Spent fuel as waste form – a summary of the SoK report.

Kastriot Spahiu

SKB, Chalmers, Sweden

Summary

- Introduction to repository science. Pillars of safety: how does a deep repository function.
- Spent fuel: mixed actinide (U, Np, Pu) and FP-oxides (Ln, Sr, Mo..), formed in reactor containing gas bubbles, segregated oxides and metal particles.
- Importance of Instant Release Fraction and how to estimate it.
- The influence of **intrinsic** (structure, burn-up) and **environmental** (H_2 in groundwater) factors on dissolution rates (source term) discussed.
- Attempt to rationalize literature data for **burn-up influence** on fuel dissolution in presence of air. The role of non-U cations shown to affect both high temperature fuel oxidation and oxidative dissolution of spent fuel or doped UO_2 (uraninite).
- A **large impact of H_2** dissolved in the groundwater is observed in tests with spent fuel or UO_2(s) doped with an α-emitter-alpha doped not discussed here due to time limit.
- The interactions between radiation and water adsorbed on the surface of actinide oxides (**interfacial radiolysis**) important in all tests. This is complicated field where better understanding is needed. Alpha radiolysis and H_2O_2, H_2 generation on water sorbed on oxide surfaces is an intrinsic property of actinide oxides.
- Recent progress in kinetic modelling of spent fuel dissolution.
- Long term changes in fuel structure due to He generation and radiation damage.

Pillars of safety

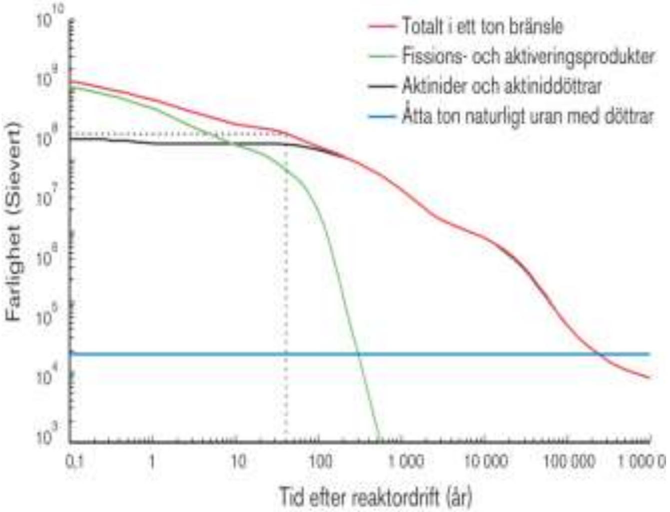
- Long term safety relies on a series of barriers:

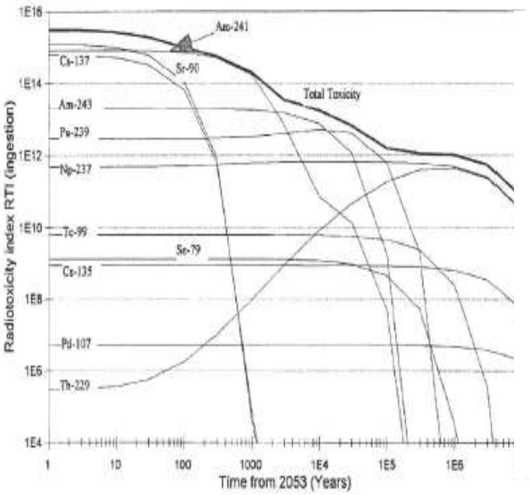
- Engineered barriers contain waste, so that short lived RN decay, and limit the release of long-lived RN.

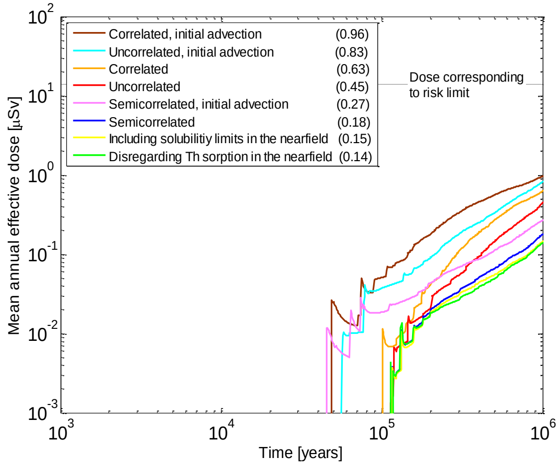
- Geological barriers retard RN migration by reducing inventory through decay and by diluting long lived RN.

- Safety assessment: First step is a scenario analysis, specifying events and processes in the repository and provides a broad description of characteristics and sequencing. Thus, possible futures of the repository are identified as well as the classes of models for quantitative safety assessment.
- The most probable vector to carry RN from the repository up to the surface and give dose to the biota is groundwater. Hence its flows (hydrology), composition (geochemistry) and other characteristics are very important for PA. A comparison of the toxicity of the waste forms with the limits established by the authorities for releases from repository, shows an enormous difference- see next slides. How can we achieve this, i.e., where is based repository safety?

Pillars of safety in a repository







- The radiotoxicity of spent fuel or vitrified waste is extremely high, the allowed releases extremely low: how does a repository manage this?

1. Very dissolution resistant waste forms and corrosion resistant canisters.
2. The major dose contributors have very low solubilities.
3. During transport in the far field both physical and chemical retardation (sorption) occur.
4. Dilution by matrix diffusion or hydrodynamic dispersion.

Pillars of safety, cont.

- The factors which contribute much to achieve this tremendous reduction, i.e., the pillars on which the safety assessment is supported are:

1. **Reduction of release rate at the source.**

-Massive canisters contribute to a) very long absolute containment (Cu-canister) or b) long containment and reducing conditions in near field (Fe-canister).

-Afterwards very dissolution resistant waste forms, such as spent fuel or nuclear glass, release only a small fraction of all RN per unit time. Extremely important to estimate spent fuel or nuclear glass dissolution rates.

-Even when the HLW waste form is dissolved, most of the major dose contributing nuclides form **compounds that are very insoluble** under near field conditions. Hence the importance of available solubility data, especially for the actinides. For solubility limited nuclides, the release rate R_N can be estimated crudely by :

$$R_N=F\ C_L$$

where F is the water exchange rate near the waste form and C_L is the elemental solubility limit. F depends on the hydrology of the host rock and properties of the backfill surrounding the waste package-that's why repositories are sited in low permeability rock(or unsaturated zone in desert). High concentrations of complexing agents in groundwater can increase the solubility limits and have detrimental effects, for this is important to know radionuclide speciation.

Radionuclide speciation

-The form in which the radionuclides exist in solution depends on their interaction with water molecules and with various ions dissolved in groundwater. Many highly charged ions ”grab” OH-groups from water molecules to form hydrolysis products and release protons. Thus e.g., $Fe^{3+}+H_2O=FeOH^{2+} + H^+$, same for $U^{4+}+H_2O=UOH^{3+}+H^+$. Carbonate present in groundwater forms usually strong complexes with actinide ions, e.g., with U(VI), such as $UO_2(CO_3)_3^{4-}$. It is clear that if $UO_2(OH)_2$(s) (schoepite) is limiting the solubility of U(VI) in distilled water, in the presence of a few millimoles carbonate in groundwater, the solubility is 100-1000 times higher, due to the strong U(VI)-carbonate complexes.

-Many of the actinides and fission products exist in many oxidation states, e. g. Pu(III), Pu(IV), Pu(V), Pu(VI), which have very different solubility and sorption properties. In general, the reduced forms of An-ions such as An(III) and An(IV) form very insoluble compounds such as Pu_2O_3(s) or UO_2(s), while the oxidized forms such as An(V) and An(VI) form relatively soluble precipitates.

- Earth was formed in absence of oxygen, thus under the water table reducing minerals dominate and the groundwater conditions are usually reducing at depth. The corrosion products of iron formed in absence of oxygen (anoxic corrosion products) contribute to enhancing further the reducing conditions in the near field.

-The actinides and some important FP (e.g., Tc or Mo) are much safer underground due to the low solubilities and strong sorption of their reduced states-an argument which could be used more in favor of a deep repository instead of interim storage.

Pillars of safety, cont.

The other factors which contribute much to achieve the reduction of dose from repository are:

2. **Retardation of radionuclides during transport.**

   The safety relevant feature of retardation during transport is that longer transport times allow for decay of larger portions of the nuclide inventory. We distinguish physical and chemical retardation.

   -Physical retardation results when nuclides advected in a water carrying zone diffuse in portions of rock with stagnant waters, the driving force being the concentration gradient. The process is called **matrix diffusion** and is an efficient retardation mechanism. While there is little doubt that matrix diffusion is a process operating in fractured media, there is debate on the spatial scales of connected matrix pore spaces.

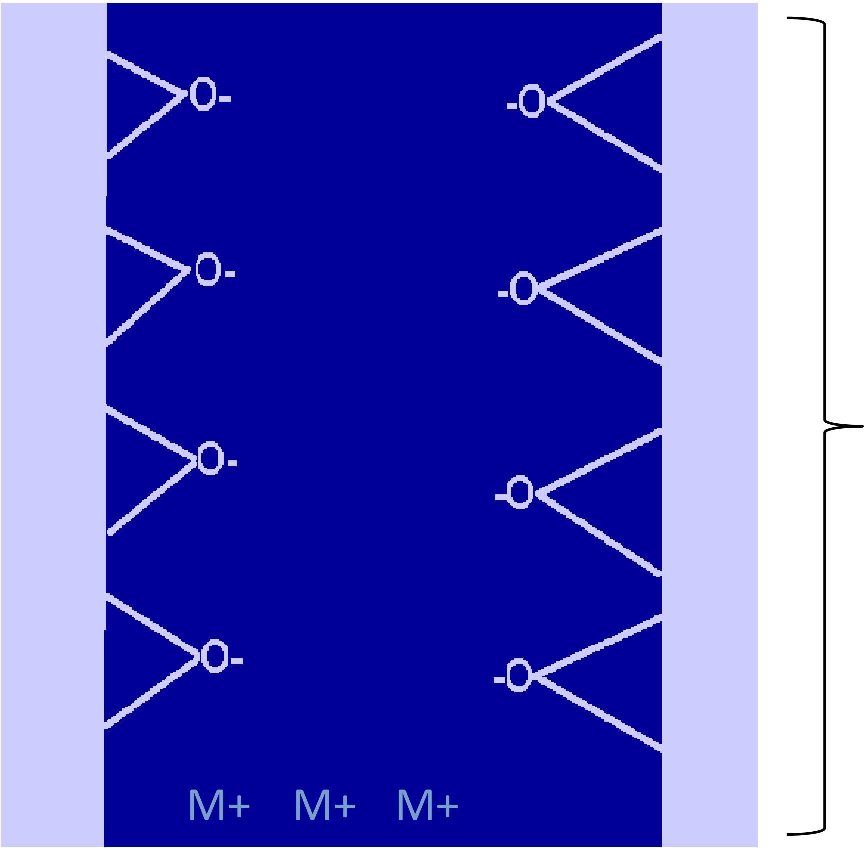
   -Chemical retardation or **sorption**. Radionuclides get fixed on different surfaces through a process called adsorption. Usually this is due to the fixation of radionuclide species on Si-OH (silanol) or Al-OH (aluminol) groups of the different minerals composing the bentonite buffer or the alumino-silicate minerals of the rock. The radionuclides which have strong hydrolysis (strong binding with OH-groups of water) also sorb strongly. Such are the low valence states or reduced forms of actinide ions, which have also strong sorption. Most of the mineral surfaces are negatively charged at near neutral pH typical for groundwaters. This is the reason why anions do not sorb and become a problem in PA.

3. **Dilution**

Dilution reduces the concentration of the surviving inventory by mixing contaminated and fresh water. This includes hydrodynamic dispersion, matrix diffusion and dilution by large bodies of water such as lakes, rivers or sea. That’s why sub-seabed disposal leads to remarkably low doses.

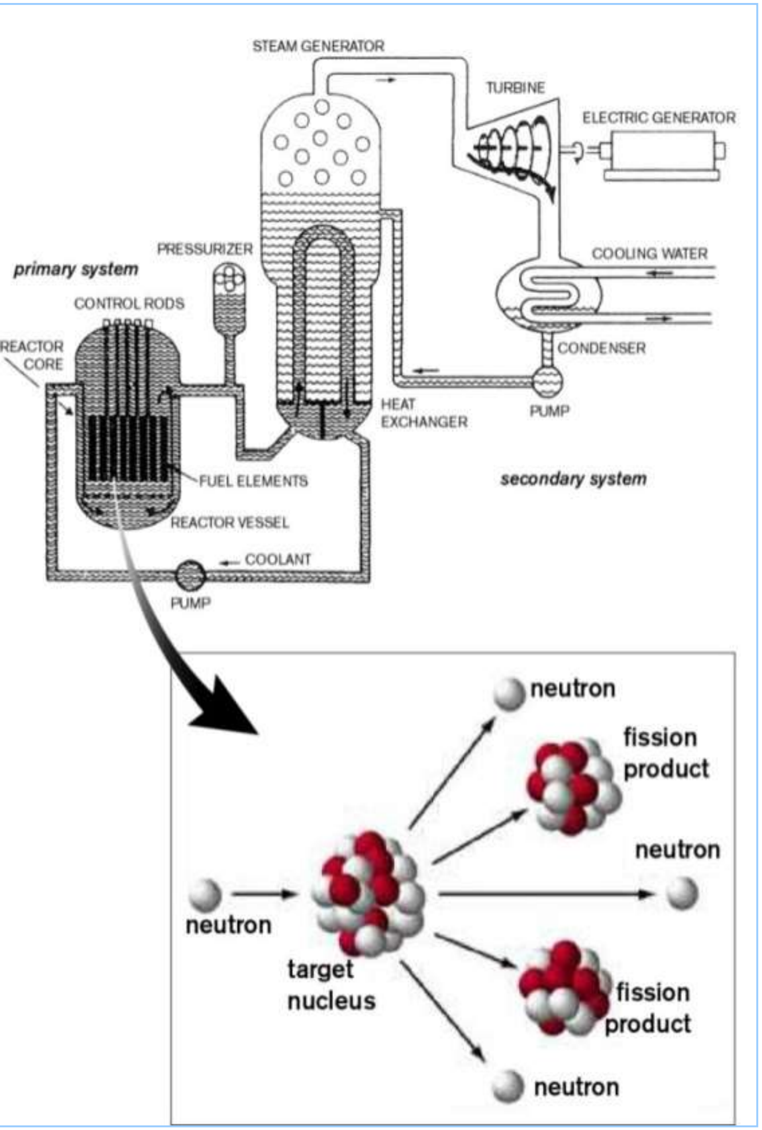
Contaminat transport in the geosphere

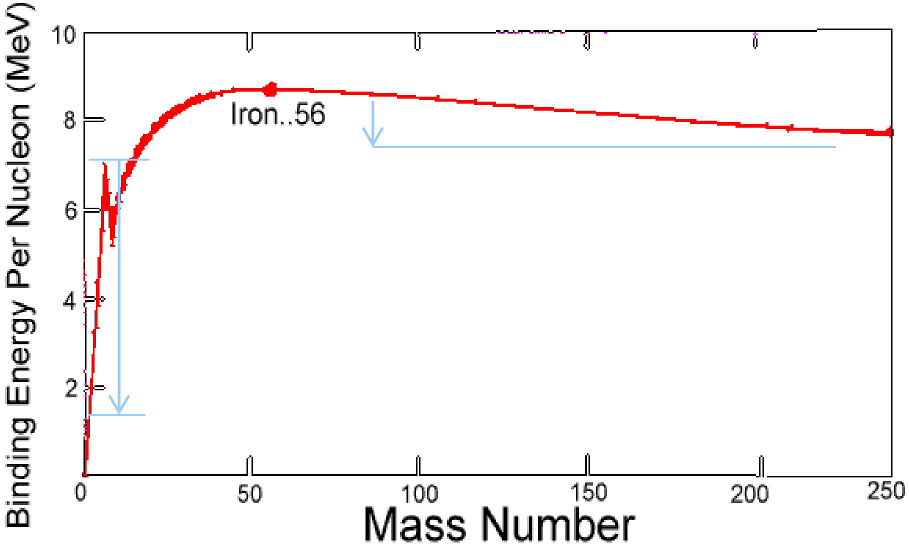
A contaminant metal is adsorbed onto the surface oxygen sites (chemical retention)

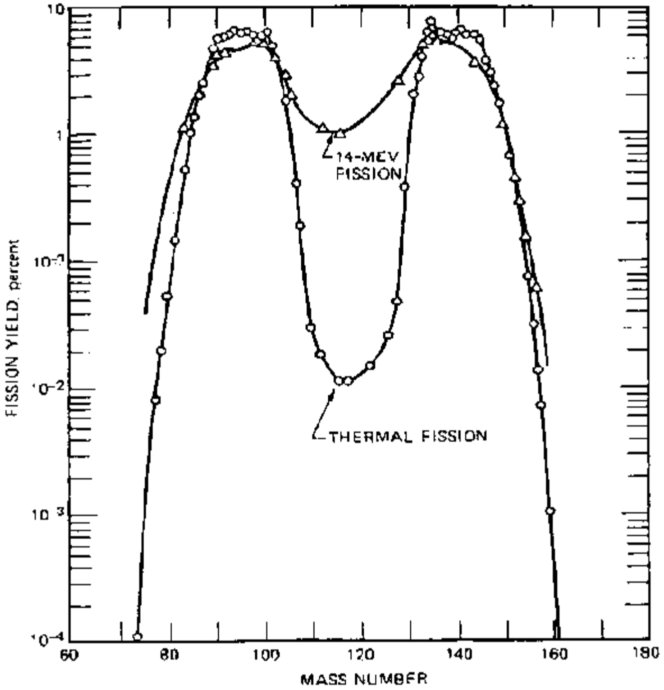


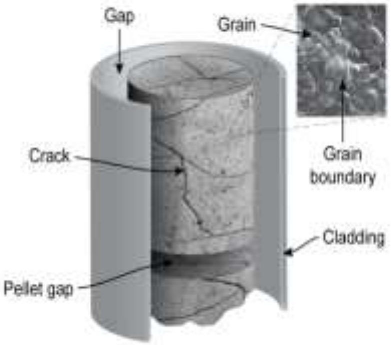
adsorption depends on the **SSA, the specific surface area** (and site density, reaction constant)

What happens with fuel in a nuclear reactor?

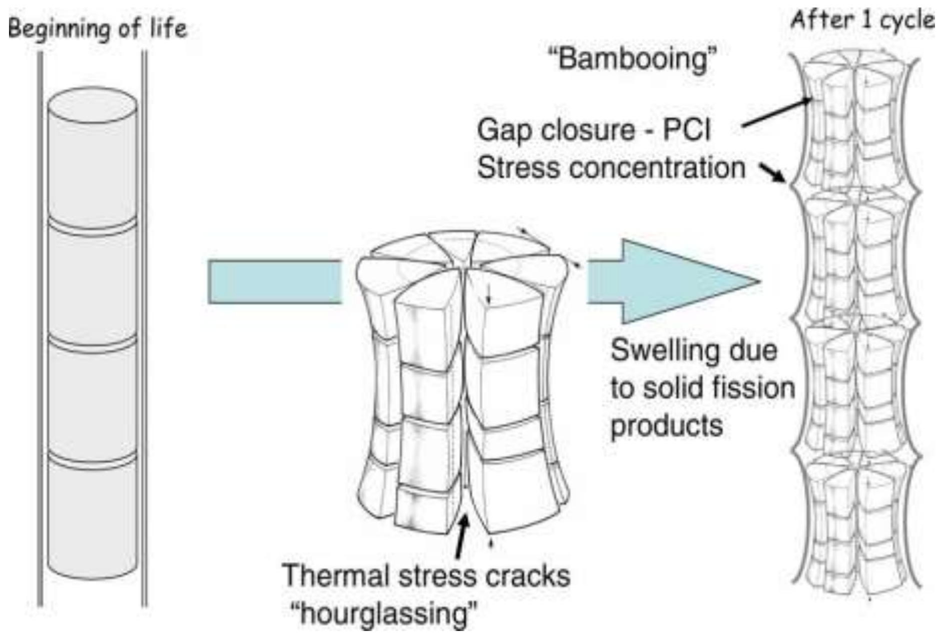








Neutron capture (rim): $^{238}U + n_0^1 \rightarrow {}^{239}Pu$


Beginning of life

After 1 cycle

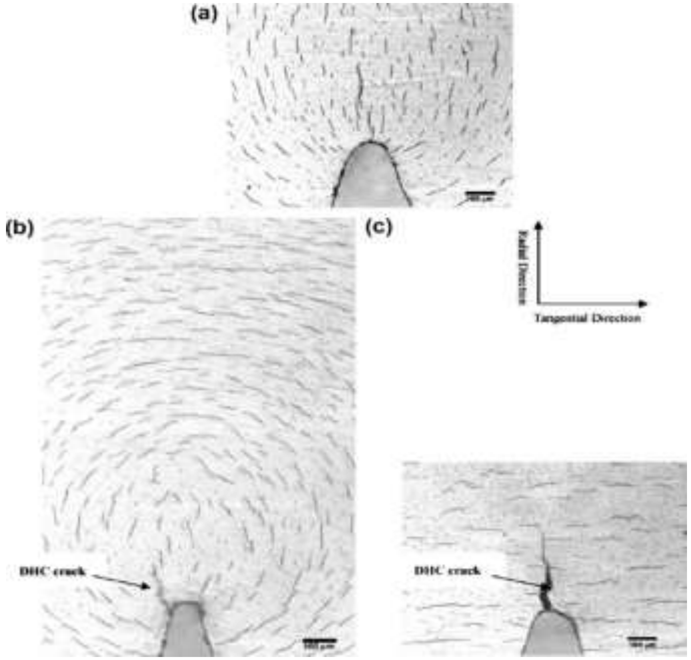
"Bambooing"

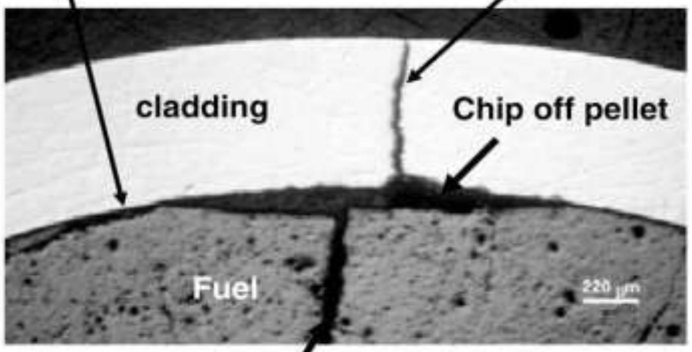
Gap closure - PCI

Stress concentration

Swelling due to solid fission products

Thermal stress cracks "hourglassing"




Gap closes due to fuel swelling

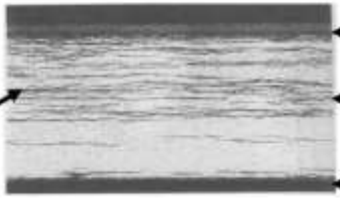
Stress-corrosion crack

Chip off pellet

Thermal-stress crack (fission-product path)

BWR - Nodular corrosion

PWR – uniform corrosion + **CRUD**


Oxide scale

cladding

Hydride

UO_2 pellet

Percent of ”new formed” elements in PWR fuel burned to 35 MWd/kg U (3,5% enrichment).

Noble gases (Kr, Xe)	16,8%
Halogenes (Br, I)	0,8%
Alkaline metals (Rb, Cs)	8,2%
Alkaline earth metals(Sr, Ba)	7,1%
Zirconium	10,1%
Y+lanthanides(La, Ce, Pr, Nd, Sm, Eu, Gd)	29,7%
ε-Ru particles (Mo, Ru, Tc, Rh, Pd)	24,7%
Rest (Te, Cd, Sn, Ag, Se, Sb)	2,6%

- (Plus other actinides (besides U-238) ca. 1% of the fuel)

Ellingham diagram for spent fuel

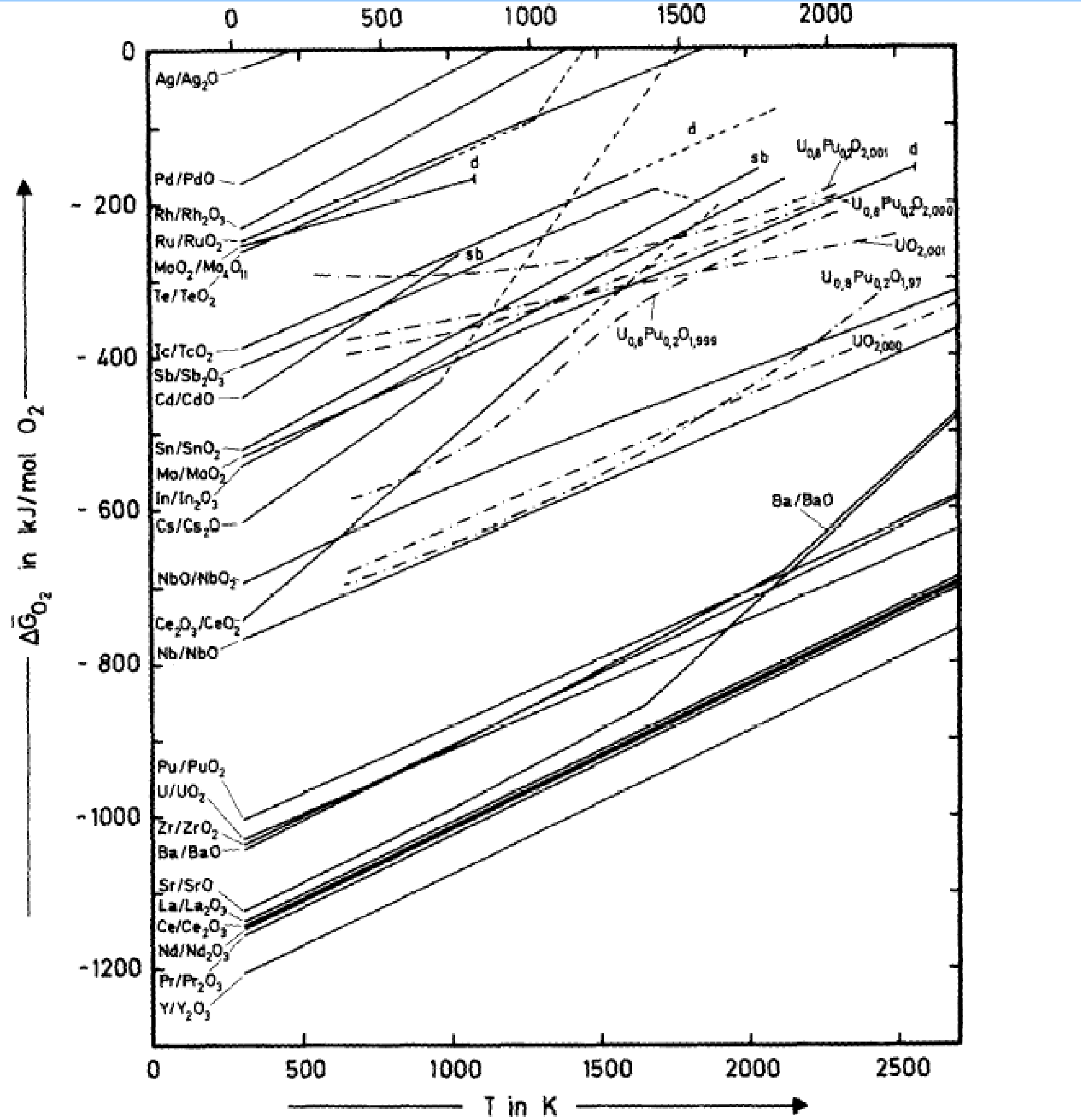
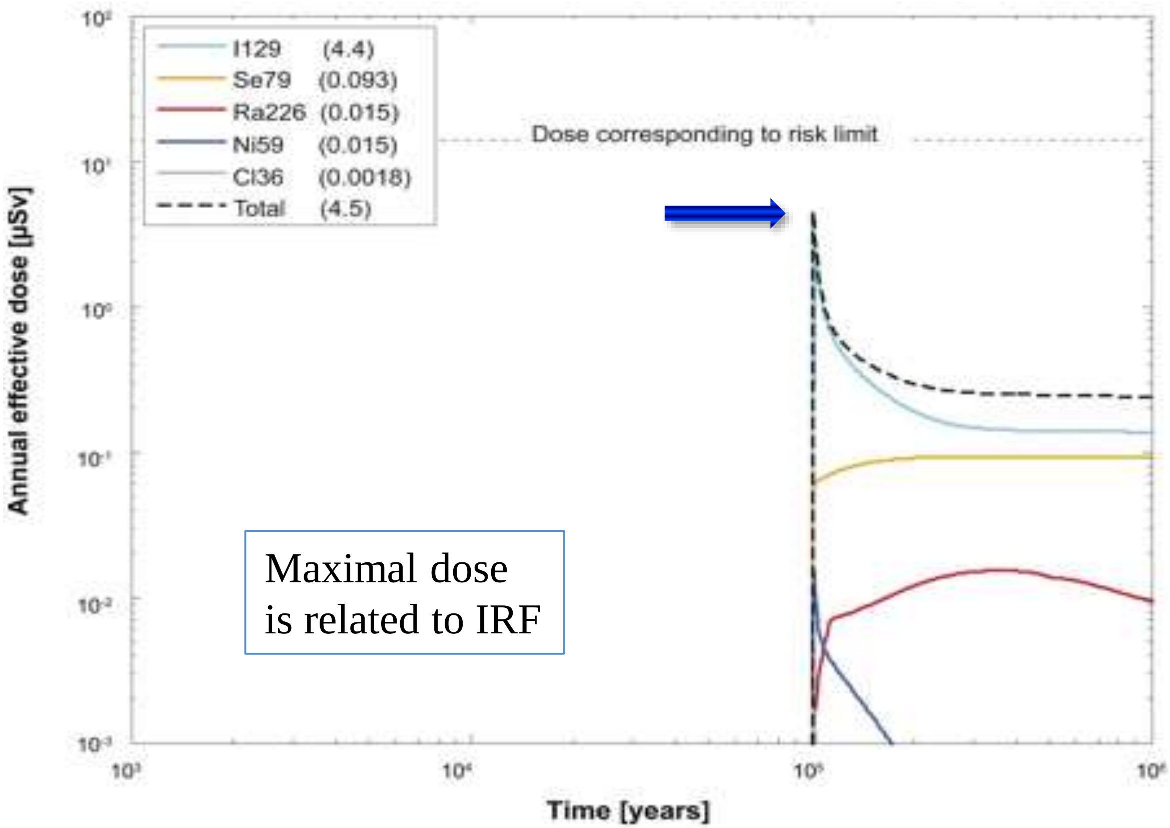


Fig. 2. Relative partial molar Gibbs free energies of oxygen of the fission product oxides and of UO_{2+x} and $U_{0.8}Pu_{0.2}O_{2\pm x}$, d: oxide decomposes, sb: oxide sublimes.

