Corrosion of spent MOX fuels under repository-relevant conditions

Giuseppe Modolo[1*], Guido Deissmann[1], Gregory Leinders[2], Thierry Mennecart[3], Christelle Cachoir[3], Karel Lemmens[3], Marc Verwerft[2], Dirk Bosbach[1]

[1]Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research – Nuclear Waste Management and Reactor Safety (IEK-6), Jülich, Germany

*g.modolo@fz-juelich.de

[2]Institute for Nuclear Materials Science, Belgian Nuclear Research Centre (SCK•CEN), Boeretang 200, B-2400 Mol, Belgium

[3]Institute for Environment, Health and Safety, Belgian Nuclear Research Centre (SCK•CEN), Boeretang 200, B-2400 Mol, Belgium

Spent fuel workshop, Ghent, Belgium, November 14-15 2019

SCK•CEN
STUDIECENTRUM VOOR KERNENERGIE
CENTRE D'ETUDE DE L'ENERGIE NUCLEAIRE

JÜLICH Forschungszentrum | INSTITUTE OF ENERGY AND CLIMATE RESEARCH

Nuclear Energy – the German perspective

terminated by 2022 – the decommissioning of all NPP will take several decades.

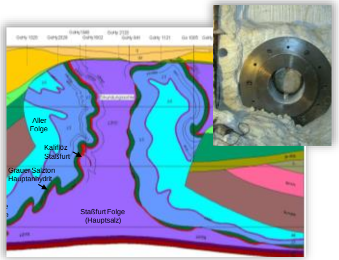
Non-heat generating waste, until 2080 (304 000 m^3)

- Repository Konrad for Germany’s low- and intermediate level waste will start operation in the next decade.

Heat-generating waste , HLW (28100 m^3)

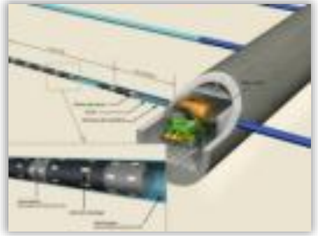
- The German repository site selection act (2017) has restarted the process for the selection of a site for Germany’s high-level waste repository (target date 2031).

Spent nuclear fuel (until 2022):	**17,220 t_{HM}**
reprocessed	6,670 t_{HM}
LWR-fuel for direct disposal (ca.10% MOX)	10,550 t_{HM}
HLW-glass (CSD-V)	670 m^3
MAW-glass (CSD-B)	25 m^3
compacted waste (CSD-C)	740 m^3
other wastes (e.g. HTRSF, RRSF)	5,710 m^3



Rock salt

Crystalline



Clay rock

MOX research in Europe

MOX form	Burn-up	REDOX	Solution	Focus of the studies	Ref.
UO_2–4.92 wt% PuO_2, cladded/decladded fuel fragnents	44.4 GWd/t_{HM}	Reducing, 1–30 mM H_2, RT, 2100 days	NaCl/2mM $NaHCO_3$	Corrosion studies in autoclaves,	**Carbol et al.** *JNM* 2009
UO_2–6.6 wt% PuO_2, decladded SF fragnents	48.8 GWd/t_{HM}	Oxidizing, +207 mV at RT, up to 3 month	DI aerated water, DI aerated water + an external γ-irradiation	Solution chemistry (water radiolysis) and surface characterization	**Jégou et al.** *JNM* 2010
MOX	63 GWd/t_{HM} 30 kW/m	Oxidizing	Air-saturated buffer solutions, pH 8.5	Leaching experiments (IFR) and correlations with fission gas release (IFR)	**Johnson et al.** *JNM* 2012
UO_2–6.6 wt% PuO_2, Segments of SF	48.8 GWd/t_{HM}	Oxidizing, +207 mV at RT, 223 + 605 days	DI aerated water/ + external γ-irradiation pH 5.5	Solution chemistry (water radiolysis) and surface characterization	**Magnin et al.** *JNM* 2015
MOX MIMAS pellets - 7.48 wt.% PuO_2	Not irradiated	Oxic (air) + anoxic (Ar) glovebox	Bicarbonate water ($NaHCO_3$ 10^{-2} M	Solution chemistry (influence of alpha) and surface characterization	**Odorowski et al.** *JNM* 2016
MOX	38 GWd/t_{HM}	Reducing	Bicarbonate water	**EU- Disco Project**	**KIT-INE**
MOX	54 GWd/t_{HM}	Anoxic: Ar	Bicarbonate water	**EU- Disco Project**	**JRC**
MOX	Unirradiadet/+ Pu-238 doped	Anoxic: Ar	Simplified COx water	**EU- Disco Project**	**CEA**

MOX research in Europe

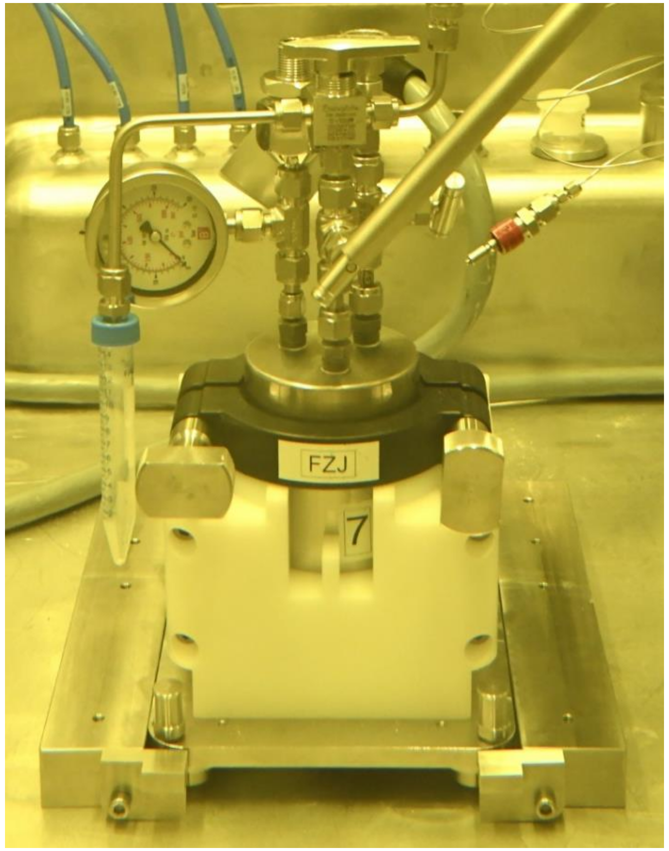
What are the main issues?

- In-reactor MOX fuel behavior is similar to that of UO_2 !
- Can the knowledge acquired for SNF-UOx be transferred to SNF-MOX (Disposal) ?
- Understanding RN release: Instant release fraction (IRF) & Long-term matrix corrosion
  - Effect of SNF history (burn up, linear power rating)
- What is the role of the Pu-rich agglomerates in spent MOX fuel?
- Most studies on MOX were carried out at oxidizing/anoxic conditions!
  - Less relevant for final disposal (reducing)

Corrosion of spent MOX fuel within the SF-ALE project

Objective: study the influence of groundwater chemistry inside waste package on spent fuel degradation and leaching

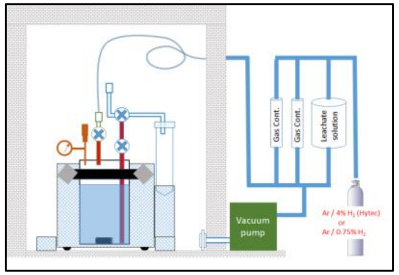
- 3 leaching experiments are carried out with well characterized MOX (Influence of BU)
- Influence of leaching solution under **reducing** conditions @ RT
- IRF and matrix corrosion
- Sampling gas and solution (>30 relevant RN)

