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Dissolution rate of MOX and Cr-doped UO_2 fuel

D. H. Wegen

JRC-ITU

London, 3rd November 2015

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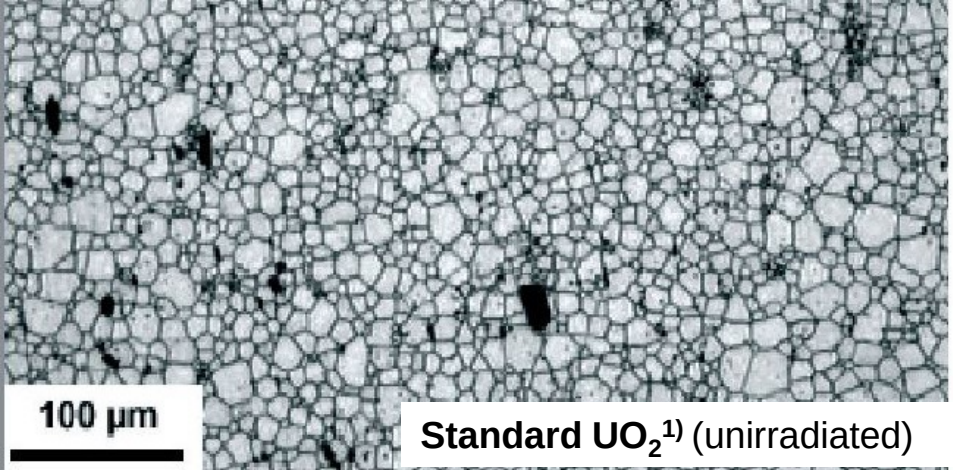
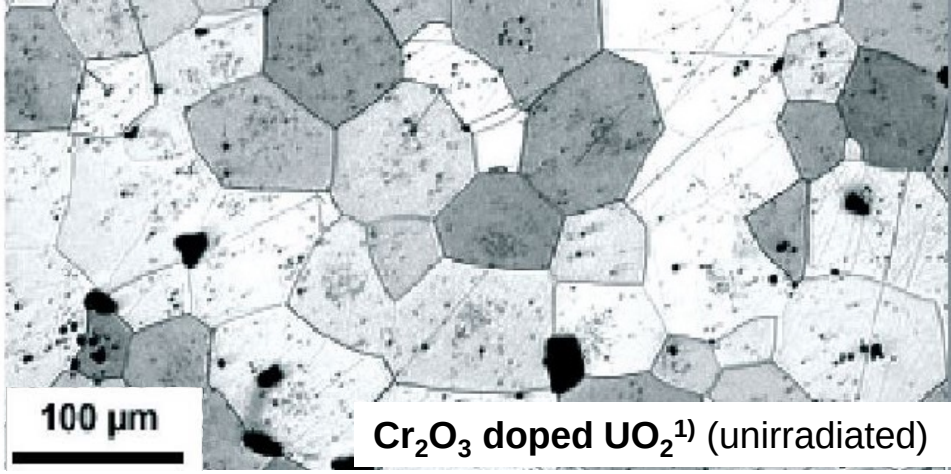


Standard UO_2[1)] (unirradiated)



Cr_2O_3 doped UO_2[1)] (unirradiated)

Standard UO_2 and Cr_2O_3-doped UO_2

Improving utilisation of nuclear fuel

- flexible reactor operation
- increase of burn-up

Enhanced fuel performance

- PCI failure risk -> attenuation of mechanical stresses
  - increased creep rate
- higher internal gas pressure -> higher fission gas retention
  - enlarged grain size

1) Y. Guérin, 2009: *Advanced UO_2 and MOX ceramics*, p. 47, in ed. J.-L. Guillet, Y. Guérin, *Nuclear fuels*, DEN Monographs, CEA and Groupe Moniteur, Paris, France

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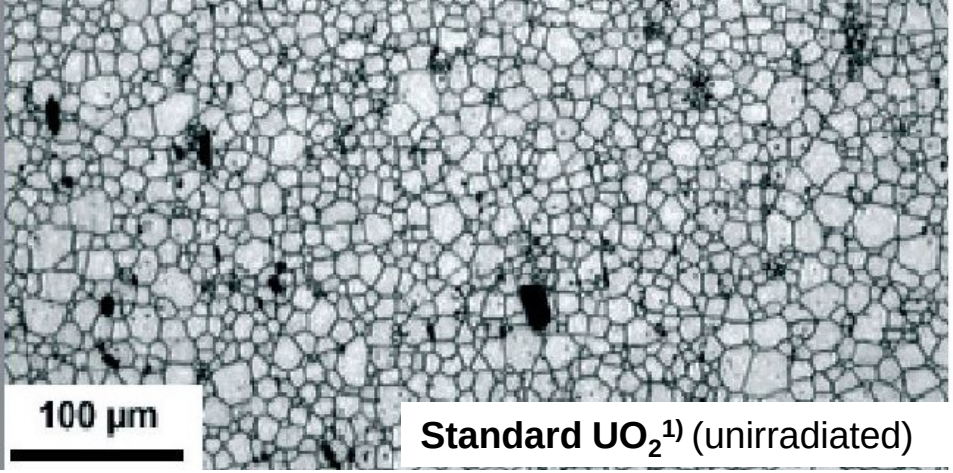

