S. Miro$^1$, S. Peuget$^1$, M. Magnin$^1$, J. Delrieu$^1$, M. Gennisson$^1$, Z. Talip$^1$, S. Perrin$^1$, J.-M. Boubals$^1$, M. Delaville$^1$, C. Jégou$^1$, M. Tupin$^2$, R. Verlet$^2$, G. Gutierrez$^2$, A. Nakayoshi$^3$, T. Washiya$^3$

$^1$CEA Marcoule, DEN/DTCD/SECM/LMPA, 30207 Bagnols-sur-Cèze cedex, France

$^2$CEA Saclay, DEN/DMN, 91191 Gif-sur-Yvette cedex, France

$^3$JAEA, 4-33 Muramatsu Tokai-mura Kaka-gun, Ibaraki, 319-1194 Japan

sandrine.miro@cea.fr
CEA: French Alternative Energies and Atomic Energy Commission

Atalante Marcoule facility

- Improve the existing treatment process
  - Optimize the recycling process
  - Reduce emissions from the plant
  - Support new fuels

- Define future treatment and recycling processes
  - Multiple recycling of plutonium
  - Minor actinide recycling

- Define matrices for waste and actinide materials
  - Immobilize ultimate radioactive waste
  - Investigate the long-term behavior of conditioning matrices
  - Synthesize actinide compounds

Chemistry of spent fuel treatment/recycling, waste management and fuel cycle processes

17 laboratories with 250 glove boxes
9 shielded lines

3 in situ Raman devices
- 2 in glove boxes
- 1 in shielding lines
Fuel characterizations laboratory:

Horiba© IHR-320 Raman spectrometer with 2 lasers: 532 nm & 660 nm

Confocal microscope equipped with 2 exchangeable turrets dedicated to:

- **Ex situ** microstructural observations (optical & Raman): equipped with 4 Olympus© objectives (x5 to x100), micro-indenter device and a Raman calibration objective.
- **In situ** high temperature Raman experiment: equipped with 3 Mitutoyo© long working distance objectives (x5 to x50) and a Raman calibration objective.

Glovebox dedicated to μ-Raman

Remote control system

Confocal microscope

Motorized stages: x, y, z and sample rotation

Optical fibbers
High Activity Wastes laboratory:

- Study the long term behavior of high level waste conditioning matrices: radiation damage and radiolysis effects (glass, ceramics, spent fuel).
- 2 shielded lines compatible with very high-activity materials from industrial facilities (ex: fuel and fuel cladding from PWR) or produced in research laboratories.
- 2 laboratories (solid characterizations and liquid analyses).

Shielded lines C18/C19

L29: Solid characterizations
- X-ray diffraction
- SEM/EDS
- Electronic Microprobe

L30: Low level radioactive liquid samples analyses
- ICP
- KPA
- Radiometry (α, β, γ)
- UV-vis
Why Raman spectroscopy?

Raman spectroscopy is a powerful technique for analyzing nuclear materials subjected to complex scenarios (irradiation, temperature and interaction with the surrounding environment).

We used this technique to:
- characterize the existing phases in service conditions.
- detect the secondary phases formed on fuel in underwater interim storage.
- follow structural evolutions generated by irradiation.

Non-contact and non-destructive technique and do not necessarily require special preparation.
Raman spectrometer coupled to a hot cell

**DHA Atalante Marcoule facility**

**DHA (Déchets de Haute Activité): High Activity Wastes**

- In situ system

- **Sample**
  - **Slave arm**
  - **Sample-holder**
  - **Sample**
  - **Laser**

- **Microscope in hot cell**
  - **Images**
    - **Spot size ~ 1 µm**

- **Green laser 532 nm**

- **DHA Atalante**
  - **Cell 505**
Raman spectroscopy: experimental acquisition modes

- **Punctual analysis**
- **Depth profile analysis**
- **Line mapping**
- **2D mapping**
I. Oxidation of fuel cladding: zirconia
   • Zirconia irradiations with external ions beams
   • Fuel cladding coming from PWR

II. Nuclear fuels
   • Uox and Mox (Irradiation damage and oxidation resistance)
     • Long-term interim storage

III. Simulated corium
   • Initial characterizations
   • Leaching experiment

Conclusions
OXIDATION OF FUEL CLADDING
Oxidation of fuel cladding: Zirconia

Industrial context

The fuel cladding in Pressurized Water Reactor

\[2\text{H}_2\text{O} + \text{Zr} \leftrightarrow \text{ZrO}_2 + 2\text{H}_2\]

Sources of radiation

\(\text{➢} \) Ionizing radiations: 99.7% of the dose induced by X, \( \gamma \) and \( \beta \)-rays.

