STUDIECENTRUM VOOR KERNENERGIE
CENTRE D'ETUDE DE L'ENERGIE NUCLEAIRE

# A general evaluation of the behavior of high-level waste forms in Supercontainer conditions

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# Outline of the presentation

- Description of the high level waste forms
- Description of the boundary conditions to which the waste forms will be exposed in the Supercontainer design
- Expected waste form behavior and uncertainties

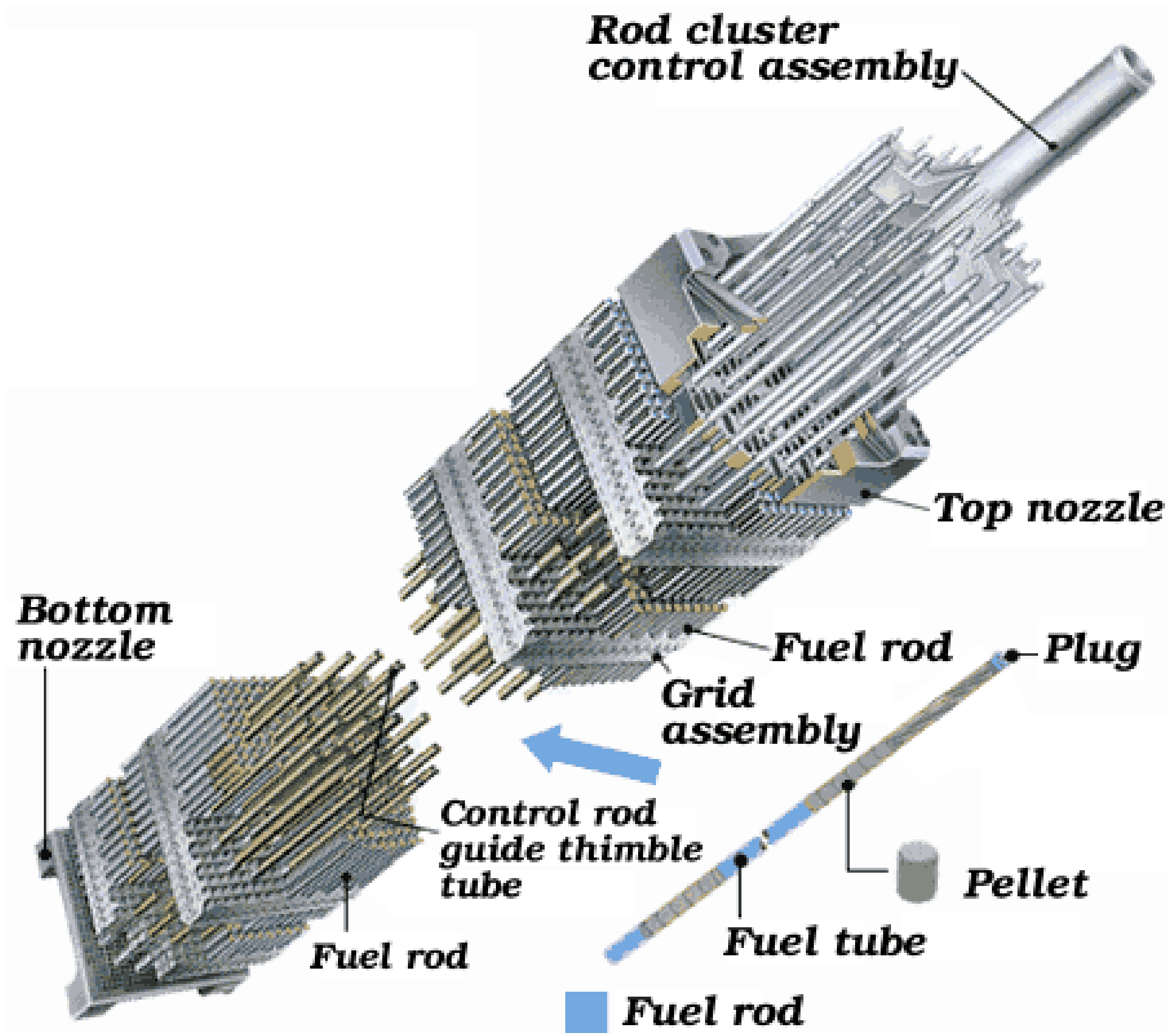
# Classes of (Very) High-Level waste (VHLW/HLW)

- *Very high-level waste (heat emitting):*
  - From nuclear energy production
  - Expected amount after 40 years electricity production:
    - 4643 tHM uranium oxide **(UOX) spent fuel** (ZAGALS)
    - 66 tHM mixed oxide **(MOX) spent fuel** (ZAGALS)
    - 390 canisters (150 L) with **vitrified very high-level waste** (ZAGALC)

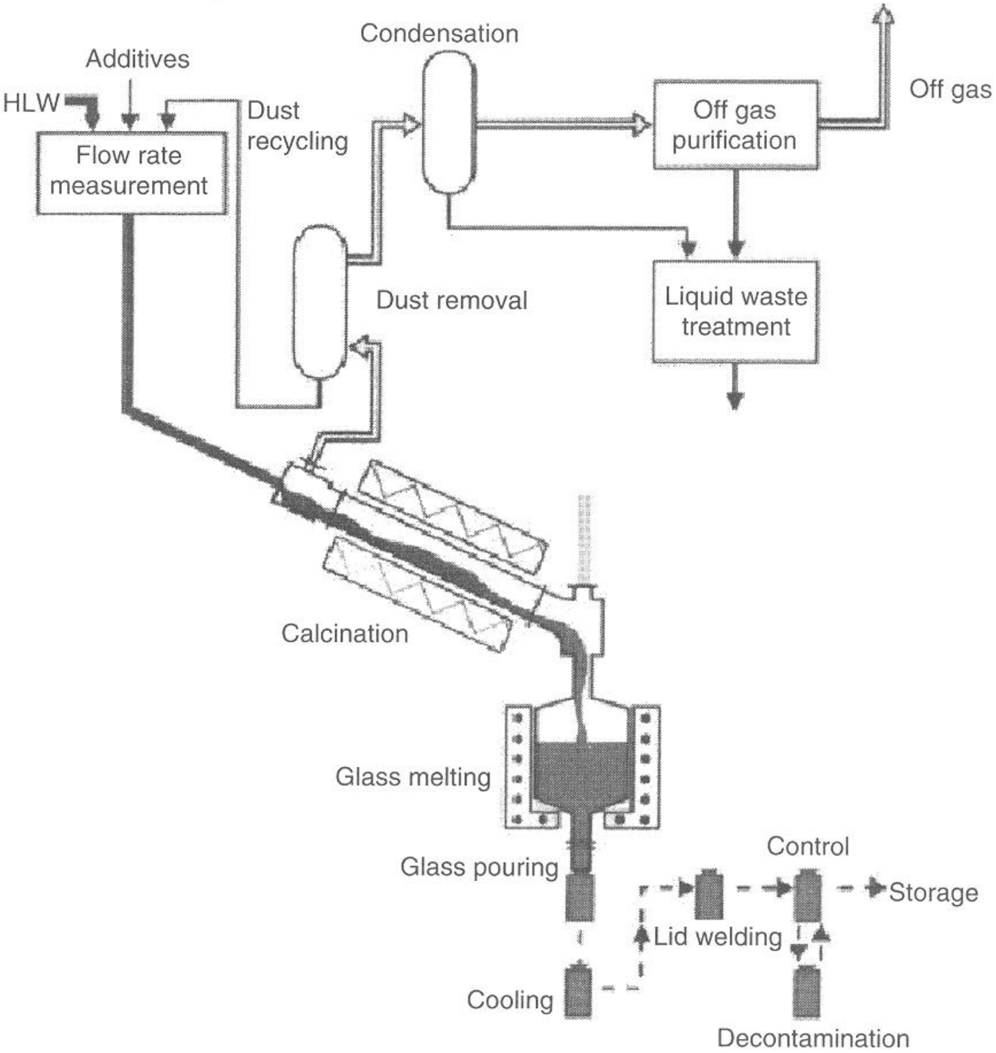
      → SON68 glass (AREVA)
- *High-level waste (less heat emitting):*
  - Historical waste from Eurochemic reprocessing pilot plant
    - **Vitrified waste**: 1501 canisters of 60L- (HAGALP1) → PAMELA glass
    - **Vitrified waste**: 700 canisters of 150L (HAGALP2 ) → PAMELA glass
    - Cement matrix: 134 canisters of 150L (HAGALP3)
    - Compacted structural/technological waste (HAGALC2)

    Not included

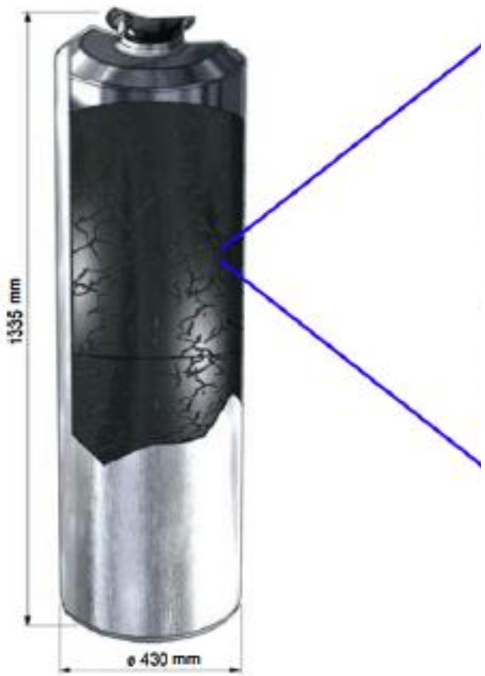
# Spent fuel assemblies placed in primary package without further conditioning