Influence of IRF in safety assessment

Example from TR-10-50, Data Report



Maximal dose
is related to IRF

- Case of a container breach after 100 000 y, due to isostatic load.
- In the rapid release fraction is e. g. the part of ^{129}I released immediately. This is only a few percent of the total I inventory, anyhow it causes a peak in the dose.
- This peak decreases slowly to the values corresponding to fuel matrix dissolution.

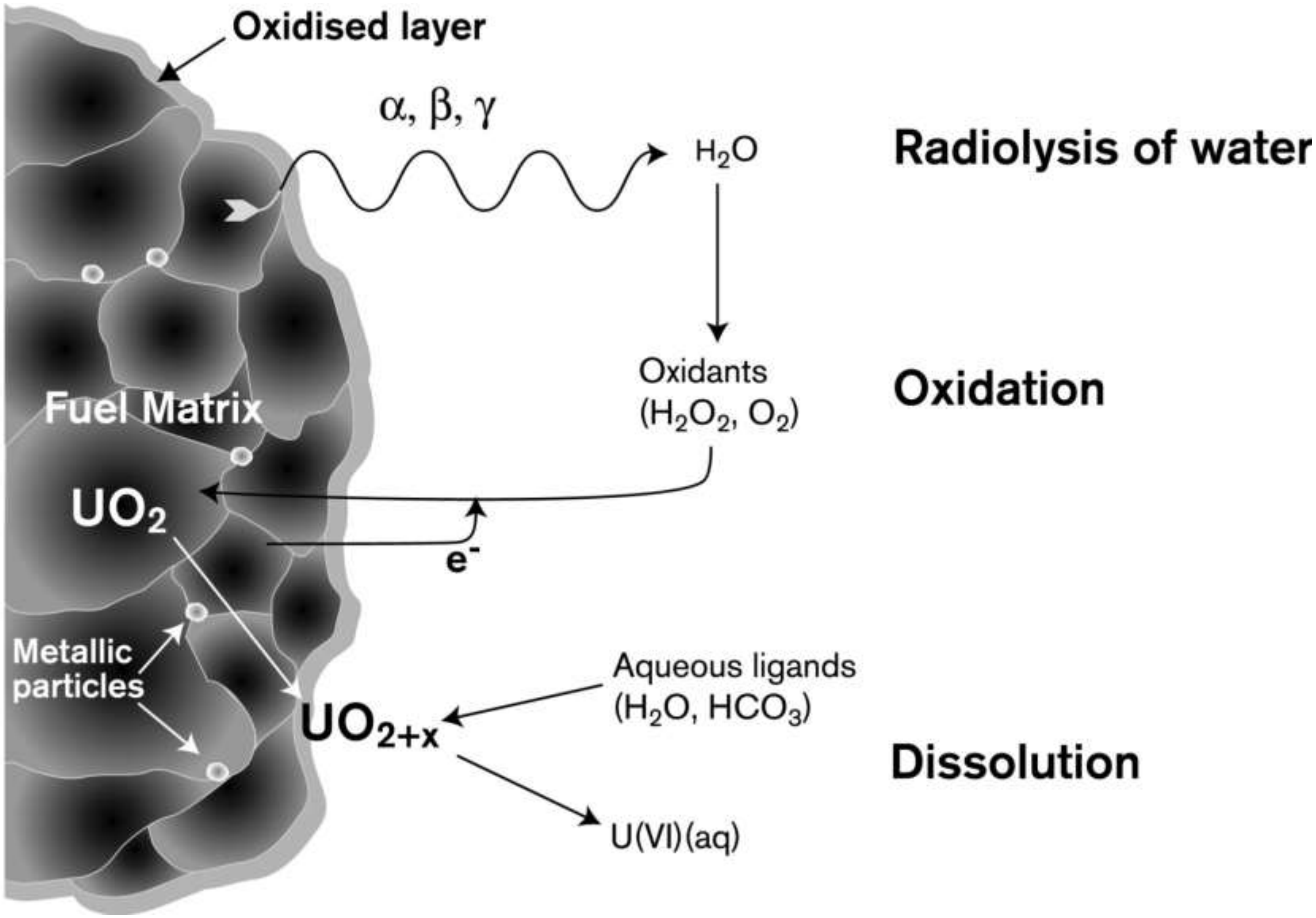
The instant release fraction

- We will look in more detail to the dissolution of the fuel matrix next slides. However, during irradiation in the reactor, a certain percentage of the volatile RN inventory has **segregated** to the gap between the fuel and the cladding and also to grain boundaries. Typical IRF isotopes are:

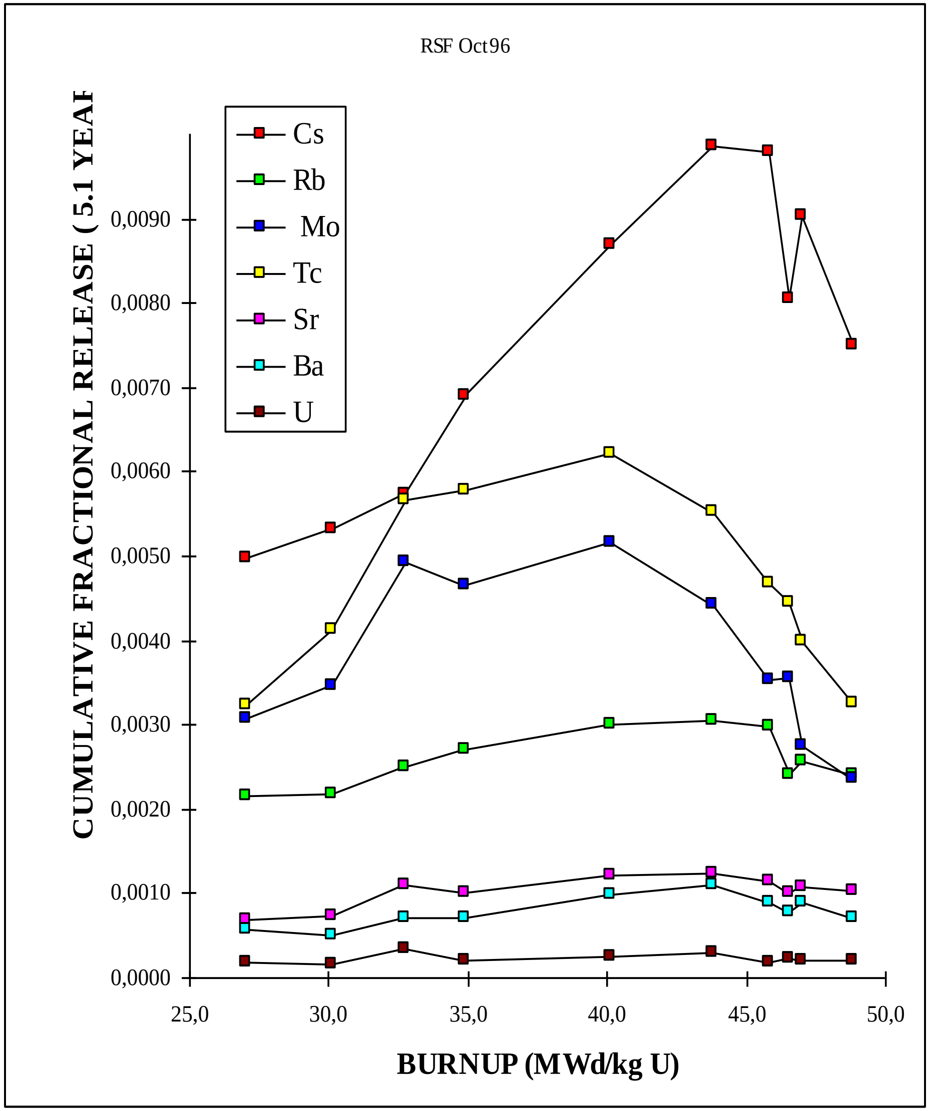
^{14}C, ^{36}Cl, ^{79}Se, ^{90}Sr, ^{99}Tc, ^{107}Pd, ^{126}Sn, ^{129}I, ^{135}Cs

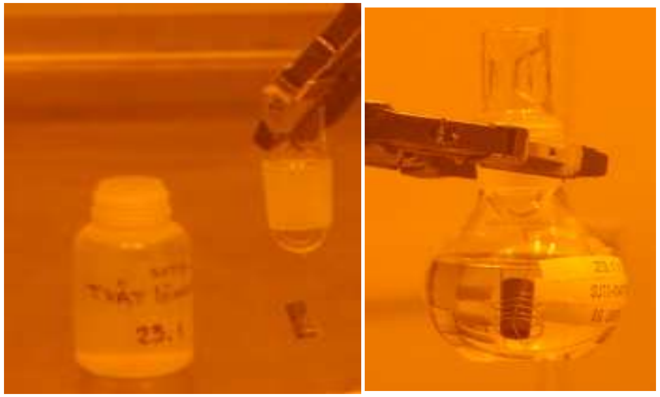
- The radionuclide fractions released to the fuel/cladding gap and to grain boundaries are somehow improperly referred to as “Instant Release Fraction”, IRF. They are released fast (weeks to months) and for PA purposes, are treated as instant release.
- There are relatively few systematic studies of the release of segregated material other than fission gases from fuel, but they have increased recently e.g. with EC project First Nuclides.
- It is generally assumed that the fission gas release and the release of other segregated nuclides are related. This seems to be a reasonable assumption for LWR fuels with a few percent FGR since gas phase diffusion determines their amounts. For some RN, assuming a 1:1 relationship will be a reasonable assumption, for others the relationship may be more complex.
- Recent micro-Xanes data by E. Curti, PSI indicate that Se is in anionic form (Se^{-2}) in the fuel.

Radiation induced fuel dissolution



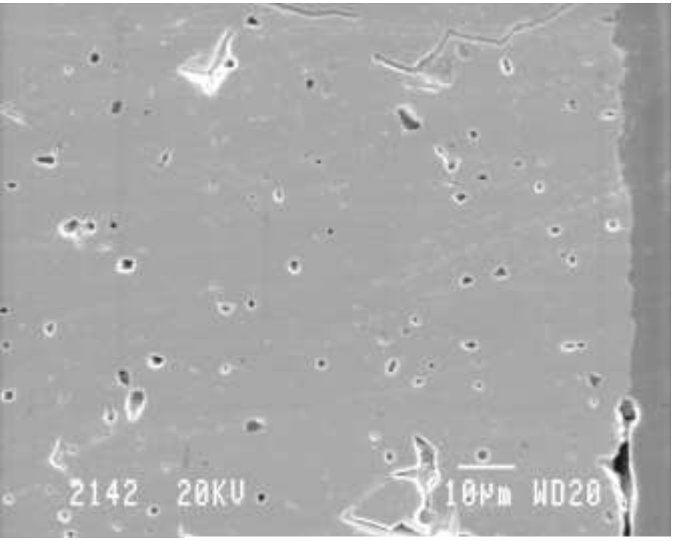
RN-releases during 5 years as function of burn-up (1997).





- Segments of fuel rods (2 pellets with cladding) +synthetic groundwater +oxidizing conditions.
- Series of sequential exposures to a static leaching solution. Results for contact periods: 7, 21, 63, 92, 180 and several 360-day periods-Series 11.
- ICP-MS isotopic analysis: fission products and actinides in leaching solution
- Release fraction = $X_{\text{Leach solution}} / X_{\text{Inventory}}$

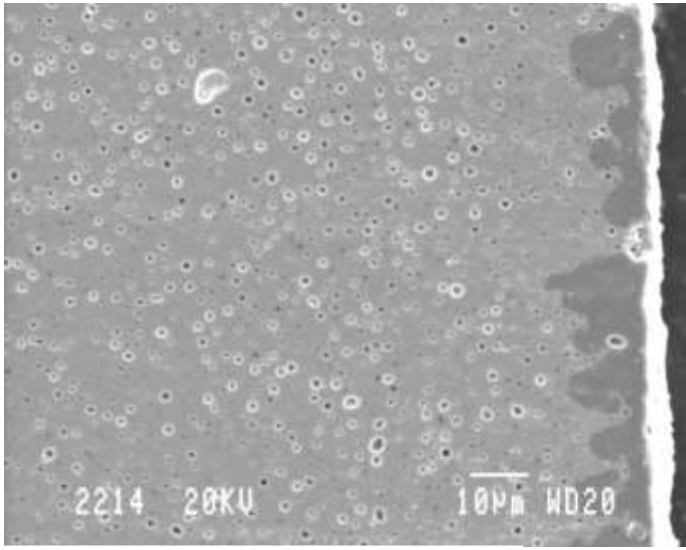
30 MWd/kg U vs. 77 MWd/kg U.

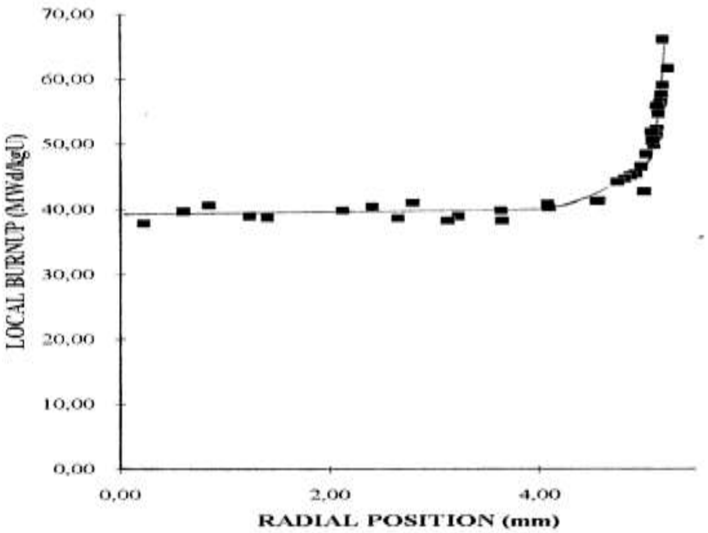


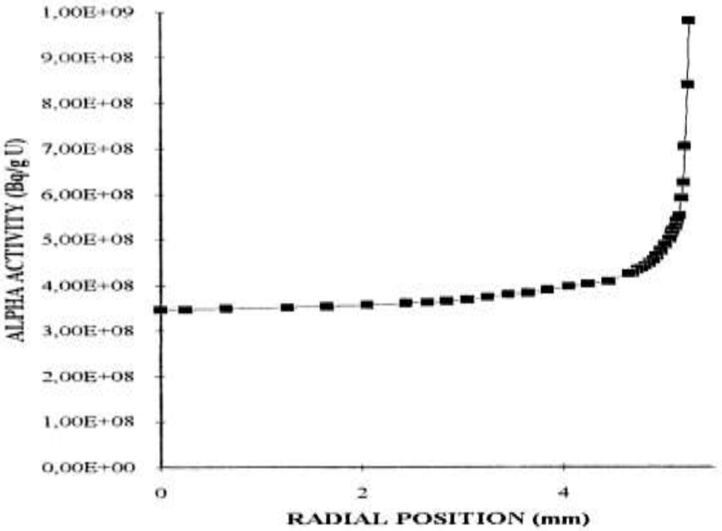
- Rim zone: porosity and small grain size

- Higher fission product and actinide occurrence.
- Higher dose rates and surface area.

Higher dissolution rates???

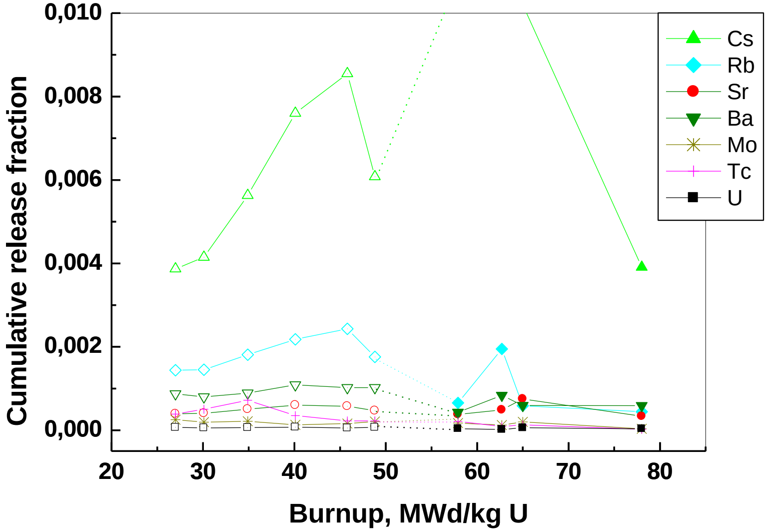






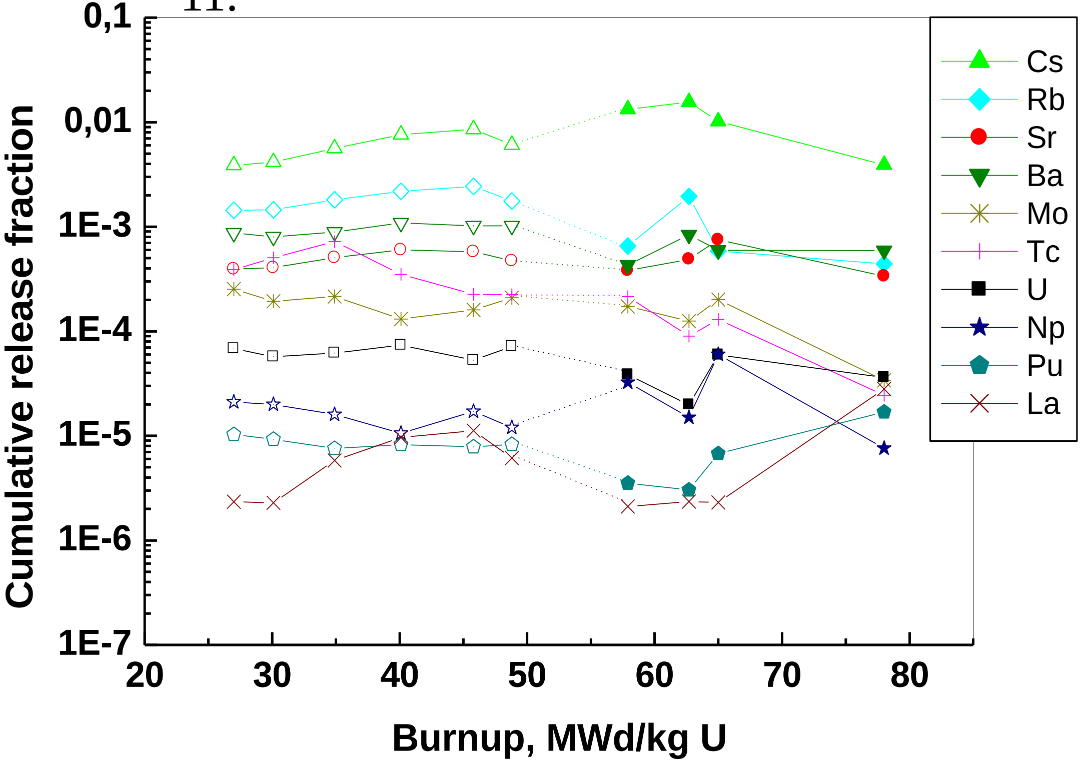
Cumulative release fractions vs. burnup for 182 days.

- **Recent results for 4 fuel samples, BU= 57.9, 62.7, 65 and 75.4 MWd/kg U**



- Cs releases are slightly higher than series 11.

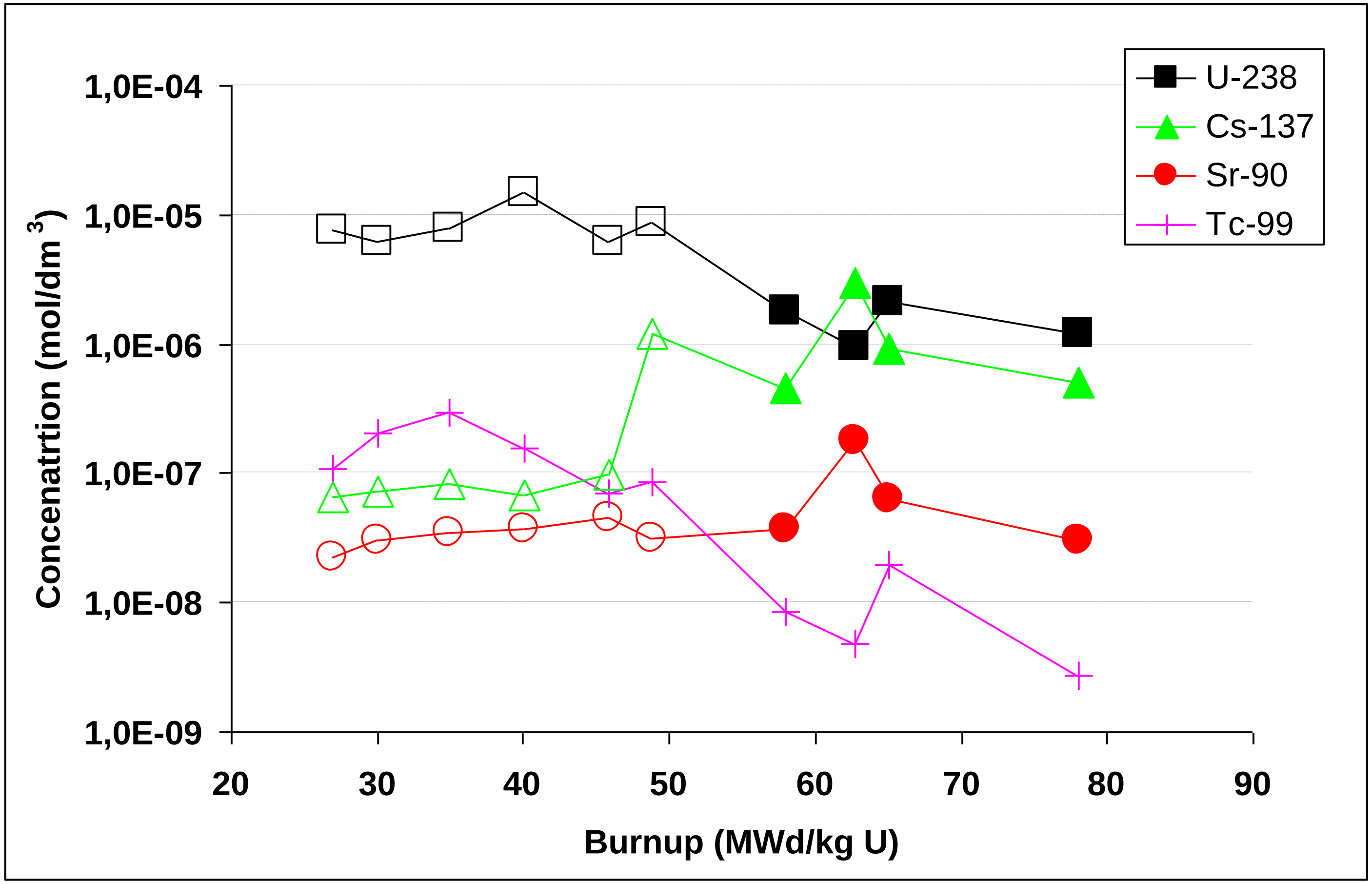
- Sr, Ba and Rb releases quite similar to series 11.



- Mo and Tc releases are lower – more difficult to oxidize?

