Release of radionuclides from spent nuclear fuel under anoxic / reducing conditions in highly alkaline solution

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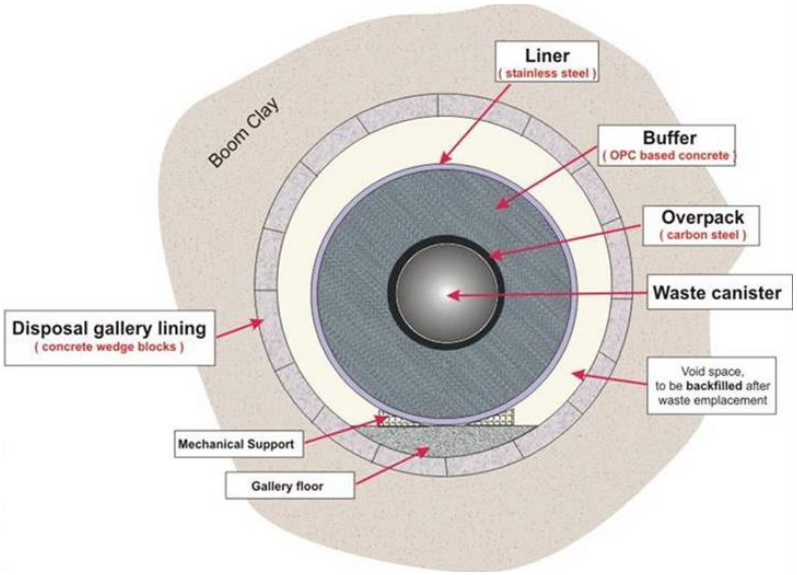
Background

- Deep underground repository for management of spent nuclear fuel (SNF) considered in many countries.
- Water access, consecutive failure of canister and loss of cladding integrity considered in long-term safety analysis.
- Assessing performance of SNF in geological disposal system requires:
  - Mechanistic understanding.
  - Quantification of radionuclides release from SNF under reducing conditions.

Belgian supercontainer concept:

- Concept for high-level radioactive waste.
- Multi-barrier concept.
- Provide favourable chemical environment to delay overpack degradation (high pH).



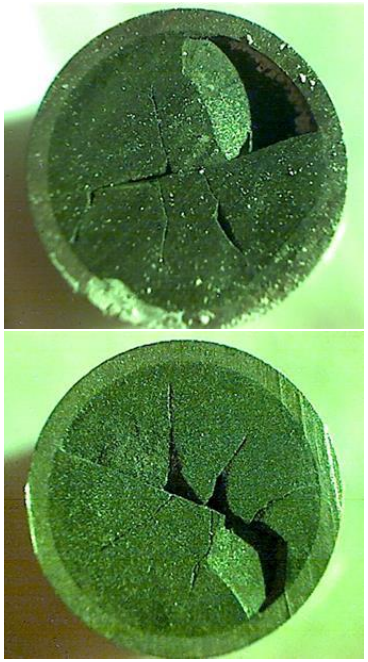
Objectives

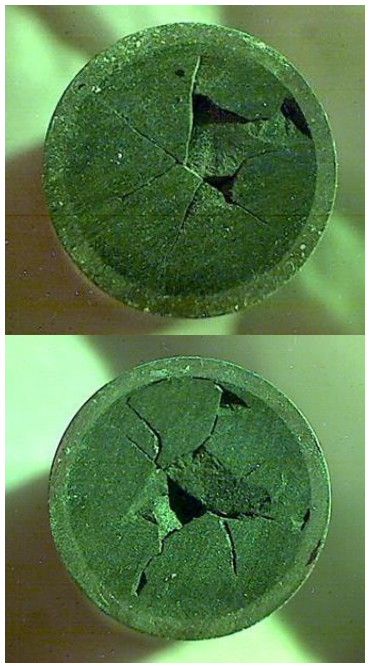
- **Matrix dissolution** of UO_2 spent nuclear fuel and **instant release fraction** (IRF) studied under anoxic/reducing and hyper alkaline conditions.
- Leaching experiments with periodical sampling of gaseous and aqueous phase.
- Three experiments under following conditions:
  - 40 bar of H_2/Ar gas mixture $\rightarrow p(H_2) = 3.2$ bar + p(Ar) = 36.8 bar.
  - 3.75 bar of H_2/Ar gas mixture $\rightarrow p(H_2) = 0.3$ bar + p(Ar) = 3.45 bar.
  - 1 bar of Ar gas $\rightarrow p(H_2) = 0$ bar + p(Ar) = 1 bar.

Materials: UO_2 fuel rod segment

Fuel rod segment irradiated in the PWR Gösgen (Switzerland):

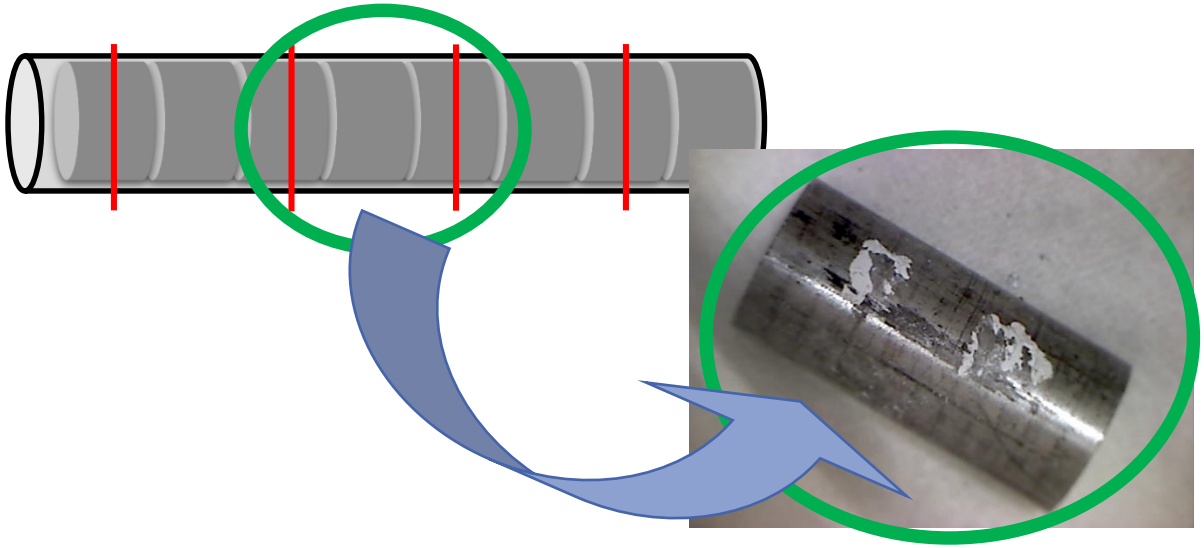
- Fuel type: UO_2 with initial enrichment of ^{235}U: 3.8%.
- Cycles: 4.
- Effective full power: 1226 days.
- Average linear power: 260 $W \cdot cm^{-1}$
- Average burn-up of: 50.4 $MWd \cdot (kgU)^{-1}$
- Cooling time: 28 years.





