Direct disposal of spent nuclear fuel.
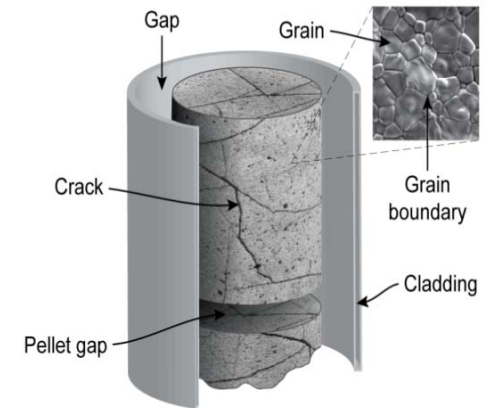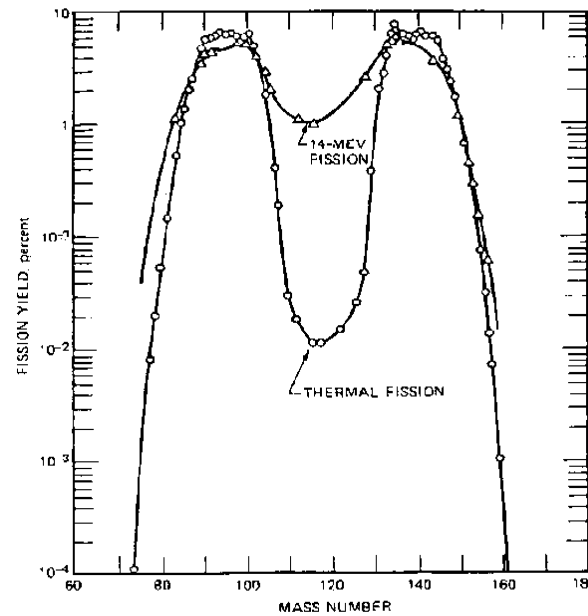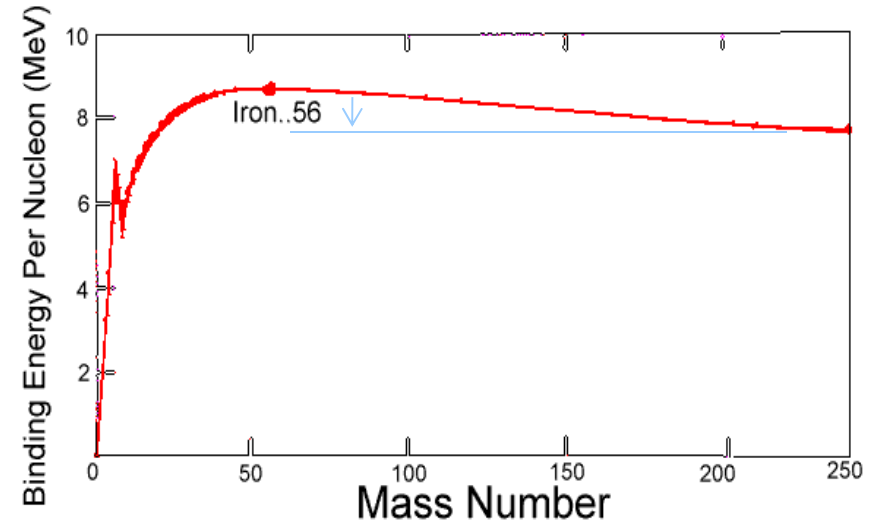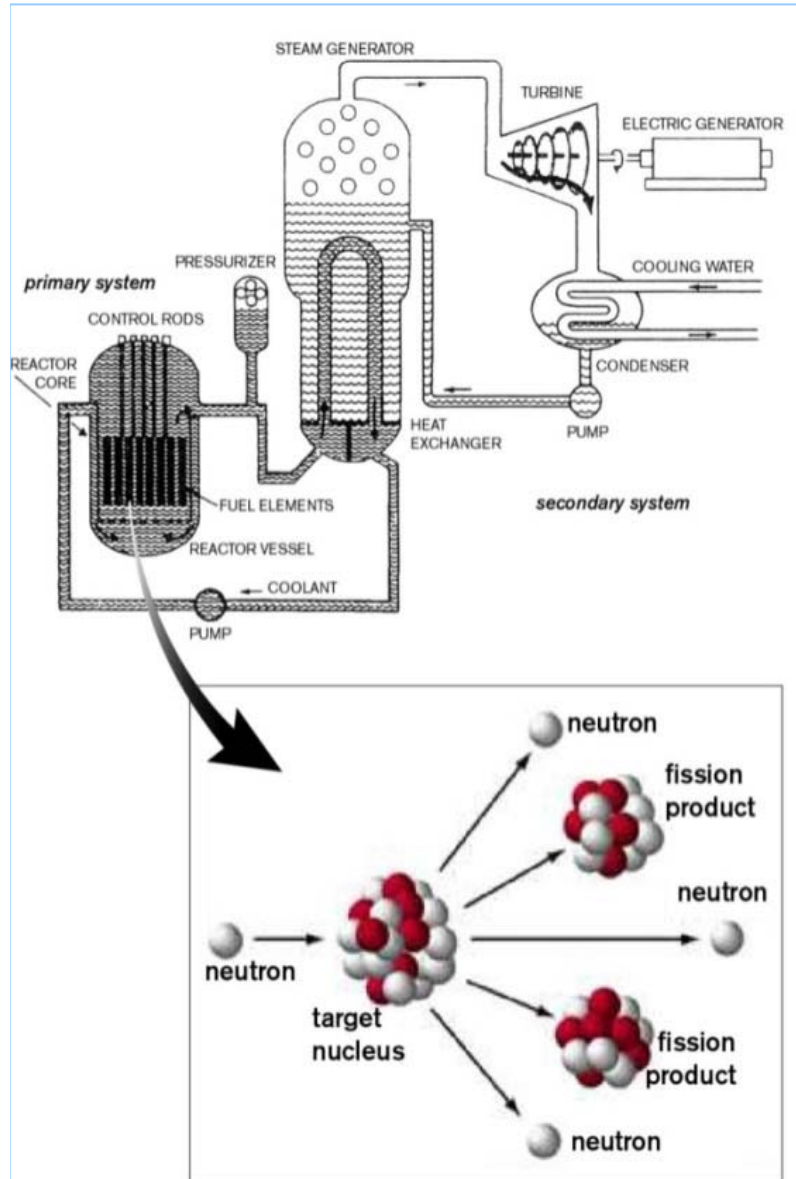
K. Spahiu, Chalmers, SKB

Lecture 2

What happens with fuel in a nuclear reactor?

Beginning of life

After 1 cycle

"Bambooing"

Gap closure - PCI
Stress concentration

Swelling due
to solid fission
products

Thermal stress cracks
"hourglassing"

(a)

(b)

(c)

Radial Direction

Tangential Direction

DHC crack

DHC crack
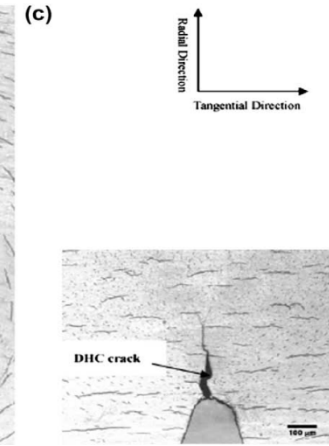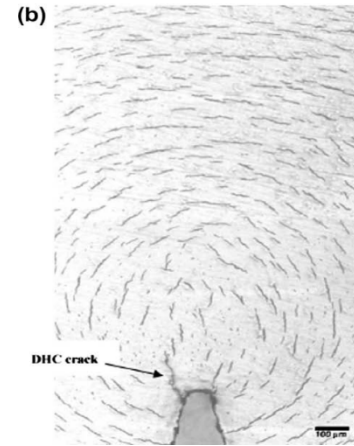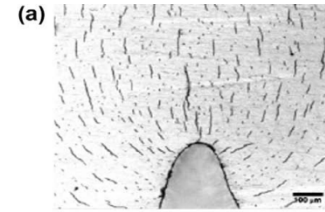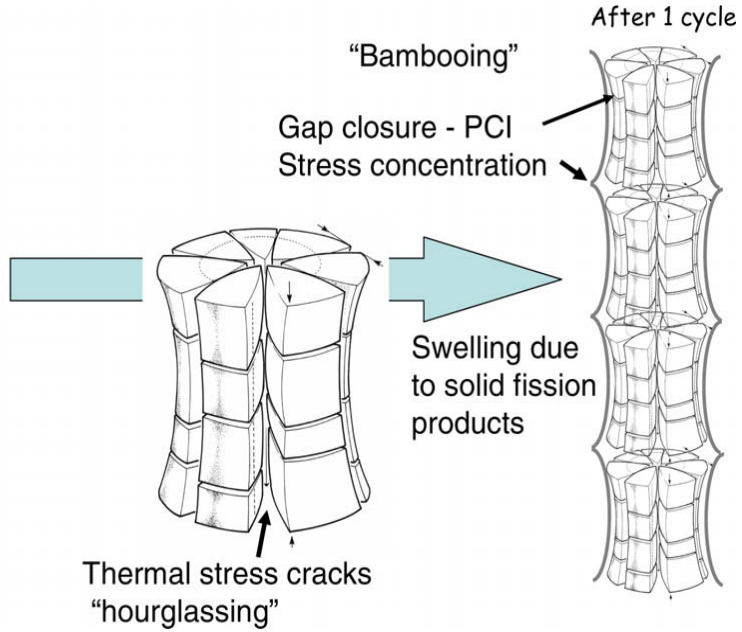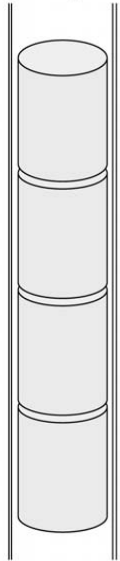
Gap closes due to
fuel swelling

Stress-corrosion crack

cladding

Chip off pellet

Fuel

220 μm
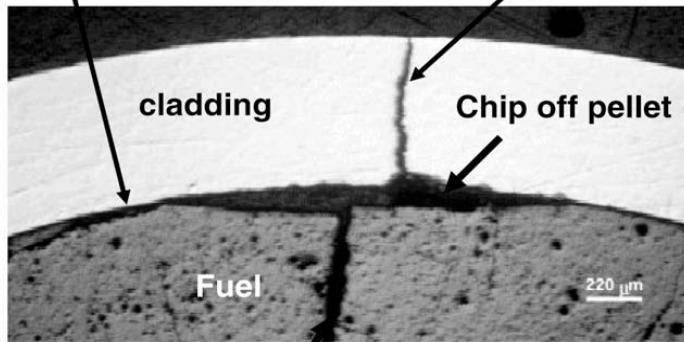
Thermal-stress crack (fission-product path)

BWR - Nodular corrosion
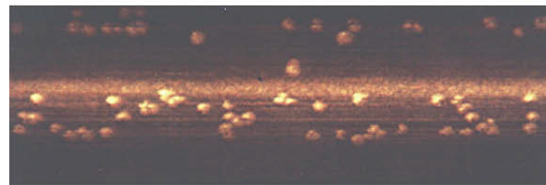
PWR – uniform corrosion + **CRUD**

Oxide scale

cladding

Hydride

UO_2 pellet

SKB
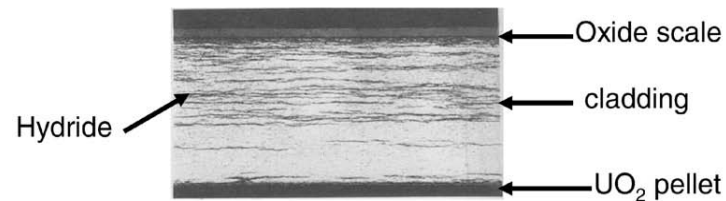
PWR fuel element and grid spacers.