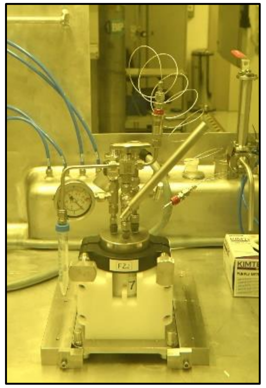


Corrosion of spent MOX fuel within SF-ALE :Timeline

2018/09

2017/04 2018/04 2019/04 2020/04





- Post-irradiation examinations

- Sample preparation
- Sample loading

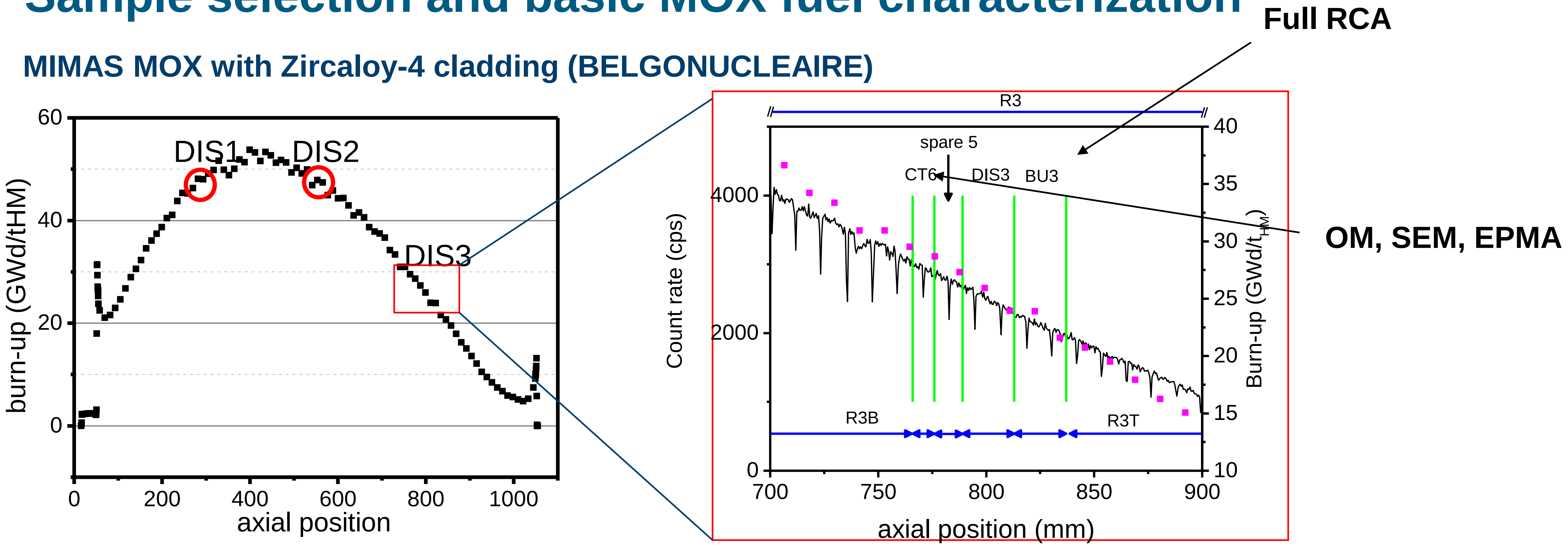
- Start of leaching experiments

- End of leaching experiments
- Rinsing and sample retrieval

- Hold-on period

Sample selection and basic MOX fuel characterization

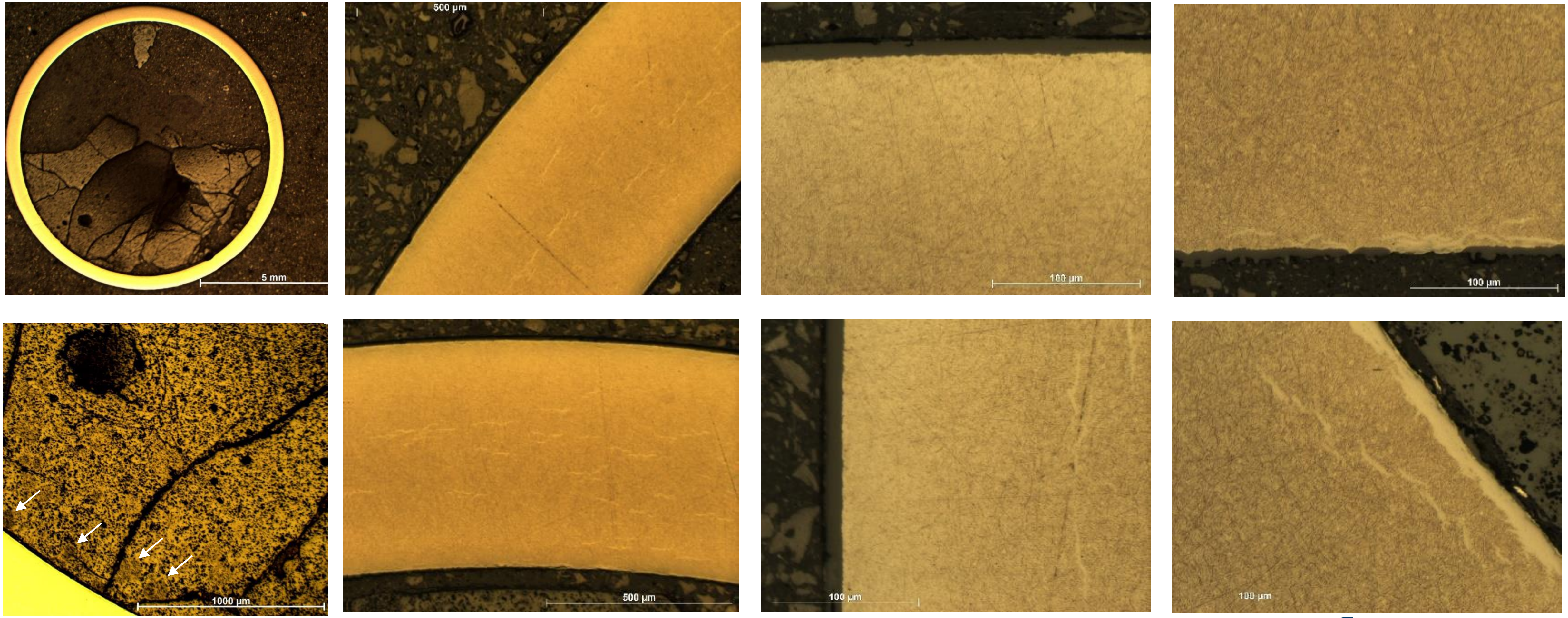
MIMAS MOX with Zircaloy-4 cladding (BELGONUCLEAIRE)



- MOX: 14.3% Pu/(U+Pu)
- Irradiated in BR-3 (1986-1987, 255-270 W/cm) and in BR-2 (1997-2011, 300-325 W/cm)
- Cladded samples: 2 * BU ~ 48 GWd/t_{HM} and 1 * 26 GWd/t_{HM}
- Representative samples for basic characterization (for DIS3: CT6, BU3)

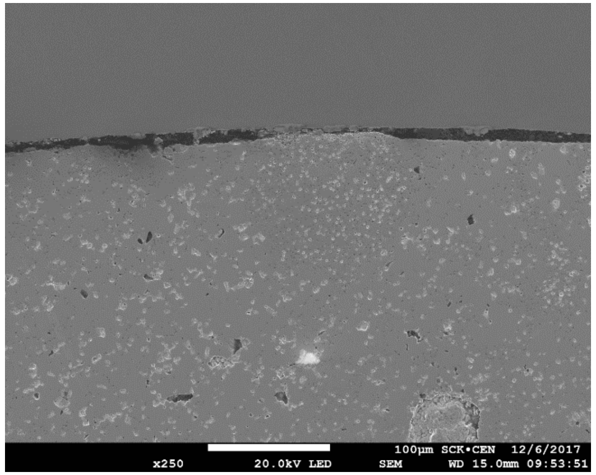
Basic MOX fuel characterization

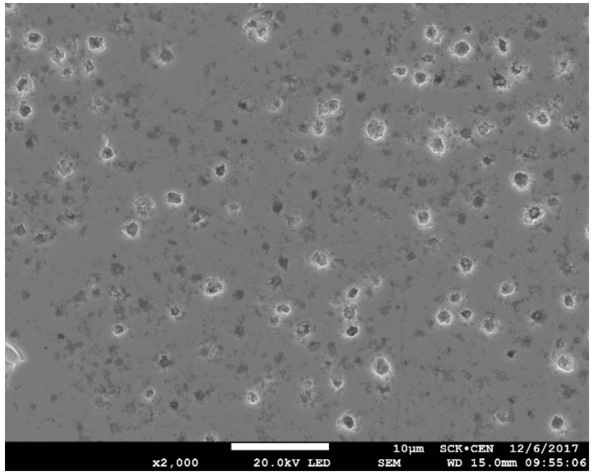
OM: macro image | **cladding hydrides** | **cladding waterside oxide** | **fuel-side corrosion**