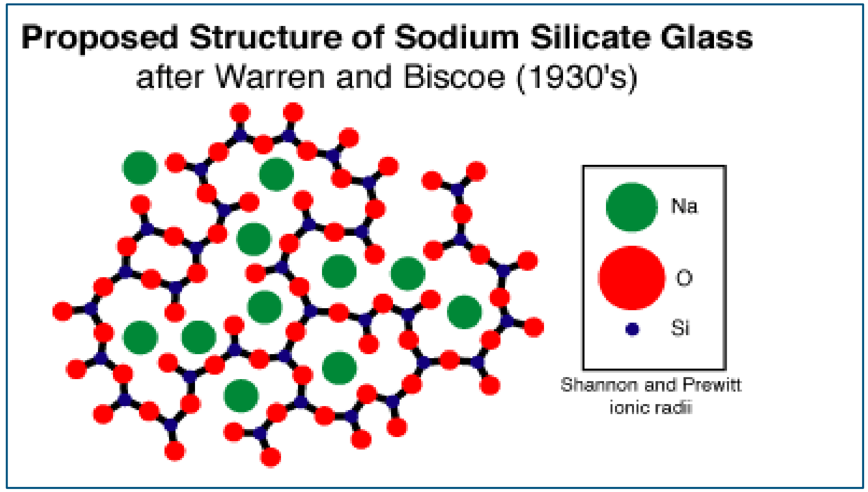


# Vitrified waste (conditioned reprocessing waste)

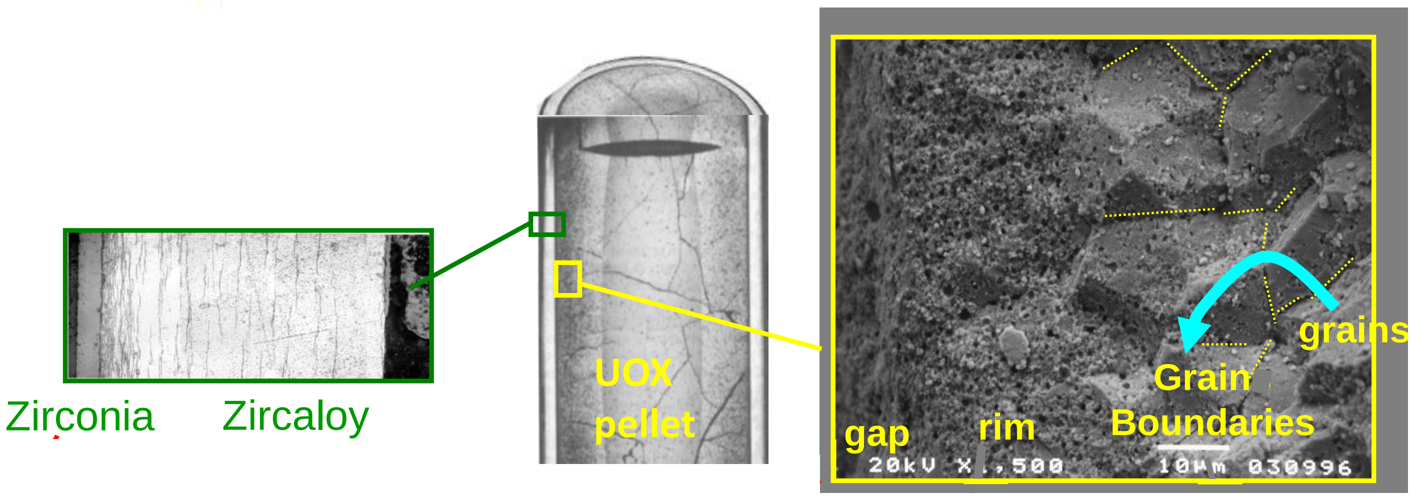



# Different microstructure of glass and spent fuel




Waste glass: homogeneous amorphous Alumino-Boro-Silicate structure trapping the radionuclides




Spent fuel: inhomogeneous, with varying radionuclides in cladding, in gap, in rim zone, in deeper (crystalline) UOX matrix, and in grain boundaries

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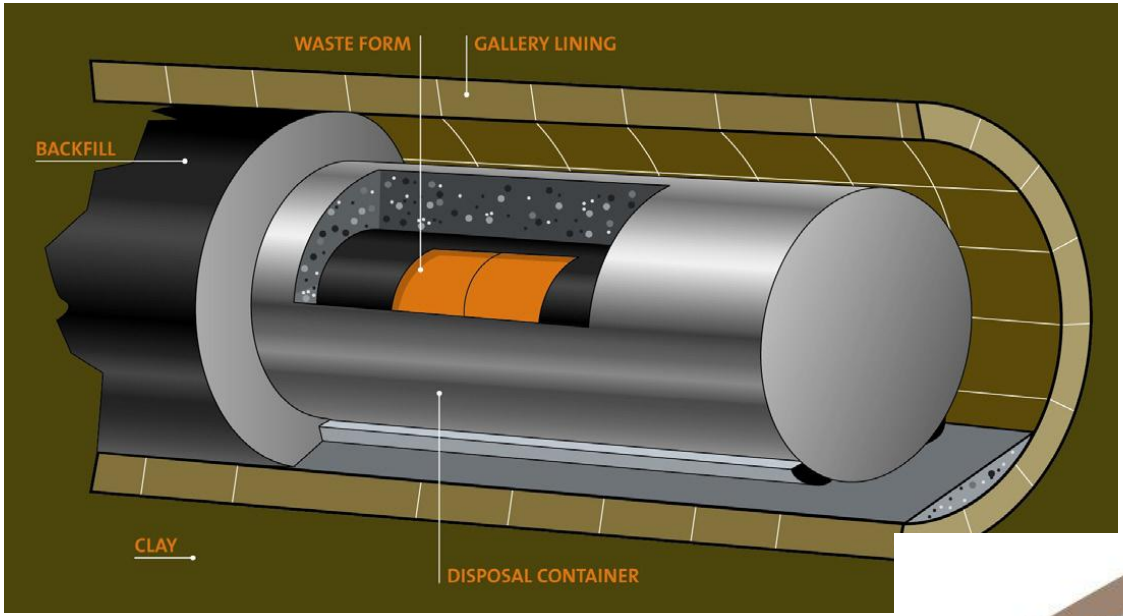
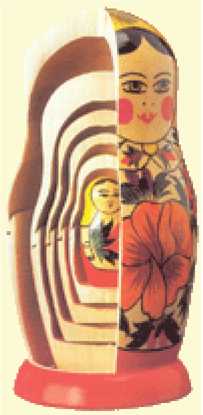
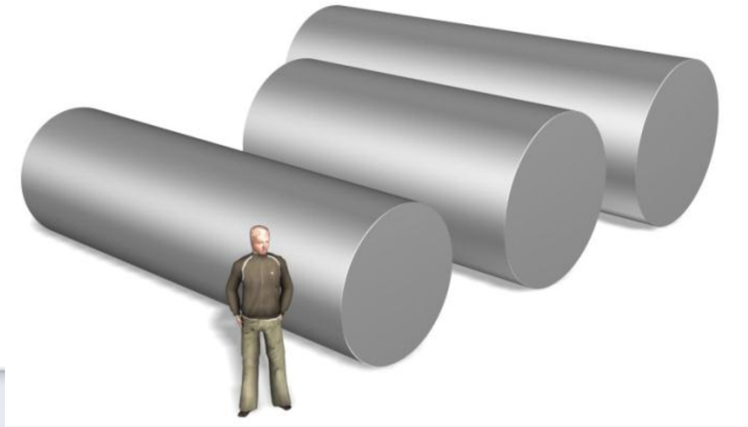
# Geological disposal of very high level waste in 'Supercontainers'

