



ESV EURIDICE GIE

19th Exchange Meeting

"Long-term evolution of high-level waste forms"

Date & Venue

Tuesday, May 6, 2013 at 13:30

Auditorium Club House SCK•CEN, Boeretang 200, BE-2400 Mol

Programme

- | | |
|-------|---|
| 13:30 | Welcome - <i>Peter De Preter</i> (ESV EURIDICE) |
| 13:40 | Research on the long-term evolution of high-level waste forms in the frame of the Belgian research programme on geological disposal of high active and/or long lived waste. - <i>Maarten Van Geet</i> (NIRAS) |
| 14.00 | A general evaluation of the high-level waste forms in Supercontainer conditions. - <i>Karel Lemmens</i> (SCK•CEN) |
| 14.30 | Experimental programme to determine the stability of vitrified waste in Supercontainer conditions. - <i>Karine Ferrand & Sanheng Liu</i> (SCK•CEN) |
| 15.00 | Coffee break |
| 15.15 | Validation and demonstration of the behaviour of vitrified waste in clay environment by the CORALUS in-situ experiments. - <i>Elie Valcke</i> (SCK•CEN) |
| 15.45 | Experimental programme to determine the stability of spent fuel in Supercontainer conditions. - <i>Christelle Cachoir & Thierry Mennecart</i> (SCK•CEN) |
| 16.15 | General conclusions and future needs for research on the long-term evolution of high-level waste forms. - ? (NIRAS) |
| 16:30 | Closure drink |

Research on the long-term evolution of high-level waste forms in the frame of the Belgian research programme on geological disposal of high active and/or long lived waste

Maarten Van Geet, Robert Gens

19th Exchange Meeting
6 May 2014

Nationale instelling voor radioactief afval en verrijkte splijstoffen



O/N is responsible for the long-term management of B&C waste

40 years of RD&D on the development of a geological repository

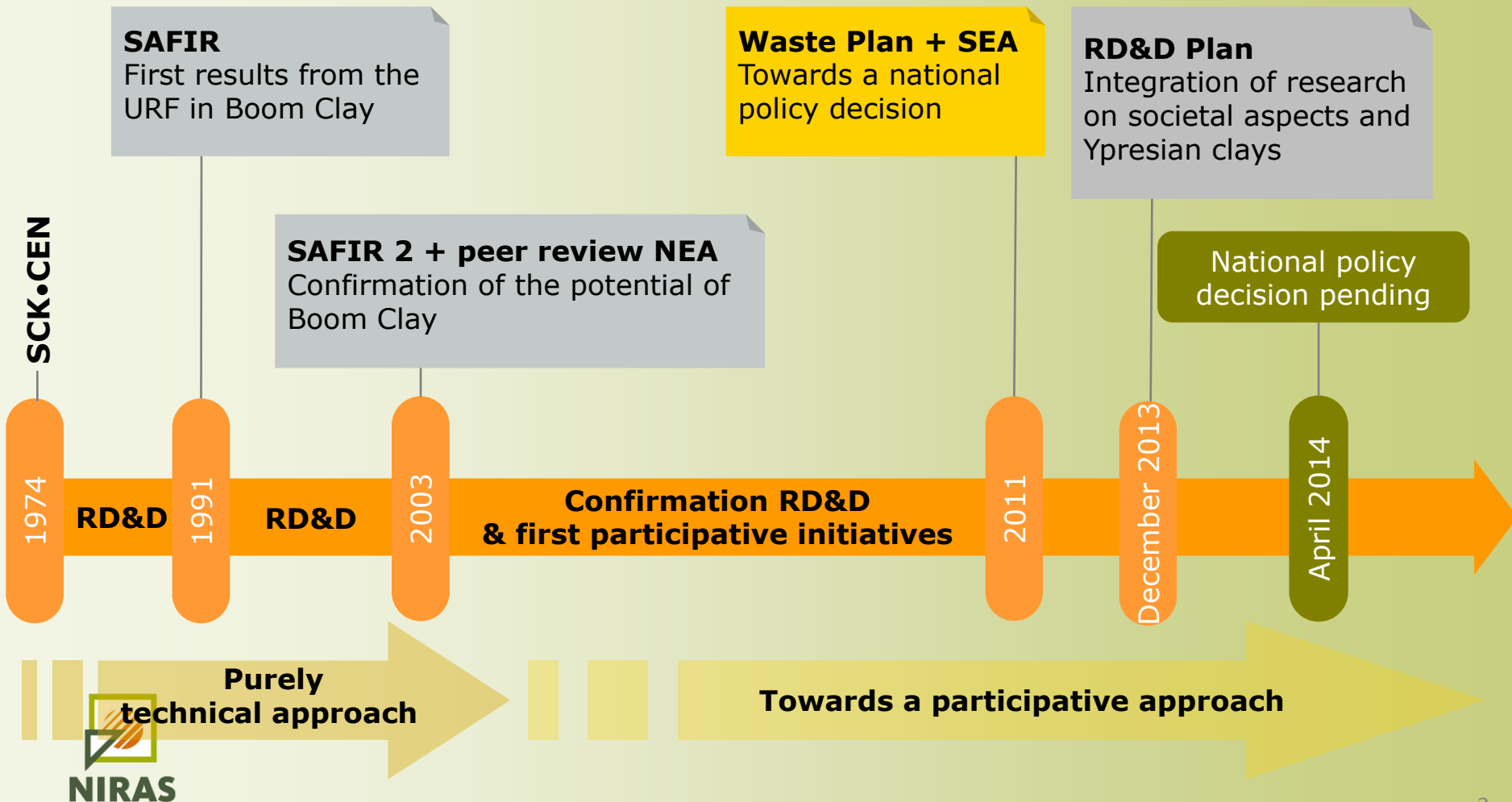
- Initiated by SCK•CEN in 1974
- In line with international recommendations
- With benefits from intensive international collaboration

Waste Plan handed over to the Federal Government in September 2011

with all elements necessary to enable the Federal Government to make a decision in principle

In the absence of decision in principle, continuation of the RD&D on geological disposal in poorly indurated clay

ONDRAF/NIRAS has synthesised the RD&D relating to geological disposal in several reports



The peer review of SAFIR 2 stated that “The Belgian programme for the disposal of B&C waste is well developed and sufficiently advanced to address the siting issue”

However, the peer review identified the need:

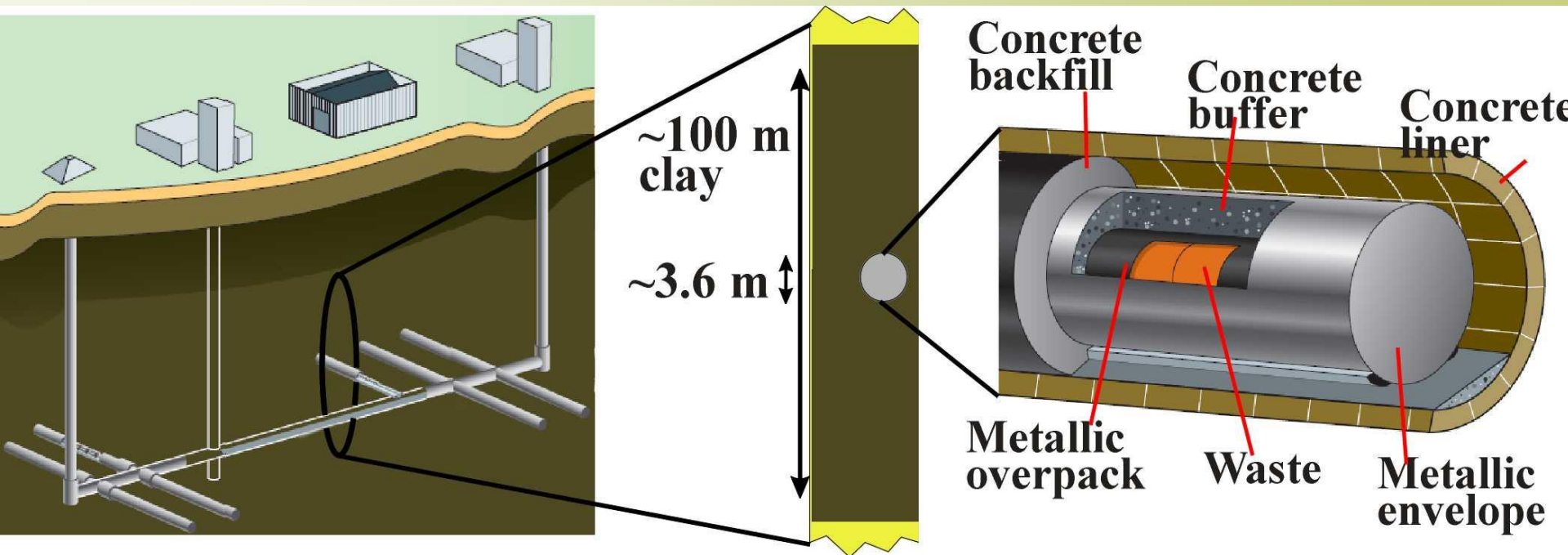
- **to refine the safety strategy and the methodology for assessing the safety**
- **to continue the RD&D to reduce the remaining significant uncertainties**
 - disposal of waste other than vitrified category C waste
 - performance of the engineered barrier system
- **to extend the programme to societal aspects**

→ O/N has thus re-evaluated its RD&D programme

Since SAFIR 2, O/N has developed a new concept for the engineered barrier system (EBS)

The supercontainer is designed to fulfil several requirements, including

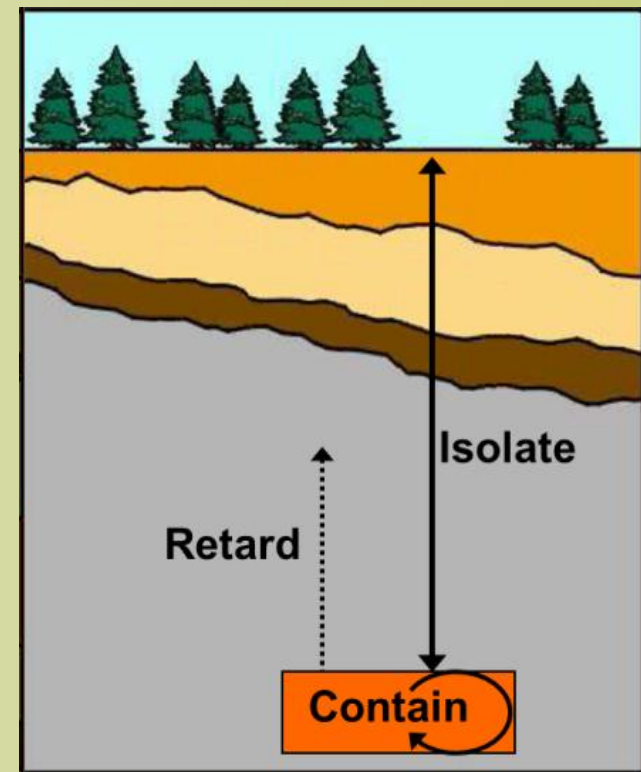
- radiological shielding,
- ease of handling and emplacement in the repository and
- containment of the wastes during the thermal phase



Since SAFIR 2, O/N has refined and formalised its safety approach

The safety strategy sets out in broad terms how it is envisaged that safe disposal will be achieved .

The disposal sytem must fulfil 3 safety functions to protect man and the environment through passive safety.



The Safety concept for C-waste (heat-emitting)

Engineered containment phase

Safety function fulfilled : engineered containment (C)

Contributing components : supercontainer

Factor determining time frame : loss of integrity of supercontain

System containment phase

Safety function fulfilled : delay and attenuation of releases (R)

R1 : limitation of contaminant releases from the waste forms

R2 : limitation of water flow through the system

R3 : retardation and spreading in time of contaminant migration

Contributing components : waste forms, engineered barrier system, Boom Clay

Factor determining time frame : dissolution properties of waste forms, transport properties of Boom Clay for contaminants

Geological isolation phase

Safety function fulfilled : isolation (I)

Contributing components : Boom Clay, geological coverage

Factor determining time frame : geological stability

Thermal phase

0

10^3

10^4

10^5

10^6



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

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

K. Lemmens*, C. Cachoir, Th. Mennecart, K. Ferrand, S. Liu
Belgian Nuclear Research Centre, SCK•CEN

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19th EURIDICE exchange meeting, , Mol, May 6th 2014

Outline of the presentation

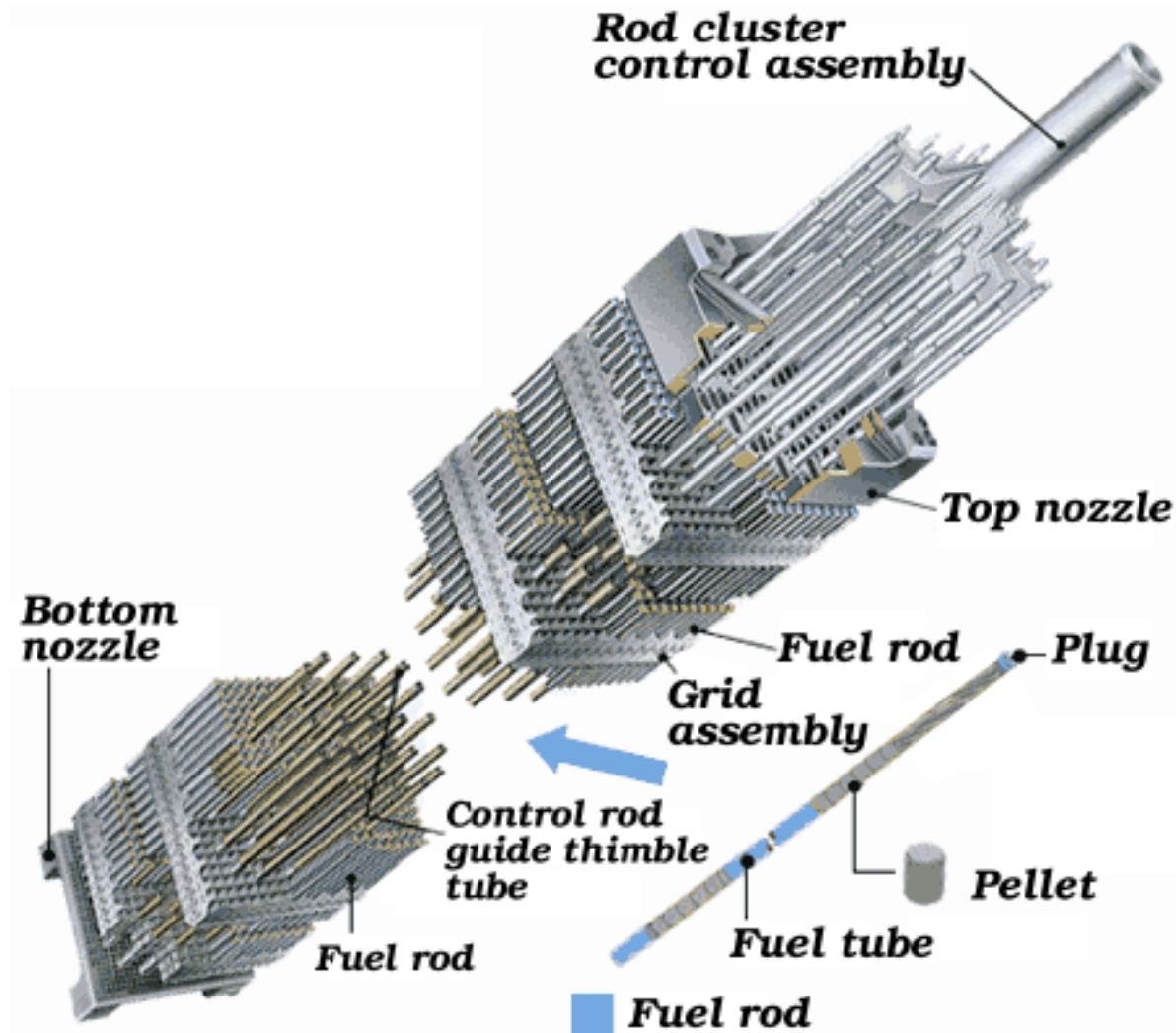
- Description of the high level waste forms
- Description of the boundary conditions to which the waste forms will be exposed in the Supercontainer design
- Expected waste form behavior and uncertainties

