Karlsruhe Institute of Technology

INE Institut für Nukleare Entsorgung

HELMHOLTZ RESEARCH FOR GRAND CHALLENGES

Spectroscopic investigation on the behavior of irradiated light water reactor fuels during prolonged dry interim storage and final disposal

K. Dardenne, M. Herm, T. König*, Y. Lin, V. Metz, T. Pruessmann, J. Rothe, D. Schild, A. Walschburger and H. Geckeis
Karlsruhe Institute of Technology - Institute for Nuclear Waste Disposal (KIT-INE)

Background

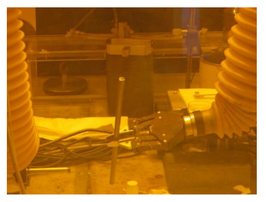
Already during irradiation, the nuclear fuel pellet and surrounding cladding will undergo changes in their morphological structure and chemical properties. Throughout utilization in a nuclear reactor, several reactions take place, which alter the initial composition of pristine UO_2 or mixed oxide (U, Pu)O_2 fuel (MOX). One of the substantial nuclear reactions is the fission of heavy nuclei (e.g., ^{235}U, ^{239}Pu) under emission of neutrons, the generation of fission products and the release of large amounts of energy. In addition, transuranium isotopes, such as neptunium, americium or curium are generated through neutron capture reactions and subsequent β^- decays, starting from ^{238}U. Moreover, the cladding tubes will incorporate hydrogen originating from the coolant surrounding the fuel rods, forming mainly circumferentially oriented hydrides in the cladding material. As the spent nuclear fuel (SNF) assembly is transferred from wet to dry storage, hydride precipitates can dissolve during the drying process and potentially reorientate in radial direction during subsequent dry interim storage as the SNF further cools down, in radial directions, potentially impacting the integrity of the zirconium-based cladding.
Throughout the geological disposal period, the contact of ground water with the highly radioactive waste form has to be considered in the long-term. Upon contact with the ingressing solution, a fraction of highly mobile fission and activation product isotopes are promptly released (e.g., the cesium isotopes, ^{36}Cl, ^{129}I) due to their heterogenous distribution in the fuel after irradiation. However, the actinides as well as matrix bound radionuclides tend to remain immobilized, as shown in various leaching experiments utilizing SNF samples in synthetic ground water solutions [1, 2]. This phenomenon is attributed to the established reducing conditions within a repository after closure and consumption of the residual oxygen. The anoxic corrosion of canister materials as well as structural parts of fuel assemblies result in the generation of hydrogen, which, in conjunction with the catalytic abilities of 4d-transition element fission product particles (i.e., Mo, Pd, Rh, Ru, Tc), is responsible for the reducing near-field conditions and thus the immobilization of the actinides and matrix bound radionuclides [3, 4].

Scope of this work

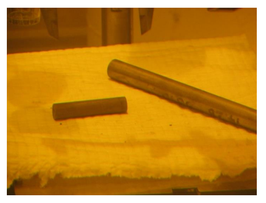
- Speciation analysis of safety relevant radionuclides (e.g., ^{36}Cl, ^{79}Se, ^{129}I) for final disposal of SNF.
- Improving the knowledge on the characteristics of 4d-transition element fission product particles (ε-particles) as well as their catalytic properties in SNF leaching experiments.
- Spectroscopic analysis of possible cladding degrading elements (e.g., chlorine, iodine, cesium) in SNF fuel rods during dry interim storage.

SNF samples

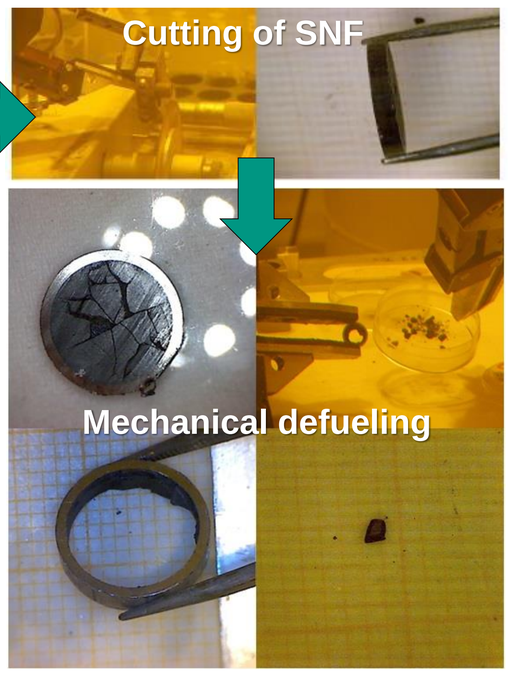
- **Fuel rod segment N0204, irradiated in PWR Gösgen (Switzerland):**
  - Fuel type: **UO_2** with 3.8% ^{235}U enrichment.
  - Cladding: Zircaloy-4.
  - Full power days: 1226 days in 4 irradiation cycles.
  - Average linear power: 260 W/cm.
  - Average burn-up: **50.4 GWd/t_{HM}**.
  - Cooling time: ~ 35 years.



