Fuel matrix dissolution in a damaged canister.

Kastriot Spahiu, Chalmers, SKB

Why hydrogen?

- **Sources of hydrogen** in the near field, e.g. spent fuel (SF) damaged canister**:**

  -Radiolysis of water: Fuel ⇒ Ionizing radiation (α, β, γ) + H_2O ⇒ Radicals ($OH^\bullet$,e-, $H^\bullet$ etc.) ⇒ Stable products mainly H_2, O_2 and H_2O_2.

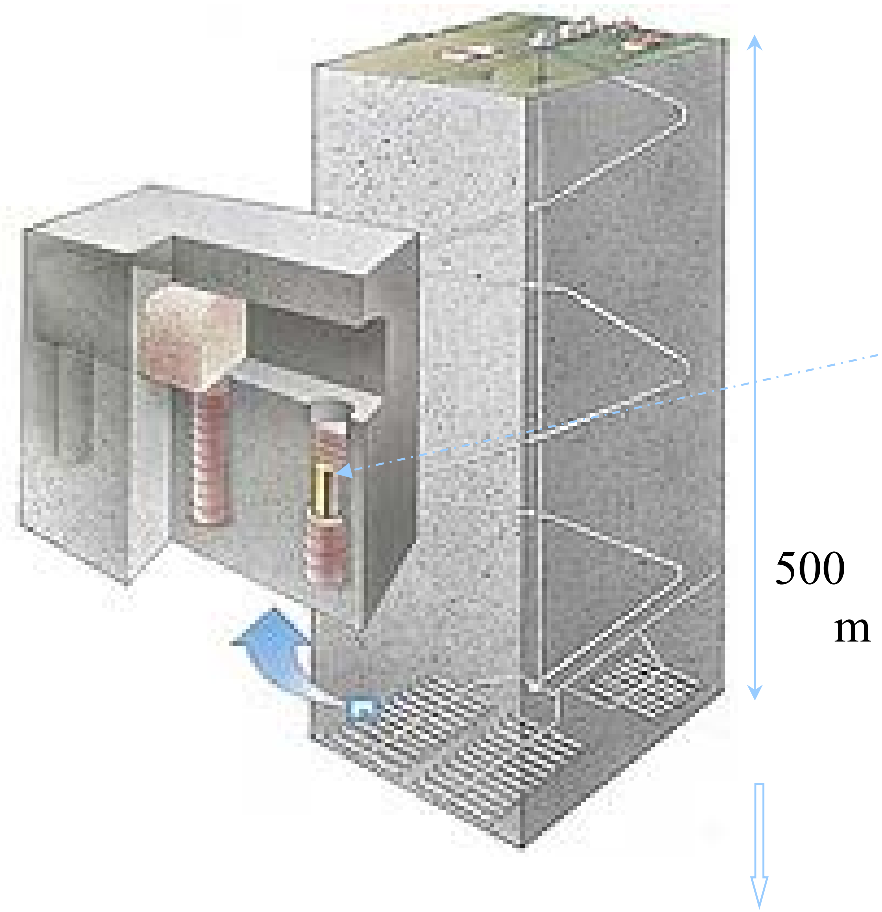
  -Anoxic corrosion of iron (the main source):

  $$3\ Fe(s) + 4\ H_2O \Leftrightarrow Fe_3O_4(s) + 4\ H_2(g)$$

- Gas phase is formed at e.g. 500 m depth when P_{H_2}~ 50 bar and $[H_2]_{diss}$~ 40 mM. Even for 1 atm. H_2, $[H_2]_{diss}$ ~ 0.8 mM, a major component of the groundwater.
- The rate of hydrogen production is higher than its depletion by diffusion through bentonite or clay. Predicted several 100 000 years H_2 saturated GW in near field.
- Work in the presence of dissolved H_2 is often reported as carried out under **reducing conditions**. No reduction of U(VI), Np(V) or Tc(VII) by dissolved H_2 at room temperature is reported in literature.
- Redox potentials at pH~8 are ~ -(300-500) mV, since the factor $(RT/nF)\cdot\log[H^+]$ in the Nernst equation is ~ $8\cdot60$ mV= - 480 mV, reducing only at Pt-electrode.

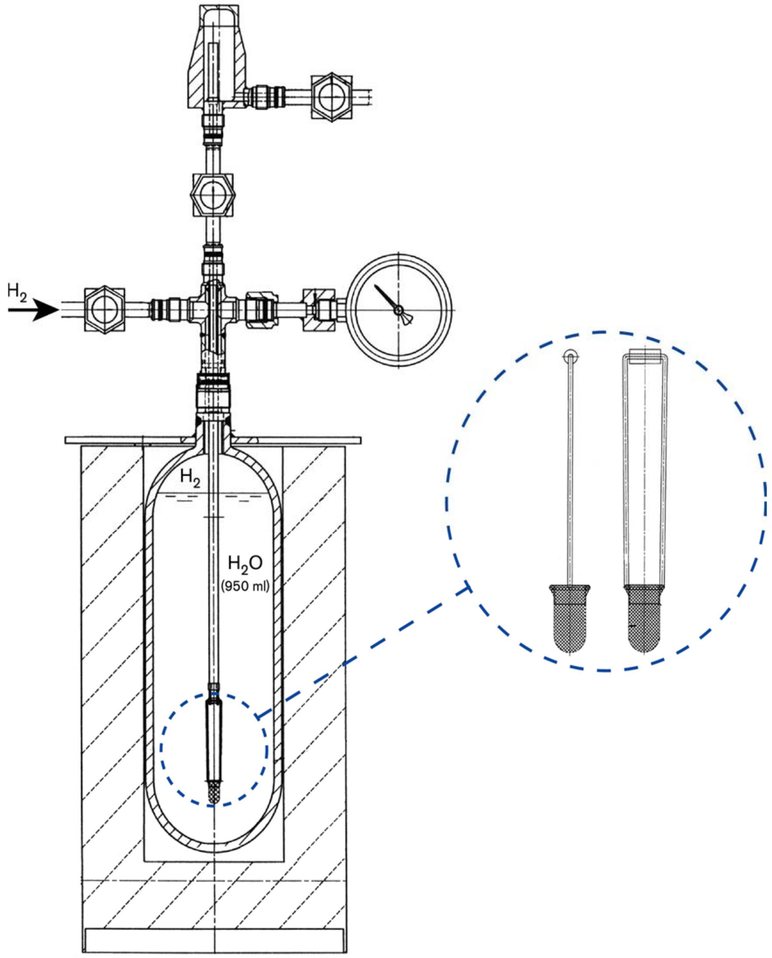
Actinide oxide mixtures (fuel or α-doped UO_2) and H_2 –why?

The KBS-3 concept of spent fuel disposal.



$$3Fe(s) + 4H_2O = Fe_3O_{4(s)} + 4H_2$$

- **500 m water column ~ 50 bar in gas bubble ~ 40 mM $[H_2]_{diss}$**
- **H_2 production rate by anoxic Fe corrosion > diffusion rate through bentonite clay.**
- **Many 10^3 y H_2-saturated near field, much higher conc. than H_2O_2, O_2 or U(VI), but H_2 inert!**



a)

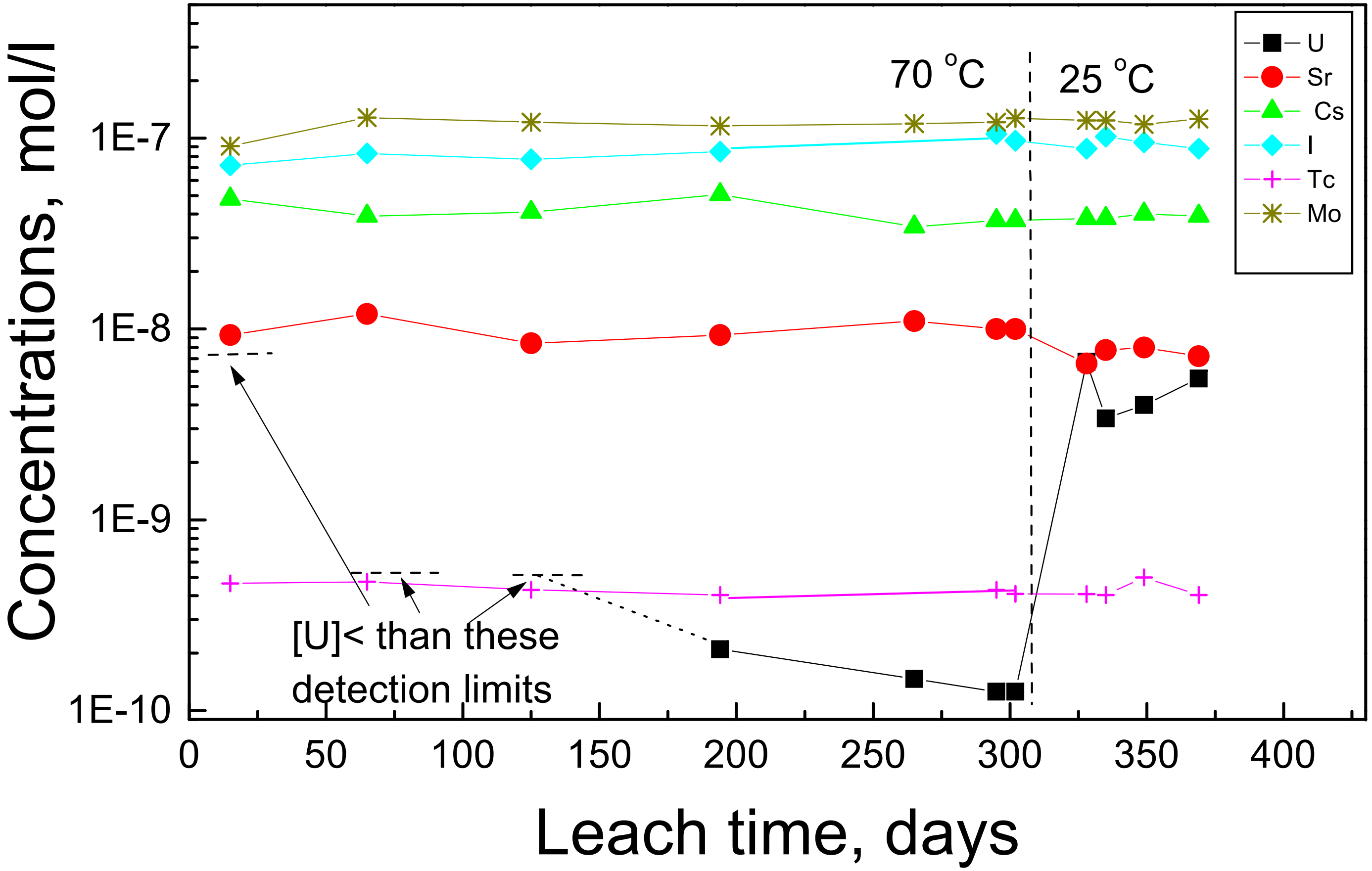
b)

a) Stainless steel autoclave used at Studsvik for leaching of fuel powder under 5 MPa H_2.