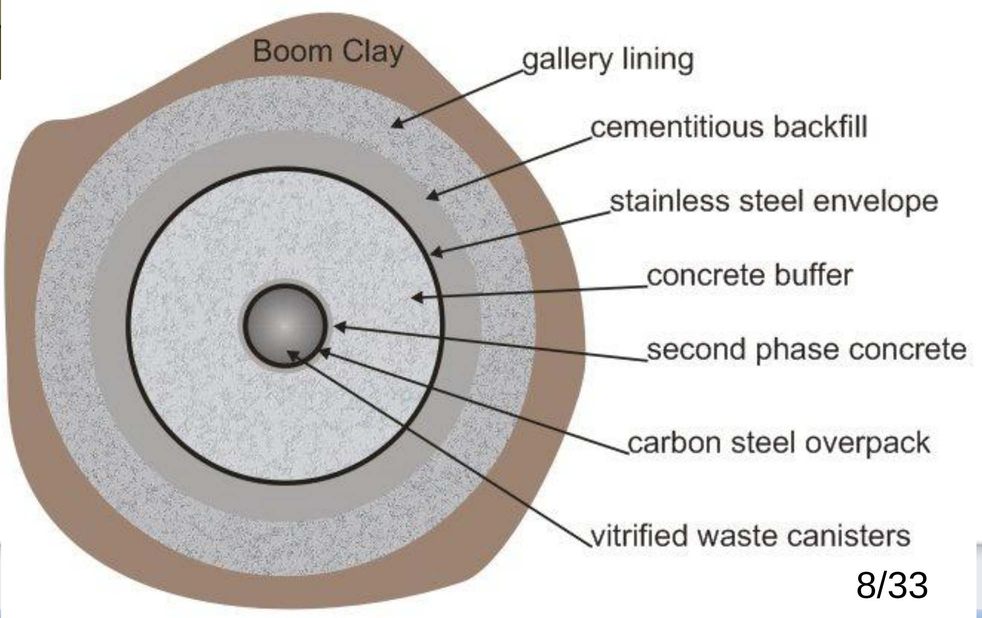



Multibarrier system



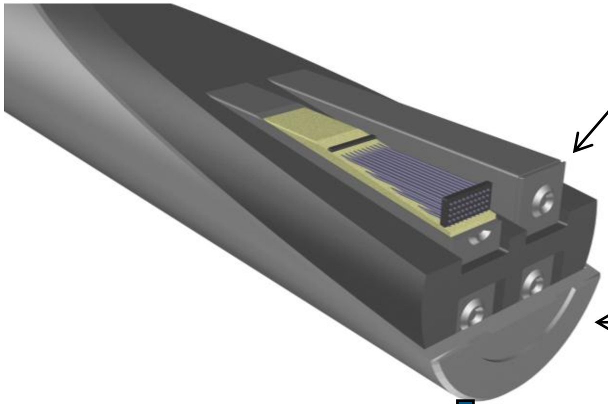
**SON68 glass (AREVA)**





# Supercontainer for spent fuel assemblies

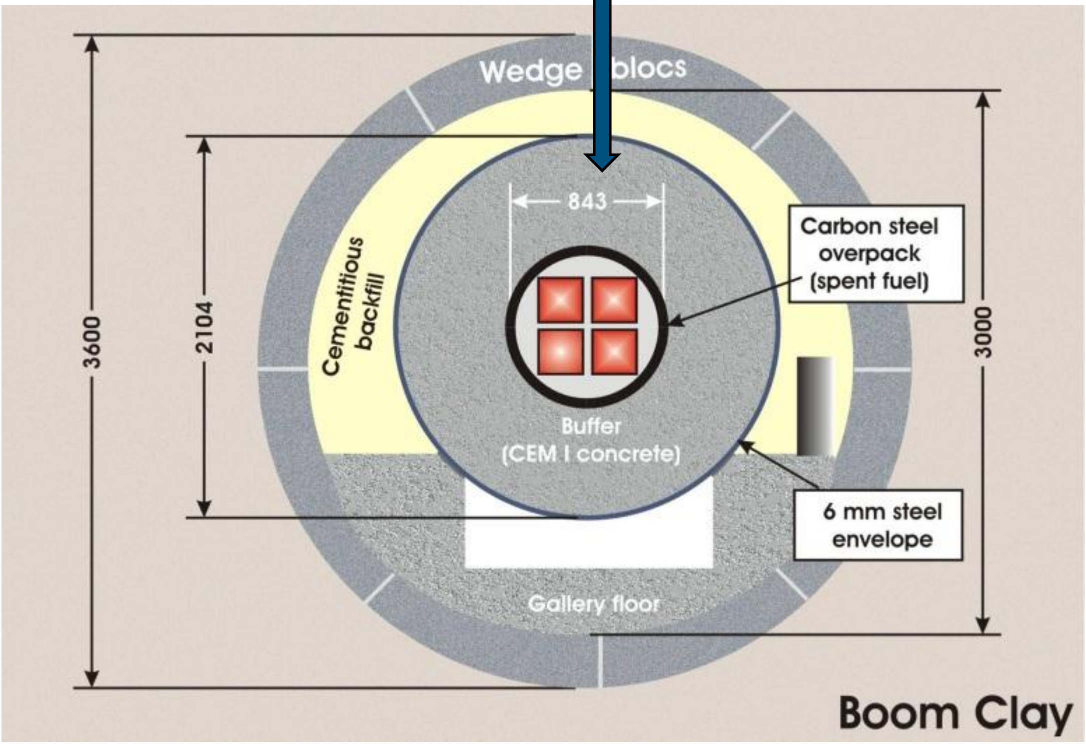
Fuel assembly



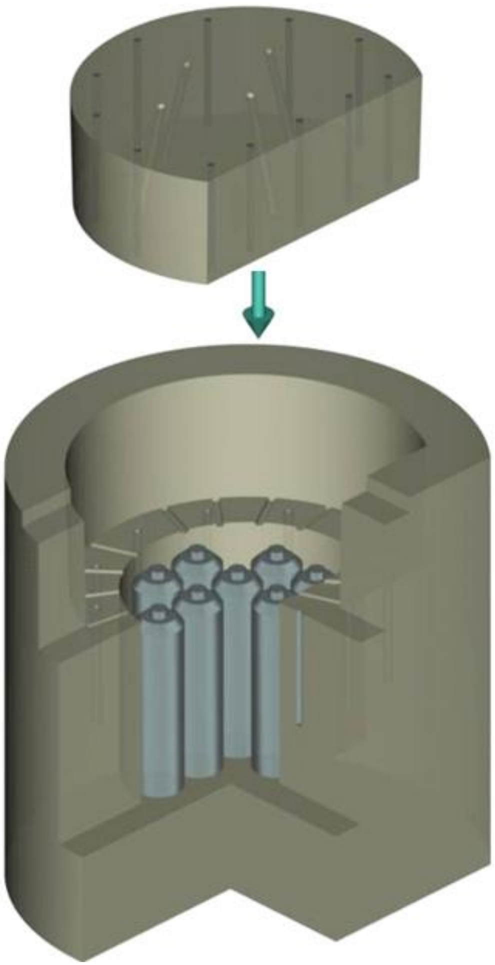
Assemblies packed in primary packages

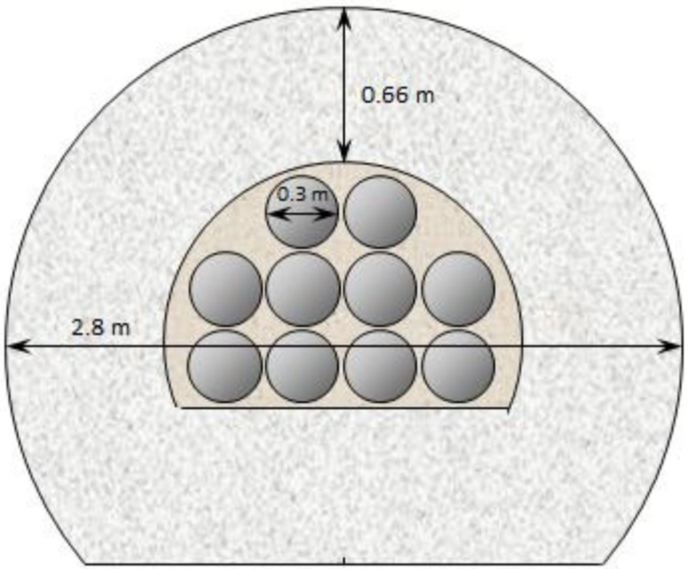
Cast iron insert

Overpack



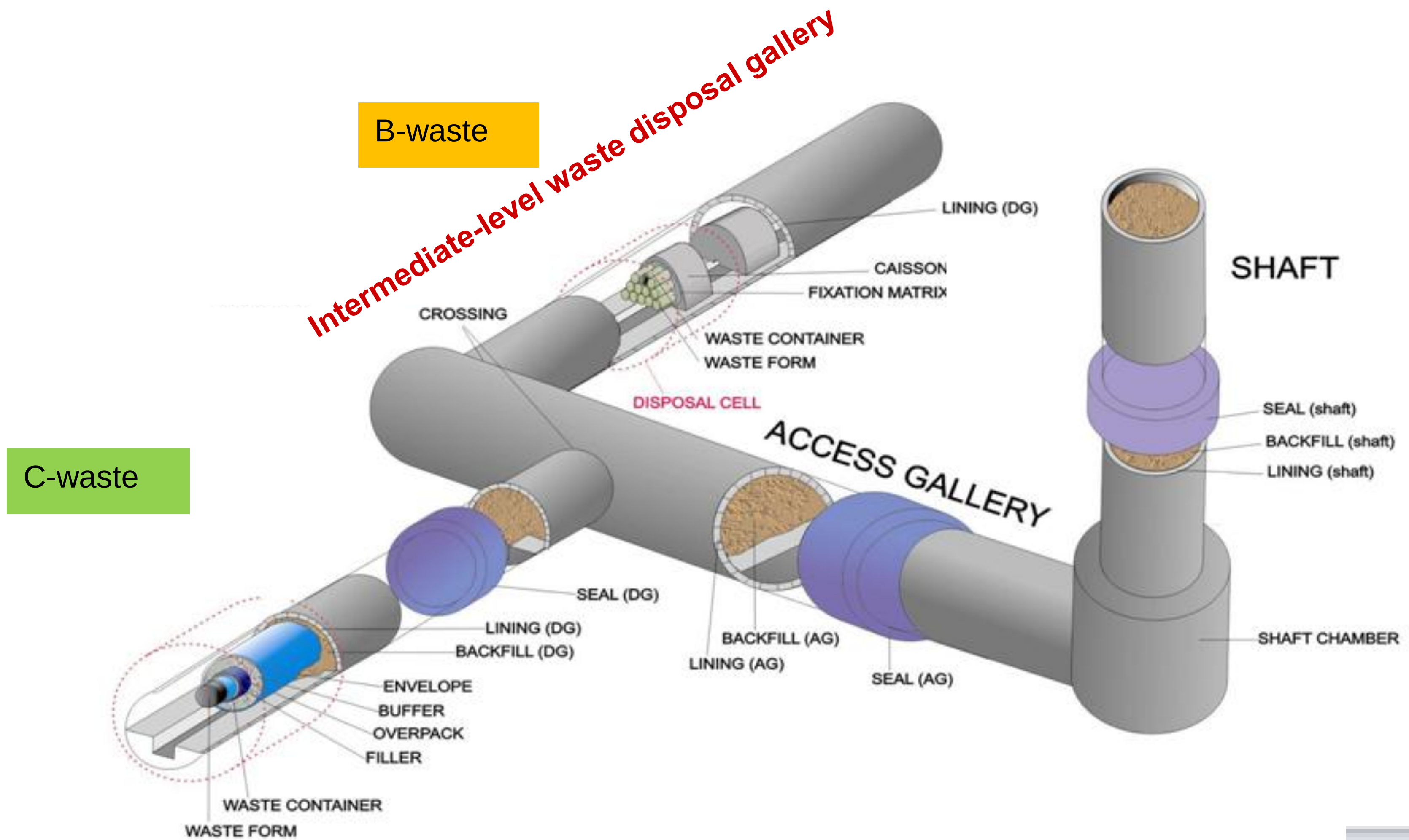
# PAMELA glass disposed of in monoliths for B-waste