CONTROL ROD GUIDE TUBE

I-BEAM ROD HOLDER

SPOT WELDS

SPRING CLIP ROD HOLDER

DIMPLE ROD HOLDER
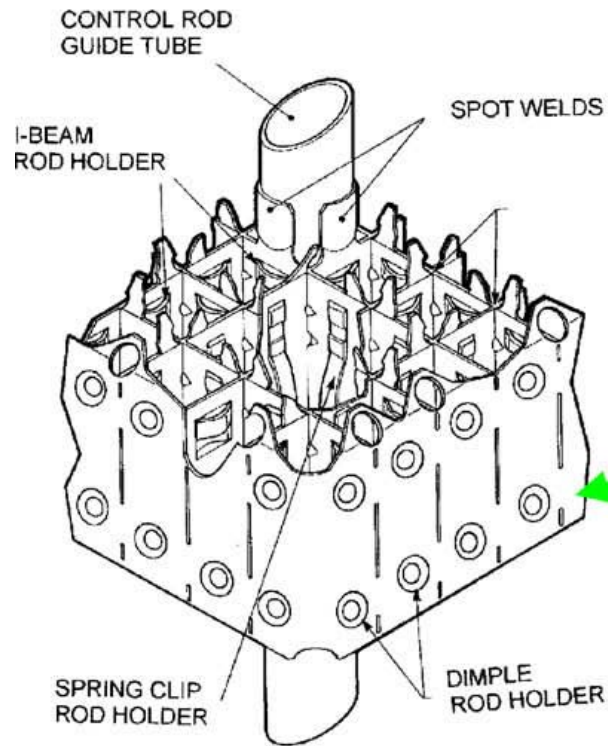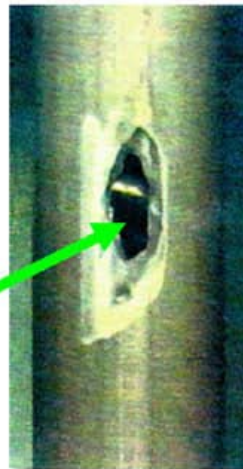
Fretting cladding breach (at grid spacer)

Grid spacers

Coolant out

Control rods

fuel assembly

Fuel rods

Coolant in

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Fuel in reactor: Clasification of fission products, Kleykamp 1985.

Neutron activation (metallic parts): $^{59}Co + {}^{1}_{0}n \longrightarrow {}^{60}Co$

Fuel: $^{14}N + {}^{1}n = {}^{14}C + {}^{1}p$, $^{35}Cl + {}^{1}n = {}^{36}Cl + \gamma$

Ellingham diagram for spent fuel
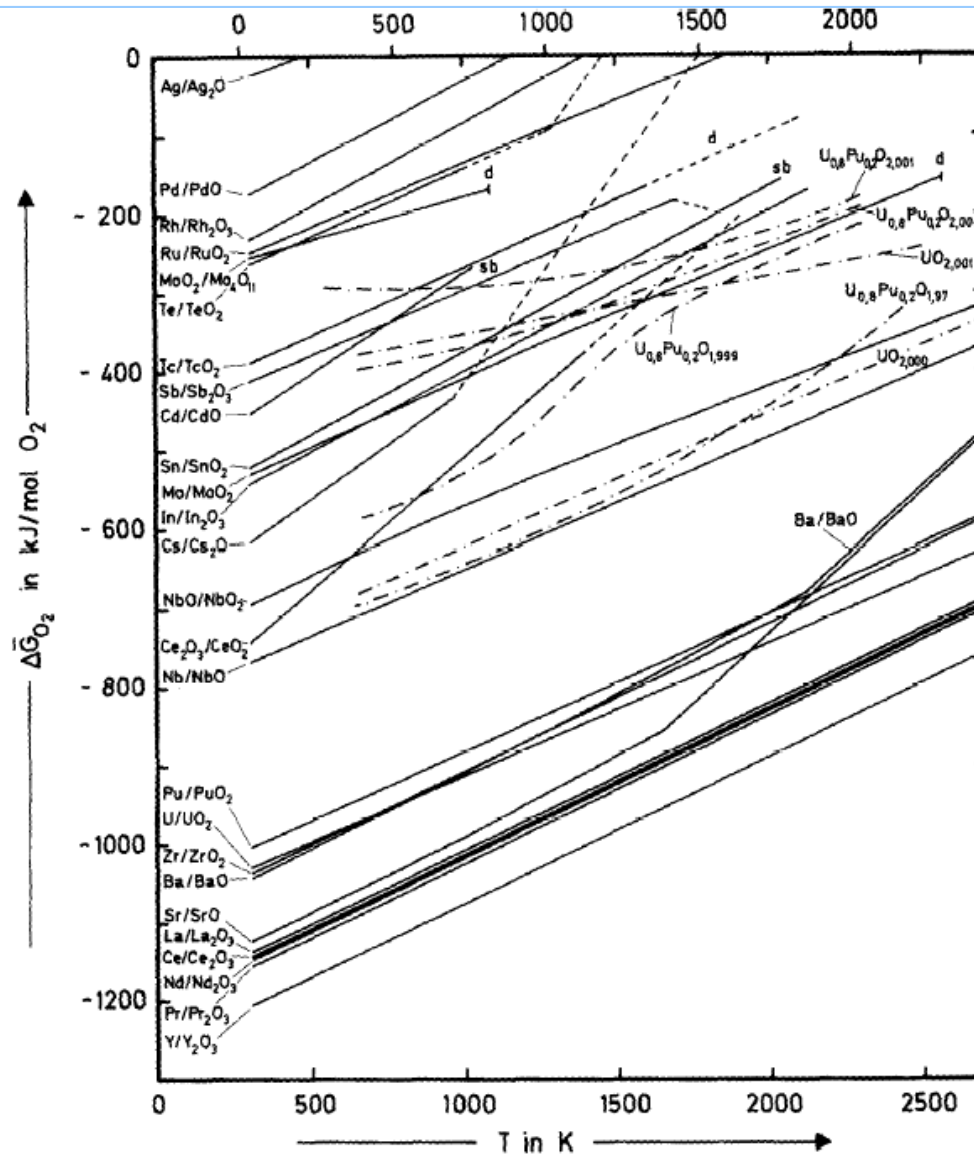
Fig. 2. Relative partial molar Gibbs free energies of oxygen of the fission product oxides and of UO_{2+x} and $U_{0.8}Pu_{0.2}O_{2\pm x}$, d: oxide decomposes, sb: oxide sublimes.
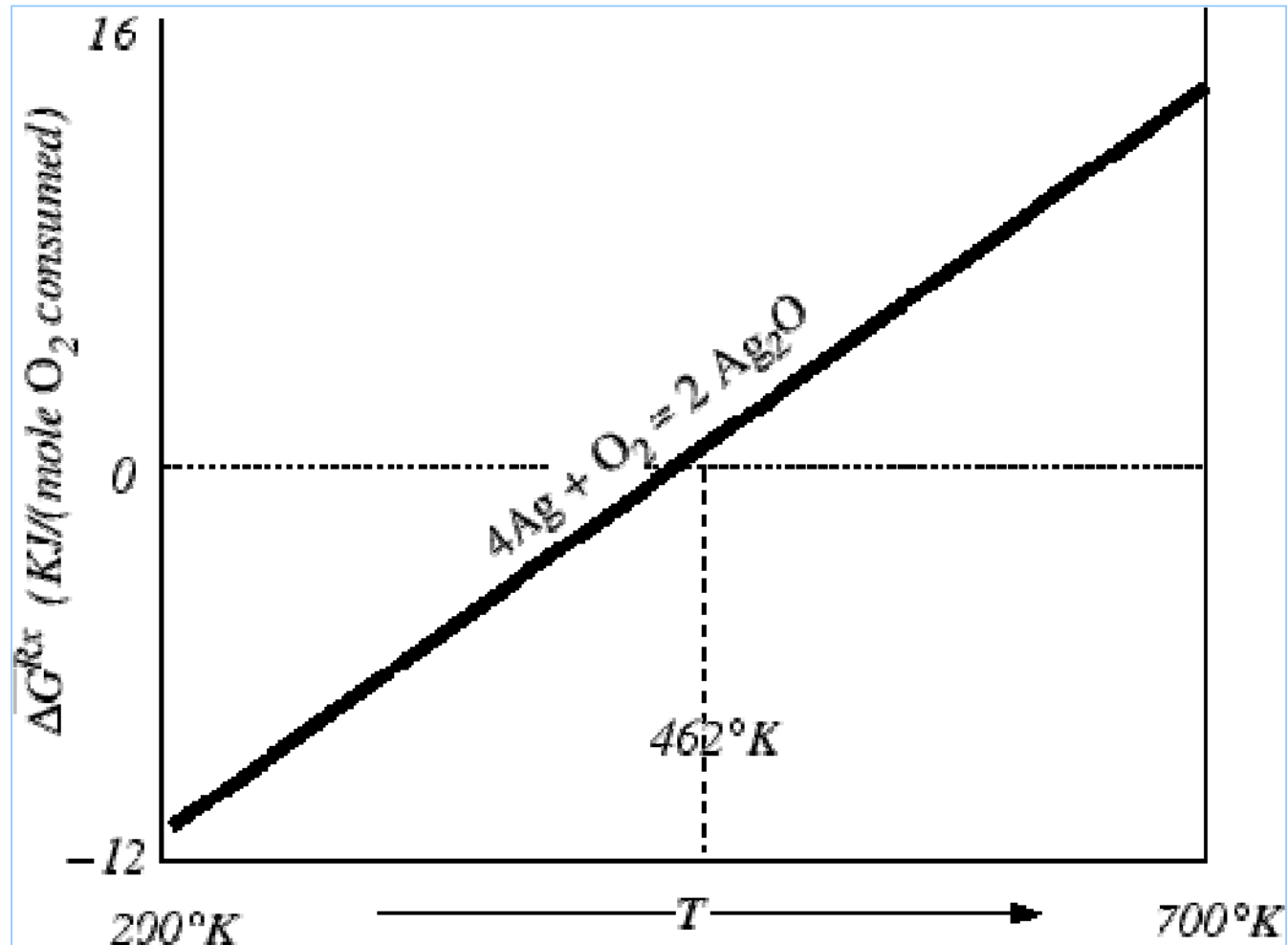
Graph of ΔG for Ag oxidation (per mole O_2) with intercept ΔH and slope –ΔS. Products favoured below 462 K (negative ΔG). $\Delta G = - RT \ln K_{eq} = RT \ln P_{O_2}$.

Burnup dependence of oxygen potential
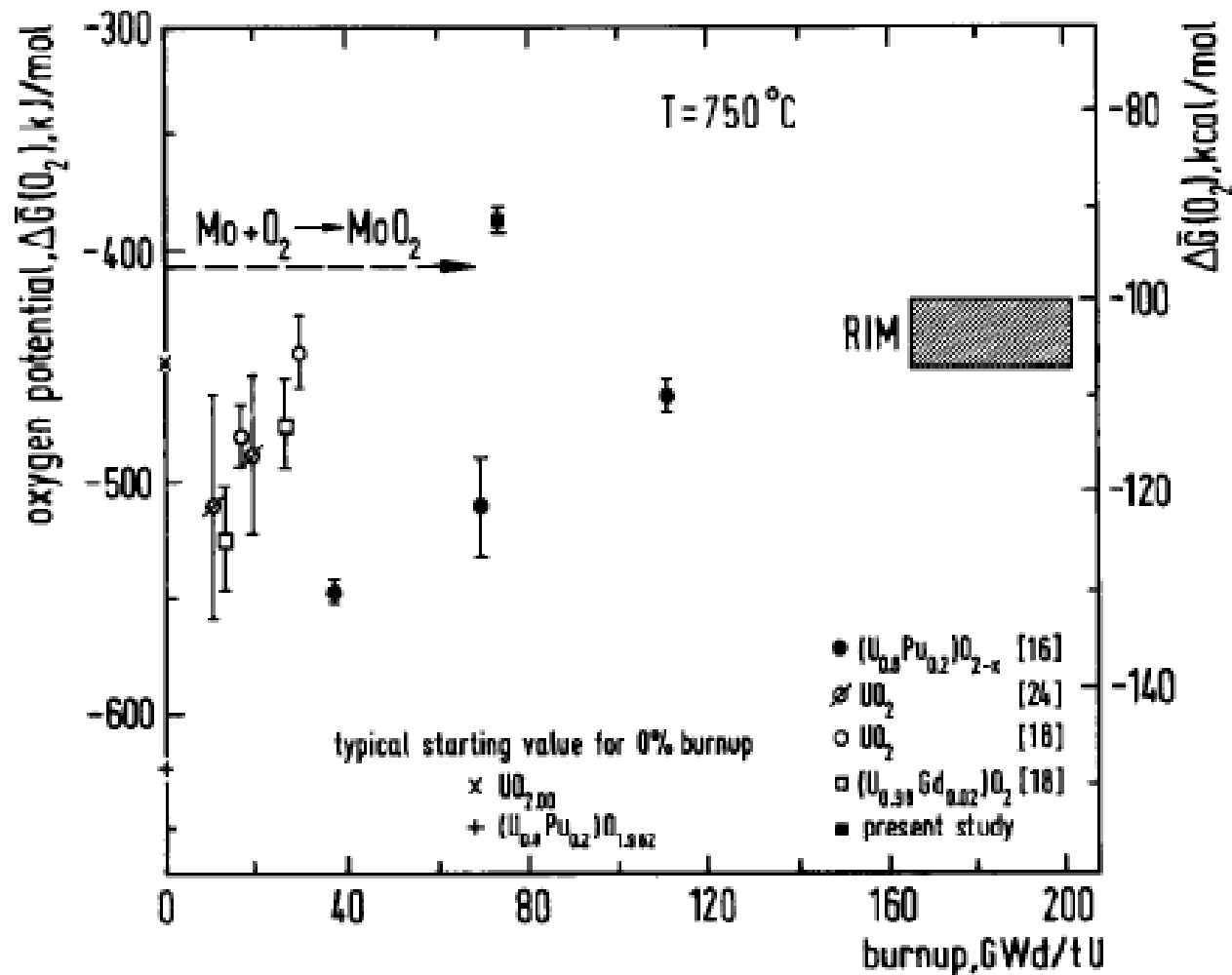
. Burnup dependence of the oxygen potential at 750°C for different irradiated oxide fuels.