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

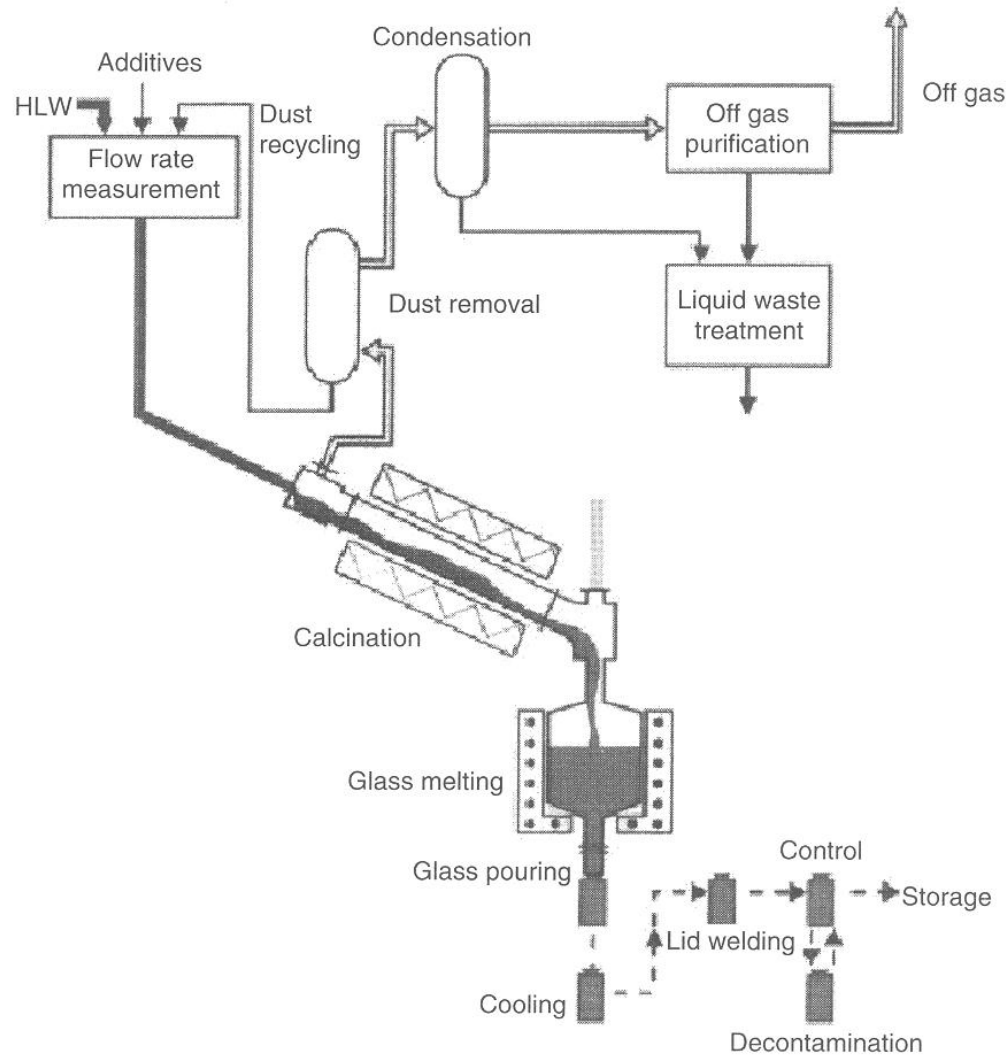
- *Very high-level waste (heat emitting):*
 - From nuclear energy production
 - Expected amount after 40 years electricity production:
 - 4643 tHM uranium oxide (**UOX**) **spent fuel** (ZAGALS)
 - 66 tHM mixed oxide (**MOX**) **spent fuel** (ZAGALS)
 - 390 canisters (150 L) with **vitrified very high-level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

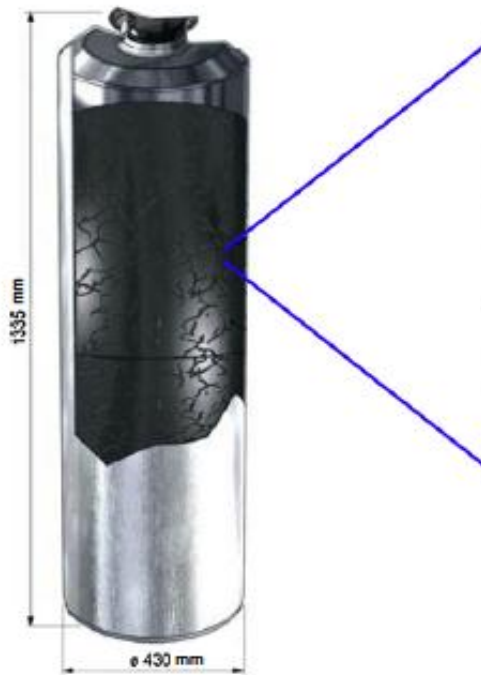
Spent fuel assemblies placed in primary package without further conditioning



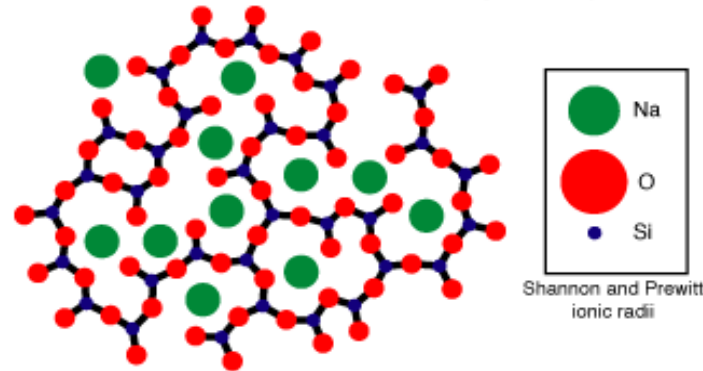
Vitrified waste (conditioned reprocessing waste)



