Direct disposal of spent nuclear fuel.

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High level waste

- **Spent fuel** contains more than 60 elements, such as:

- Fission gases or volatile products: Kr, Xe, I, Br.

- Metallic precipitates (ε- phase): Mo, Tc, Pd, Ru, Rh etc.

- Oxide precipitates: Cs, Rb, Ba, Zr, Te etc.

- Oxides dissolved in $UO_2(s)$ matrix: An, REE, Sr, Zr.

- **Vitrified waste** contains all fission products (16 % weight), small amounts of U and Pu due to non ideal separation and all other actinides as Np, Am, Cm distributed in the glass matrix (0.6% An-oxides).

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 retards RN migration reducing inventory by decay and dilute 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. If one compares the toxicity of the waste forms with the limits established by the authorities for releases from repository, there is an enormous difference-see next slides. How can we achieve this, i.e. where is based repository safety?
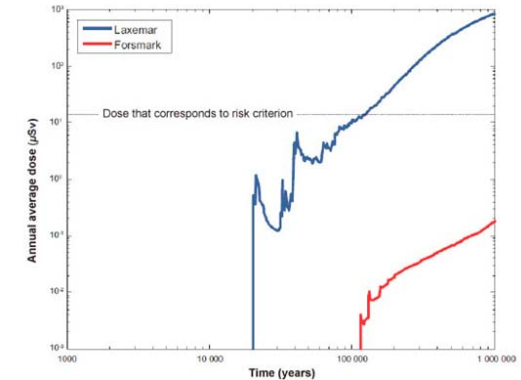
Pillars of safety in a repository
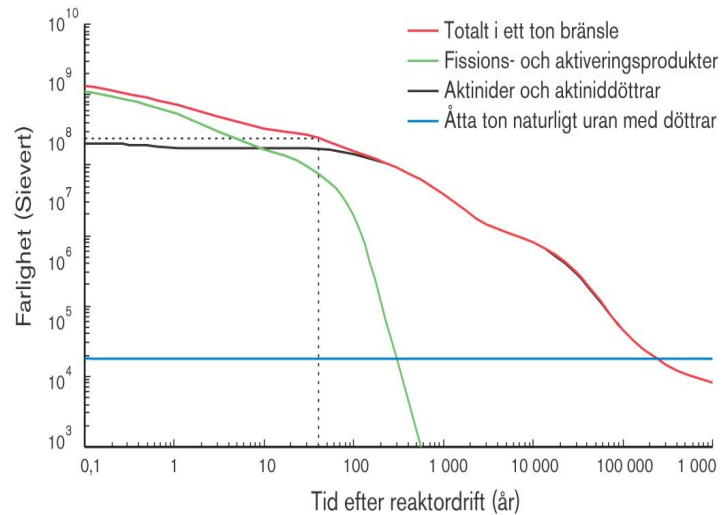
a)
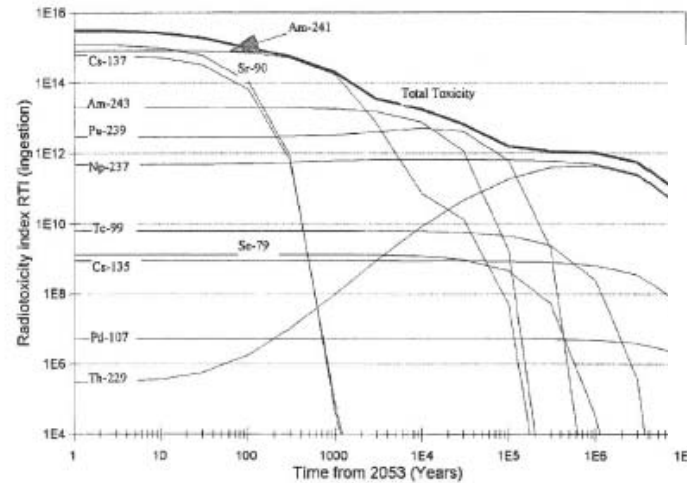
b)

c)

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

1. Very dissolution resistent 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 retadation (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.

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Pillars of safety, cont.

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

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. Usually 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**

The two previous mechanisms eventually reduce radionuclide fluxes to the biosphere by allowing for decay during release and transport, dilution reduces the concentration of the surviving inventory by mixing contaminated and fresh water. Three mechanisms lead to dilution:

-The first is hydrodynamic dispersion in the host rock caused by spatial variability of water velocities. Dispersion smears out the radionuclide breakthrough curve and so contributes to dilution. If radionuclide transit time is large compared to half-life, dispersion becomes important because only the fast-running portion of the nuclide survives decay. Not very important for PA, since large repository scale dispersion is not well understood.

-Second is dilution caused by matrix diffusion. Also here, through diffusion kinetics, the concentration-time distribution is smeared out and a dilution in the fracture water results.