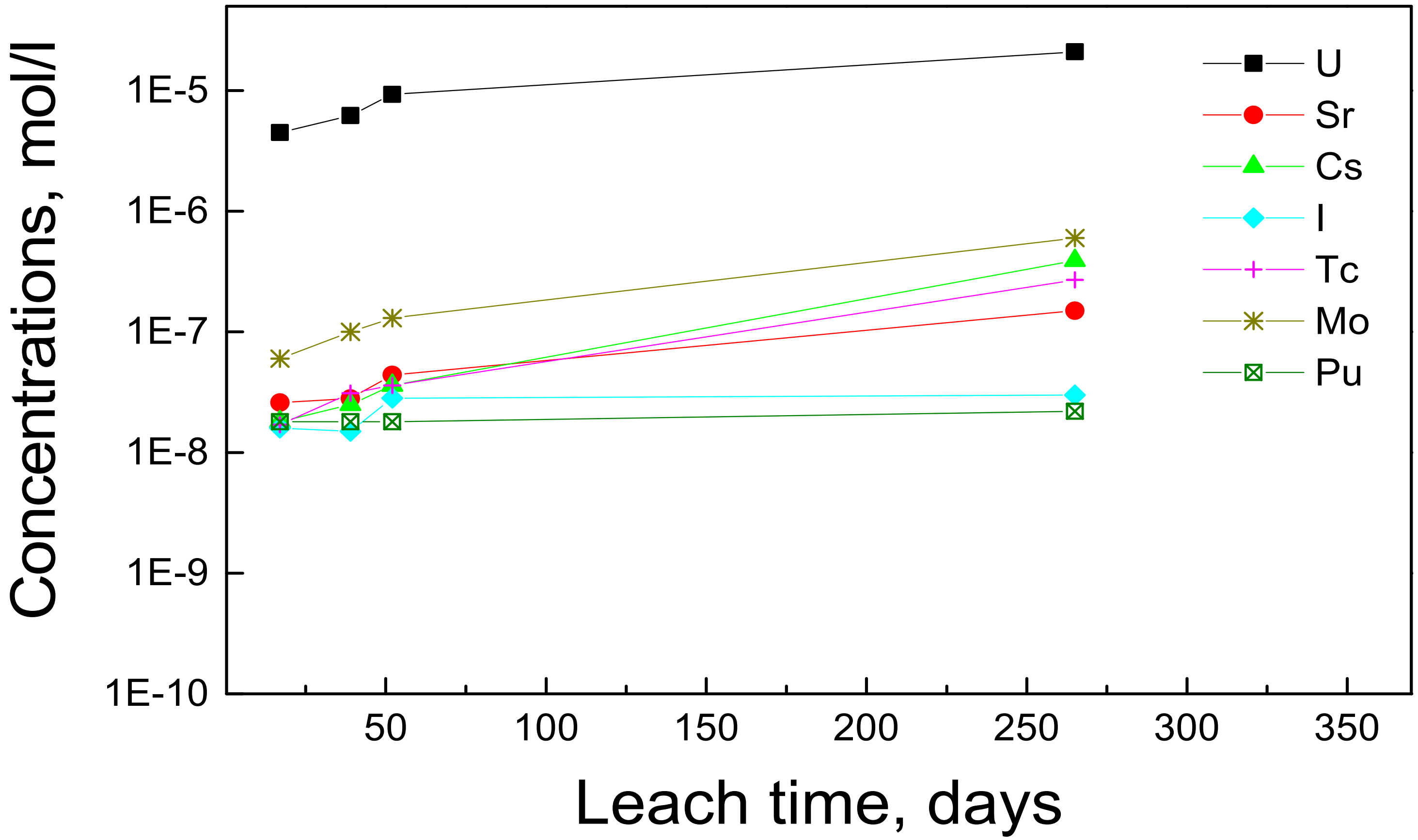
b) Picture of the gold basket and central lock.

Data from the first spent fuel leaching under hydrogen at Studsvik, 1998-1999.

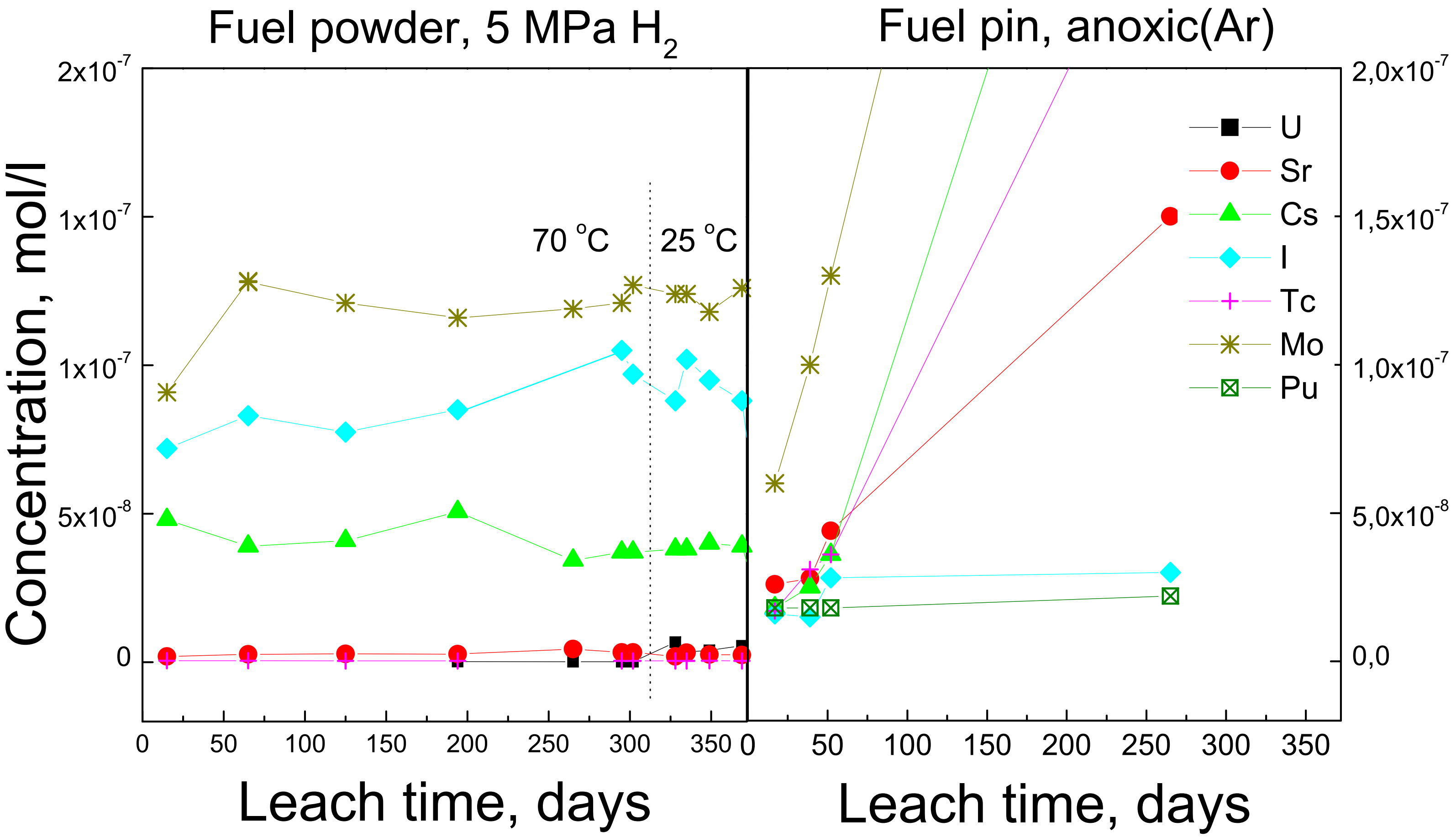
Fuel powder leaching in 10 mM NaCl, 2 mM HCO_3^-, 5 MPa H_2(g), 70 and 25 °C.



Fuel pin leaching in 10 mM NaCl, 2 mM HCO_3^-, and Ar+2% CO_2 atmosphere.



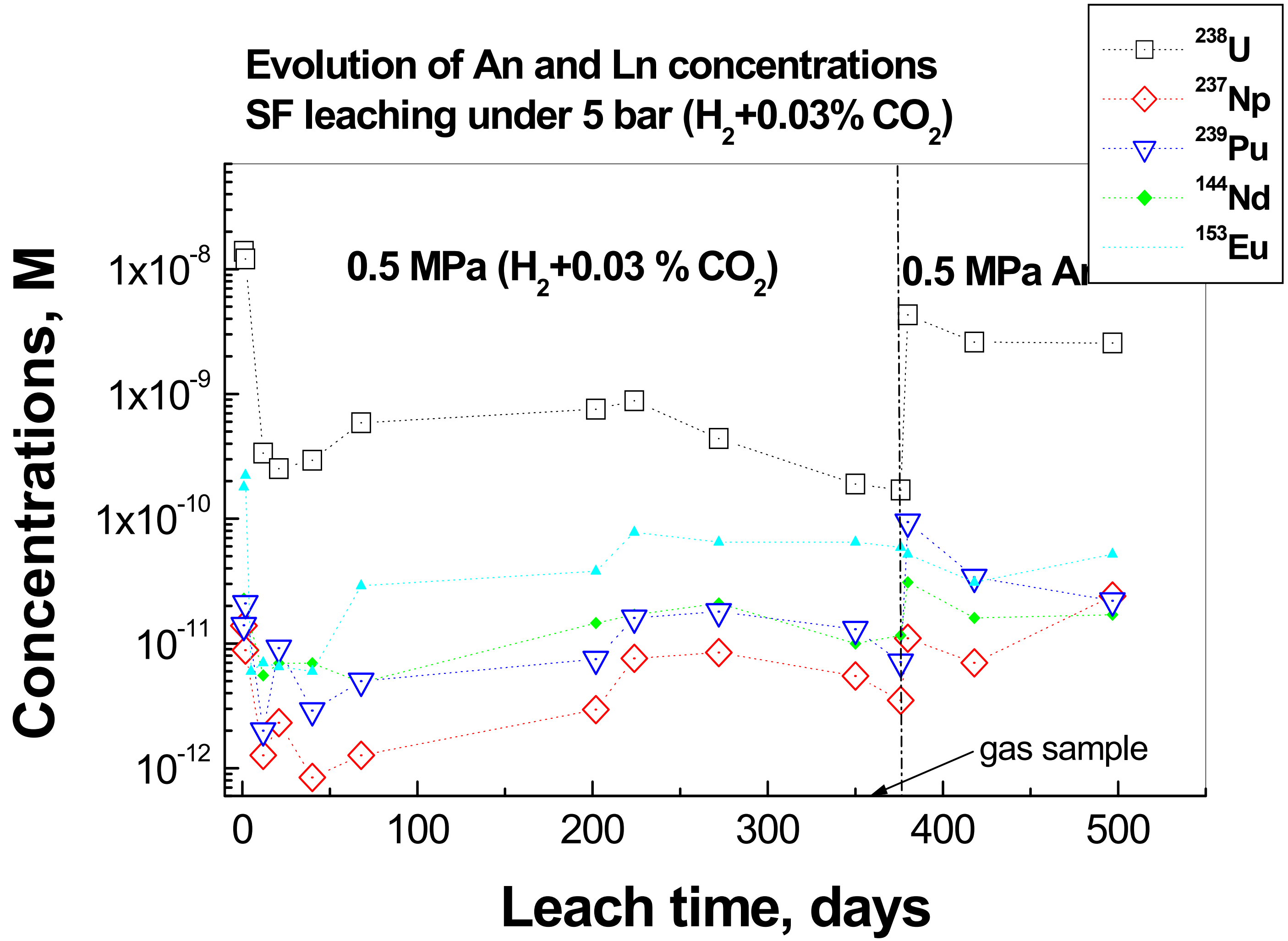
Same data as previous figures, but linear scale for C = 0 - $2 \cdot 10^{-7}$ M.
Right figure presents the same interval for Ar leaching of fuel segment.



Stainless steel autoclave

Quartz lined , quartz sampling tube with internal filter, Peek drop collector.
S.F.: ~1.7 g powder 0.25-0.5 mm, Ringhals D07-S14, burnup ~ 43 MWd/kgU.

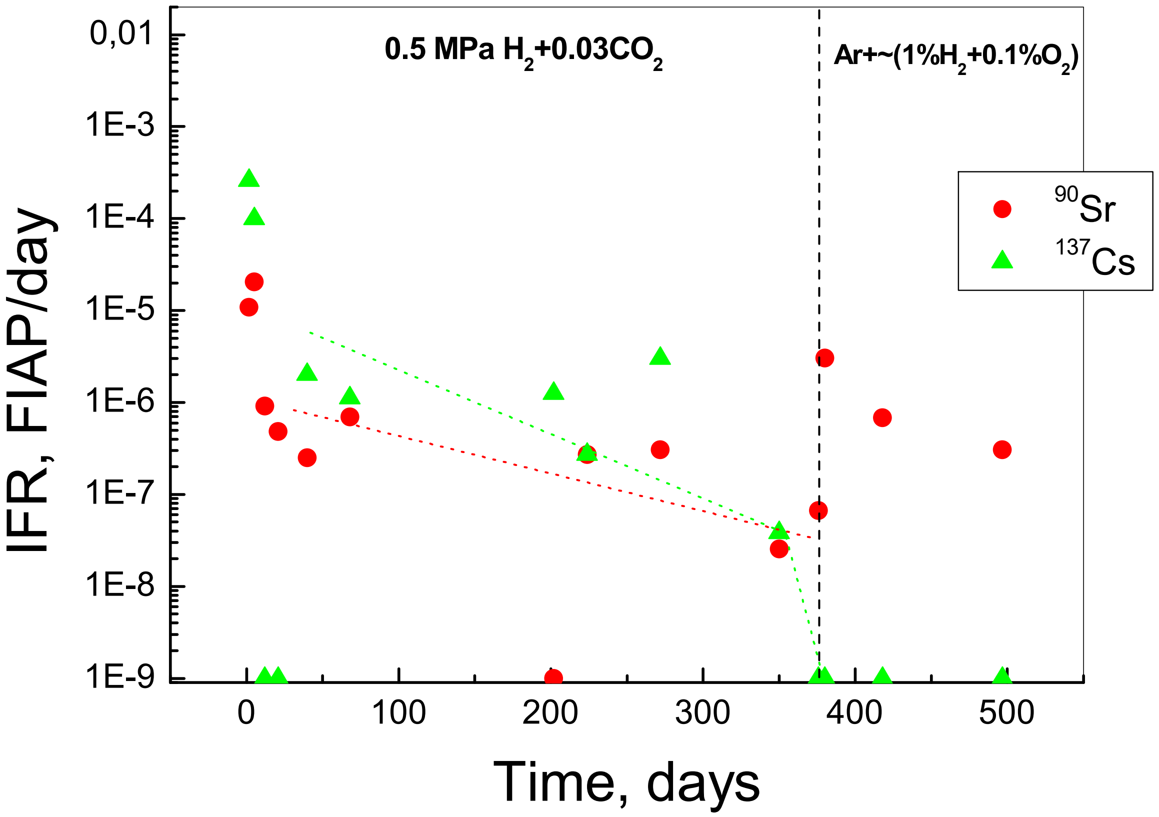
Evolution of An and Ln concentrations SF leaching under 5 bar (H_2+0.03% CO_2)



How to draw conclusions from autoclave tests?