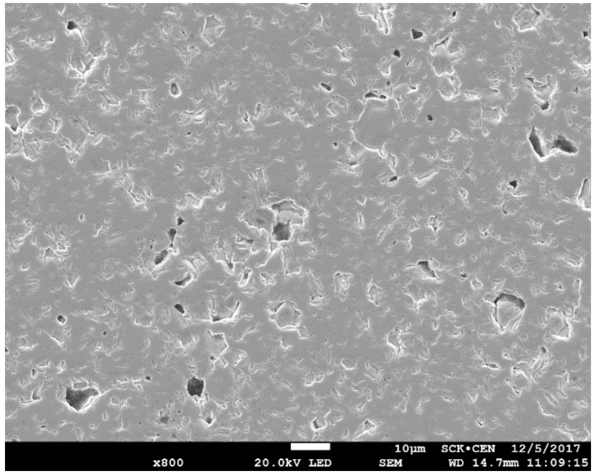
Basic MOX fuel characterization

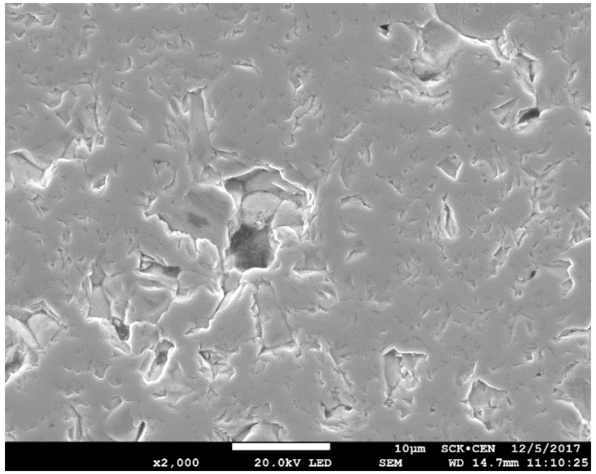
SEM: Pu-rich island



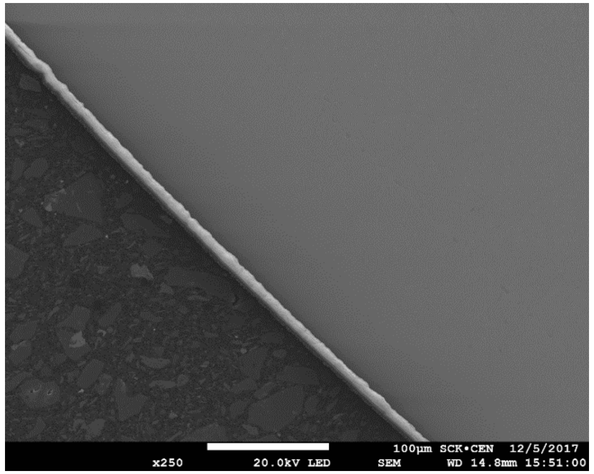


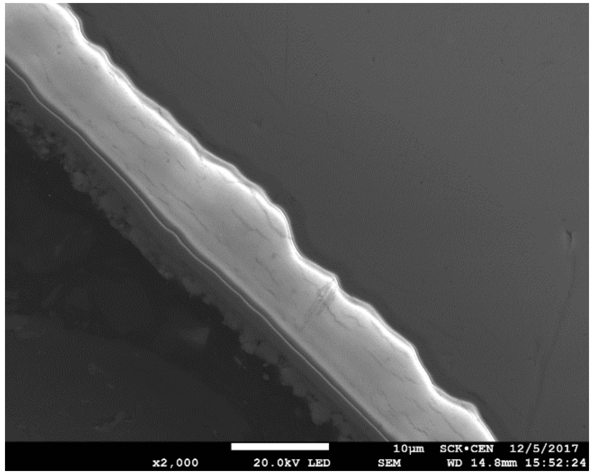
small particles at mid-rad



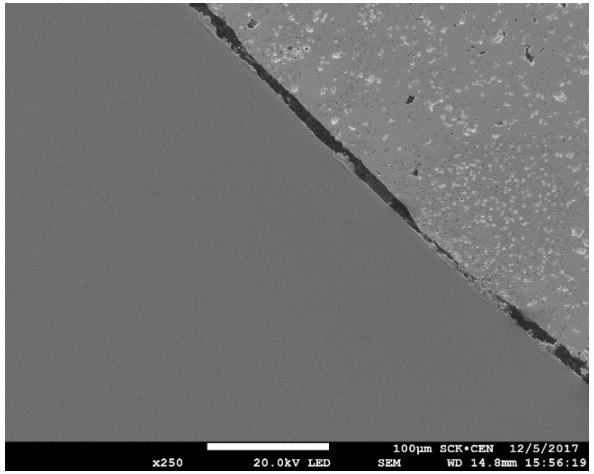


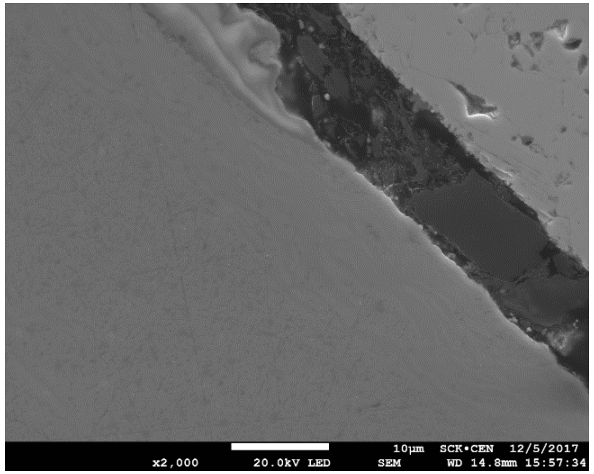
cladding waterside oxide





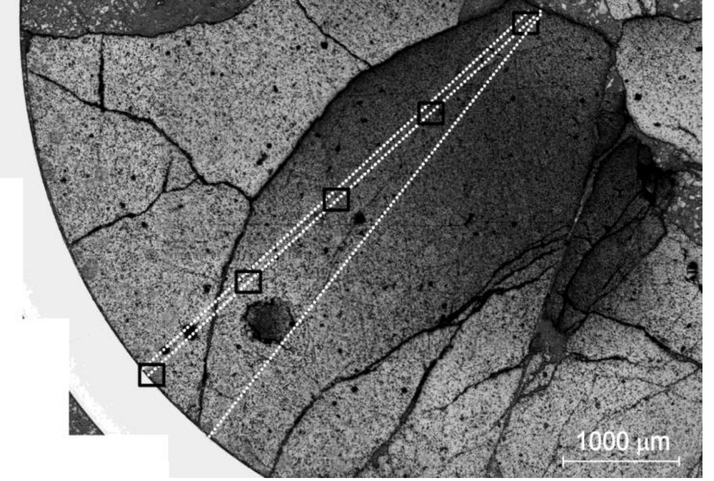
fuel-side



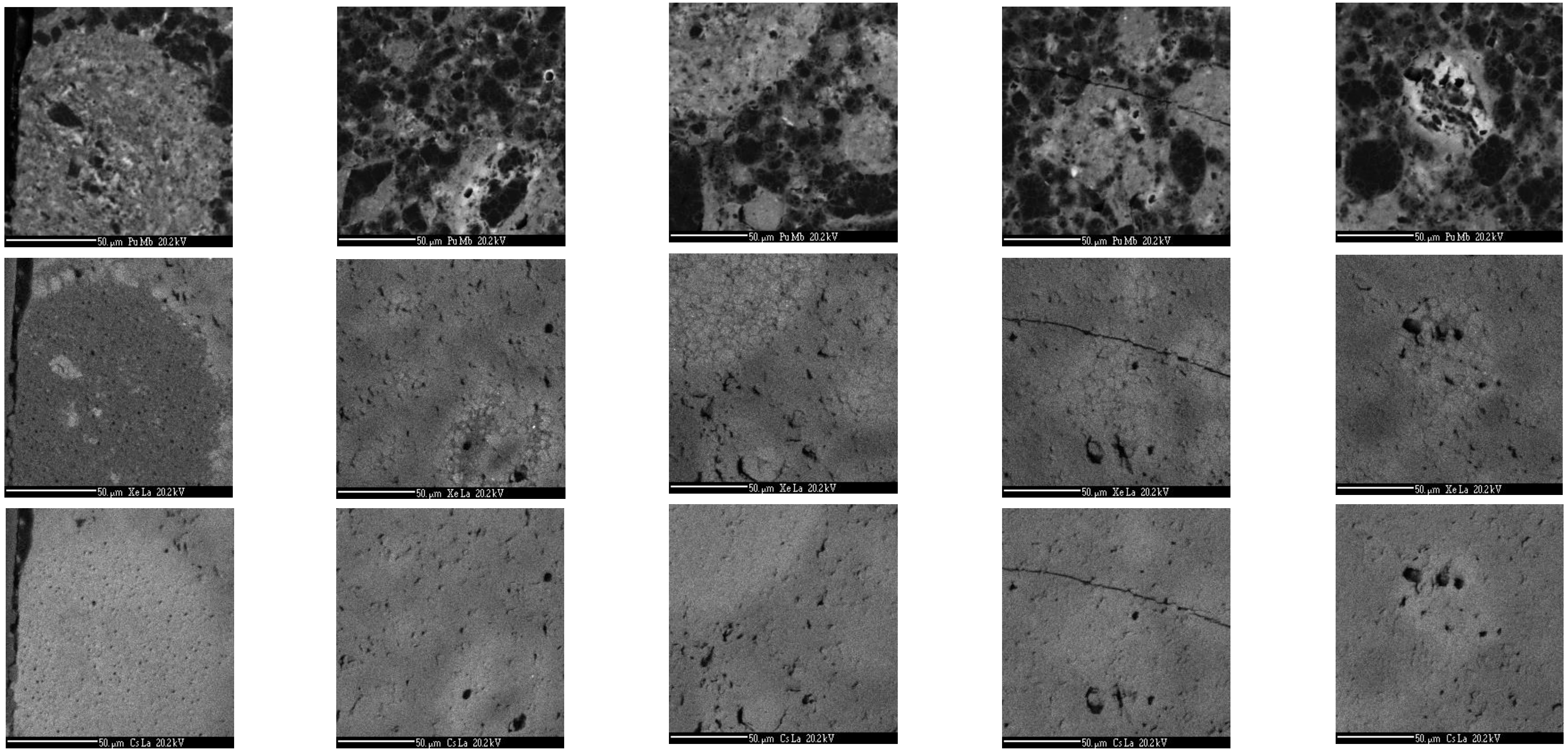