-However, very important becomes the dilution of nuclides along the pathway to man by large bodies of water, such as lakes, rivers or the sea. This is the reason why sub-seabed disposal leads to remarkably low doses.

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Dose relevant nuclides

- The set of dose relevant nuclides excludes RN in very low concentrations or very short lives. For all nuclides in this list, solubility products, sorption and diffusion coefficients in cementitious or bentonite near field and sorption and diffusion coefficients in the far field are needed.

- Dose relevant nuclides in spent fuel are produced through:

  -Fission of ^{235}U and ^{239}Pu produces fission products (FP).

  -Neutron capture by ^{238}U and higher actinides produces transuranium elements.

  -Neutron activation of structure material produces activation products.

1. Fission products.

- Ternary fission events(~2 in 1000) produce a third nuclide of low mass (^{1}H to ^{21}Ne). Thus total fission yield for ^{235}U is 200.2%.

- The majority of the 977 FP listed in databases have very short half lives, in the range of msec. (30 %), sec. (28 %) or min. (16 %).

- Cumulative fission yield (total no. of atoms of a nuclide produced directly or through decay of precursors in 100 fissions) with $T_{1/2}$ >30 days and fission yields >0.0001% for ^{235}U and ^{239}Pu are shown in next slides.

- For ^{235}U, such FP number is much smaller: 97 stable, 16 short lived (30 d < $T_{1/2}$ < 3 y), 8 medium lived (3 y < $T_{1/2}$ < 100 y), 9 long lived ($T_{1/2}$>5000y). Similar numbers for thermal fission of ^{239}Pu.

- Thus for ^{239}Pu fission, there are 107 stable isotopes, 18 short lived, 8 medium and 9 long lived isotopes.

- With cumulative fission yields >0.001% for both U and Pu we have: 7 long lived FP (^{79}Se,^{93}Zr, ^{99}Tc,^{107}Pd,^{126}Sn,^{129}I,^{135}Cs) and 7 medium lived FP (^{3}H, ^{85}Kr, ^{90}Sr,^{121m}Sn, ^{137}Cs, ^{151}Sm, ^{155}Eu)- these are generic candidates for dose relevant nuclides. ^{10}Be, ^{14}C and ^{113m}Cd not important as FP (low yields), but are produced also by neutron activation in reactor.

- Chemistry of FP we should know (excluding gases) include only 10 elements: **Se, Sr, Zr, Tc, Pd, Sn, I, Cs, Sm, Eu**.

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Dose relevant nuclides (cont.)

2. Transuranium elements

Formed in reactor through neutron capture by non-fissile ^{238}U or sometimes by fissile ^{235}U or ^{239}Pu.

- $^{238}U+^1n \rightarrow {}^{239}U(23.5min) \rightarrow {}^{239}Np+\beta^-(2.35d) \rightarrow {}^{239}Pu+\beta^-$

- $^{235}U+^1n \rightarrow {}^{236}U+^1n \rightarrow {}^{237}U(6.75d) \rightarrow {}^{237}Np+\beta^-$

- $^{239}Pu+^1n \rightarrow {}^{240}Pu+^1n \rightarrow {}^{241}Pu+^1n \rightarrow {}^{242}Pu+^1n \rightarrow {}^{243}Pu(4.96h) \rightarrow {}^{243}Am+\beta^-$

Thus, by repeated neutron capture and subsequent beta decays, the transuranium elements **Np, Pu, Am, Cm** and **Cf** are produced in reactor. Together with naturally occurring Th and U this group is called "Actinides" after Ac, the first element of this row in the table.

- All actinides decay in four decay chains through many steps to stable ^{206}Pb, ^{207}Pb, ^{208}Pb and ^{209}Bi (very long $T_{1/2}$ to ^{209}Tl). Some of the long lived decay products with $T_{1/2}$ longer than 100 days are potentially dose relevant, i.e. ^{231}Pa, ^{228}Th, ^{229}Th, ^{230}Th, ^{227}Ac, ^{226}Ra, ^{228}Ra, ^{210}Po, ^{210}Pb. This adds 10 RN or 6 elements to the list of potentially dose relevant ones: **Pa, Th, Ac, Ra, Po and Pb.**

3. Activation products.

Neutrons in a reactor are captured by stable nuclides in the structural materials in the reactor, i.e. $^{59}Co+^1n={}^{60}Co$. This "neutron activation" process produces many RN, some of them are long lived enough and produced in such amounts that they become dose relevant in repository. Important nuclides with half-lives longer than 100 years and sufficient production are: ^{10}Be, ^{14}C, ^{36}Cl, ^{41}Ca, ^{59}Ni, ^{63}Ni, ^{79}Se, ^{93}Zr, ^{94}Nb, ^{93}Mo, ^{108m}Ag, ^{166m}Ho. Two of these are produced also by fission: ^{79}Se and ^{93}Zr. This leaves 10 RN or 9 new elements for the list: **Be, C, Cl, Ca, Ni, Nb, Mo, Ag, and Ho**.