H. Matzke, J. Nucl. Mater. 208(1994) 18-24.

Chemical state of fission products in fuel.

- The fission process creates fission products of valences lower than IV, e.g. Nd(III) or Sr(II). Their occupation of the place of an U(IV) should result in excess oxygen in the matrix. In this case the neighboring U atom is formally U(V), leading to stronger attraction and shortening of U-O distances. Similar effects observed for atoms such as Pu or Ce, which are easier reduced to Pu(III) than U. The lattice parameter of LWR fuels at constant O/M ratio decreases with increasing burnup.

- The oxygen potential of the fuel increases during burnup, but very little. No oxidation as increased x in UO_{2+x} is observed and oxygen potential is buffered around the values for $Mo(s)+O_2=MoO_2(s)$ equilibrium. At the end of the radiation, the fuel is nearly stoichiometric and the oxygen potential is slightly lower at the rim than in the center. At high temperatures, Zr of the cladding also acts as excess oxygen getter, forming $ZrO_2(s)$.

- Another important factor is the solubility of the newly formed oxides in $UO_2(s)$. Thus Ln_2O_3 oxides (RE oxides) are usually very soluble in $UO_2(s)$ even at high content, so the lanthanides are always in solid solution with UO_2 and do not segregate. ZrO_2 is very soluble in PuO_2, while its solubility in UO_2 is limited and temperature dependent. $MoO_2(s)$ is very little soluble in $UO_2(s)$ and the same holds for Tc, while Cs has a maximum solubility of about 1 at%. Sr is more soluble, up to 10 at%, while Ba is around 2 at% and Nb around 3 at%.

- It should be kept present that fissions create fission products in the whole pellet, then there is a very strong thermal diffusion gradient from the center towards the gap, where the temperature approaches this of the coolant. Gaseous fission products migrate from the center of the grain towards grain boundaries and further towards the gap. It is extremely important to have accurate diffusion rates at the given temperatures in order to judge nuclide distribution. For example, Cs(s) melts at 28.5 C and boils at 678.4 C; iodine melts at 114 C and boils at 184 C. These temperatures are low as compared to fuel temperatures in the reactor.

Chemical state of fission products in fuel (contd).

- Several other processes, such as e.g. radiation damage, should be considered while making thermodynamic predictions for the chemical state of fission products in fuel. Thus, CsI is never observed in spent fuel, even though it should form according to thermodynamic data. The same holds for $Cs_2(U,Pu)O_4$, predicted by phase studies in the Cs-U-O system, but never observed as a ternary oxide in spent fuel. The lower the O/M ratio and oxygen potential, the higher is Cs partial pressure resulting in transport to the gap. Diffusion coefficient of iodine is higher than this of Xe, and iodine releases are usually higher than these of Cs, which is partially dissolved in the matrix.

- Mo, Tc, Ru, Rh, Pd form metallic inclusions, called also "white inclusions" or ε-phase particles. Mo and Ru are the main components in ε-particles and both can migrate as $MoO_3(g)$ and $RuO_3(g)$. Pd metal has high vapor pressure and is not contained in particles according to its fission yield. These metallic particles are very important hydrogen catalysts during fuel dissolution under repository conditions.

- Zr is usually dissolved in UO_2 and distributed homogeneously. Sr is predominantly dissolved in UO_2, while only a small fraction of Ba-oxide is dissolved in UO_2; the majority of Ba is precipitated in "grey phases" perovskite type oxides $(Ba_{1-x-y} Sr_x Cs_y)(U, Pu, Zr, Mo, RE)O_3$. Grey phases are typical for fuel which has experienced very high temperatures, usually not observed in standard LWR fuel. Sr content in the grey phases increases with a decrease of the local oxygen potential.

- Other phases occur in the gap between fuel and cladding by condensation of volatile fission products and by chemical interaction of fission products with cladding (e.g. $ZrI_4(s)$ or $ZrH_x(s)$).

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The instant release fraction

- During irradiation in the reactor, a certain percentage of the RN inventory has **segregated** to the gap between the fuel and the cladding and also to grain boundaries. Of these RN, the behaviour of fission gases is best known and a number of studies on FGR has been published. The behaviour of other potentially segregated nuclides is far less well known and this is a concern, because they will be released more rapidly than the ones embedded in the fuel matrix.

- The radionuclide fractions released to the fuel/cladding gap and to grain boundaries are somehow improperly referred to as "Instant Release Fraction", IRF. More appropriate would be "Rapid Release Fraction" since the release from the grain boundaries may continue for extended periods of time. For PA purposes, both fractions are frequently treated as instant release.

- There are relatively few systematic studies of the release of segregated material other than fission gases from fuel. In the Canadian program, Stroess-Gascoyne(1996) published data on the rapid release of ^{137}Cs, ^{90}Sr, ^{99}Tc, ^{129}I and ^{14}C from Candu fuel. Much less studies were available in this period for LWR fuel, the situation is somehow better after 2000. A couple of recent studies will be described.

- 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. For some RN, assuming a 1:1 relationship will be a reasonable assumption, for others the relationship may be more complex-to be discussed later.

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The instant release fraction

- Based on literature data (Johnson&McGinnes 2002), the following RN need to be considered for rapid release after 1000 y-in parenthesis their half-life in years:

$$^{14}C(5.73\cdot10^3),\ ^{36}Cl(3.0\cdot10^5),\ ^{79}Se(3.77\cdot10^5),\ ^{99}Tc(2.1\cdot10^5),\ ^{107}Pd(6.5\cdot10^6),$$

$$^{126}Sn(2.3\cdot10^5),\ ^{129}I(1.57\cdot10^7),\ ^{135}Cs(2.3\cdot10^6)$$

- The two first originate mainly from neutron activation of nitrogen and chlorine impurities in the fuel. Selenium would be volatile as Se(s), Tc and Pd are certainly segregated in metallic particles, while I and Cs are partially accumulated in the gap.

- Very few data are available on ^{14}C releases from LWR, Johnson&Tait proposed 10% as bounding value and 5% as best estimate. The EU-project CAST expected to improve the situation.

- There are almost no data on ^{36}Cl release from LWR fuel, therefore the data of J. Tait on releases from Candu fuel are used to estimate its releases.

- The release fractions for **Tc** and **Pd**, which are part of the metallic ε-particles are assumed as for Candu fuel (Johnson&Tait), with a best estimate 0.2% and bounding value 1% of the inventory as IRF.

- The data of Wilson(1990), PNNL, USA report "less than" values for ^{126}Sn, indicating no real evidence for Sn segregation at low to moderate burnup. The vapor pressure of tin is relatively low($10^{-3.3}$ atm. at 2000 °C), hence tin may be part of metallic particles. Thus for both ^{121}Sn and ^{126}Sn best estimate is 0.03% and a bounding value of 0.1%.

- The radionuclides $^{129}I, ^{135}Cs, ^{137}Cs, ^{108m}Ag$ and ^{113m}Cd a 1:1 correlation with FGR is used pessimistically. The gap and grain boundary fraction of ^{108m}Ag and ^{113m}Cd is negligible as compared to the releases from control rods.

- ^{79}Se is a typical example where new data on its characterization in the spent fuel as Se^{2-} ions substituting oxygen atoms in the fuel lattice give support to the below detection limit values measured and to discarding it as an IRF member in the future. EXAFS data obtained by E. Curti et al. 2015.