Basic MOX fuel characterization

EPMA: radial maps and profiles for Pu/fission products



Periphery (rim) | ¼ radius | ½ radius | ¾ radius | fuel center



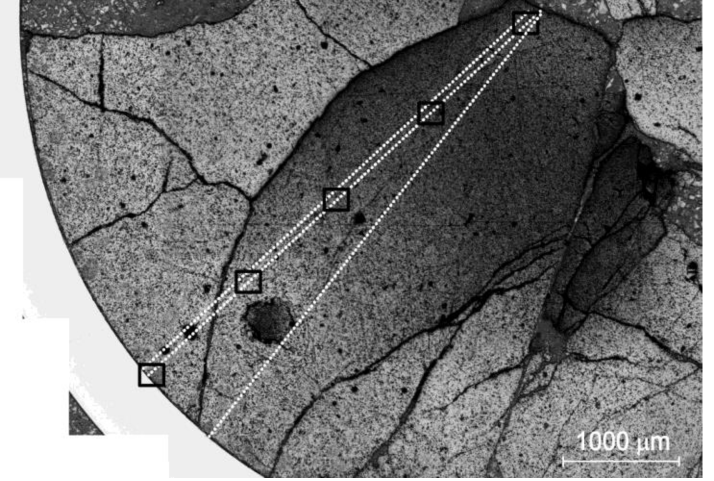
Pu

Xe

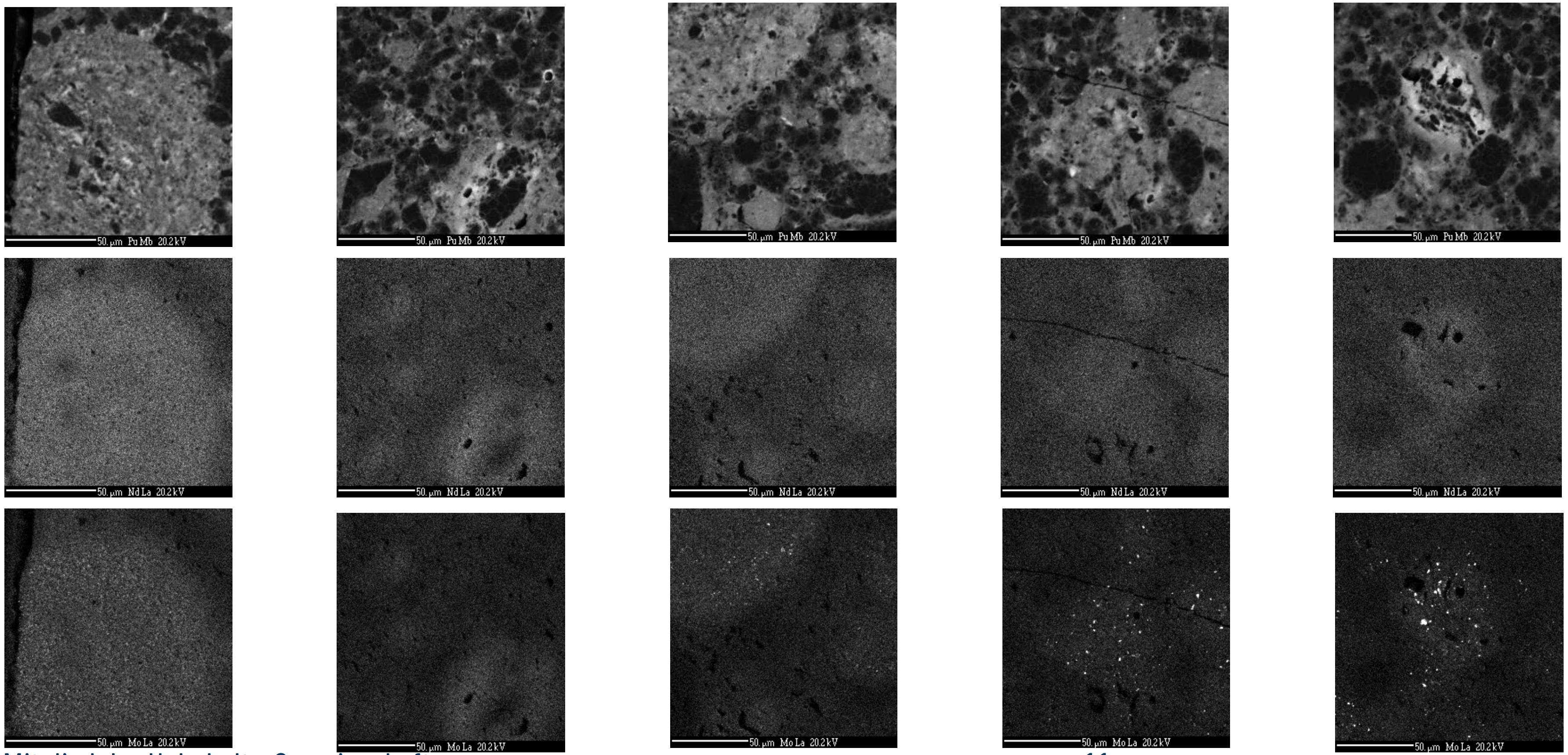
Cs

Basic MOX fuel characterization

EPMA: radial maps and profiles for Pu/fission products



Periphery (rim) | ¼ radius | ½ radius | ¾ radius | fuel center



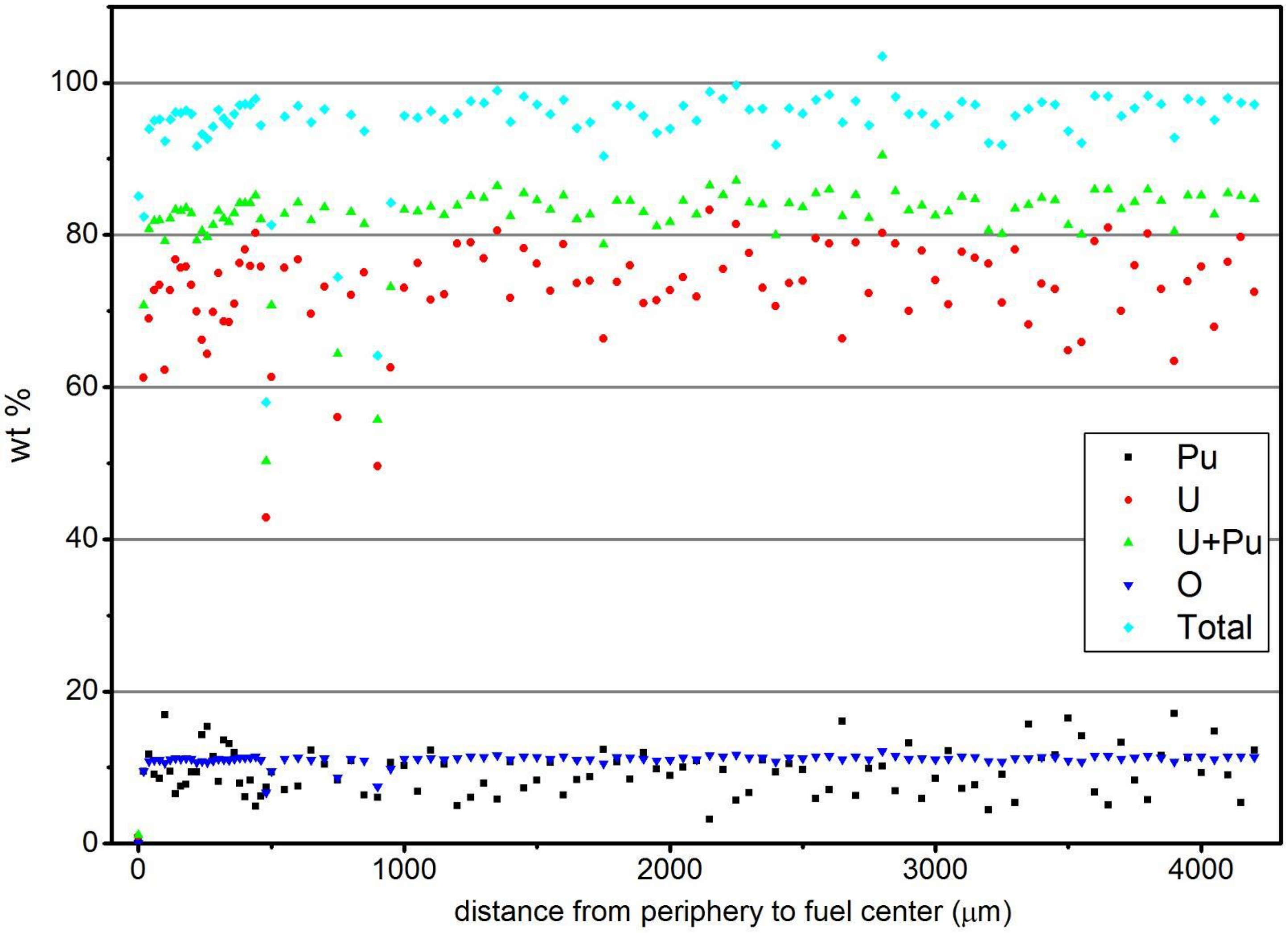
Pu