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Repository conditions

- Deep groundwaters are oxygen free and reducing.

- Post-closure oxygen is consumed by e. g. pyrite in bentonite:

$$FeS_2(s) + 3.75O_2 + 3.5H_2O + 4\ CO_3^{2-} \Rightarrow Fe(OH)_3(s) + 2\ SO_4^{2-} + 4\ HCO_3^-$$
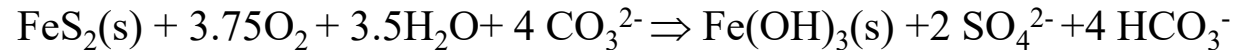
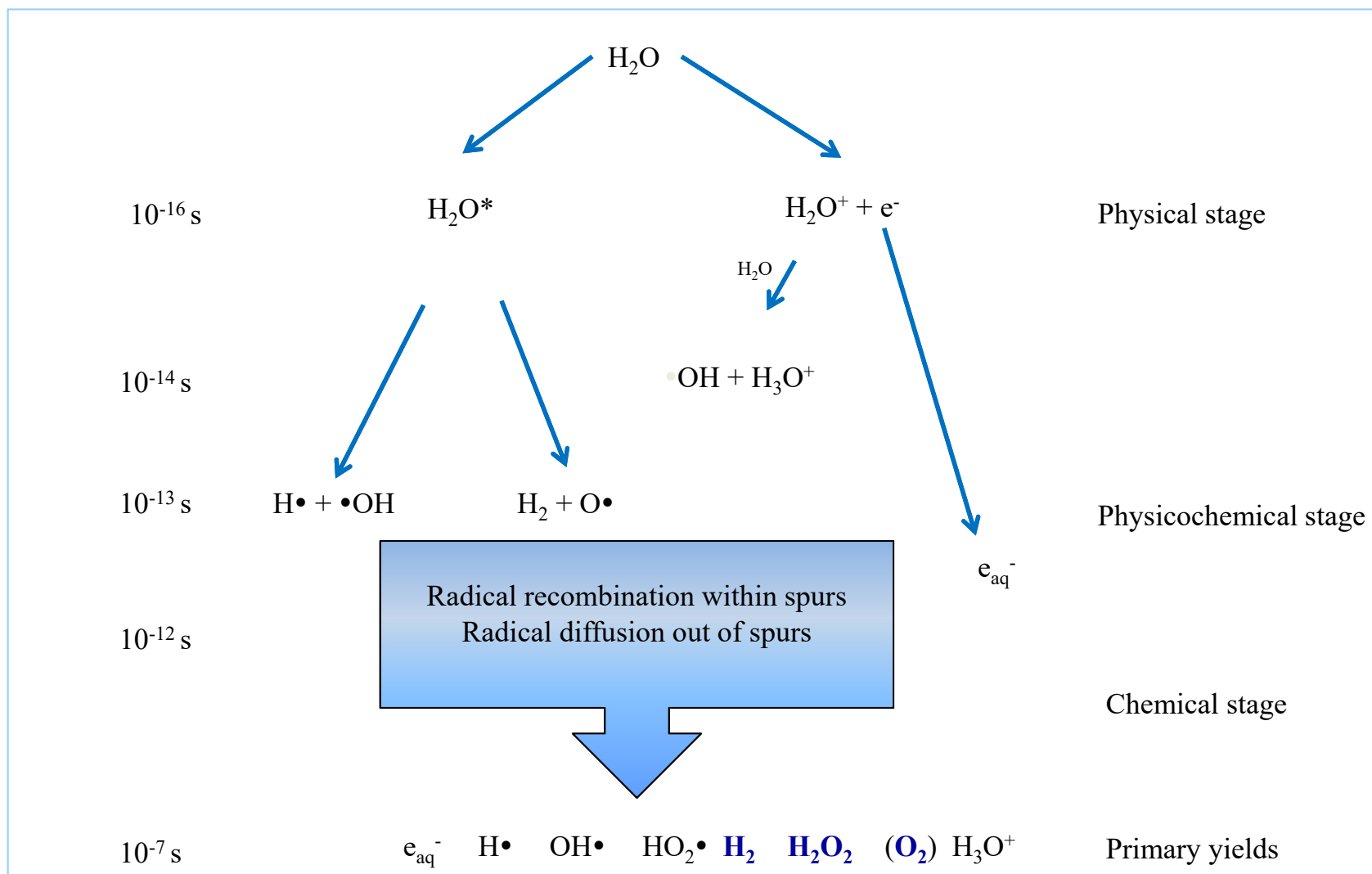 and kinetic studies predict 7-120 years time.

- Recent studies in granitic bedrock show that bacteria assure total oxygen consumption in a few days.

- Iron and magnetite on the surface of iron are potential reductants of high capacity, not fully studied.