Experimental: cutting of specimens

- Cut from mid to mid pellet positions (20 mm length samples).
  → one complete pellet plus two half pellets (two inter-pellet gaps).



- Three SNF samples with Zircaloy cladding cut from the fuel rod segment:
  - in hot cell under N_2 atmosphere (with an O_2 content < 1%).
  - slow dry cutting to limit heating (friction between blade and pellet).
- Cut samples stored in Ar atmosphere (prevent oxidation of surfaces).

Experimental: design of leaching experiments

- Young Cement Water with Ca (YCWCa) prepared according to SCK-CEN.
  → except reduction of [Ca] from 7.0×10^{-4} M to 4.8×10^{-4} M.
- pH 13.5.
- Washing step and seven samplings.

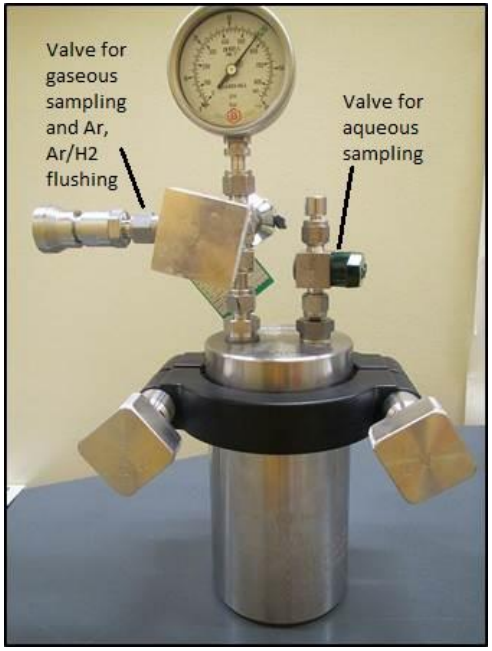
YCWCa	[Na]	[K]	[Ca]	[Al]	[Si]
Theoretical (M)	1.4×10^{-1}	3.7×10^{-1}	4.8×10^{-4}	6.1×10^{-4}	3.0×10^{-4}
Experimental (M)	1.35×10^{-1}	3.41×10^{-1}	3.84×10^{-4}	b.d.l*	b.d.l*

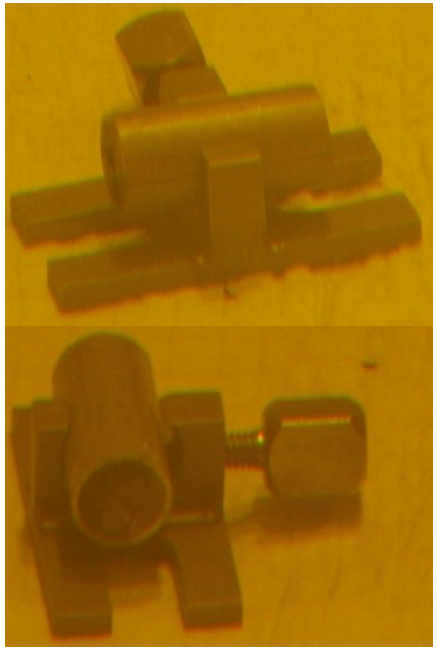
*b.d.l: below detection limit

sample #	Interval (days)	Total time (days)
1	1	1
2	20	21
3	60	81
4	90	171
5	120	291
6	180	471
7	240	711

Experimental: design of leaching experiments

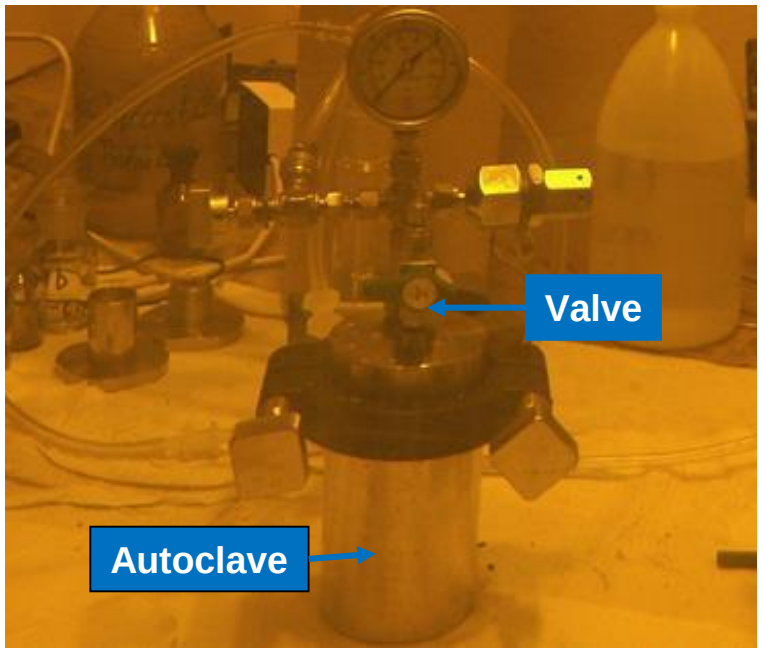
- **Autoclaves:** Ti-lined (total volume of 250 mL) with 2 valves in the lid to allow sampling of gases and liquids.
- **Initial volume of solution:** 220 mL in autoclave.
- Complete replenishment after one day (washing step).
- Start of experiments: Feb./Mar. 2017 // End of experiments: April 2019.