  - U releases are lower than series 11 – no clear trend with burnup can be seen

Oxidative dissolution: Concentrations as a function of burnup



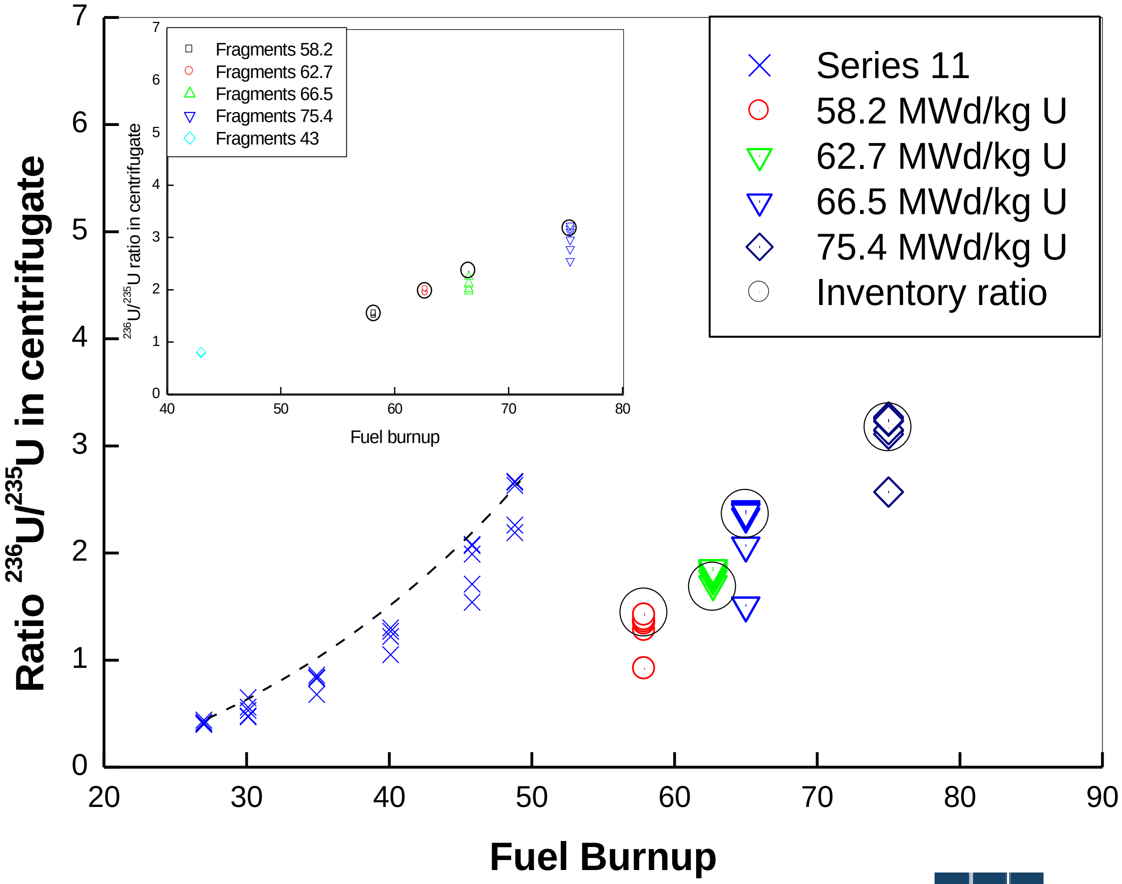
- **No secondary U mineral phases expected to affect U releases under 92 days (fourth contact period)**

Corrosion sites? ^{236}U/^{235}U ratio vs. burnup.

- ^{236}U/^{235}U ratio increases with the irradiation process
- Higher in the rim zone (burnup up to 2.5 times higher than the pellet average*)
- Increase in the ^{236}U/^{235}U ratio with number of contact periods (same observation in series 11)
- Series 11; ^{236}U/^{235}U is below the pellet average ratio ⇒ less corrosion in the rim zone and increases towards average value.
- Insert shows data for de-cladded fuel

$$^{235}\mathrm{U} + \mathrm{n} \rightarrow 2\ \text{fiss.products} + 2\text{-}3\ \mathrm{n}$$

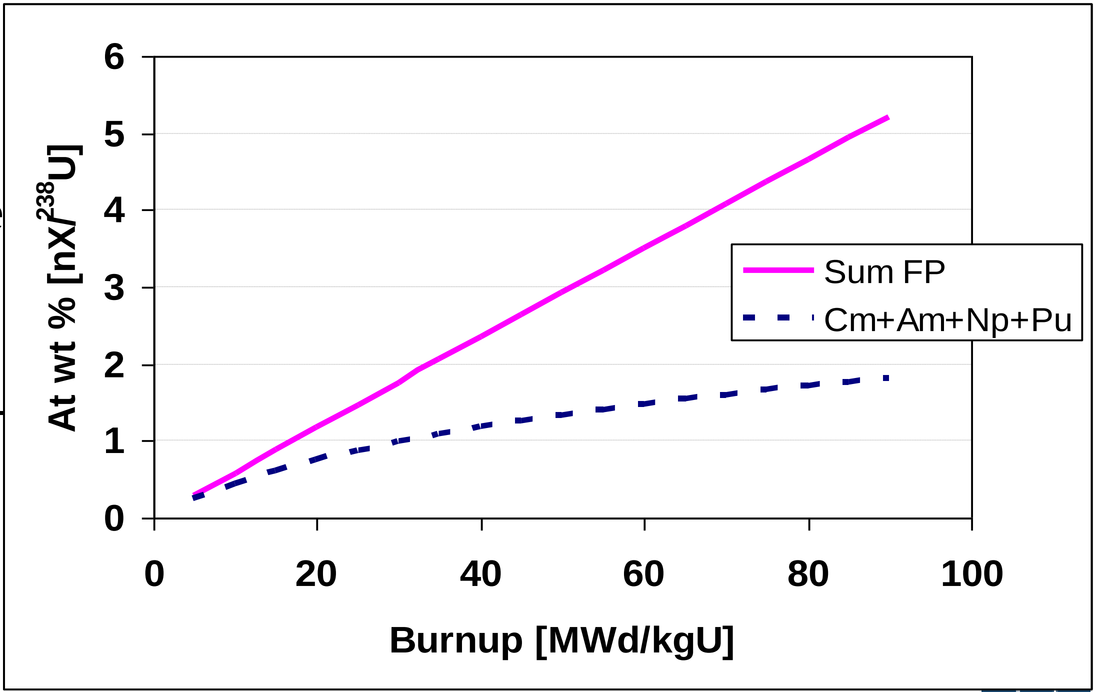
$$^{235}\mathrm{U} + \mathrm{n} \rightarrow {}^{236}\mathrm{U}$$



*H. Matzke, J. Spino, *J. Nucl. Mater.* **248** (1997) 170

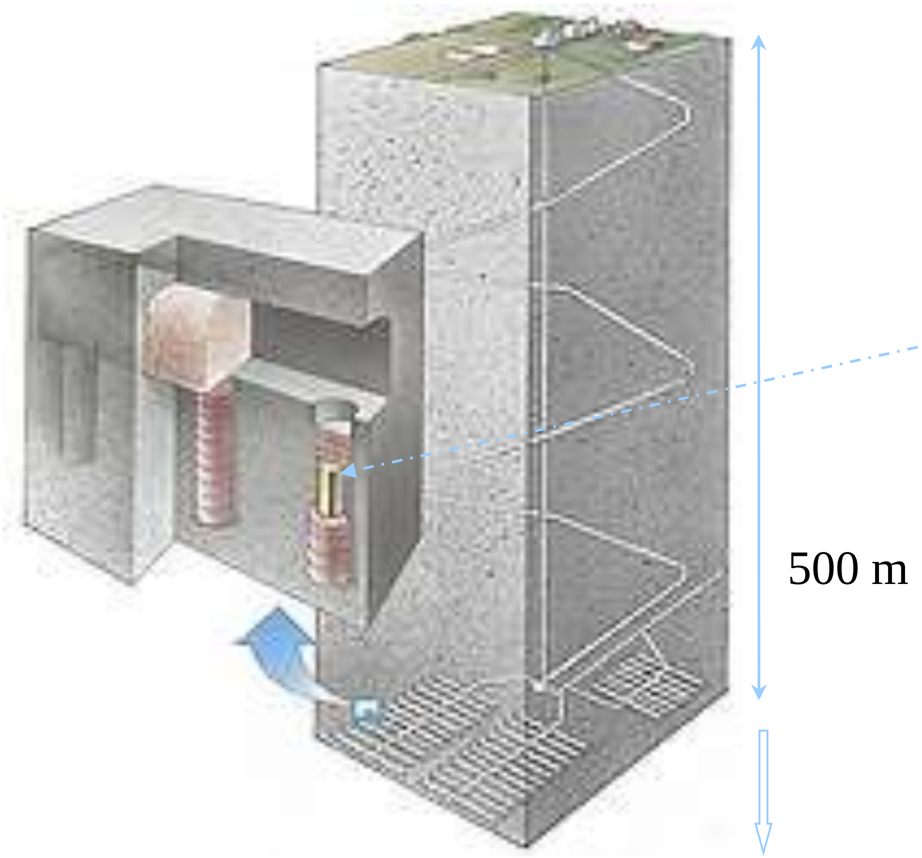
Summary on burnup influence.

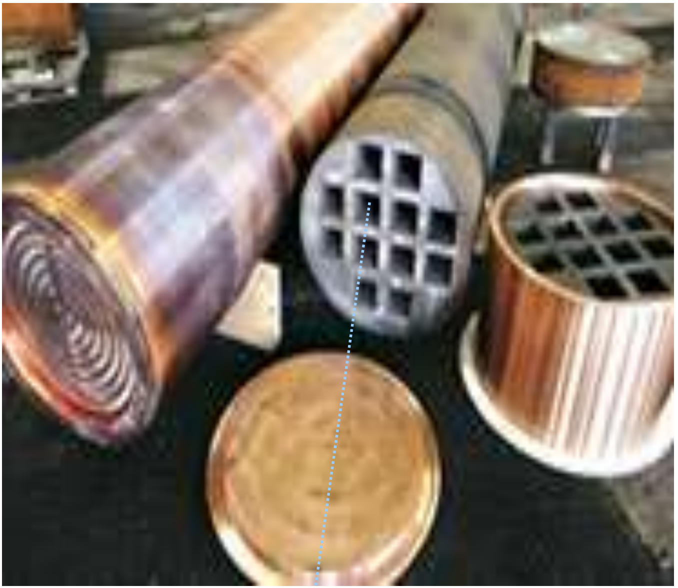
- Increase of burnup and linear power rate cause increase of fission gas release and IRF.
- First four data sets show that the releases from high burnup fuels are not systematically higher than those from series 11 (lower burnup fuel).
  - Similar trends observed from other work (Hanson et al.2008, Jegou et al.2004, Clarens et al.2008) ⇒ Higher releases from intermediate burnup fuel.
  - The increased dopant concentration counteracts oxidative dissolution, despite increased surface area and dose rates.
  - Several recent publications have confirmed the role of non-U cations in the inhibition of interstitial O injection during fuel oxidation.



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

KBS-3 deep repository concept for spent fuel.

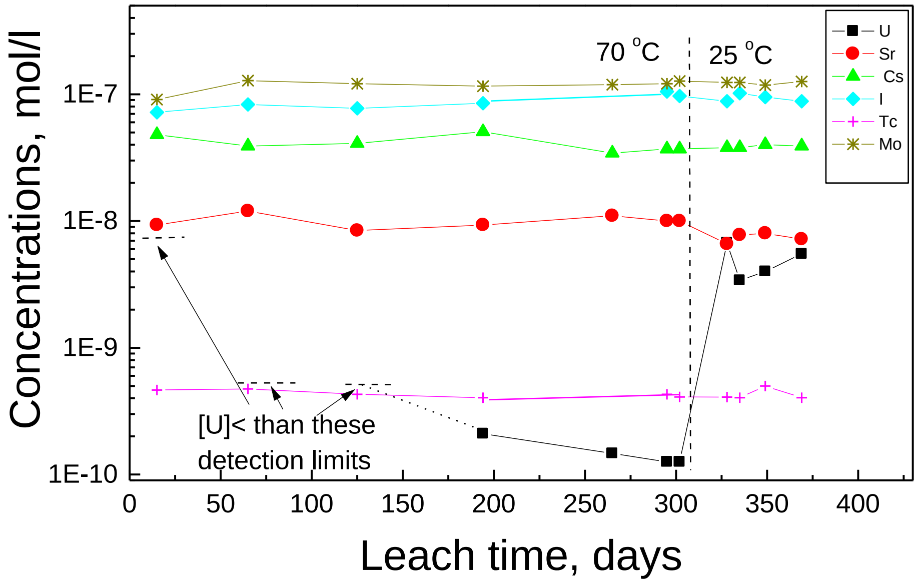


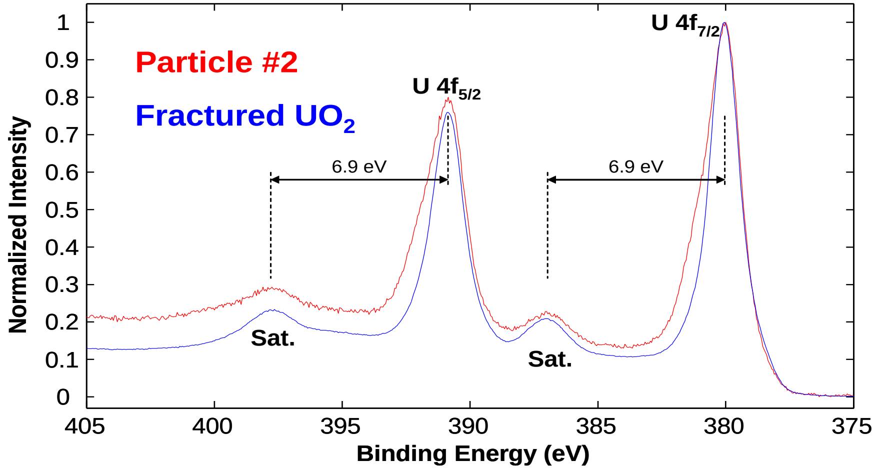


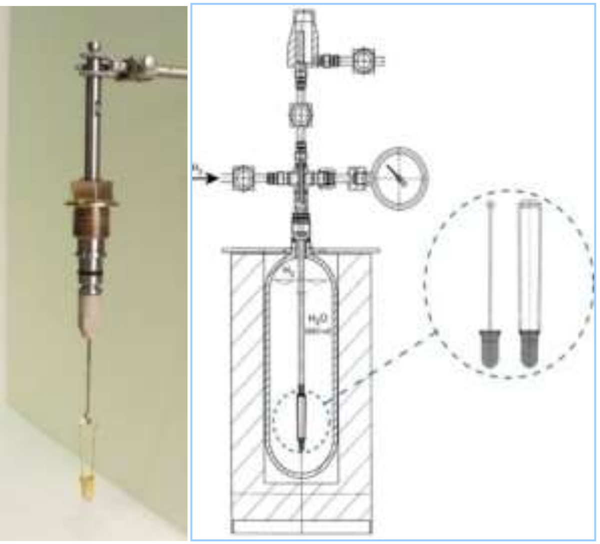
$$3Fe(s) + 4H_2O = Fe_3O_{4(s)} + 4H_2$$

- 500 m water column~ 50 bar in a gas bubble~ 40 mM $[H_2]_{diss}$
- H_2 production rate from anoxic Fe corrosion > diffusion rate through bentonite clay.
- Many 10^3 years H_2-saturated near field, much higher conc. than H_2O_2, O_2 eller U(VI), but H_2 is inert!
- The first test of spent fuel under 50 bar H_2 was started in 1998 based on erroneous assumptions.

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

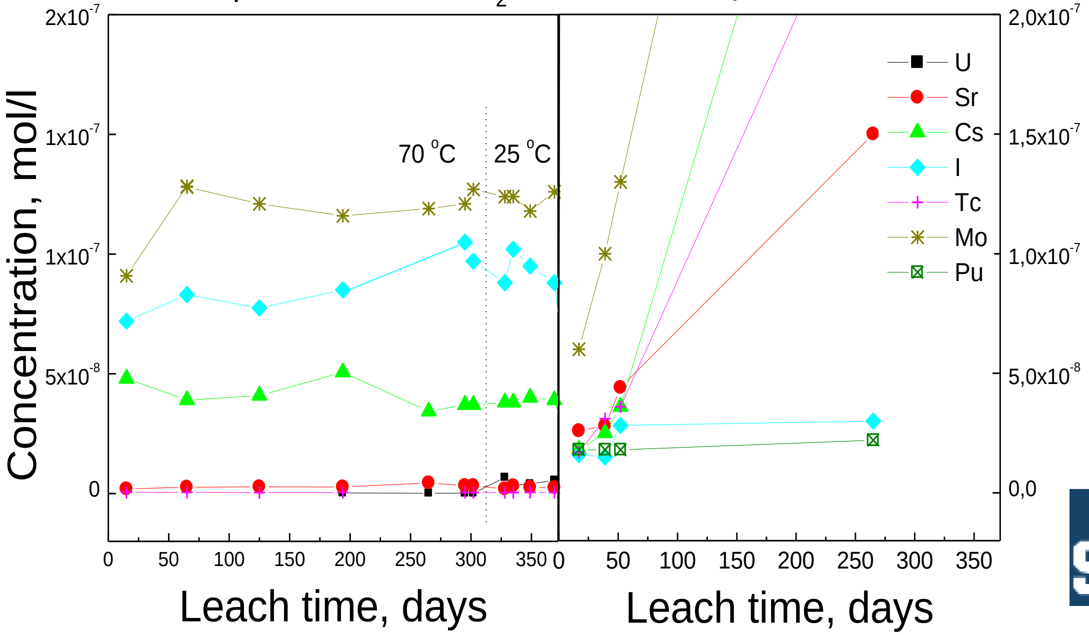






Fuel powder, 5 MPa H_2

Fuel pin, anoxic



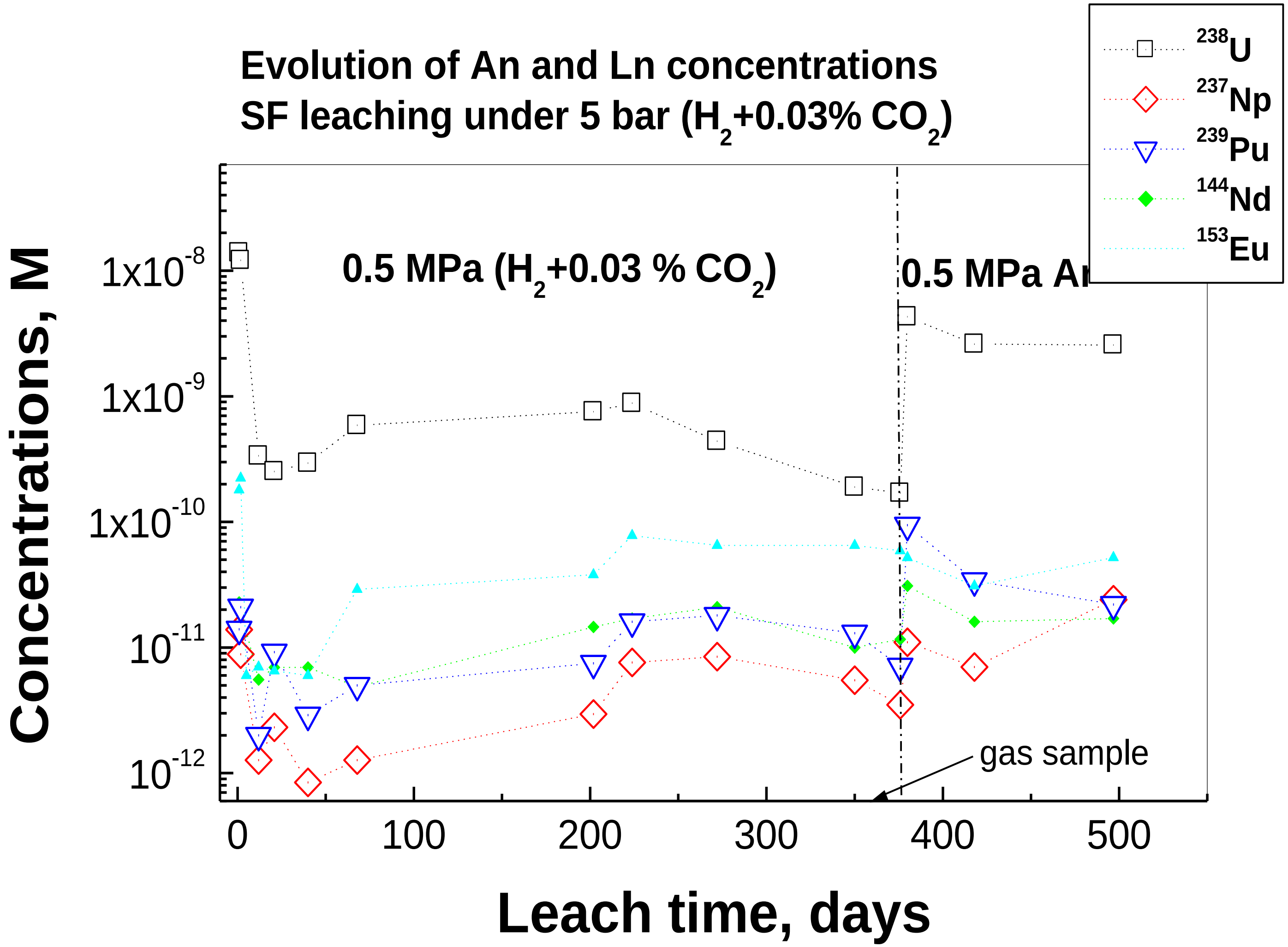
How to draw conclusions from autoclave tests?

- 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, a glass frit filter is used in sampling tube intake and the solution 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 most of the nuclide is in 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 etc. it can be used to estimate the release rate of this radionuclide.

Conclusions from autoclave tests-contd.

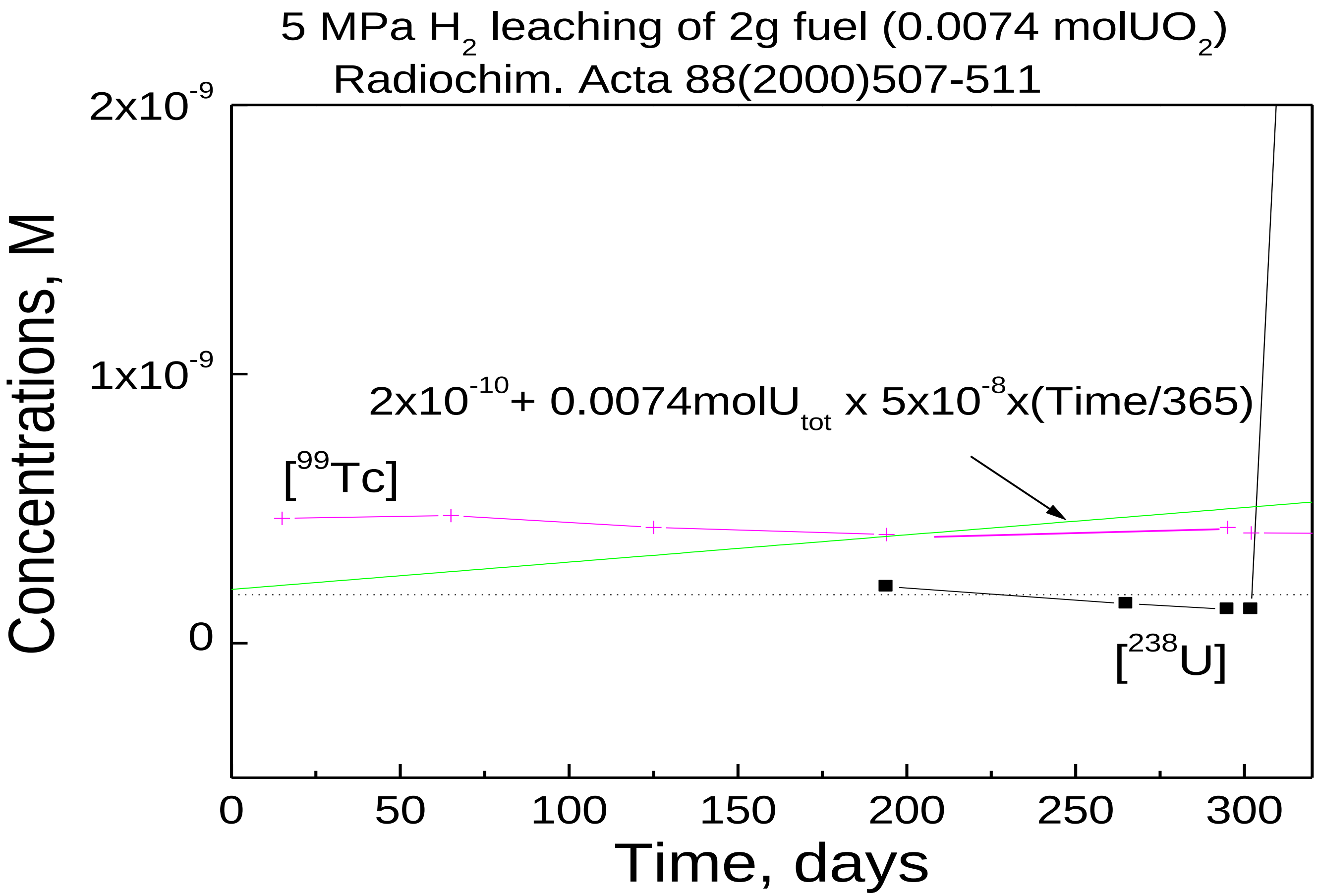
- The concentrations of actinides and lanthanides, as well as those of certain redox sensitive fission products such as Tc, Mo etc. are important to report in order to judge about the redox state of the given actinide or fission product. Thus, there are no U(VI) compounds which have a solubility lower than 10^{-7} M, one such insoluble U(VI) compound is uranophane, a calcium-uranyl silicate.
- Thus, 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 practically 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 $10^{-10.9}$ M.

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

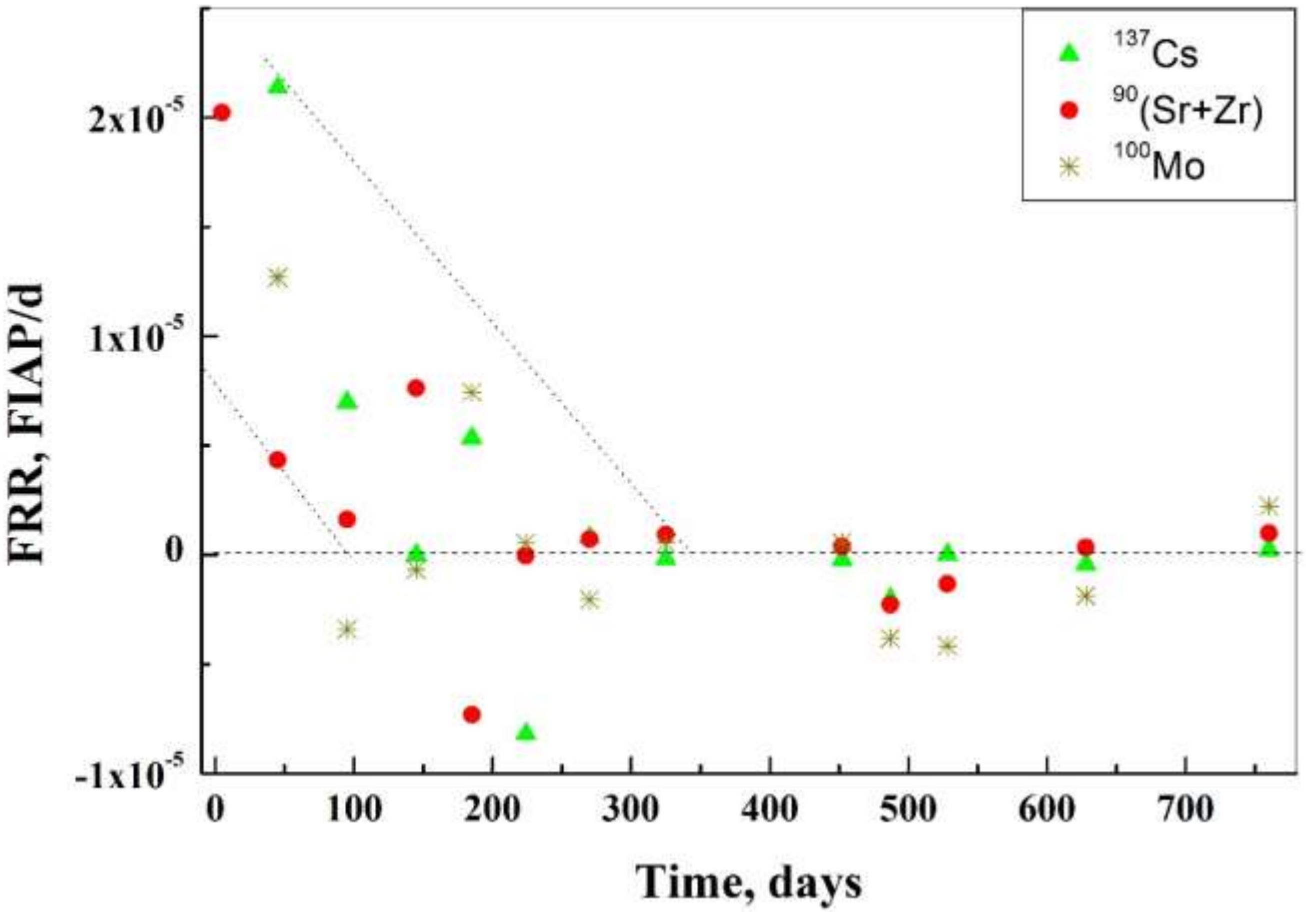


Spahiu et al., Radiochim. Acta 92 (2004) 625

Why it is not reasonable to use rates lower than 10^{-8}/year.