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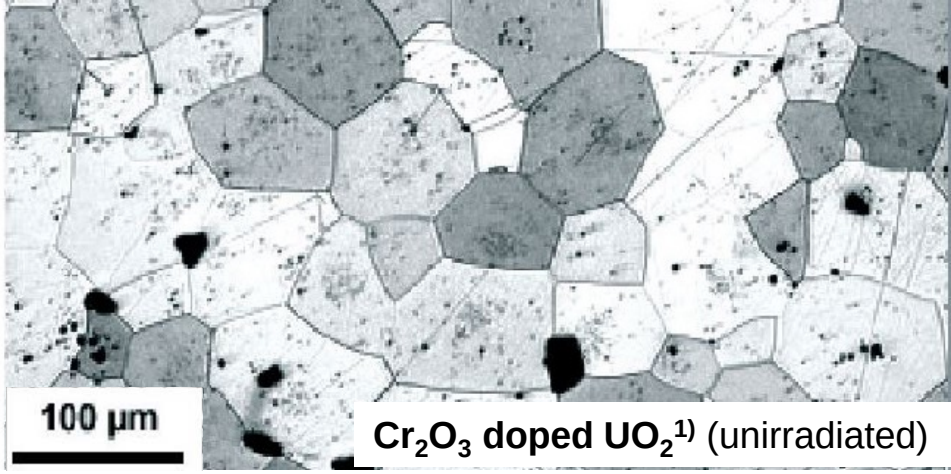


Cr_2O_3 doped UO_2[1] (unirradiated)

Cr_2O_3-doped UO_2

Fission gas retention

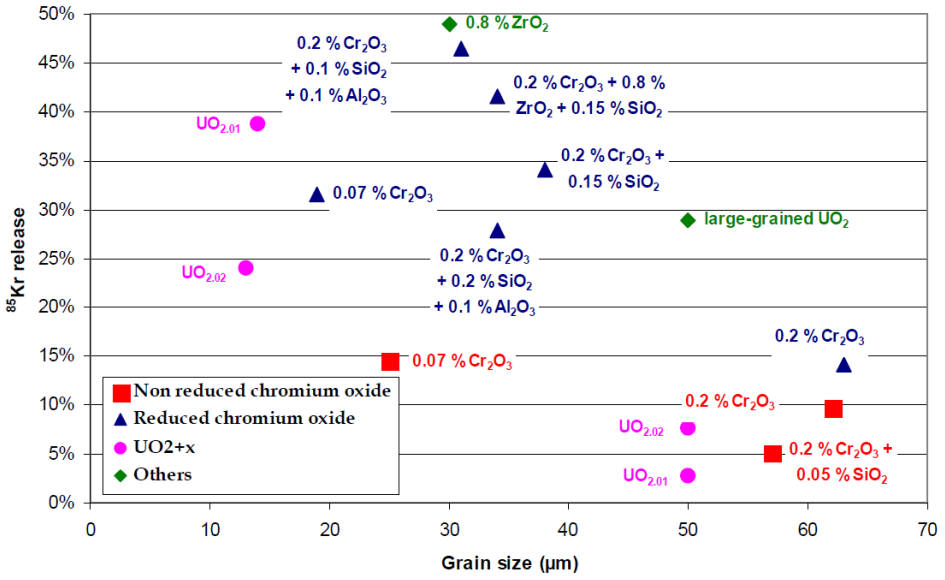
post-irradiation annealing test

large grained UO_2 not sufficient

intragranular bubble formation

structural defects due to

- hyperstoichiometry (UO_{2+x})
- second phase precipitates (0.2% Cr_2O_3 doped fuel)



^{85}Kr release results after annealing tests of 5 hours at 1700° C on irradiated UO_2 fuel (10 GWd/t_U)[2]

2) S. Valin et al., 2003: *Synthesis of the results obtained on the advanced UO_2 microstructures irradiated in the tanox device*, in: *Advanced fuel pellet materials and designs for water cooled reactors*, IAEA. IAEA-TECDOC-1416, Vienna, Austria, 2004.

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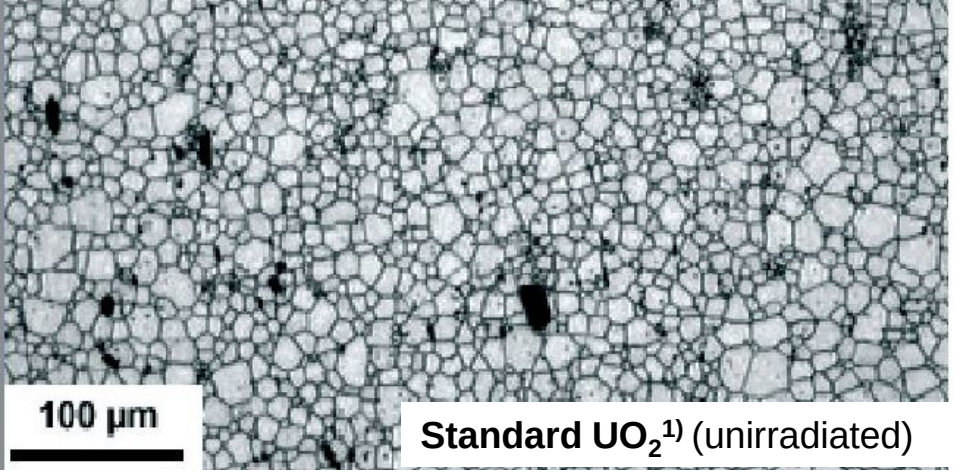