- Under such conditions the $UO_2(s)$ matrix is stable and has a very low solubility, $3\ 10^{-9}$ M U for pH>4 (groundwaters have usually near neutral pH, buffered by the presence of minerals such as calcite, $CaCO_3(s)$). In this case, the volume of water inside the damaged canister($\sim 1m^3$) is in equilibrium with $UO_2(s)$:

$$UO_2(s) + 2H_2O = U(OH)_4(aq)$$
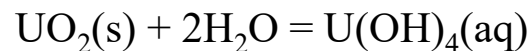
and with the low repository flows (max 300 L/year), the amount of released U is negligible.

- The problem is that spent fuel has an inherent α, β and γ radiation field which causes **water radiolysis.** Water radiolysis produces oxidants, which cause oxidative dissolution of fuel.

Radiolysis of water

H_2O

H_2O^* $H_2O^+ + e^-$ Physical stage

10^{-16} s

H_2O

$\cdot OH + H_3O^+$

10^{-14} s

$H\cdot + \cdot OH$ $H_2 + O\cdot$ Physicochemical stage

10^{-13} s

e_{aq}^-

Radical recombination within spurs
Radical diffusion out of spurs

10^{-12} s

Chemical stage

10^{-7} s e_{aq}^- $H\cdot$ $OH\cdot$ $HO_2\cdot$ $\mathbf{H_2}$ $\mathbf{H_2O_2}$ $\mathbf{(O_2)}$ H_3O^+ Primary yields

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Radiolytic scheme for pure water

	Chemical Reactions			Rate coefficients $(M^{-1}s^{-1}$ or $s^{-1})$
25	$e^-_{aq} + OH$	$\rightarrow$	OH^-	3.0×10^{10}
26	$e^-_{aq} + H_2O_2$	$\rightarrow$	$OH + OH^-$	1.1×10^{10}
27	$e^-_{aq} + O_2^- + H_2O$	$\rightarrow$	$HO_2^- + OH^-$	$1.3 \times 10^{10}/[H_2O]$
28	$e^-_{aq} + HO_2$	$\rightarrow$	HO_2^-	2.0×10^{10}
29	$e^-_{aq} + O_2$	$\rightarrow$	O_2^-	1.9×10^{10}
30	$e^-_{aq} + e^-_{aq} + 2H_2O$	$\rightarrow$	$H_2 + 2OH^-$	$5.5 \times 10^9/[H_2O]$
31	$e^-_{aq} + H + H_2O$	$\rightarrow$	$H_2 + OH^-$	$2.5 \times 10^{10}/[H_2O]$
32	$e^-_{aq} + HO_2^-$	$\rightarrow$	$O^- + OH^-$	3.5×10^9
33	$e^-_{aq} + O^- + H_2O$	$\rightarrow$	$OH^- + OH^-$	$2.2 \times 10^{10}/[H_2O]$
34	$e^-_{aq} + O_3^- + H_2O$	$\rightarrow$	$O_2 + OH^- + OH^-$	$1.6 \times 10^{10}/[H_2O]$
35	$e^-_{aq} + O_3$	$\rightarrow$	O_3^-	3.6×10^{10}
36	$H + H_2O$	$\rightarrow$	$H_2 + OH$	1.1×10^1
37	$H + O^-$	$\rightarrow$	OH^-	1.0×10^{10}
38	$H + HO_2^-$	$\rightarrow$	$OH + OH^-$	9.0×10^7
39	$H + O_3^-$	$\rightarrow$	$OH^- + O_2$	1.0×10^{10}
40	$H + H$	$\rightarrow$	H_2	7.8×10^9
41	$H + OH$	$\rightarrow$	H_2O	7.0×10^9
42	$H + H_2O_2$	$\rightarrow$	$OH + H_2O$	9.0×10^7
43	$H + O_2$	$\rightarrow$	HO_2	2.1×10^{10}
44	$H + HO_2$	$\rightarrow$	H_2O_2	1.8×10^{10}
45	$H + O_2^-$	$\rightarrow$	HO_2^-	1.8×10^{10}
46	$H + O_3$	$\rightarrow$	HO_3	3.8×10^{10}
47	$OH + OH$	$\rightarrow$	H_2O_2	3.6×10^9
48	$OH + HO_2$	$\rightarrow$	$H_2O + O_2$	6.0×10^9
49	$OH + O_2^-$	$\rightarrow$	$OH^- + O_2$	8.2×10^9
50	$OH + H_2$	$\rightarrow$	$H + H_2O$	4.3×10^7
51	$OH + H_2O_2$	$\rightarrow$	$HO_2 + H_2O$	2.7×10^7
52	$OH + O^-$	$\rightarrow$	HO_2-	2.5×10^{10}
53	$OH + HO_2^-$	$\rightarrow$	$HO_2 + OH^-$	7.5×10^9
54	$OH + O_3^-$	$\rightarrow$	$O_3 + OH^-$	2.6×10^9
55	$OH + O_3^-$	$\rightarrow$	$O_2^- + O_2^- + H^+$	6.0×10^9
56	$OH + O_3$	$\rightarrow$	$HO_2 + O_2$	1.1×10^8
57	$HO_2 + O_2^-$	$\rightarrow$	$HO_2^- + O_2$	8.0×10^7
58	$HO_2 + HO_2$	$\rightarrow$	$H_2O_2 + O_2$	7.0×10^5
59	$HO_2 + O^-$	$\rightarrow$	$O_2 + OH^-$	6.0×10^9
60	$HO_2 + H_2O_2$	$\rightarrow$	$OH + O_2 + H_2O$	5.0×10^{-1}
61	$HO_2 + HO_2^-$	$\rightarrow$	$OH + O_2 + OH^-$	5.0×10^{-1}
62	$HO_2 + O_3^-$	$\rightarrow$	$O_2 + O_2 + OH^-$	6.0×10^9
63	$HO_2 + O_3$	$\rightarrow$	$HO_3 + O_2$	5.0×10^8
64	$O_2^- + O_2^- + 2H_2O$	$\rightarrow$	$H_2O_2 + O_2 + 2OH^-$	$1.0 \times 10^2/2[H_2O]$
65	$O_2^- + O^- + H_2O$	$\rightarrow$	$O_2 + 2OH^-$	$6.0 \times 10^8/[H_2O]$
66	$O_2^- + H_2O_2$	$\rightarrow$	$OH + O_2 + OH^-$	1.3×10^{-1}

