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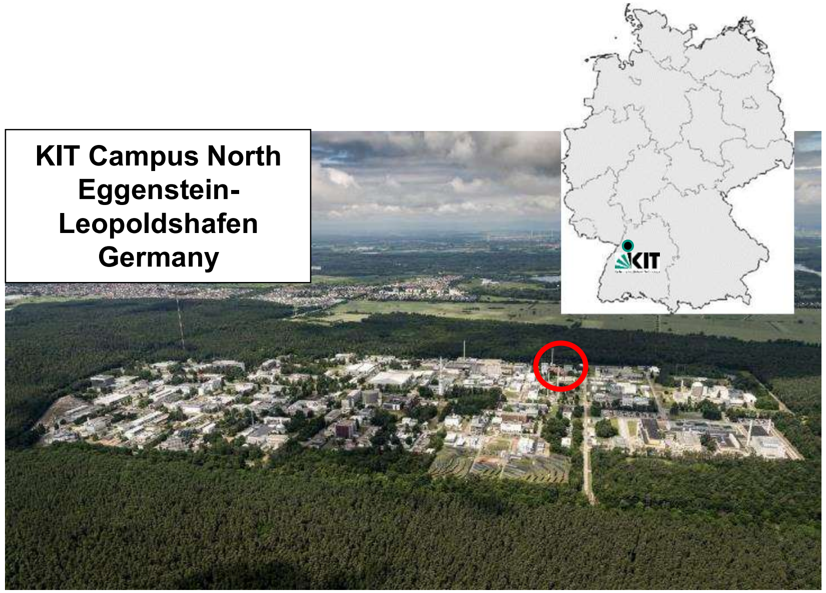
Long-term dissolution experiments with medium and high burn-up spent UO_X and MOX fuels under conditions expected in a deep geological repository

T. König, R. Dagan, E. González-Robles, M. Herm, V. Metz, A. Walschburger and H. Geckeis

Karlsruhe Institute of Technology (KIT), Institute for Nuclear Waste Disposal (INE), P.O. Box 3640, 76021 Karlsruhe Germany

The Institute for Nuclear Waste Disposal (KIT-INE)


KIT Campus North
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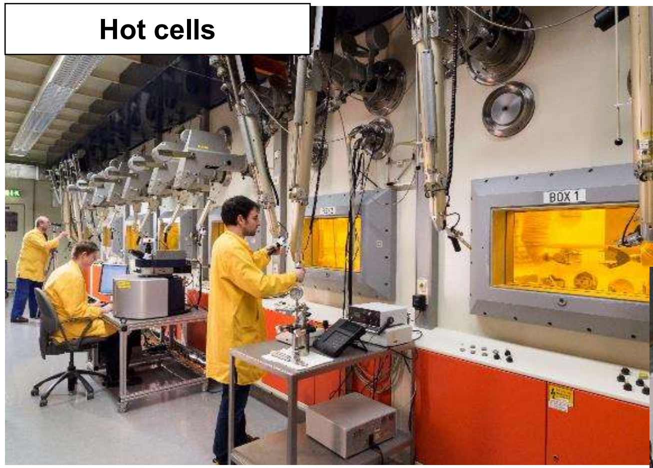
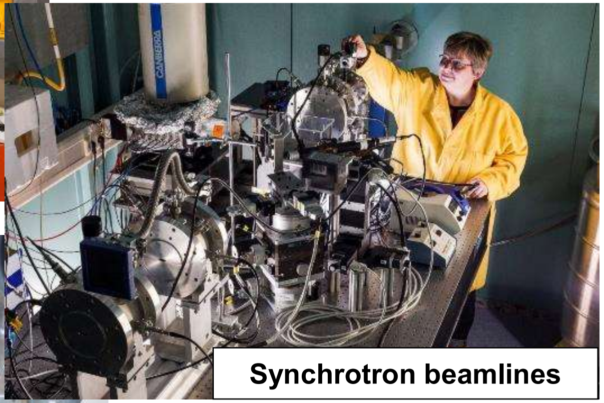
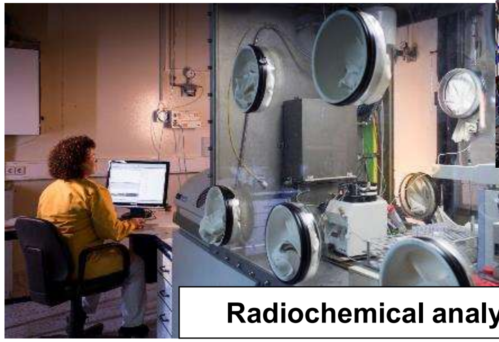

Hot cells


Synchrotron beamlines


Radiochemical analytics

1980 - 2020
INE - 40
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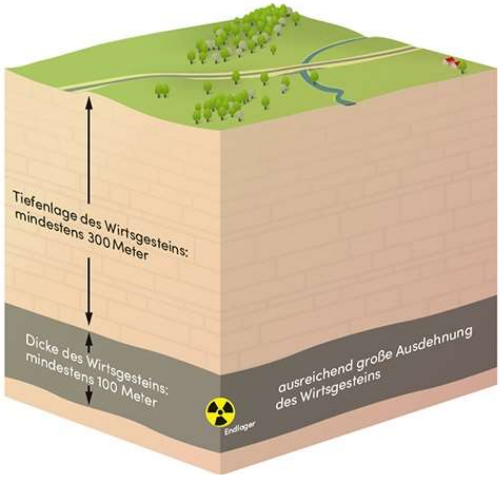
→ ~120 colleagues and many students, interns, guest scientists, etc.