Nd

Mo

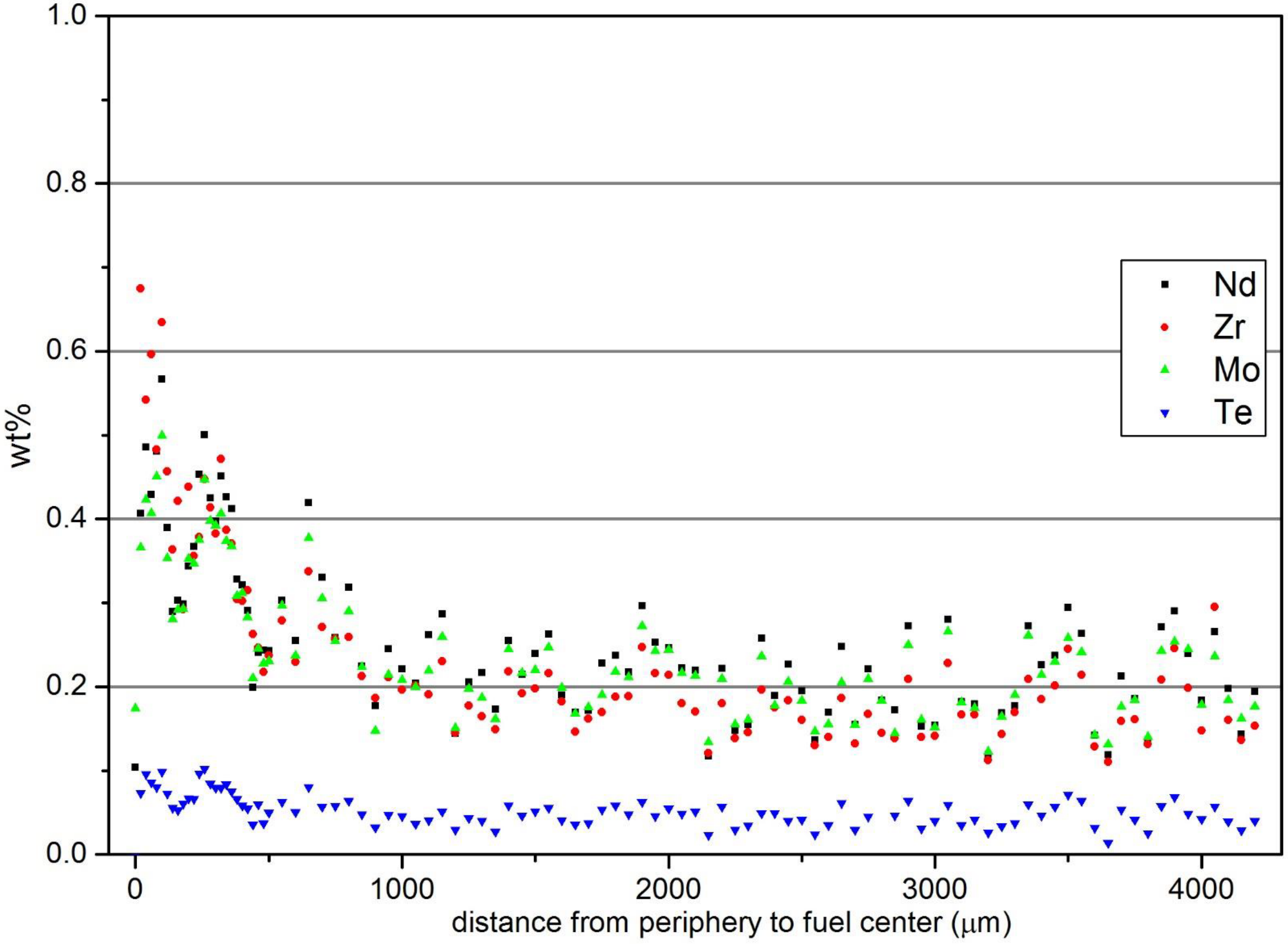
Basic MOX fuel characterization

EPMA line scans: Averaged radial composition for U, Pu, and O

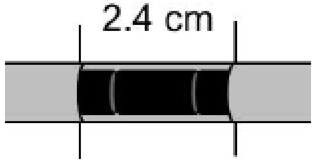


Basic MOX fuel characterization

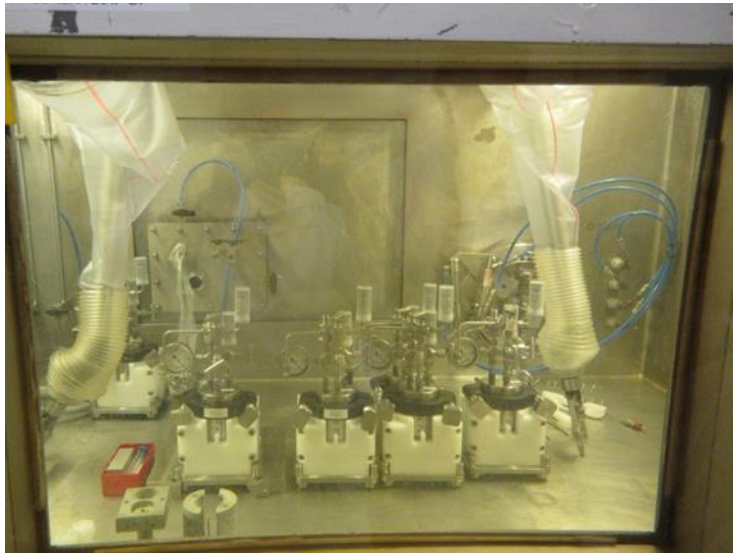
EPMA line scans: Averaged radial composition for Nd, Zr, Mo, and Te

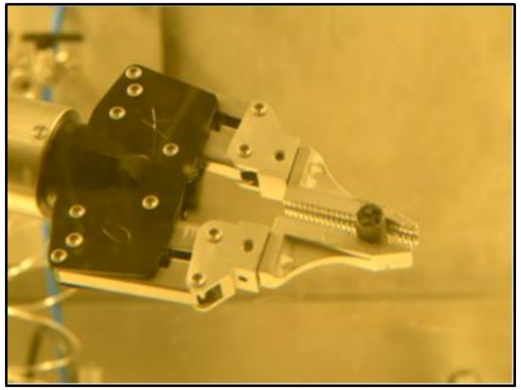


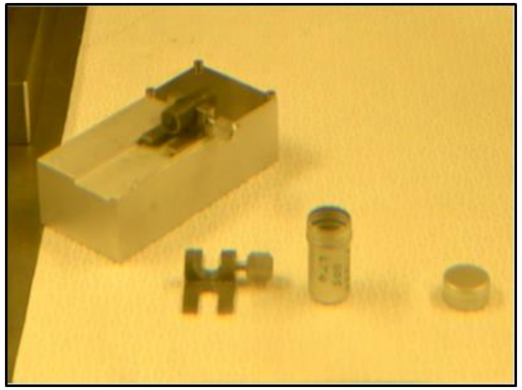
Loading of the autoclaves and start leaching