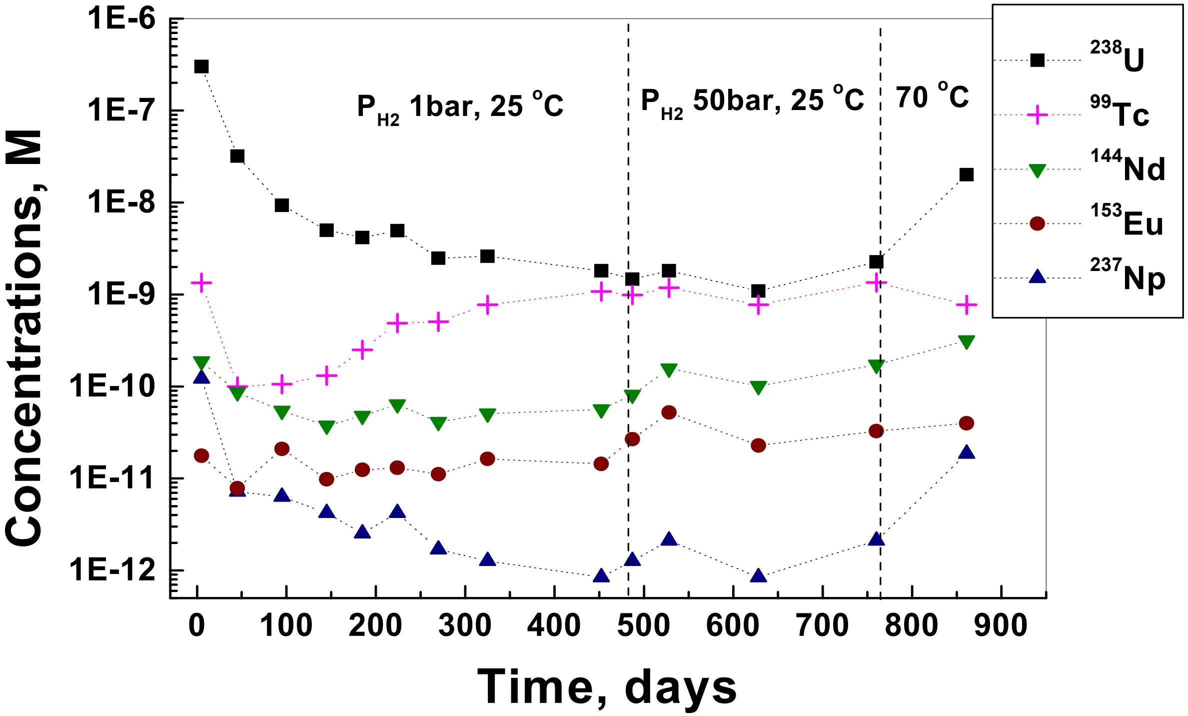
- During the autoclave leaching of the fuel sample under H_2, solution samples are withdrawn from the autoclave and analyzed. Usually the first sample is calculated to have a volume equal to the solution remaining in the sampling tubes from the previous sampling and is discarded, while the two consequent samples are analyzed by ICP-MS or γ-spectroscopy.
- In order to avoid dissolution of fuel fines which would give high unrealistic values, ultracentrifugation is used and the supernatant is immediately acidified to avoid radionuclide loss in container walls due to sorption. This is especially important if An(III), An(IV) or Ln(III) are present in the solution-the losses from sorption could be such that the majority of the nuclide is in the vessel walls and very little in the solution.
- If in consecutive samplings the concentration of a radionuclide increases, from this increase the amount released in solution during a certain time interval can be calculated and together with the surface area of the fuel, its radiation field etc. it can be used to estimate the release rate of this radionuclide.
- The concentrations of actinides and lanthanides, as well as those of certain redox sensitive fission products such as Tc, Mo etc. are important to report in order to judge about the redox state of the given actinide or fission product. Thus, there are no U(VI) compounds which have a solubility lower than 10^{-7} M, one such insoluble U(VI) compound is uranophane, a calcium-uranyl silicate. If we measure U concentrations in the range 10^{-9} M which stay for a long time constant, it means that they result from equilibrium with UO_2(hydr, am) and there is no U(VI) in solution. If the concentration is 10^{-8}M, there is a part of U(10^{-9} M) which is U(IV), while the rest is U(VI) in solution. When the concentrations of Mo reach 10^{-9} M starting from higher levels, then we can conclude that the molybdate (MoO_4^{2-}) ion which is usually released from the pre-oxidized fuel layer is reduced to Mo(IV) as MoO_2(s) which has a solubility around 10^{-9} M and the same holds for Tc, which is released as Tc(VII) per-technetate ion (TcO_4^-) from the pre-oxidized fuel layer. The other actinide oxides have also similar solubilities, NpO_2(s) at about 10^{-9} M while PuO_2(s) about 10^{-10} M.

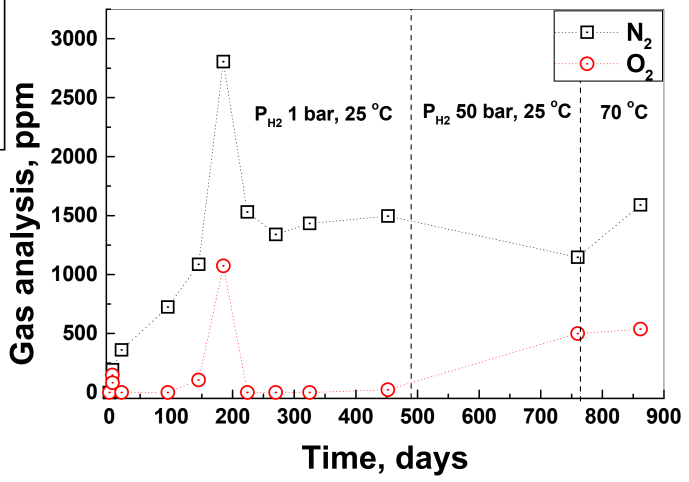
The kinetics of release of Cs and Sr under 5 bar H_2 or Ar.



Negative values of Incremental Fractional Release (IFR) plotted in x-axis.

4U6: Starting conditions: $p(H_2)$ = 1 bar, T = 25 °C; SF (∅ = 250-500 µm)