\(\text{➢} \) Displacement cascades created by neutrons estimated to 3 dpa per year in the metal.

\(\text{➢} \) Fission products for the internal oxide layer.
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.

**Oxidation of fuel cladding: Zirconia**

**Industrial context**

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.

Corrosion performance of alloy M5 and Zr-4 fuel rods in PWR. The burnup acceleration at 35 corresponds approximately to a life time of around 3 years of the fuel rod in reactor.

Oxidation rate of Zr-4 alloy, in autoclave (346 and 354 °C), PWR reactor or in corrosion loops (with similar PWR hydrodynamic conditions).
Oxidation of fuel cladding: Zirconia

In situ Raman

(Coll. M. Tupin 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 collisions

Follow the irradiation damage under ion beam irradiation.
Raman spectrometer coupled to the triple beam chamber

**In situ** configuration

JANNUS Saclay facility

**JANNUS**: Joint Accelerators for Nano-science and Nuclear Simulation
Oxidation of fuel cladding: Zirconia

*In situ* Raman

(Coll. M. Tupin CEA/DMN)

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

**ZrO$_2$ irradiated Au 12-MeV**

- Monoclinic
- Tetragonal

Disappearance of the monoclinic phase, in agreement with DRX.

**Monoclinic reference**

**Tetragonal phase**

**Cross-section**

**Metal**

**Oxide**

**Phase diagram**

- 1.0 E15
- 9.5 E14
- 8.3 E14
- 7.4 E14
- 6.5 E14
- 5.8 E14
- 4.6 E14
- 3.6 E14
- 3.1 E14
- 2.6 E14
- 2.1 E14
- 1.5 E14
- 9.6 E13
- 6.7 E13
- 4.3 E13
- 2.5 E13
- 1.7 E13
- 9.2 E12
- 2.7 E12
- 9.0 E11
- Virgin

**Defects band (oxygen vacancies)**

**Metal**

- 360°C and 187 bars

**Monoclinic**

**Tetragonal**

**Phase diagram**

**Oxidation of fuel cladding: Zirconia**

*In situ* Raman

*(Coll. M. Tupin CEA/DMN)*

- **Comparison 12 MeV Au and 1 MeV H irradiations**

- **Evolution of the defects band according to** \((dE/dx)_{e}\) or \((dE/dx)_{n}\)

---

### Table: Ion Energy, \(R_p\), Dpa (max), \(S_e/S_n\)

<table>
<thead>
<tr>
<th>Ion</th>
<th>Energy</th>
<th>(R_p)</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.**

- **Intensity of the 712 cm\(^{-1}\) band of an oxide layer formed on a Zy-4 in PWR conditions according to** \((dE/dx)_{e}\).

- **Intensity of the 712 cm\(^{-1}\) band of an oxide layer formed on a Zy-4 in PWR conditions according to** \((dE/dx)_{n}\).

---

**The ballistic effects are responsible to the creation of defects \(\Rightarrow\) defects are probably oxygen bi-vacancies \([Vo, Vo']\).**

The spectrum observed is the result of a strong disorder in the oxygen sub-lattice of the zirconia tetragonal phase.

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.

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

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

After re-oxidation, defects disappear and the oxidation rate of the irradiated sample comes back to that of the non-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 ZrO$_2$**

(Coll. M. Tupin CEA/DMN)

---

Rod cross-section

External ZrO$_2$

Coating

Metal

Video: Carte lumière normale

Cursor spectrum: Cursor spectrum

Intensity (counts)

Wavenumber (cm$^{-1}$)

Monoclinic zirconia

Defects band

Monoclinic ZrO$_2$

12 MeV-$10^{15}$ Au.cm$^{-2}$

Reference

P$_2$/c

9Ag + 9Bg

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.