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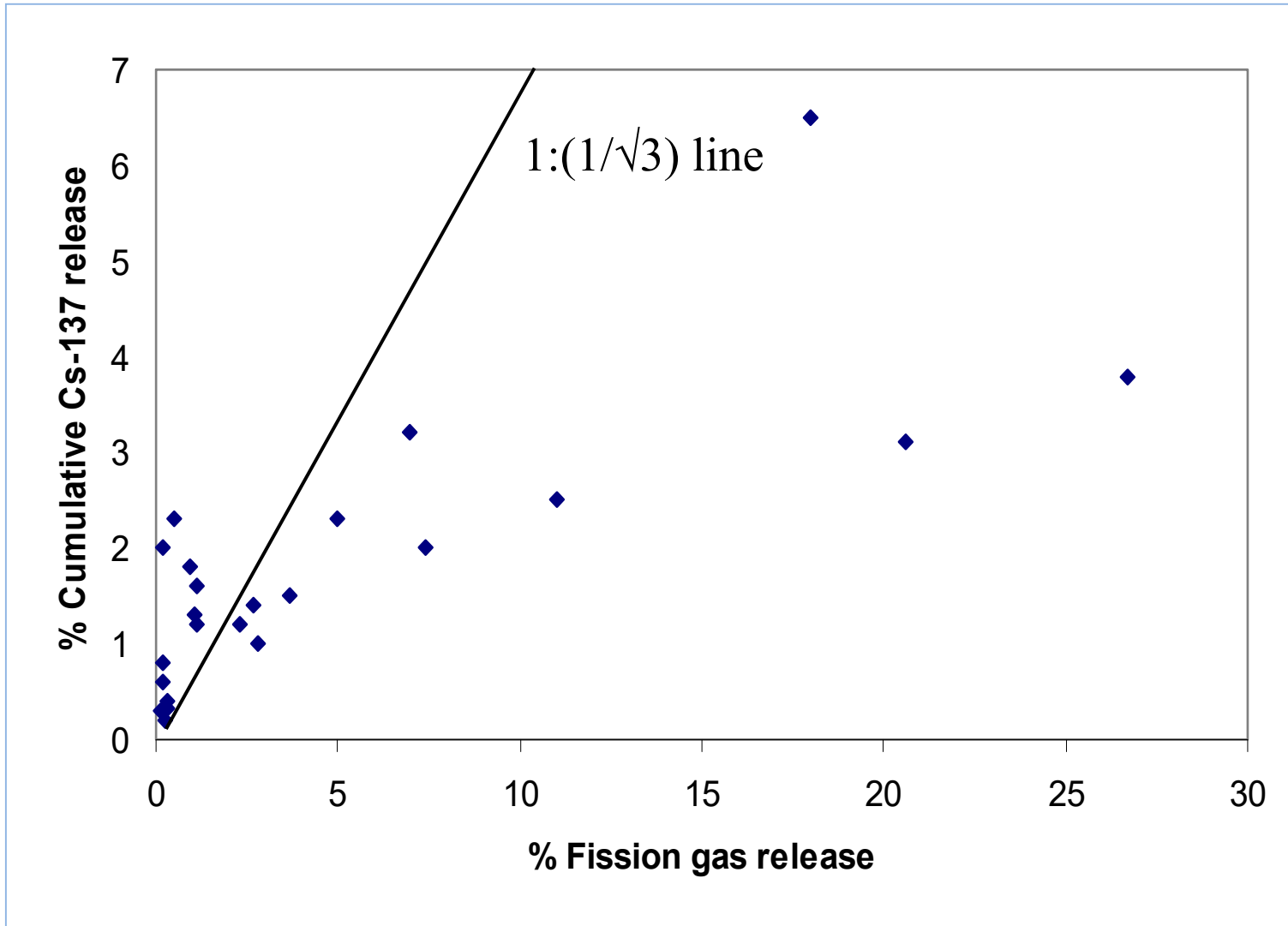# Cumulative RF vs Cumulative Contact Time
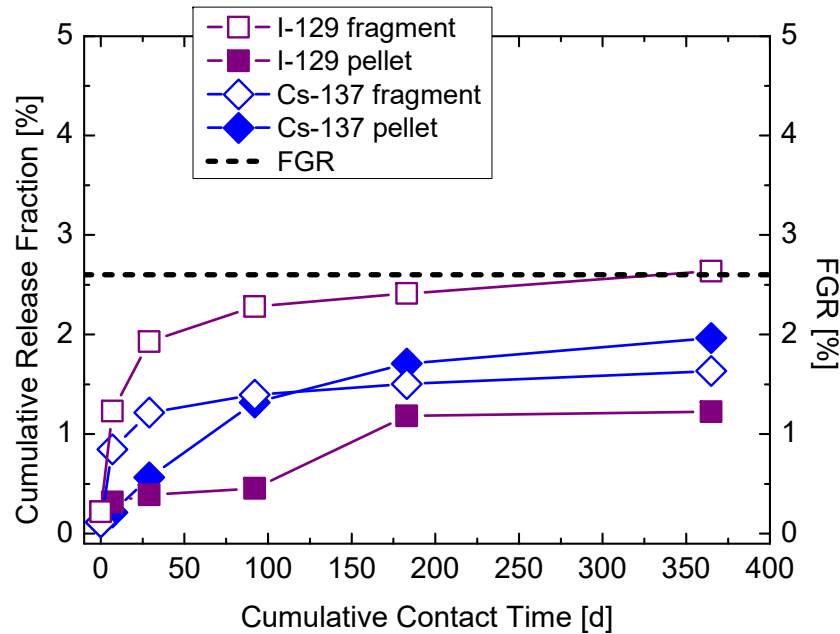
66.5 MWd/kgU fuel samples
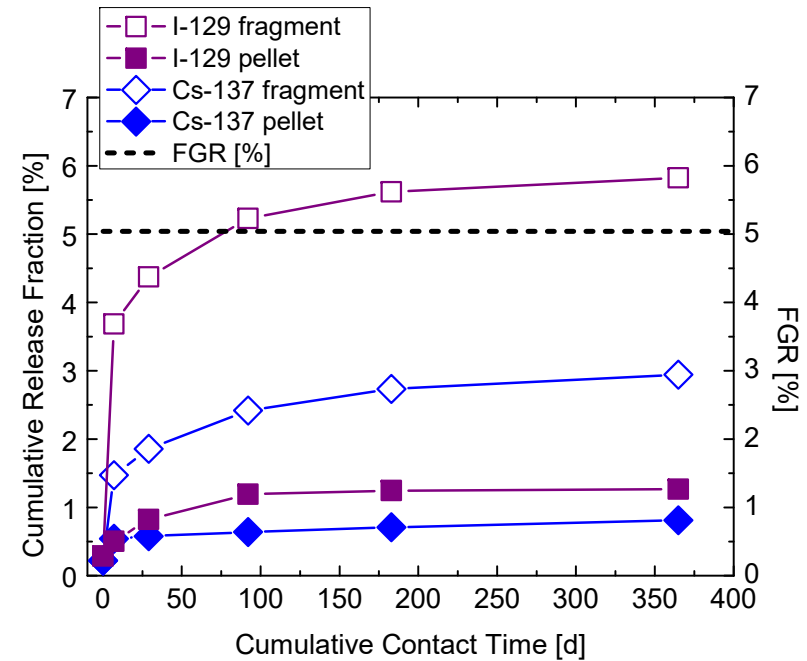
75.4 MWd/kgU fuel samples

- Cumulative RF of ^{129}I and ^{137}Cs levels out with time.

- The ^{129}I release approaches the FGR value.

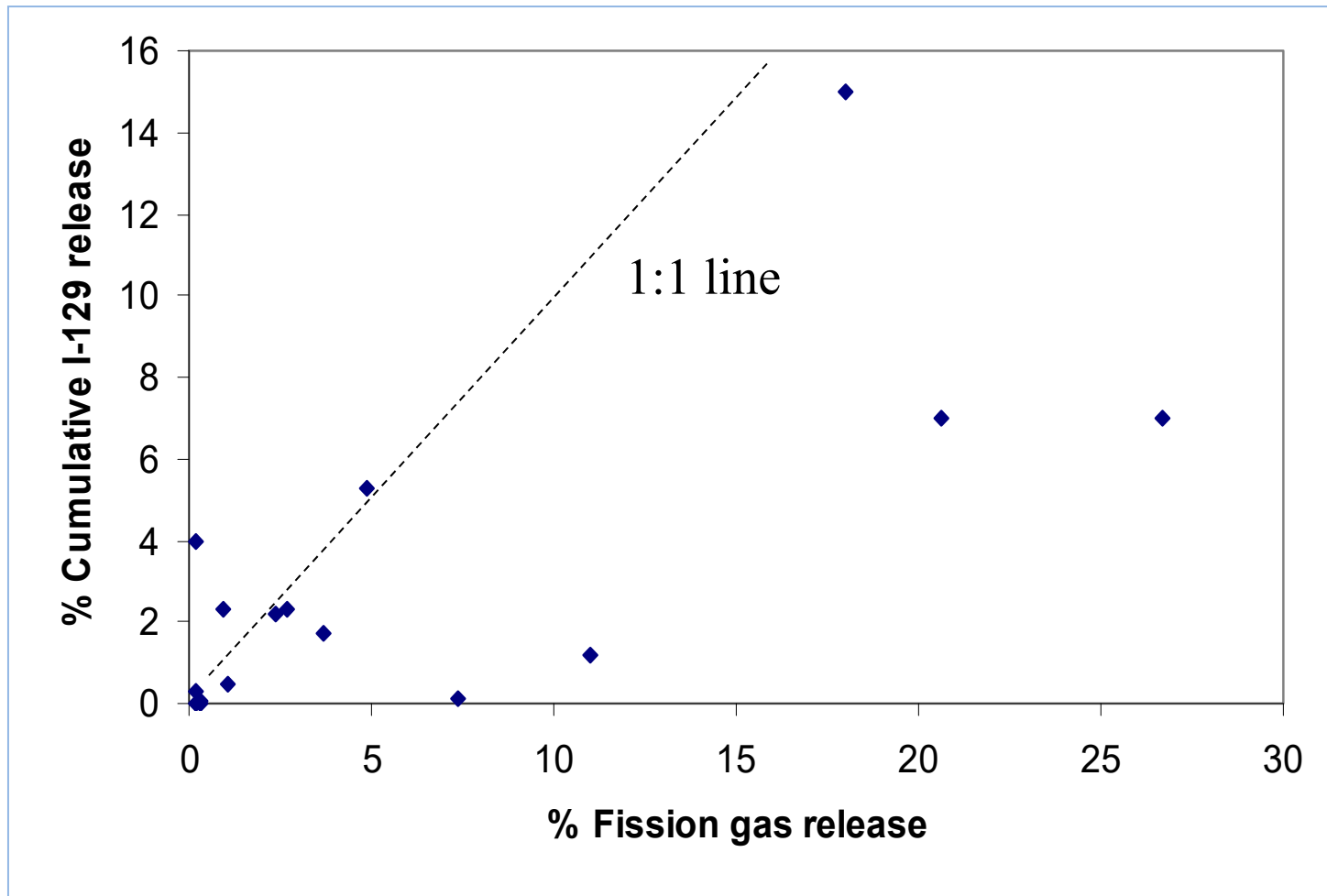- Lower RF for pellet samples than for fragment samples (75 MWd/kgU)

All data for Cs, including HBU data and MOX

$1:(1/\sqrt{3})$ line

% Cumulative Cs-137 release (y-axis)

% Fission gas release (x-axis)

$D_{Cs}/D_{Xe} = 0.33$ (Lassman et al., Fission gas behaviour in water reactor fuels, pp. 321-334, NEA 2002)
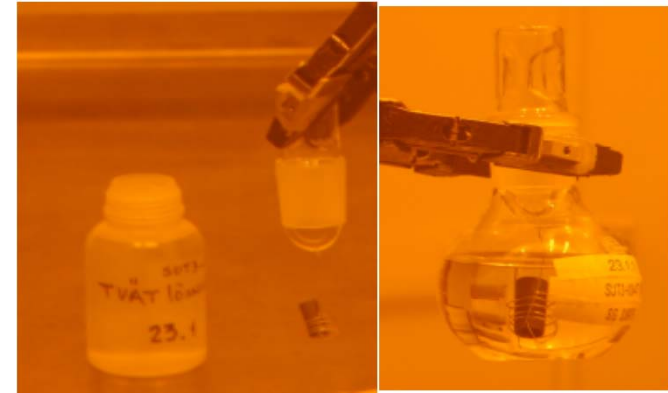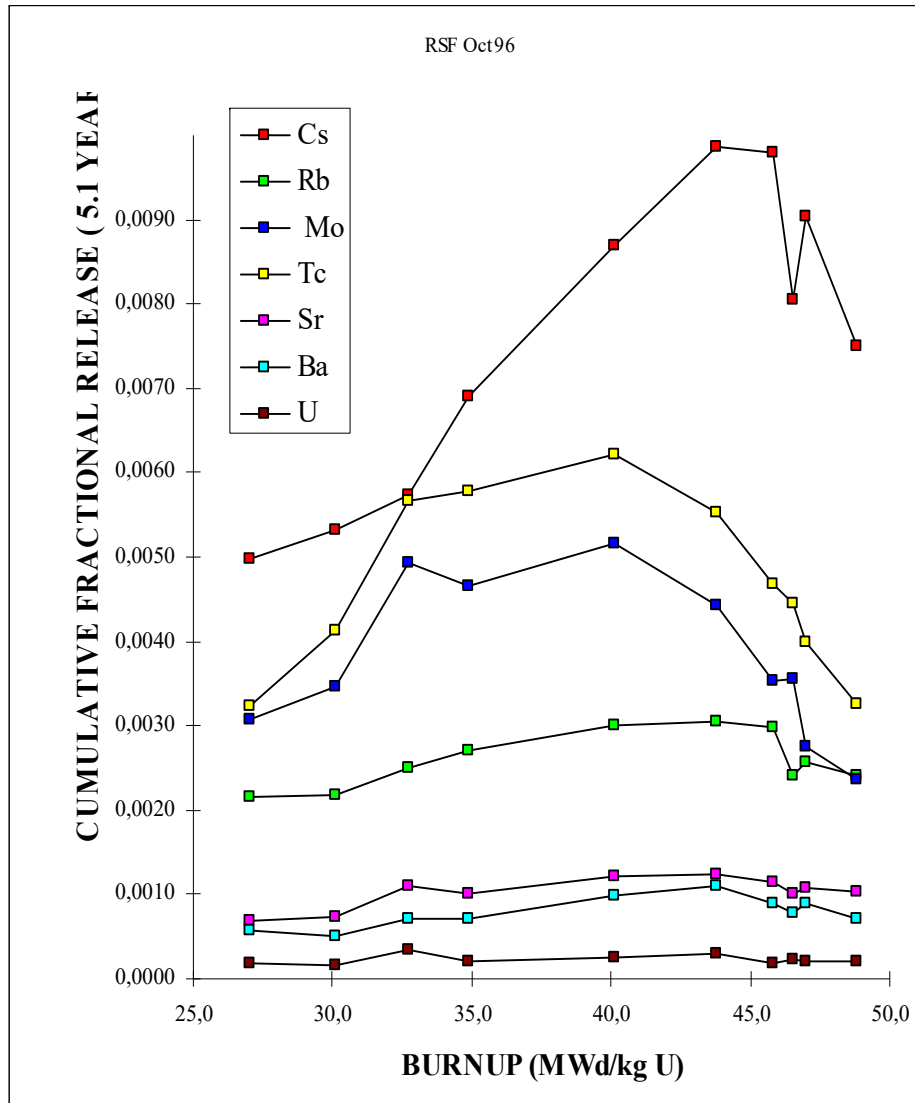
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FGR vs. I-129 release


All available data for iodine release

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# Releases during 5 years as function of burn-up (1997)-series 11.