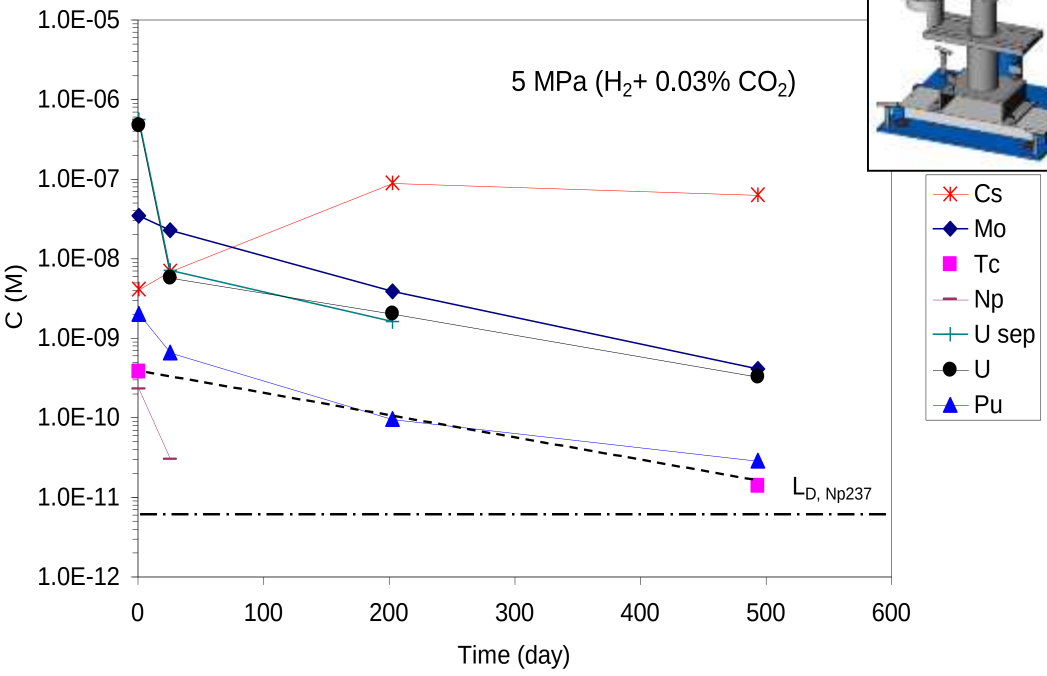
Fractional release rates of Cs, (Sr+Zr) and Mo, 1 bar H_2 (Ekeroth et al. 2020)



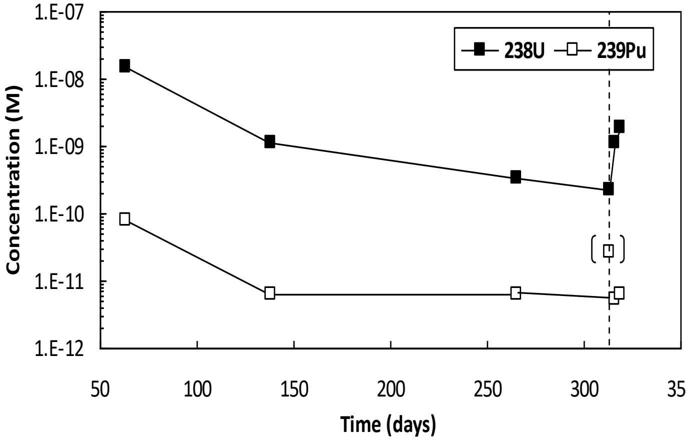
Matrix dissolution rate 10^{-6}/y corresponds to 0.0012 ppb ^{90}Sr increase per year!

Dissolution of MOX(Mixed OXide) or HBU(High BurnUp) fuel under H_2.

MOX fuel (48 MWd/kgHM) leaching, ITU



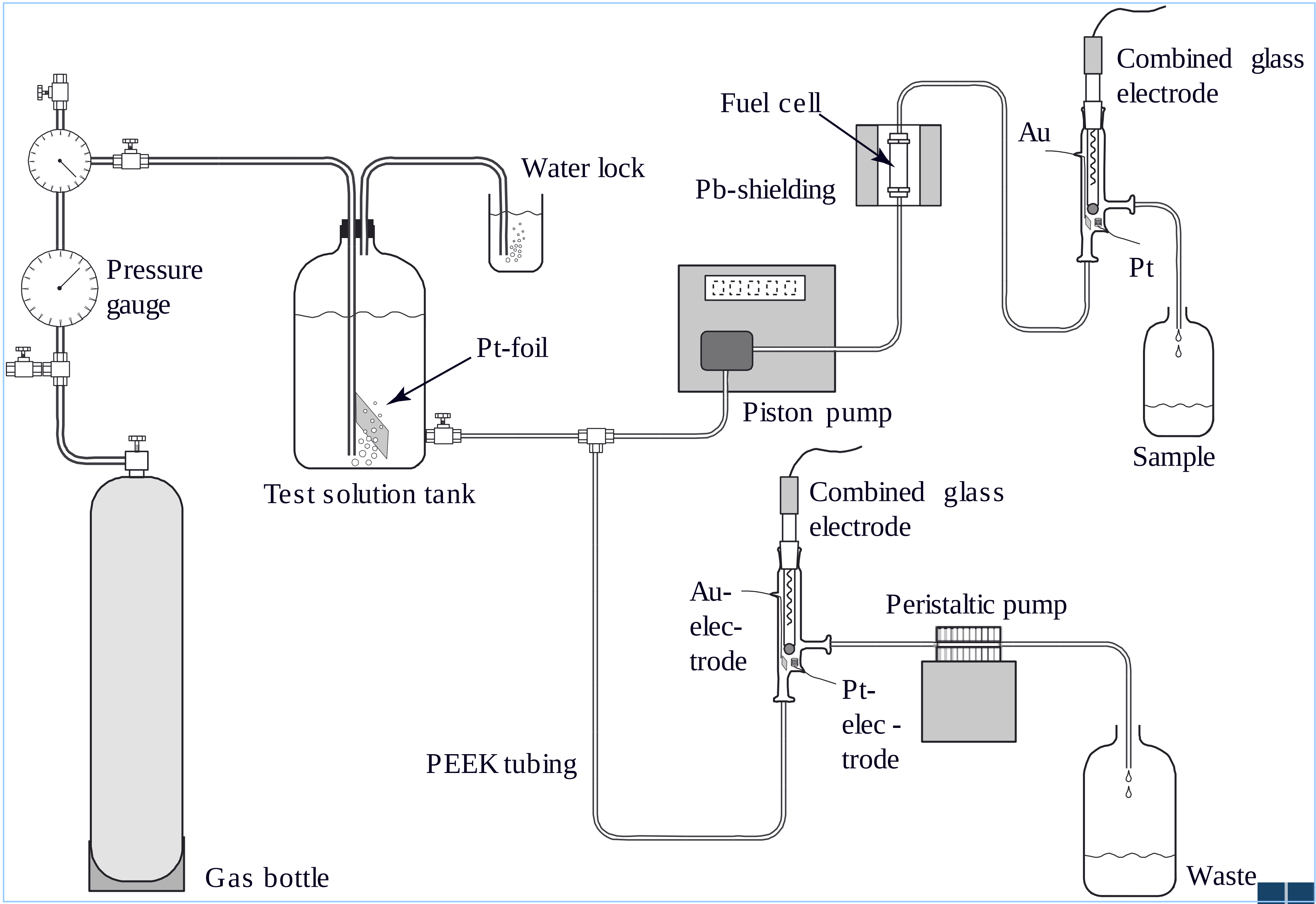
HBUfuel (67 MWd/kg U) rim leaching, ITU



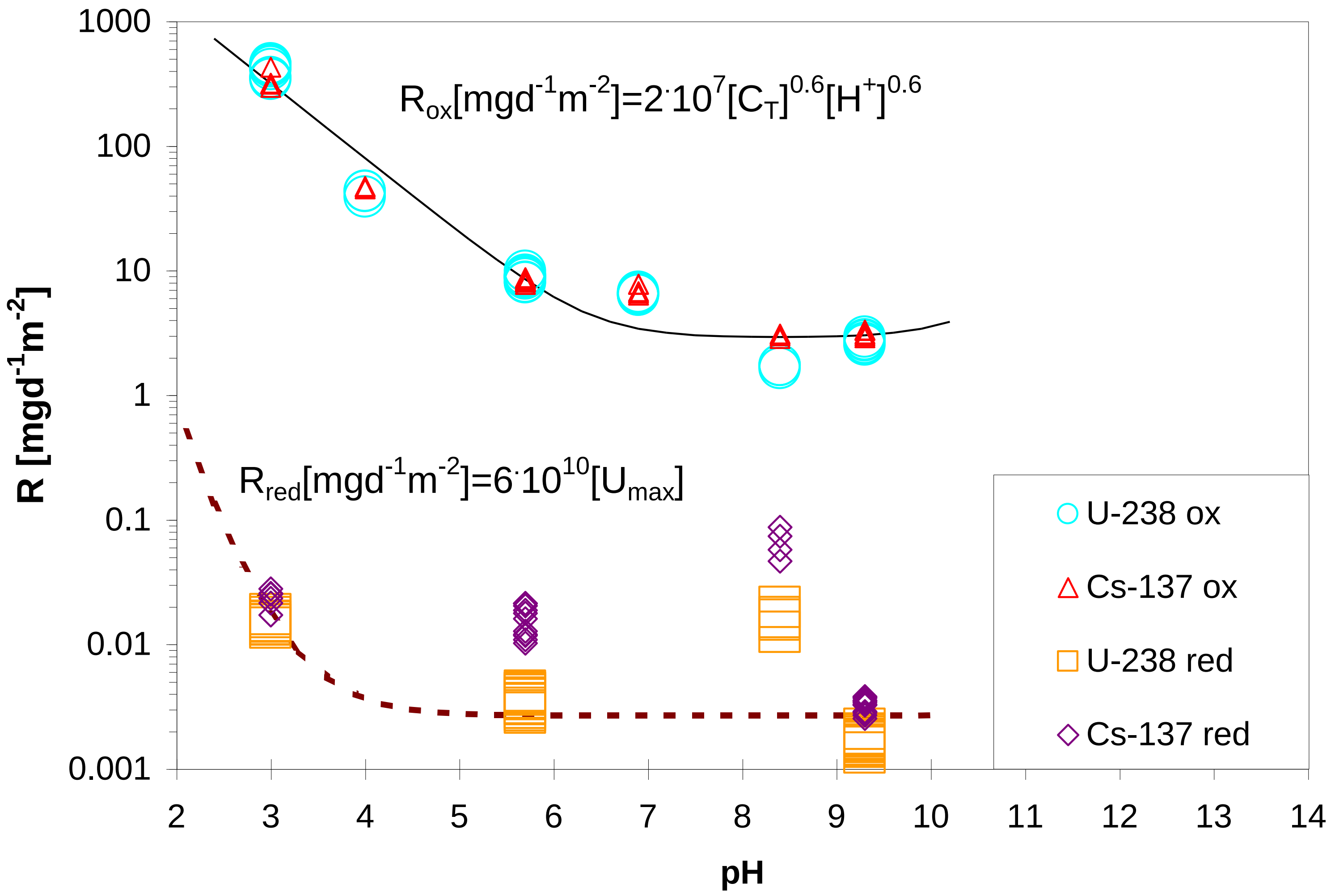
Carbol et al et al., J. Nucl. Mater. 392(2009) 45

Fors et al. J. Nucl Mat. 333(2009) 344

Schema of the flow through experimental setup



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

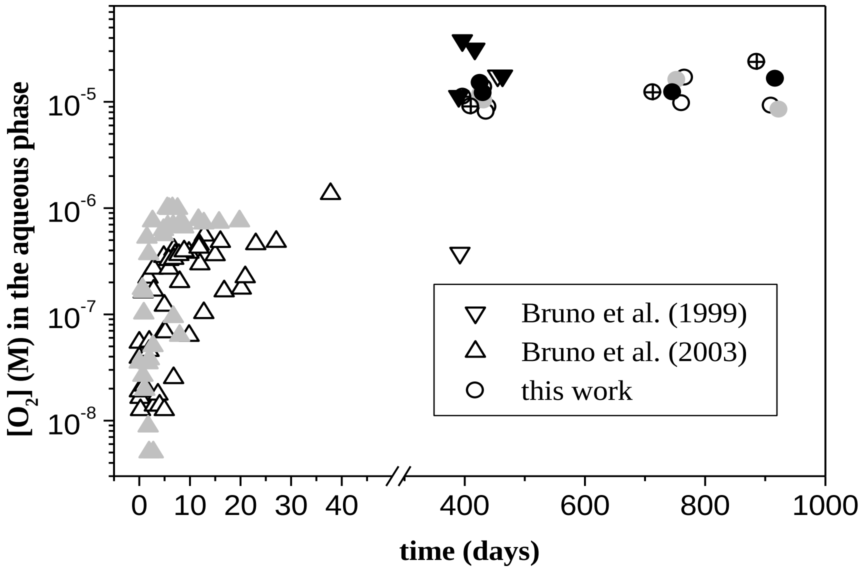


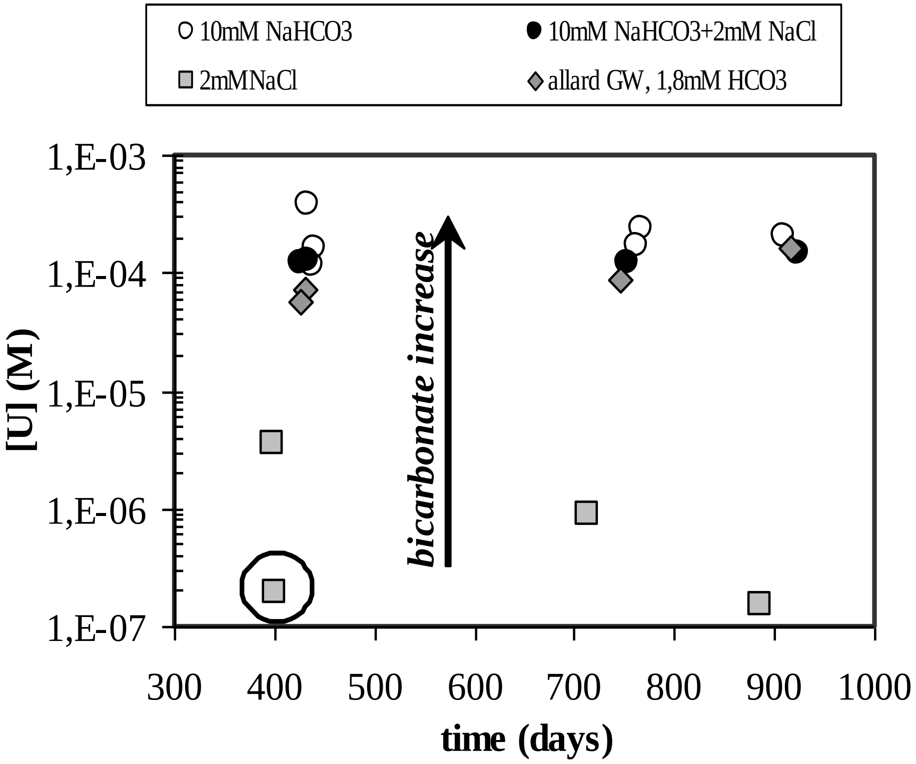
U_{max} corresponds to UO_2(s) solubilities measured by Parks&Pohl, 1988.

Oxidative versus non-oxidative dissolution of spent fuel: relative importance.

- Geochemical testing of minerals (e.g., oxides) usually involves dissolution rates determined in acidic solutions via flow through tests.
- One should be careful in applying such data for spent fuel dissolution in a repository: the flow rates are so low that any influence of the **non-oxidative dissolution** of UO_2(s) is negligible. This is because one very quickly reaches equilibrium, where such dissolution rate is equaled by the precipitation rate and no more U(IV) is released. On the other hand, the **oxidative dissolution** rate is usually orders of magnitude higher and depends mainly on the oxidant concentration at the surface of the solid and other factors.
- By applying non-oxidative dissolution rates as measured in (Röllin et al, 2001) for fuel in the repository, dissolution rates of 10^{-5}/year are obtained. On the other hand, the lowest flow in the experiment (0.02 ml/min) corresponds to a flow of ~6.5 m^3/hour for a canister in the repository! Such flows are un-realistic (max 300 l/y in a granitic repository).
- Röllin et al. 2001 verified that the rates corresponded to undersaturated conditions, while later tests by Ekeroth et al. 2020 with the same fuel and 1 bar H_2 pressure proved that this amount of dissolved H_2 was sufficient to completely cancel oxidative fuel dissolution.

Glass ampoules sealed with 2 g fuel and ~30 ml solution

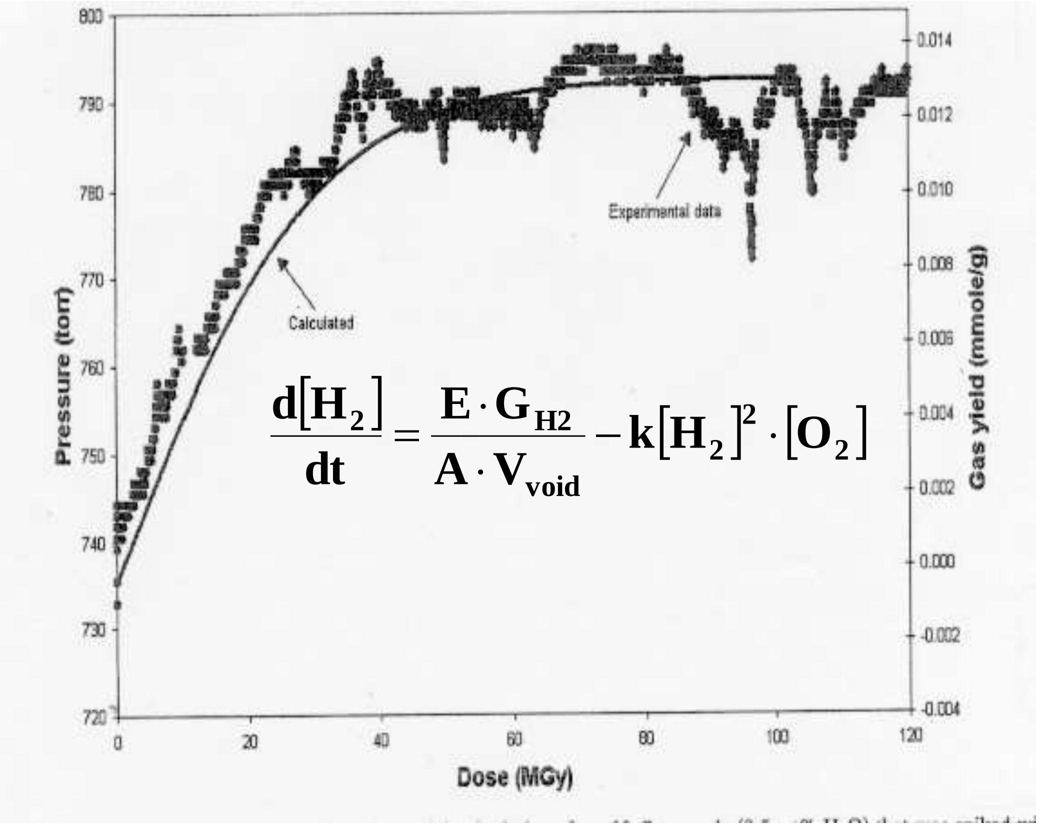




Eriksen et al, J. Nucl. Mat. 375(2008)331

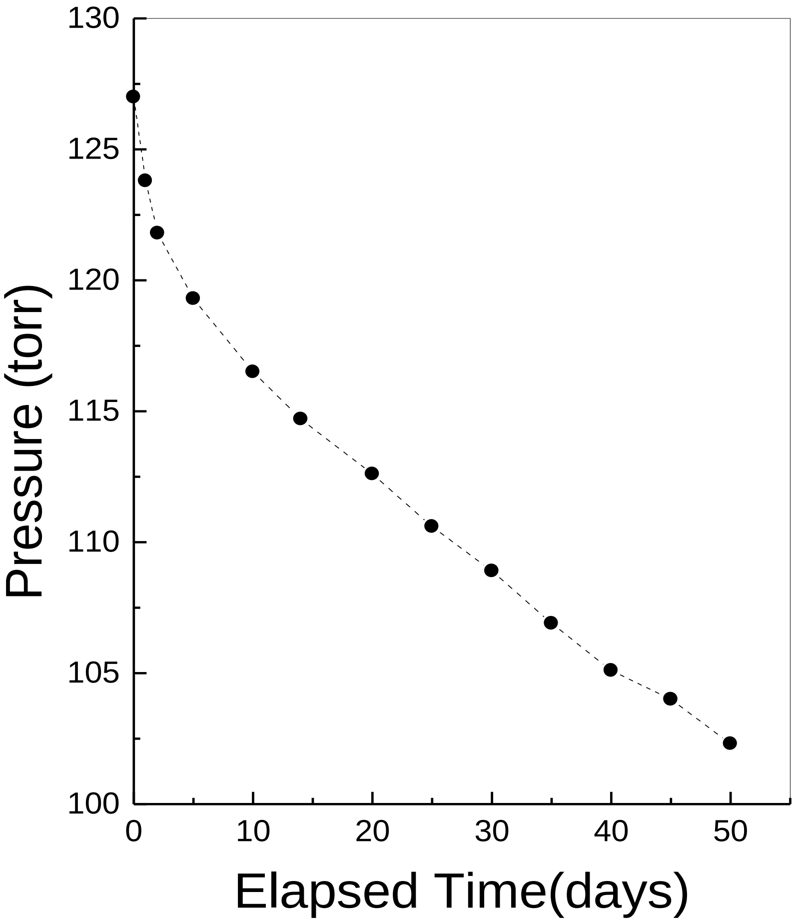
Recombination reactions

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



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

2:1 mixture D_2+O_2 over $PuO_2(s)$, 25 °C [Haschke et al., J. All. Comp. 1996].



Modelling of fuel dissolution

- Geochemical (equilibrium) models or electrochemical models, which are based on the measurement of the equilibrium corrosion potential and use the measured current to determine the dissolution rate, have been used earlier.
- Radiolytic (kinetic) models use:

  -Experimental rate constants for molecular and radical species and radiolytic yields (G-factors or G-values) for all radical and molecular species.

  - The dose rate.
- Calculate steady state concentrations of all species present by solving a system of linear diff. equations of the type: $-dC_i/dt = k C_i$. Good results in homogeneous systems, initially solid phase was treated by solubilizing the first solid layers.
- Progress made in the a modelling of the dose rate profile for all radiations from the spent fuel surface and in the experimental determination of interfacial rate constants, including noble metal particle catalyzed reduction by H_2.
- H_2O_2 confirmed as the dominating oxidant of the fuel matrix and its catalytic decomposition on oxide surfaces investigated. Linear free energy relationships of oxidation potential with second order rates used to obtain rates for very fast radicals.
- Modern modelling approaches make possible to determine critical H_2 concentrations for fuels of different age, which completely cancel oxidative fuel dissolution.
- This is probably the field where most progress has been made in the last 15 years.

Potential modification of radionuclide location

- In the frame of the French PRECCI research program (1999-2006) the redistribution of fission products in the spent fuel due to athermal diffusion caused by alpha decays was largely discussed.
- Hypothesis:

  based on H. Matzke´s publications: JNM (1983), IAEA Report (1991) :

  $$D_{athermal} \propto N_{defects} \propto E_{released}$$

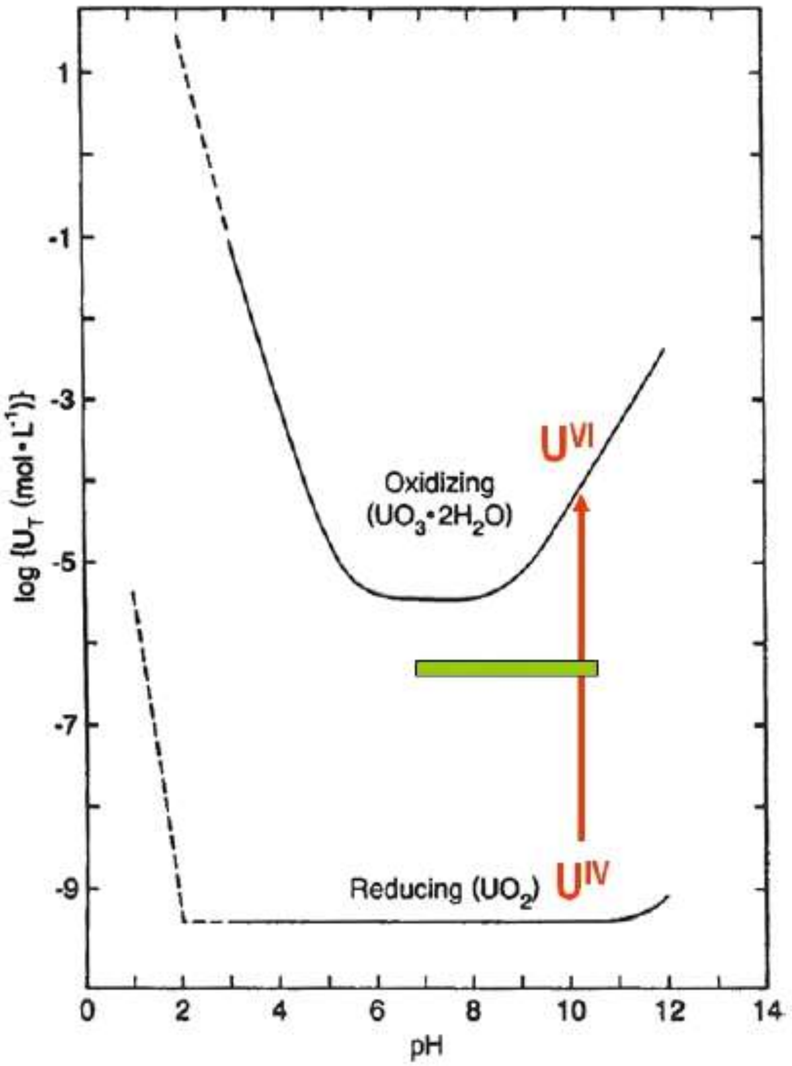
- From in reactor data: $D_{athermal} \approx 10^{-22}\ m^2/s$
- Characteristic path for 10 000y:

  $\sqrt{D_{athermal} \cdot t} \approx 6\ \mu m \Rightarrow$ half mean grain diameter

- Significant modification of Cs, I inventories can not be excluded.
- Later modeling and experimental data showed that the athermal diffusion due to α-decay is negligible and $D_{athermal} < 10^{-26}\ m^2/s$.
- Similarly, potential damage caused by He accumulation shown by many modelling studies (Ferry et al. 2008, 2010, 2016) and a natural analogue study (Roudil et al. 2008) to be negligible for UO_2 fuel.