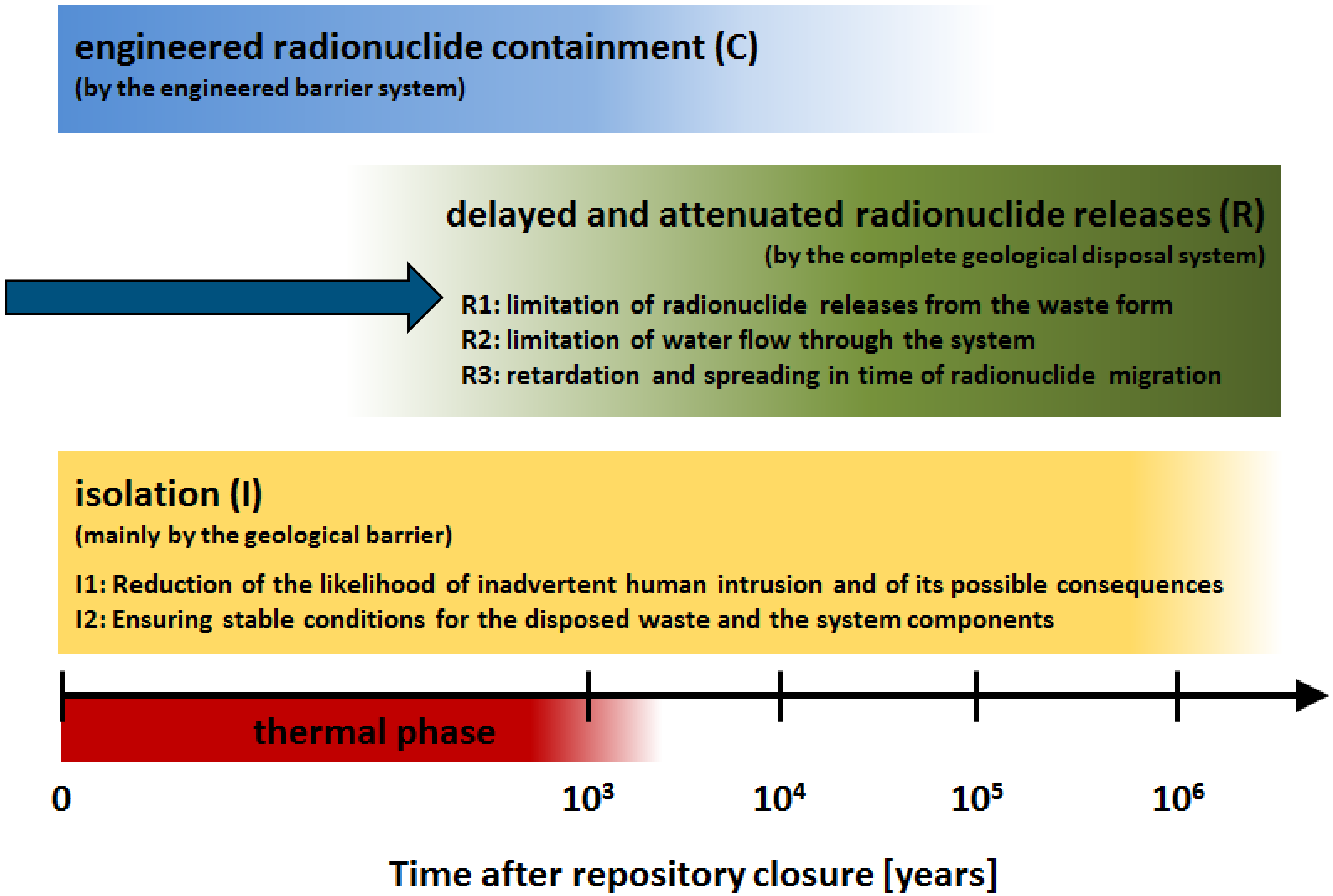


# The repository architecture

| | No further reprocessing | Full reprocessing |
|---|---|---|
| | gallery length (m) | gallery length (m) |
| **UOX spent fuel** | **14222.2** | **-** |
| **MOX spent fuel** | **792.0** | **-** |
| **V-HLW glass (AREVA)** | **792.7** | **6544.7** |
| **HLW glass (PAMELA)** | **172.5** | **1387.5** |



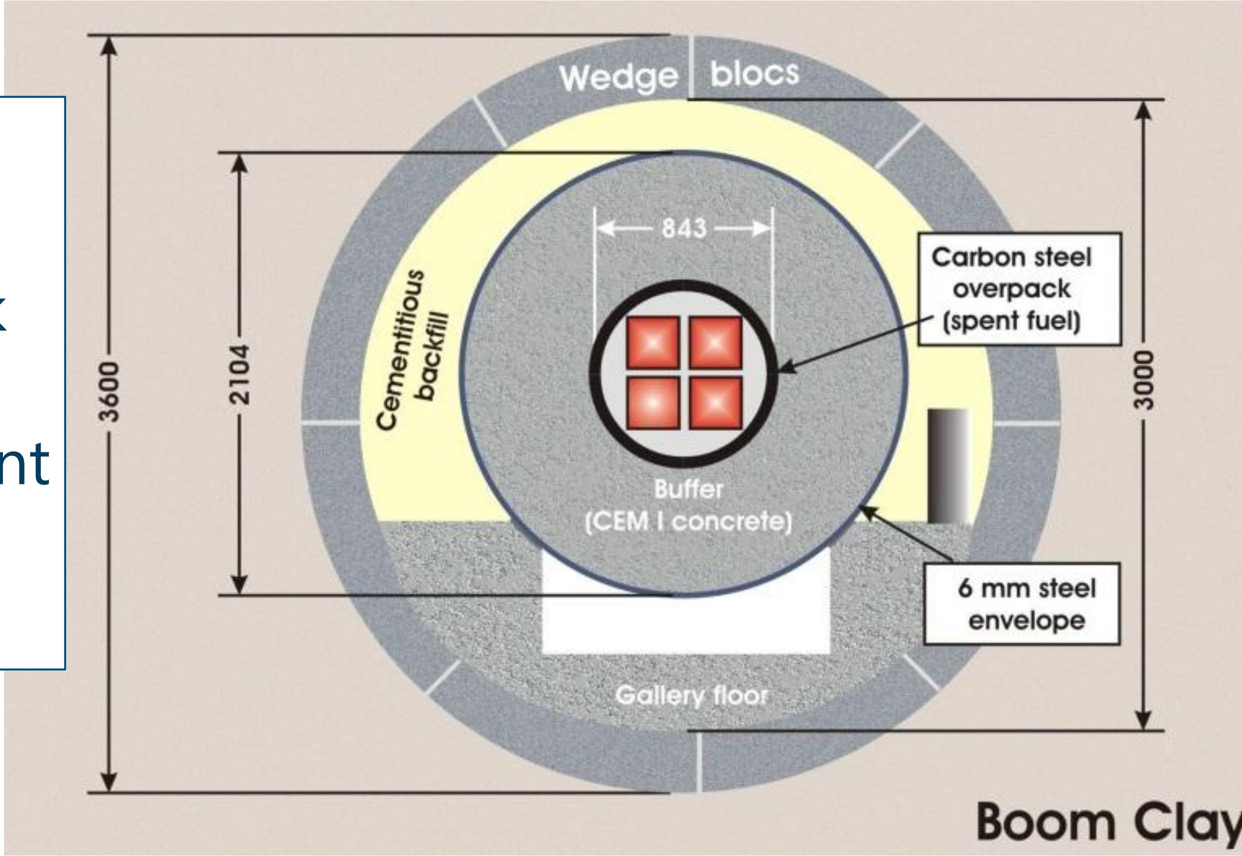
# Safety concept: Glass and spent fuel matrix limit radionuclide release (R1)