Final disposal of SNF

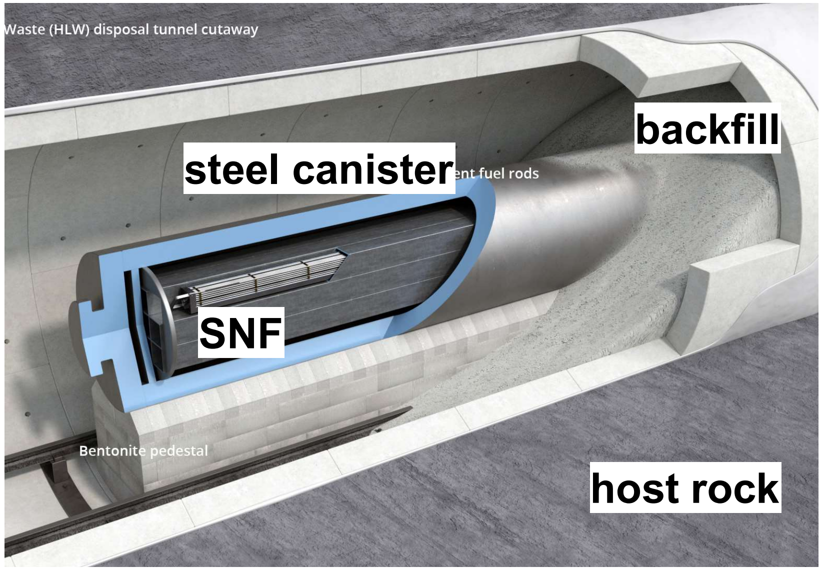
- Direct disposal of spent nuclear fuel (SNF) in deep geological repositories considered in many countries.
- Water access, consecutive failure of canister and loss of cladding integrity considered in long-term safety analysis of deep underground repositories.
- Assessing performance of SNF in geological disposal system requires:
  - Process understanding of **SNF dissolution** and **rates**.
  - **Quantification of radionuclides release** from SNF under **reducing conditions**.



https://www.einblicke.de/fileadmin/images/magazin/Einblicke_6/Kriterien_zur_Endlagersuche.jpg (aufgerufen am 04.04.2022).

Deep geological repository

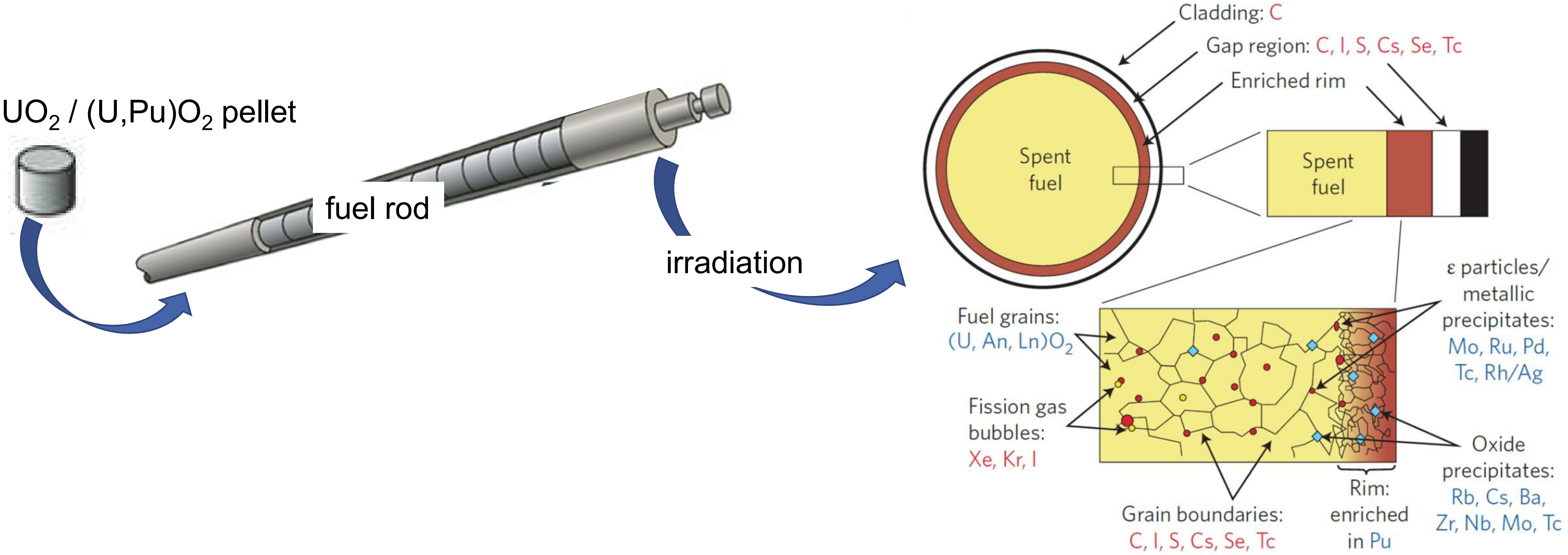
- Multibarrier concept: technical (e.g. waste matrix, cladding), geo-technical (e.g. buffer, backfill) and geological barriers (e.g. host rock, overburden).
- Oxygen trapped in deep geological repository after its closure will be consumed e.g. by bacteria, reducing minerals and aerobic corrosion of outer layers of waste canisters.
- Subsequently, ground water in contact with metallic canisters leads to **anaerobic corrosion of metals**, mainly corrosion of iron:
→ H_2 pressure build-up ≥ 50 bar in repository.



https://www.grimsel.com/gts-information/waste-disposal-overview/the-engineered-barrier-system (02.11.2021).