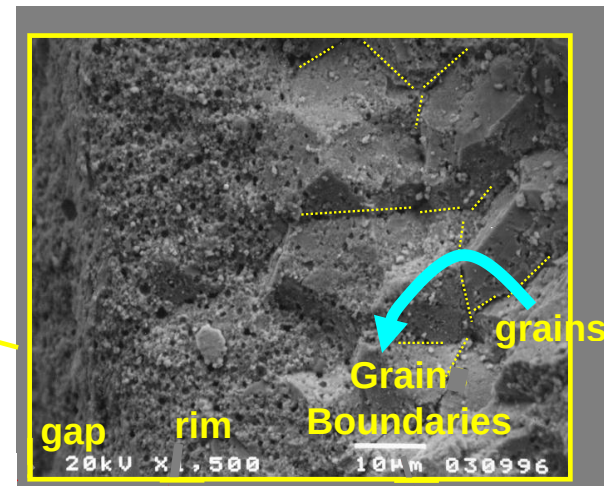
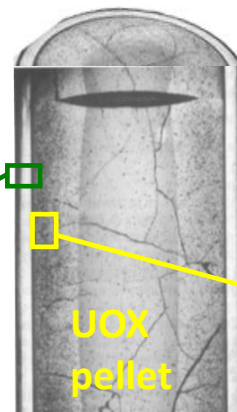
Different microstructure of glass and spent fuel



Proposed Structure of Sodium Silicate Glass
after Warren and Biscoe (1930's)



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

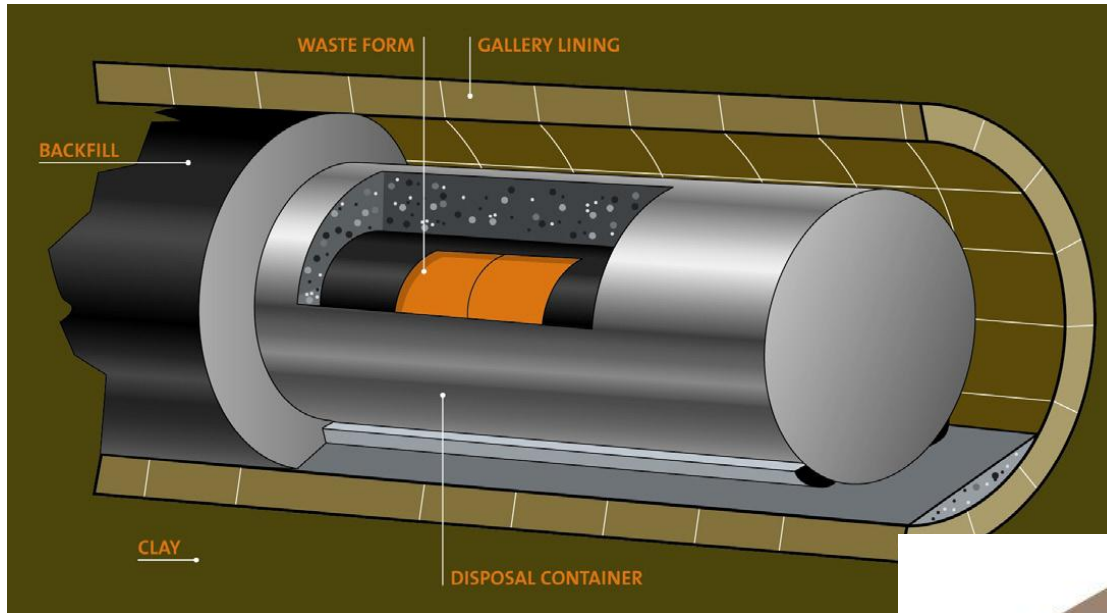


Spent fuel: inhomogeneous, with varying radionuclides in cladding, in gap, in rim zone, in deeper (crystalline) UOX matrix, and in grain boundaries

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

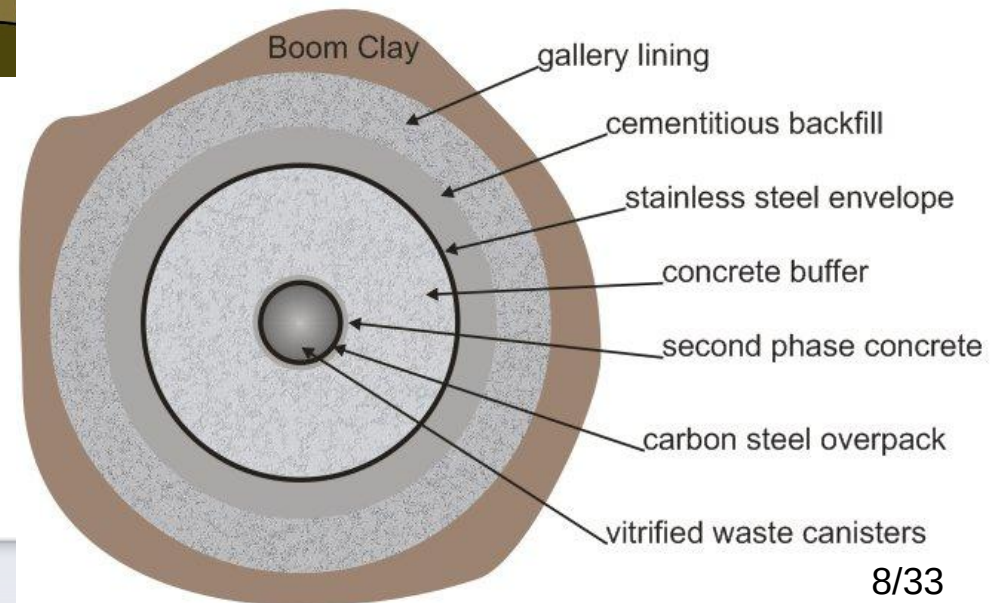
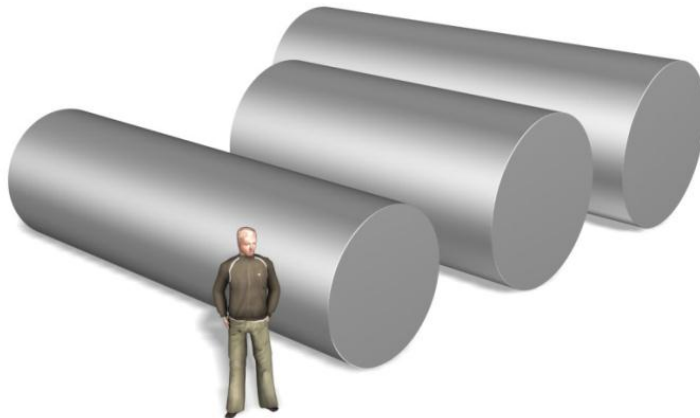
Geological disposal of very high level waste in 'Supercontainers'