- 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.

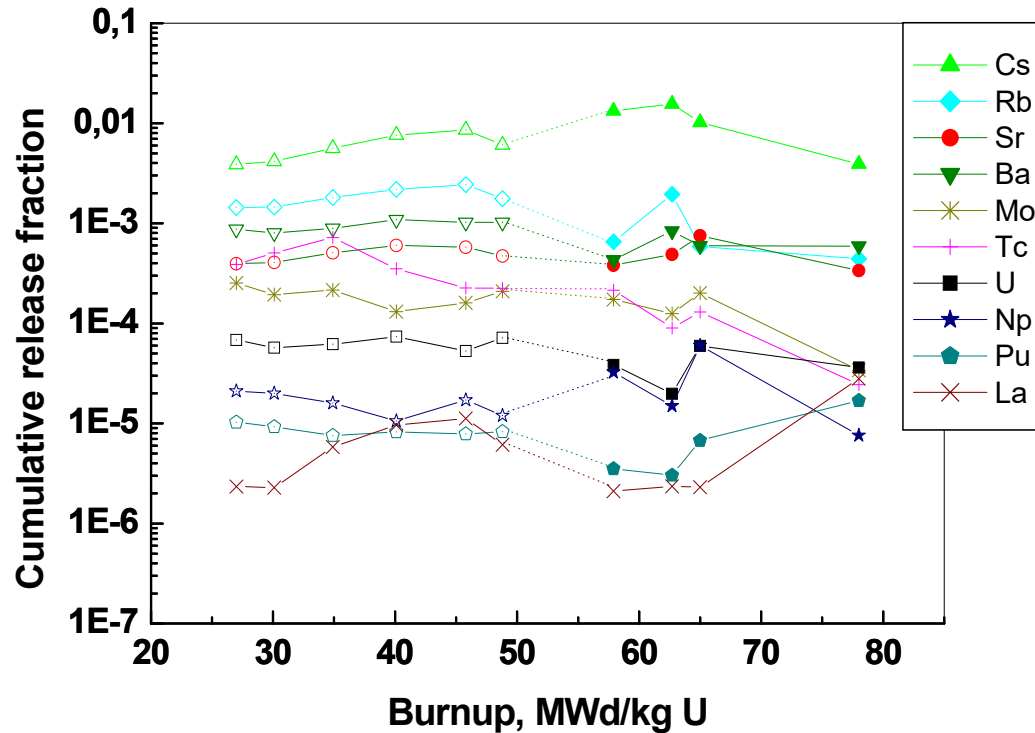- Release fraction = $X_{\text{Leach solution}} / X_{\text{Inventory}}$
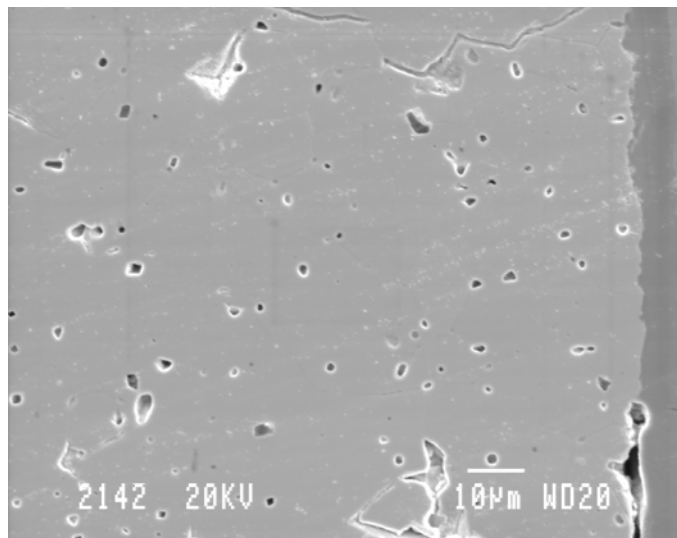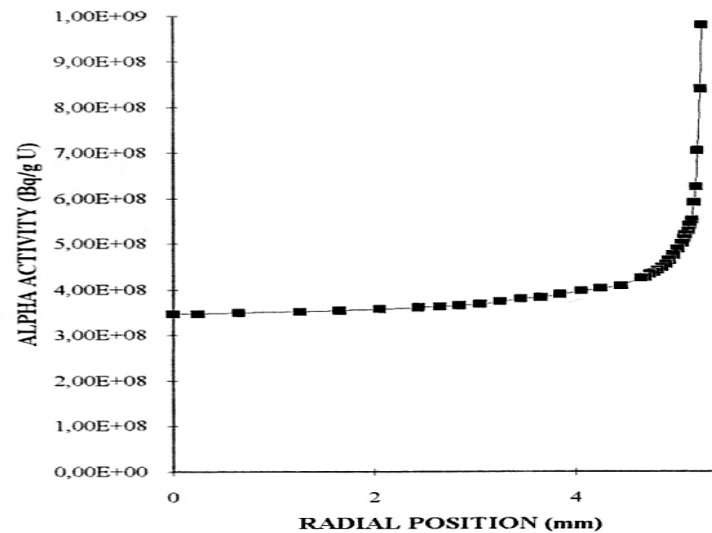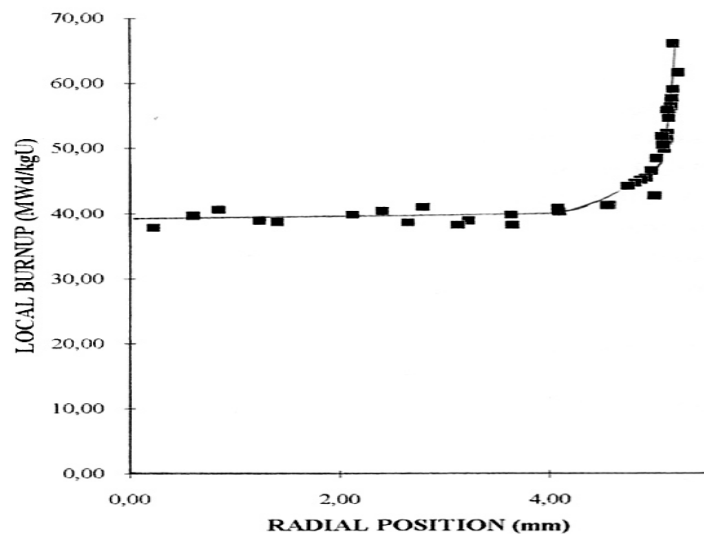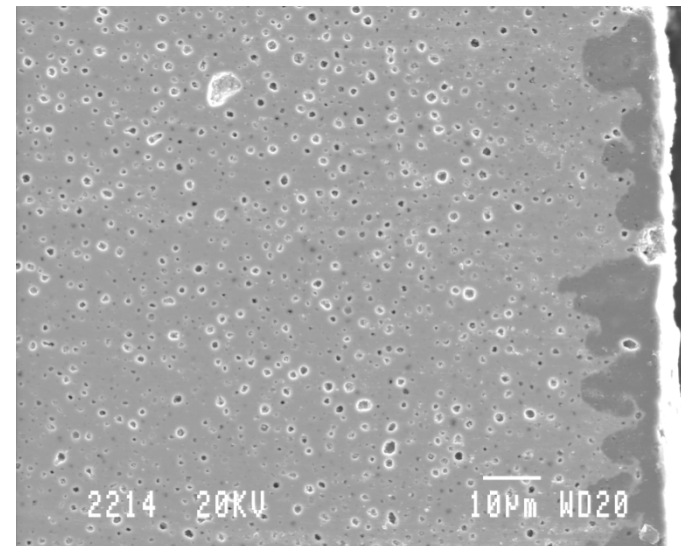
Results for 4 fuel samples, BU= 57.9, 62.7, 65 and 75.4 MWd/kg U

a)Cumulative release fractions vs. burnup for 182 days.

b) Concentrations as function of burnup
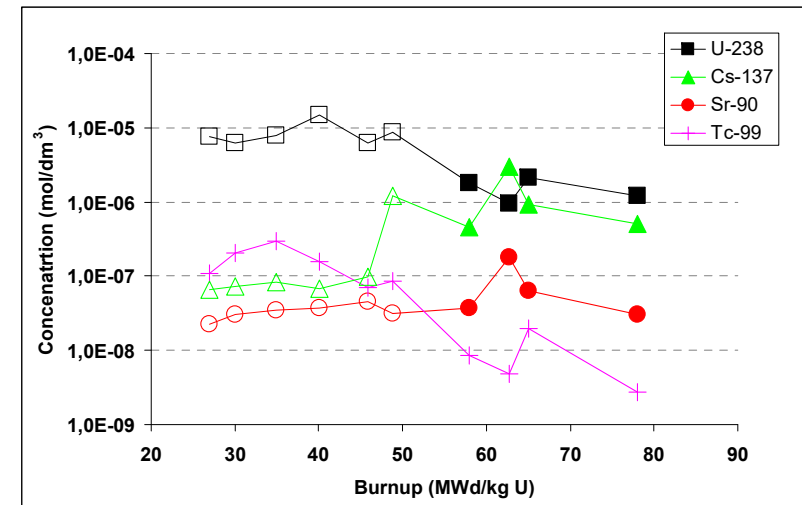
•No secondary U mineral phases expected to affect U releases under 92 days (fourth contact period).

- Cs releases are higher than series 11(IRF increase).
- Sr, Ba and Rb releases quite similar to series 11.
- U releases are lower than series 11.
- Mo and Tc releases are lower – probably closed gap?

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

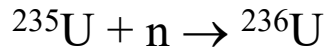$$^{235}U + n \rightarrow 2 \text{ fiss.products} + 2\text{-}3 \text{ n}$$
$$^{235}U + n \rightarrow {}^{236}U$$

• $^{236}U/^{235}U$ ratio increases with the irradiation process due to the above processes.

• Higher in the rim zone (burnup up to 2.5 times higher than the pellet average*)

• Increase in the $^{236}U/^{235}U$ ratio in solution with number of contact periods (the same observed for series 11).

• Series 11; $^{236}U/^{235}U$ is below the pellet average   ratio $\Rightarrow$ less corrosion in the rim zone and increases towards average value.

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

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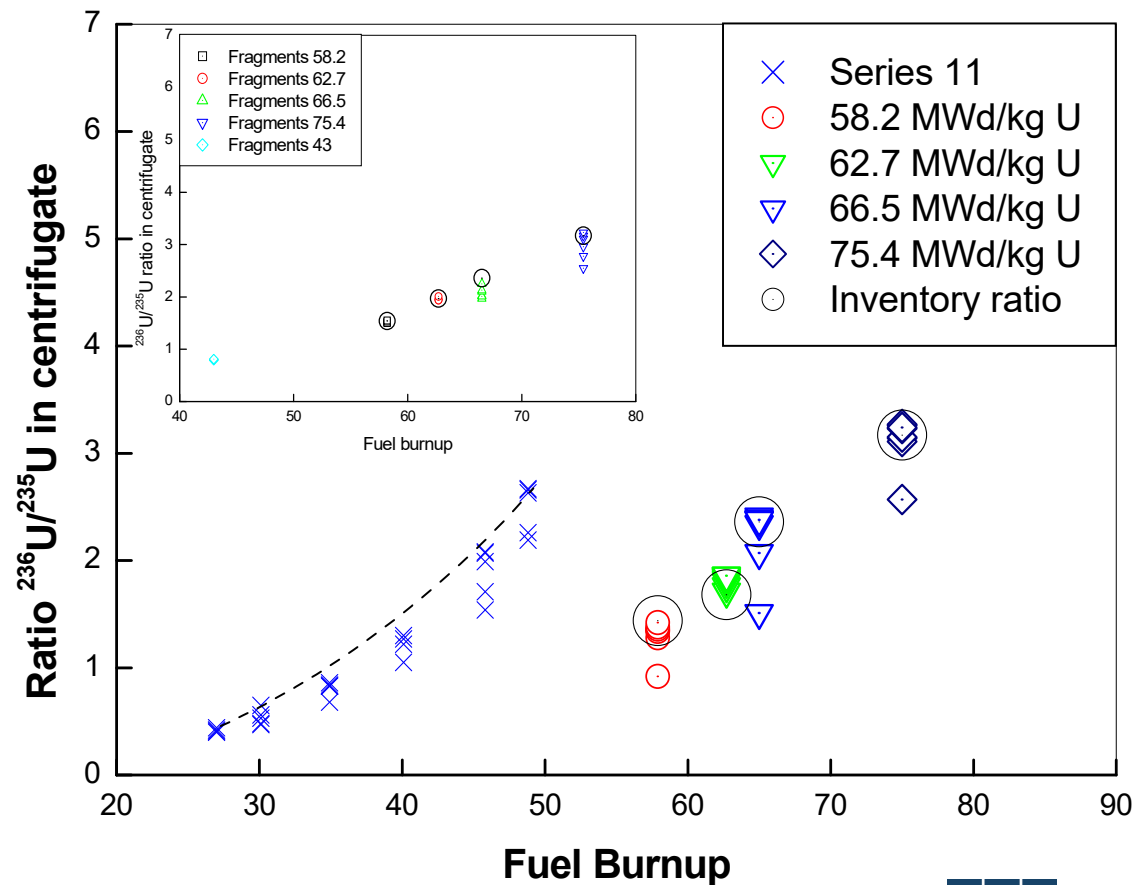
Burnup influence on fuel oxidation and leaching

- It is clear that increased burnup, especially combined with high power rating, causes higher IRF.