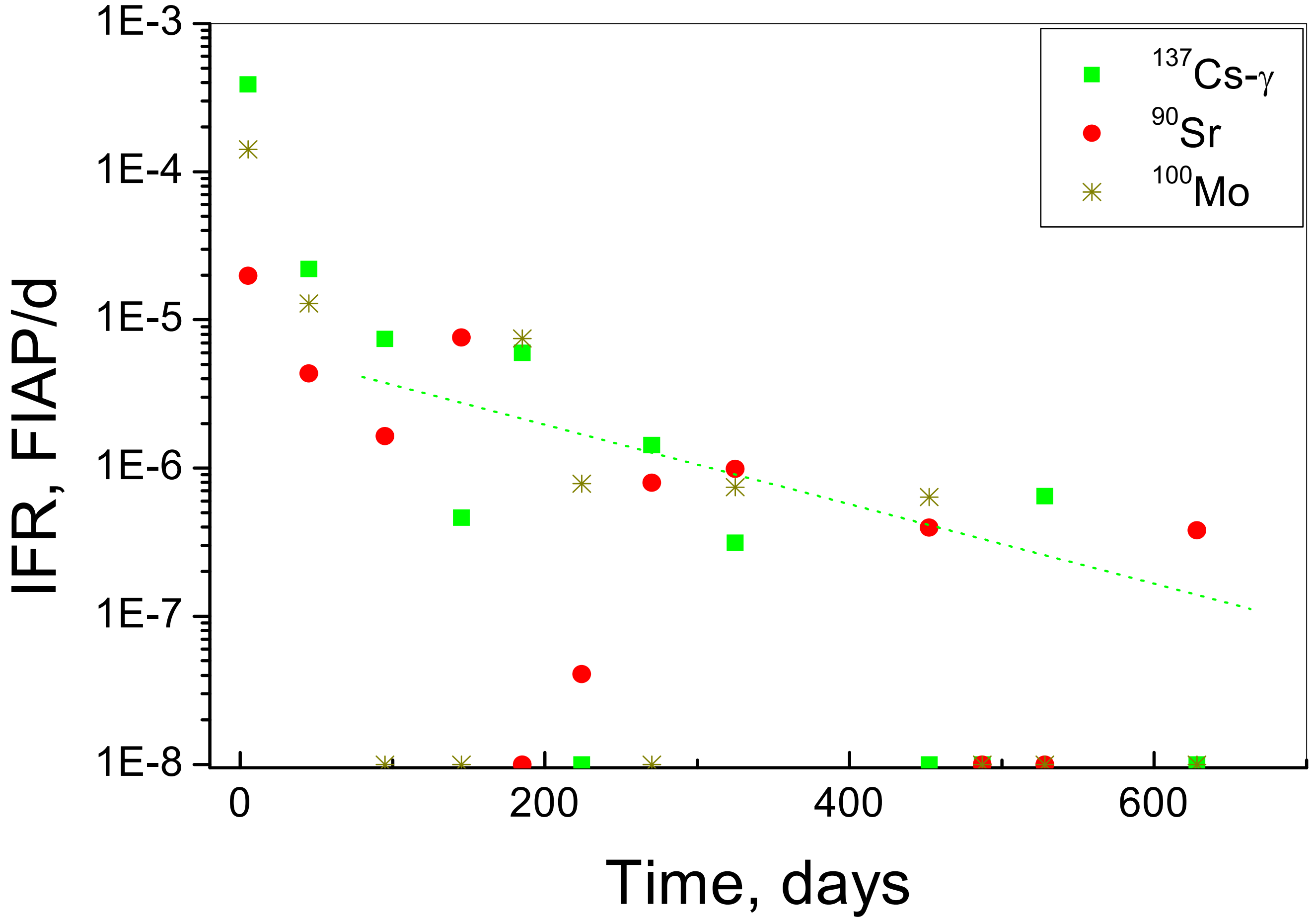




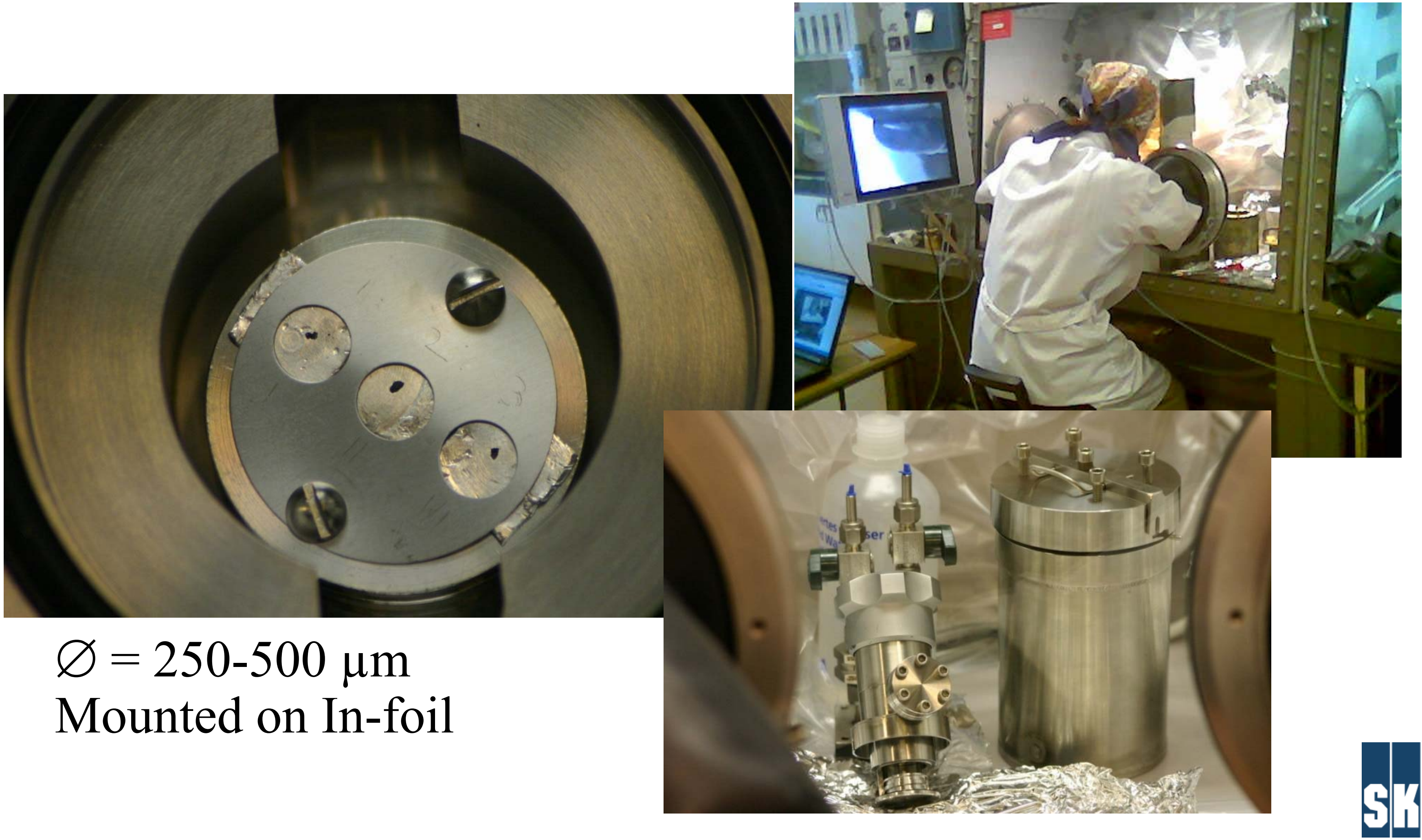
- The [U] decrease is steadily accompanied by Tc (initially), Nd, Eu and Np (co-precipitation?), despite air intrusion
- The H_2 pressure increase seems to have no evident influence on the system, probably also due to measurable O_2 levels.

SKB

IFR for Cs, Sr, Mo, 1 bar H_2

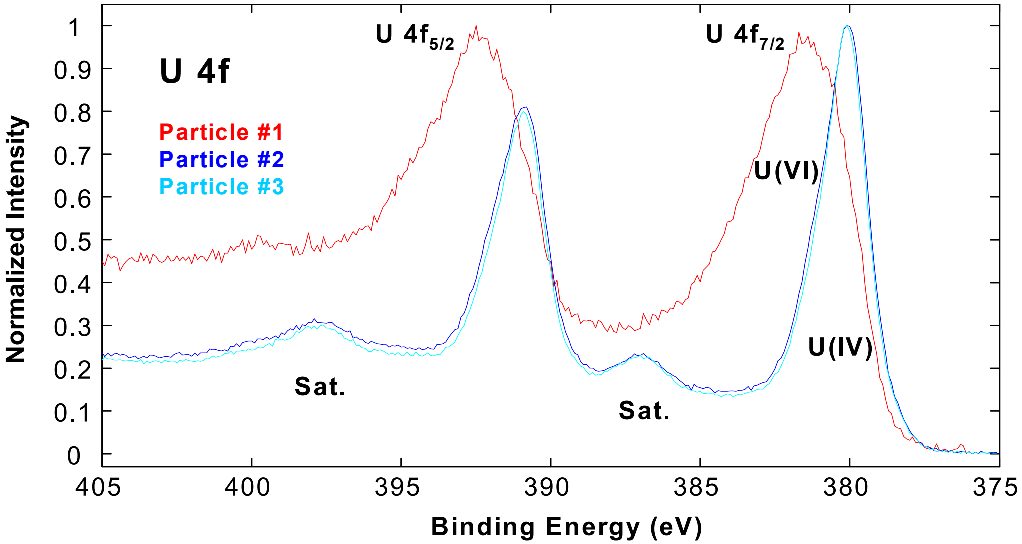


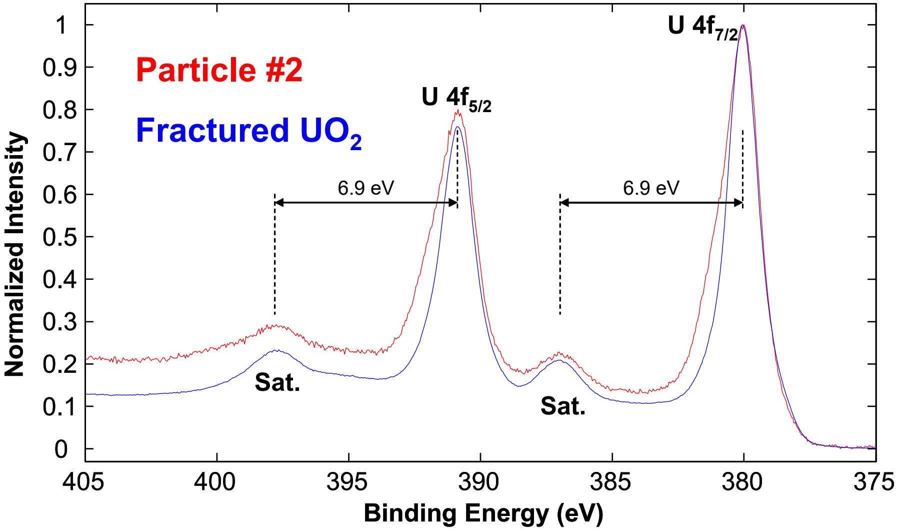
4U6: Preparation for XPS analysis on non-leached and leached spent fuel fragments



∅ = 250-500 μm
Mounted on In-foil

4U6: XPS results on non-leached (#1) and leached SF fragments (#2, #3) (INE).

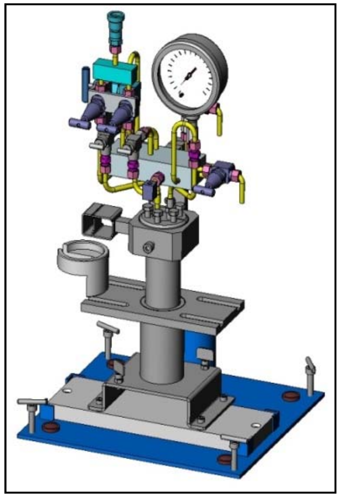


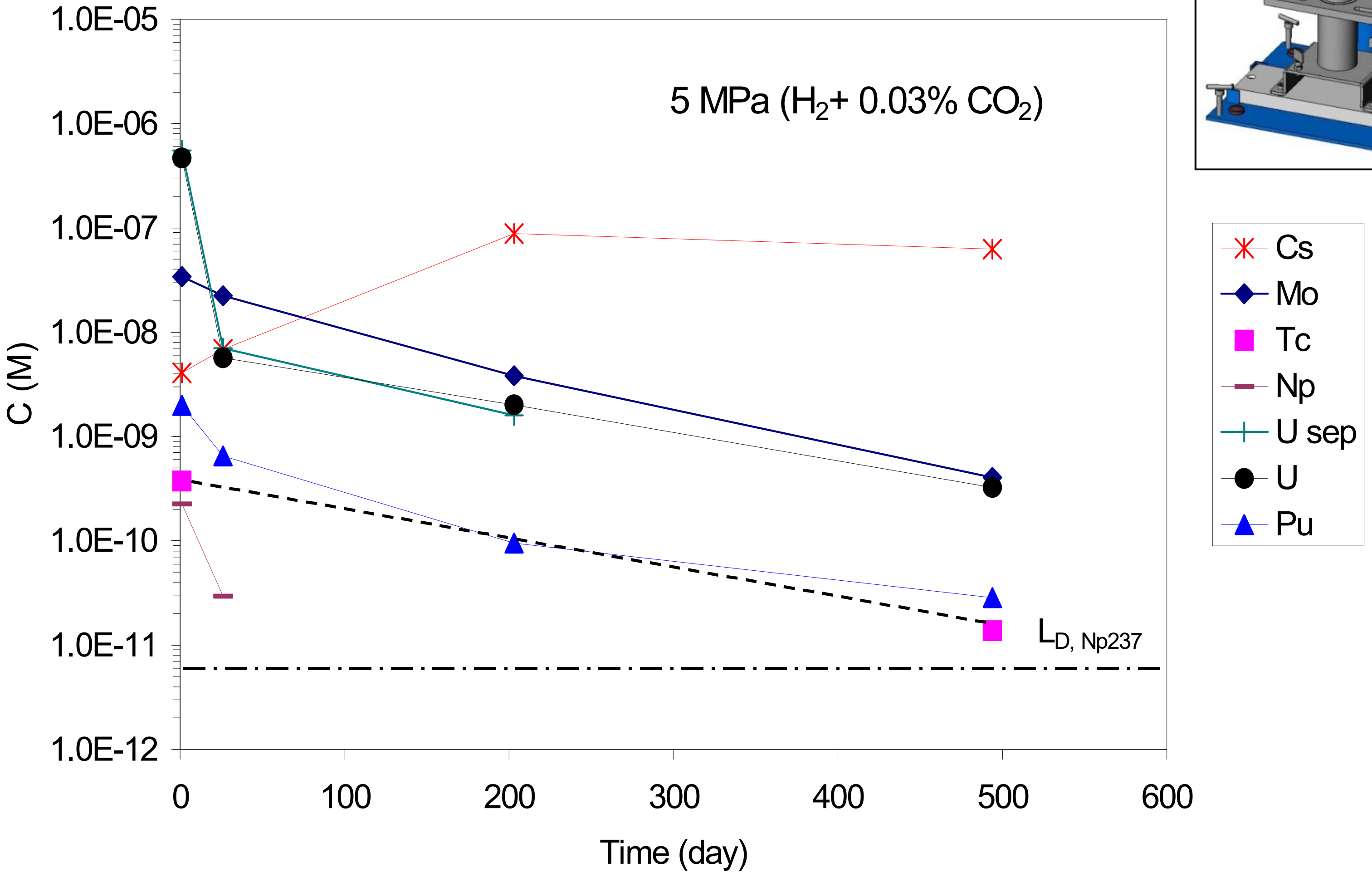


- XPS results show that the initial [U] derives from a pre-oxidized surface layer (particle #1). Cs was also found on particle #1. Dissolution of the pre-oxidized layer results in initial increase of FIAP for Cs, (Sr+Zr) and Mo.
- The surface of leached fragments (particle #2 and #3) are almost identical to pure UO_2. No Cs could be detected.

MOX fuel leaching under H_2,ITU

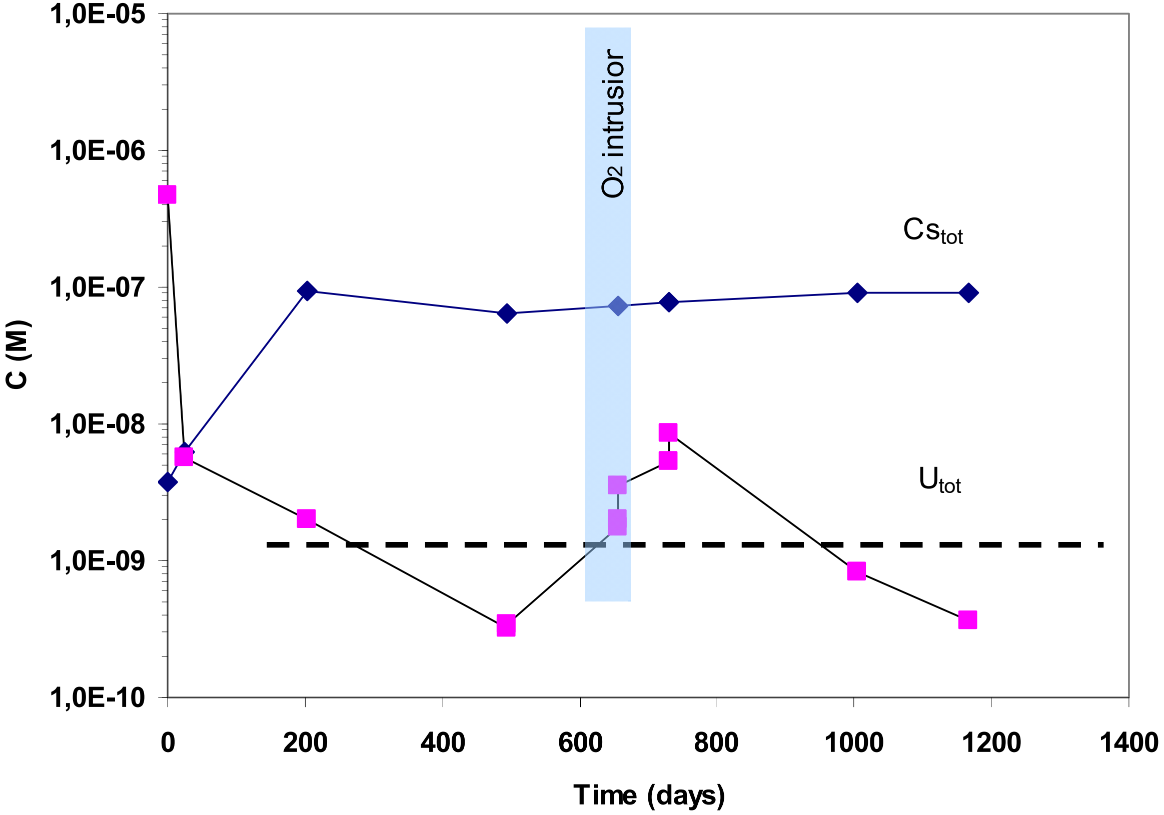
Simple synthetic GW solution, 10 mM NaCl + 2 mM $NaHCO_3$.