---

Oxidation of fuel cladding: Zirconia

- **External ZrO$_2$**

(Coll. M. Tupin CEA/DMN)
Oxidation of fuel cladding: Zirconia

- **Internal ZrO₂**

(Coll. C. Ciszak CEA/DEC)

---

**Internal ZrO₂**

Rod cross-section

---

**Monoclinic ZrO₂**

**Tetragonal ZrO₂**

Phase transformation

*Reference* [Electron Probe Micro Analysis](J. M. Costantini et al. JAP, 2006)

---

Defects band

---

12 MeV·10¹⁵ Au.cm⁻²

---

C. Ciszak et al. JNM 2018

Electron Probe Micro Analysis
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.

- **Monoclinic**

- **Tetragonal**

- **UO₂**
NUCLEAR FUEL
Uox and Mox spent nuclear fuel

Industial context

Fabrication Uox and Mox

Lifetime in reactor

Interim storage

Geological disposal conditions

1. Radiation damage
2. Chemical effects
3. Radiolysis effect at the solid/water interface

Raman spectroscopy efficient to study these effects
Nuclear fuel

- Irradiation damage

(Coll. C. Sabathier CEA/DEC)

**UO$_2$ irradiated 4-MeV Kr– 160°C**

In situ Raman

**T$_{2g}$**

Defects triplet

G. Gutierrez

*J. Nucl. Mater. 2018*
This defects triplet appears after irradiation in reactor?

MOX MIMAS (U, Pu)O$_2$ (7 wt. % Pu)

Self-radiation damaged
Annealing (1273 K for 16 h under Ar/He)
Annealing (1273 K for 32 h under Ar/He)

- T$_{2g}$ wavenumber
- defects triplet

Nuclear fuel

➢ Mox

(Z. Talip, M. Magnin, S. Peugeot, M. Gennisson CEA/DE2D)

MOX MIMAS (U, Pu)O₂ (7 wt. % Pu)

Optical microscope image

➢ T₂g position in Pu agglomerate and disappearance of the 2LO band.

Comparison of the optical microscope image and EPMA results of UO₂ matrix, coating phase and Pu agglomerate

➢ T₂g position versus Pu content in agreement with the lattice parameter.

<table>
<thead>
<tr>
<th>EPMA (Electron Probe MicroAnalysis)</th>
<th>RAMAN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pu content (%)</td>
<td>T₂g</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>
</tr>
<tr>
<td>0.11</td>
<td>447</td>
</tr>
<tr>
<td>0.1</td>
<td>447</td>
</tr>
<tr>
<td>0.07</td>
<td>447</td>
</tr>
<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>

Comparison of the measured and calculated T₂g positions for the damaged MIMAS MOX disk.

Nuclear fuel

➢ Mox

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

- MOX MIMAS (U, Pu)O₂ (7 wt. % Pu)
  - map xy 100x60 µm
  - step 2µm: time: 2x20 s
Nuclear fuel

➢ Oxidation resistance

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

Oxidation resistance of the (U, Pu)O₂ matrix.

Temperature (K)

2-theta angle [°]


After oxidation (conditions: laser power 2.8 mW and exposure time 10x60s)

Increasing Pu content inhibits the M₃O₈ phase formation for the oxidized MIMAS MOX sample.

M₄O₉

UO₂ matrix
Pu < 2.7%

M₃O₈

Coating phase
Pu < 10%

M₄O₉

Pu agglomerate
Pu < 20%
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 (UO$_4$.4H$_2$O).

M. Magnin et al. 462 (2015) 230-241

Storage pool (high $\gamma$ dose) (ph 5-5.5)
Nuclear fuel

➢ Long-term interim storage

**PRECCI project (CEA/EDF)**

Segment of failed fuel rod stored during 15 years in storage pool.

Water interaction

15 years in water

Atalante

PWR fuel cladding

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

Perforated zone 400 µm x 100 µm

Secondary phases U(VI)

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

Uranyl with Zr or FP?
SIMULATED CORIUM
In the case of severe accident, the materials of the nuclear reactor (nuclear fuel, cladding, metallic alloys, structural materials, etc…) could melt to form complex and aggressive mixtures called corium.