Multibarrier system



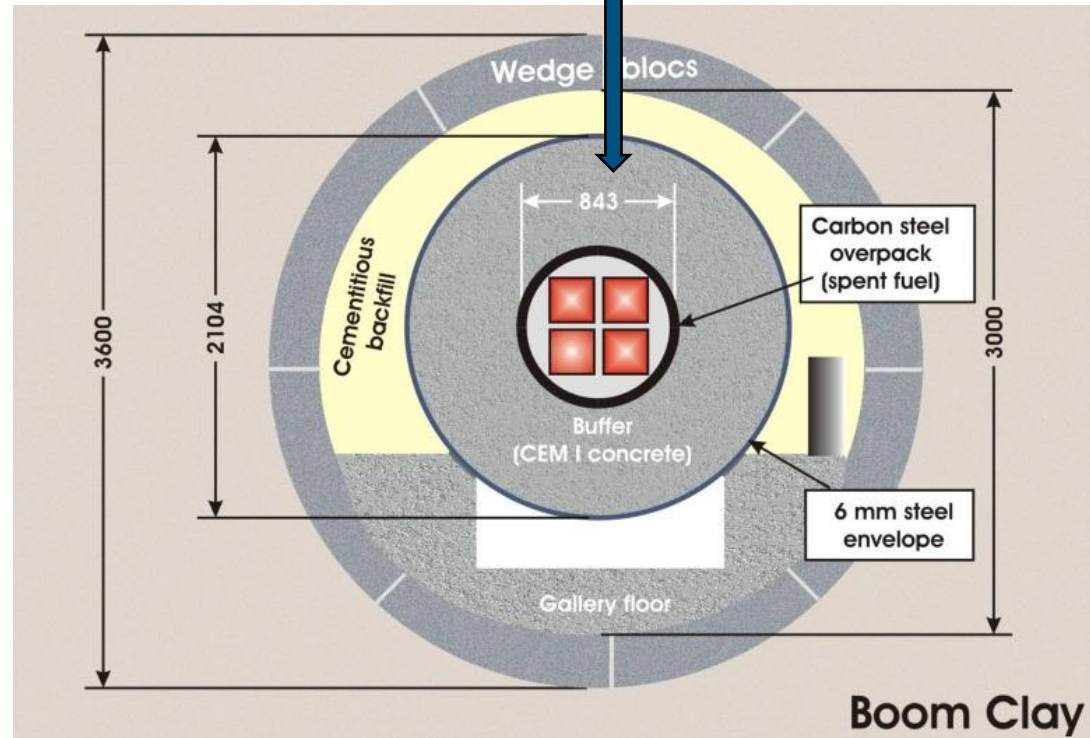
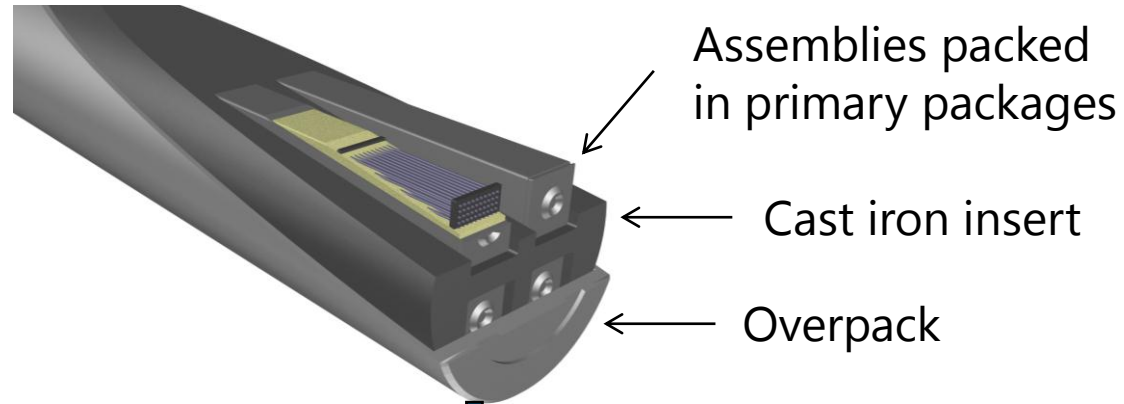
SON68 glass (AREVA)



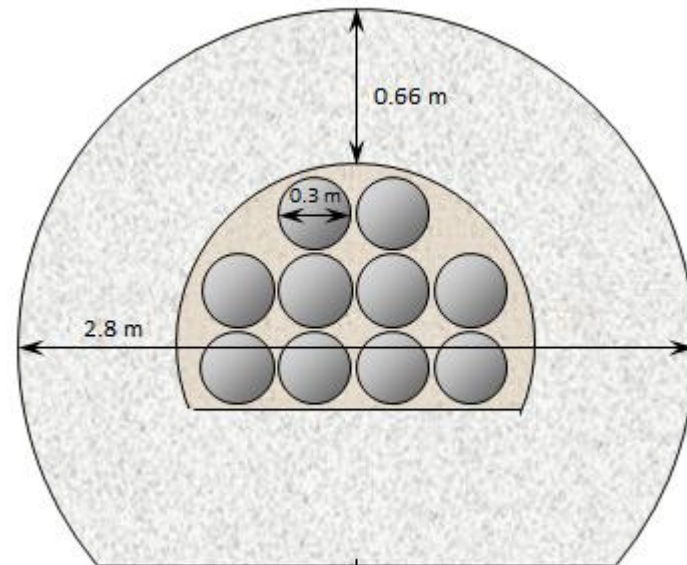
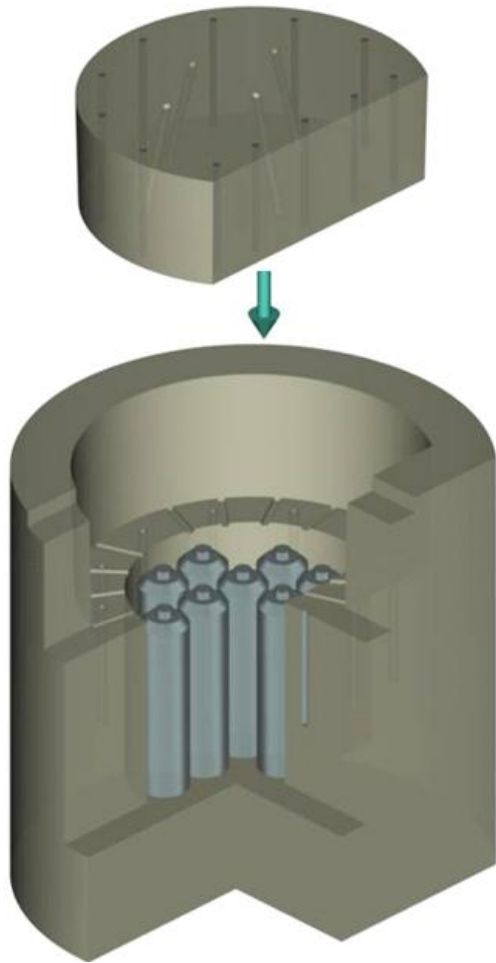
Supercontainer for spent fuel assemblies