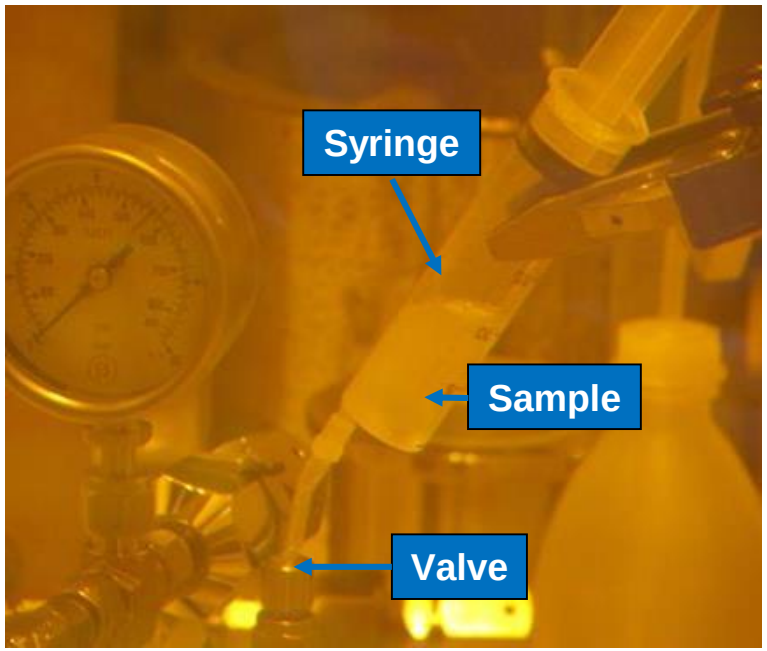




Experimental: liquid sampling

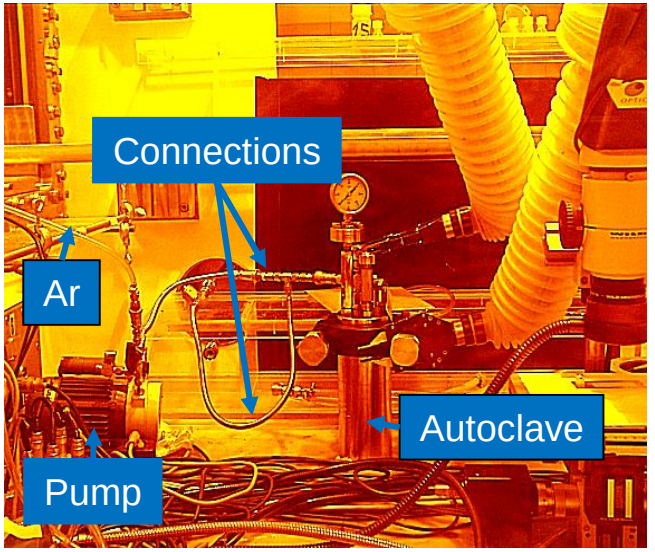
- 10 mL aliquots are taken in static regime.
- Autoclave purged with Ar during sampling.
- Non-filtered and ultra filtered (10 kD, 2-3 nm) samples.
- Dilution and Cs-removal (ammoniummolybdatophosphate, AMP) necessary.

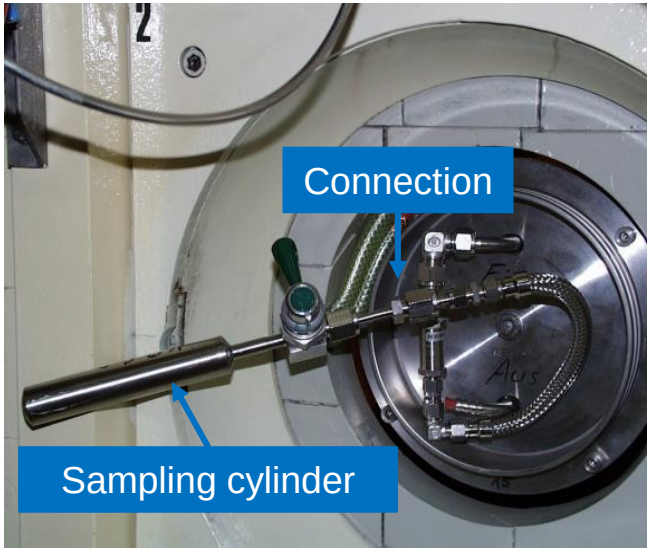




Experimental: gas sampling

- Autoclave connected to vacuum pump.
- Sampling cylinder placed outside the hot cell.
- Connections purged with Ar.
- Overpressure reduction to 1 bar in autoclave.
- Opening the valve of the autoclave and, at the same time, the valve of the sampling cylinder.
- Gas sample released from the autoclave to the sampling cylinder within two minutes.
- Gas phase is renewed after each sampling (pseudo-dynamic regime).