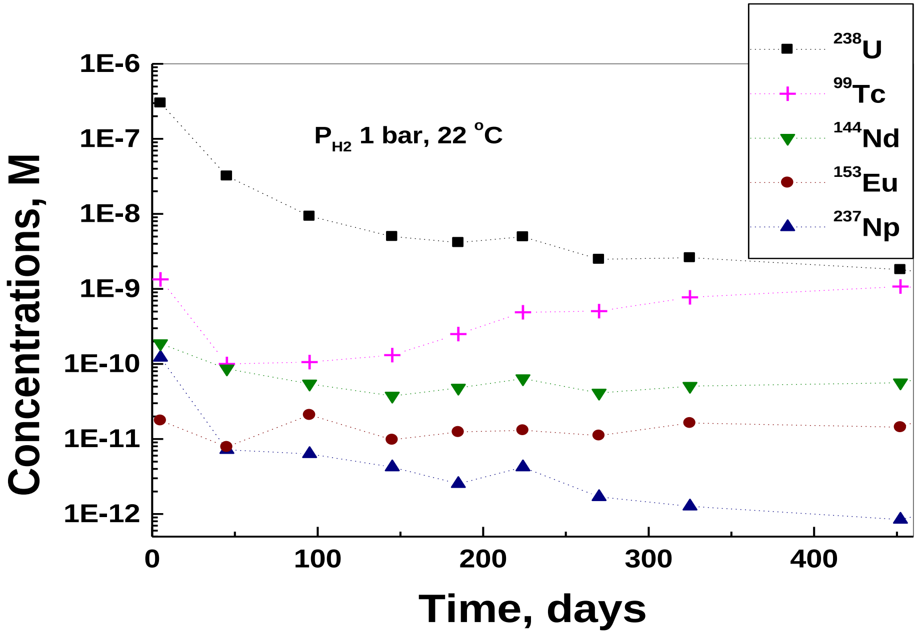
Thank you!

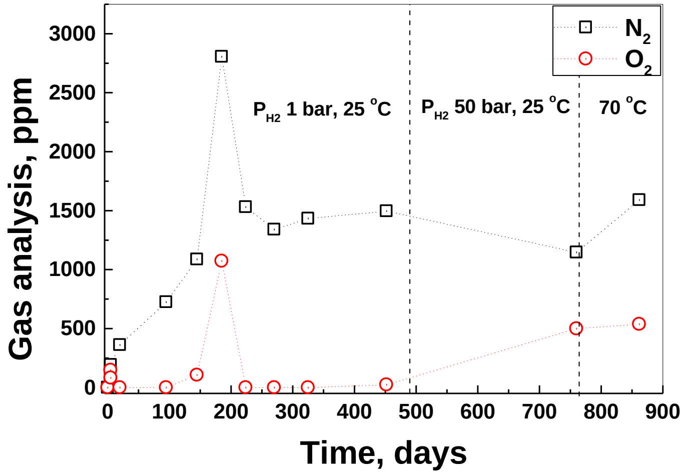
UO_2(s) and $UO_3.2H_2O$(s) solubilities-U(IV) and U(VI).



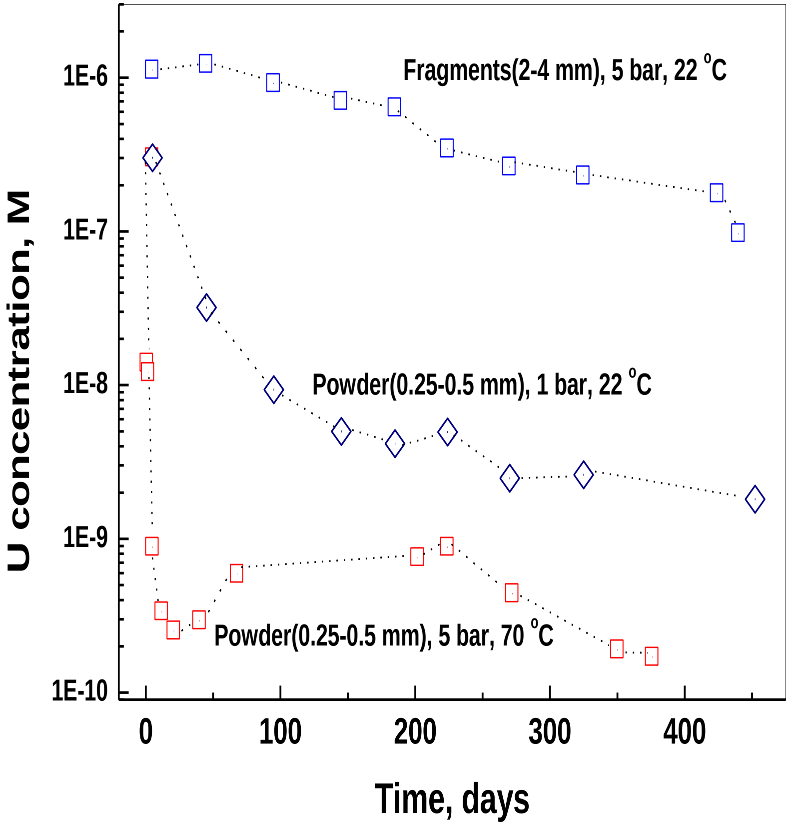
- More than 4 orders of magnitude difference in U concentrations in water.
- Solubility of schoepite increases more than two orders of magnitude in presence of 2 mM carbonate, no change for UO_2(s).
- Advantageous for repository to have reducing conditions and keep U low.

Leaching of fuel powder under 1 bar H_2, 22 C.



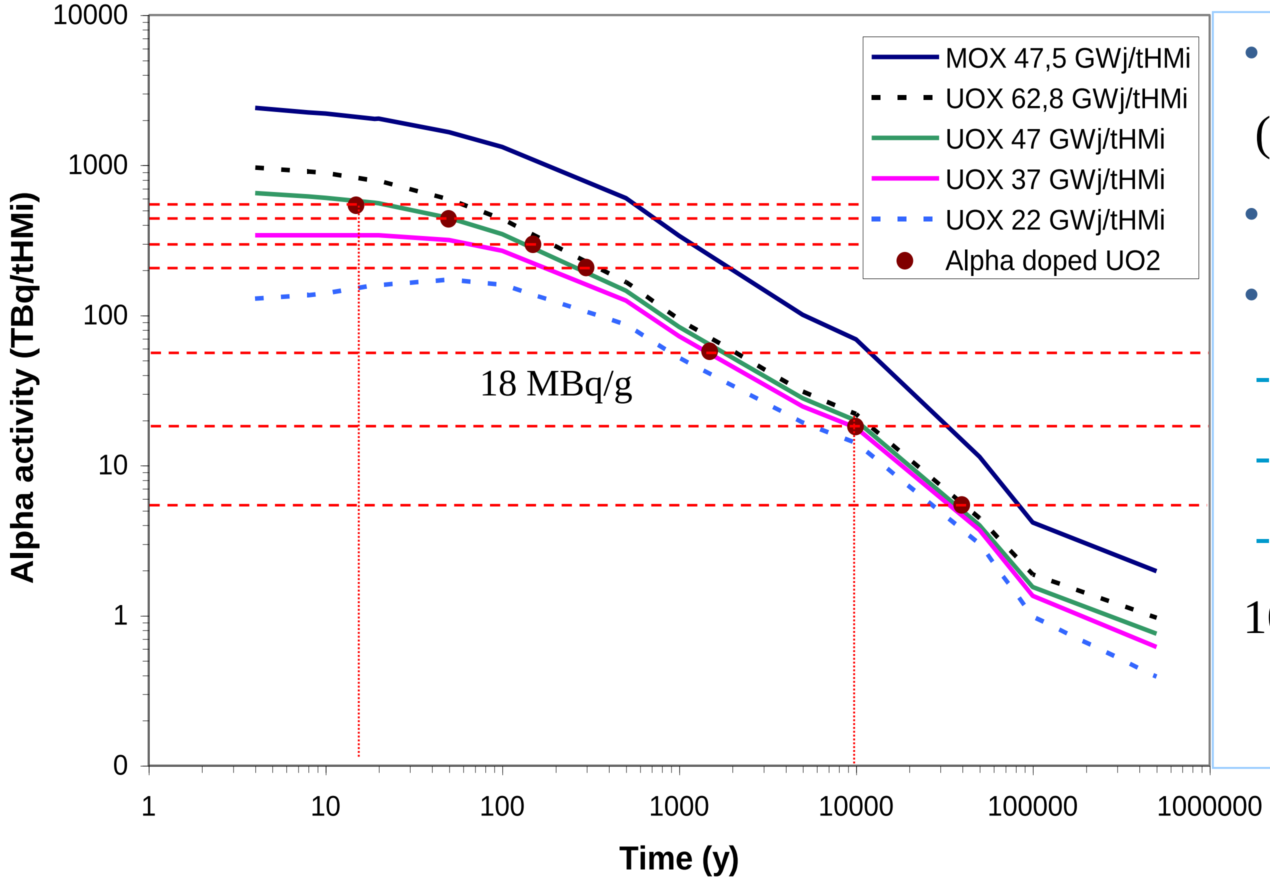


Influence of surface area and T on the decrease of [U] in solution.



Ekeroth et al., J. Nucl Mater. 531 (2020) 151981

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 (%),

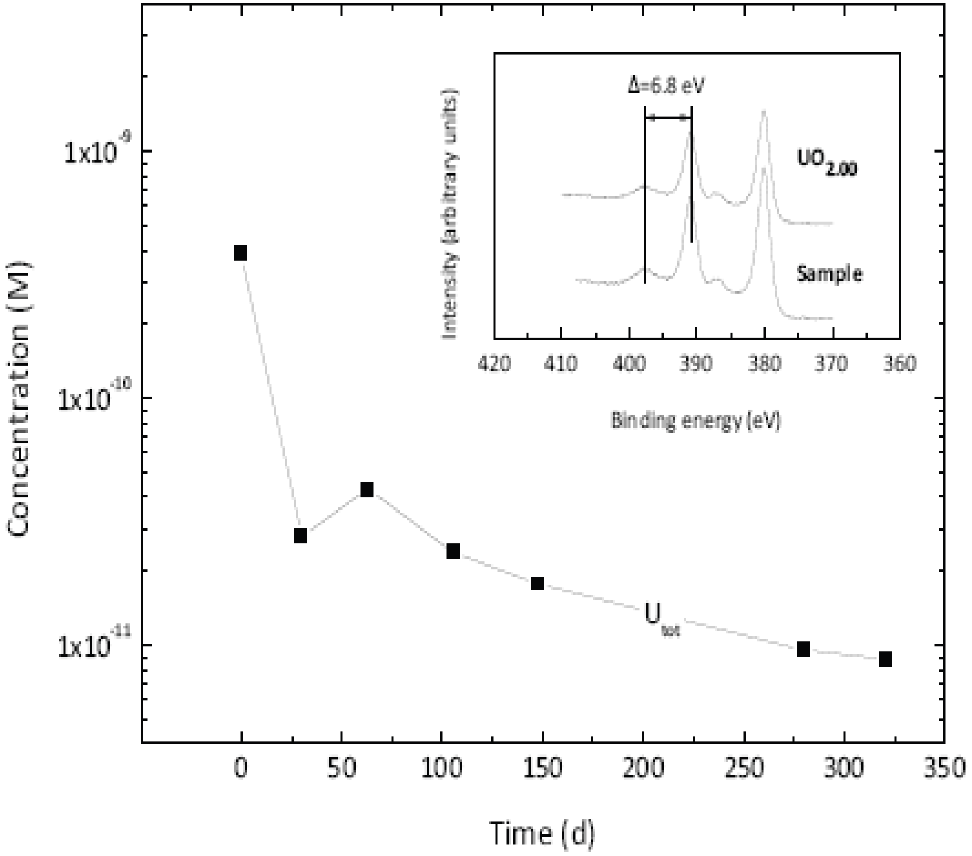
-specific activity (MBq/g)

-or fuel age mimicked (y)

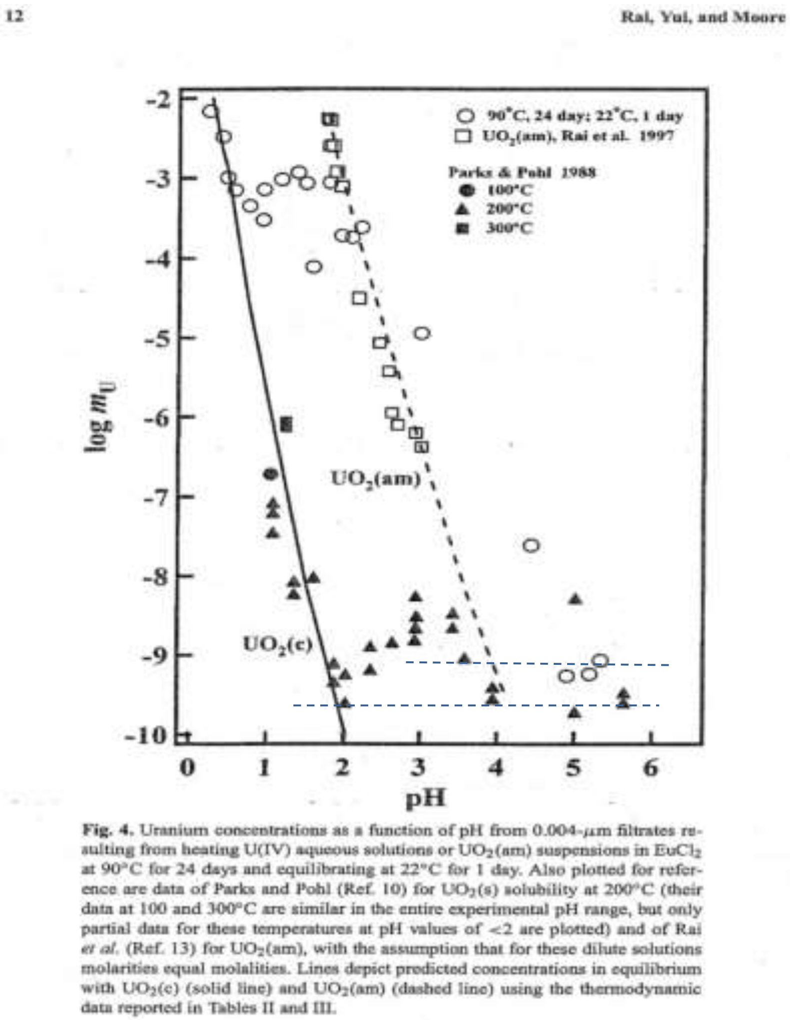
10% ^{233}U = 33 MBq/g = 3000 y

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

XPS of the pellet surface after test; comparison with UO_2 solubility (Rai et al., 2003)



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

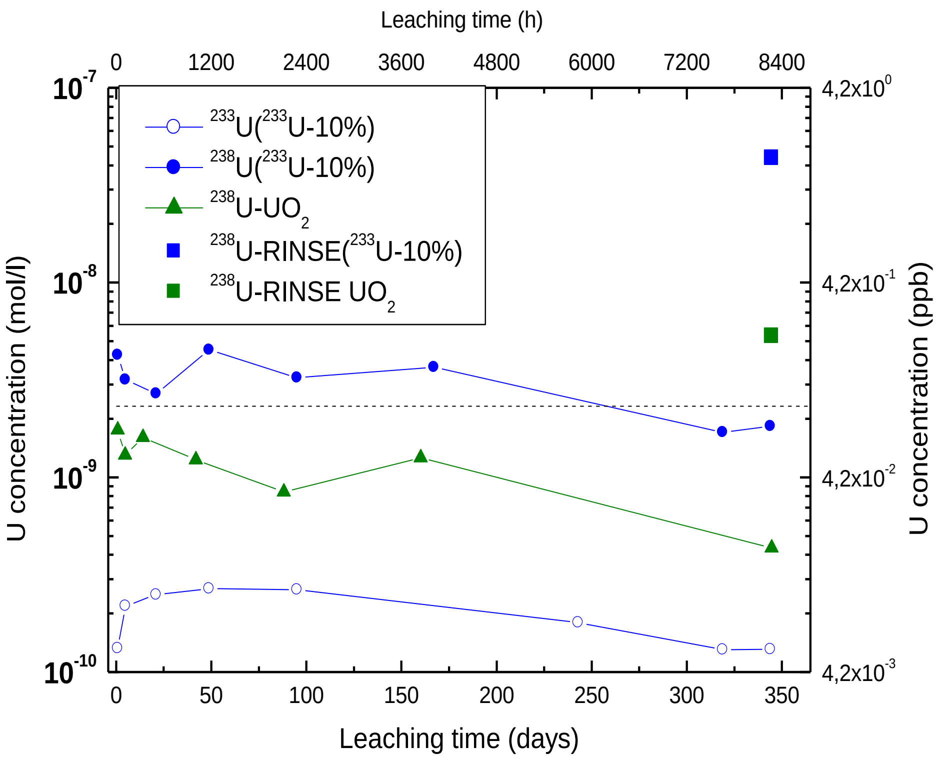


12 Rai, Yui, and Moore

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.

a) ITU -Static leaching of 10% ^{233}U doped UO$_2$ in H$_2$ gas mixtures

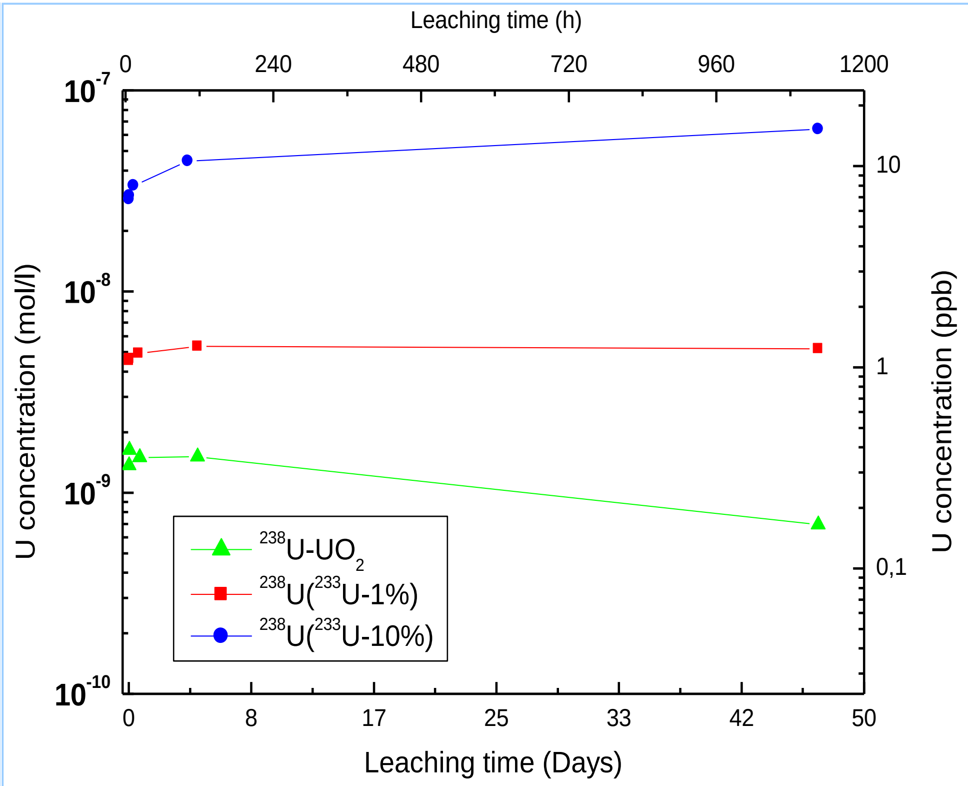
Static leaching of 0 and 10% ^{233}U doped UO$_2$ in carbonated dilute GW flushed with Ar + 6% H$_2$ gas mixtures ([H$_2$]~0.05 mM).



Carbol et al., SKB TR-05-09, 2005.

b)Unclear H$_2$ effect: Threshold of α-activity observed in carbonate solutions under Ar.

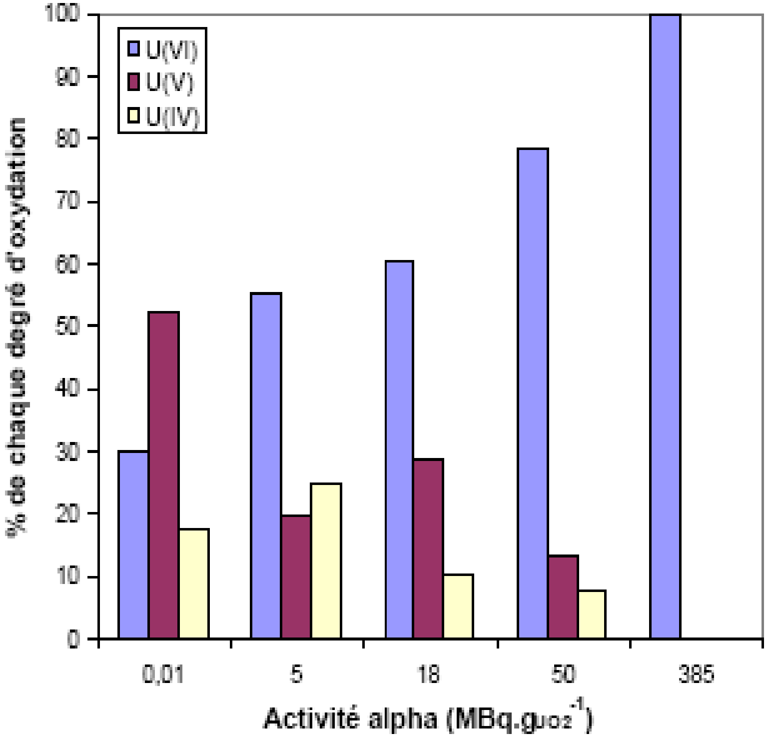
Static leaching of 0, 1 and 10% ^{233}U doped UO$_2$ under Ar+0.02%CO$_2$,



Rondinella et al, Mat Res Symp Proc. 2004.

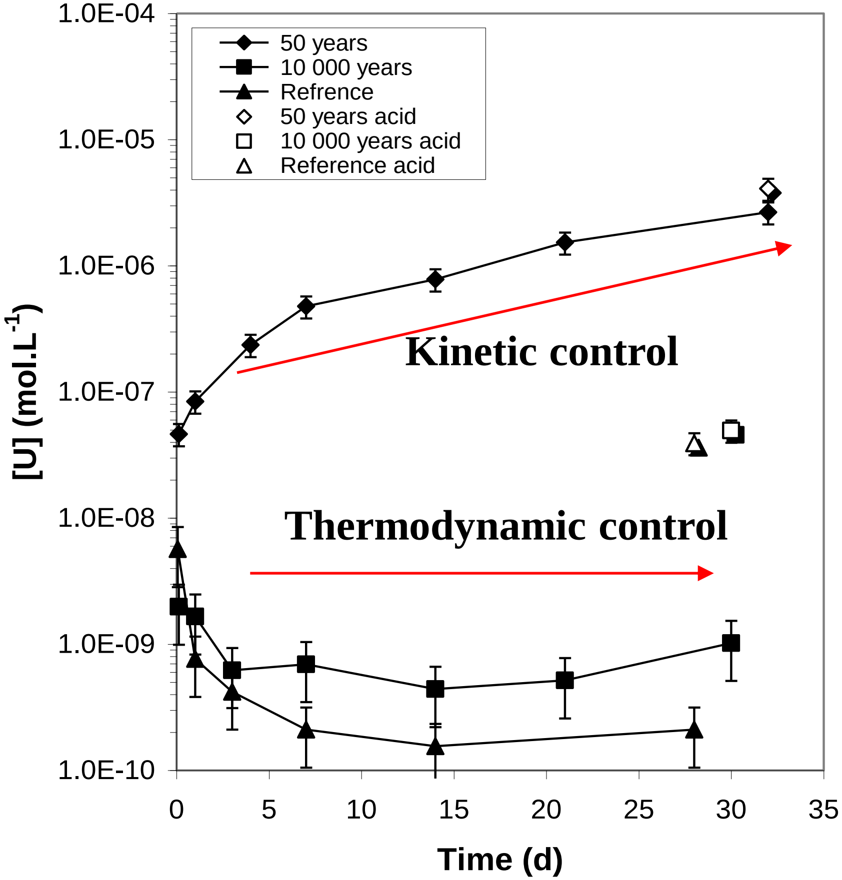
Muzeau et al., J. Alloy Comp. 467(2009)578.

XPS surface analysis after annealing and storage



Test in carbonate solutions under Ar.

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



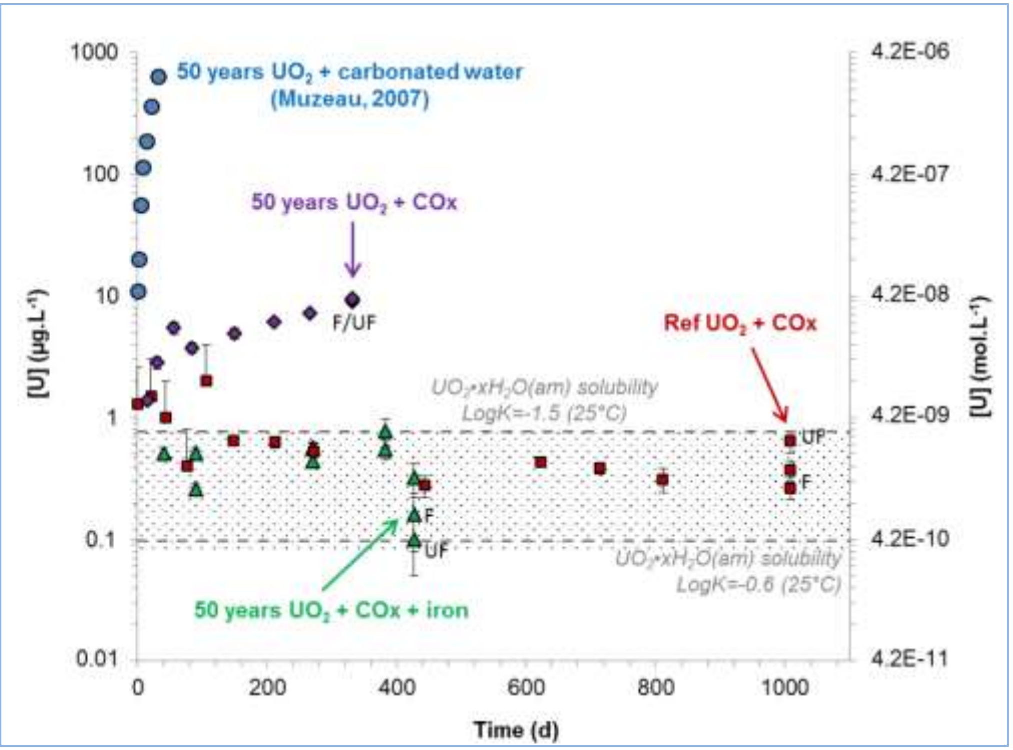
Data from tests with(U,Pu)O_2(s) in presence of Fe(s).

