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

Boom Clay

Wedge blocs
Carbon steel overpack (spent fuel)
6 mm steel envelope
Buffer (CEM I concrete)
Cementitious backfill
Gallery floor

Fuel assembly
PAMELA glass disposed of in monoliths for B-waste
The repository architecture

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<th>No further reprocessing</th>
<th>Full reprocessing</th>
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<td>UOX spent fuel</td>
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<td>MOX spent fuel</td>
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<td>-</td>
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<td>V-HLW glass (AREVA)</td>
<td>792.7</td>
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<td>HLW glass (PAMELA)</td>
<td>172.5</td>
<td>1387.5</td>
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Safety concept: Glass and spent fuel matrix limit radionuclide release (R1)

engineered radionuclide containment (C)
(by the engineered barrier system)

delayed and attenuated radionuclide releases (R)
(by the complete geological disposal system)

R1: limitation of radionuclide releases from the waste form
R2: limitation of water flow through the system
R3: retardation and spreading in time of radionuclide migration

isolation (I)
(mainly by the geological barrier)

I1: Reduction of the likelihood of inadvertent human intrusion and of its possible consequences
I2: Ensuring stable conditions for the disposed waste and the system components

thermal phase

Time after repository closure [years]

0 10³ 10⁴ 10⁵ 10⁶
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

Interim storage

Gallery construction

Thermal phase  Post-thermal phase

pH ~13.5 \rightarrow pH \sim 12.5 \rightarrow pH \sim 12 \rightarrow pH \sim 9

H_2 gas formation

Overpack perforation

Confined system  Open system

End of Life  T_0 Disposal closure  $10^3$  $10^4$  $10^5$  $10^6$  $10^7$ Years
Expected pH evolution [Wang, 2009]

Young concrete water pH 13.5

Evolved concrete water pH 12.5

Old concrete water pH <12

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 H₂ gas evolution [Yu and Weetjens, 2012] relevant for spent fuel stability

![Graph showing dissolved hydrogen over time](image)

**Expected H₂ gas evolution**

- **Overpack**
  - Dissolved hydrogen (mol/l)
  - Time (years)

**H₂ Saturation**

- \([H_2] > 0.5\, \text{mM} (0.7\, \text{bar})\) up to 10⁶ years

**H₂ Experimental Conditions**

- \([H_2] > 2.5\, \text{mM} (3.2\, \text{bar})\) after 10⁶ years

**Alternative, lower corrosion rate**

- 0.01 µm.year⁻¹ (carbon steel)

  - \([H_2] > 0.5\, \text{mM} (0.7\, \text{bar})\) up to 10⁶ years
  - \([H_2] > 2.5\, \text{mM} (3.2\, \text{bar})\) after 10⁶ years
Test materials

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$_2$ $\rightarrow$ 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\(\times\) to 40\(\times\) external surface area due to cracks
\(\rightarrow\) 0.2 – 1.7 cm\(^2\).g\(^{-1}\)

Spent fuel: large total surface area due to cracks, surface roughness and accessible grain boundaries
\(\sim\) 10 cm\(^2\).g\(^{-1}\)

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

Spent fuel: surface area relevant only for oxidative UO\(_2\) matrix dissolution

\(^*\)Surface area not relevant when dissolution is solubility (\(\rightarrow\) diffusion) limited
Dissolution rate of waste glass (g.m\(^{-2}\)day\(^{-1}\))

SON68, 30°C

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

Effect of pH

Effect of Ca

Forward rate
KOH
pH 13.5
0.23 g.m\(^{-2}\) d\(^{-1}\)

pH 12.5
0.13 g.m\(^{-2}\) d\(^{-1}\)

pH 11.5
0.07 g.m\(^{-2}\) d\(^{-1}\)

Initial rate
Cement water pH 13.5 (YCWCa)
0.04-0.08 g.m\(^{-2}\) d\(^{-1}\)

Cement water (YCWCa) with cement pH 13.5

0.0032-0.0094 g.m\(^{-2}\) d\(^{-1}\)

Temporary effect of cement
0.0085 g.m\(^{-2}\) d\(^{-1}\) pH 13.5 (YCWCa, unconfined)

0.00057 g.m\(^{-2}\) d\(^{-1}\) (confined)

0.0021 g.m\(^{-2}\) d\(^{-1}\) pH 12.5 (ECW)

0.00005 g.m\(^{-2}\) d\(^{-1}\) pH 11.5 (OCW)

Effect of pH

(max. rate)
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

Dissolution rate (g/m²d)

- KOH pH 13.5
- KOH pH 12.5
- KOH pH 11.5
- Cement water pH 13.5
- Young cement water pH 13.5
- Evolved cement water pH 13.5
- Mock-up
- Young cement water pH 13.5 (confined glass)
- Old cement water pH 11.5

Dissolution rates are shown on a logarithmic scale, with values ranging from 0.0001 to 1 g/m²d. The chart includes mock-up, short term, long term, and evolved cement water conditions.

- Mock-up: X.10⁴ yrs
- Old cement water pH 11.5: X.10⁵ yrs
- Young cement water pH 13.5 (confined glass): <10000 yrs

Life time glass block
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

![Graph showing dose river pathway (Sv/a) over time after canister failure (years). The graph includes lines for MD in 1000 years, 10000 years, 100000 years, 500000 years, and 1000000 years. The full reprocessing assumption is 3915 HLW canisters and $^{79}$Se migrates as selenate.]
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)

UO$_2$ matrix dissolution

Instant release
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)
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

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