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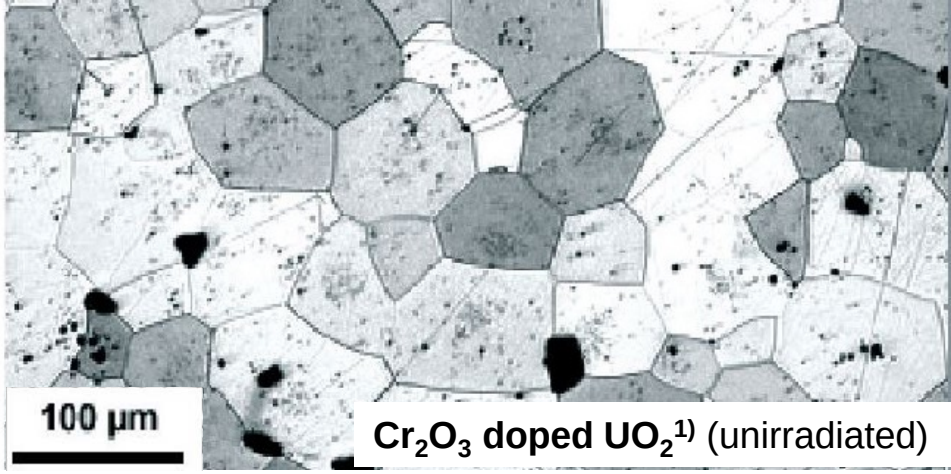


Cr_2O_3 doped UO_2[1)] (unirradiated)

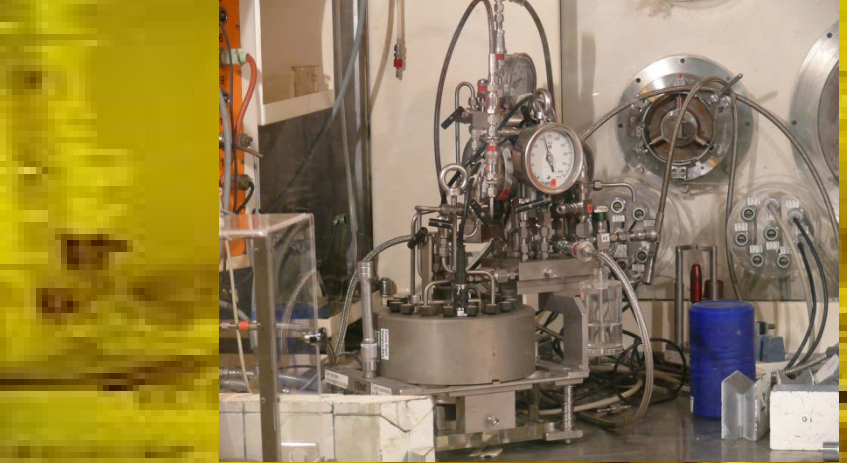
Leaching behaviour of irradiated Cr_2O_3-doped UO_2

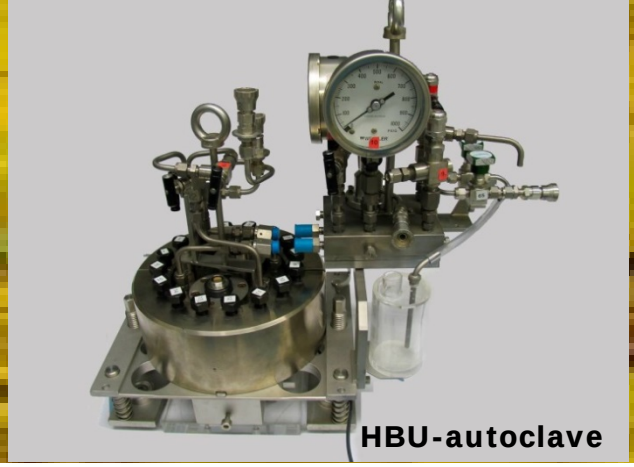
Some data available for oxidising conditions e.g.[1-3)]

Proposal to decrease the uncertainty related to the release of radionuclides from irradiated Cr_2O_3-doped UO_2 fuel

- **reducing conditions (30 bar H_2)**
- **well characterized fuel (incl. irradiation history)**
- **determine the long-term dissolution rate**
- **comparison with un-doped UO_2 fuel tested under similar conditions**

