Fission Product behaviour in \( \text{UO}_2^{+/-x} \) by atomic scale simulations

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Context of FP Multiscale modelling in IRSN-PSN-RES/SAG

To investigate basic mechanisms for FP migration.

To understand the behavior of fission products in UO2+/-x, atomic scale simulations are employed. This context involves the use of various computational tools and codes for multiscale modeling.

- **Atomistic** simulations focus on the detailed atomic scale, using codes like VASP, LAMMPS, and Home made codes.
- **Meso-scale** modeling includes finite element simulations using codes like TRANSURANUS, FRAPCON, and MEPHISTA, which considers phase field, grain size, and gas porosities.

These tools and models are used to investigate the basic mechanisms of fission product migration in nuclear materials.
A major issue: FP’s migration in UO₂ and UO₂⁺ₓ

- U and FP migration activation energy (generally) decreases from UO₂ to UO₂⁺ₓ
  - Decrease of defects formation energy and decrease of migration energy.
- This will depend on the defects clusters configuration
  - FP in V_U or Schottky defects in UO₂
  - I₀ or even more likely quadri-interstitials (cub-octahedrons) in UO₂⁺ₓ.
- DFT and classical MD (static) simulations in 3 configurations
  - To understand basic mechanisms and to help in defining reliable interatomic potentials

![Diagram showing configurations VU, Schottky, and Quadri-interstitials]

- Uranium, ● Oxygen, ○ Oxygen interstitial, □ PF/Uranium (migration)
Incorporation and migration energies in UO$_2$ and UO$_{2+x}$

From first-principle simulations: DFT-VASP; 144 atoms; PAW; GGA+U (not for FP)

- U, Zr and Mo “stabilized” by oxygen (both for incorporation and migration)
- Ba not so dependant of O configuration

<table>
<thead>
<tr>
<th></th>
<th>U</th>
<th>Ba</th>
<th>Zr</th>
<th>Mo</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$E_{\text{inc}}$ (eV)</td>
<td>$E_{\text{mig}}$ (eV)</td>
<td>$E_{\text{inc}}$ (eV)</td>
<td>$E_{\text{mig}}$ (eV)</td>
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<tr>
<td>$V_U$</td>
<td>-13.3</td>
<td>4.7</td>
<td>-7.8</td>
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<tr>
<td>Schottky</td>
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<td>5</td>
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<td>Quadri-interstitial</td>
<td>-13.7</td>
<td>2.2</td>
<td>-6.8</td>
<td>2.1</td>
</tr>
</tbody>
</table>

From classical MD: LAMMPS; 144 atoms; Grimes-Catlow interatomic potentials

- Stabilization by oxygen not reproduced for Zr and U

<table>
<thead>
<tr>
<th></th>
<th>U</th>
<th>U$^{(1)}$</th>
<th>Ba</th>
<th>Zr</th>
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<tr>
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<td>$E_{\text{inc}}$ (eV)</td>
<td>$E_{\text{mig}}$ (eV)</td>
<td>$E_{\text{inc}}$ (eV)</td>
<td>$E_{\text{mig}}$ (eV)</td>
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<td>-86.15</td>
<td>10.9</td>
<td>-37.8</td>
<td>7.4</td>
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</tbody>
</table>

Interatomic potentials


\[ U(r_{ij}) = \frac{1}{4\pi\varepsilon_0} \sum_{ij} \frac{q_i q_j}{r_{ij}} + A \exp\left(-\frac{r_{ij}}{\rho}\right) - \frac{C_{ij}}{r_{ij}^6} \]

- Long-range Coulomb potential
- Short ranged pair potential: Buckingham form

- Parameters adjusted. Formal constant charges.


\[ U(r_{ij}) = \frac{1}{4\pi\varepsilon_0} \sum_{ij} \frac{z_i z_j e^2}{r_{ij}} + A_{ij} \exp\left(-\frac{r_{ij}}{\rho_{ij}}\right) - \frac{C_{ij}}{r_{ij}^6} + D_{ij} \left[1 - \exp\left(\beta_{ij} (r_{ij} - r_{ij}^*)\right)^2 - 1\right] \]

- Coulomb potential
- Buckingham form
- Morse potential

- Non formal constant charges and a covalent part.

DFT simulations able to help in understanding the nature of bondings in UO₂ and UO₂⁺ₓ including FP

See details in Poster session PA5
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Uranium ($6s^26p^65f^36d^17s^2$) “stabilized” by oxygen bonding (and Zr too)

- Bonding between s, p, d and f-orbital of uranium with s and p orbital of oxygen (hybridization) in valence bands

- Localized non-bonding orbital at the Fermi level corresponding to no overlapping f uranium occupied-orbital.

- Occupation of non-bonding localised upper orbital corresponding of f Uranium orbital directional lobes

- Lower charge transfer between U and oxygen.

- Additional bondings with I$_0$ which stabilize the structure.

- And higher charge transfer between U and oxygen.