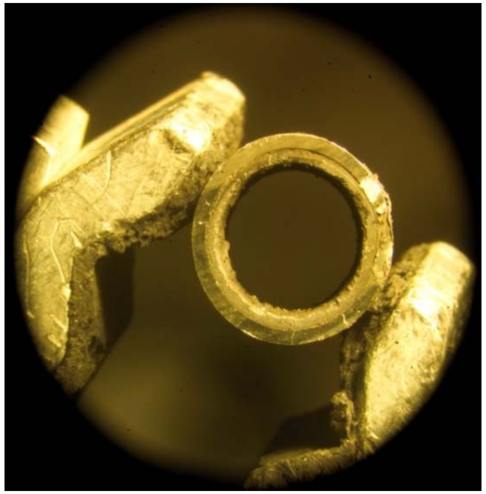


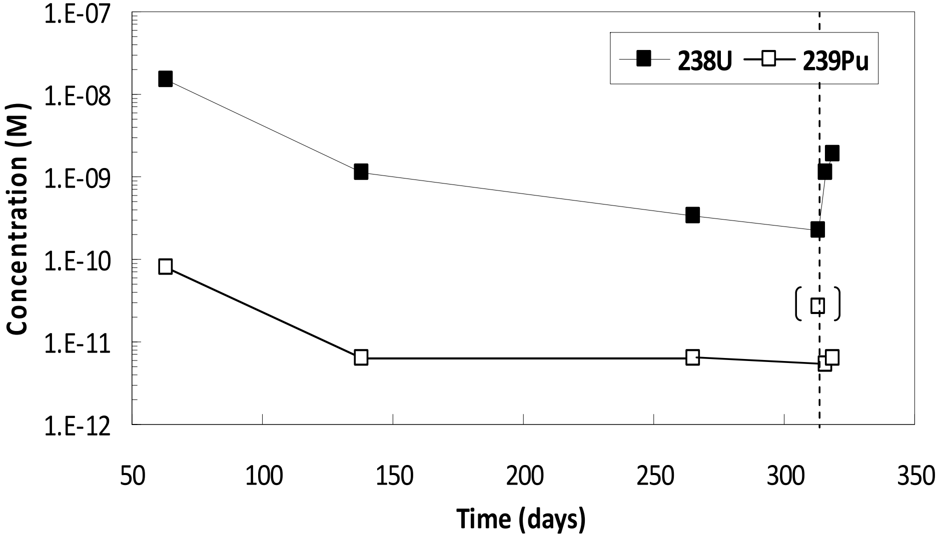
Carbol et al, J. Nucl. Mater. 233(2009)234-238.

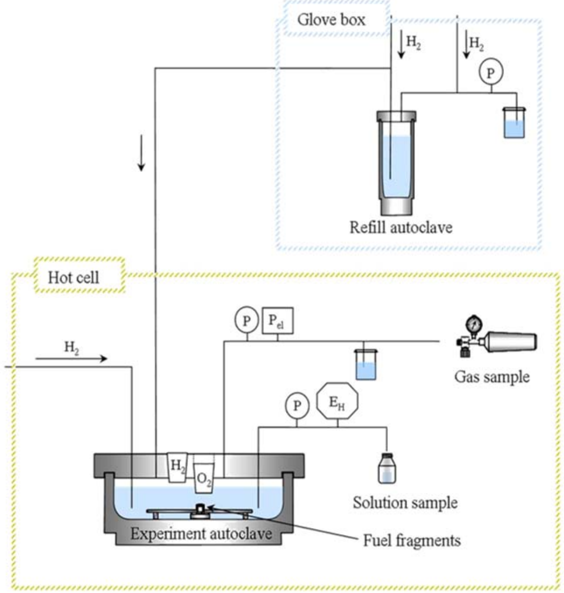
Long term Cs and U data from the MOX test.

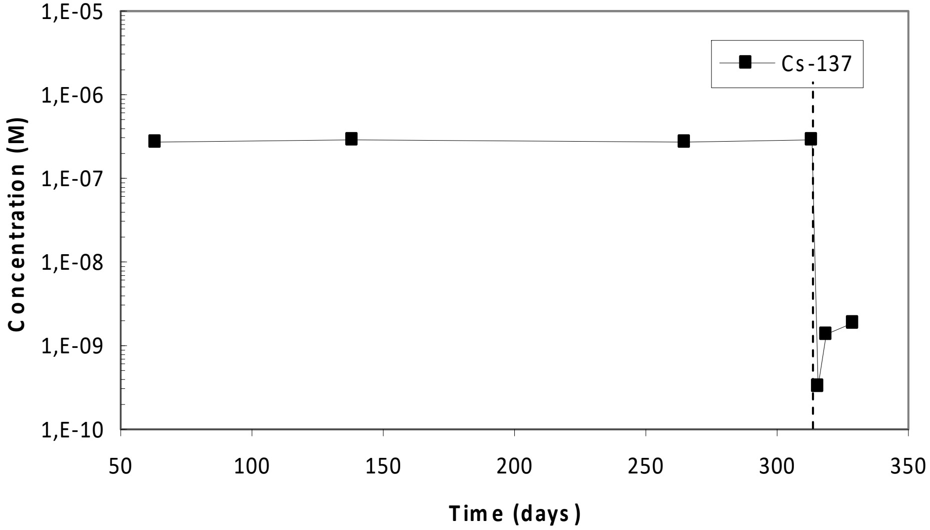


Leaching of rim containing fraction of HBU fuel (67 MWd/kg), ITU.



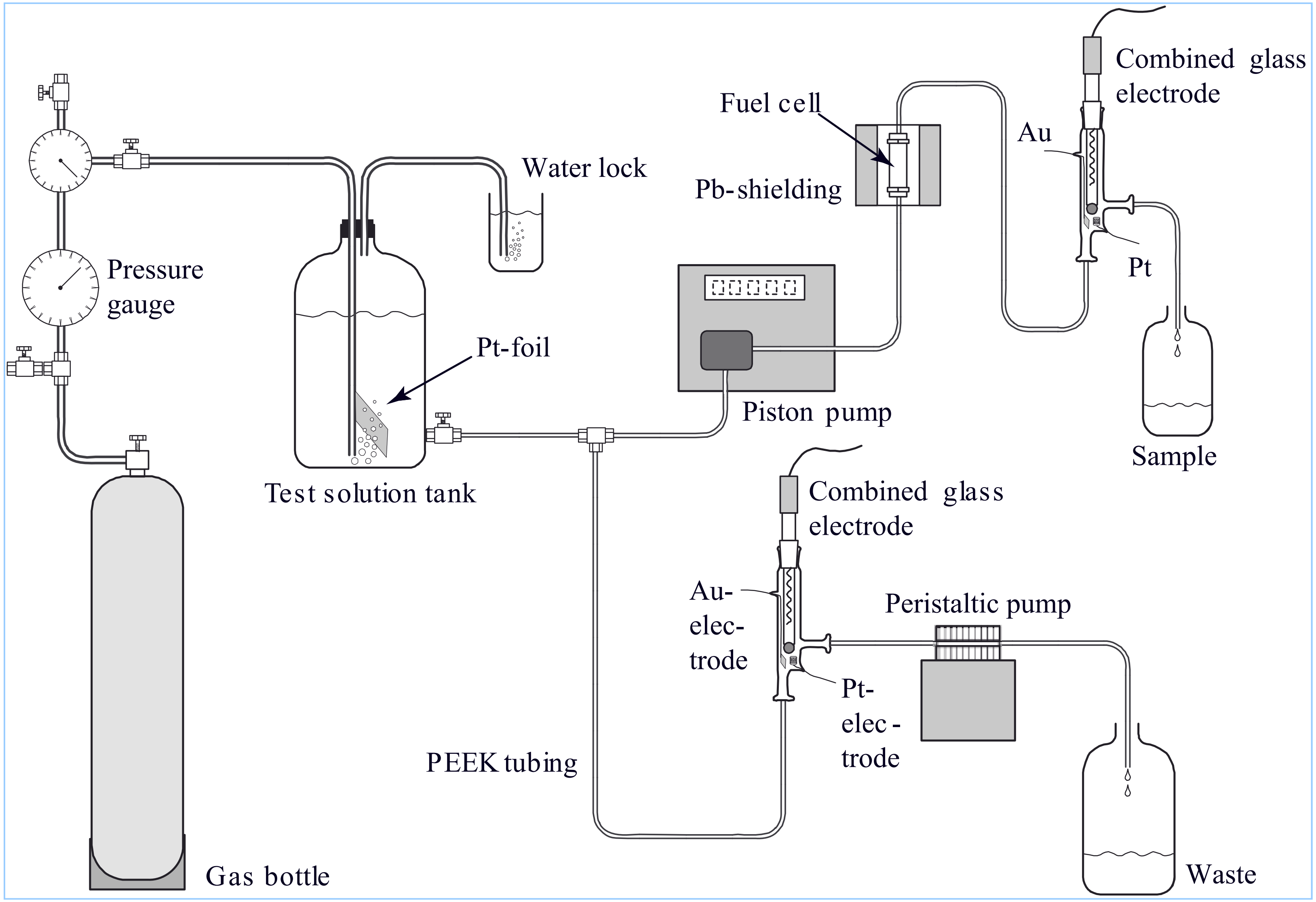






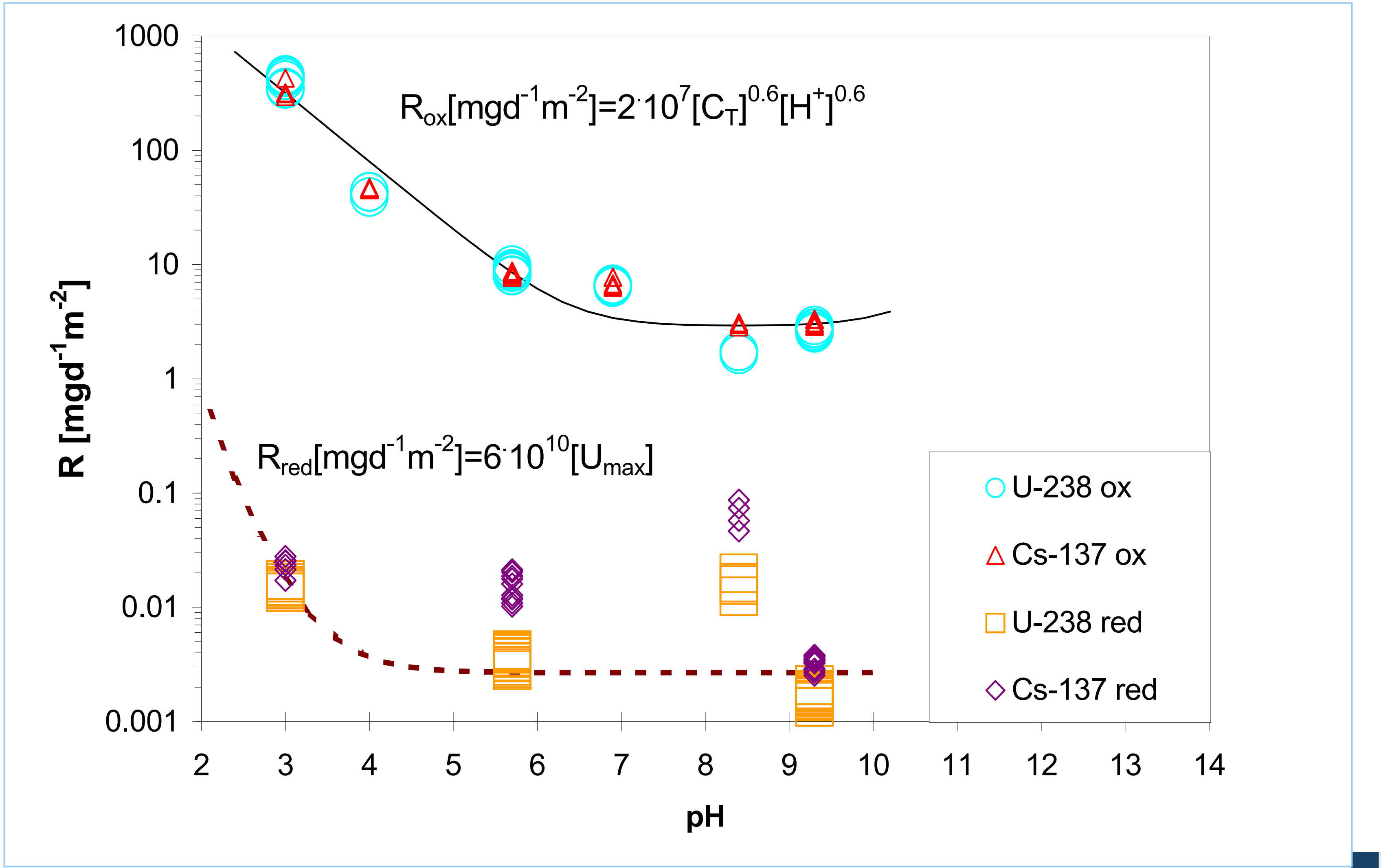
Fors et al, J. Nucl. Mater. 233(2009)234-238.