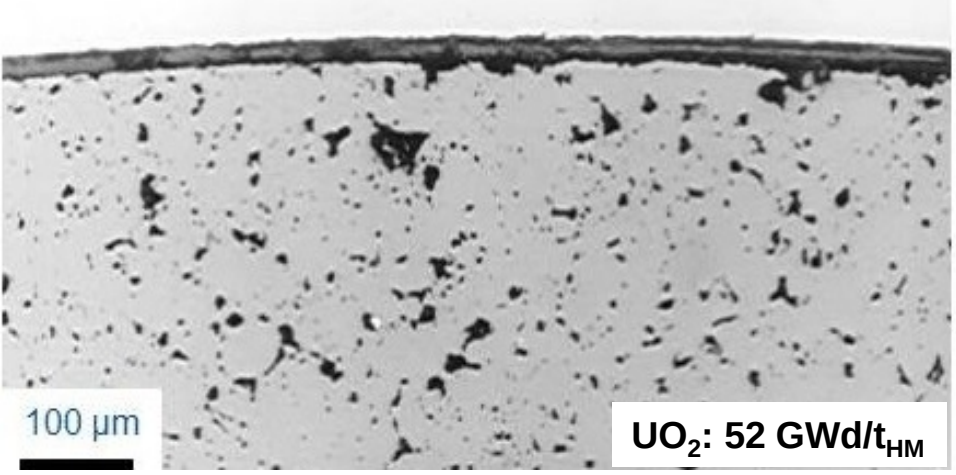
1) Roth, O., et al. (2013). *Effects of matrix composition on instant release fractions from high burn-up nuclear fuel. M*RS Proceedings 1518: 145-150.
2) O. Roth, et al. (2014). *Effects of matrix composition and sample preparation on instant release fractions from high burnup nuclear fuel.* MRS Proceedings 1665: 261-266
3) K. Nilsson (2014). *Oxidative dissolution of doped UO_2 and H_2O_2 reactivity towards oxide surfaces - A kinetic and mechanistic study*. KTH Royal Institute of Technology. Licentiate. . Stokholm, Sweden.

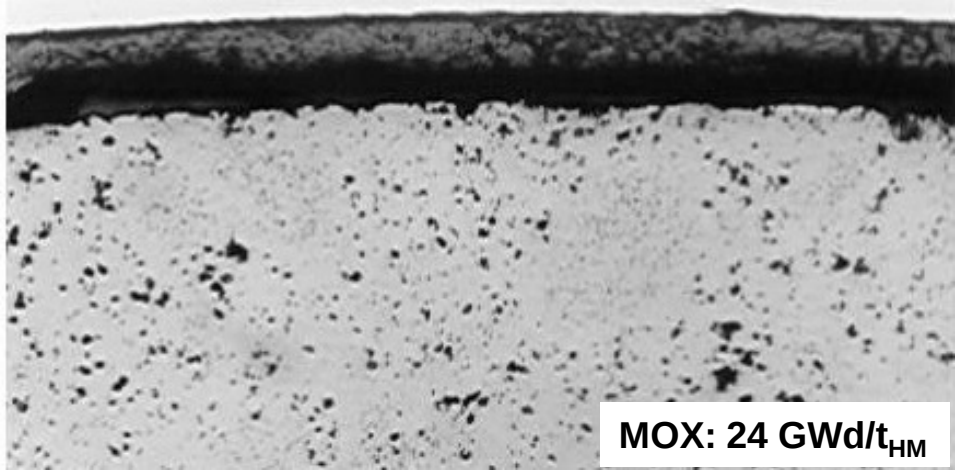




Cr_2O_3-doped UO_2 fuel experiment

Fuel:	Cr_2O_3-doped UO_2 fuel
	burn-up approx. 60 GWd/t_{HM}
	decladded pellet disc fragments
	1 mm thick (surface area estimated)
Leachant:	start volume 400 ml, 10 mM NaCl, 2mM HCO_3^-
	pH 8.2, E_h approx. -300 mV_{SHE} measured during sampling
Gas phase:	30 bar H_2/0.03% CO_2
Duration:	1-1.5 years
Conditions:	HBU-autoclave (lined with PEEK)
Sampling:	20 min, day 1, 7, 70, 360, 420, 480, 540
	matrix corrosion





MOX compared to UO_2-fuel

Higher linear power level

Higher centreline temperature

Smaller grainsize

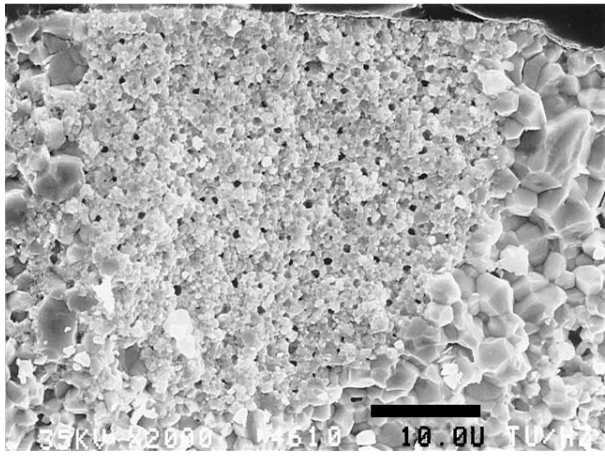
Heterogeneous fissile material distribution