Fuel assembly

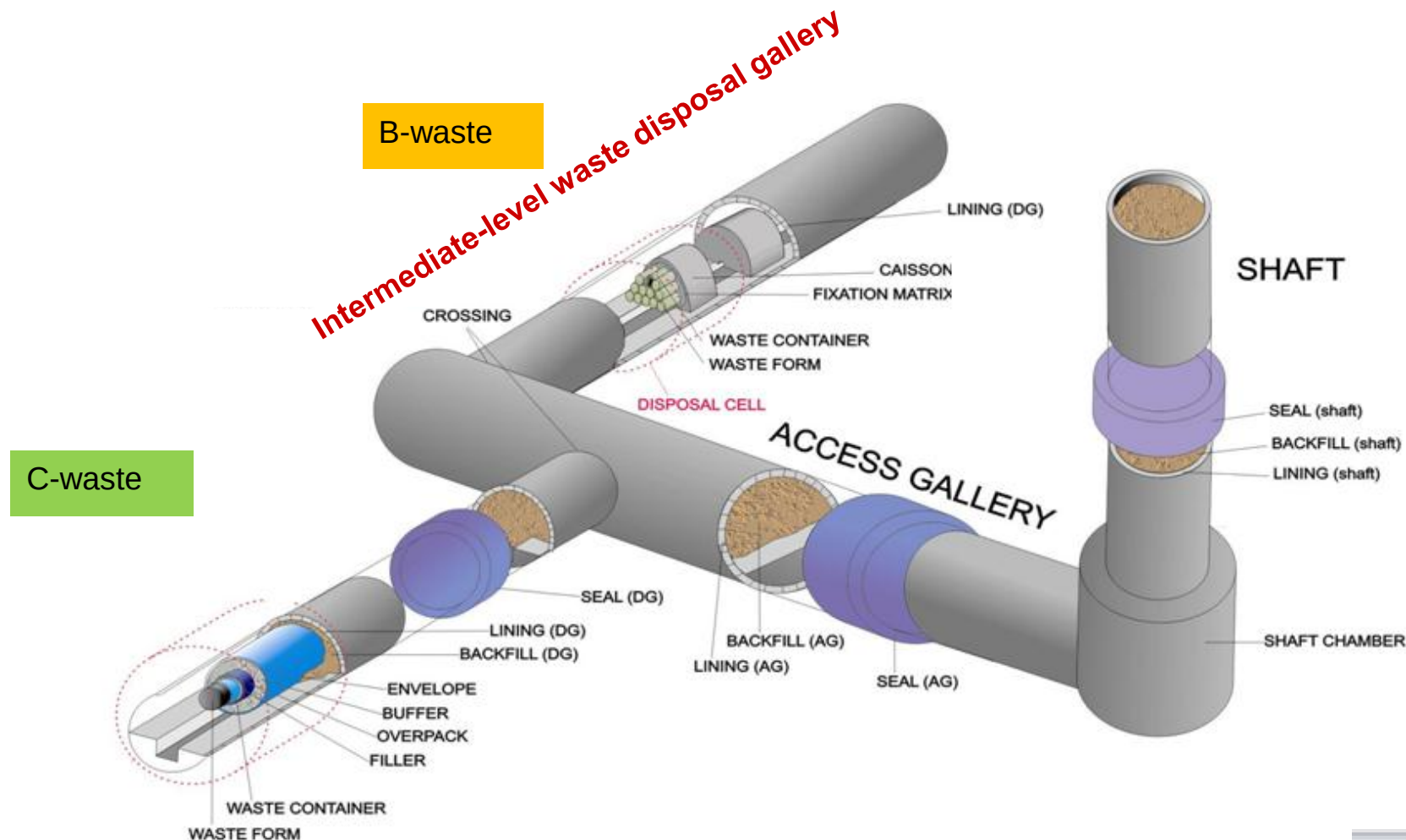


PAMELA glass disposed of in monoliths for B-waste



	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

The repository architecture



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)

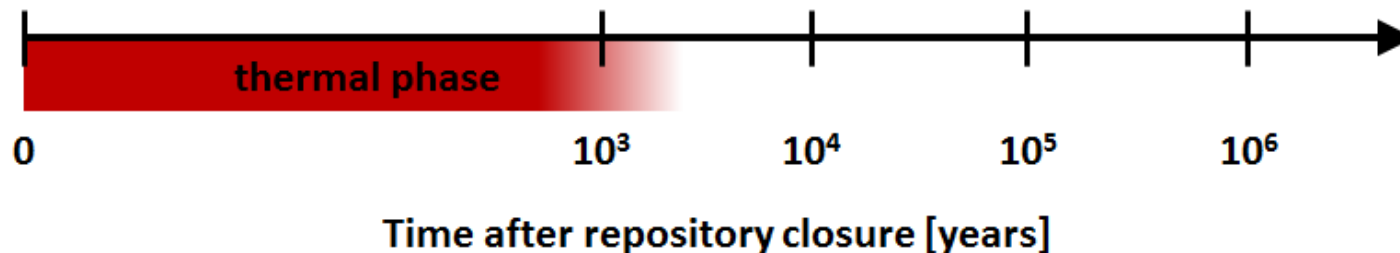
(by the complete geological disposal system)

- 
- 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)

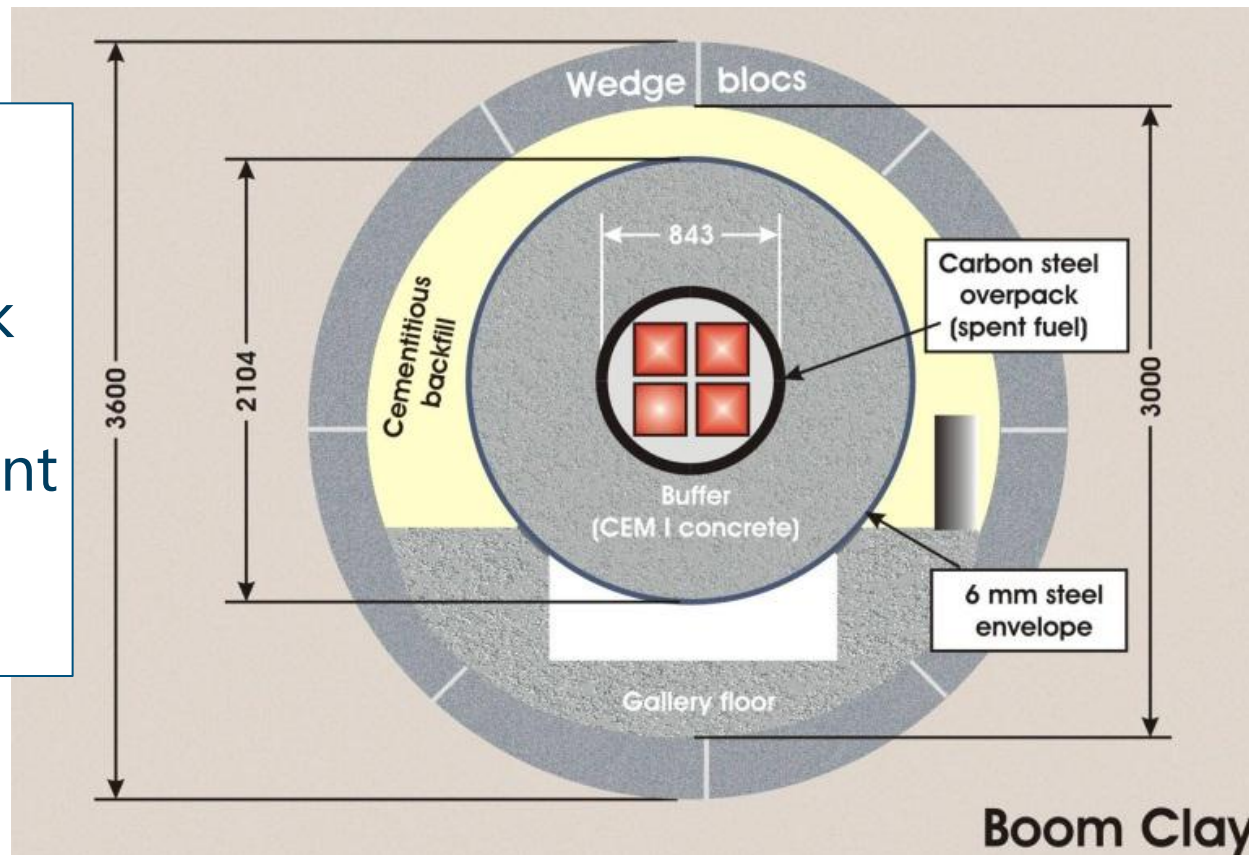
- I1: Reduction of the likelihood of inadvertent human intrusion and of its possible consequences
- I2: Ensuring stable conditions for the disposed waste and the system components