Schema of the flow through experimental setup



Röllin et al., J. Nucl. Mater, 111(2001)222-333

U, Cs based dissolution rates, different pH and redox conditions.



Characteristics of fuel leaching for $[H_2] > 0.8$ mM - the role of surfaces.

- **Observed: a)** Complete absence of **O_2, H_2O_2 b)** Decreasing with time: concentrations of U, Np, Pu, Tc,… and release rates of Sr,Cs,… **c)** Reduction of the UO_2 surface (α, γ or fuel + H_2).
- **Radiolytic modelling** predicts only a decrease of the levels of radiolytic oxidants and of U release.
- Evidence on fuel surface reduction of radionuclides with $H_{2,diss}$.

-**Chalmers**: 99% of precipitated U on fuel surface, very little in vessel rinse.

- **INE-FZK**: Co-dissolution test SF+Fe in 5 M NaCl under Ar from start and 2.8 bar H_2 after 4 years. Fe(s), Fe_3O_4 and GR as corrosion products, absence of U sorption/precipitation on Fe.

- In the case of SF, β- and γ-radiations also present and ε-particles in UO_2 matrix.
- -Recent tests **INE**: Br^- addition to 5 M NaCl scavenges OH-radicals, reacting 250 times faster than H_2. Measured oxidizing bulk solution under γ-radiation. Only surface processes responsible for absence of radiolytic O_2 or U oxidation in spent fuel case.
- - Brczkowski et al, J. Nucl Mat. 346(2005)16: Electrochemistry of **SIMFUEL electrodes** under low $P_{H\,2}$. Eriksen et al, J. Nuc.Mat. 2007, Trummer et al, 2008: Effect of **Pd inclusions on UO_2**. Cui et al, Radiochim Acta 2004**. extracts from fuel** ε-particles, tests with 10 % H_2.

-The galvanic coupling with UO_2 protects all or is there any effect of the AnO_2 surface itself?

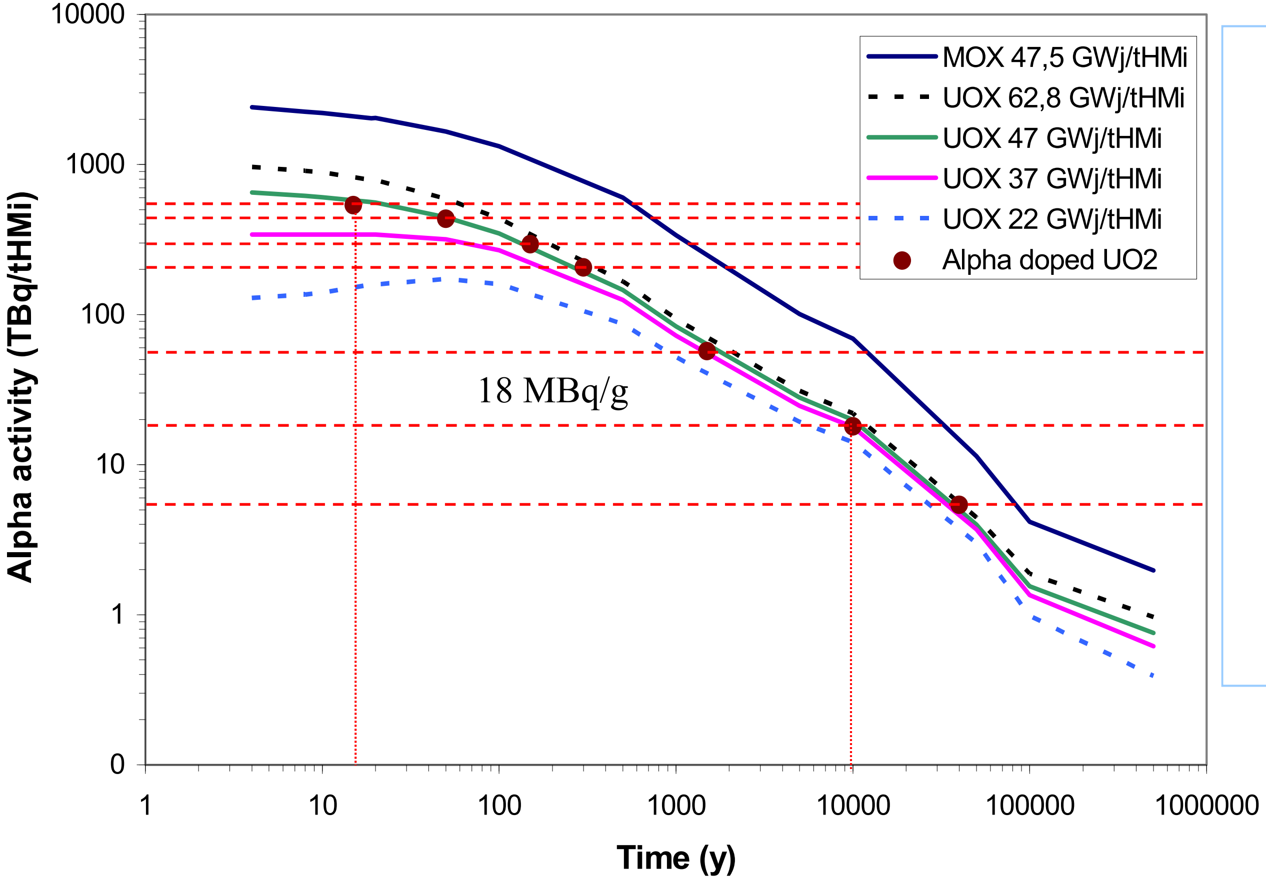
- Fuel tests with lower $[H_2]$ (0.06, 0.08, 0.24 mM): presence of H_2O_2, increasing Cs, Sr, Mo.

How to imitate old spent fuel (e.g. 1000 y old)?

- In fresh spent fuel a few years after discharge the β-γ radiation is very strong and dominates. Both these radiations have low LET(Linear Energy Transfer), i.e. long range and are radical rich.
- In our PA analysis the first contact of fuel with water is predicted after several (hundred) thousand years, so the authorities have raised the question of the difference of the fuel radiation field used in spent fuel experiments and the real radiation that will be present when it contacts groundwater in a damaged container.
- In this case the alpha radiation dominates, while the β,γ-radiations have decayed to insignificant levels.
- Alpha radiation is a high LET radiation and produces mainly molecular products H_2O_2 and H_2, as well as a few radicals outside the alpha tracks.
- Therefore the last years several experiments testing so-called alpha doped UO_2, i.e. UO_2(s) mixed homogeneously with various amounts of an alpha emitting isotope, such as ^{233}U or ^{238}Pu have been carried out under various conditions.
- Up to now, it has not been possible to add inactive fission products together with the alpha emitting isotope, so the solid phase imitates well the alpha radiation levels of “old” spent fuel, on the other hand is more easy to oxidize than spent fuel because of the absence of lower valence cations in the UO_2 matrix.

Alpha activity decay with time in spent fuel

Studies with α- doped UO_2



- Actinide oxide mixtures:

$(^{238}U + ^{233}U \text{ or } ^{238}Pu)O_2(s)$

- Mimic α-field of old fuel.
- Referred to by:

- dopant content (%),

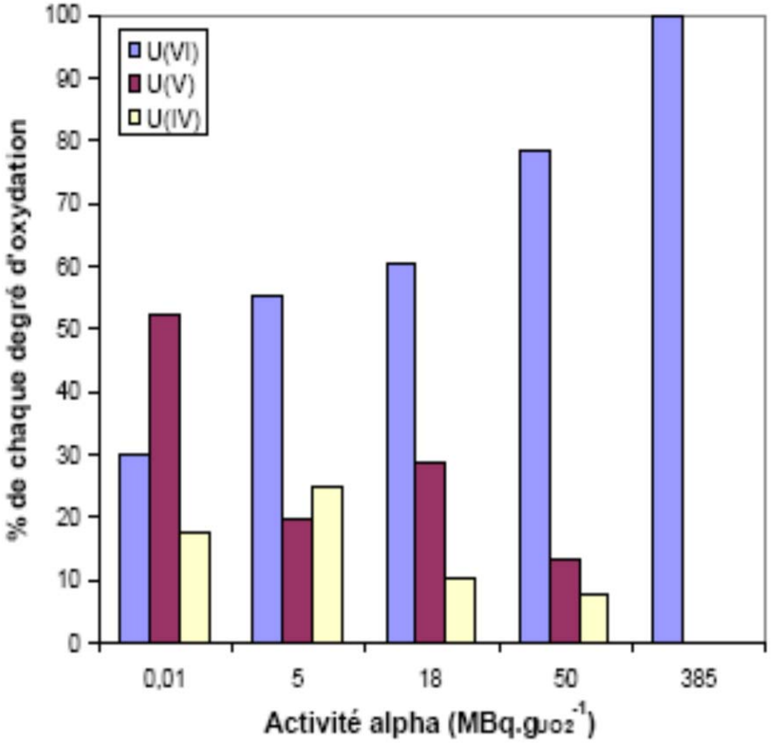
-specific activity (MBq/g)

-or fuel age mimicked (y)

10% ^{233}U = 33 MBq/g = 3000 y

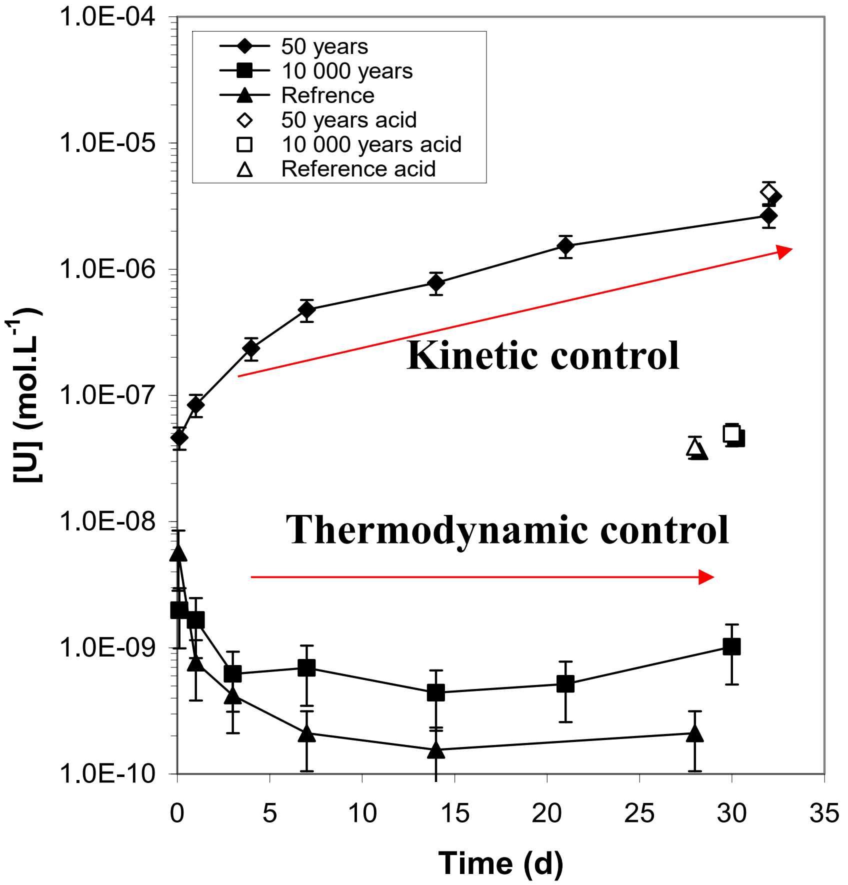
Muzeau et al., J. Alloy Comp. 467(2009)578.

XPS surface analysis after annealing and storage



Test in carbonate solutions under Ar.