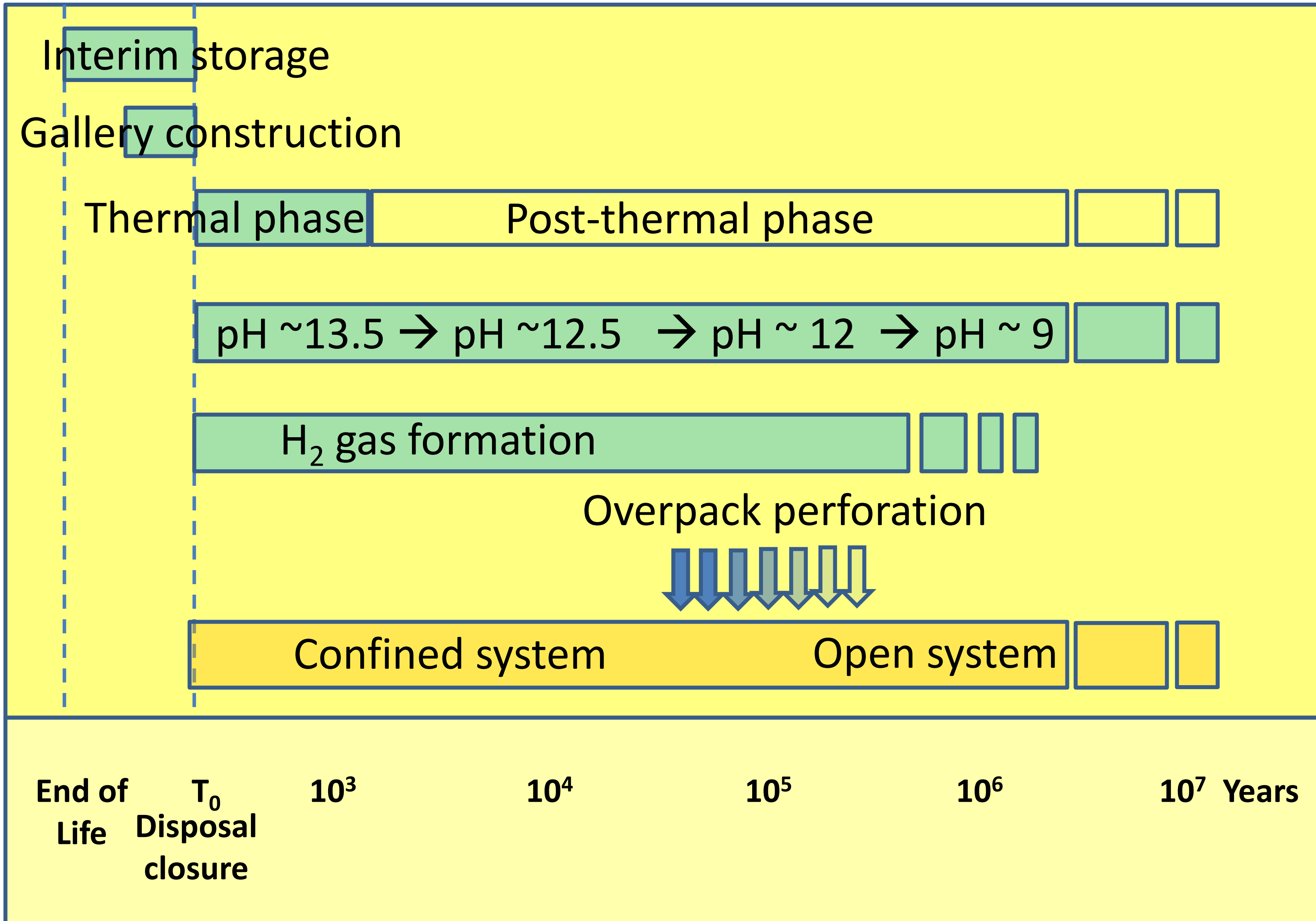
# The Supercontainer disposal design requires a specific evaluation of expected glass and spent fuel dissolution behavior

Concrete stabilizes carbon steel overpack

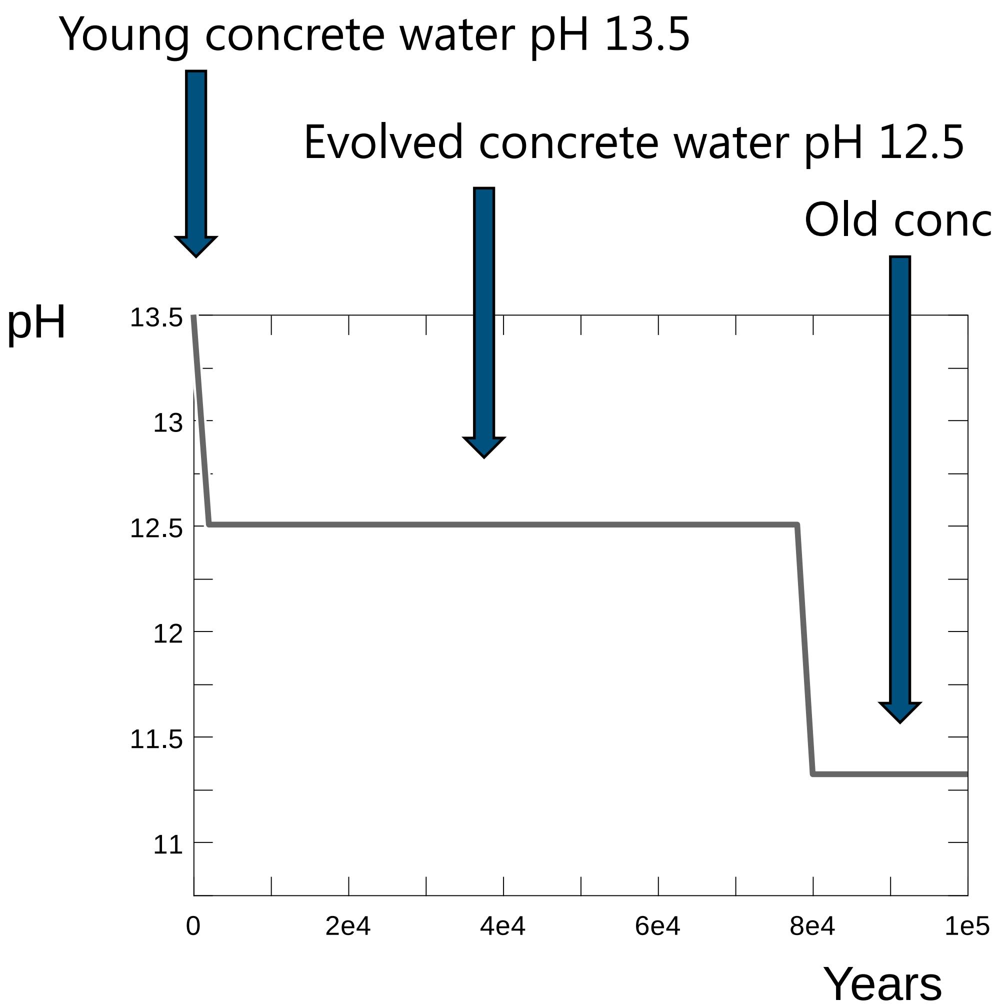
Effect on glass and spent fuel dissolution ?



# Boundary conditions depend on expected evolution



# Expected pH evolution [Wang, 2009]



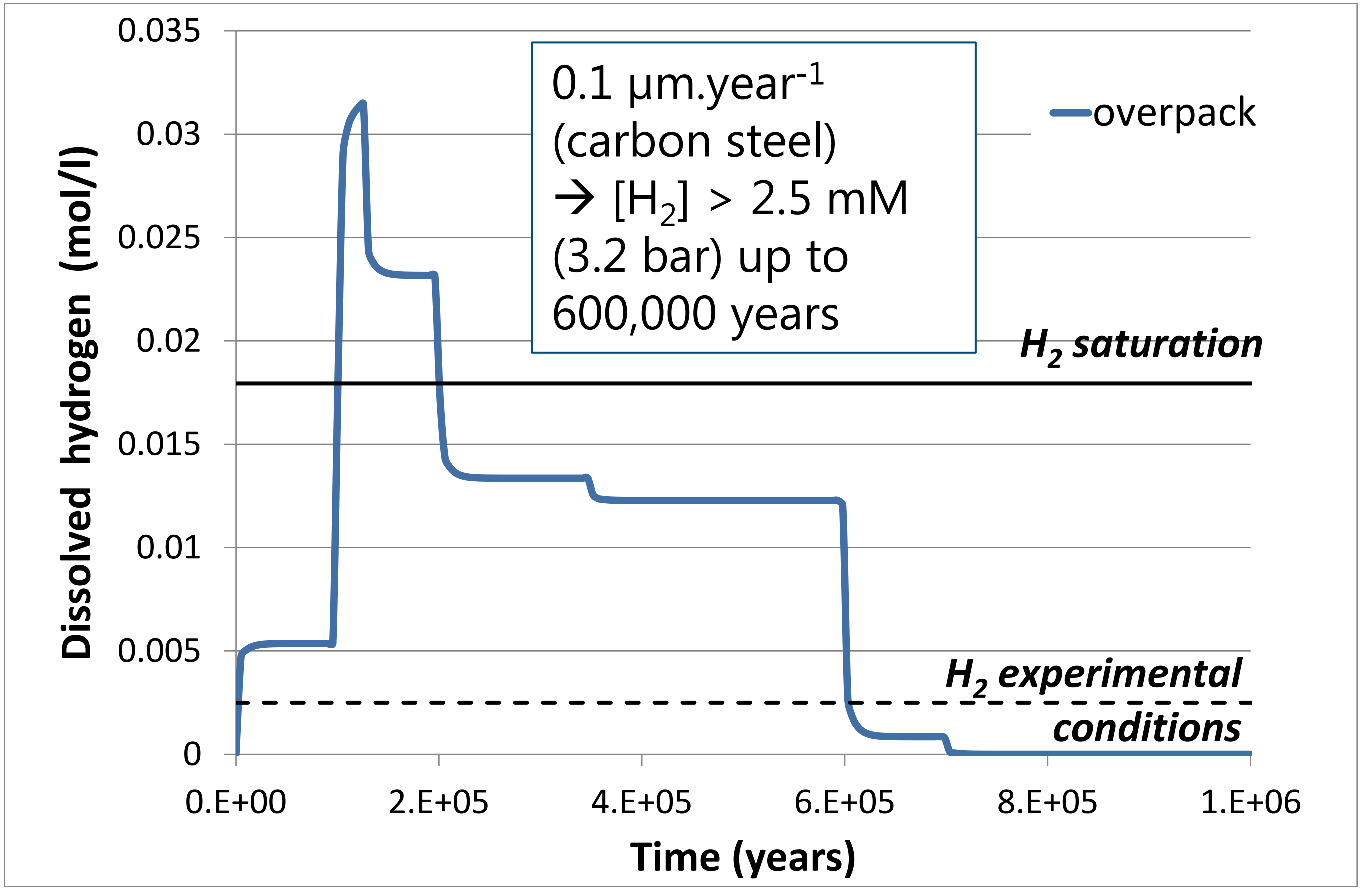

If perforation overpack after 50,000 years : pH 12.5

If perforation overpack after 100,000 years: pH <12

But sustained pH 13.5 (12.5) possible if clogging of concrete pores by carbonatation