Composition and distribution of radionuclides in SNF

- Radionuclides are heterogeneously distributed in spent nuclear fuel.



UO_2 / $(U,Pu)O_2$ pellet

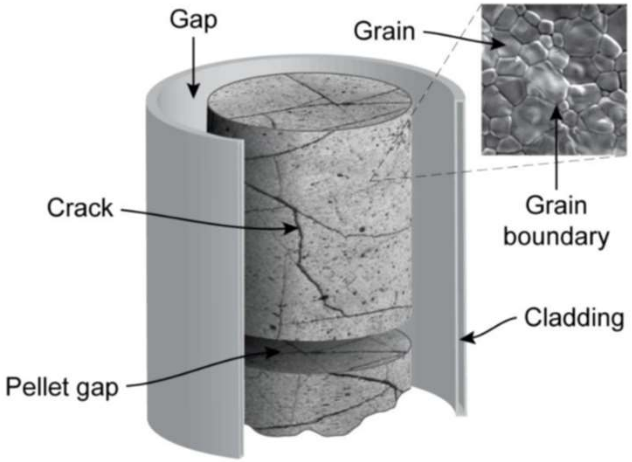
fuel rod

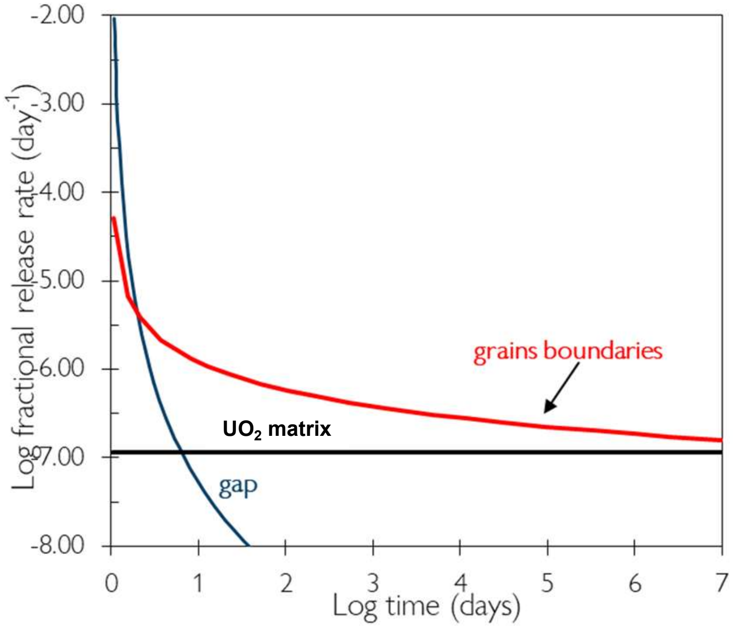
irradiation

Buck et al. (2004) and Bruno et al. (2006); The McGraw-Hill companies.

SNF-water interaction in deep geological repository

- In order to derive a source term model, dissolution and alteration processes of SNF can be grouped into two stages:
  - (1) instantaneous release (IRF) due to waste package and cladding failure: fission gases (**Xe**, **Kr**), volatile/long-lived elements (**I**, **Cs**, **Cl**) present in **gap** and **grain boundaries**.
  - (2) long-term release as result of dissolution of **UO_2 matrix**: actinides (**Pu**, **Np**), lanthanides, segregated oxides (**Rb**, **Tc**) and metallic precipitates (**Ru**, **Pd**, **Tc**).