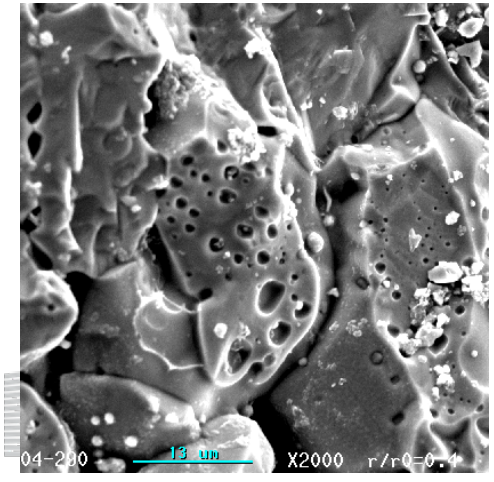
Plutonium rich agglomerates with high burn-up

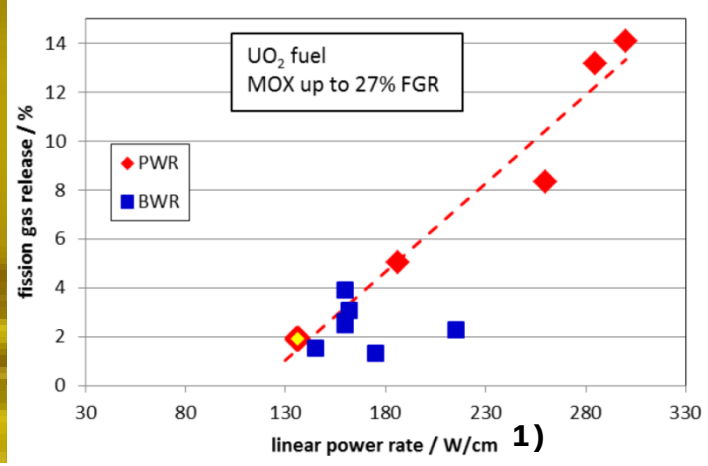
Restructuring of mixed oxide

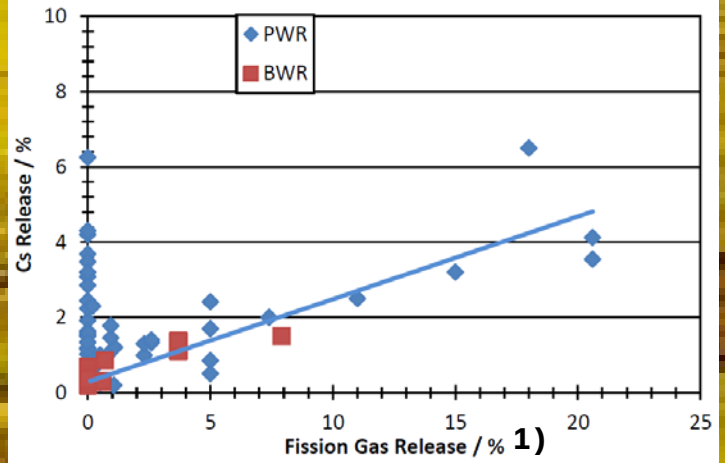
- further division of grains
- gas bubbles at intergranular locations
- metallic precipitates

Higher fission gas release









MOX fuel leaching experiment

UO_2-fuel

- radionuclide inventory depend on burn-up
- fission gas (FG) release correlated to linear power rate
- FG release seems to correlate with release of volatile fission products (e.g. ^{137}Cs)
- release of volatile FP's correlated to linear power rate
- fission gas in the plenum average release from all fuel in a rod
- power history can be locally different in a fuel rod

-> locally different IRF possible

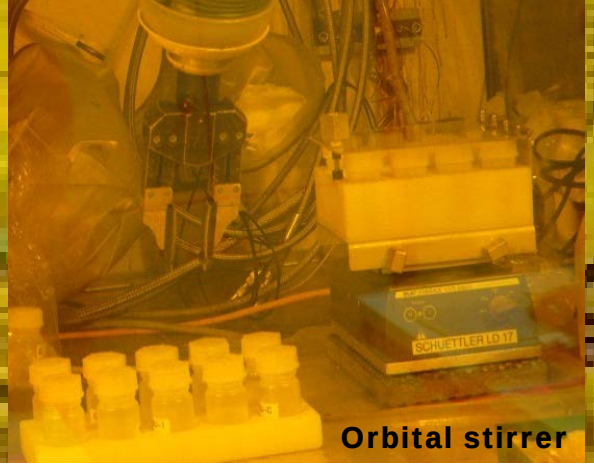
1) AMPHOS21+KIT-INE, *State of the art report.* FIRST-Nuclides Deliverable (D-N° :5.1), 2014.

MOX fuel leaching experiment

Proposal to decrease the uncertainty related to the release of radionuclides from irradiated MOX fuel

- **samples from MOX fuel at well-defined locations**
- **well characterized commercial fuel (incl. irradiation history, FGR)**
- **determination of IRF**
- **determine the matrix dissolution rate**


PEEK sample holder



Orbital stirrer

MOX fuel static corrosion experiment

Fuel:	commercial MOX fuel burn-up 40 - 60 GWd/t_{HM} 2-4 mm cladded segment
Leachant:	(50±1) ml , 1mM $NaHCO_3$ + 19mM NaCl pH : 8.4±0.1, T : (25±5) ° C
Gas phase:	air, oxidising condition
Duration:	120-300 days (cumulated time)
Conditions:	PE-bottles with PEEK sample holder
Sampling:	complete replenishments IRF, matrix corrosion

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Analysis of leaching solutions