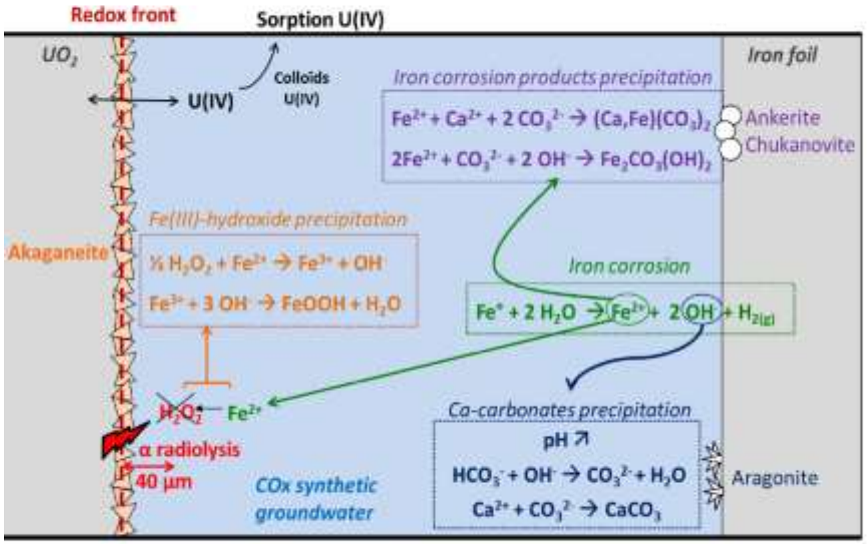
New results obtained with 385 MBq/g α-doped UO_2, simulating 50-year-old fuel.

Similar results with fresh MOX with 7% Pu, Ph.D. thesis of M. Odorowski or fresh MOX with 27% Pu, Ph.D. thesis of V. Kerleguer at CEA Marcoule.

All radiolysis effects counteracted in presence of a Fe-foil!

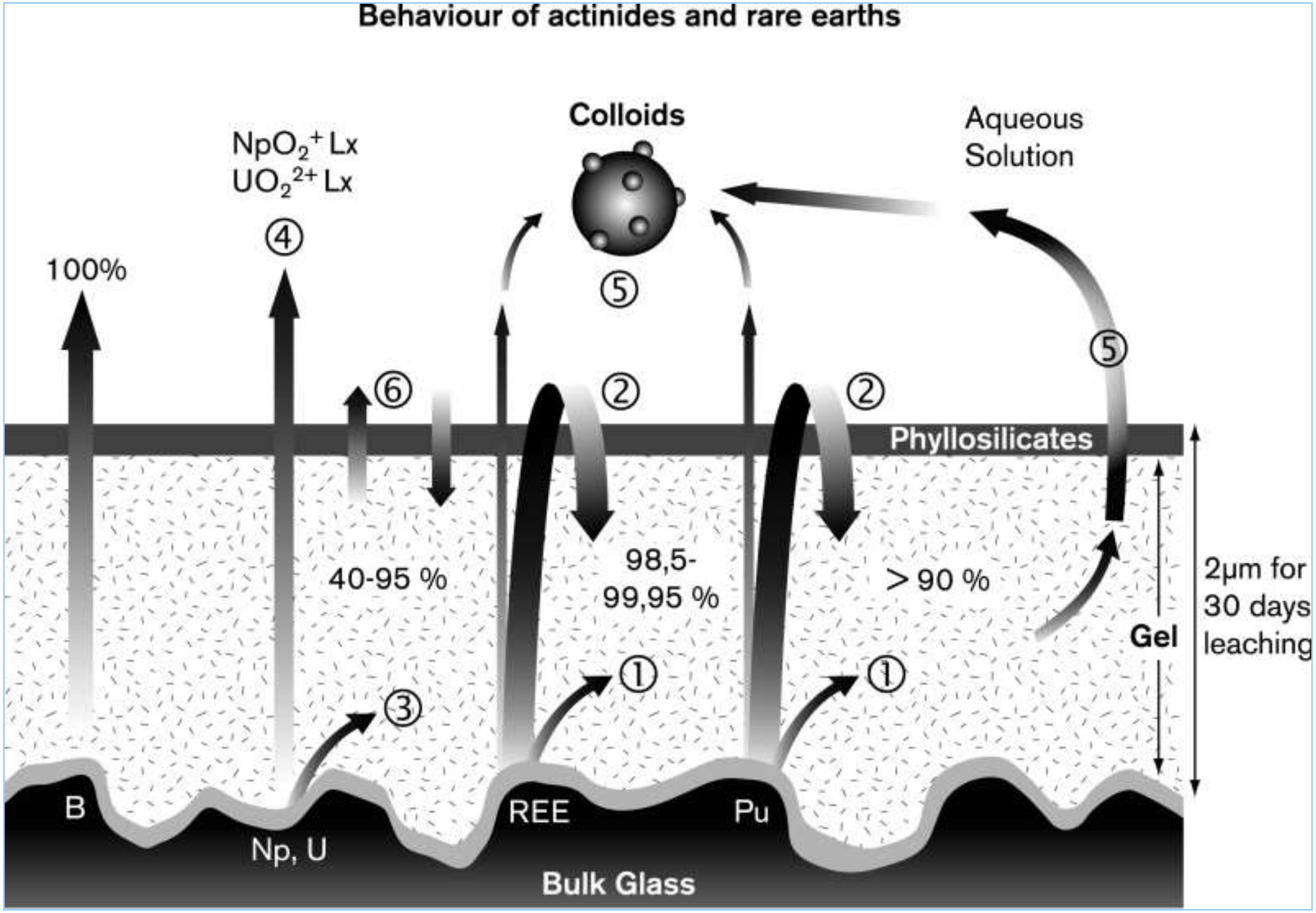
- No U on Fe(s) means no U(VI) was released in solution.
- Fe(III) solids on the surface of the un-irradiated MOX pellet.
- High Fe(II) concentrations in presence iron hydroxocarbonates (e.g. chukanovite)



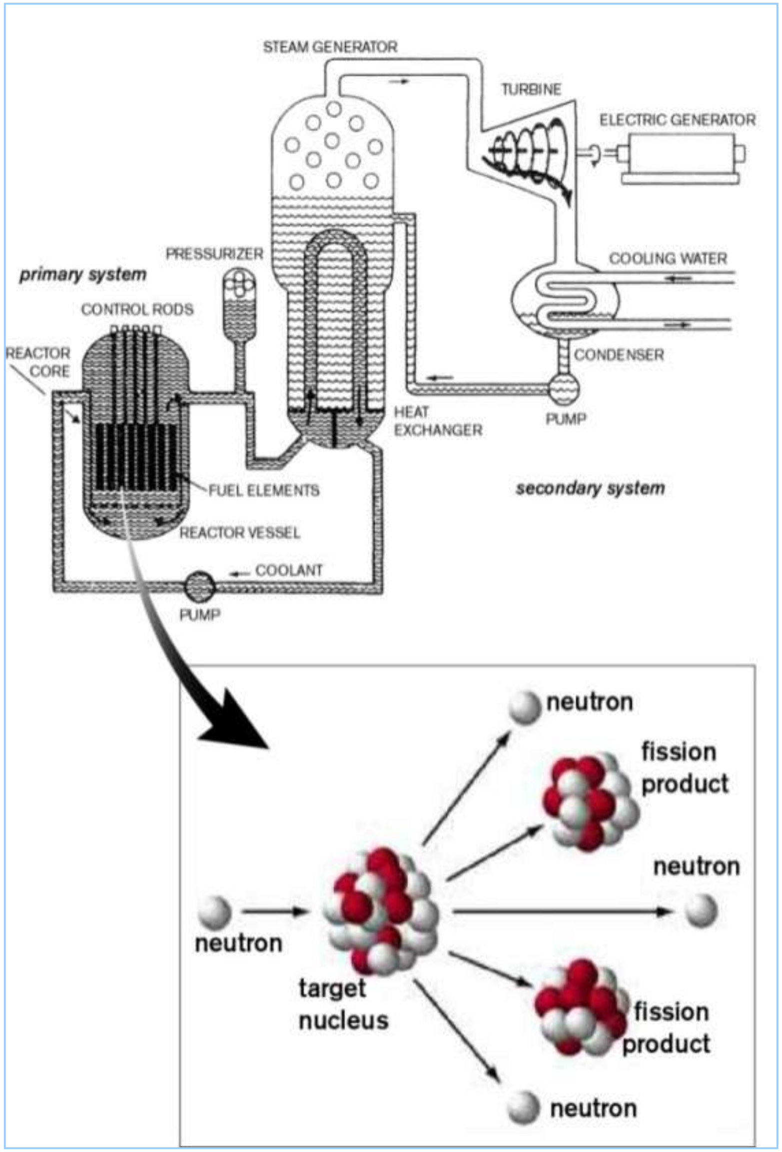


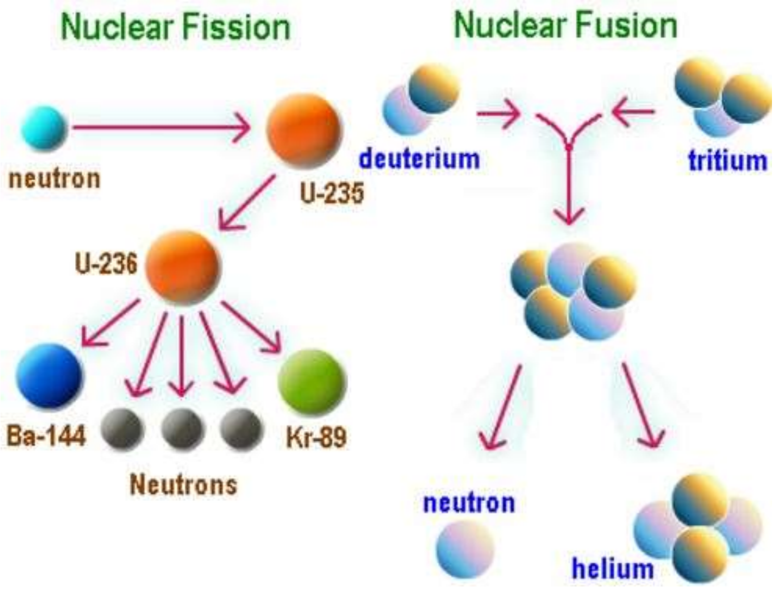
Odorowski et al. Geochim. Cosmochim. Acta, 219(2017)1-21.

Vitrified waste dissolution



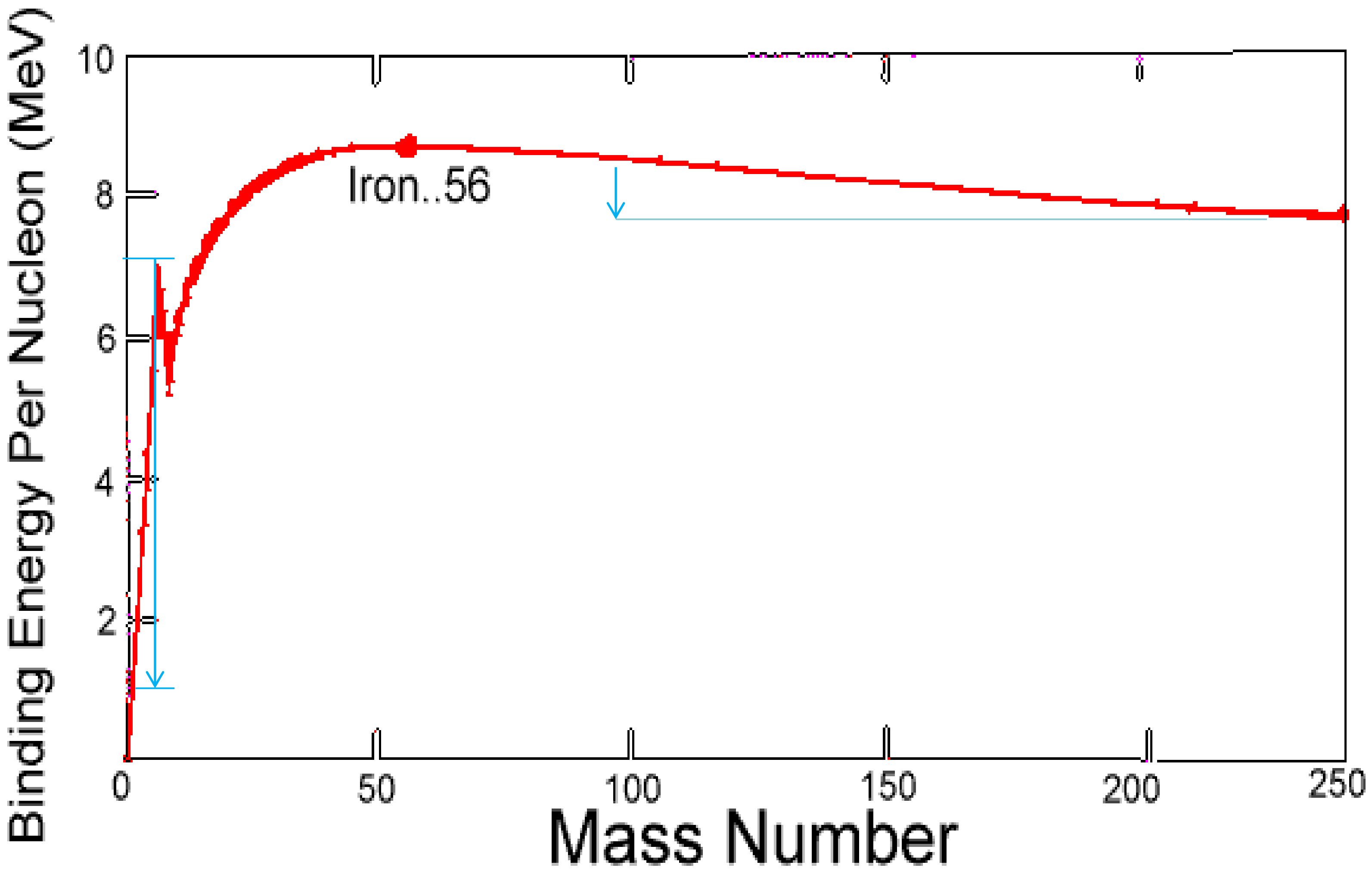
Schema of a nuclear reactor, fission and fusion.





Neutron capture (rim): $^{238}U + n_0^1 \rightarrow {}^{239}Pu$

Atomic nuclei have different stability

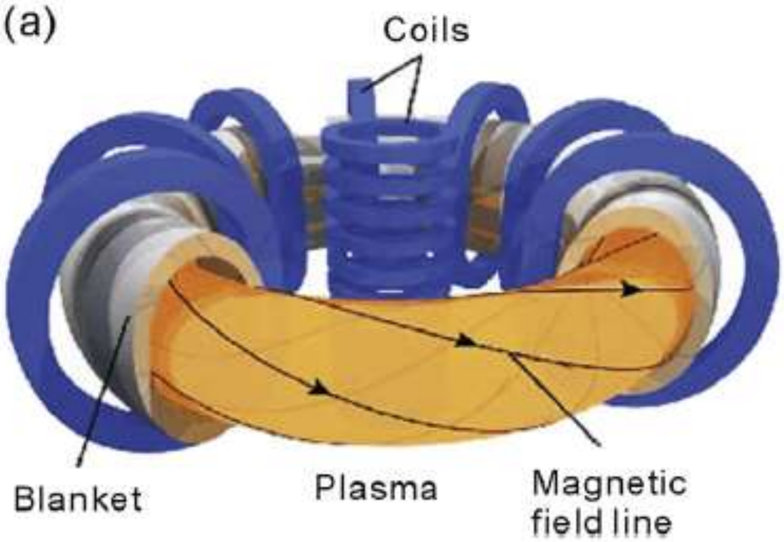


Fission: $^{235}U + ^{1}n = 2FP + 2.1\ ^{1}n$

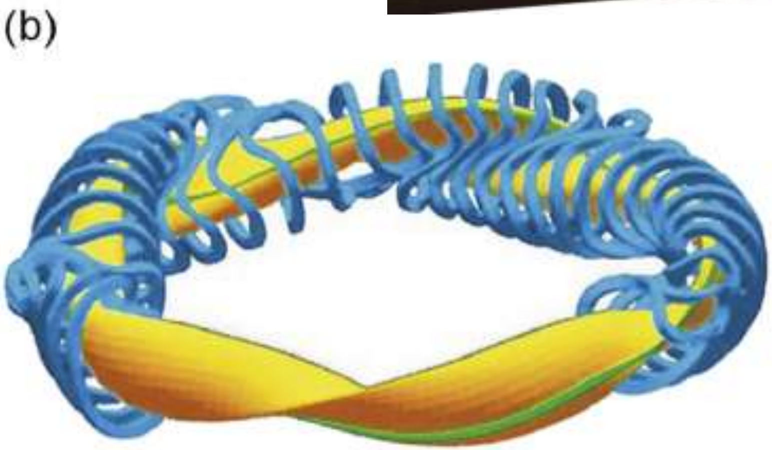
Fusion: $^{3}T + ^{2}D = ^{4}He + ^{1}n + 17.6$ MeV

Nuclear fusion reactors

Fermi calculated in 1944 that 50 million °C are sufficient for the D-T reaction. ITER(right) will be 24 m high and 30 m wide, contain ca. 850 m^3 plasma.

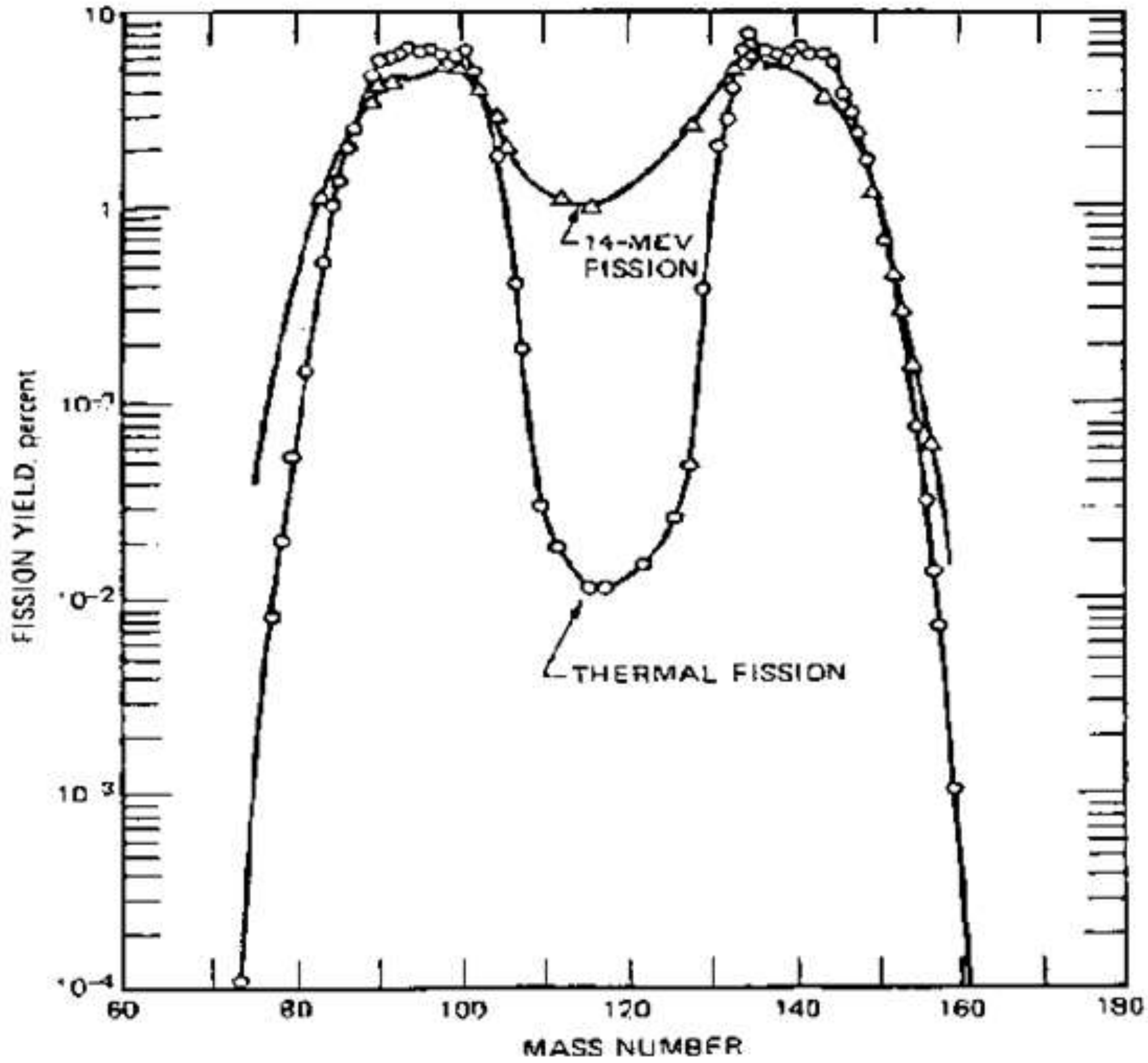


a) Tokamak (ITER)

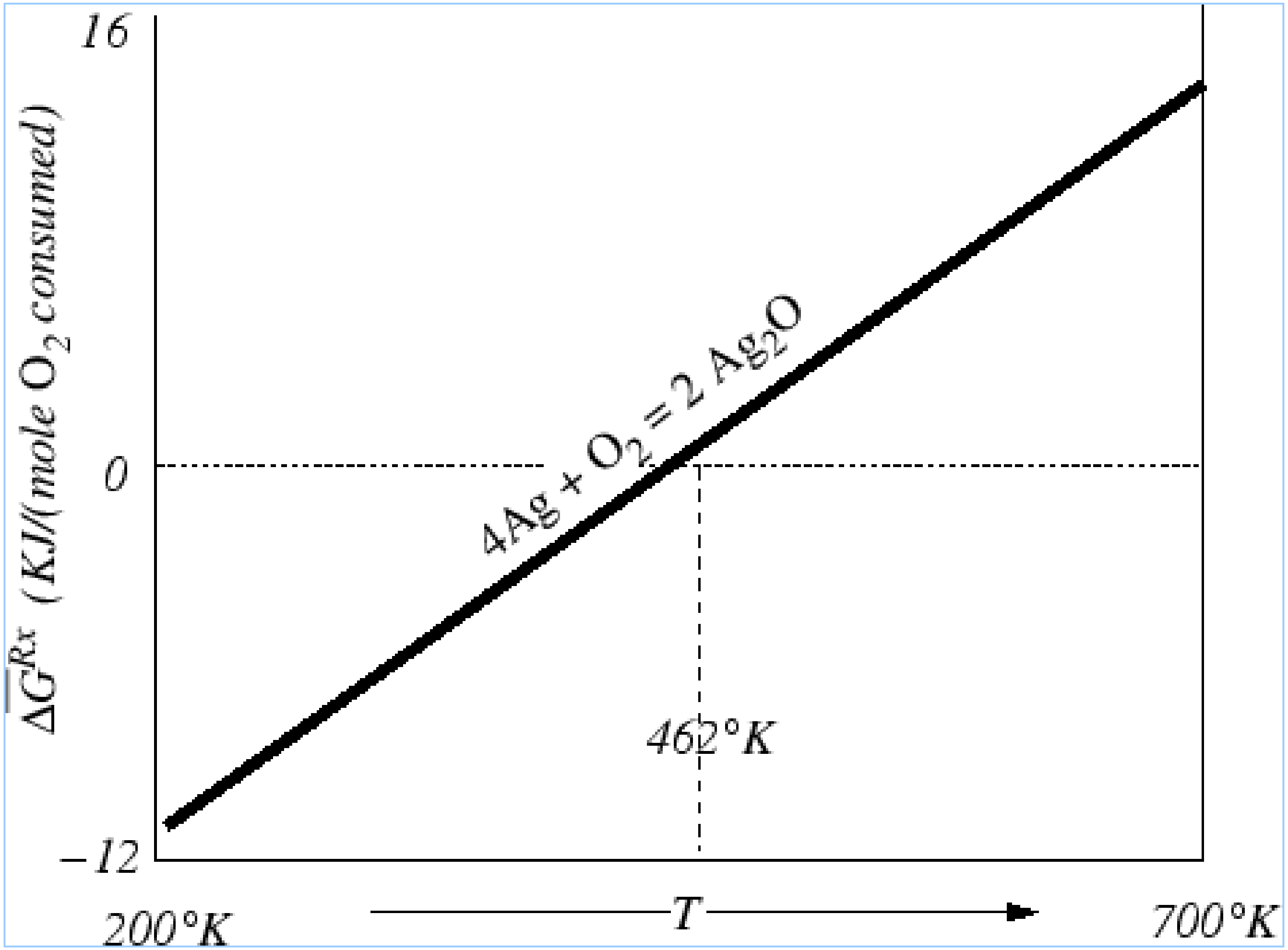


b) Stellerator (Wedelstein 7)

Fission yields for ^{235}U



Observe the maxima at masses ~90 and ~137

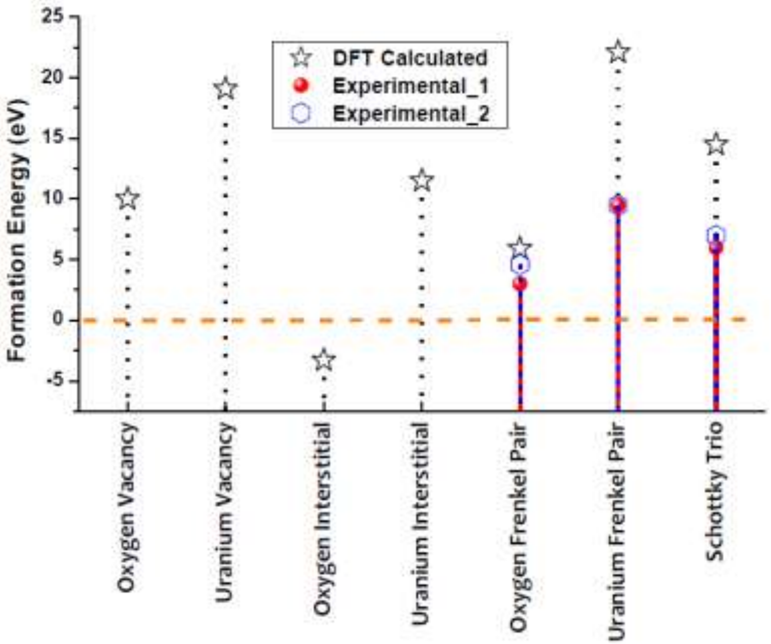


Graph of ΔG for Ag oxidation (per mole O_2) with intercept ΔH and slope –ΔS.
Products favoured below 462 K (negative ΔG). (ΔG = ΔH -T ΔS)

Autoclave tests at Studsvik.