Three Mile Island, 1979

Tchernobyl, 1986

Fukushima, 2011

This molten core in the reactor steel vessel forms a mixture called in-vessel corium. In the worst case, this mixture can pierce the vessel and pour onto the concrete underneath the reactor, leading the formation of the ex-vessel corium.

The meltdown process

1. If the cooling system which pumps water fails, water level can drop and expose fuel rods.

2. ~2000°C, the zirconium can melts, exposing uranium oxide which also melts ~3000°C.

3. The reactor becomes ever hotter, as it melts in the bottom of the vessel.

4. In a worst-case, the corium interact with the concrete containment wall.
Severe nuclear accident in Fukushima Daïchi Nuclear power station.

Fuel in unit 1 through 3 has melted due to a loss of all power supply and a subsequent failure in emergency cooling systems. Some parts of the melted fuels are assumed to drop down to the concrete basement which is a bottom of the primary containment vessel through the lower part of the reactor pressure vessel.

In mid-and-long term roadmaps towards decommissioning, a policy of fuel debris retrieval will be decided. After a removal, medium or long term storages of corium, are one of possible options.

This option may include that the fuel debris may be transported in deionized water and also stored in the same kind of condition.

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

- **Samples**

(CEA/DE2D and JAEA)

**COLIMA (COrium LIquid and MAterials) facility**

- Study of core-melting accidents in PWR: corium/materials interaction and release of aerosols from the corium.
- The hot crucible induction technique: the crucible is heated by an inductive heater (few kHz), it transmits the heat to the total load, till it reaches the liquidus temperature. The crucible is intended to received about a few kg of corium.
- The samples are simulant debris with depleted U and inactive simulant of FP.
- Different kinds of corium can be melted in this facility: in or ex-vessel corium, according to the scientific objectives of the experiments.

*F. Parozzi et al Nuclear Engineering and Design 261, 2013, 346-351*
Simulated Corium

Sample

(CEA/DE2D and JAEA)

Simulated in-vessel corium

- Experimental conditions:
  - Temperature ~ 2760°C during 8h.
  - Ar-H₂ atmosphere

Loading composition of COLIMA CA-U3:

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UO₂</td>
<td>1665.8</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>260</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.5748</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>21.0223</td>
</tr>
</tbody>
</table>

Simulated Fission Products

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Mass (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SrO</td>
<td>1.851</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>1.0592</td>
</tr>
<tr>
<td>Rh₂O₃</td>
<td>0.9599</td>
</tr>
<tr>
<td>TeO₂</td>
<td>1.191</td>
</tr>
<tr>
<td>BaO</td>
<td>3.0101</td>
</tr>
<tr>
<td>CeO₂·ZrO₂</td>
<td>9.6379</td>
</tr>
<tr>
<td>Pr₂O₃</td>
<td>2.3362</td>
</tr>
<tr>
<td>Nd₂O₃</td>
<td>6.1689</td>
</tr>
</tbody>
</table>

Samples analysed at the CEA Marcoule:

- Morphology of Colima 3 sample shows the presence of holes and white phases

The main elements: uranium (~ 76 %) zirconium (~ 4%)

Colima facility

W crucible

Upper level of the corium melt

Broken crucible

Fragment

Polished sample
Simulated Corium ➢ Storage

(CEA/DE2D and JAEA)

SEM (Scanning Electron Microprobe) observations:

- Matrix rich in uranium, zirconium and oxygen with different U/Zr ratio.
- Grey phase is metallic tungsten.

EDS analyzes:

<table>
<thead>
<tr>
<th></th>
<th>U</th>
<th>Zr</th>
<th>O</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix in weight %</td>
<td>78.41</td>
<td>7.42</td>
<td>13.24</td>
<td>0.22</td>
</tr>
</tbody>
</table>

SEM observations show a matrix and a grey phase.
X-Ray diffraction analysis (LMAC/DEN):

Diffractometer Bruker Xas D8 Advance with a cathode in copper.