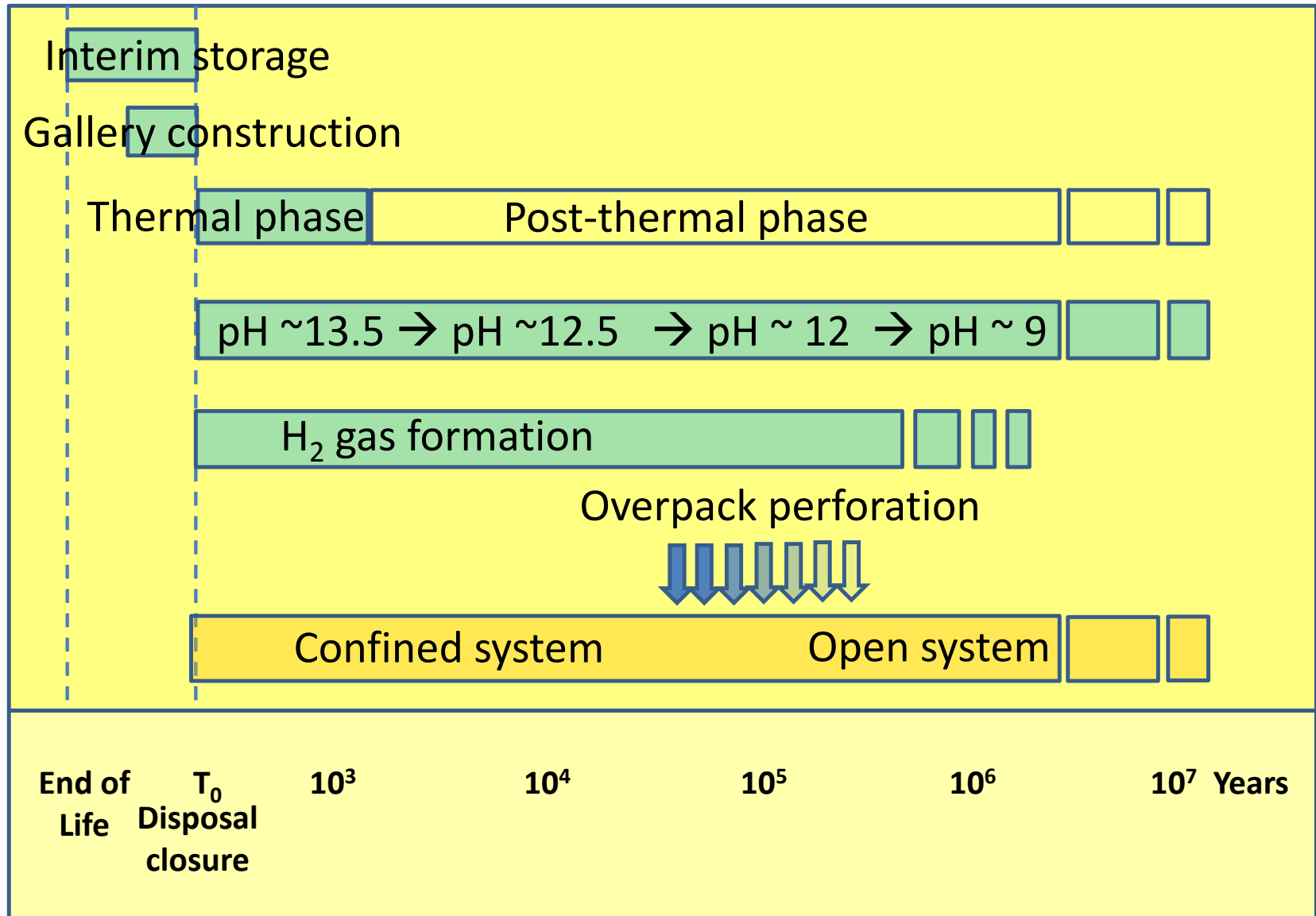
The Supercontainer disposal design requires a specific evaluation of expected glass and spent fuel dissolution behavior

Concrete stabilizes
carbon steel overpack

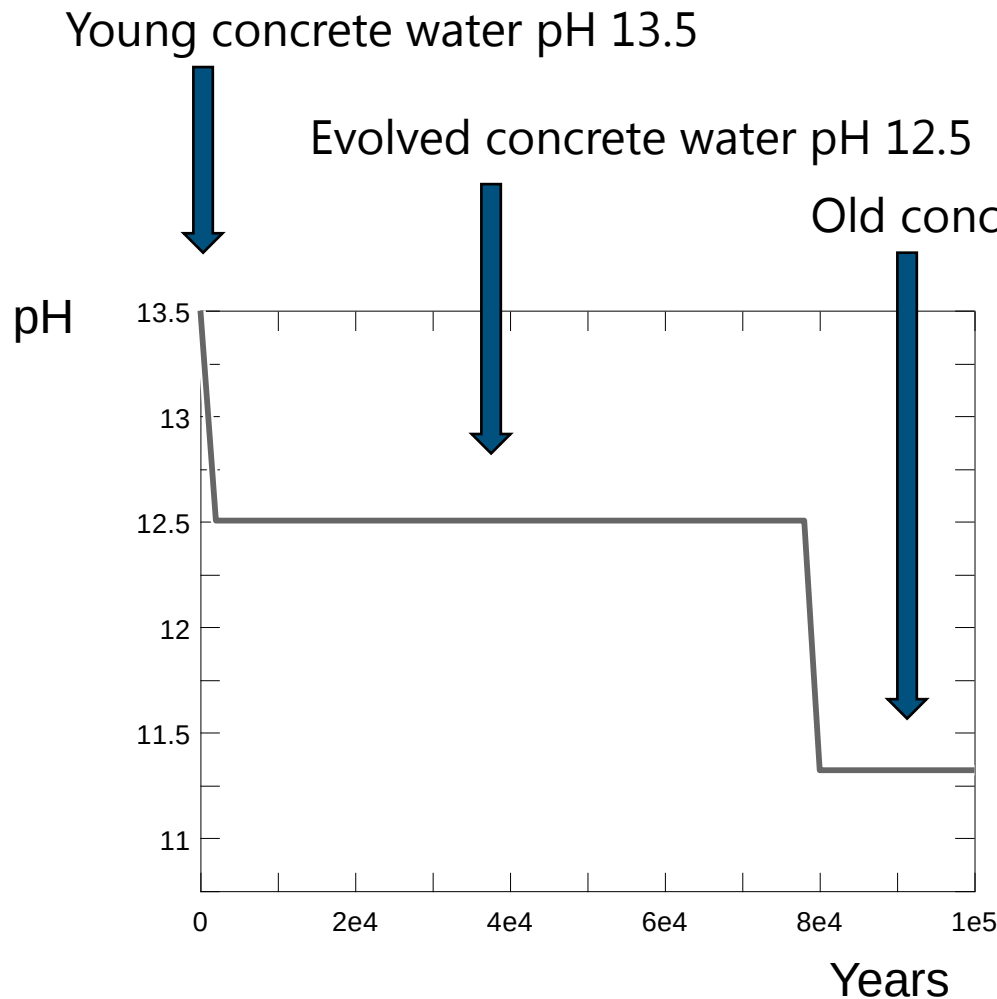
Effect on glass and spent
fuel dissolution ?