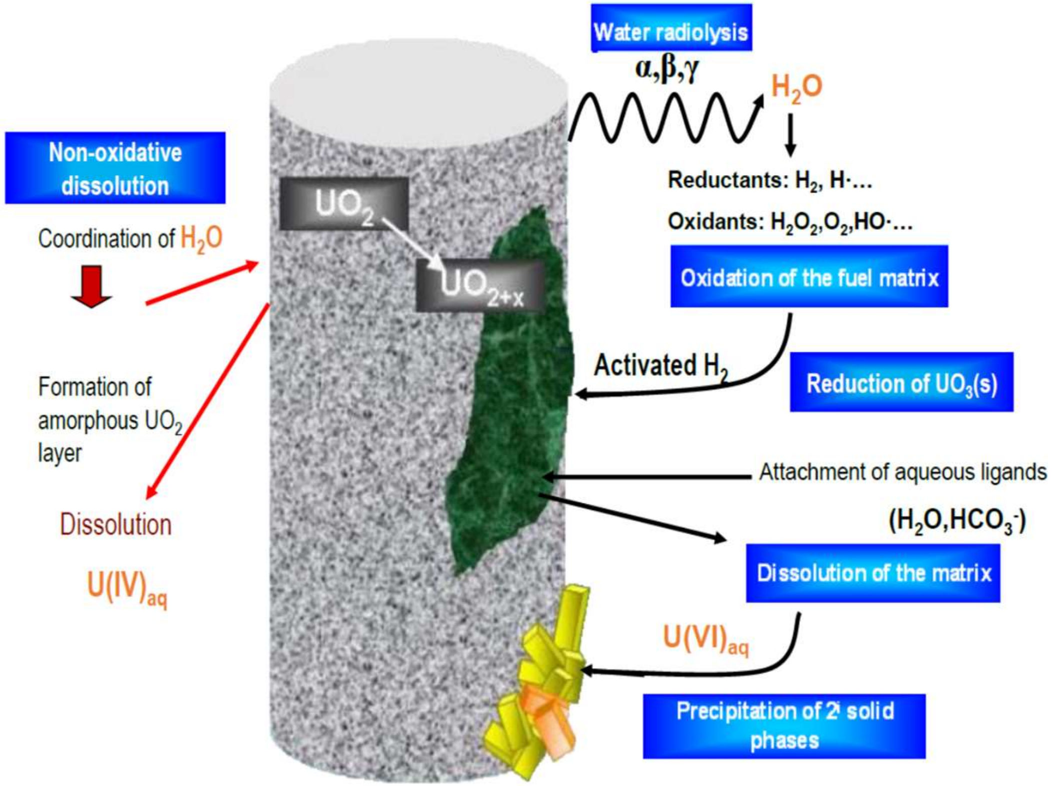




Pastina et al. (2021)

Radiolysis based matrix dissolution

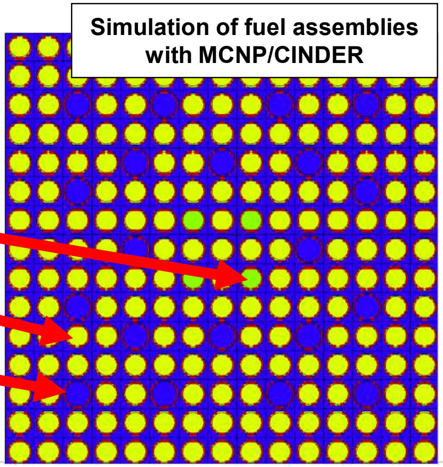
- Most radionuclides produced during irradiation of nuclear fuel in a reactor are trapped in the UO_2/(U,Pu)O_2 crystalline matrix.
- Matrix alteration models (MAM) developed.
- Radiolysis enhanced oxidative dissolution of SNF.
  → U(IV) to U(VI).
- Activated, dissolved H_2 counteracts matrix dissolution.
  → reduction of U(VI) to U(IV) in vicinity of SNF.
- Precipitation of secondary phases (probably U(VI)):
  e.g. $UO_{3(s)}$ on SNF surface.
- Non-oxidative dissolution leads to an amorphous, more soluble layer of U(IV) on SNF surface:
  e.g. $U(OH)_{4(am)}$.



Pastina et al. (2021)

Objectives of experiments performed for final disposal of SNF

- Determination of matrix dissolution of SNF under relevant disposal conditions, including hydrogen overpressure and comparison of [U] with respective uranium solubility data.
- Determination of instant release fraction (IRF) of SNF under relevant disposal conditions (incl. hydrogen overpressure).
- Determination of radionuclide inventory in SNF/cladding using experimental and theoretical methods:
    - Radiochemical inventory analysis.
    - Inventory calculations using:
        - MCNP/CINDER.
        - webKORIGEN.



Simulation of fuel assemblies with MCNP/CINDER

Green pins
investigated fuel segments

Yellow pins
generating power and flux without burn-up

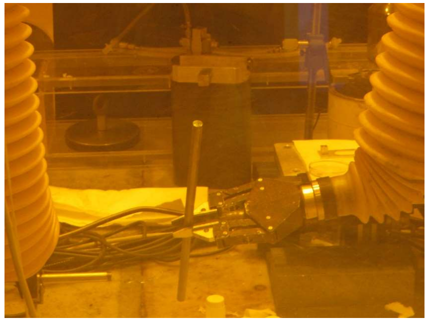
Guide tubes:
filled with water (control rods extracted)

Blue:
water of primary circuit

Fuel characteristics and irradiation data

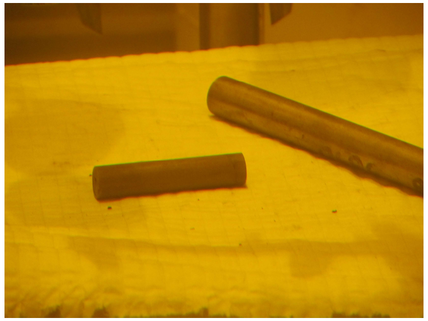
Fuel rod 1108 irradiated in the PWR Gösgen (Switzerland):

- **Fuel type:** UO_2 with 3.8 % initial U-235.
- **Cycles**: 4.
- **Effective full power**: 1226 days.
- **Average linear power:** 260 $W \cdot cm^{-1}$.
- **Average burn-up of:** 50.4 GWd/t_{HM}.
- **Fission gas release (puncturing):** 8.5 %.



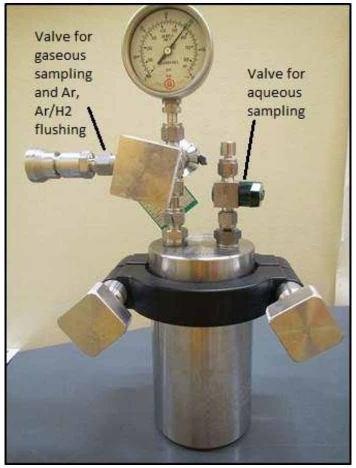
Fuel rod 5810 irradiated in the PWR Obrigheim (Germany):

- **Fuel type:** MOX with 3.2 % Pu (OCOM[*]).
- **Cycles**: 4.
- **Effective full power**: 1157 days.
- **Average linear power:** 200 $W \cdot cm^{-1}$.
- **Average burn-up of:** 38 GWd/t_{HM}.
- **Fission gas release (puncturing):** 6 %.