Experimental: measurement of RN

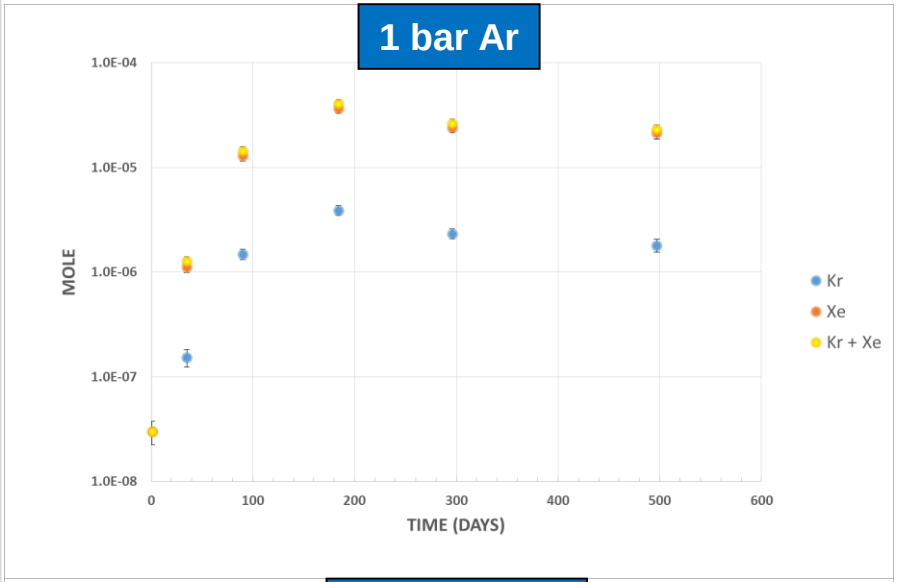
- **α-spectroscopy:** ^{238,239,240,242}Pu and further α-emitters.
- **γ-spectroscopy:** ^{144}Ce, ^{154,155}Eu, ^{241}Am, ^{134,137}Cs, ^{60}Co, ^{129}I.
- **LSC:** ^{241}Pu, ^{90}Sr.
- **HR-ICP-MS:** ^{99}Tc, ^{235,238}U, ^{237}Np, ^{239,240,241,242}Pu, ^{241,243}Am, ^{244}Cm.
- **gas-MS:** fission gases Kr, Xe, H_2, Ar, radiolytic O_2 and also intrusion of air checked (N_2).

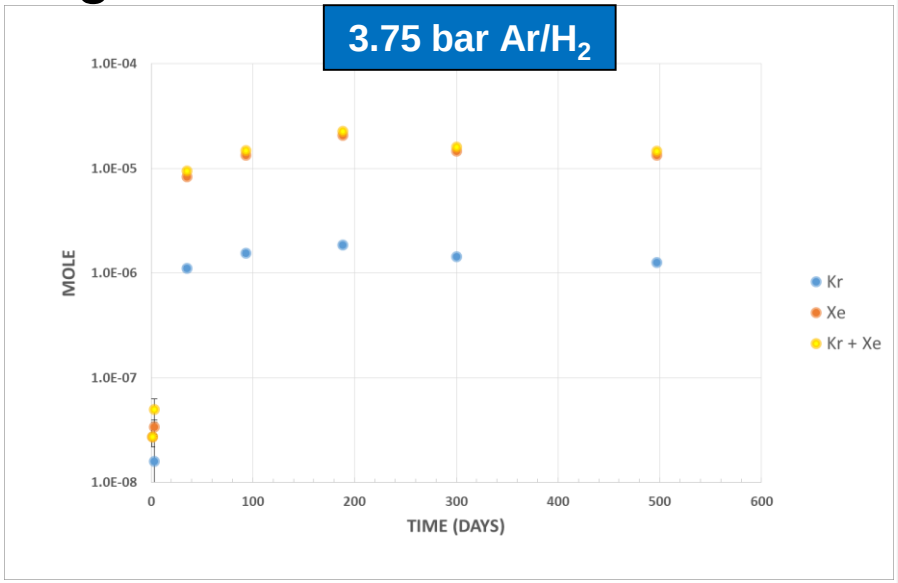
Results: SNF inventory calculation

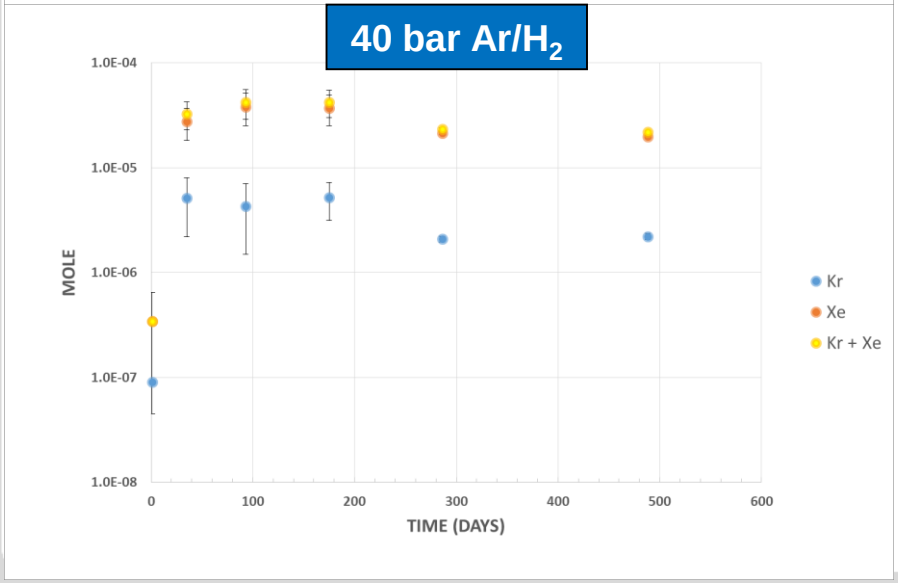
- KORIGEN code.
- Cooling time: 28 years.
- Inventory of Kr, Xe and Kr+Xe was calculated taking into account the inventory released into the plenum.

	mol/g_{UO2}
Kr	4.6E-06
Xe	4.8E-05
Kr + Xe	5.2E-05
Sr-90	3.8E-06
Cs-137	6.2E-06
U-238	3.4E-03
Np-237	2.8E-06
Pu-239	2.1E-05
Am-243	8.4E-07
Cm-244	1.2E-07