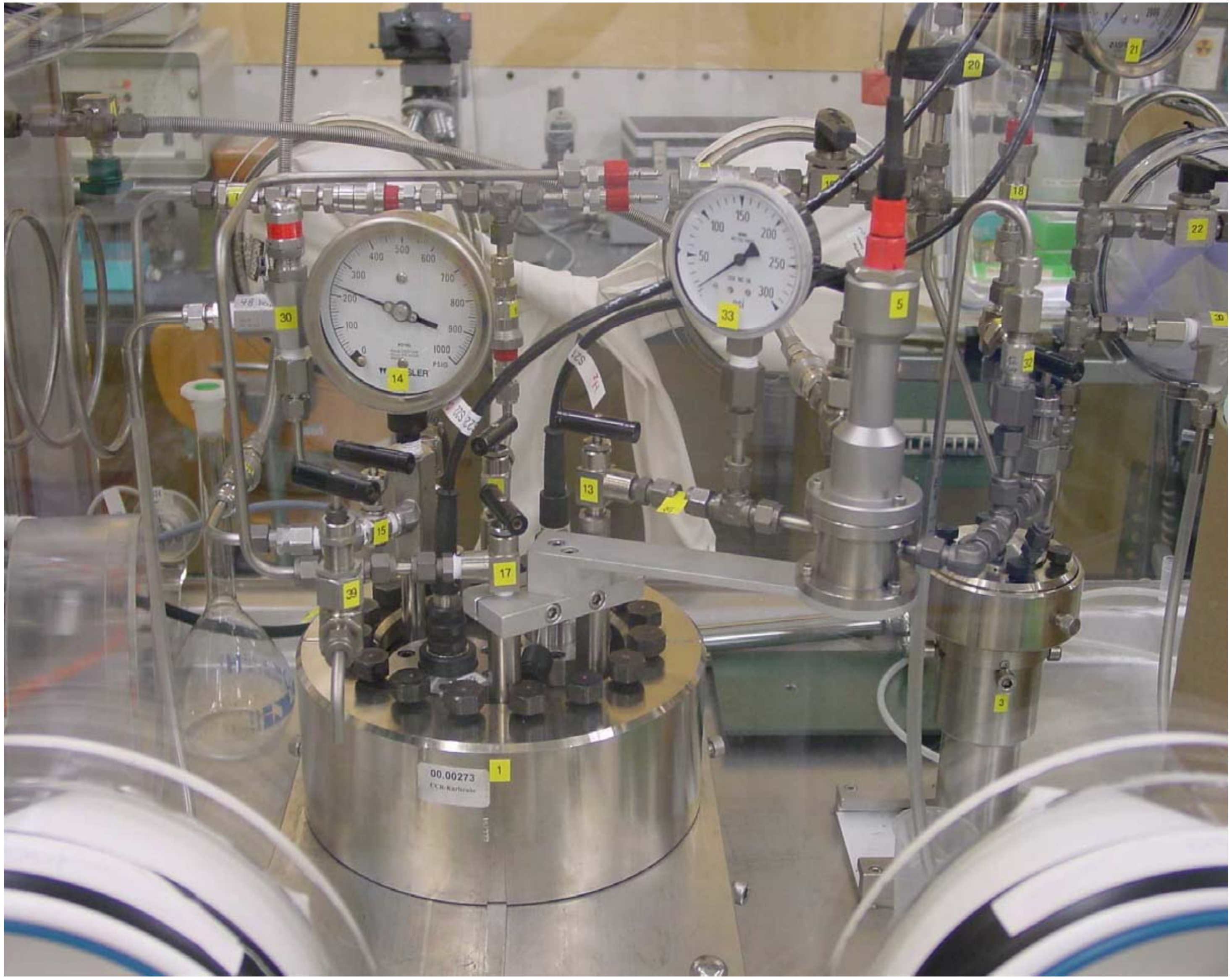
New **threshold**: 18 MBq/g or 10 000 y



Kinetic control

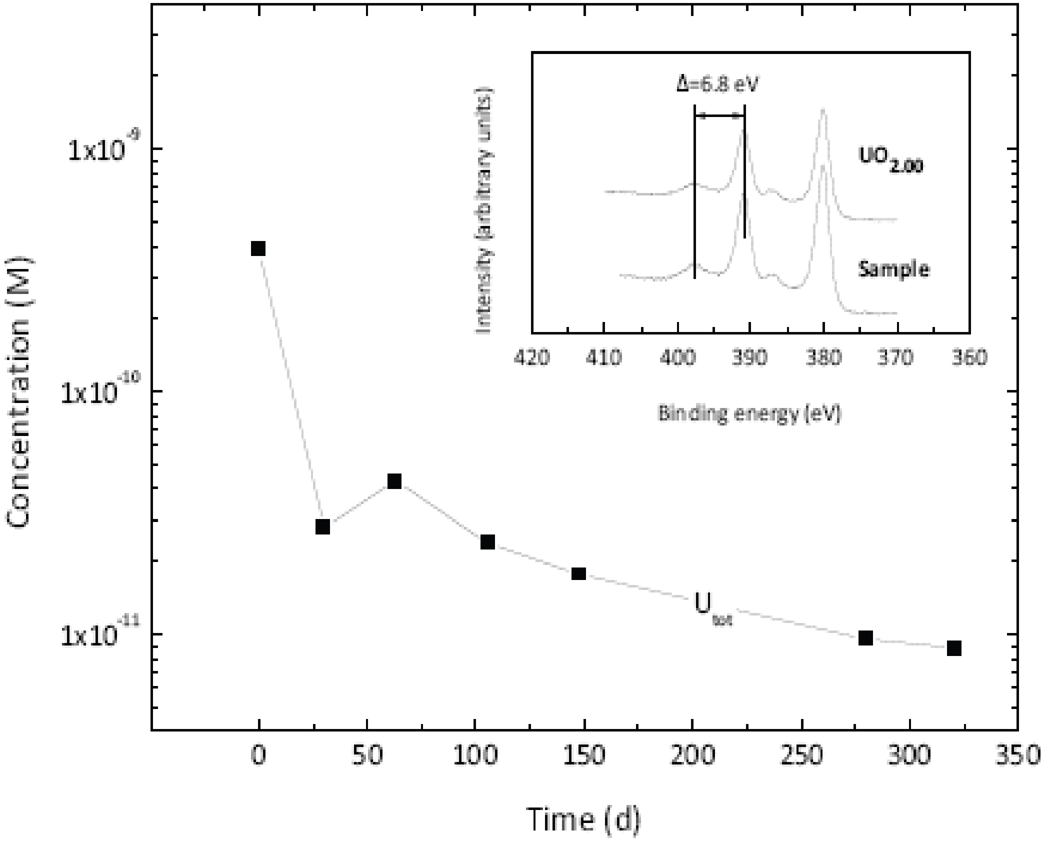
Thermodynamic control

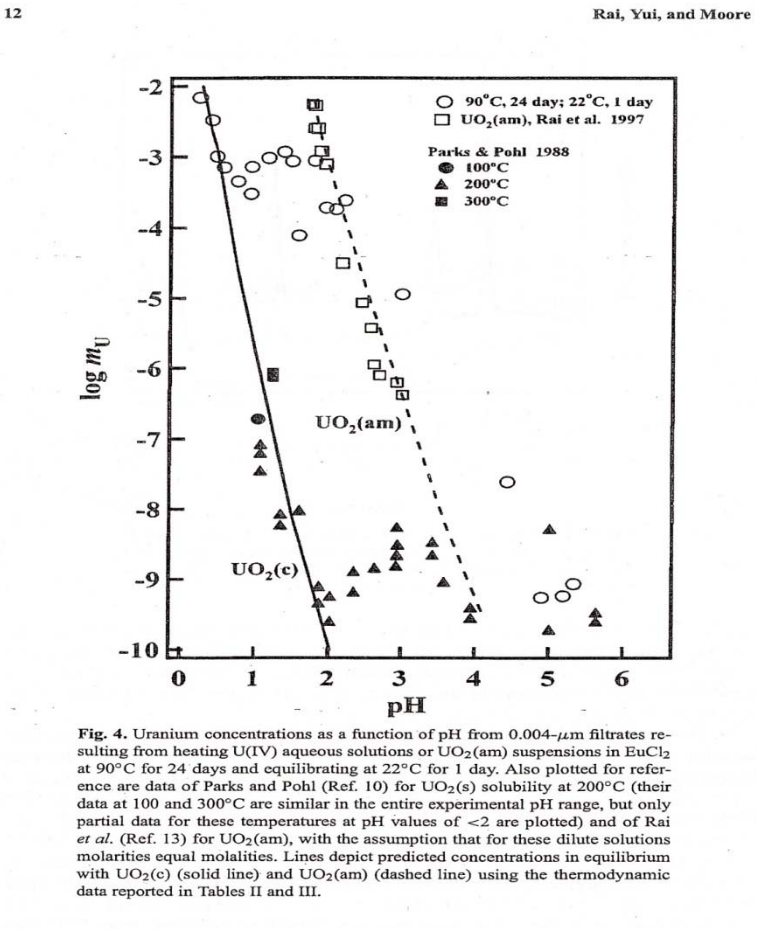
Autoclave test (ITU) with 10% ^{233}U doped pellet under H_2 and Ar.



ITU-Measured total U concentrations, 10% ^{233}U pellet leached under H_2.

Insert- XPS of the pellet surface after test. **Right**-Inactive UO_2 solubilities, Rai et al. 2003.





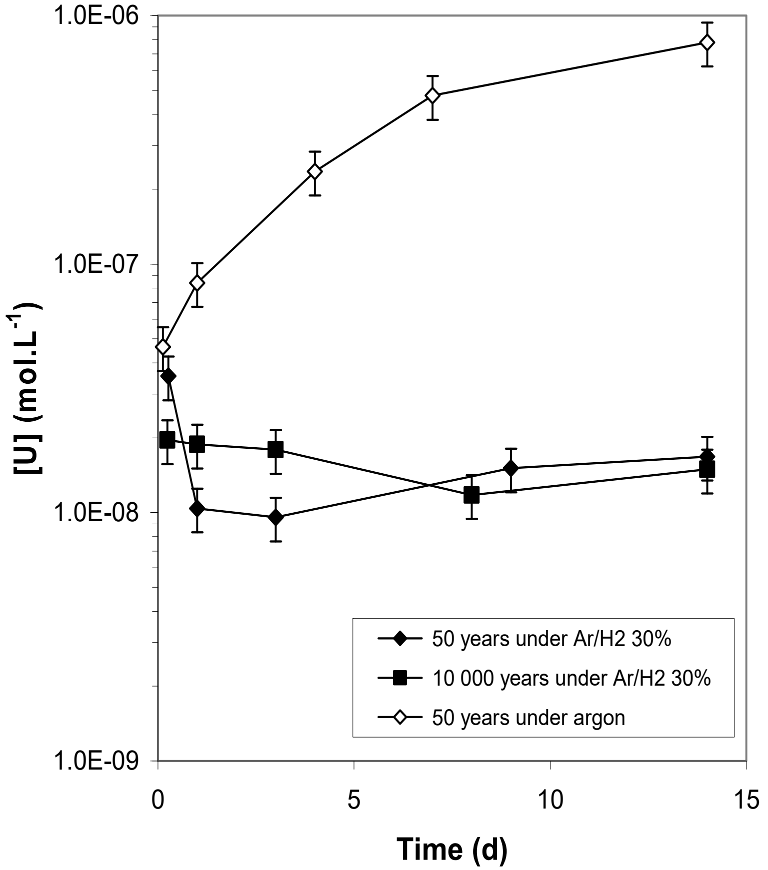
12 Rai, Yui, and Moore

Fig. 4. Uranium concentrations as a function of pH from 0.004-μm filtrates resulting from heating U(IV) aqueous solutions or UO_2(am) suspensions in $EuCl_2$ at 90°C for 24 days and equilibrating at 22°C for 1 day. Also plotted for reference are data of Parks and Pohl (Ref. 10) for UO_2(s) solubility at 200°C (their data at 100 and 300°C are similar in the entire experimental pH range, but only partial data for these temperatures at pH values of <2 are plotted) and of Rai *et al.* (Ref. 13) for UO_2(am), with the assumption that for these dilute solutions molarities equal molalities. Lines depict predicted concentrations in equilibrium with UO_2(c) (solid line) and UO_2(am) (dashed line) using the thermodynamic data reported in Tables II and III.