Leaching experiments with SNF

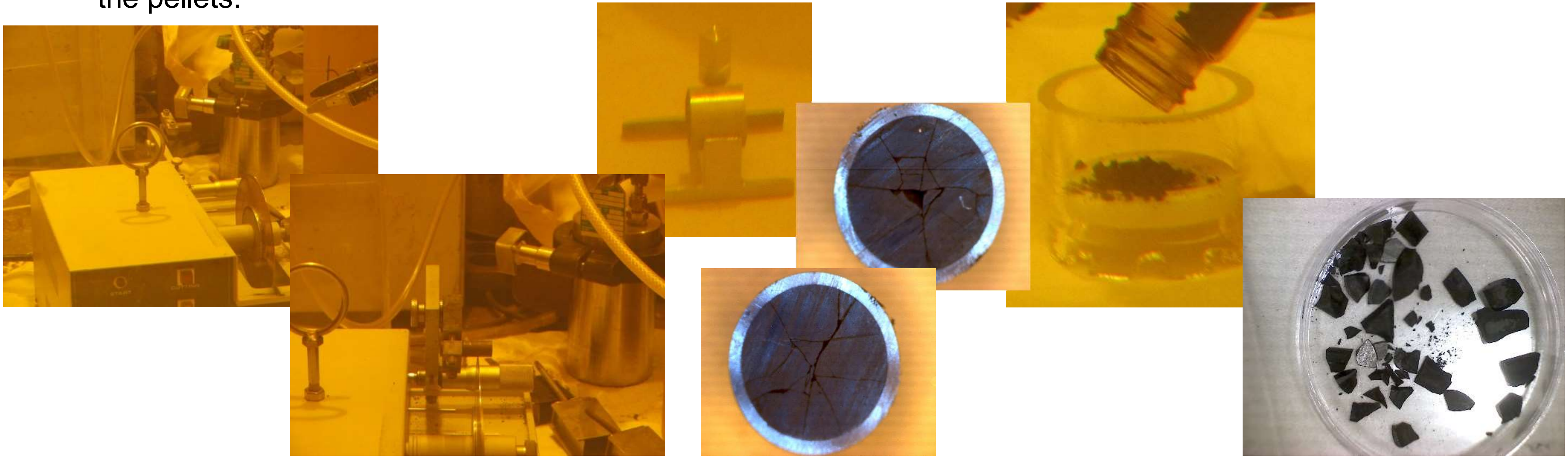
- **Autoclaves:** Stainless steel vessel with titanium liner and lid (total volume of 250 mL) with 2 valves in the lid to allow sampling of gases and liquids.
- Static experiments with periodic samplings (10–15 mL and no refilling of the solution).
- **Leaching solution:** Mainly use of synthetic ground waters in leaching experiments with SNF.
  - Young cement water with calcium as proxy for cementitious ground water (pH 13.5).
  - **Bicarbonate water as proxy for granitic ground water (pH 8.5).**
  - Concentrated NaCl as proxy for salt brines.
- **Atmosphere:** anoxic or reducing (Ar/H_2).
- **Total pressure in autoclave:** up to 40 bar (partial pressure of H_2 3.2 bar).



Preparation of SNF samples

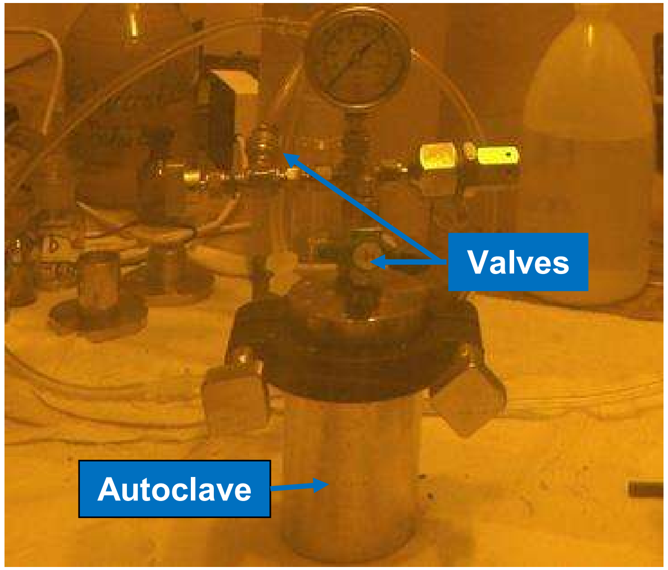
SNF samples cut from the fuel rod segments:

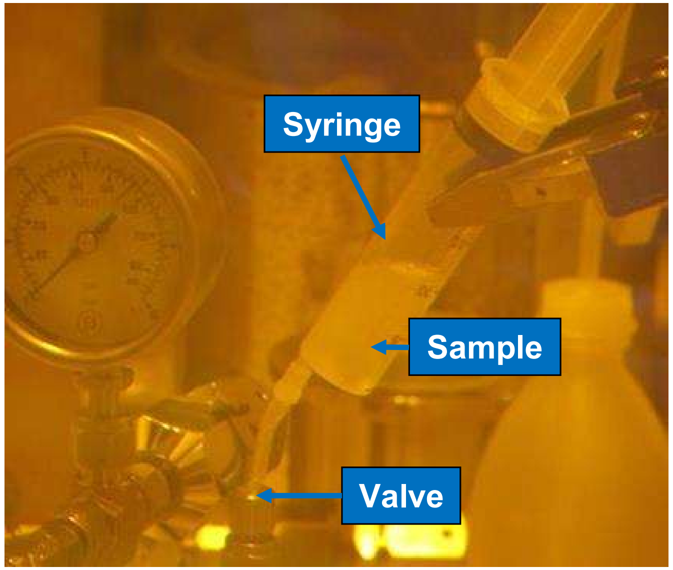
- Low speed saw with diamond blade.
- Absence of cooling liquid and slow cutting to limit any heating as a result of friction between the blade and the pellets.

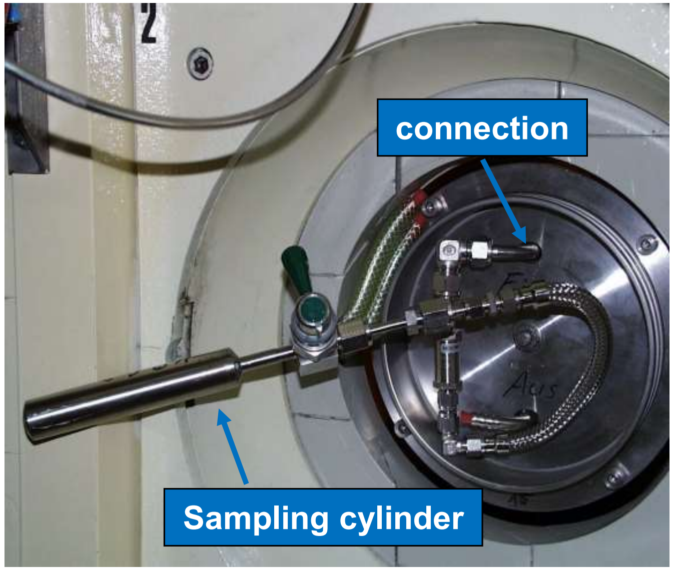


Sampling and analytics of aqueous and gas phases

- Measurement of: **Sr-90**, **I-129**, **Cs-137**, **U-238**, **Pu-239**.
- Measurement of **lanthanides, other minor actinides**, **fission and activation products (e.g., Cl-36), pH**.
- Measurement of gas composition, in particular **fission gases** (Kr, Xe) by means of gas-mass spectrometry (radiolytic production of O_2 and intrusion of air checked using nitrogen as proxy).







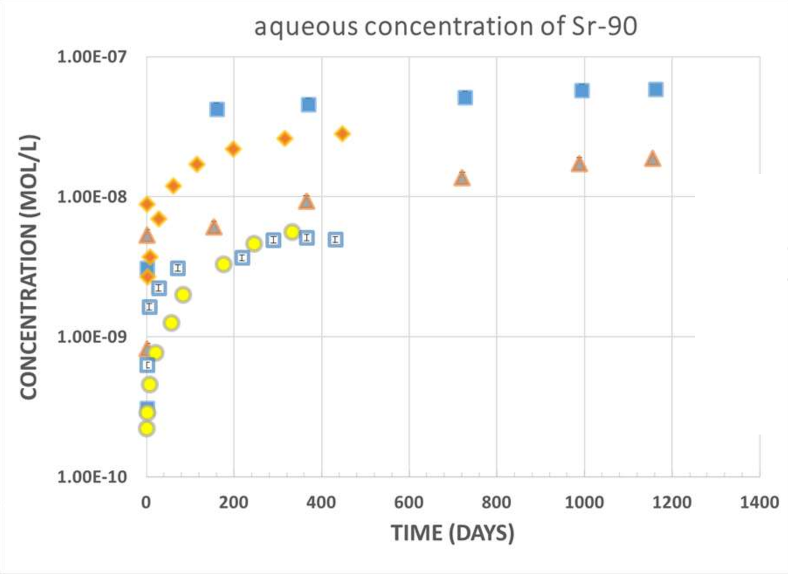
SNF inventory calculations & radiochemical determination

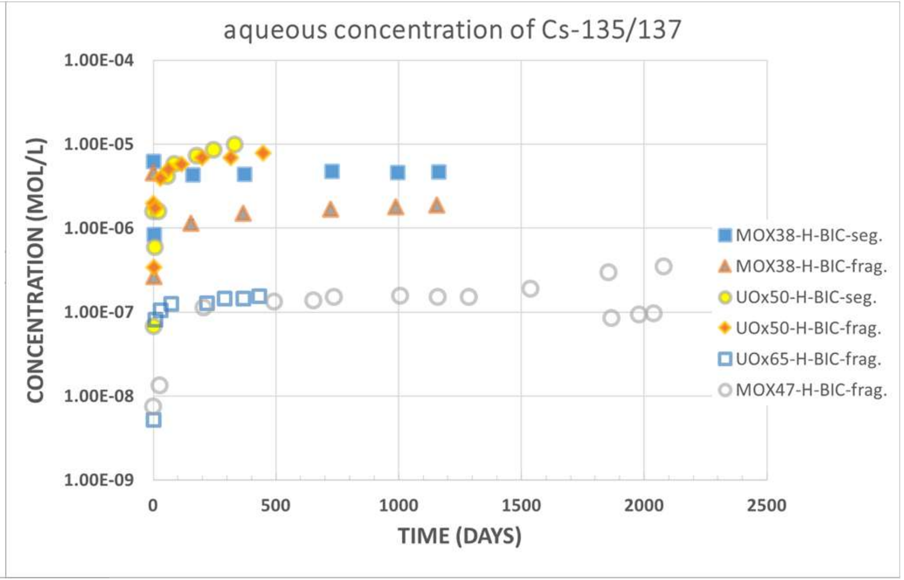
- Calculated radionuclide inventory [mol/g_{HM}] for both fuel types:
  - **MCNP/CINDER for Gösgen UO_X** fuel (50.4 GWd/t_{HM}).
  - **webKORIGEN for Obrigheim MOX** fuel (38.0 GWd/t_{HM}).
- Inventories of Kr and Xe were calculated taking into account the inventory released into plenum:
  - **8.3 % for Gösgen UO_X** fuel.
  - **6.0 % for Obrigheim MOX** fuel.