Results: moles released of fission gases



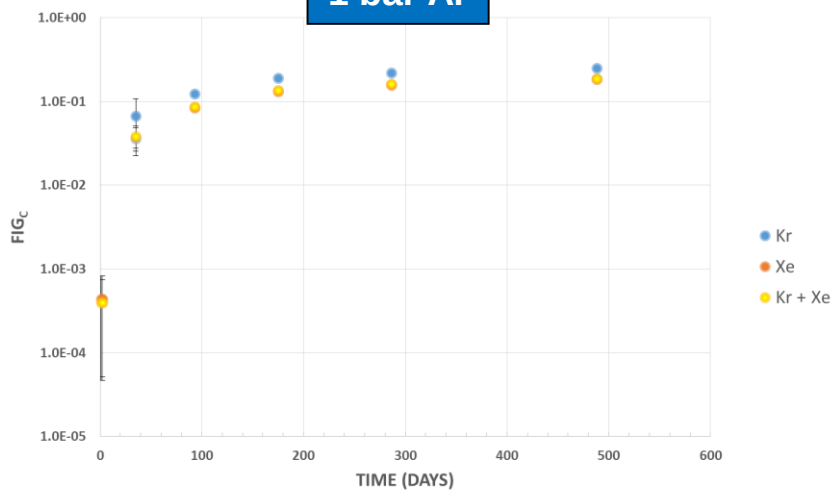




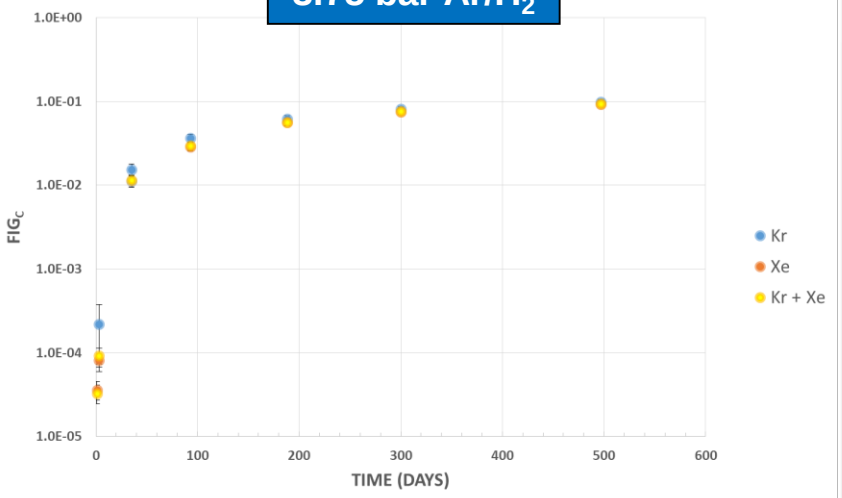
- Kr below detection limit in wash cycle of all experiments.
- Fission gas release decreasing after about 200 days of leaching.

Results: cumulative release fraction of FG

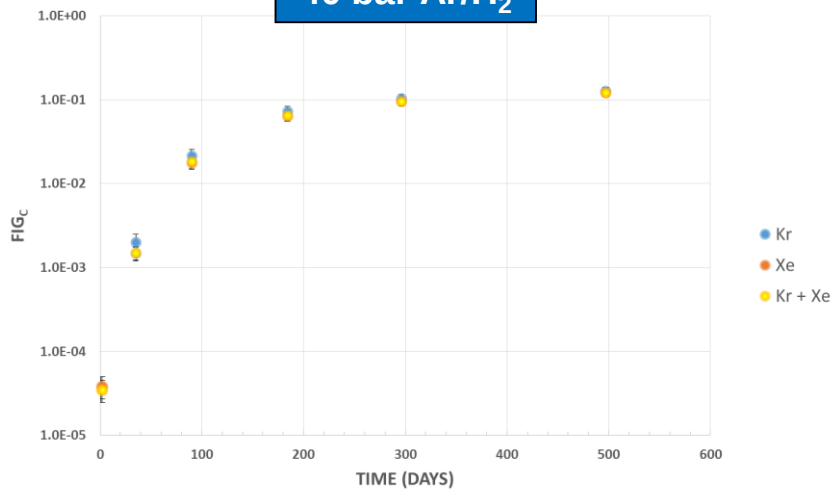
1 bar Ar



3.75 bar Ar/H_2



40 bar Ar/H_2

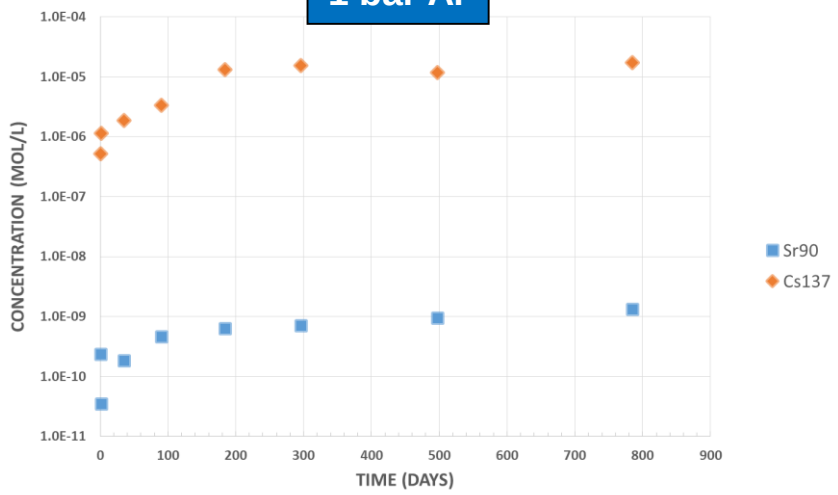


- Fission gases release (cumulative) in % after 500 days of leaching:

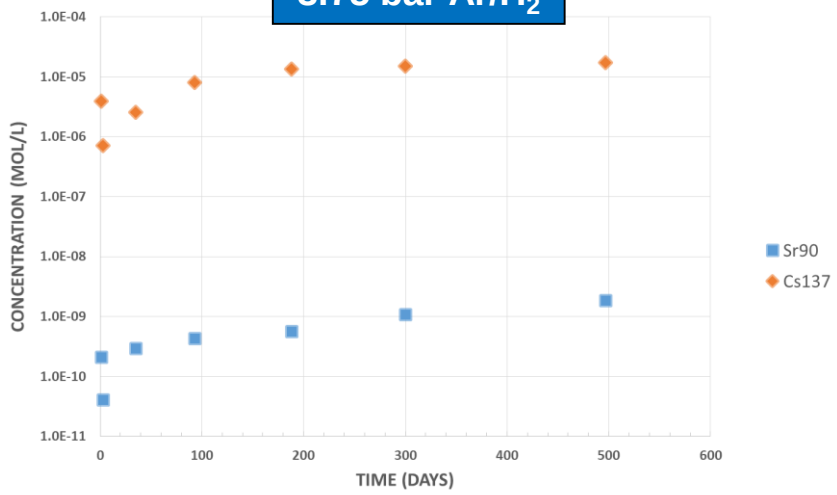
	40 bar Ar/H_2	3.75 bar Ar/H_2	1 bar Ar
Kr (%)	24.9 ± 6.2	9.9 ± 0.6	12.8 ± 1.0
Xe (%)	18.4 ± 2.8	9.4 ± 0.5	12.2 ± 0.9
Kr + Xe (%)	18.9 ± 2.7	9.4 ± 0.5	12.3 ± 0.9

Results: concentration of ^{90}Sr & ^{137}Cs in solution

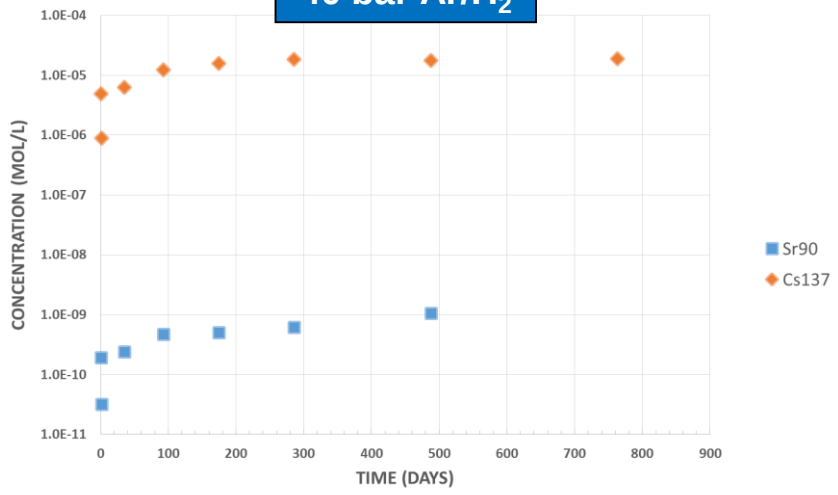
1 bar Ar



3.75 bar Ar/H_2



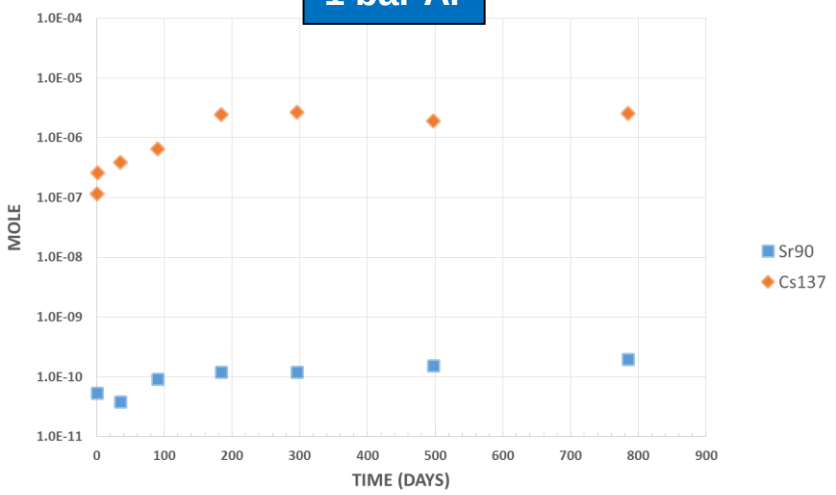
40 bar Ar/H_2



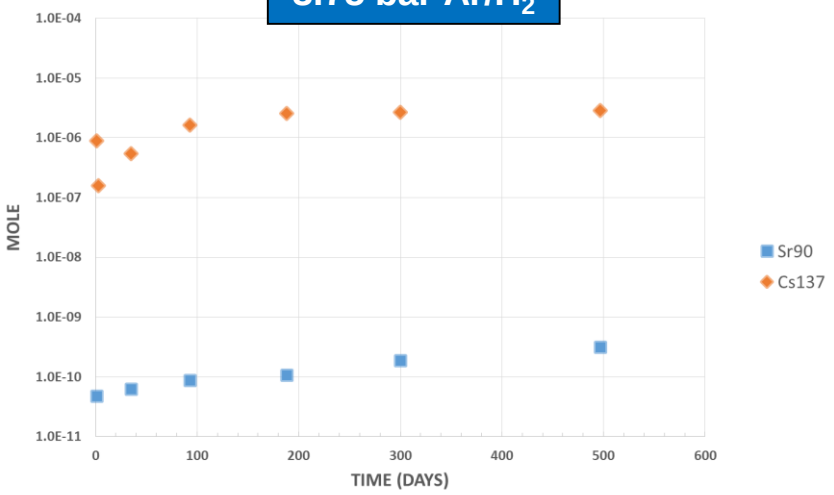
- ^{137}Cs and ^{90}Sr concentrations similar in the three experiments at same time step.
- Concentration of ^{90}Sr and ^{137}Cs after 780 days of leaching still increasing.