A PLAUSIBLE EXPLANATION FOR THE STABILIZATION OF THE UO_2 LATTICE BY RARE EARTH DOPING (RE^{III}) DOPING

- Lattice contraction due to incorporation of RE on the U sublattice?
- Ionic radius of RE^{III} > ionic radius of U^{IV}. Lattice expansion more likely.
- Perhaps over-ridden by RE^{III}-O_V cluster formation
- RE^{III} incorporation introduces an effective negative charge. Leads to repulsion of O interstitials and/or attraction of O vacancies. This reduces the number of available vacancies



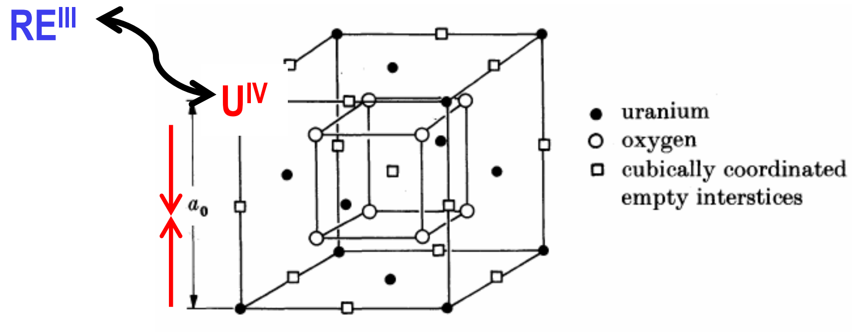


FIGURE 1. The unit cell of UO_2.

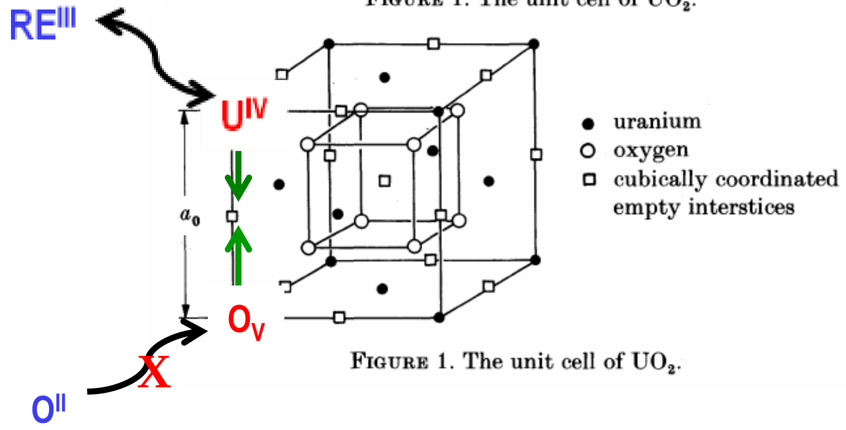


FIGURE 1. The unit cell of UO_2.

Since oxidation involves O^{II} injection into O_V sites RE doping leads to retarded UO_2 oxidation

Systematic studies on oxidative fuel dissolution as function of burn-up.

- **Jegou et al. J. Nucl. Mat. 326 (2004) 144-155** : Sr releases in static leaching UOX fuel pins of 22-60 MWd/kgU burnup in carbonated groundwater.

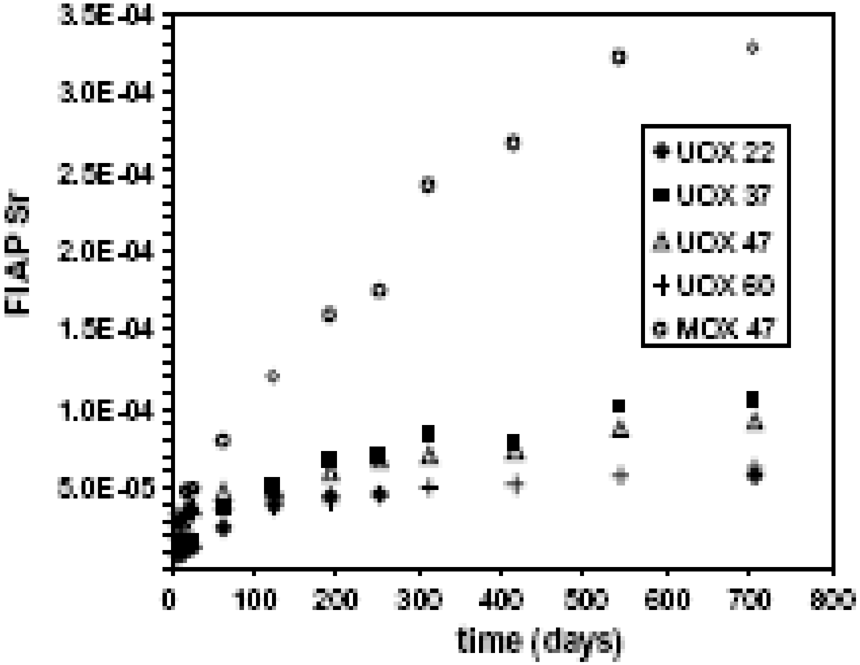


Fig. 2. Cumulative released strontium fractions.

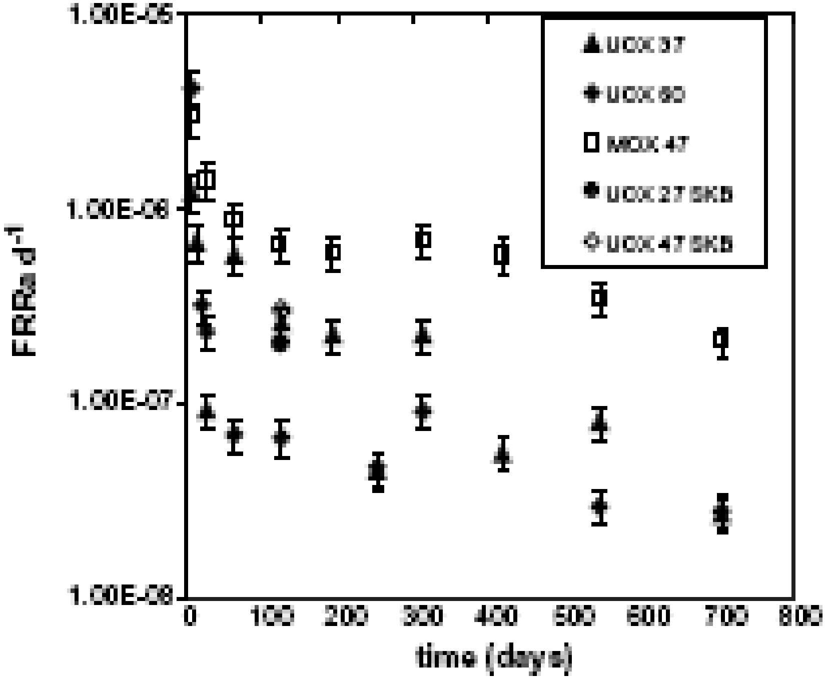
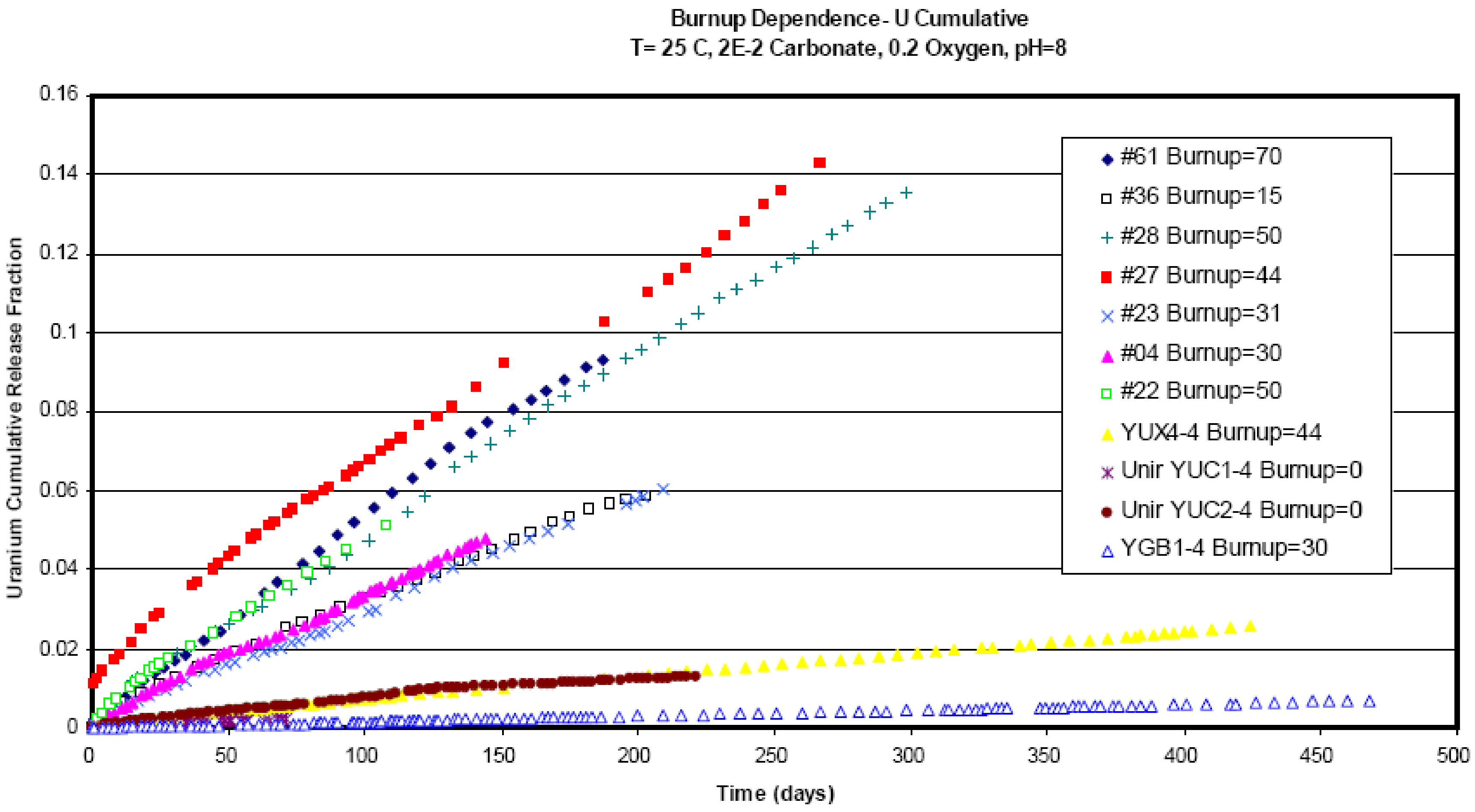


Fig. 3. Average fractional release rate FRR$_s$ (d^{-1}) for strontium.

Cumulative U release in from flow-through tests at PNNL

B. Hanson, Proc. IHLLW Conf. Las Vegas (2008) p.404-411.

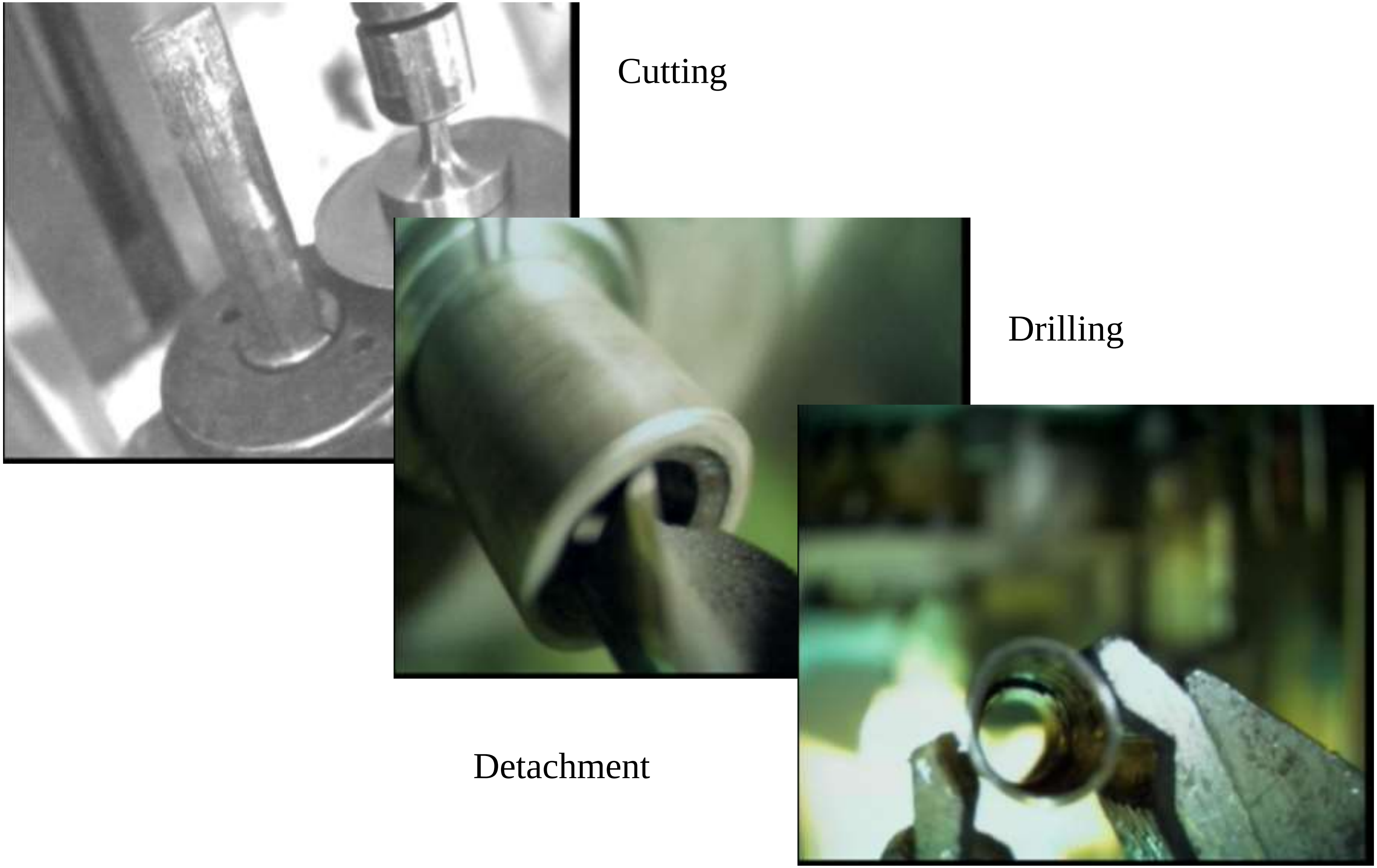


All samples are powders except for YUX4-4 and YGB1-4

ITU-ENRESA tests in NF-PRO comparing central (core) versus outer part leaching.

Sample preparation

- Clarens et al. Mat. Res. Soc. Symp. Proc. 1107(2008) 439-446

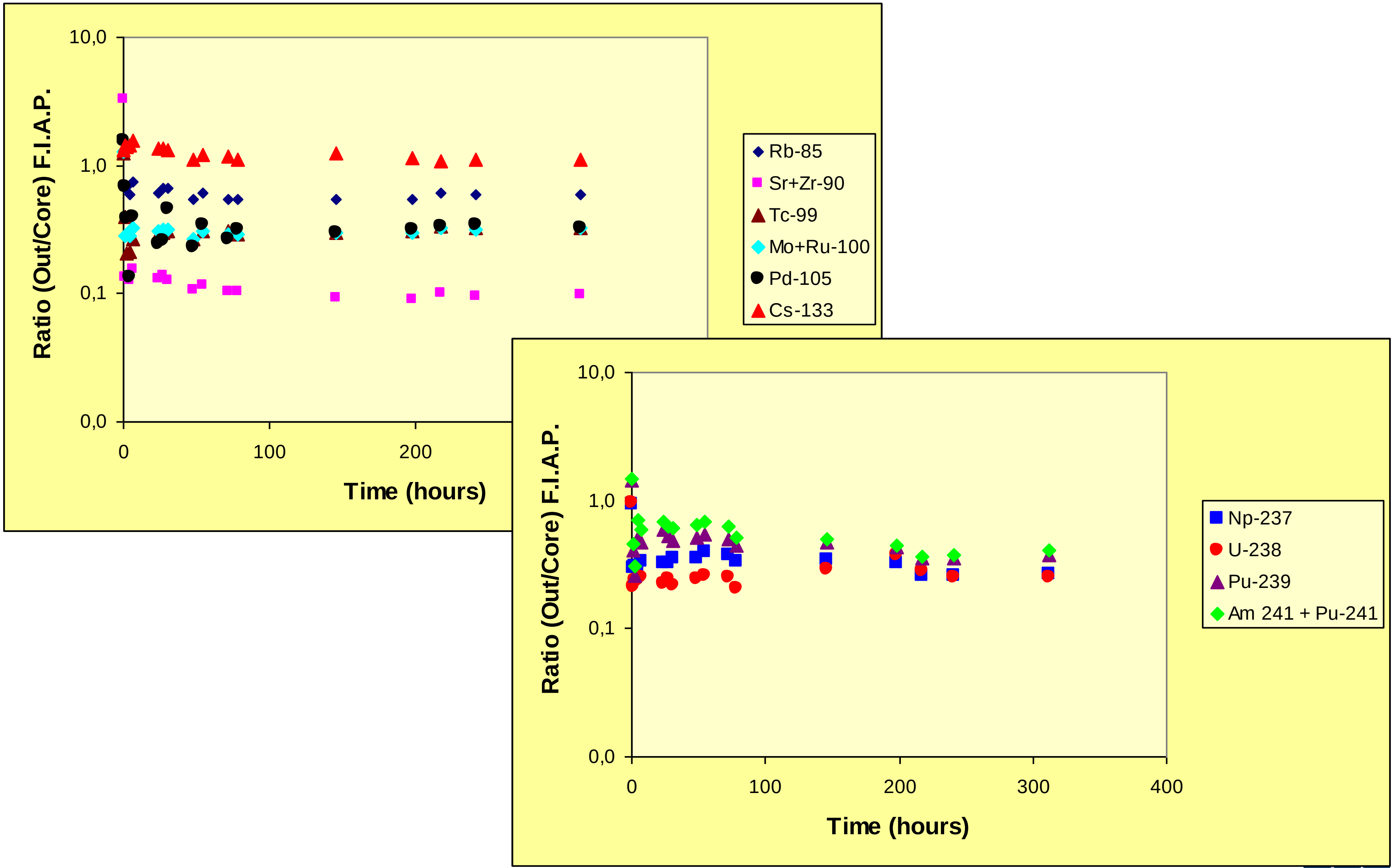


Cutting

Drilling

Detachment

Out (RIM) vs core sample releases (ratio < 1 means less release from outer part)



More difficult to fully oxidize high burn-up fuel at high temperature.

B. Hanson, PNNL-1173 Report, 1998.

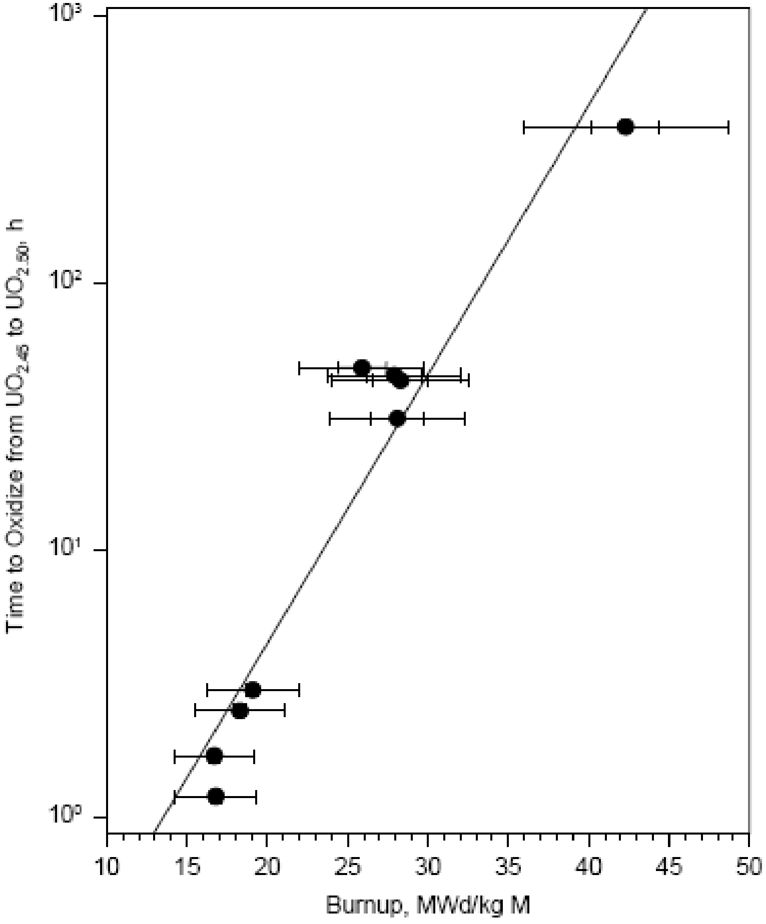


Figure 5.11. Time to Oxidize LWR Fragments from $UO_{2.45}$ to $UO_{2.50}$ at 305°C as a Function of Burnup (Burnup from ^{137}Cs Analysis)

Cobos et al. J. All. Comp. 271-273(1998) 610.

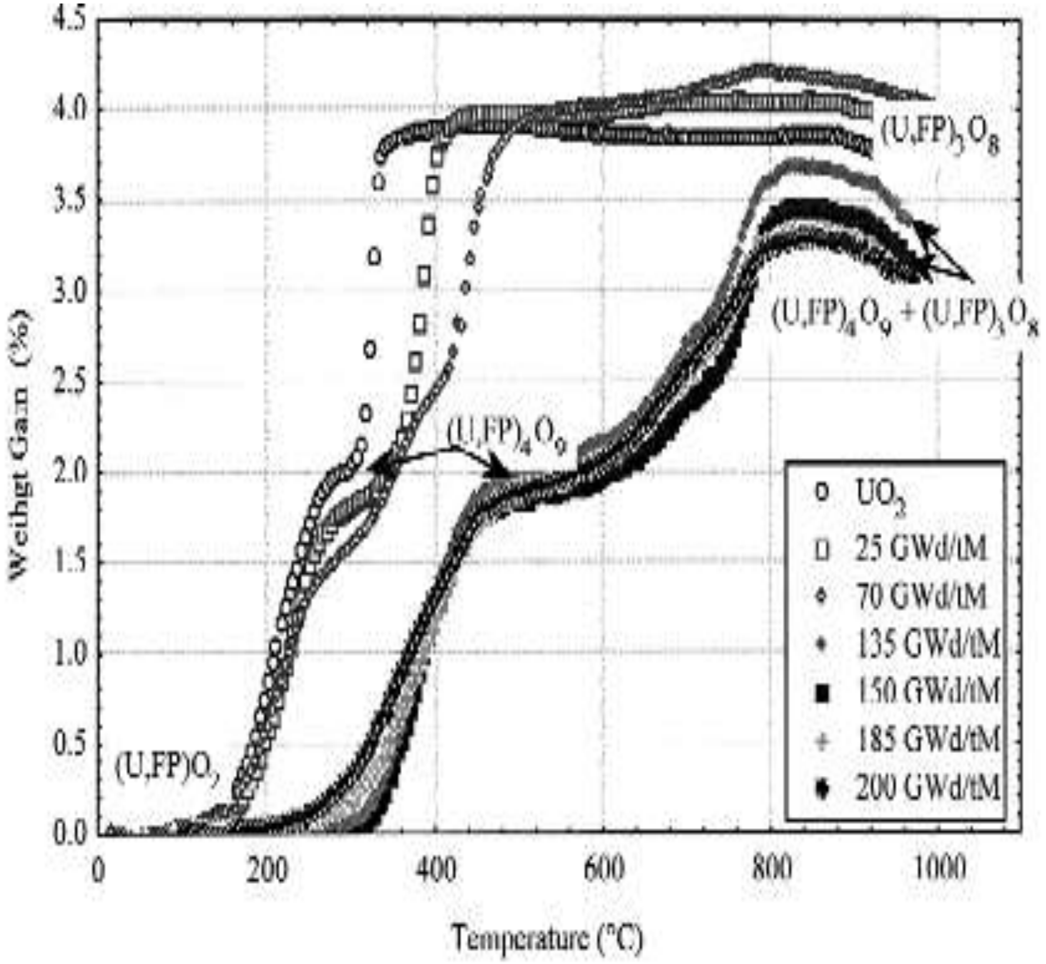


Fig. 2. Oxidation kinetics of unirradiated UO_2 and simulated spent fuels. Starting material: powdered pellets (mesh #220).

Dissolution rates of uraninite as function of other cation content.

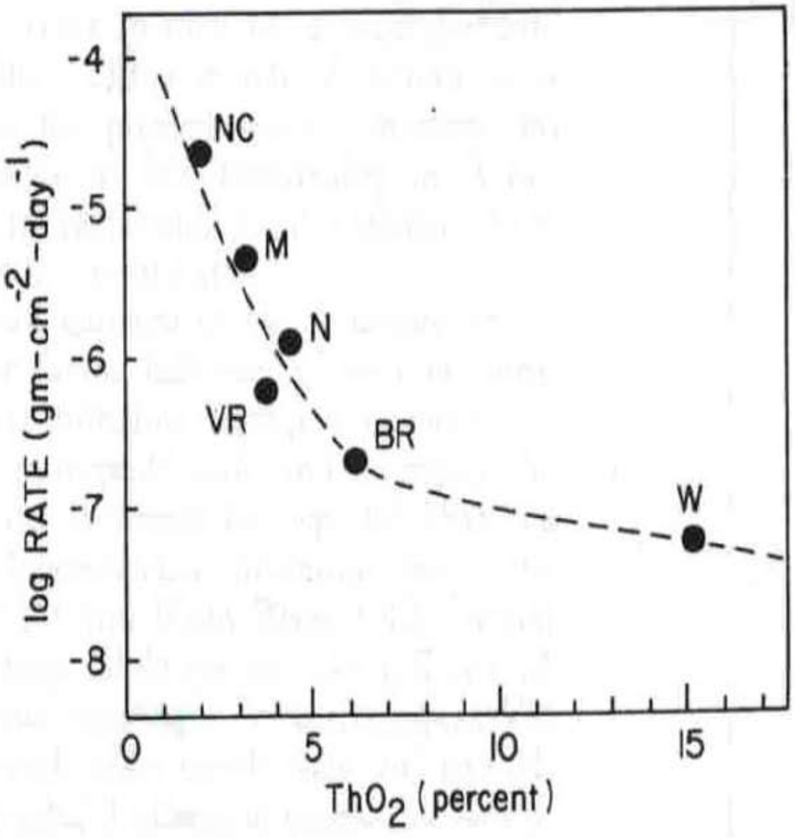


FIG. 4. Rate of uraninite dissolution as a function of uraninite ThO_2 content. ($T = 23°C$, ambient air, distilled water.)

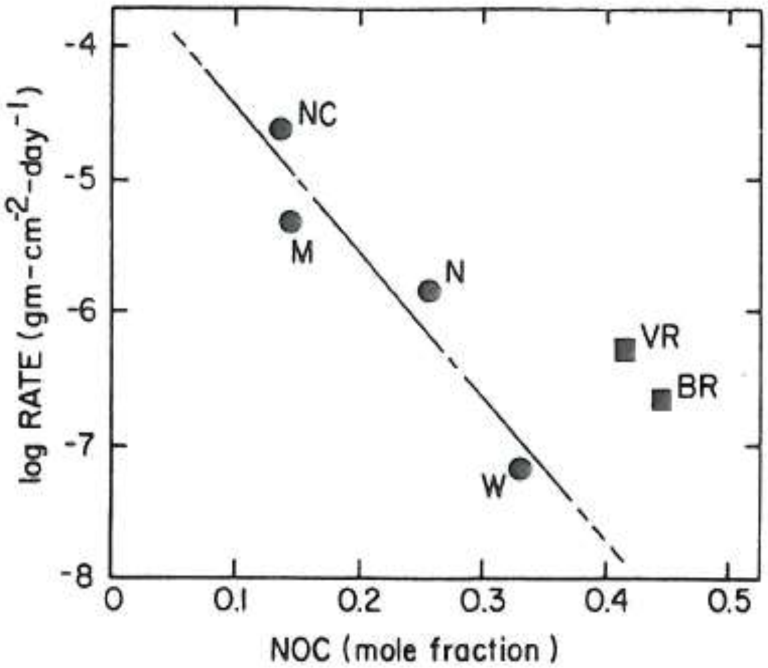


FIG. 5. Rate of uraninite dissolution as a function of non-uranium cation mole fraction (NOC). ($T = 23°C$, ambient air, distilled water.) Samples indicated by square symbols (BR and VR) were not considered in the analysis because of marked sample heterogeneity.