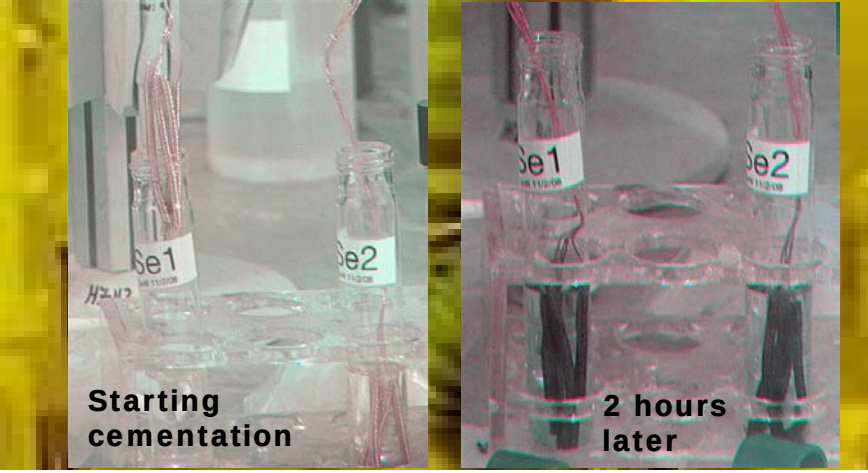
Radionuclides:

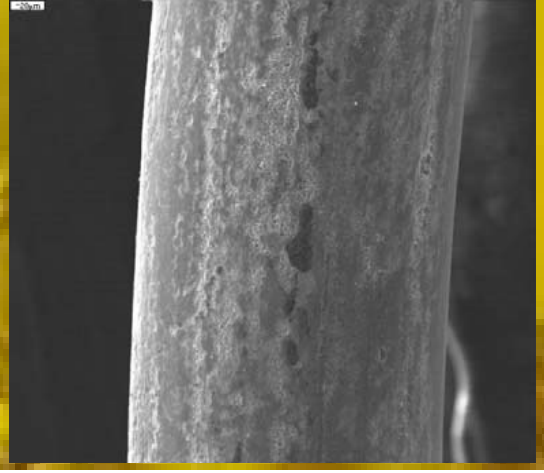
^{79}Se, ^{90}Zr, ^{90}Sr, ^{99}Tc, ^{100}Mo, ^{105}Pd, ^{106}Ru/^{106}Rh, ^{110m}Ag, ^{125}Sb, ^{127}I, ^{129}I, ^{133}Cs, ^{134}Cs, ^{137}Cs, ^{139}La, ^{140}Ce, ^{141}Pr, ^{143}Nd, ^{154}Eu, ^{155}Eu, ^{237}Np, ^{238}U, ^{239}Pu, ^{240}Pu, ^{241}Pu/^{241}Am

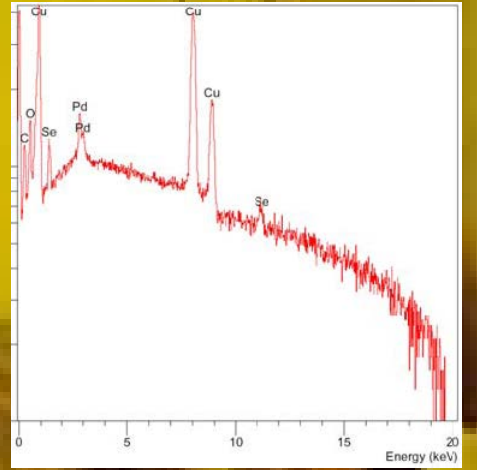
Stable elements:

Ti, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Zr, Mo, Ag, Pd, Sn, Ba, Nd

Technique: ICP-MS, Liquid Scintillation Counting, γ-spectrometry







Separation and purification of ^{79}Se

Selective deposition of Se out of high active PUREX raffinate by reductive cementation on Cu (Reinsch test) [1)]

Results:

- ICP-MS + EDX confirmed: Se (+ Pd) deposited
- ICP-OES: >85% of Se-carrier was recovered
- γ-spectrometry: Cs decontamination factor ~50000

1) G. Jörg et al., *Preparation of radiochemically pure ^{79}Se and highly precise determination of its half-life*, Applied Radiation and Isotopes 68(2010)2339–2351

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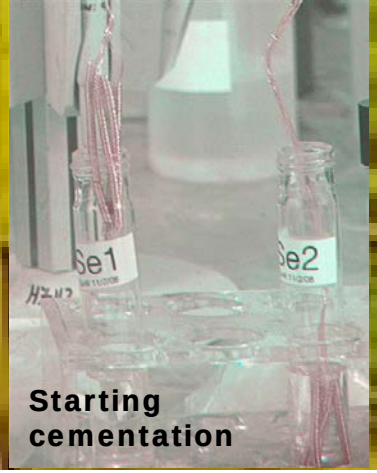