Pastina&LaVerne, J. Phys. Chem. A 233(2001) 2344.

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Radiolysis of water
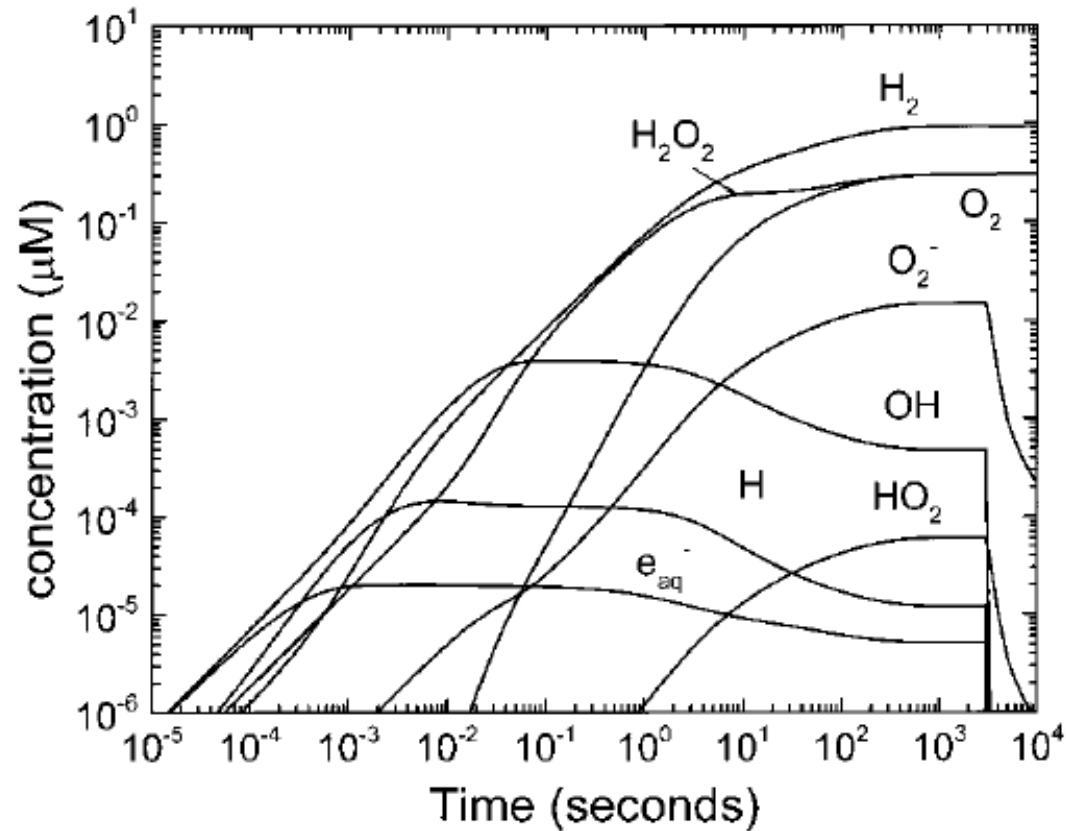
Temporal dependence of water decomposition product
concentrations for a 1 h γ-radiolysis (25 rad/s) of neat water.

Pastina&LaVerne, J. Phys. Chem. A 105 (2001) 9316-9322.

Fuel leaching experiments under oxidizing conditions.

- Relatively simple experiments, except that they are carried out in a hot cell: one places the fuel sample in a flask with solution and waits.