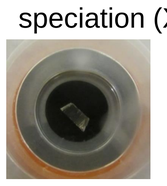
- **Fuel rod 5810, irradiated in PWR Obrigheim (Germany):**
  - Fuel type: **MOX** with 3.2% Pu_{fiss} enrichment.
  - Cladding: Zircaloy-4.
  - Full power days: 1157 days in 4 irradiation cylces.
  - Average linear power: 200 W/cm.
  - Average burn-up: **38.0 GWd/t_{HM}**.
  - Cooling time: ~ 38 years.

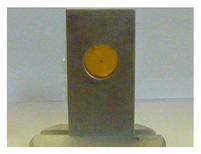


Sample preparation



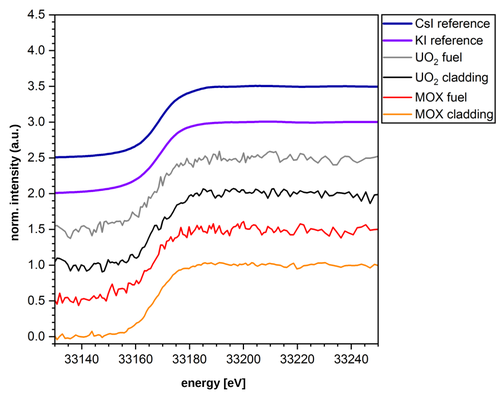
- Shielded box infrastructure with transfer lock system allowing for:
  - Conditioning and extraction of HLW sample fragments: **SNF**, vitrified waste concentrates.
  - Application of complementary spectroscopic tools to determine RN distribution and / or speciation (XPS, SEM-EDX, Raman, **XAS**).





INE beamlines licensed for working with 10^6 times the exemption limit / up to 200 mg of fissile ^{235}U/^{239}Pu!

Chlorine & iodine

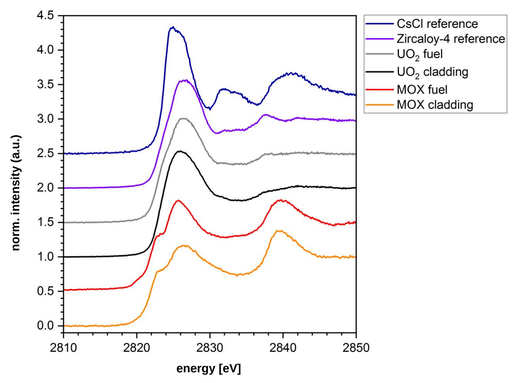


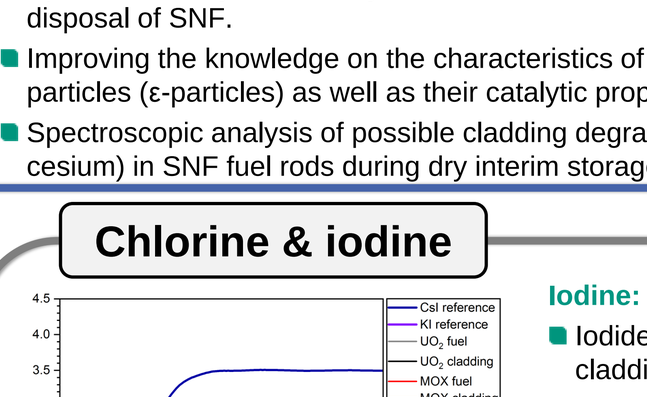
Iodine:

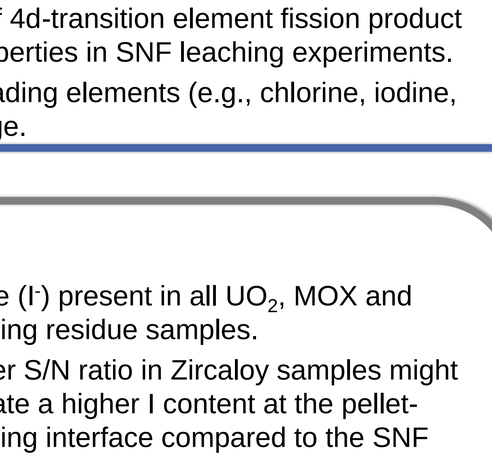
- Iodide (I^-) present in all UO_2, MOX and cladding residue samples.
- Higher S/N ratio in Zircaloy samples might indicate a higher I content at the pellet-cladding interface compared to the SNF bulk.
- As predicted in the literature, iodine formed inside the fuel and the interface layer might be present as CsI (iodate to be ruled out).