Iono-covalent bonding and charge transfer depends on O atoms configuration
The same for molybdenum ($4d^{5}5s^{1}$) but crystal field (Tc and Ru too)

- Hybridization between oxygen $p$ orbital and Mo $T_{2g}$ $d$
- Molybdenum $E_{g}$ orbital directed toward the faces of oxygen atoms cubes.
- Lower hybridization between oxygen $p$ orbital and Molybdenum $T_{2g}$ $d$ and less charge transfer.
- New unoccupied localized states near Fermi level and decrease of stability.
- Higher hybridization between oxygen $p$ orbital and Mo $T_{2g}$ orbital and higher charge transfer due to $l_{0}$.

Again Iono-covalent bonding and charge transfer depending on O atoms configuration
Barium \((6s^2)\) somewhere different (Cs too)

- Hybridization between oxygen s and p orbital and Ba s and p orbital
- Charge transfer (important) from s oxygen orbital.
- Ba DOS not modified (and charge transfer only weakly)
- An effect due to uranium neighbours (like U in Schottky)

**The covalent part of bonding is weaker. The charge transfer depends weakly on O atoms configuration.**
The oxygen atoms configuration in the saddle point position will explain the differences in migration energies.

In the saddle point position the oxygen environment will change with the nature of the trap site:
- More oxygen atoms close to the moving atom at the saddle point from Schottky site to quadri-interstitial.

From the previous results:
- U, Zr, Mo migration energies are decreased in case of O-rich environment because of higher hybridization and charge transfer.
- Ba and Cs migration energies only weakly depend on O environment.
- Transfer from inner s-type orbital and charge transfer unaffected by oxygen environment.

What about U and FP migration?
Example of Barium migration

For migration via Schottky: no significant DOS and charge transfer modification

- For migration via Schottky: no significant DOS and charge transfer modification
- A steric effect

For migration via Quadri-interstitial: no significant DOS and charge transfer modification

- For migration via Quadri-interstitial: no significant DOS and charge transfer modification
- A steric effect
Example of Zirconium (4d²5s²) migration

Migration via Schottky: localized non-bonding level and lower charge transfer

- Migration via Schottky: localized non-bonding level and lower charge transfer
  - Emig = +6.8 eV
  - Bader = +2.20

Migration via Quadri-interstitial: no significant DOS and charge transfer variation: low migration energy

- Migration via Quadri-interstitial: no significant DOS and charge transfer variation: low migration energy
  - Emig = +0.8 eV
  - Bader = +2.48
As a conclusion

- Cation-oxygen bonding in UO$_2$ and UO$_{2+x}$ is of iono-covalent type and depends on the relative configuration of cations and oxygen atoms
- The charge transfer depends on the relative configuration of cations and oxygen atoms
  - Significantly for U, Zr, Mo (Tc, Ru)
  - Only weakly for Ba, Cs
- Interatomic potentials including both a covalent part and a variable-charge model are recommended like described in:

  **Bulk, surface and point defect properties in UO$_2$ from a tight-binding variable-charge model**

  G Sattonnay and R Tétot
  Université Paris-Sud 11, ICMMO/LEMHE, Bât. 410, F-91405 Orsay Cedex, France

- The work will be pursued in this direction in IRSN for the definition of interatomic potentials for FP in UO$_{2(+/-)x}$
Thank you for your attention.
Point defects in UO$_2$+/-x

Energy (arbitrary units)

Composition (O at.%)  66.5  67.0  67.5  68.0

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<thead>
<tr>
<th>Defect Type</th>
<th>Raw Energy (eV)</th>
<th>Effective Energy (UO$_2$-x)</th>
<th>Effective Energy (UO$_2$)</th>
<th>Effective Energy (UO$_2$+x)</th>
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FPs mobility and speciation in high temperature annealing mode

<table>
<thead>
<tr>
<th>Case</th>
<th>Xe-I-Cs-Sb-Te</th>
<th>Mo-Ru</th>
<th>Ba-Sr</th>
<th>Zr-RE</th>
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<tr>
<td>Case 3</td>
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<td>4.7</td>
<td>6.4</td>
<td>6.8</td>
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</table>
P(O₂) dependence on FPs mobility in normal reactor operations

- Case 1: $E_{\text{act}} = 5.2\text{eV (Xe, Cs, I, Sb, Te)}$, 6eV (Mo, Ru), 7eV (Ba, Sr), 8eV (Zr and RE)
- Case 2: $E_{\text{act}} = 2\text{eV (Xe, Cs, I, Sb, Te)}$, 3.5eV (Mo, Ru), 4.5eV (Ba, Sr), 5.5eV (Zr and RE)
- Experimental from Walker et al., J. Nucl. Mater. 345 (2005) 192-205

Fuel oxygen potential: 100GWd/t (MFPR v1.5.2)
Ba steric effects

\[ \text{Cs-O} = 2.07 \, \text{\AA} \]

\[ \text{E}_{\text{mig}} = +0.1 \]

\[ \text{Ba-O} = 2.44 \, \text{\AA} \]

\[ \text{E}_{\text{mig}} = +2.1 \]