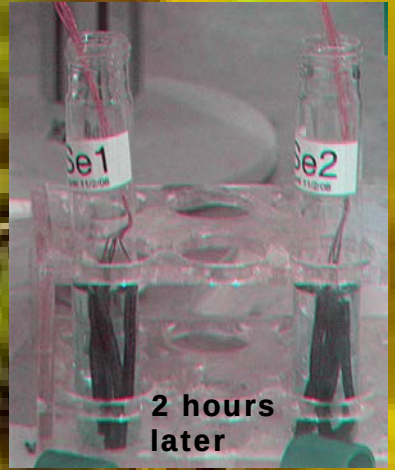

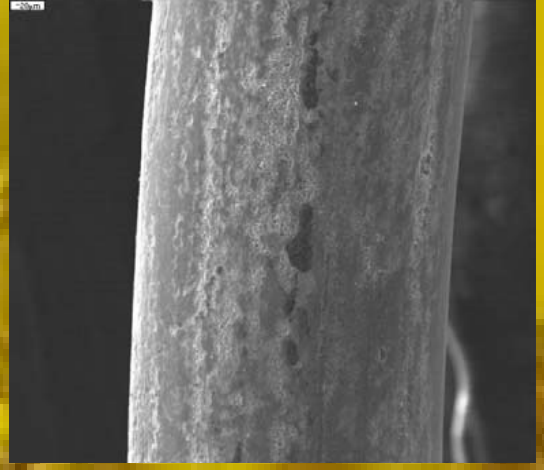

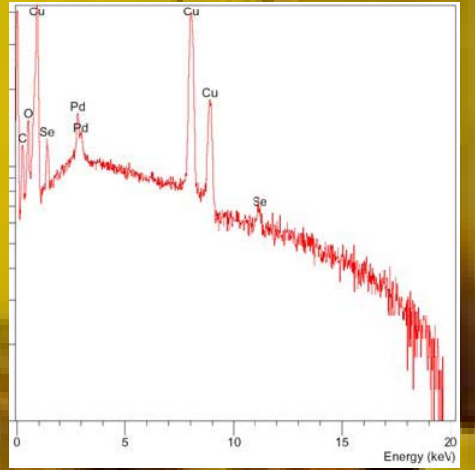

Separation and purification of ^{79}Se

Further purification possible[1)]

(1) Deposition of ^{79}Se/carrier-Se from high active raffinate on metallic Cu → (2) Dissolution of deposited Se in KCN solution by formation of KSeCN → (3) Precipitation of Se by addition of formic acid in excess of cyanide → (4) Suspension of precipitate in 8 M HCl → (5) Dissolution of residue in conc. HNO_3 → (6) Evaporation to dryness and dissolution of residue in 4.5 M HCl, addition of Ru(III) hold-back carrier → (7) Ion exchange separation on DOWEX 2x10, 100-200 mesh, elution with 4.5 M HCl → (8) Precipitation of Se from eluate by addition of Sn(II) → (9) Dissolution of precipitate in conc. HNO_3 → (10) Transfer into micro-flask and evaporation to dryness → (11) Sublimation of residue at 250 °C → (12) Dissolution of sublimate in conc. HNO_3 = ^{79}Se stock solution

1) G. Jörg et al., *Preparation of radiochemically pure ^{79}Se and highly precise determination of its half-life*, Applied Radiation and Isotopes 68(2010)2339–2351

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	Interference	Mode	Gas/Reaction
^{79}Se	$^{79}Br^+$; $^{158}Gd^{2+}$, $^{40}Ar^{39}K^+$; $^{38}Ar^{40}ArH^+$; $^{63}Cu^{16}O^+$	REACTION	O_2; O_2 /He; O_2/Ar; O_2/N_2
^{77}Se	$^{39}K^{38}Ar^+$ $^{61}Ni^{16}O^+$, $^{59}Co^{18}O^+$ $^{76}GeH+$, $^{76}SeH+$ $^{40}Ar37Cl^+$, $^{40}Ca^{37}Cl^+$ $^{154}Sm^{+}+$, $^{154}Gd^{++}$		
^{78}Se	$^{78}Kr^+$; $^{40}Ca^{38}Ar^+$; $^{62}Ni^{16}O^+$;$^{41}K^{37}Cl^+$;$^{156}Gd^{++}$, $^{156}Dy^{++}$; $^{38}Ar^{40}Ar^+$; $^{39}K^{39}K^+$		
^{80}Se	$^{80}Kr^+$; $^{40}Ca^{40}Ar^+$; $^{64}Ni^{16}O^+$ $^{64}Zn^{16}O^+$; $^{32}S_2{}^{16}O^+$, $^{32}S^{16}O_3{}^+$ $^{79}BrH^+$;$^{45}Sc^{35}Cl^+$; $^{160}Gd^{++}$; $^{60}Gd^{++}$;$^{40}Ar^{40}Ar^+$;$^{40}Ca^{40}Ca^+$		
^{82}Se	$^{82}Kr^+$; $^{42}Ca^{40}Ar^+$;$^{66}Zn^{16}O^+$; $^{32}S^{34}S^{16}O^+$; $^{34}S^{16}O_3{}^+$;$^{81}BrH^+$; $^{45}Sc^{37}Cl^+$;$^{162}Dy^{++}$;$^{162}Er^{++}$		