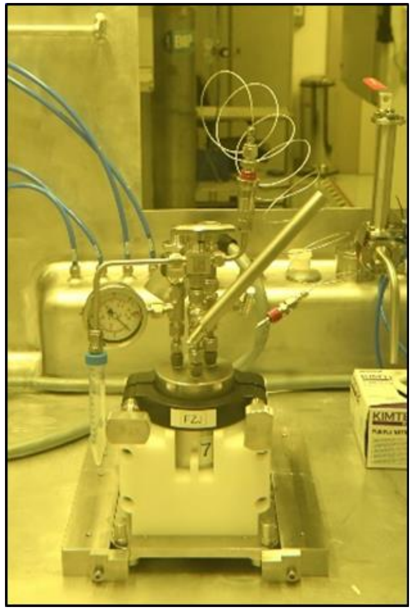


MIMAS MOX with Zircaloy-4 cladding









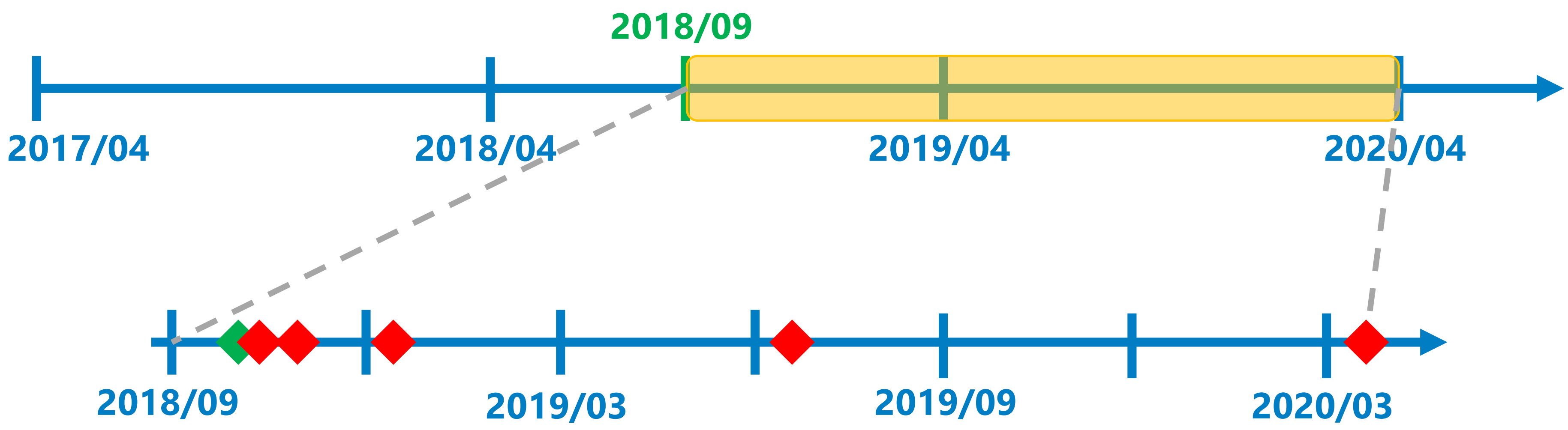
250 mL Ti-lined stainless VA steel autoclaves

Autoclave:	7	8	9
Sample ID:	F6677-DIS1	F6677-DIS2	F6677-DIS3
Fuel type:	MOX	MOX	MOX
Burn-up:	47.6 GWd/t_{HM}	47.9 GWd/t_{HM}	25.8 GWd/t_{HM}
Dissolution liquid:	YCW, pH=13.5[1)]	BC, pH=7.4[2)]	BC, pH=7.4[2)]
Dissolution gas:	Ar / 4% H_2, 40 bar	Ar / 4% H_2, 40 bar	Ar / 4% H_2, 40 bar

[1)] *Young Cement Water with Calcium – light composition*

[2)] *Bicarbonate solution type "First-Nuclides"*

Timeline: Leaching experiments

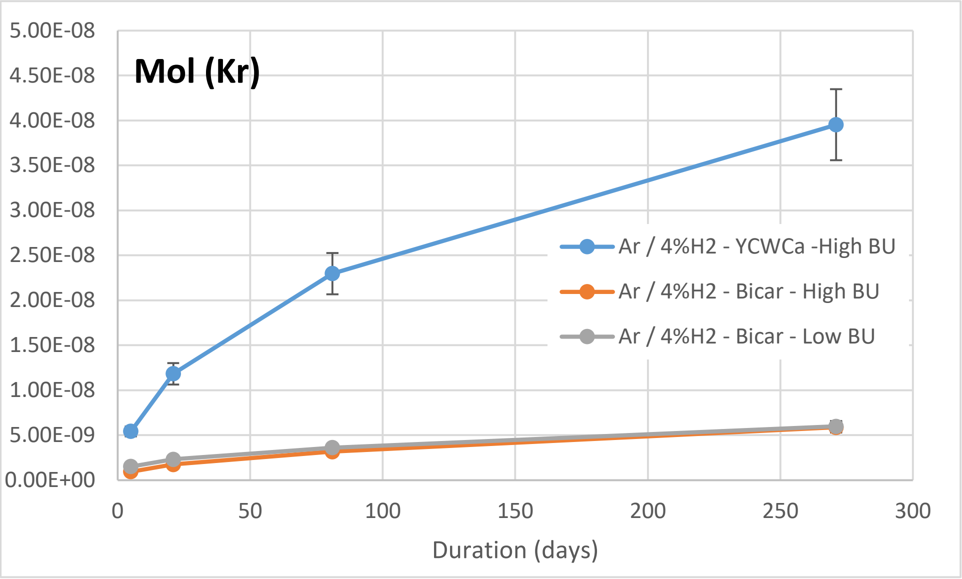


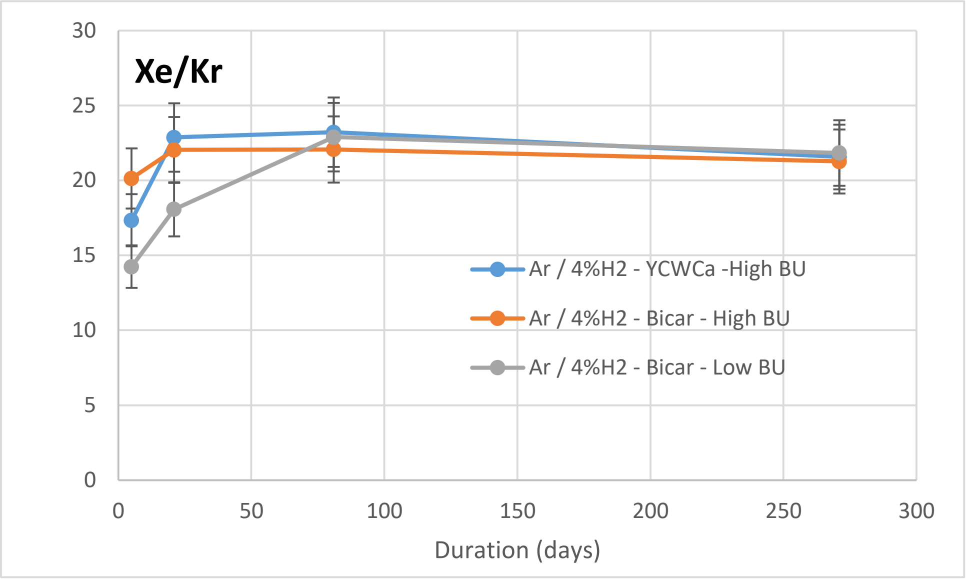
1. +5 days (renewal of leaching medium)	-> IRF	**solution**✓	gas ✓
2. +21 days	-> IRF	**solution**✓	gas ✓
3. +82 days = 2 months + 21 days	-> IRF + matrix	**solution**✓	gas ✓
4. +271 days ≈ 9 months	-> matrix		gas ✓
5. +544 days ≈ 1.5 years	-> matrix		

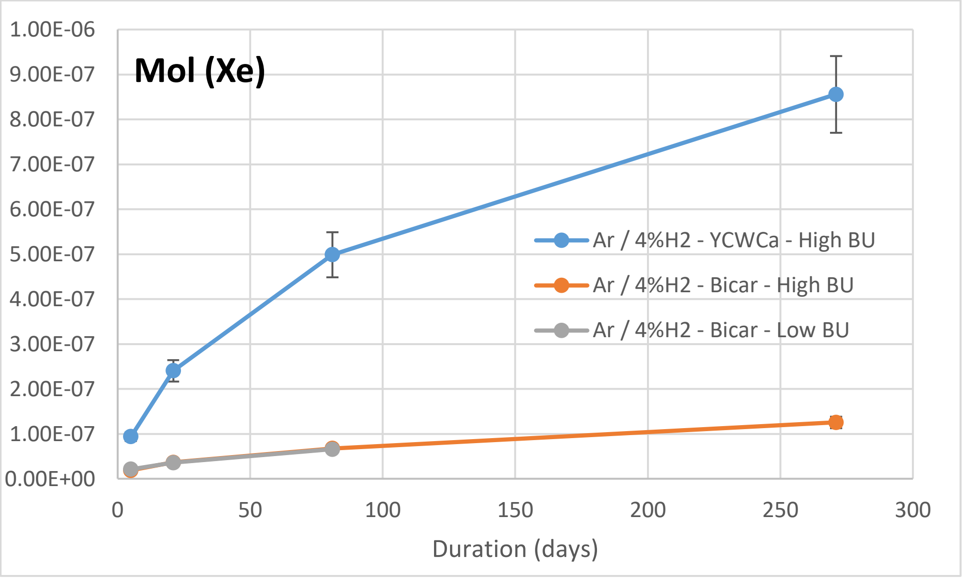
Radiochemical analysis matrix

Method	Elements to be analyzed
Alpha spectrometry	Cm-242, Cm-244, Pu-238 + Am-241, Pu-239 + Pu-240
Gamma spectrometry	Cs-134, Cs-137, Co-60, Mn-54, Ce-144, Am-241, Nb-94
Liquid scintillation counting	C-14, Sr-90, Cl-36, Ni-63, Ni-59
TIMS	U-233, U-234, U-235, U-236, U-238, Pu-239, Pu-240, Pu-241, Pu-242, Pu-244
ICP-MS	Be-10, Tc-99, Pd-105, Pd-106, Pd-108, Zr-90, Zr-91, Zr-94, Mo-95, Mo-96, Mo-97, Mo-98, Ru-100, Ru-101, Ru-102, Ru-104, Cd-111, Cd-112, Cd-114, Nb-93, Rh-103, Ag-107, Ag-109, Sn-118, Sn-120, Te-126, Cs-133, I-129
Gas mass spectrometry	H_2, N_2, O_2, Ar, Kr-83, Kr-84, Kr-85, Kr-86, Xe-131, Xe-132, Xe-134, Xe-136