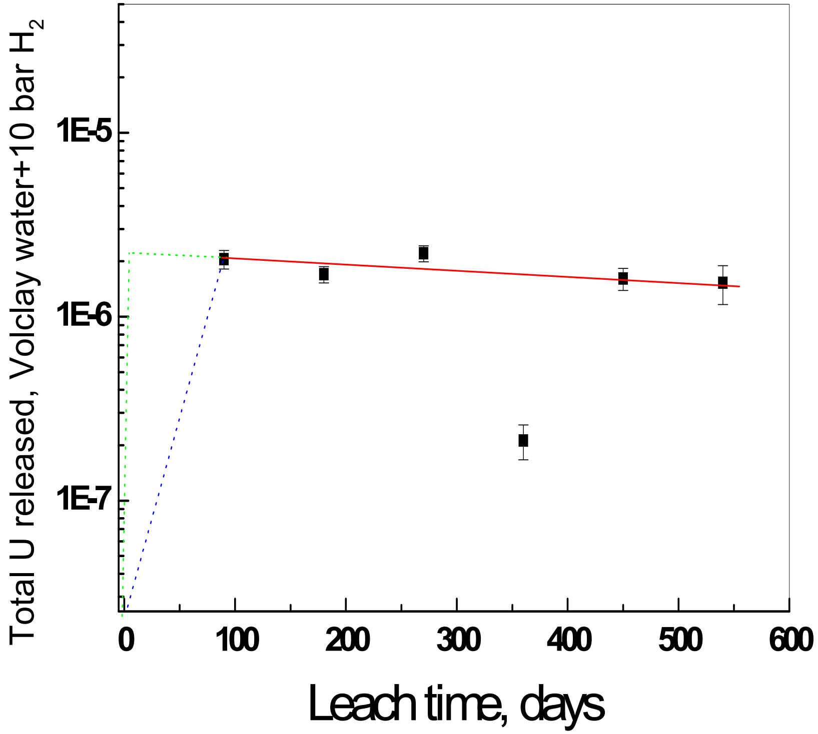
Carbol et al, Geochim. Cosmochim. Acta 73 (2009) 4366

Back to H_2: Two tests with highly doped UO_2

Muzeau, 2009: α–doped UO_2 (385 MBq/g or 50 y fuel) tested in carbonate solutions under Ar or 1 bar H_2



SCK.CEN: UO_2 powder (245 MBq/g or 150 y fuel) tested in carbonate solutions under 10 bar H_2



Reactivity of α-emitting AnO_2 surfaces

- The property of causing **recombination of O_2 with H_2** on alpha particle emitting light actinide surfaces more general than in our tests.
- Haschke et al. 1997 report consumption of 2:1 D_2+O_2 mixtures to form water on the surface of ^{239}**PuO_2**. LANL studies show that these recombination reactions over pure and impure actinide oxides occur at much faster rates than radiolysis events [Kelly and Paffet, WM´02 Conf.].
- **NpO_2** doped with ^{244}Cm consumes H_2 by reacting it with O_2 [Icenhour et al, Nucl. Techn. 146(2004)206].
- Bauhn et al. 2018 used D_2 to prove production of increasing concentrations of HDO in water contacting SIMFUEL or 24%Pu fresh MOX pellets:

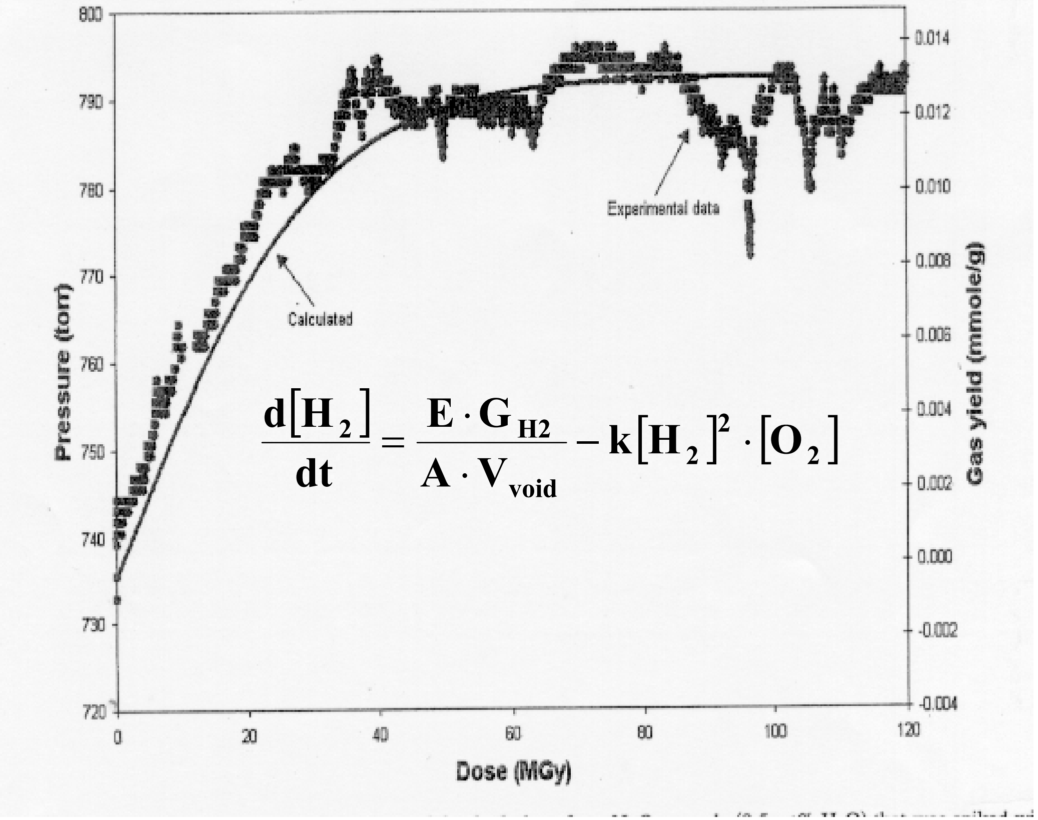
$$H_2O_2 = 2OH\cdot(\text{sorbed})$$

$$2OH\cdot + D_2 = 2HDO$$

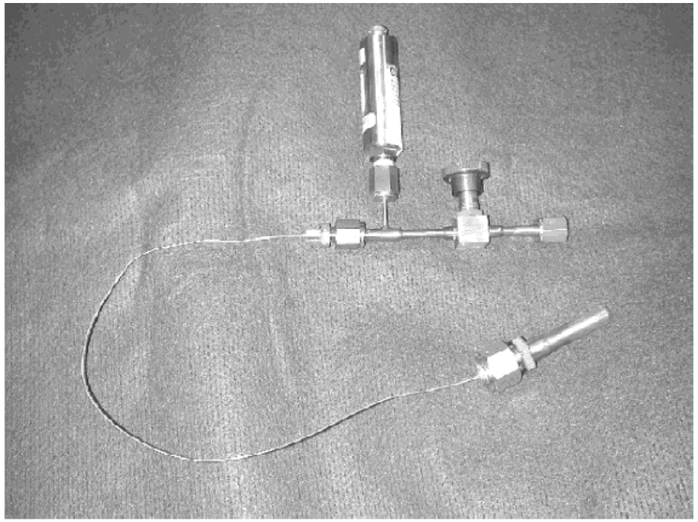
- The undoped **UO_2** surfaces may have a limited capability to activate H_2 but no effect on H_2+O_2 [Devoy et al, MRS 2004] or H_2+ H_2O_2 [Nilsson et. al. JNM 2007] could be detected (basic catalysts poisoned by water). This seems to be a property **of the radioactive** actinide oxide surfaces.

Recombination reactions

Radiolytic gas production from water sorbed on ^{244}Cm doped $NpO_2(s)$ [Icenhour et al., Nucl. Tech. 2004]

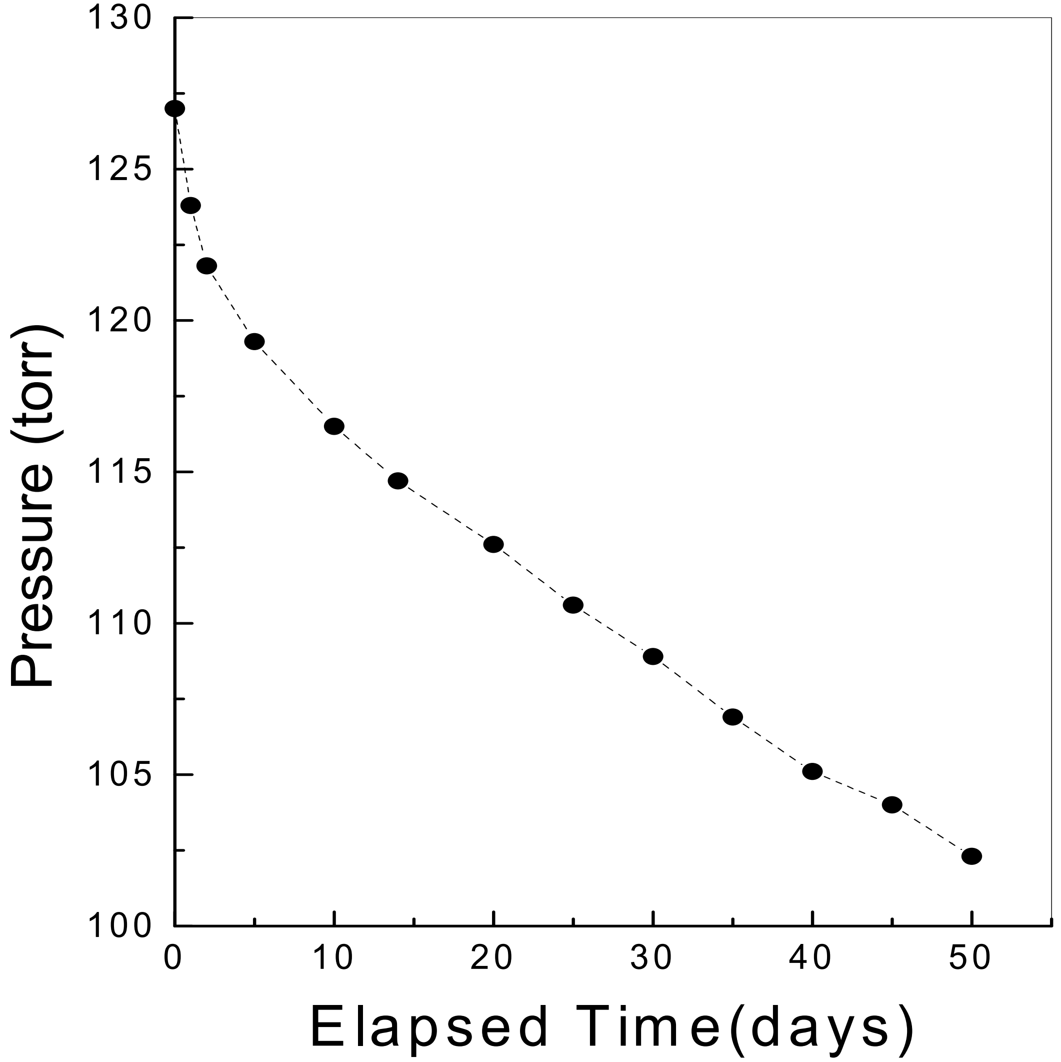


$$\frac{d[H_2]}{dt} = \frac{E \cdot G_{H2}}{A \cdot V_{void}} - k[H_2]^2 \cdot [O_2]$$



Photograph of experimental aparatus.

PuO_2(s) causes recombination of H_2 with O_2 to form water.



PVT experiment:

2:1 mixture D_2+O_2

over PuO_2(s), 25 °C.

Haschke et al., J. All.Comp.1996.

Interfacial radiolysis

- Experimental and modelling studies on homogeneous water radiolysis carried out for decades, mechanistic studies of radiolysis of water sorbed on surfaces of oxides is quite recent.
- Study of γ-radiation induced H_2 generation in oxides, [Petrik et al, J. Phys Chem, 2001].

  Oxides with band gap ~5eV show increased H_2 production due to excitons causing dissociation of water molecules (H-O-H bond energy 5.1 eV). Possible $H_2+OH\cdot = H_2O+H\cdot$
- UO_2(s) included in another study [LaVerne et al., J.Phys. Chem. 2003], reporting much higher radiolytic yields of H_2 (>10 fold) from adsorbed water than from free water, while O_2 production below detection limit on UO_2 and ZrO_2 surfaces.
- Energy, charge and matter can be transferred through the interface, while catalytic or steric effects can alter the reactivity or decomposition of adsorbed molecules. Excitons, slow electrons or recombination of electron-hole pairs mentioned as potential sources of high H_2.
- [Stutz et al, J.Phys Chem, 2004]: effect of oxygen vacancies (created by sputtering UO_2(s) surface with heavy ions) in hydrogen evolution following water adsorption. Similar ones created by alpha recoil atom. Contribute to the release of hydrogen by dissociative adsorption of a water molecule.
- Difficult to propose mechanism from fuel studies, mechanistic studies as interfacial radiolysis ones may contribute in the quantification and understanding of the observed effects.

Thank you!

SKB