Results: moles released of ^{90}Sr & ^{137}Cs

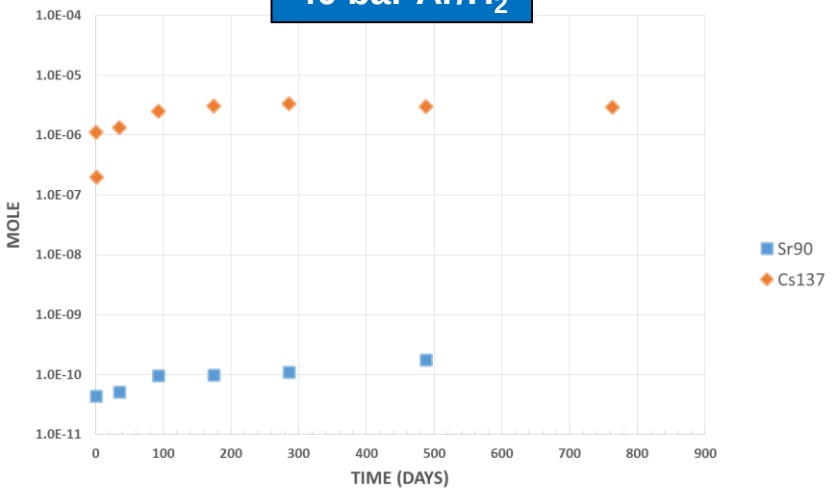
1 bar Ar



3.75 bar Ar/H_2



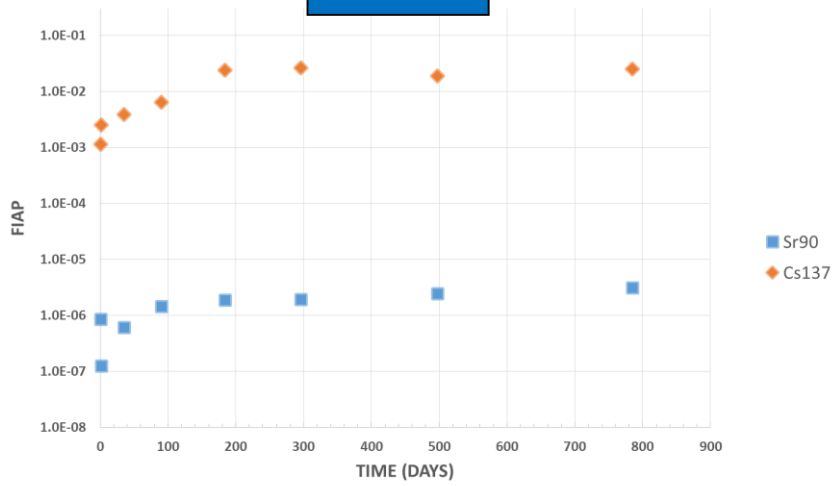
40 bar Ar/H_2



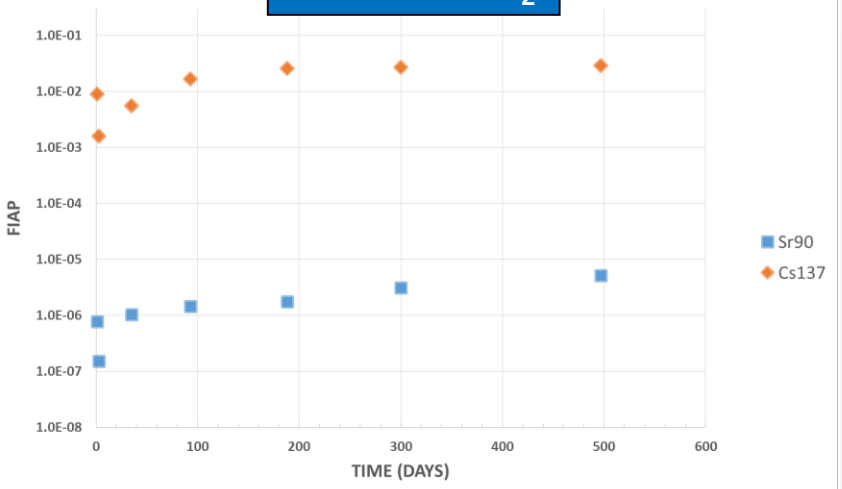
- The mole released in solution follow the same trend as the measured concentrations.
- After 780 days of experiment there are still moles of ^{90}Sr and ^{137}Cs released into the solution.