- A few systematic studies on oxidative **fuel dissolution** as function of burn-up show similar trends, i. e. samples of intermediate burnup 37-44 have highest releases of matrix bound nuclides.

- Jegou et al. J. Nucl. Mat. 326 (2004) 144-155 **:** Sr releases in static leaching UOX fuel pins of 22, 37, 47, 60 MWd/kgU burnup in carbonated groundwater were highest for 37 and lowest for the 60 MWd/kgU sample.

- B. Hanson, Proc. IHLLW Conf. Las Vegas (2008) p.404-411**:** Cumulative U releases in flow-through tests with 20 mM carbonate solutions of fuel powders with burnups 15, 30, 31, 44, 50, 70 MWd/kg U are highest for the 44 MWd/kg U sample.

- Clarens et al., Mat. Res. Soc. Symp. Proc. 1107(2008) 439-446**:** Compared releases from the drilled central part of the pellet with the outer ~1 mm part containing the rim: higher releases of both FP and actinides from the central part.

- Rates of oxidative dissolution of **natural uraninite** (Grandstaff, Econ. Geol. 71 (1976) 1493), **Gd-doped UO_2** (Casella et al, IHLWM Conf. Proc. (2008) 388) or **SIMFUEL**(He et al., Can. J. Chem., 85 (2007) 702), reported to decrease proportionally to the dopant concentration .

- Reported increasing difficulty to fully **oxidize at high temperature spent fuel** (Hanson, PNNL-1173 Report, 1998) or **SIMFUEL**(Cobos et al, J. All. Comp. 271(1998) 610) with increasing burnup (i.e. dopant concentration).

- Most probably for high burnup spent fuel, the increased dopant concentration counteracts the oxidative dissolution, in spite of increased surface area and dose rates. Mazeina et al, J. Nucl. Mater. 373(2008) 39 report increased stability of $U(Ca$ or $Y)O_2$ solid solutions towards oxidation.

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Fuel leaching and redox conditions.

a) **Eh** determined by atmospheric oxygen and radiolytic oxidants.

- Under **oxidizing** (air) conditions: $[O_2]_{diss} = k\,P_{O2} \approx 2.7 \cdot 10^{-4}$ M.

   This is orders of magnitude higher than the concentration of radiolytic oxygen

   (Eriksen et al, 1997 experimentally determine $[O_2]_{rad} \approx 10^{-7}$ M after ~10 days).

- **Anoxic conditions (Ar).** Glove box or vessel flushed with Ar or N_2 with ~1 ppm O_2 in the gas phase. In this case:

   $[O_2]_{diss} = k\,P_{O2} \approx 10^{-9}$ **to** 10^{-11} **M.** This is anyhow lower than radiolytic oxygen after ~10 days.

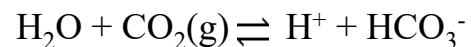   Even such small amounts of O_2 create strongly oxidizing conditions.

   $$2\,H_2O \Leftrightarrow 4\,H^+ + O_2(g) + 4e^-, \qquad \log K = -82.8$$
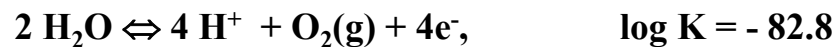
   Thus: $-82.8 = 4 \log [H^+] + \log P_{O2} + 4 \log [e^-]$

   $20.7 + (\log P_{O2})/4 = pH + pe$

   For pH=8, anoxic conditions: pe = 20.7- pH -2.5 = 10.2 or $E_h \approx 59.16$ pe = **+ 612 mV**.

b) **pH** determined by carbonate equilibria:

   $H_2O + CO_2(g) \rightleftharpoons H^+ + HCO_3^-$

   $$K_{a1} = \frac{[H^+] \cdot [HCO_3^-]}{P_{CO_2(g)} \cdot a_{H_2O}} = 10^{-7.75} \qquad (at \qquad I = 0.01 \cdot M)$$
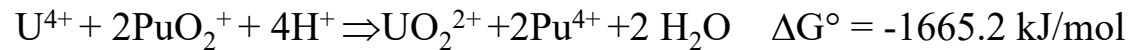
Real and laboratory anoxic conditions.
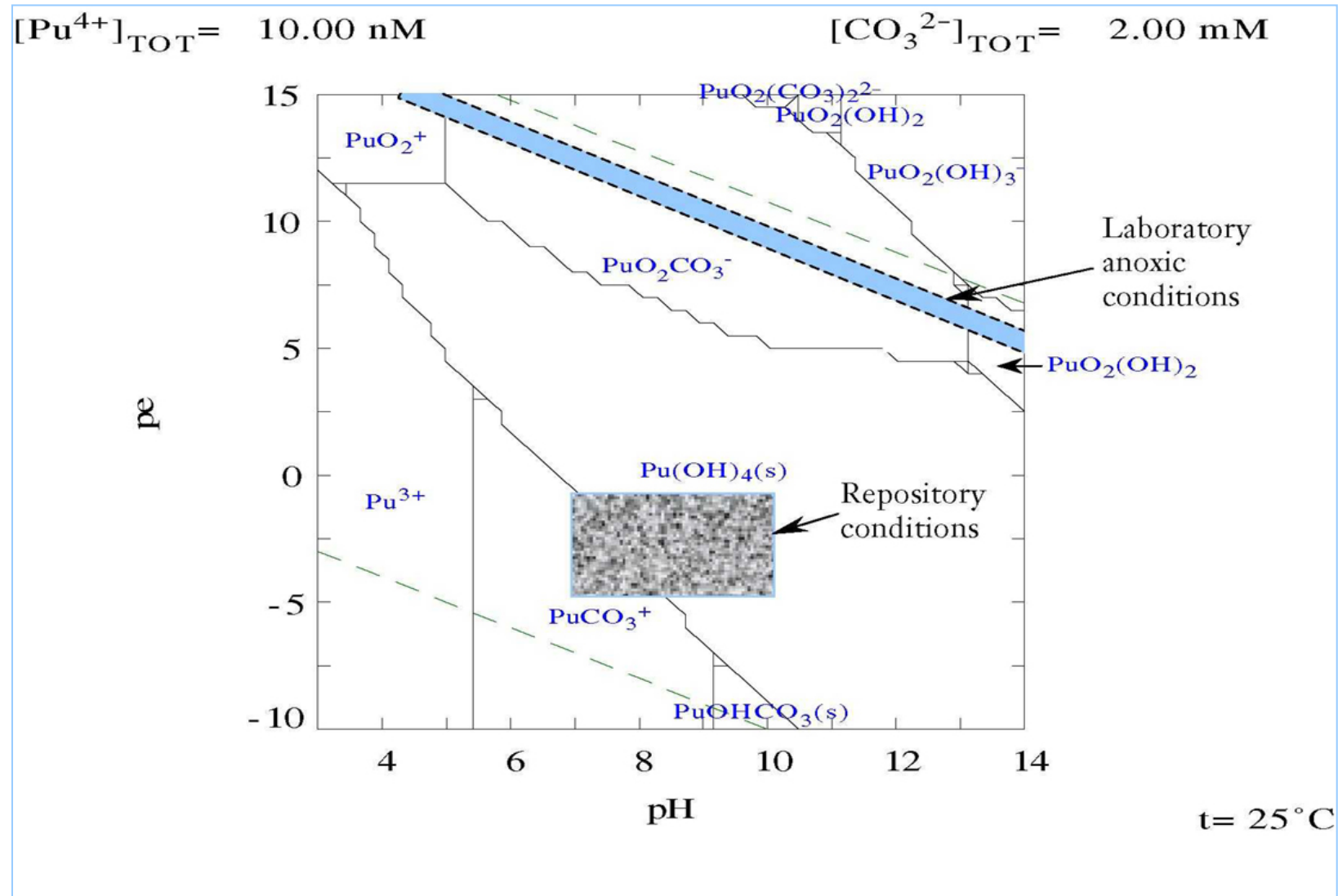
Redox kinetics

- Good knowledge of thermodynamics (speciation, redox potentials). Thus U(IV) should reduce

  Np(V), Pu(V):

$$U^{4+} + 2NpO_2^+ + 4H^+ \Rightarrow UO_2^{2+} + 2Np^{4+} + 2\ H_2O \quad \Delta G^\circ = -2163.1\ kJ/mol$$

$$U^{4+} + 2PuO_2^+ + 4H^+ \Rightarrow UO_2^{2+} + 2Pu^{4+} + 2\ H_2O \quad \Delta G^\circ = -1665.2\ kJ/mol$$

  and even more so does $UO_2(s)$.

- Is this kinetically feasible?

- Does soluble Fe(II) or magnetite reduce Np(V), Tc(VII) or $UO_2(CO_3)_3^{4-}$ within reasonable time scales?

- In all fuel dissolution models, an oxidative fuel dissolution is assumed. Then it is difficult to argue that while releasing uranium as oxidized U(VI), some minor fuel matrix component such as other actinides or fission products will not also be released in their oxidized forms.

- There is a lot of reductants with high reductive capacity in the near field. However, some experimental information that a reduction of the oxidized forms of the radionuclides occurs is necessary. This helps supporting the thermodynamic conclusions that the radionuclides are reduced in the near field, hence have low solubilities and sorb strongly.