Results gas sampling: Xe, Kr





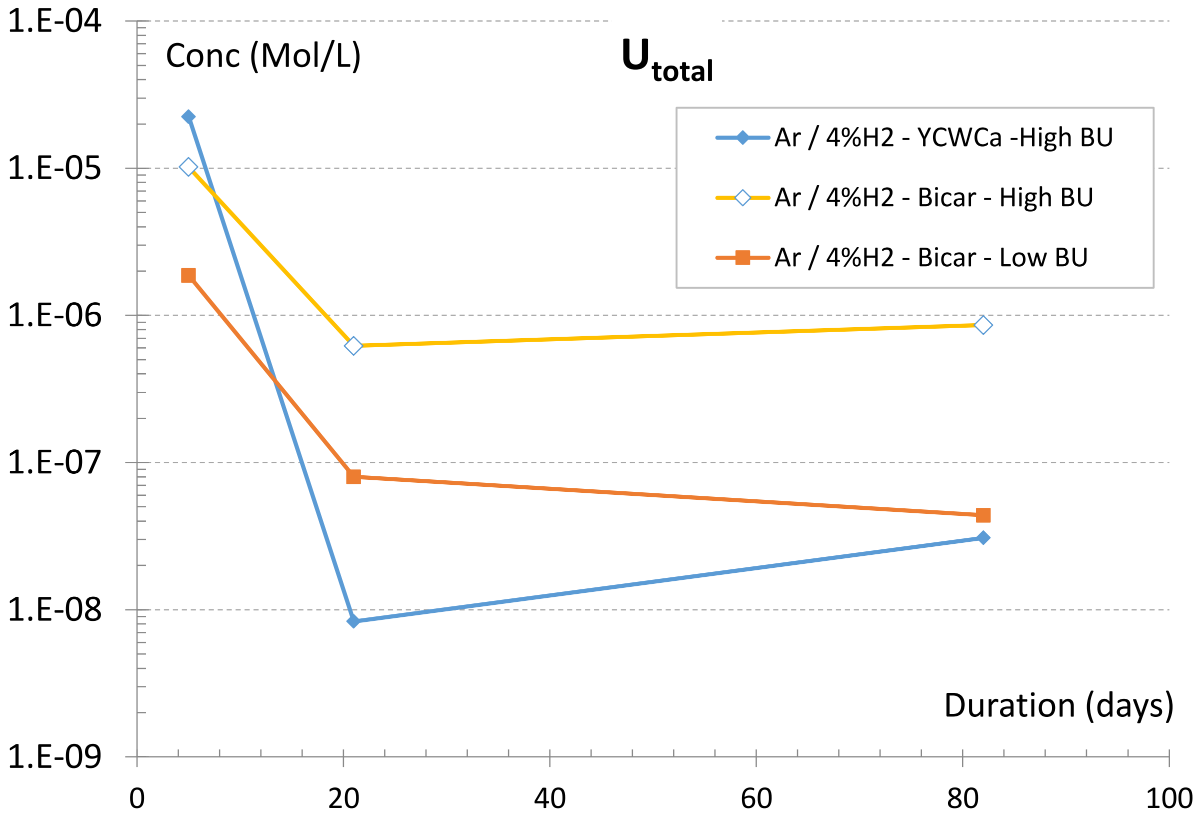


- Continous release (as for UOx)
- Xe/Kr ≈ 22

(for Pu-239: Xe/Kr:18.6, Pu-241: Xe/Kr: 23.2)
White et al. JNM 288, 2010

YCWCa: Young Cement Water with Calcium – light composition
Bicar: Bicarbonate solution type “First-Nuclides”

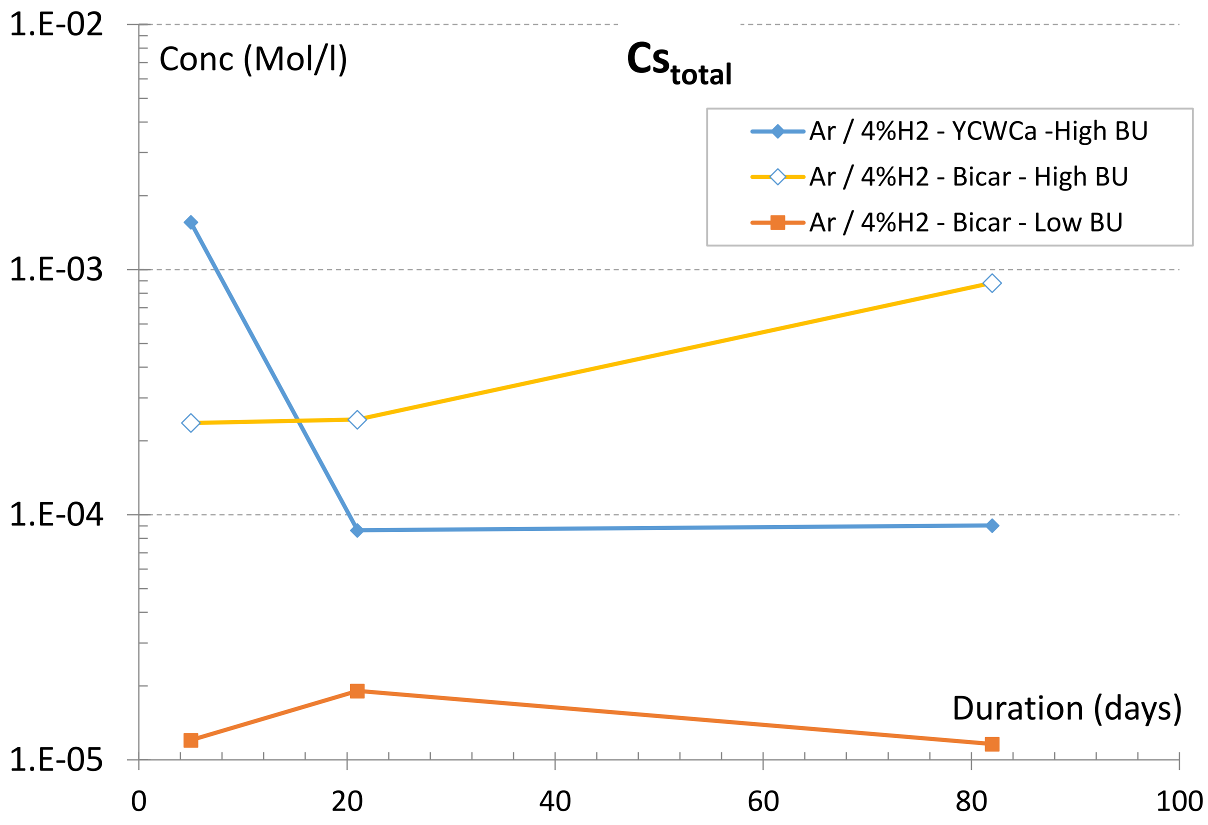
Results leaching experiments: U, Pu

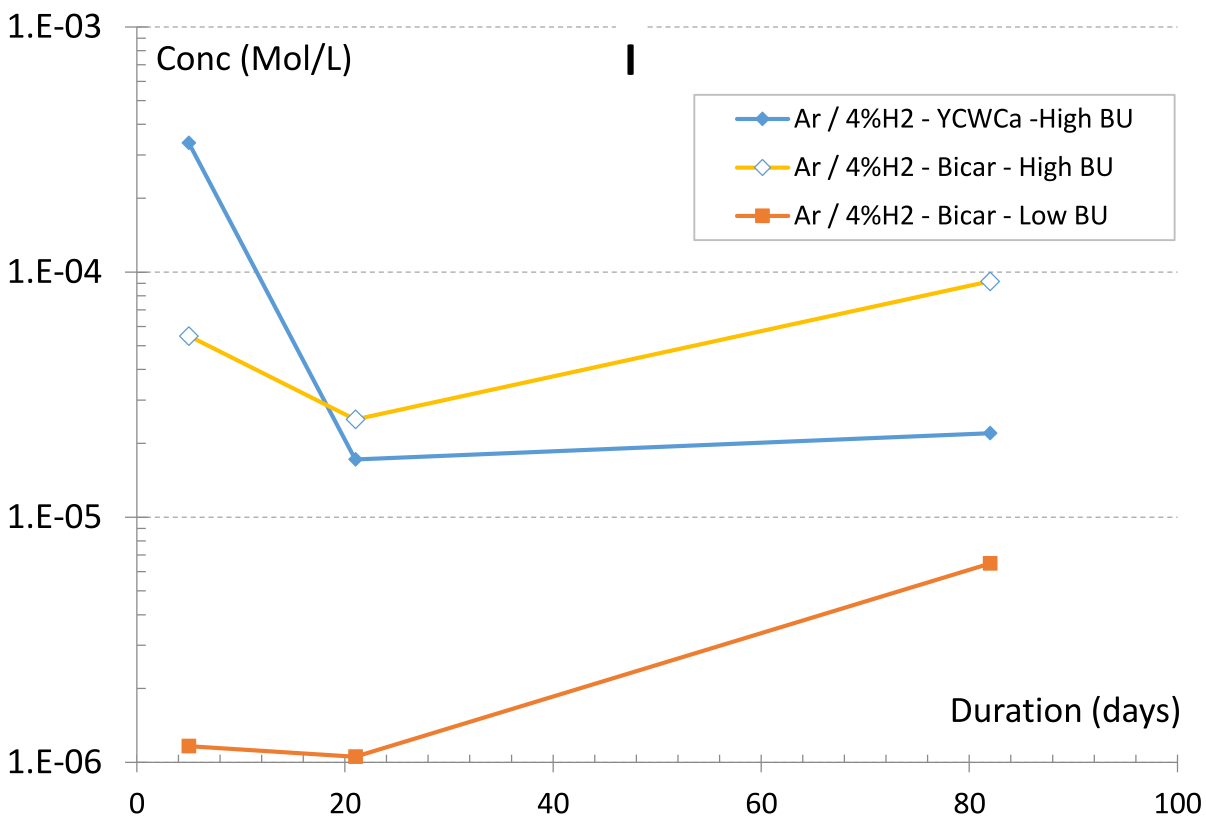


- High initial release of U (as for UOx)
- Pu concentrations below the DL ($<10^{-9}$M)