	50.4 GWd/t_{HM} UO_X [mol/g_{HM}]		38.0 GWd/t_{HM} MOX [mol/g_{HM}]	
	Calc.	**Exp.**	**Calc.**	**Exp.**
Kr	5.60E-06	5.44E-06	2.16E-06	tba
Xe	5.90E-05	5.40E-05	3.86E-05	tba
^{90}Sr	3.34E-06	4.96E-06	1.36E-06	tba
^{129}I	1.84E-06	2.85E-06	1.82E-06	2.55E-06
^{137}Cs	7.24E-06	5.87E-06	4.65E-06	5.32E-06
^{238}U	3.88E-03	4.05E-03	3.74E-03	3.78E-03
^{237}Np	3.19E-06	3.87E-06	1.59E-06	1.83E-06
^{239}Pu	2.80E-05	2.41E-05	6.35E-05	5.14E-05
^{241}Am	6.01E-06	7.65E-06	2.90E-05	2.64E-05
^{243}Am	1.02E-06	1.38E-06	6.81E-06	3.79E-06
^{244}Cm	1.98E-07	2.09E-07	1.10E-06	5.84E-07

Fission products release to solution (in molar concentration)

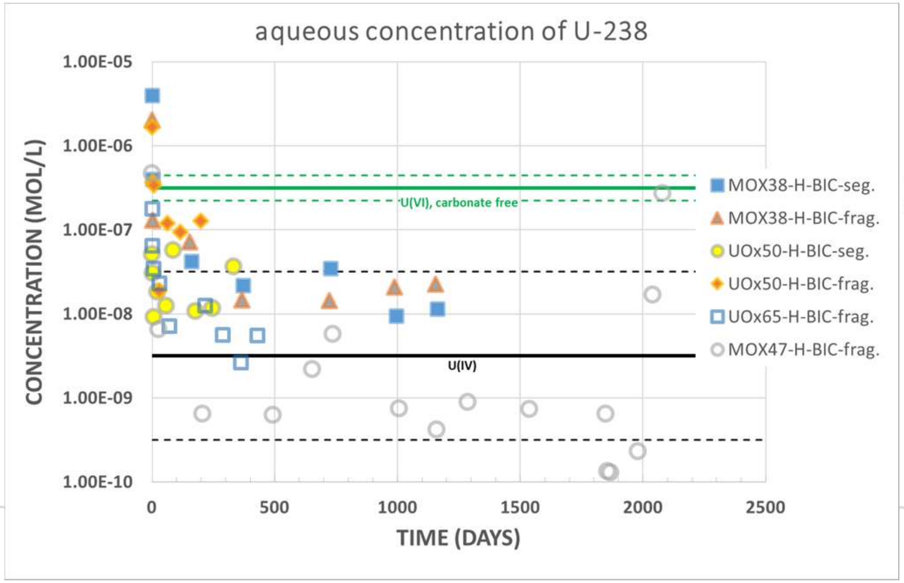
- Concentration of Sr-90 and Cs-135/137 in solution after 1156 days of leaching MOX fuel.
- Fast release of Sr-90 and Cs-135/137 in first 400 days of leaching seen in all experiments.
- Release of strontium and caesium diminish with time but clearly continue slowly, towards concentration plateau in the long-term.
- Good agreement of p.w. data with literature (spent MOX / UO_2 fuels) [Carbol et al., 2009].

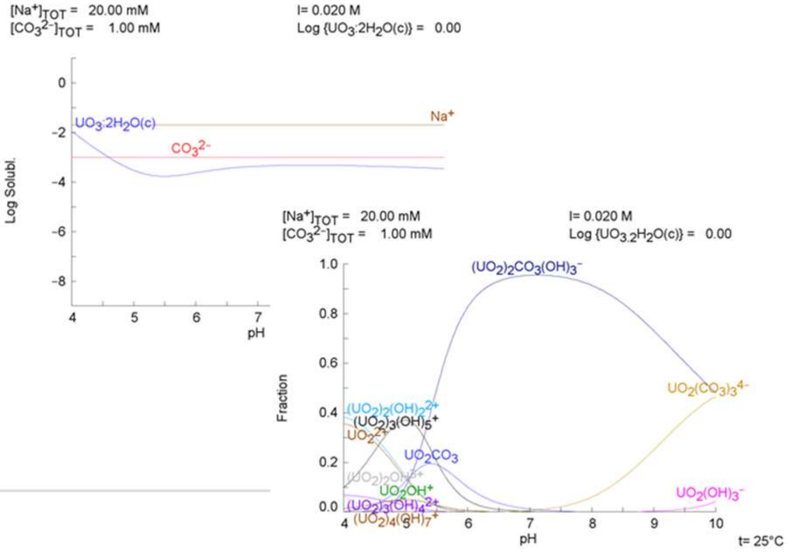




Uranium release to solution (in molar concentration)