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Soluble Fe(II) as reductant

- Np concentrations in 1% H_2 -Ar(g) saturated Fe(II) solution. Initial concentrations: Fe(II)=$1.6 \cdot 10^{-4}$ M, NpO_2^+=$6.7 \cdot 10^{-7}$ M
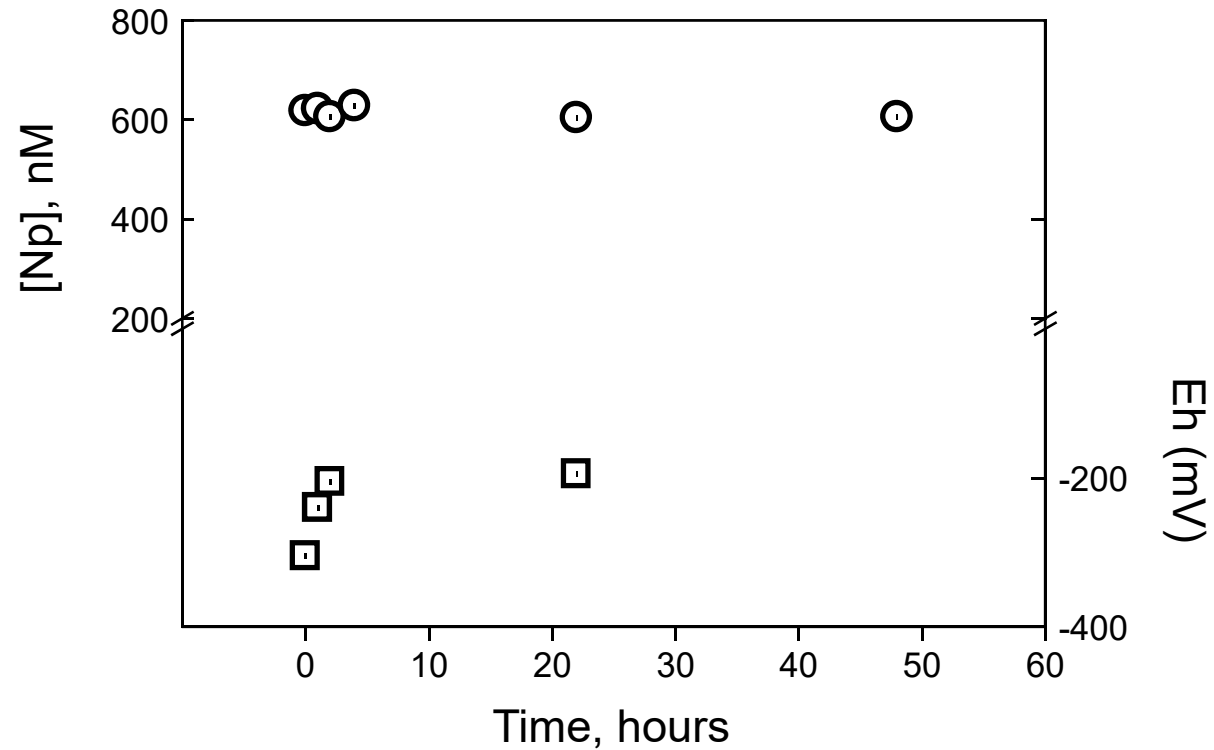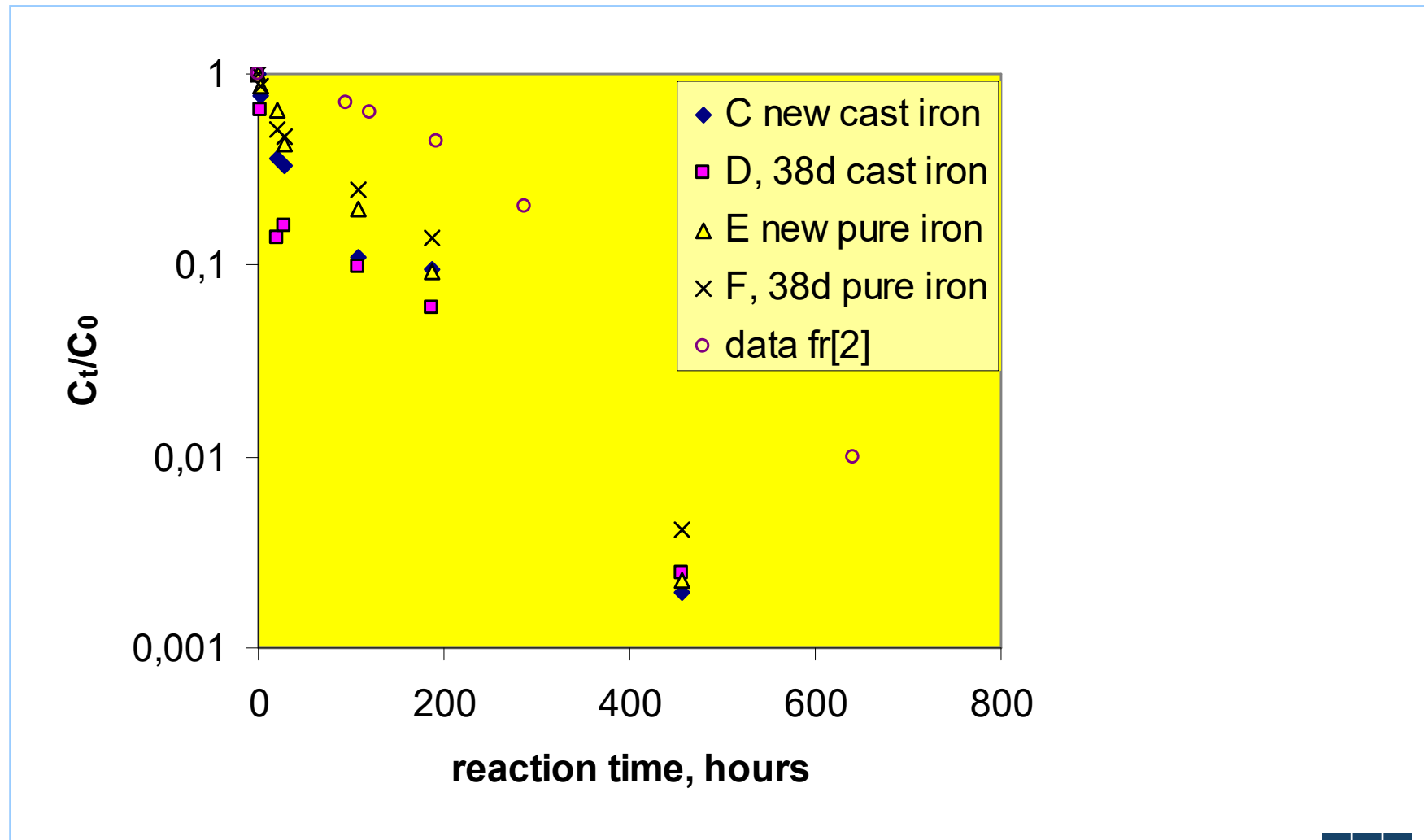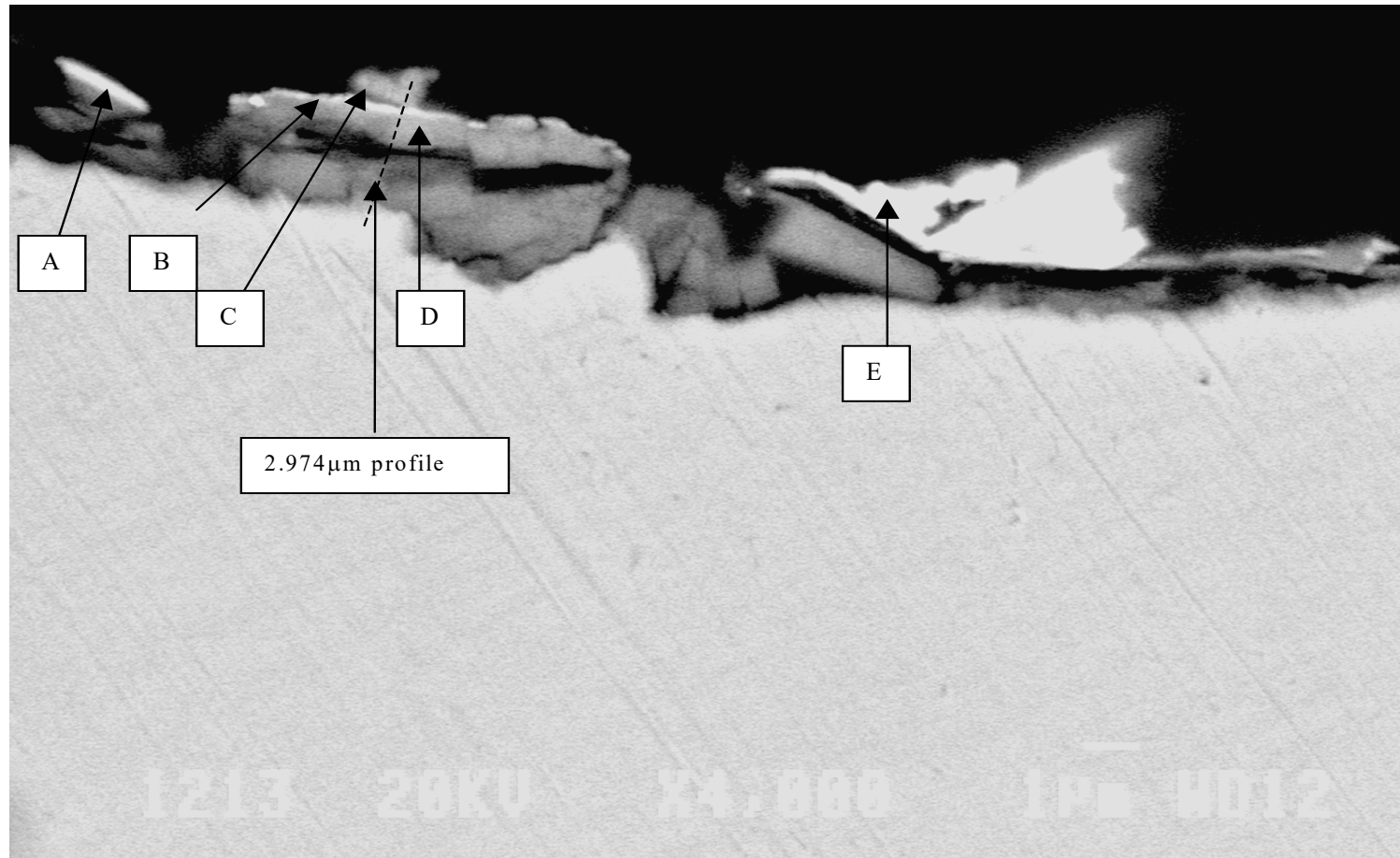
Magnetite as a reductant for Np(V).
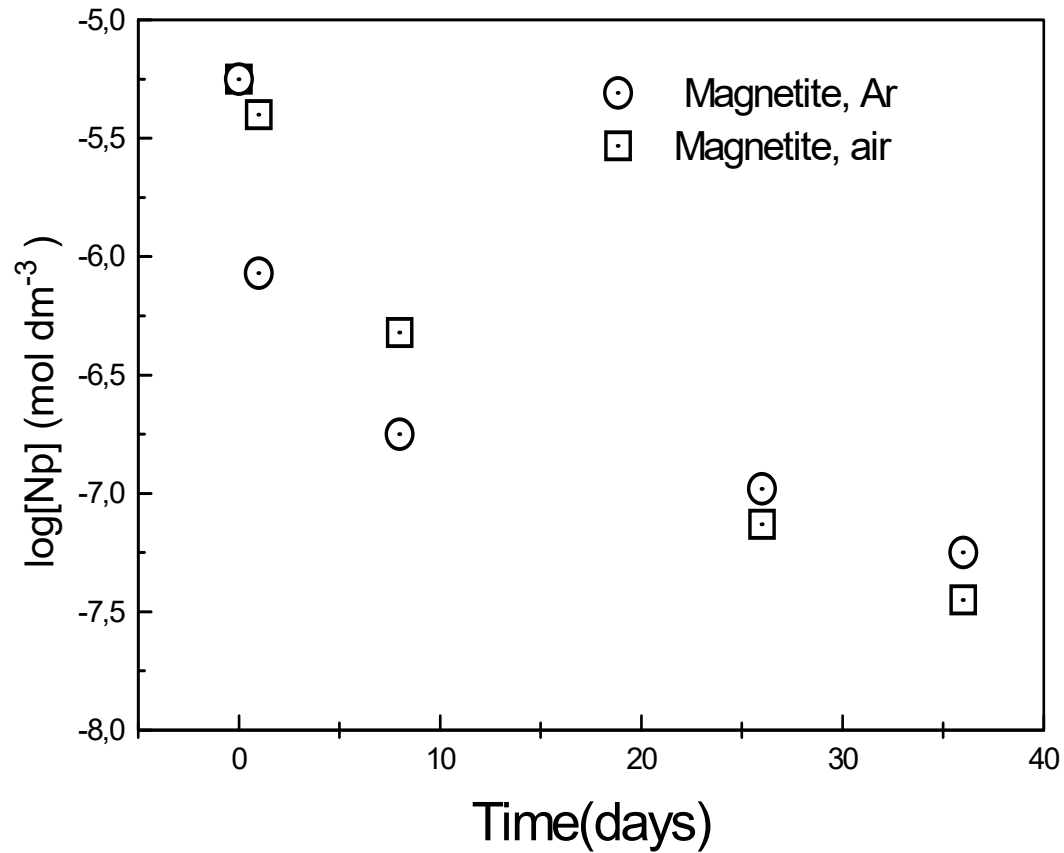
U(VI) removal kinetics, C_t/C_0 vs time, t.

1.06 cm^2 iron foils / 4.0 cm^2 cast iron coupons, reacted for 12 h (new)/38 d in 20 ml SGW before adding 1ppm U(VI). C-F: bottles described in Table 1. The open circles show the data from ref. [2], in which V(ml)/ S(cm^2) is 4 times higher.