- After the determined time interval has passed, the fuel sample is moved to another similar flask and the solution is analyzed for all radionuclides in the fuel inventory, which can be quite difficult for some nuclides which are released in very small amounts.

- First radionuclides which are outside the UO_2 matrix pass into the solution(Cs&I). This takes a few days.

- The solution will slowly be saturated with uranium. This takes a few months.

- As uranium passes into solution, other radionuclides in the fuel matrix also pass into solution.

- In the presence of O_2, U(IV)(green) is oxidized to U(VI)(yellow).

- U(VI) can enter solution as UO_2^{2+} (uranyl) or uranyl complexes, depending on pH and water composition.

- In neutral and mildly alkaline solutions uranyl carbonate complexes dominate if the solution contains carbonate.

- The solubility limiting phase for U(VI) is schoepite (uranyl hydroxide).

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Spent fuel leaching experiments in hot cell.

- Complicated systems (several phases, An + many FP in the solid, synthetic GW solutions and radiation). Necessary to determine matrix alteration rates, i.e. source term.

- U releases can not be used: insoluble Ca-Mg-U(VI) - silicate or oxide phases may form or $CaCO_3$(s) precipitates due to CO_2 depletion in glove box atmosphere. For this reason, later we avoided Ca, Mg and used constant pCO_2 in the autoclave and ampoule leaching.

- The inventory of the fuel under study must be known in order to quantify the fraction released in solution. At Studsvik fuel samples consisting of 2 fuel pellets were cut from a fuel rod and also half of an adjacent pellet for inventory determination. The inventory is determined by dissolving completely the half pellet in acidic mixtures and analyzing the solution by ICP-MS and radiometric methods. At Studsvik the fuel inventory is reported in microgram nuclide per gram U, which can easily be converted in gram or mol nuclide per gram or mol fuel.

- The fuel sample together with cladding is cut to contain half pellet-whole pellet-half pellet. This sample is hang with a Pt-wire in the stopcock of the flask containing 400 ml leaching solution to have the fuel sample surrounded with water.

- After the time determined for leaching period has passed, the fuel sample together with the stopcock is transferred to a new flask with 400 ml fresh solution. The solution in the flask is analyzed by ICP-MS and radiometric methods for all nuclides.

- The results of the analysis are reported as molar concentrations for the actinides and lanthanides, while for fission products such as Cs and Sr they are reported as Fraction of the Inventory in the Aqueous Phase, FIAP. After several consecutive leaching periods, the Cumulative Fractional Release, which the sum of all FIAP for the given nuclide, is plotted against Cumulative time, which is the sum of all time intervals for the leaching.

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# FIAP and IFR for release kinetics.

- The Fraction of Inventory in the Aqueous Phase (FIAP) is usually used for characterizing the release on non-redox sensitive radionuclides, such as Cs, Sr, Rb, Ba etc. FIAP is calculated based on the volume of solution in the leaching vessel and the concentration of the radionuclide in it-this gives the inventory in the aqueous phase and the content or inventory of this nuclide in the fuel sample.

- Usually the inventory in the fuel sample is given related to the amount of heavy metal (U for UO_2 fuel), while we usually know the weight of the fuel sample W, thus a conversion factor f_{HM} relating the atomic mass of U(238) and the molecular mass of its oxide (270) is needed.

- Below two formulas for the FIAP of the nuclide i are given for the case when the concentration in solution C_i is given mol/L and the inventory in fuel IF_i is given in microgram/g U, while in the second formula the specific activity Ai in the aqueous phase (Bq/L) is used and AI_i is the specific nuclide activity inventory in the fuel (Bq/g heavy metal).

$$FIAP_i = \frac{C_i \cdot V}{W \cdot IF_i \cdot f_{HM}} \qquad\qquad FIAP_i = \frac{A_i \cdot V}{W \cdot AF_i \cdot f_{HM}}$$
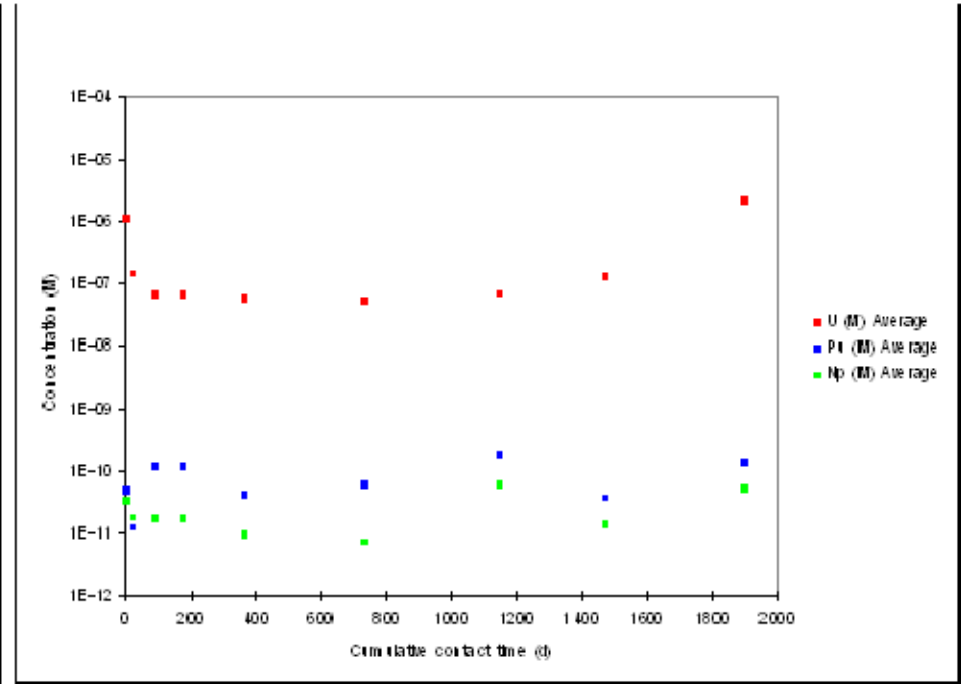
- The Incremental Fractional release takes into account the sampling volume and corrects for it. IFR(t) expresses the release rate of a nuclide during the time interval between the samplings:

$$IFR(t) = \frac{FIAP(t) - FIAP(t-1) \cdot \left(1 - \frac{V_{sample}(t-1)}{V_{soln}(t-1)}\right)}{\Delta t}$$

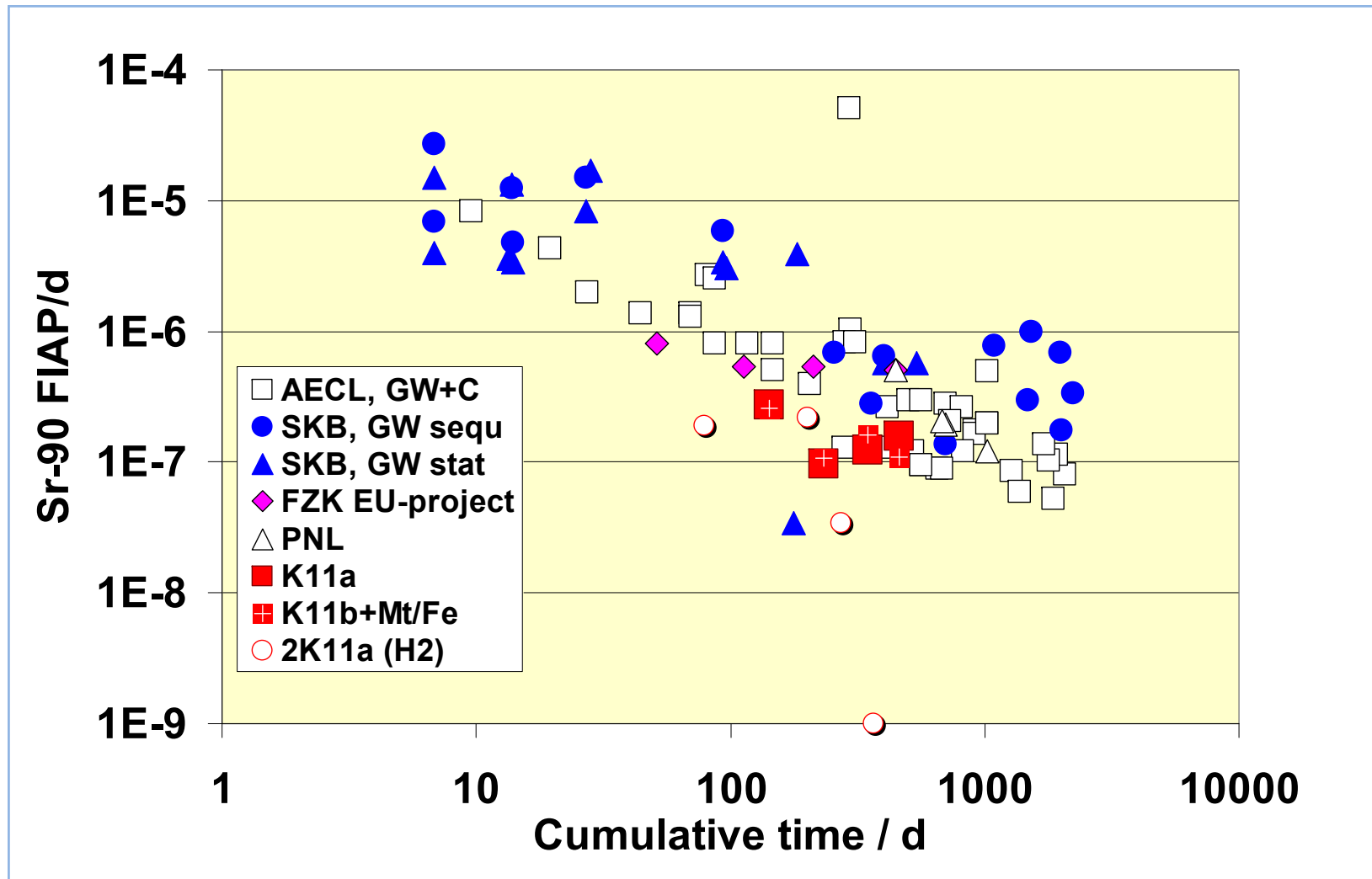# U, Pu, Np concentrations during fuel leaching in presence of air
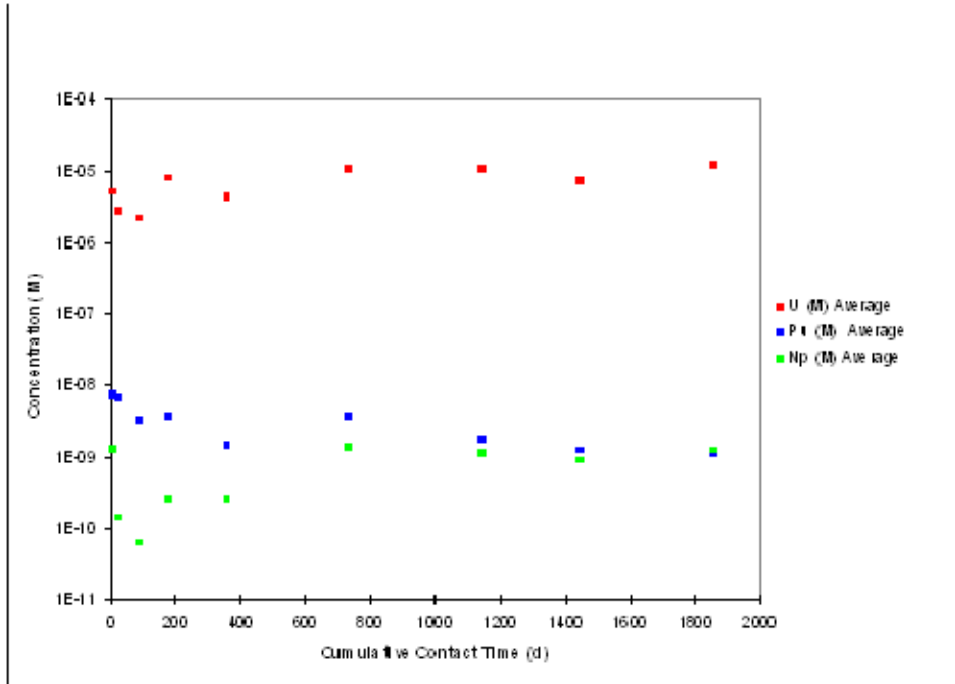
a) In synthetic granitic (Allard) water