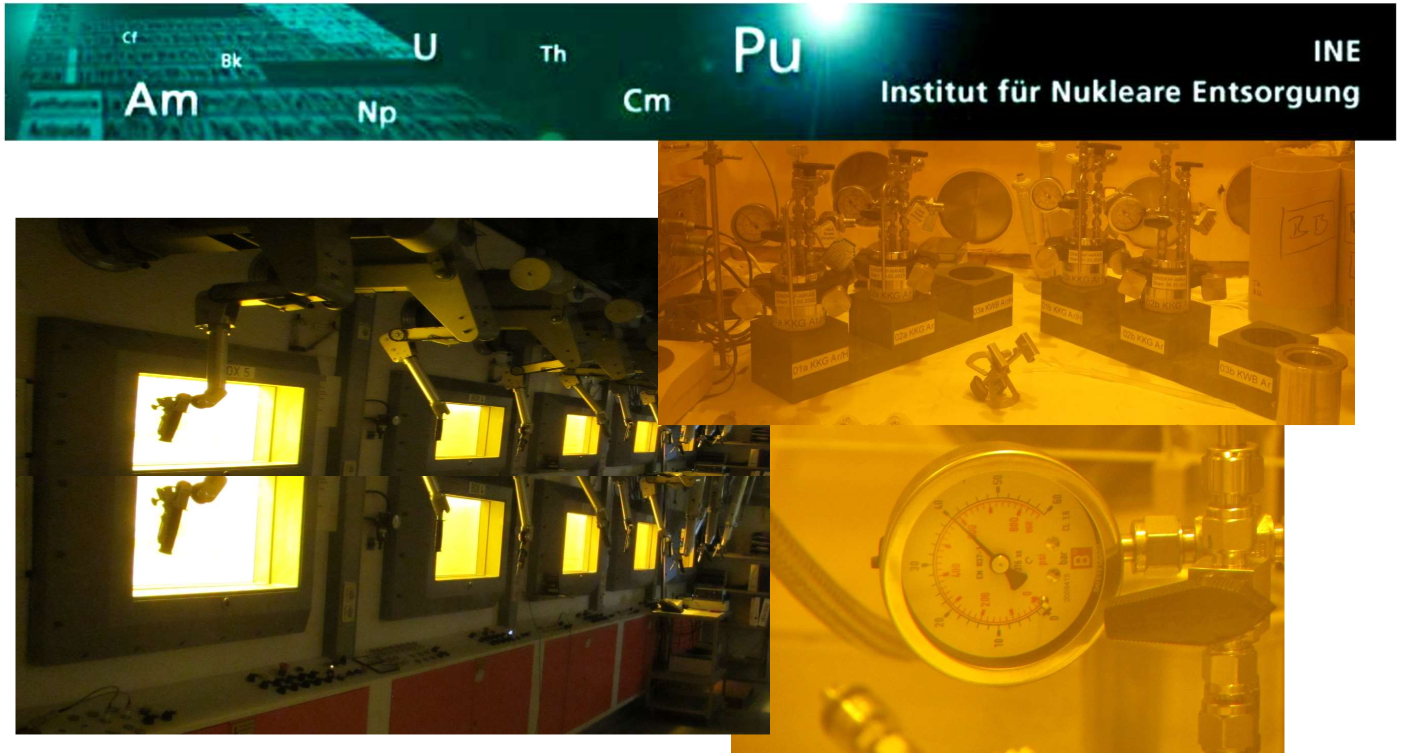
- Concentration of uranium in solution after 1156 days of leaching MOX fuel.
- Large scatter at beginning in all experiments (e.g. pre-oxidised fuel layers).
- [U-238] approach towards solubility limit of U(IV) within uncertainty in all experiments.
- For comparison: U(VI) solubility in systems with carbonate (≥ 1 mM) much higher according to NEA-TDB calculations using $UO_3 \cdot 2H_2O$(cr), $Na_2U_2O_7 \cdot H_2O$(cr) or UO_2CO_3(cr) as solid phase controlling solubility in 19 mM NaCl + 1 mM $NaHCO_3$ solutions.





Summary

- Radiochemical inventory determination in good agreement with data obtained from calculations.
- Leaching experiments in autoclaves were performed using irradiated UO_X and MOX fuel in bicarbonate water and under hydrogen overpressure.
- Strontium and caesium show fast, initial release in all experiments. Then release slows significantly down but continuous release observed.
- Solubility of actinides approaches towards solubility limits of respective An(IV) solid phases in the long-term.
- Inhibition of matrix dissolution is attributed to presence of hydrogen.
- Based on p.w. and literature data on leaching experiments performed with spent MOX fuels or spent UO_X fuels under reducing conditions, no significant difference between dissolution behaviour of the studied MOX and UO_X fuels can be seen.



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Modern Spent Fuel Dissolution and
Chemistry in Failed Container Conditions

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Thank you for your kind attention!

This work received funding from the Euratom research and training programme 2014-2018 under grant agreement No **755443** and the European Union's Horizon 2020 research and innovation programme under grant agreement No **847593.**