→ both young concrete water (pH 13.5) and evolved concrete water (pH 12.5) considered

# Expected $H_2$ gas evolution [Yu and Weetjens, 2012] relevant for spent fuel stability




| | |
|---|---|
| Alternative , lower corrosion rate<br>0.01 µm.year$^{-1}$ (carbon steel) | → $[H_2]$ > 0.5 mM (0.7 bar) up to $10^6$ years<br>→ $[H_2]$ > 2.5 mM (3.2 bar) after $10^6$ years |

## Glass

- Tests with the real active vitrified HLW practically impossible (and relatively irrelevant)
- Simulated inactive glass with reference composition (SON68 glass, SM539 glass, SM513 glass)
- Possible: doping the glass with radioactive tracers

## Spent fuel

- Tests with real spent fuel (hot-cells) overestimate long-term dissolution rate (without $H_2$ gas) due to high $\beta,\gamma$ radiation
- Simulated fuel : depleted $UO_2$ or $UO_2$ doped with alpha emitters (U-233, Pu-238); test batches F1 (young fuel) to F6 (old fuel)
- Structure real spent fuel (grain boundaries, rim, composition) $\neq$structure $UO_2$ → tests with real spent fuel required

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# Main axes of the research programme supported by ONDRAF/NIRAS

- Study of glass/spent fuel dissolution mechanisms in Supercontainer boundary conditions (system understanding)
- Determine dissolution rates under Supercontainer boundary conditions (to be used in combination with surface area of glass/spent fuel)
- Validate knowledge with tests under ‘realistic’ conditions (e.g. tests in mock-ups, *in situ* experiments in Hades)

⇒ Evaluate dissolution rates, considering known mechanisms and natural analogues, to estimate (range of) realistic/robust dissolution rates (life time) under *in situ* conditions for specified evolution scenario’s.

# Two main parameters determine waste form life time: Surface area ($m^2$)* and dissolution rate ($g.m^{-2}day^{-1}$)

Glass: total surface area 5× to 40× external surface area due to cracks

→ 0.2 – 1.7 $cm^2.g^{-1}$

Spent fuel: large total surface area due to cracks, surface roughness and accessible grain boundaries

~10 $cm^2.g^{-1}$

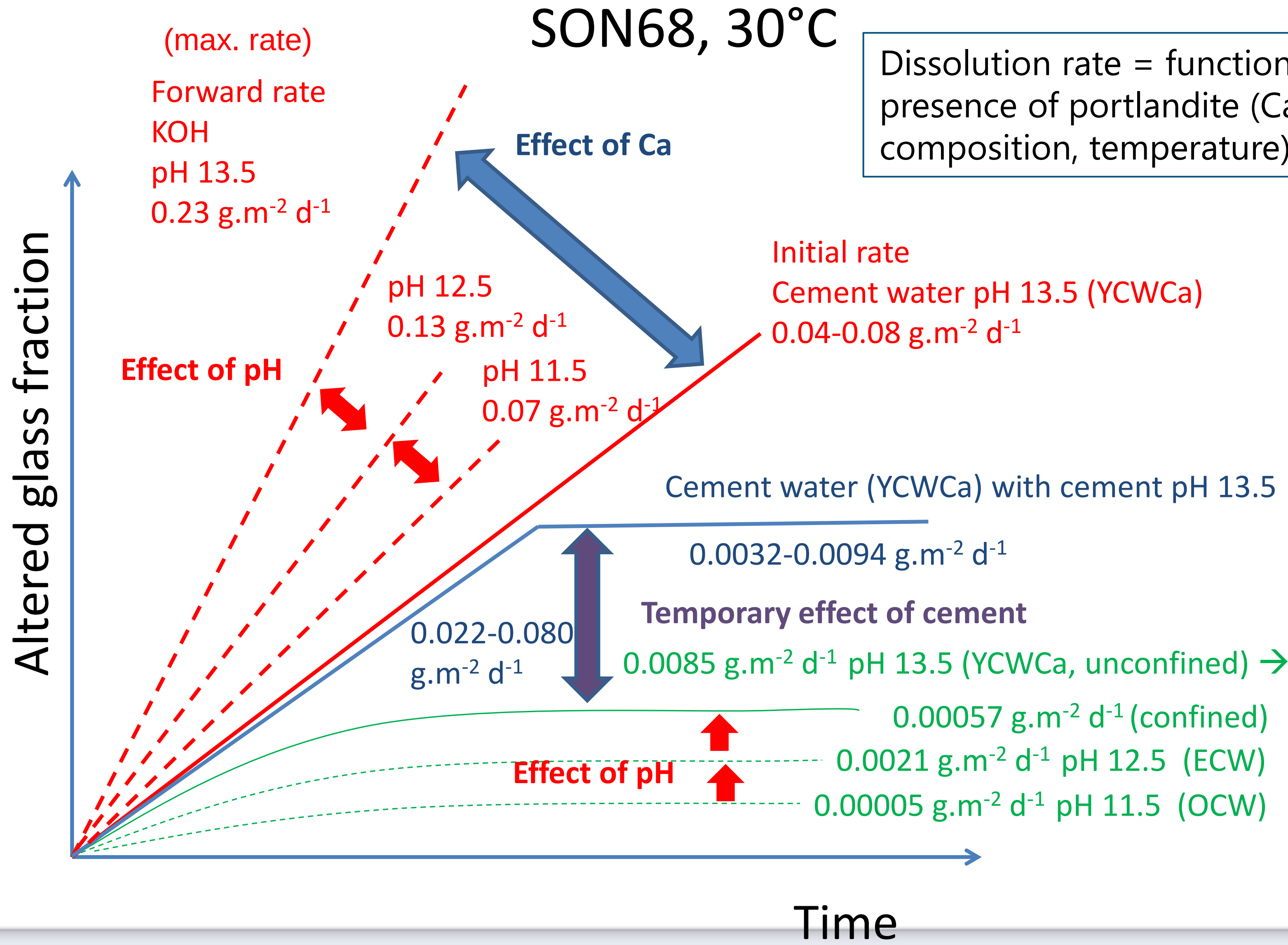
Glass: internal glass surfaces (narrow cracks) can be filled with precipitation products → small contribution

Spent fuel: surface area relevant only for oxidative $UO_2$ matrix dissolution

*Surface area not relevant when dissolution is solubility (→ diffusion) limited

# Dissolution rate of waste glass ($g.m^{-2}day^{-1}$)

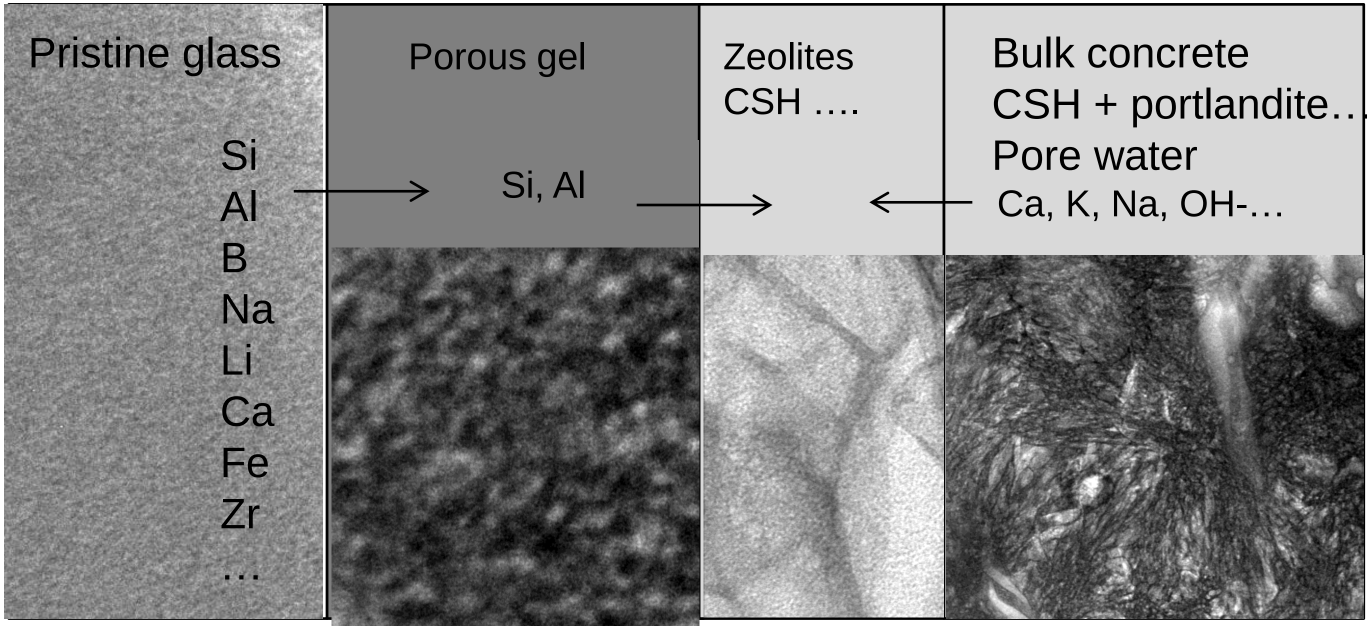
Dissolution rate = function of (pH, presence of portlandite (Ca), glass composition, temperature) a.o.