b) In distilled water

Sr release rates during oxidative fuel leaching-all data.

Loida et al., Mat Res. Soc. Symp. Proc. 343 (2012) 233

Summary on spent fuel leaching in air.

- Only a few countries carried out systematic fuel leaching studies: due to the necessity to work with highly radioactive spent fuel these studies are usually expensive and require extremely good planning because small negligence's or mistakes can compromise the whole study.

- Pioneering work was carried at AECL, Canada, at PNNL and ANL in USA and Studsvik, Sweden in the 80´es, reporting the first data on fuel dissolution rates. There are enormous difficulties connected with the experimental measurement of spent fuel surface area by using e.g. the BET method. The surface area is necessary to use geochemical methods to express the fuel dissolution rate, see later on flow through leaching. In any case, the use of the Cumulative release fractions is to be preferred to other methods, as discussed in a paper of Hanson&Stout, MRS. Symp. Proc. 2004.

- We discovered later that the use of synthetic groundwater solutions caused precipitation on the surface of the fuel even when the solution concentrations indicated no saturation. This is due to the formation of very insoluble compounds of calcium uranyl silicates, such as soddyite and uranophane. In case Ar flushing is used in carbonate containing solutions, one expels CO_2 decreasing the total carbonate in solution, rising the pH and precipitating calcite $CaCO_3(s)$.

- The major result from these leaching studies for use in PA was the determination of long term fuel dissolution rates of the order of 10^{-5}-10^{-4}/ year, based on the release rates of Sr of $\sim 10^{-7}$/ day x 365day/year= 3.65 10^{-5}/year. We used dissolution rates of 10^{-5}-10^{-4}/year in our PA.

- These are quite low dissolution rates and were used in all SKB safety assessments until 1997. During this time, we could afford also a case with immediate dissolution of all the fuel ("instant coffee" model). New scenarios with bentonite erosion and container corrosion, as well as scenarios with an early canister shear would give high doses to biosphere with these dissolution rates, so we had to do more complicated experiments to reproduce repository conditions. The presence of air makes γ-radiolysis more aggressive.

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Thank you!