Chlorine:

- Chloride (Cl^-) present in all UO_2, MOX and cladding residue samples.
- Unlike iodine, chlorine does not seem to be associated with cesium (cf. CsCl reference).
- Differences in pre-edge region between UO_2 and MOX samples.
- Interference with Ru L_3 edge in case of both MOX samples probably due to presence of ε-particles and/or higher Ru fission yield from ^{239}Pu.

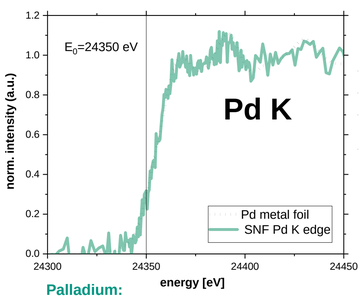




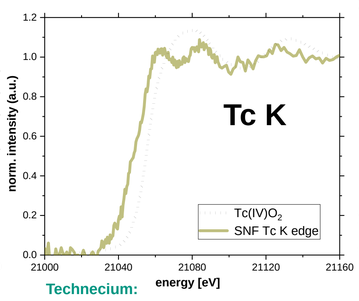


- SEM-EDX and XPS analysis of halogen-rich agglomerates present on SNF cladding.
- Possible impact on cladding integrity via chemically assisted stress corrosion cracking.

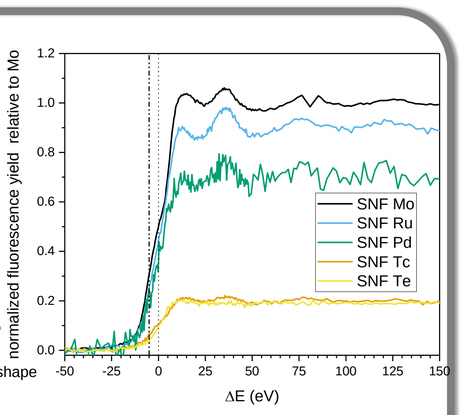
ε-particles

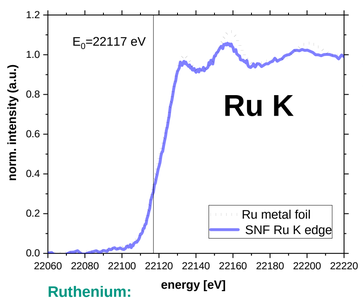


Palladium:
- metallic state – Pd(0)
- exact coincidence with hcp-Pd metal

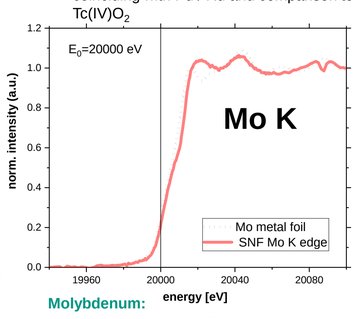


Technecium:
- metallic state – Tc(0) deduced from edge shape coinciding with Pd / Ru and comparison to Tc(IV)O_2



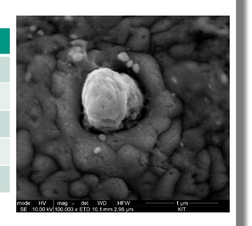


Ruthenium:
- metallic state – Ru(0)
- 4d metal hcp structure



Molybdenum:
- metallic state – Mo(0)
- different fine structure compared to hcp metals
- Mo assumed to exist in other phases

element	at%	calc.*
Mo	**0.324**	**0.324**
Ru	0.223	0.203
Pd	0.135	0.114
Tc	0.056	0.072
Te	0.017	0.040



Determination of at% conc.:
- Mo as internal standard
- XANES edge step
- Fluorescence yield
- Absorption coefficients for excitation and fluorescence in UO_2 matrix

Conclusions & Outlook

- Agglomerates present in the interaction layer between fuel and cladding consist, amongst others, of halogen-rich mixed phases (Cl and I), as well as Cs, Te, U and Pu.
  - ➡ Possible impact on cladding integrity via stress corrosion cracking or pitting corrosion in conjunction with other cladding degrading phenomena.
- Chlorine and iodine are present as Cl^- and I^- in SNF and interaction layer on Zircaloy.
  - ➡ Readily soluble species contribute to Instant Release Fraction of SNF.
- Elements associated with ε-particles (e.g., Pd, Tc, Ru) are present in their metallic state.
  - ➡ Further experiments planned (i) to investigate properties of ε-particles and (ii) to elucidate hydrogen activation effect on suppression of matrix dissolution.

This work has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement N°847593.

[1] González-Robles et al., MRS Advances, 62, 4163-4168 (2016).
[2] Mennecart et al., J. Nucl. Mater., 154811 (2024).
[3] Cui et al., Appl. Catal., B, 94, 173-178 (2010).
[4] Carbol et al., GCA, 73, 4366-4375 (2009).