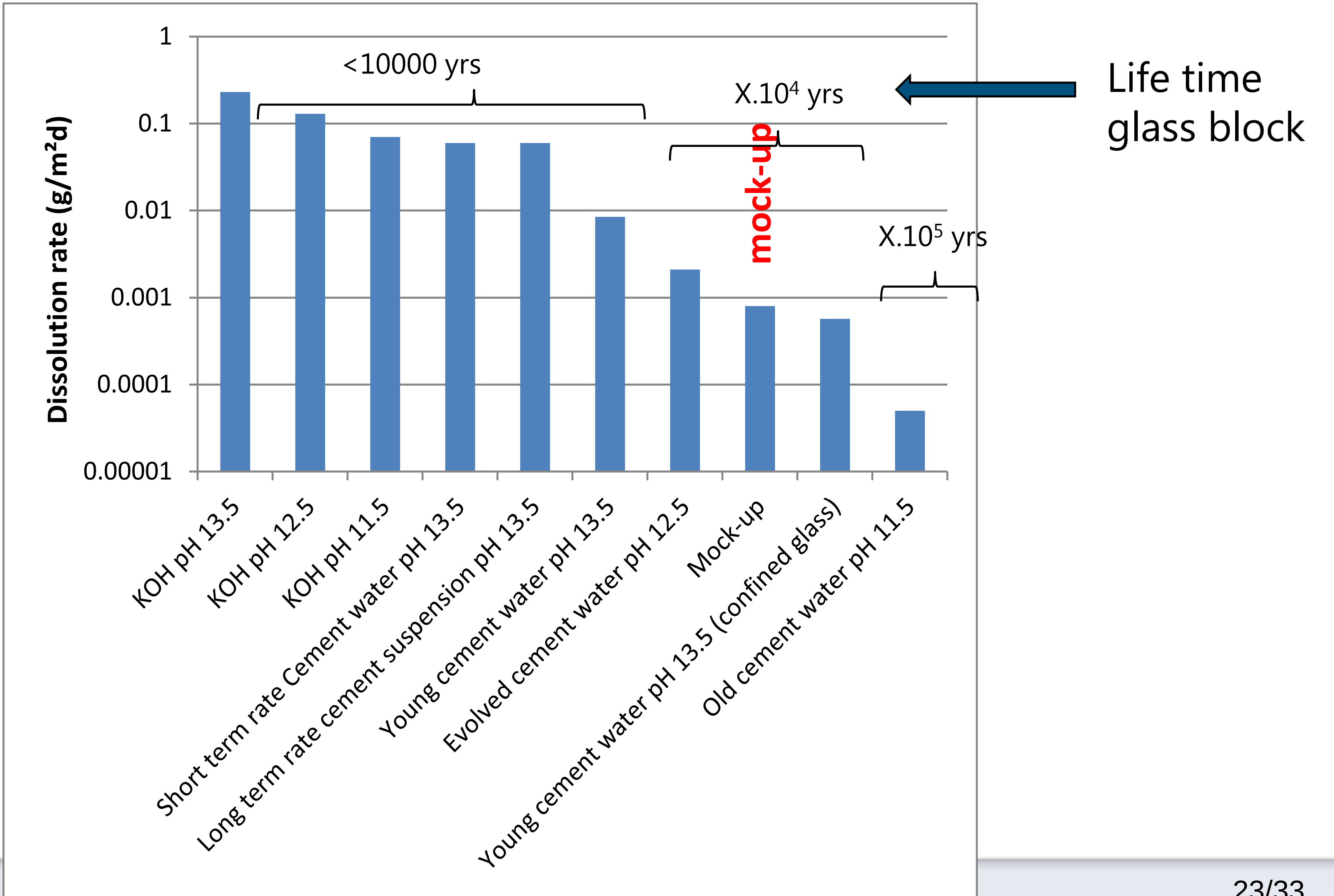
# Main rate controlling mechanism and uncertainties (glass)

- Dissolution driven by transformation of glass in other phases, but these are +/- amorphous → no good thermodynamic data
- Dissolution rate decreases by formation of altered interface between pristine glass and concrete → transport problem (diffusion)

➡ No detailed predictions possible (conservativeness required)

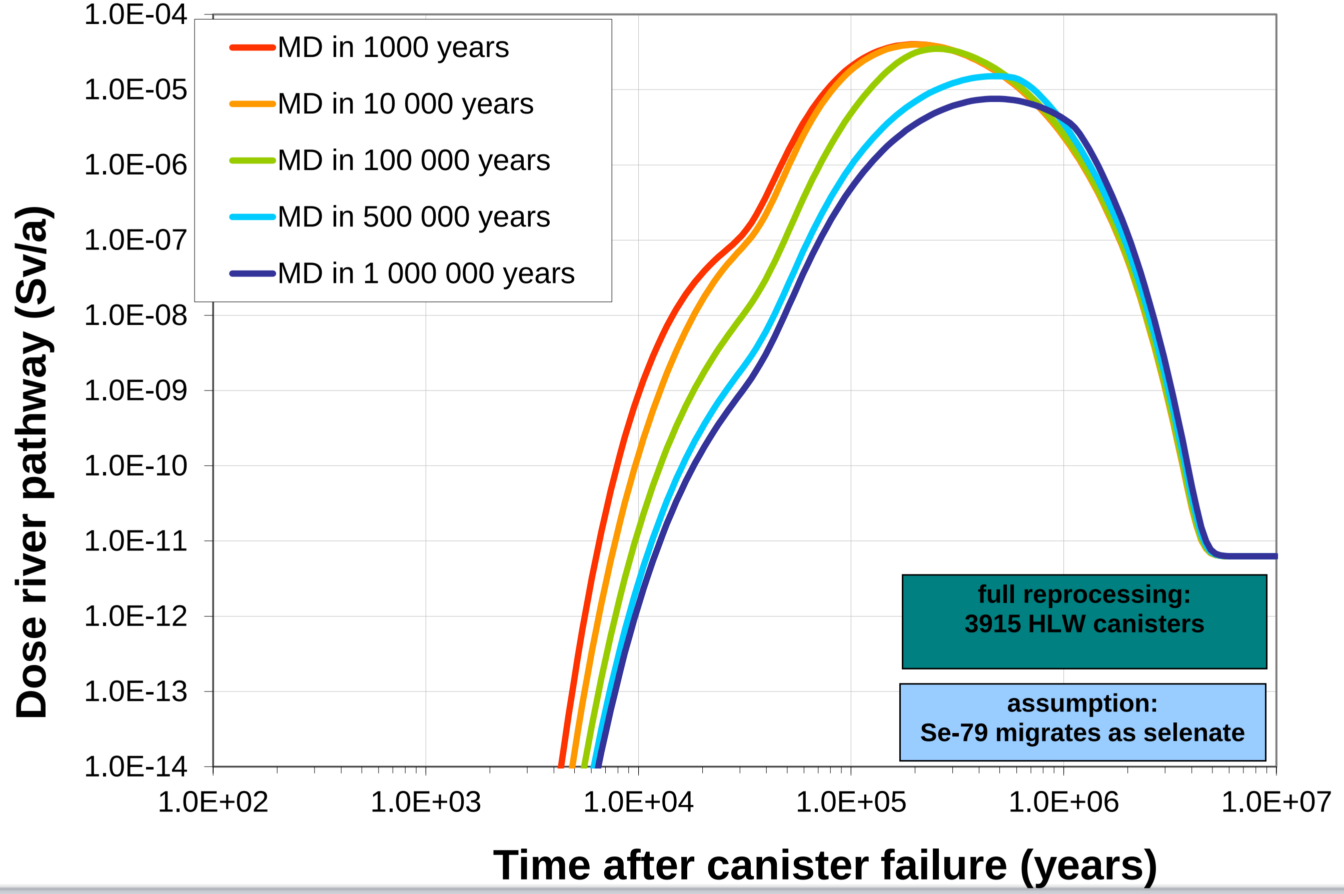


# Compilation of experimental dissolution rates for reference glass SON68 in high pH/cement conditions at 30°C



# Relation with safety evaluation:
## Life time glass block → Release rate of radionuclides → Diffusion through concrete and Boom Clay layer → Biosphere

Example: Calculated $^{79}$Se dose via river pathway for various assumptions of glass life time