YCWCa: Young Cement Water with Calcium – light composition
Bicar: Bicarbonate solution type “First-Nuclides”

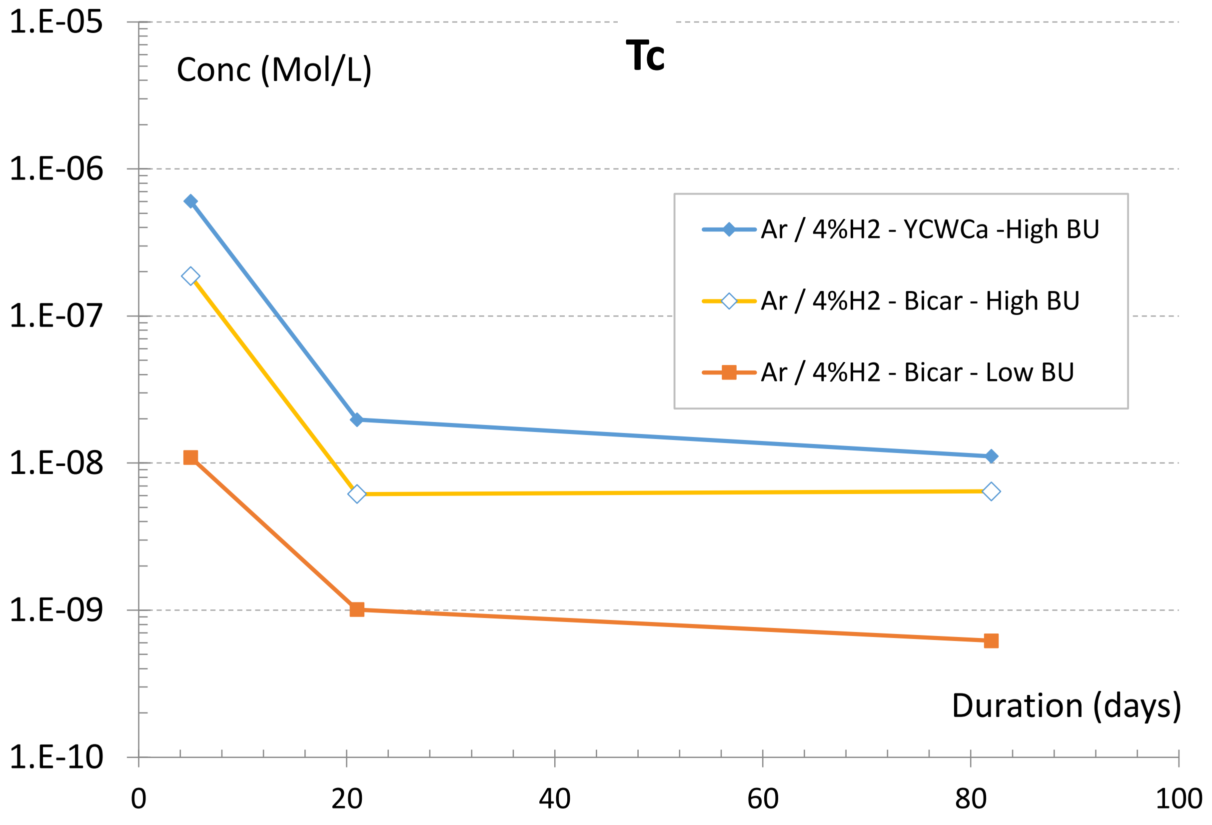
Results leaching experiments: Cs, I

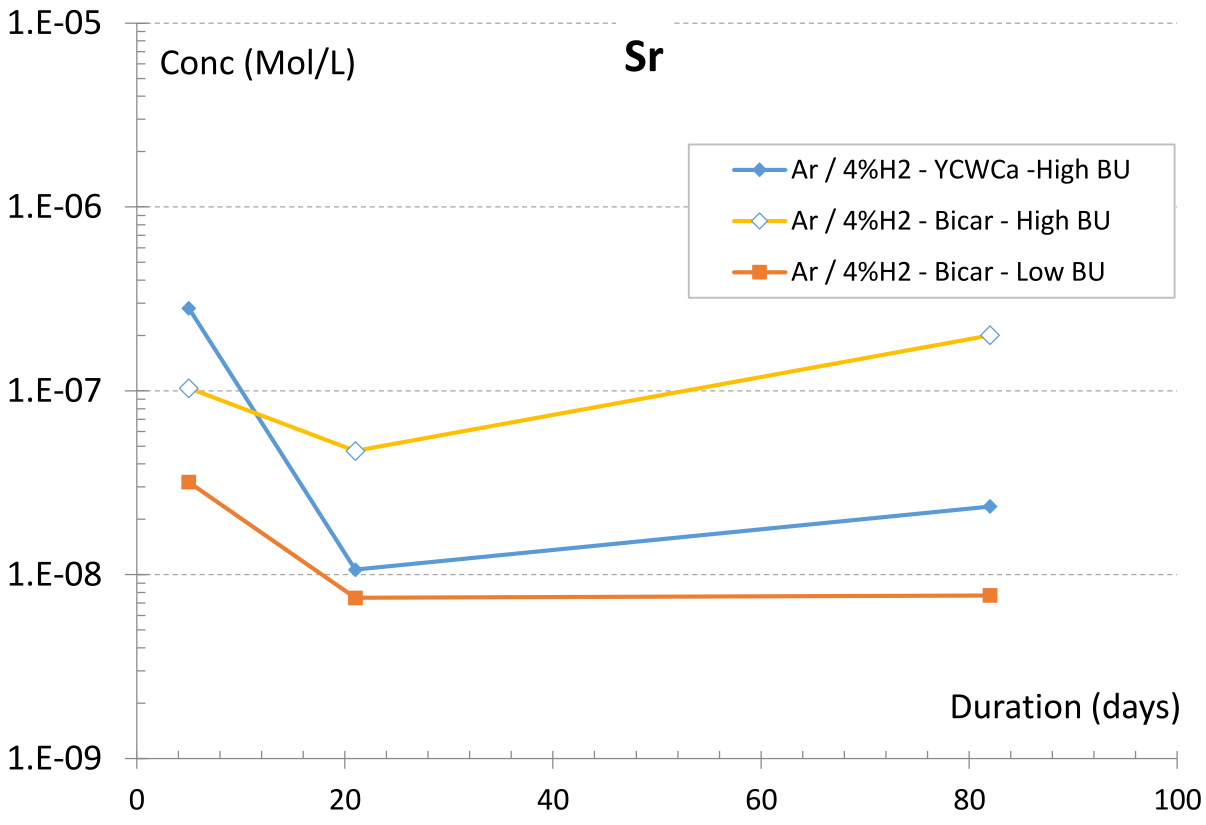




YCWCa: Young Cement Water with Calcium – light composition
Bicar: Bicarbonate solution type “First-Nuclides”

Results leaching experiments: Tc, Sr





YCWCa: Young Cement Water with Calcium – light composition
Bicar: Bicarbonate solution type “First-Nuclides”

Conclusion and Outlook

- Dissolution experiment with fully characterized MOX fuel successfully started
- 3 MOX experiments running in parallel under specific conditions
- Continuous release of fission gases (Xe, Kr) (cf. results of UOx)
- Results from puncturing and inventory (RCA, calculations) pending:
  - ➢ important for FIAP (FG) and FIAP (IRF/Matrix)
- Continuous experiment (1.5 years)
- Post leaching characterization planned
  - ➢ Raman, SEM etc. for secondary phases and microstructure evolution

ACKNOWLEDGEMENTS

Thanks to …

Gerry Cools, Guy Cornelis, Ben Gielen,

Pieter Schroeders, Janne Pakarinen, Felix Brandt…

Thank you for your kind attention!