Identification of phases:

⇒ Cubic (U, Zr)O$_2$ phase: U$_{0.85}$Zr$_{0.15}$O$_2$ and U$_{0.65}$Zr$_{0.35}$O$_2$

The diffraction peaks are anisotropic, which indicates a variation of the lattice parameters and their stoichiometry

⇒ Tungsten phase
Raman analyzes:

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

**Inclusions**
- No phase detected
- Confirm the metallic state

Simulated in-vessel corium
Simulated Corium

Sample

(CEA/DE2D and JAEA)

Simulated ex-vessel corium

- Experimental conditions:
  - Temperature ~ 2000°C
  - Nitrogen atmosphere

- Loading composition of COLIMA CA-U4:

<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>

Colima facility

The main elements:
- uranium (~ 52 %)
- zirconium (~ 16.5%)

Fuel
Claddings
Metallic alloys
Concrete

Simulated Fission Products

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Mass (g)</th>
</tr>
</thead>
<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>RuO₂</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 analysed at the CEA Marcoule:

Morphology of Colima 4 sample shows a very porous material which the presence of different phases

Fragment
Polished sample
Simulated Corium ➢ Storage

*(CEA/DE2D and JAEA)*

Simulated ex-vessel corium

SEM (Scanning Electron Microprobe) observations:

SEM observations show a matrix composed of small spherical grains (< 5 µm) in which are inserted bigger inclusions.

- Matrix rich in uranium, zirconium and oxygen with different U/Zr ratio.
- Inclusions composed of grains rich in Fe and Cr, with a heterogeneous distribution: the external part richer in chromium whereas the inner part is richer in iron.

**Fragment**

**Polished sample**

**Matrix**

**Spherical inclusions**
X-Ray diffraction analysis (LMAC/DEN):

Diffractometer Bruker Xas D8 Advance with a cathode in copper.

⇒ Cubic (U, Zr)O$_2$ phase: U$_{0.65}$Zr$_{0.35}$O$_2$ and U$_{0.7}$Zr$_{0.3}$O$_2$

The diffraction peaks are anisotropic, which indicates a variation of the lattice parameters and their stoichiometry

⇒ ZrO$_2$ (zirconia).
Simulated Corium ➤ Storage

(CEA/DE2D and JAEA)

Colima 4 (EDS)

- U-rich phase
- Fe/Cr phase
- Zr-rich phase

<table>
<thead>
<tr>
<th>Phase</th>
<th>Element</th>
<th>EDS wt (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium</td>
<td>Uranium</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>Zirconium</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td>(15)</td>
</tr>
<tr>
<td>Zirconium</td>
<td>Uranium</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>Zirconium</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td>(21)</td>
</tr>
</tbody>
</table>

TMI-2 Molten-core (EDX)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Element</th>
<th>EDXA wt (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uranium</td>
<td>Uranium</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>Zirconium</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td>(13)</td>
</tr>
<tr>
<td>Zirconium</td>
<td>Uranium</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>Zirconium</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td>(20)</td>
</tr>
</tbody>
</table>

X-ray diffraction reveals the presence of a cubic (Urich, Zr)O_{2+x}, and tetragonal (Zrich, U)O_2

D. Bottomley, Hotlab 2017
G. Bart, OECD-CSNI, 1992
Simulated Corium ➢ Storage

Simulated ex-vessel corium

Matrix (U, Zr, O)

(U, Zr)O$_2$

Fluorite structure

- Matrix (U, Zr)O$_2$ crystallizes in the fluorite structure
- The position of the T2g depends on the U/Zr ratio

Matrix (Zr, U, O)

(Zr, U)O$_2$

Tetragonal phase

- (Zr, U)O$_2$
- The crystallographic structure must be determined
Simulated Corium ➢ Storage

(CEA/DE2D and JAEA)

Leaching conditions:

Scheme of the leaching device

Leaching experiments:
- deionized water
- at 25°C
- in air
- under $\gamma$ irradiation.

Photo of the preparation of Colima leaching experiment in hot cell

Fragments ➢ Sample holder ➢ Reactor ➢ Co-source

➢ Solution samples are periodically transferred to the liquid analysis laboratory
➢ At the end of the experiment, the colima samples are analyzed by Raman spectroscopy
Simulated Corium ➢ Storage

(CEA/DE2D and JAEA)

- SEM (Scanning Electron Microprobe): Precipitation of phases included Zn on the sample.
- Raman analyzes after leaching:

Outlook

Model materials ➔ Irradiation damage ➔ Leaching behavior ➔ Corium samples
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 probably the secondary phases formed after interaction with the surrounding environment.
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.