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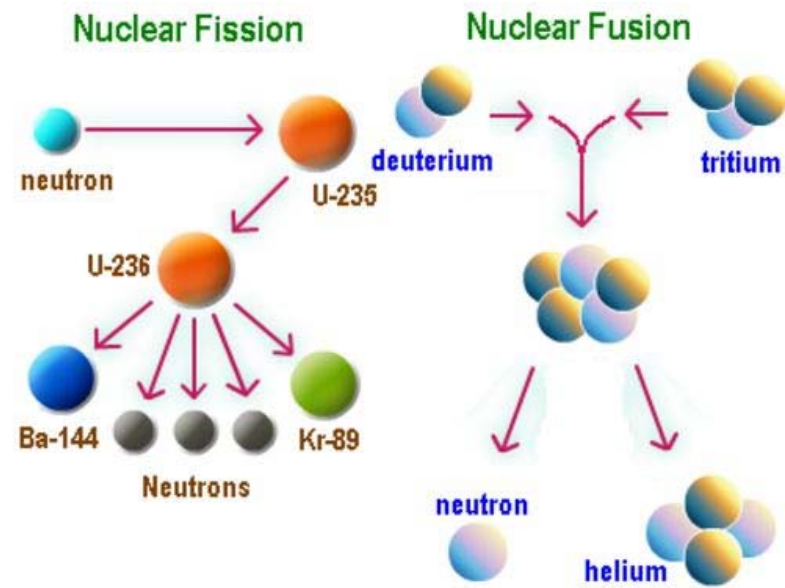# UO$_2$(cr) from soluble U(VI) on green rust formed on Fe(s)

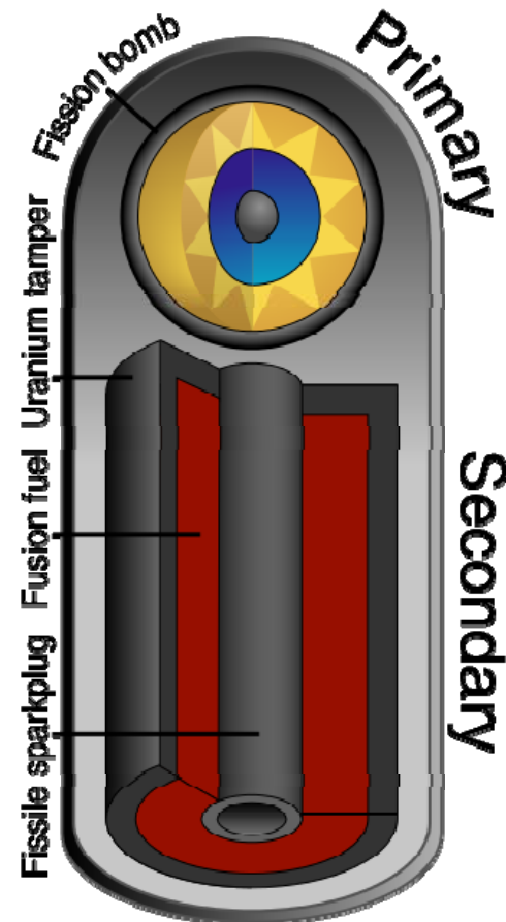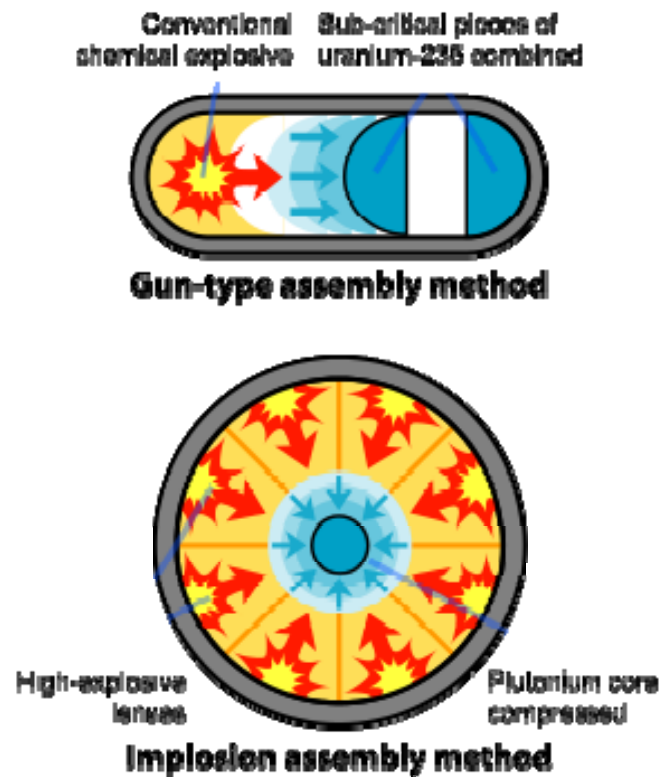A-E and the profile are analysed by SEM-EDS

Thank you!

Fission and fusion
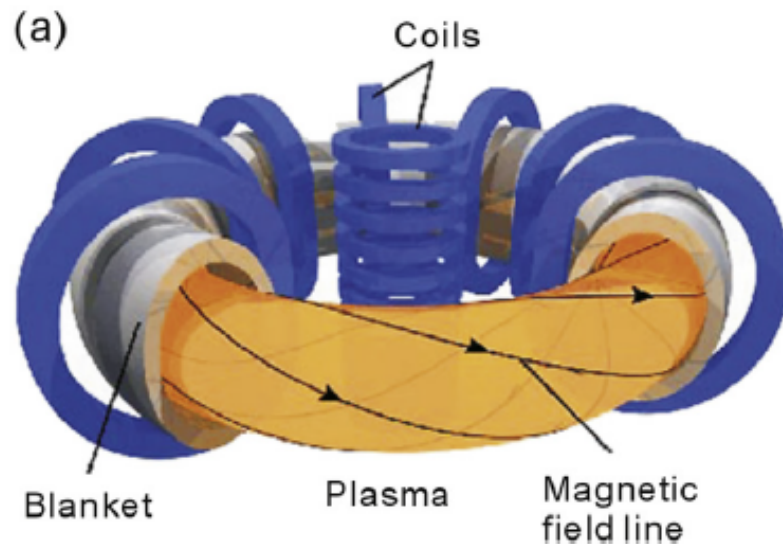
Atomic and hydrogen bombs.

b) Teller-Ulam device(H-bomb)
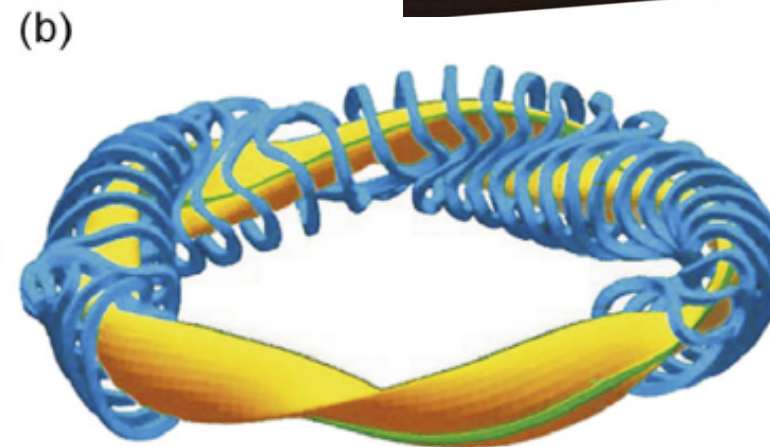
a) Atomic bomb

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) Coils, Blanket, Plasma, Magnetic field line
(b)

a) Tokamak (ITER)

b) Stellerator (Wedelstein 7)

SKB

Chemical state of fission products in fuel.

Oxygen potential of UO_2, UO_{2+x} and spent fuel – H. Matzke, J. Nucl. Mat. 208(1994)18-26.
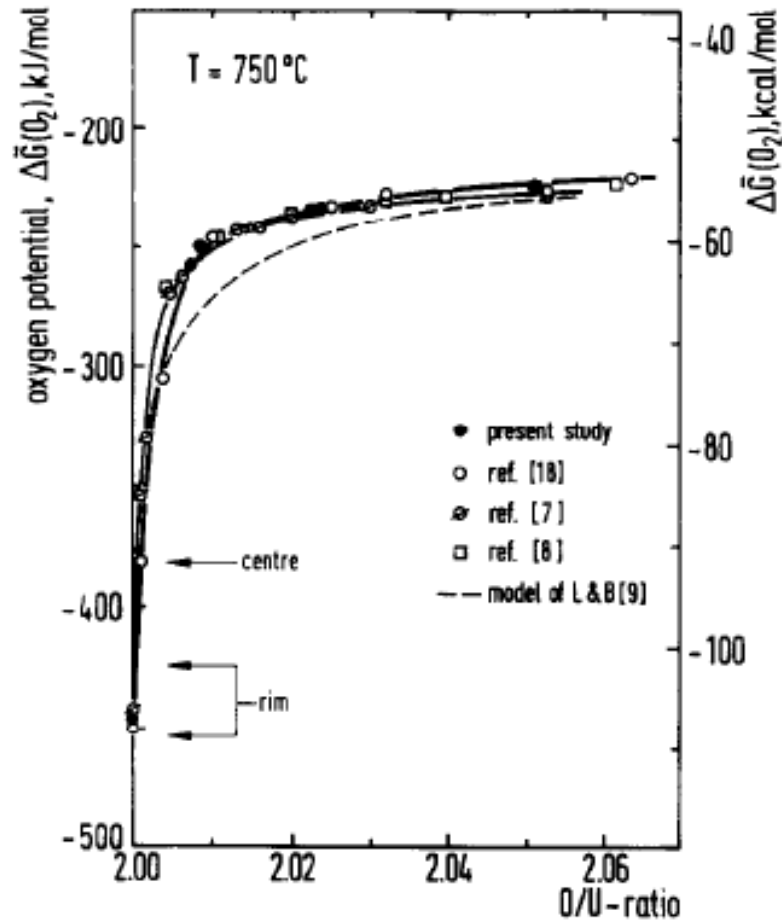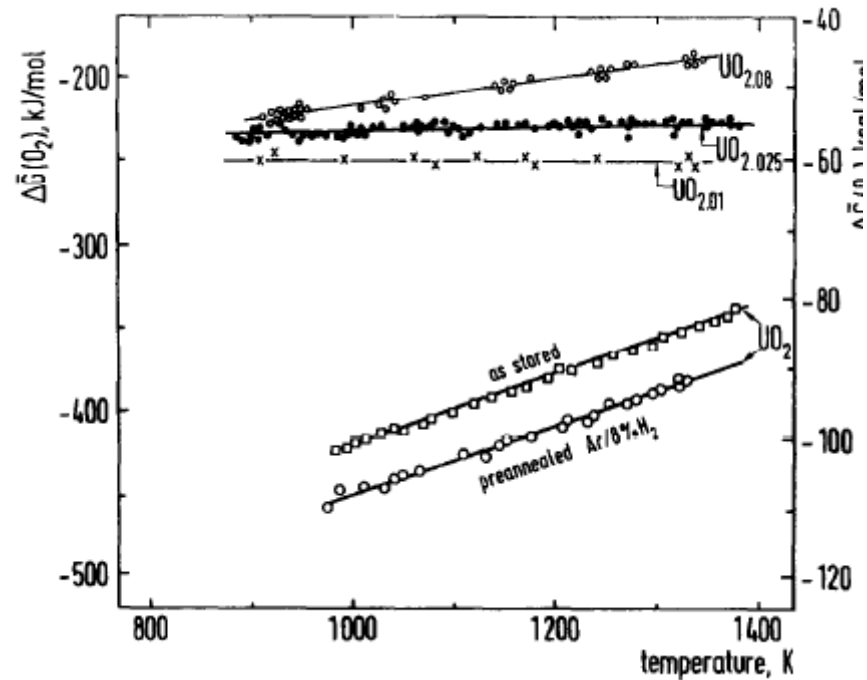

Fig. 5. Oxygen potential data for unirradiated UO_{2+x} at 750°C, including the data for unirradiated UO_{2+x} obtained in the present study with the modified cell as well as the results for the high burnup rim specimens.

Oxygen potential of sintered UO_{2+x}, nominally stoichiometric UO_2 and UO_2 stored in lab air.