D.Grandstaff, A kinetic study of the dissolution of uraninite, Econ. Geol. 71(1976) 1493-1506.

Role of doping on oxidative dissolution of Gd-doped UO_2 or SIMFUEL

- Casella et al., IHLWM Conf. Proc. (2008) 388-394

- He et al., Can. J. Chem., 85 (2007) 702-714

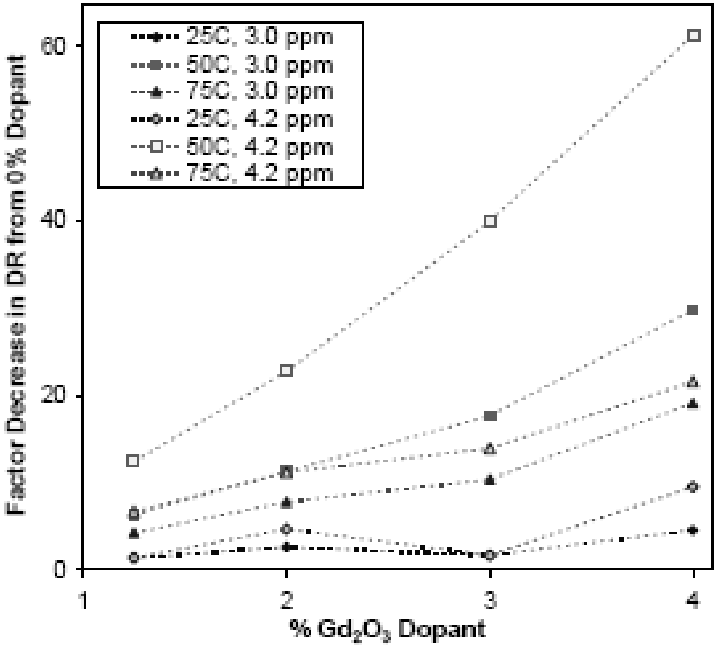
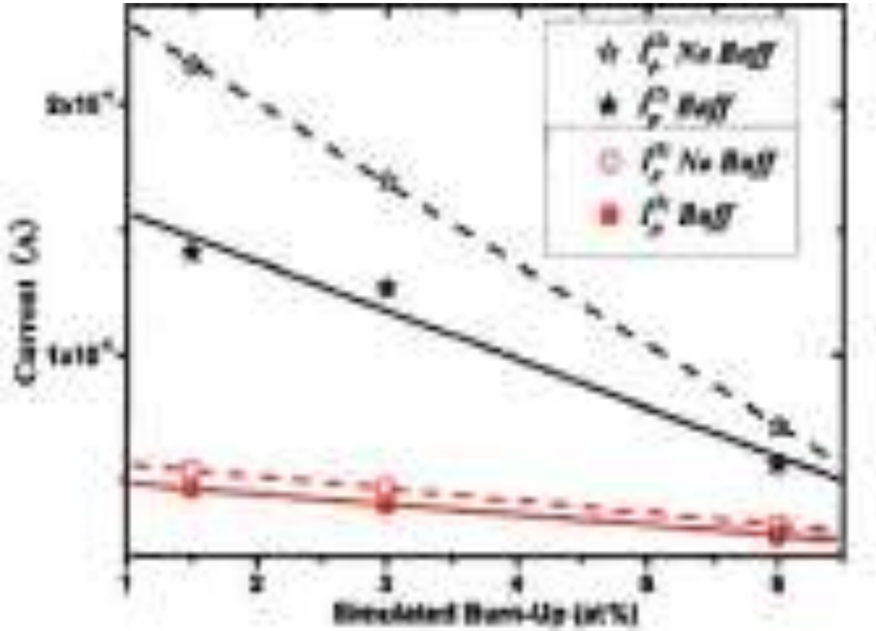
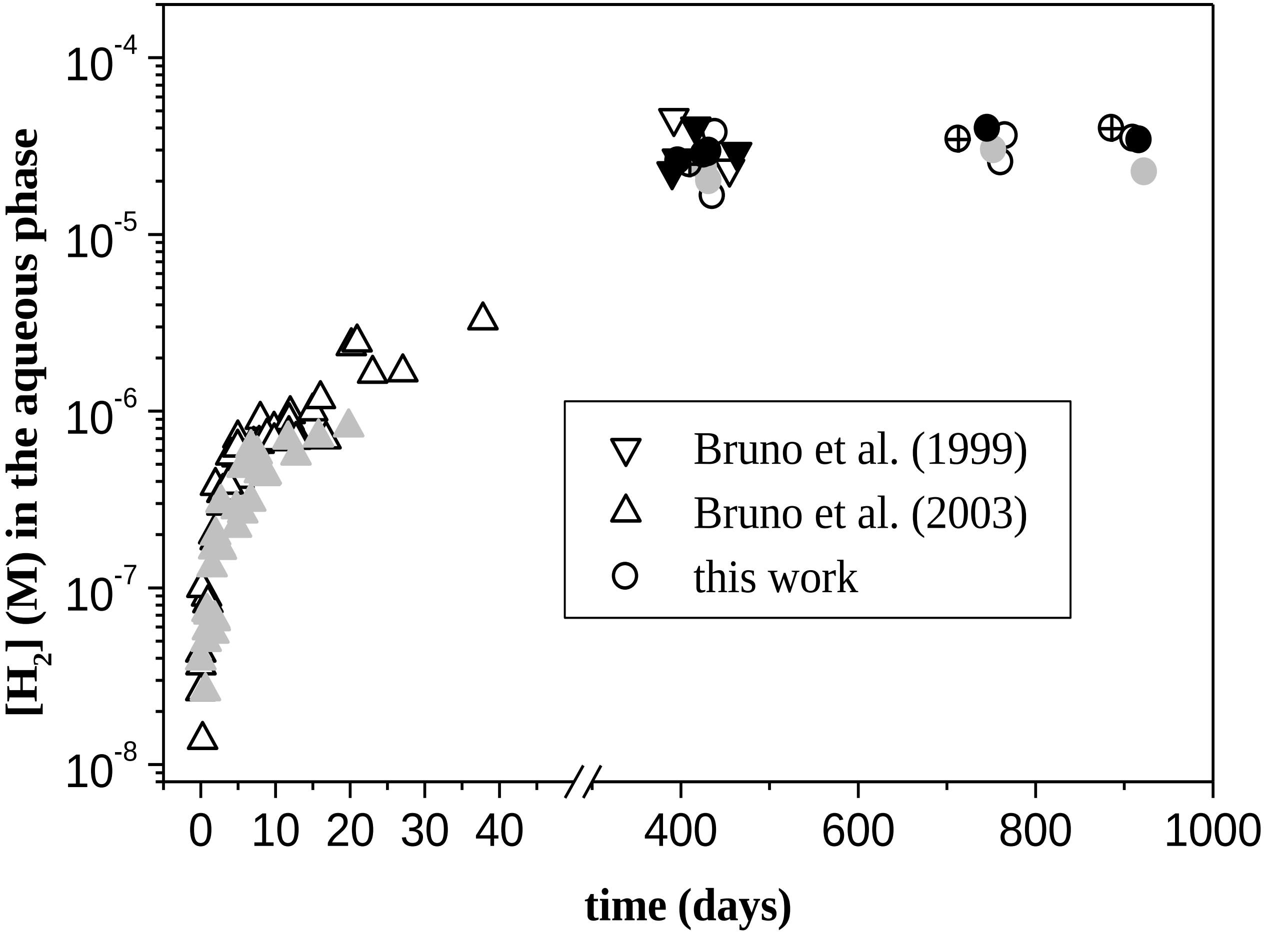


Fig. 7. Factor decrease of normalized dissolution rates from powder samples relative to undoped UO_2 as the dopant level of Gd_2O_3 is increased.

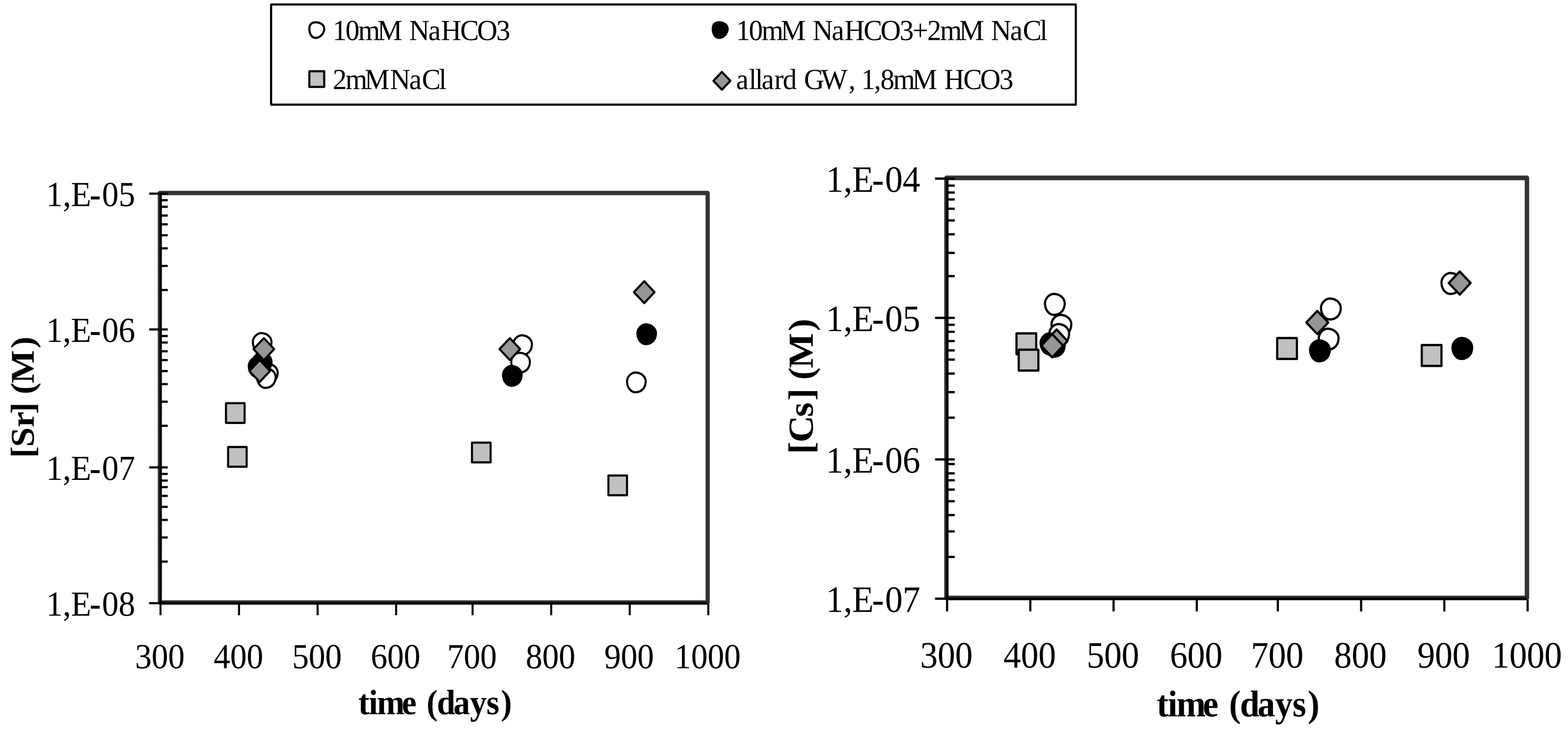


Current densities for oxidation ($UO_2 \rightarrow UO_{2+x}$, red) and dissolution ($UO_2 \rightarrow UO_2^{2+}$, black) as function of simulated BU.

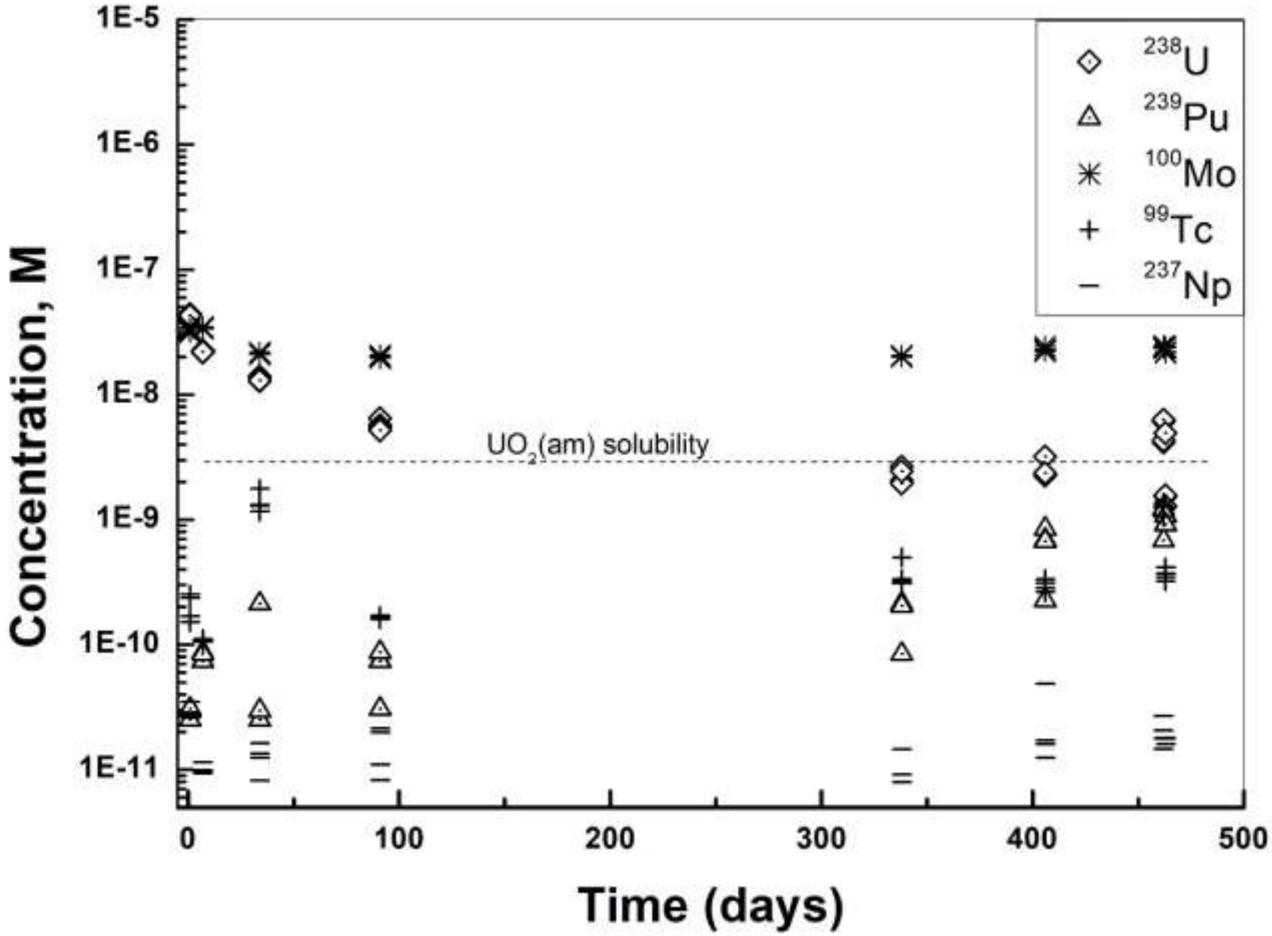
H_2 concentrations in long time leaching of fuel in sealed ampoules.



Sr and Cs concentrations during long term leaching of fuel in ampoules.



Concentrations of actinides and some FP



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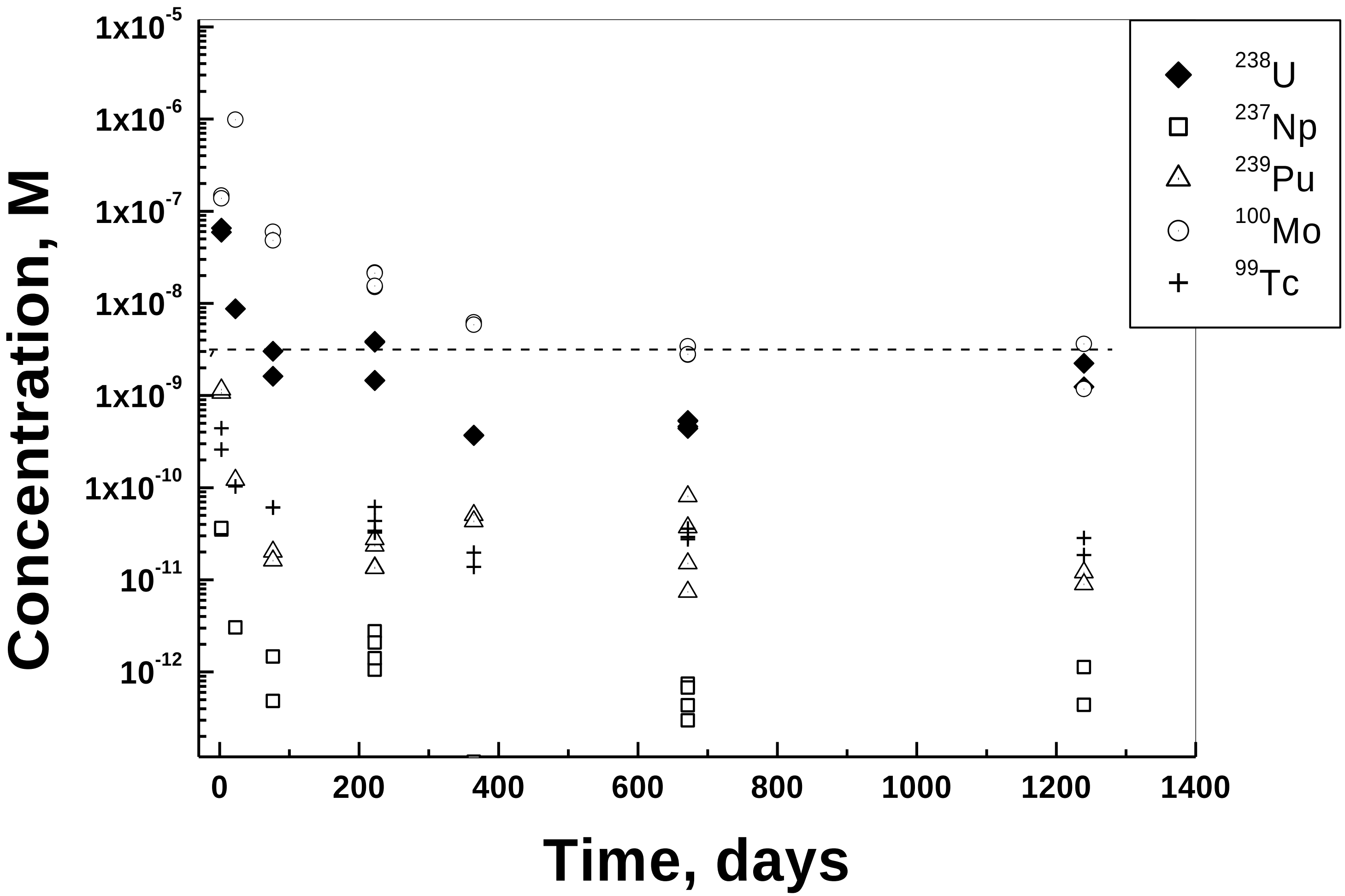
Leaching of fuel in presence of Fe(s) and Ar at start.



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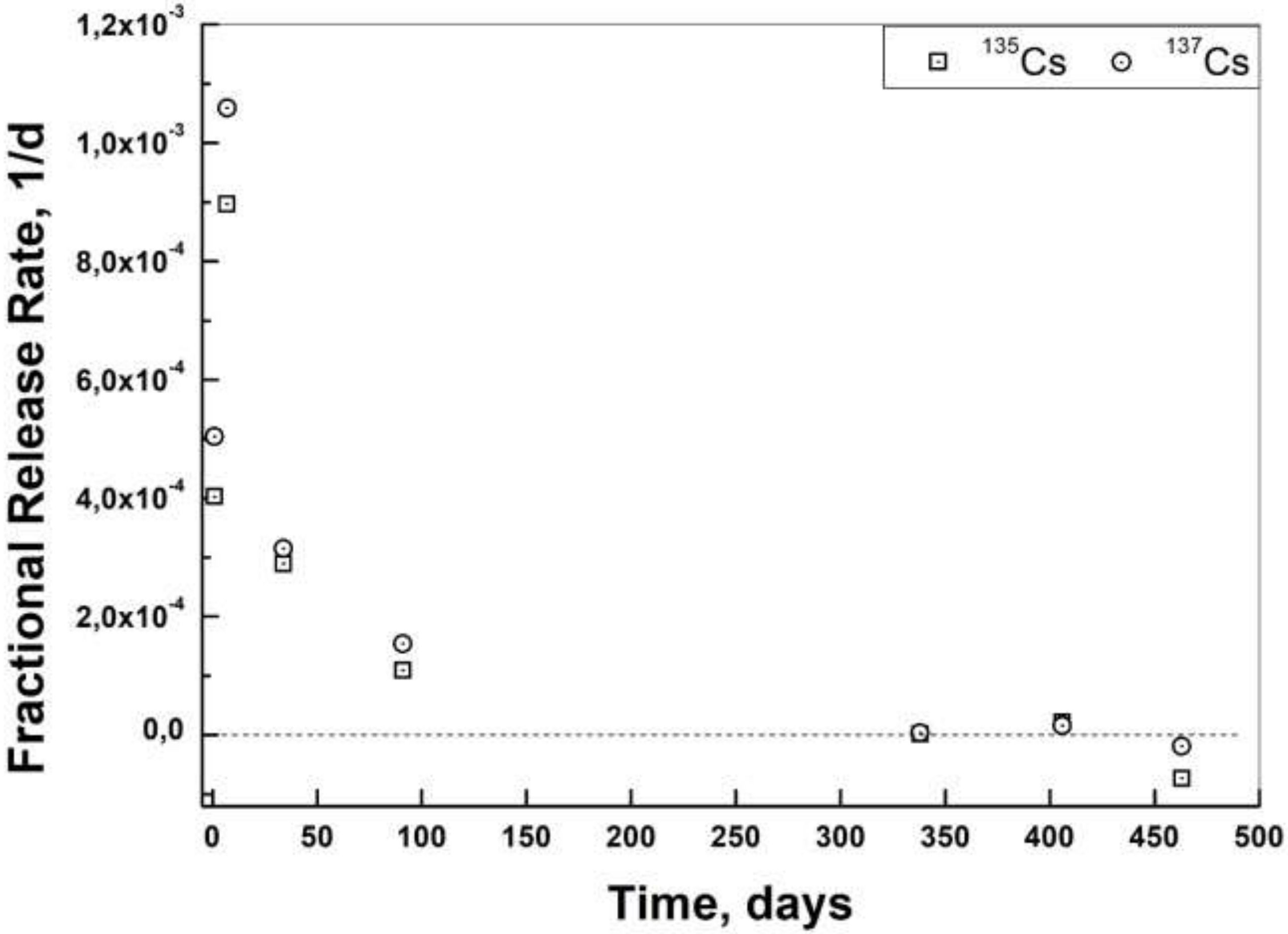
FRR of Cs from leaching of 75 MWd/kgU fuel under 50 bar H_2.



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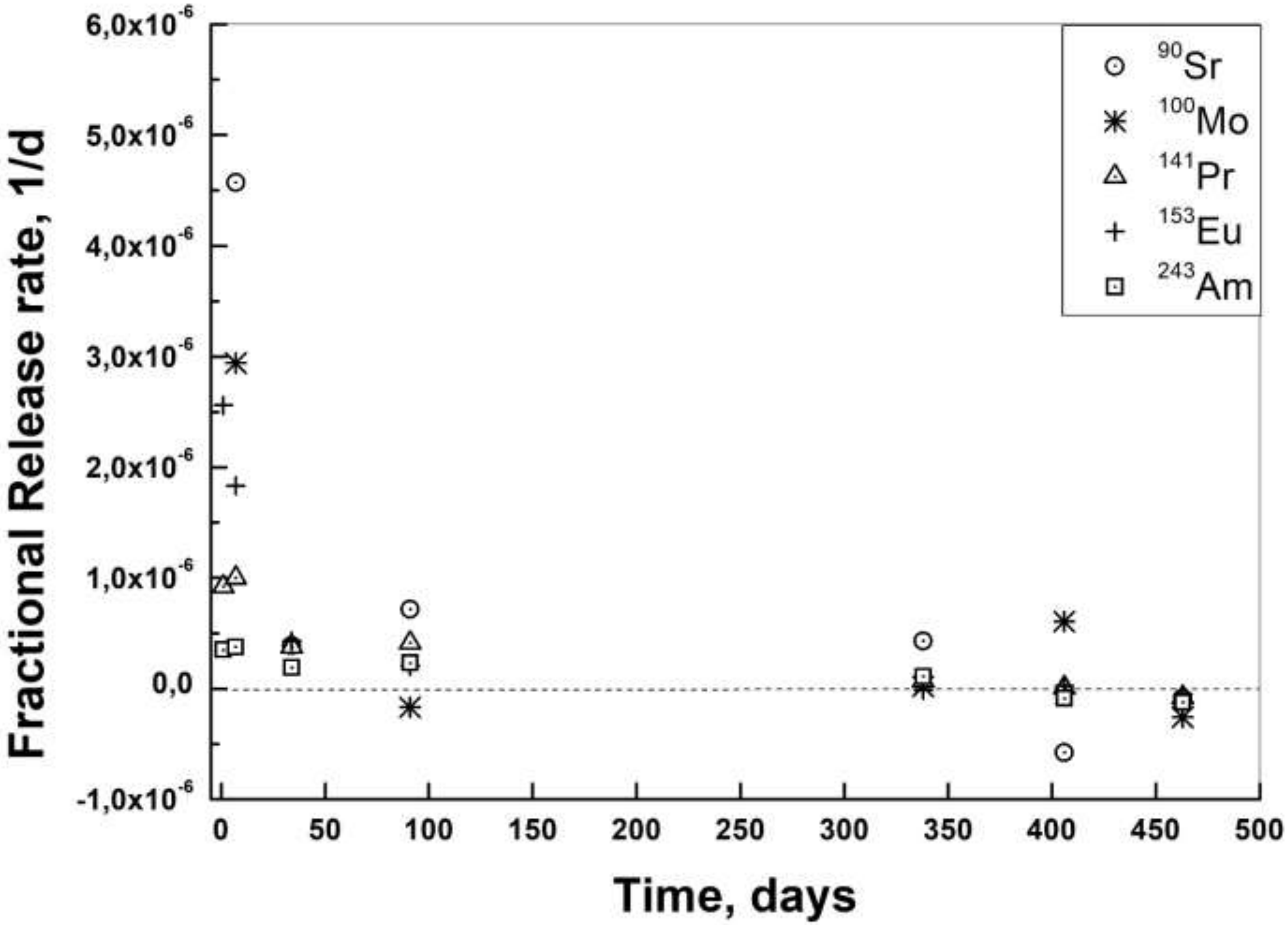
FRR from leaching of 75 MWd/kgU fuel under 50 bar H_2:



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