^{79}Se Quantification and Standardisation

ICP-MS NexION: Collision / Reaction Cell Technology

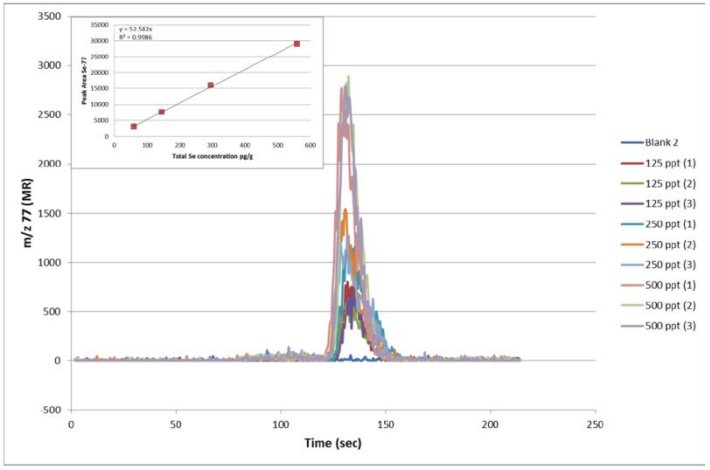
- Minimise the effect of many
- potential spectral interferences

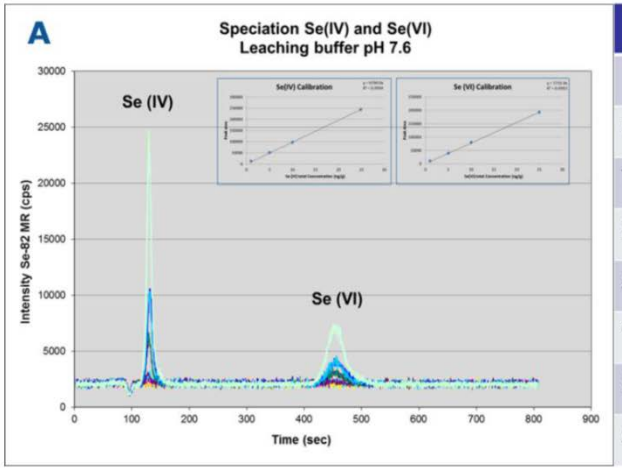
Isotope dilution mass spectrometry

- ^{78}Se & ^{82}Se enriched certified standards
- Double IDMS

Flow Analysis-Automated Platforms for Radionuclide Analysis[1)]

1) Aldave de las Heras et al., *Development of methods for the determination of ß emitters (^{79}Se, ^{126}Sn, ^{135}Cs, ^{90}Sr) based on sequential injection flow analysis coupled to ICP-MS.* In ed. B. Kienzler et al., *Final 3rd Annual Workshop Proceedings.* FIRST-Nuclides Deliverable (D-N° :5.4), pp. 95-103, 2014.



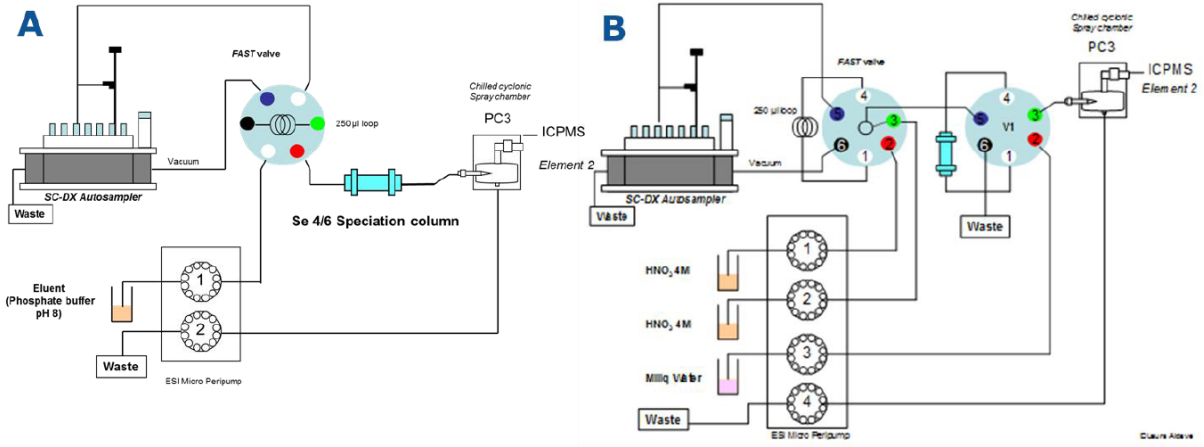


B **Analytical figures of merit:**

	Se (IV)	Se(VI)
Repeatibility (%)	0.2 -1	
Total Se		
Detection limits (pg/g)	23.5	25.3
Absolute amount (pg)	5.9	6.3
^{82}Se		
Detection limits (pg/g)	2.2	2.3
Absolute amount (pg)	0.5	0.6

Determination of ^{79}Se

Flow Analysis-Automated Platforms for Radionuclide Analysis[1)]



System configurations for speciation analysis (A) and for pre-concentration and/or separation (B) purposes

1) Aldave de las Heras et al., *Development of methods for the determination of ß emitters (^{79}Se, ^{126}Sn, ^{135}Cs, ^{90}Sr) based on sequential injection flow analysis coupled to ICP-MS.* In ed. B. Kienzler et al., *Final 3rd Annual Workshop Proceedings.* FIRST-Nuclides Deliverable (D-N° :5.4), pp. 95-103, 2014.

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