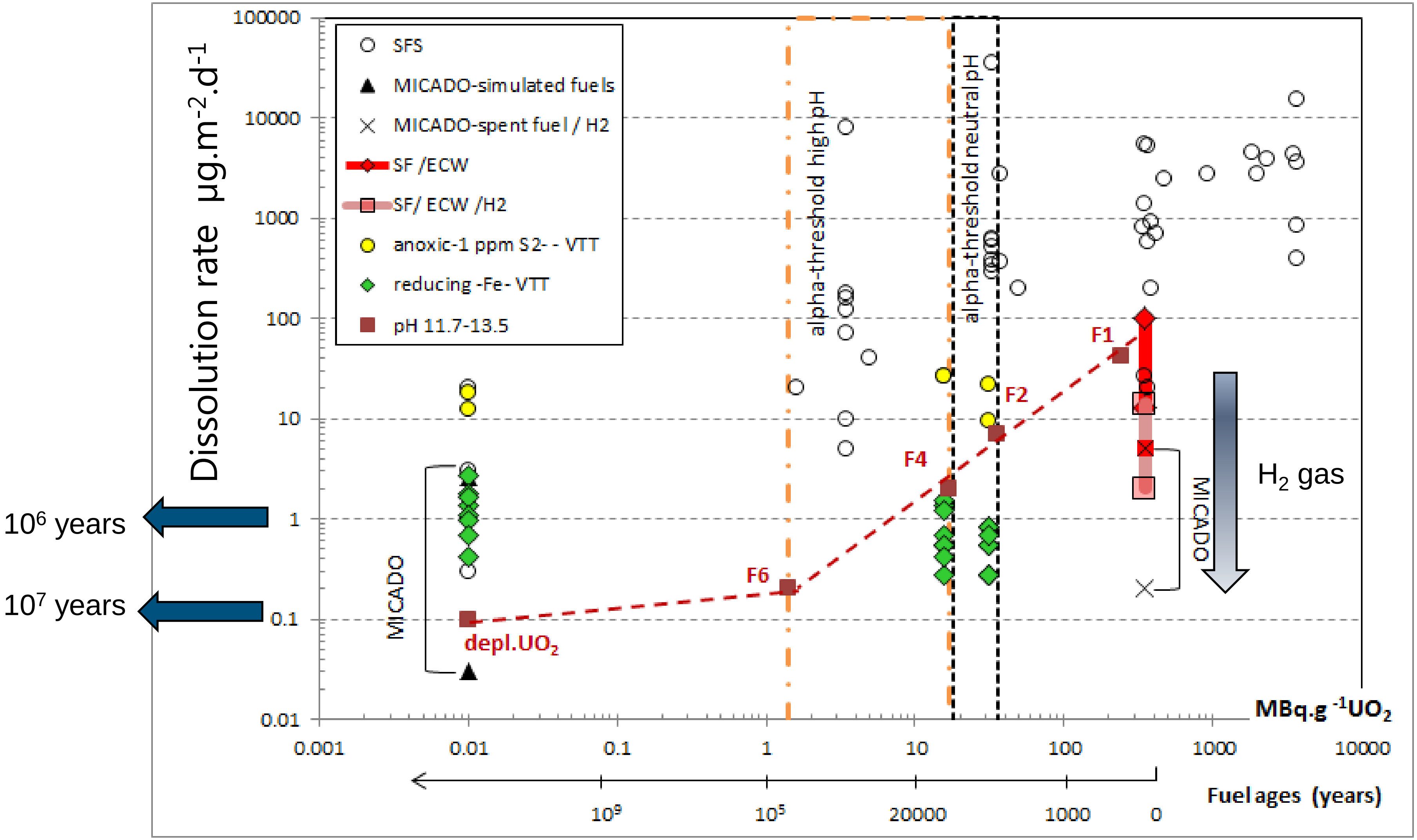


# To decrease conservativeness of dissolution rate estimations

- Better description of formed secondary phases to improve glass dissolution model
- Study of transport parameters (link with concrete studies)
- Tests in realistic geometries (evolution of small cracks)
- Effect of altered cement (C-S-H) on glass dissolution kinetics

# Spent fuel (UOX) matrix dissolution rate

Dissolution rate = function of fuel activity versus redox conditions



# Main rate controlling mechanism and uncertainties (spent fuel)

- Dissolution driven by radiolytical oxidation of $UO_2$ matrix
  - Possibly favorable effect of Ca (protective layer)
  - Possibly unfavorable effect of high pH (U(VI) hydroxo-complexes)
  - $H_2$ gas suppresses radiolytical fuel oxidation
  - $UO_2$ solubility not affected by high pH
  - Similar dissolution rates as in other media (pH < 11)

⇒ **Similar behavior as in other media**

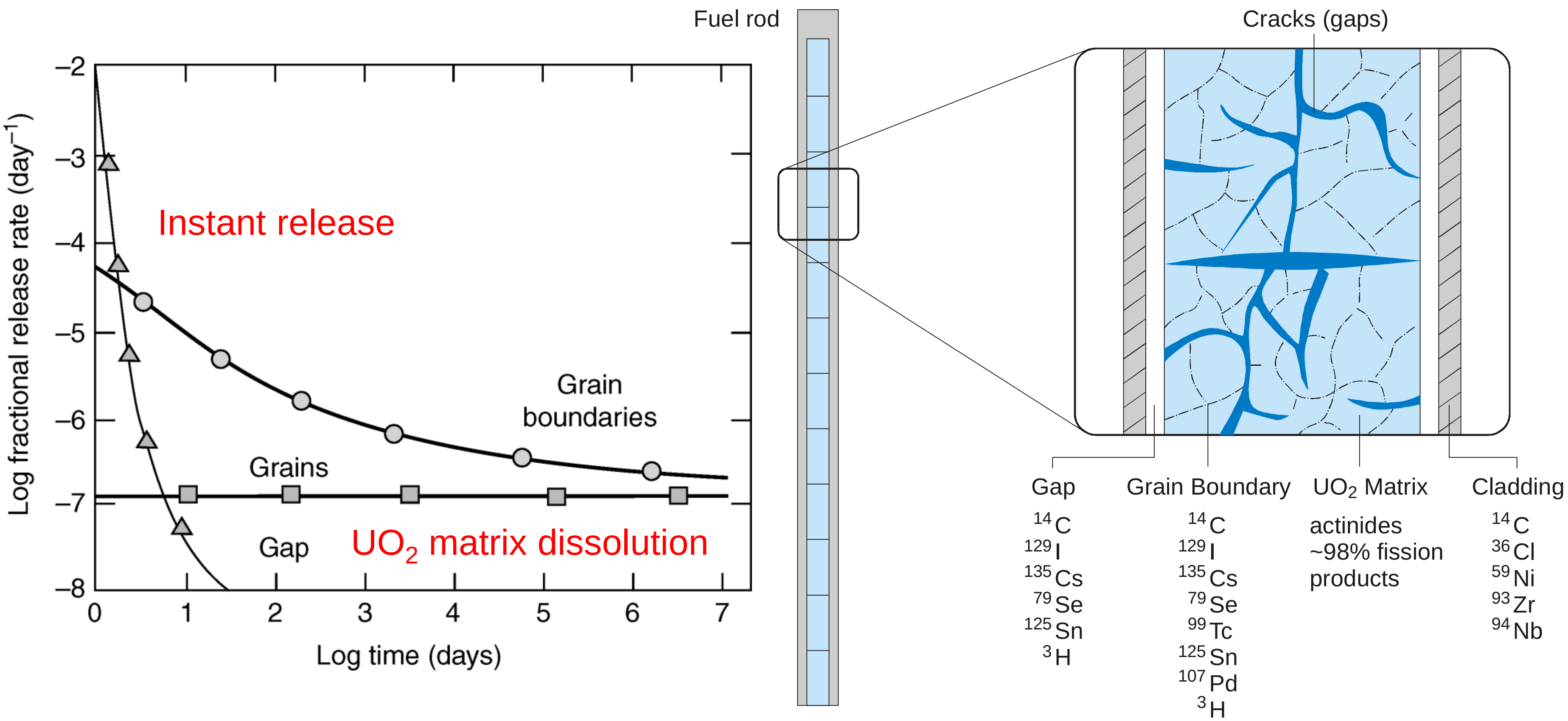
- Exact mechanisms not known
  - Radiolytical species and redox potential effects at high pH ?
  - Ca adsorption or secondary phase precipitation ?
  - Formation of colloids ?
  - Conditions under which U(VI) hydroxo-complexes play a role ? (only for young fuel without $H_2$ gas ?)
  - Minimum $H_2$ concentration required for dissolution suppression ?

## Other uncertainties (glass & spent fuel)

- (Partial) confinement by overpack
- Metallic corrosion
- pH decrease in buffer (glass) + other cement types
- Carbonatation of concrete
- Temperature decrease (30 → 16°C)
- Radionuclide precipitation
- Calcite aggregates (glass)
- Initial surface area + evolution
- Waste composition effects (glass)
- Representativeness of tested materials
- High pressure effects
- Long term alteration resumption (glass)
- Long term radiation effects
- Few studies on MOX fuel

# Extra source term from spent fuel : Instantly Released radionuclides Fraction (IRF)

Instant Release Fraction: soluble radionuclides at accessible sites (not incorporated in $UO_2$ matrix)



# Instant Release Fraction (spent fuel)

- Measured by short term tests with real spent fuel
- Correlated with fission gas release
- Influenced by fuel characteristics (Burnup, in-reactor temperature…)
- Sometimes very pessimistic assumptions, based on total inventory in gap and grain boundaries, or in oxidized cladding surface
- Typical values :

  2 to 4 % for $^{129}I$ and $^{135-137}Cs$

  10 % for $^{14}C$ (fuel), 20 % for $^{14}C$ (cladding)

# Instant Release Fraction (spent fuel)
## Remaining questions

- Many data from CANDU fuel (Canadian fuel with natural uranium)
- More data necessary, especially for high burnup fuel and for MOX
- Very generalized approach for IRF estimations (e.g. no distinction between different types of fuel assemblies, no distinction between water compositions)

  → Similar IRF values for all disposal designs

- Investigated further in EU project First Nuclides

Related question:

- Better estimation of specific surface area of fuel
  (surface normalization difficult → fractional release)

## What will be shown next

Next presentations will summarize and illustrate the methods used to come to the given dissolution mechanisms and rates :

- Experimental program to determine the stability of vitrified waste in Supercontainer conditions. - *Karine Ferrand (experimental) & Sanheng Liu (geochemical modeling)*
- Validation and demonstration of the behavior of vitrified waste in clay environment by the CORALUS *in situ* experiments. - *Elie Valcke*
- Experimental program to determine the stability of spent fuel in Supercontainer conditions. - *Christelle Cachoir ($UO_2$ matrix dissolution) & Thierry Mennecart (Instant Release from spent fuel)*
- General conclusions and future needs for research on the long-term evolution of high-level waste forms. – *Robert Gens, Maarten Van Geet (ONDRAF/NIRAS)*

# Thank you for your attention

Work supported by ONDRAF/NIRAS and the European Commission