Results: release fraction of ^{90}Sr and ^{137}Cs

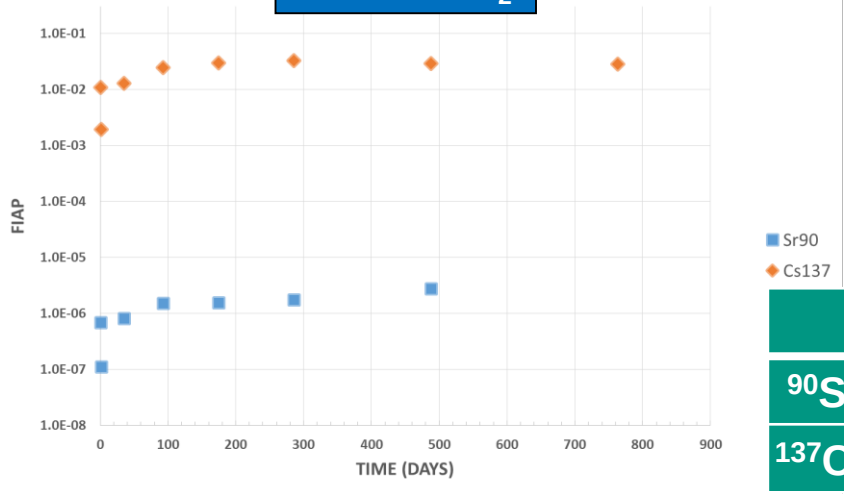
1 bar Ar



3.75 bar Ar/H_2



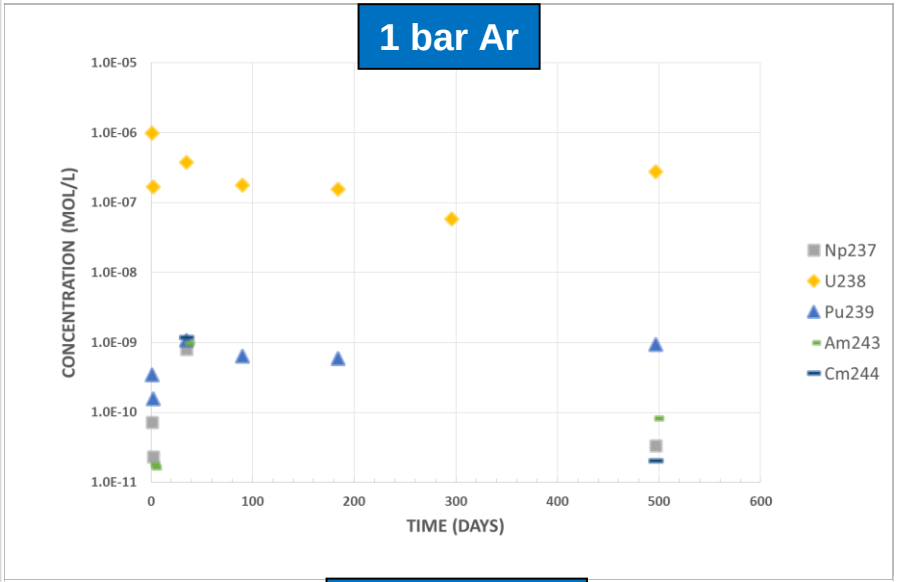
40 bar Ar/H_2

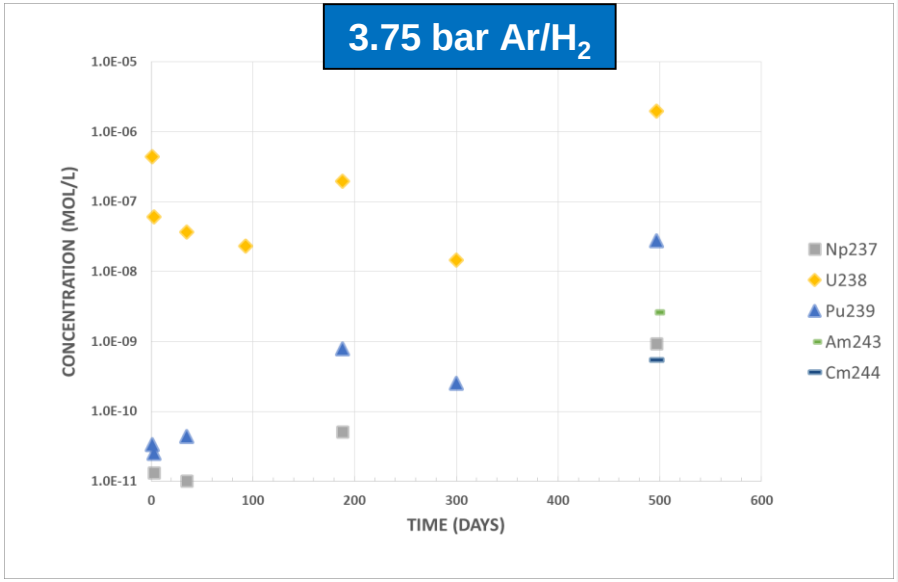


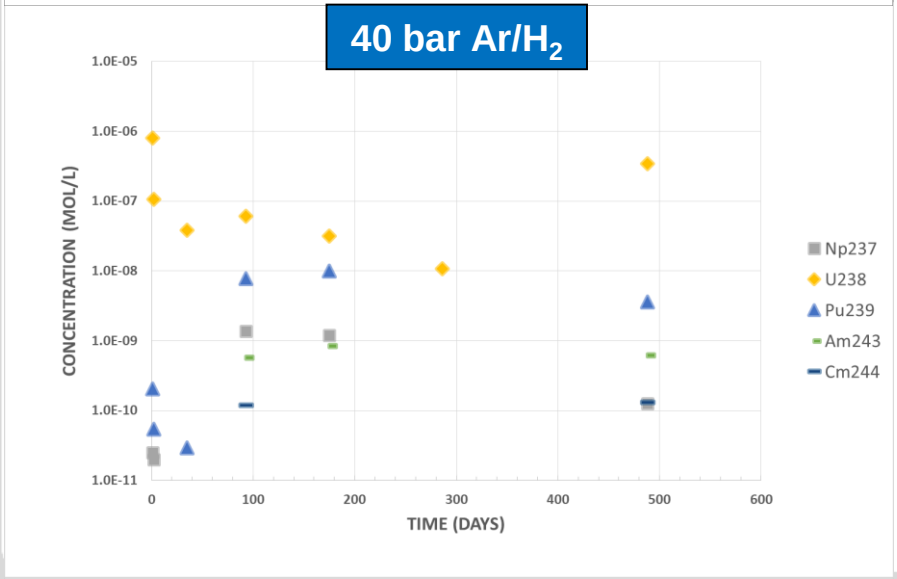
- Release fraction in % for wash step and last sampling:

	40 bar Ar/H_2	3.75 bar Ar/H_2	1 bar Ar
^{90}Sr (%)	7×10^{-5} / 2×10^{-4}	8×10^{-5} / 3×10^{-4}	9×10^{-5} / 2×10^{-4}
^{137}Cs (%)	1.1 / 3.3	0.9 / 2.7	0.1 / 2.6

Results: concentration of actinides in solution







- [U] constant between 10^{-8} and 10^{-7} M in all experiments and [An] in pure Ar experiment seem constant.
- ^{237}Np, ^{239}Pu and ^{243}Am reach concentration plateau between 10^{-10} and 10^{-8} M after 100 days of leaching in 40 bar Ar/H_2 experiment.
- [An] in 0.3 bar H_2 + 3.45 bar Ar experiments seem to increase.

Conclusions and outlook

- The IRF of fission gases , ^{90}Sr and ^{137}Cs has been determined over 500 days of leaching.
- There is still a release of fission gases, ^{90}Sr and ^{137}Cs in the 3 experiments as indicated by the mole and fraction released into the solution and into the gas phase.
- Concentration of actinides in all experiments significantly lower than in experiments performed under oxic conditions.
- Actinides concentrations constant in pure Ar experiment.
- Indications for similar behavior in 40 bar Ar/H_2 experiment.
- Increase of actinide concentrations in 3.75 bar Ar/H_2 experiment.

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