irradiated glasses with heavy ions.
Nuclear fuel

▶ *In situ* Raman

(C. Onofri and C. Sabathier CEA/DEC)

**UO₂ irradiated 4-MeV Kr– 160°C**

- Rapport d’aires
- Fluence (ions.cm⁻²)
- Aires (U₁+U₂+U₃)/T₂g
- Defects triplet
- T₂g
- 443 cm⁻¹
- 445 cm⁻¹

**Fluence (ions.cm⁻²)**

<table>
<thead>
<tr>
<th>Fluence (ions.cm⁻²)</th>
<th>Intensity (a. u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.8E15</td>
<td></td>
</tr>
<tr>
<td>4.8E15</td>
<td></td>
</tr>
<tr>
<td>2.9E15</td>
<td></td>
</tr>
<tr>
<td>1.952E15</td>
<td></td>
</tr>
<tr>
<td>1.03E15</td>
<td></td>
</tr>
<tr>
<td>7E14</td>
<td></td>
</tr>
<tr>
<td>4.96E14</td>
<td></td>
</tr>
<tr>
<td>2.95E14</td>
<td></td>
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<tr>
<td>1.08E14</td>
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<tr>
<td>6.6E13</td>
<td></td>
</tr>
<tr>
<td>4.83E13</td>
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<tr>
<td>3.04E13</td>
<td></td>
</tr>
<tr>
<td>2.1E13</td>
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</tr>
<tr>
<td>1.33E13</td>
<td></td>
</tr>
<tr>
<td>9.45E12</td>
<td></td>
</tr>
<tr>
<td>7.52E12</td>
<td></td>
</tr>
<tr>
<td>5.39E12</td>
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<tr>
<td>3.17E12</td>
<td></td>
</tr>
<tr>
<td>2.15E12</td>
<td></td>
</tr>
<tr>
<td>1.09E12</td>
<td></td>
</tr>
<tr>
<td><strong>virgin</strong></td>
<td></td>
</tr>
</tbody>
</table>

**Nombre d’onde (cm⁻¹)**

- 443 cm⁻¹ T₂g
- Defects triplet
- 445 cm⁻¹

**Aires (U₁+U₂+U₃)/T₂g**

- 6.8E15
- 4.8E15
- 2.9E15
- 1.952E15
- 1.03E15
- 7E14
- 4.96E14
- 2.95E14
- 1.08E14
- 6.6E13
- 4.83E13
- 3.04E13
- 2.1E13
- 1.33E13
- 9.45E12
- 7.52E12
- 5.39E12
- 3.17E12
- 2.15E12
- 1.09E12
- virgin

**Nombre d’onde (cm⁻¹)**

- 300
- 400
- 500
- 600
- 700

**Intensité (a. u.)**

- 6.8E15
- 4.8E15
- 2.9E15
- 1.952E15
- 1.03E15
- 7E14
- 4.96E14
- 2.95E14
- 1.08E14
- 6.6E13
- 4.83E13
- 3.04E13
- 2.1E13
- 1.33E13
- 9.45E12
- 7.52E12
- 5.39E12
- 3.17E12
- 2.15E12
- 1.09E12
- virgin
Oxidation of fuel cladding: Zirconia

\(\text{Internal ZrO}_2\)

(C. Ciszak CEA/DEC)

Internal ZrO\(_2\)

Rod cross-section

Video: Image avant carto interne 2

Cursor spectrum: Cursor spectrum

Metal

zirconia

UO\(_2\)

Defects band

Eletronic Probe Micro Analysis

Monoclinic ZrO\(_2\)

Tetragonal ZrO\(_2\)

Electron Probe Micro Analysis

C. Ciszak et al. JNM, submitted

Electron Probe Micro Analysis
This defects triplet appears after irradiation in reactor?

- Depleted UO$_2$ irradiated 4 MeV-Kr 1E17 ions.cm$^{-2}$
- UO$_2$ nuclear fuel (burnup 47 GWd/t)

Self-radiation damaged 0.08 dpa
Self-radiation damaged 0.006 dpa
Annealed

MOX MIMAS (7 wt.% Pu)
Zircaloy-4 corroded in autoclave in PWR simulated conditions:

Liquid water at 360°C and a pressure of 187 bars with 2 ppm in mass of lithium from LiOH and 1000 ppm in mass of boron from H3BO4.

After 40 days a 1.5 µm thick oxide layer is formed on the metal.

Irradiation of zirconia

<table>
<thead>
<tr>
<th>Ion</th>
<th>Energy</th>
<th>Rp</th>
<th>Dpa (max)</th>
<th>S_e/S_n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au^{5+}</td>
<td>12 MeV</td>
<td>1.6</td>
<td>13</td>
<td>0.7</td>
</tr>
<tr>
<td>H^+</td>
<td>1 MeV</td>
<td>9.2</td>
<td>0.03</td>
<td>2500</td>
</tr>
</tbody>
</table>
For the same dpa and not the same fluence, we observe the same Raman spectra.

The ballistic effects are responsible to the creation of defects $\Rightarrow$ defects are probably oxygen bi-vacancies $[V_o, V_o^*]$. The spectrum observed is the result of a strong disorder in the oxygen sub-lattice of the zirconia tetragonal phase.

\[ J.-M. \ Costantini \ et \ al. \ JNM, \ 440(2013) \ 508-514. \]