Boundary conditions depend on expected evolution



Expected pH evolution [Wang, 2009]



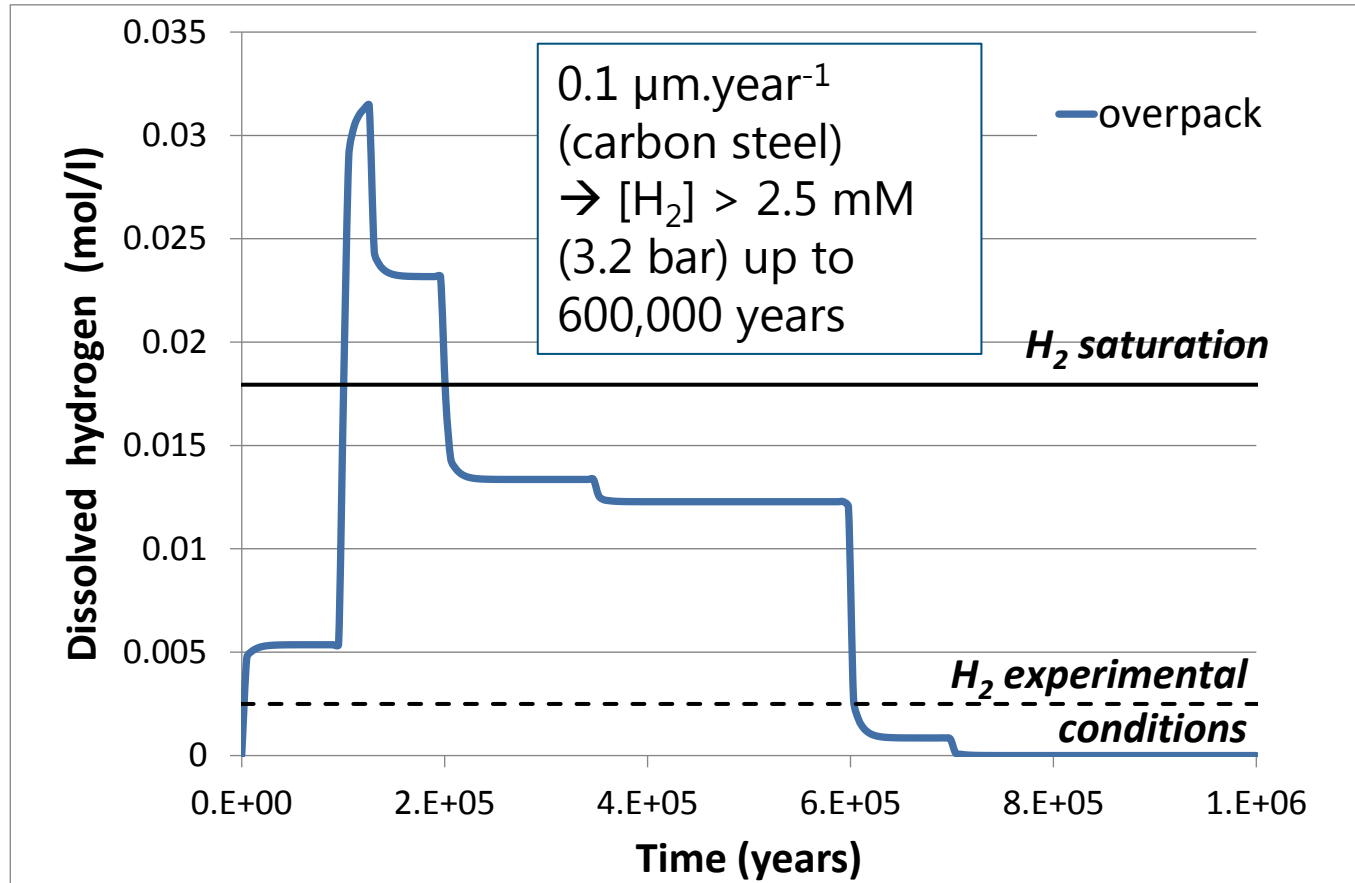
If perforation overpack after 50,000 years : pH 12.5

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
0.01 $\mu\text{m}.\text{year}^{-1}$ (carbon steel)

$\rightarrow [H_2] > 0.5 \text{ mM}$ (0.7 bar) up to 10^6 years
 $\rightarrow [H_2] > 2.5 \text{ mM}$ (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 β, γ 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

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

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 ($\text{g} \cdot \text{m}^{-2} \cdot \text{day}^{-1}$)

Glass: total surface area
 $5\times$ to $40\times$ external surface
area due to cracks

→ $0.2 - 1.7 \text{ cm}^2 \cdot \text{g}^{-1}$



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

$\sim 10 \text{ cm}^2 \cdot \text{g}^{-1}$

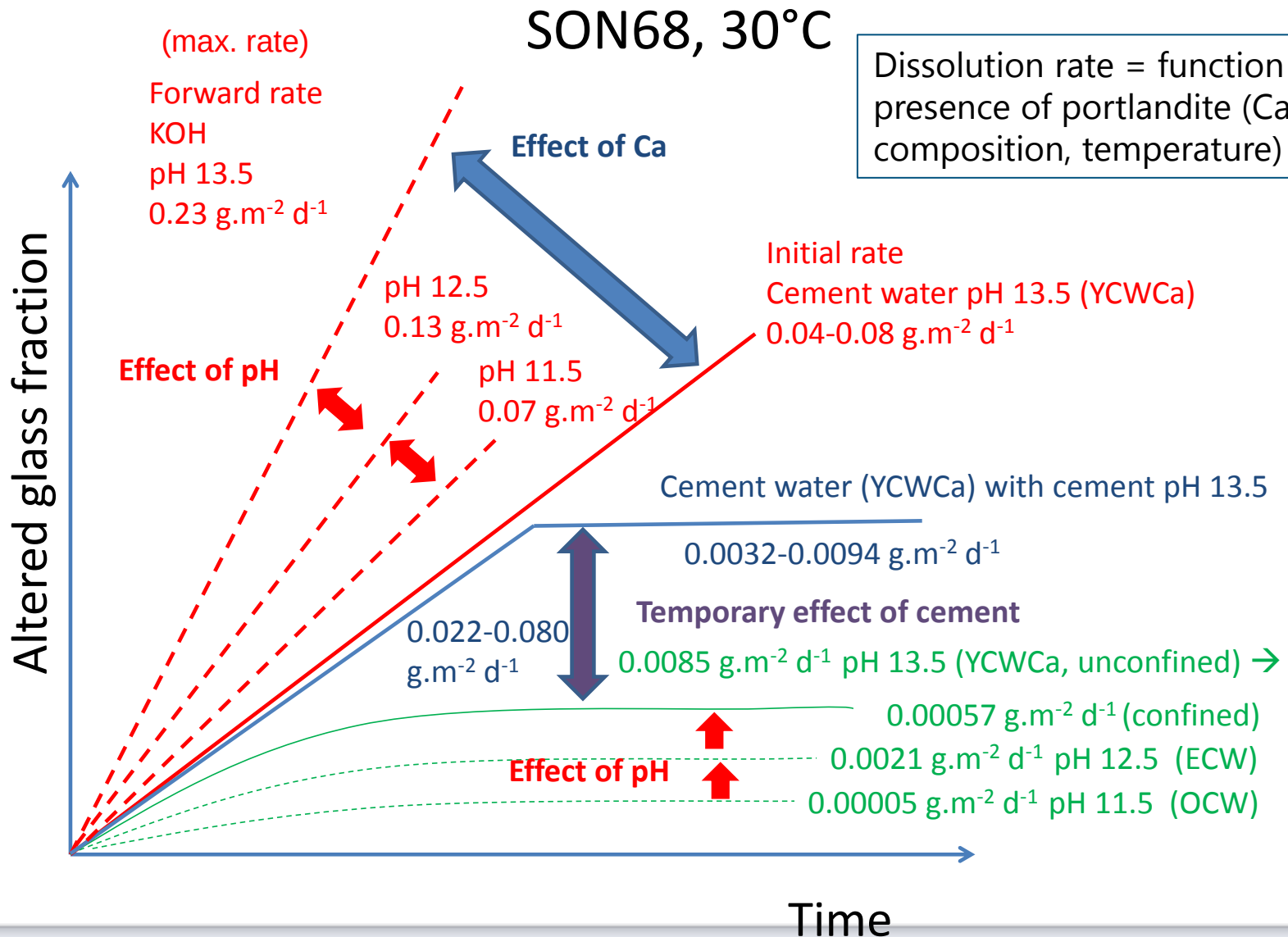


Glass: internal glass surfaces (narrow cracks) can be filled
with precipitation products → small contribution

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

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

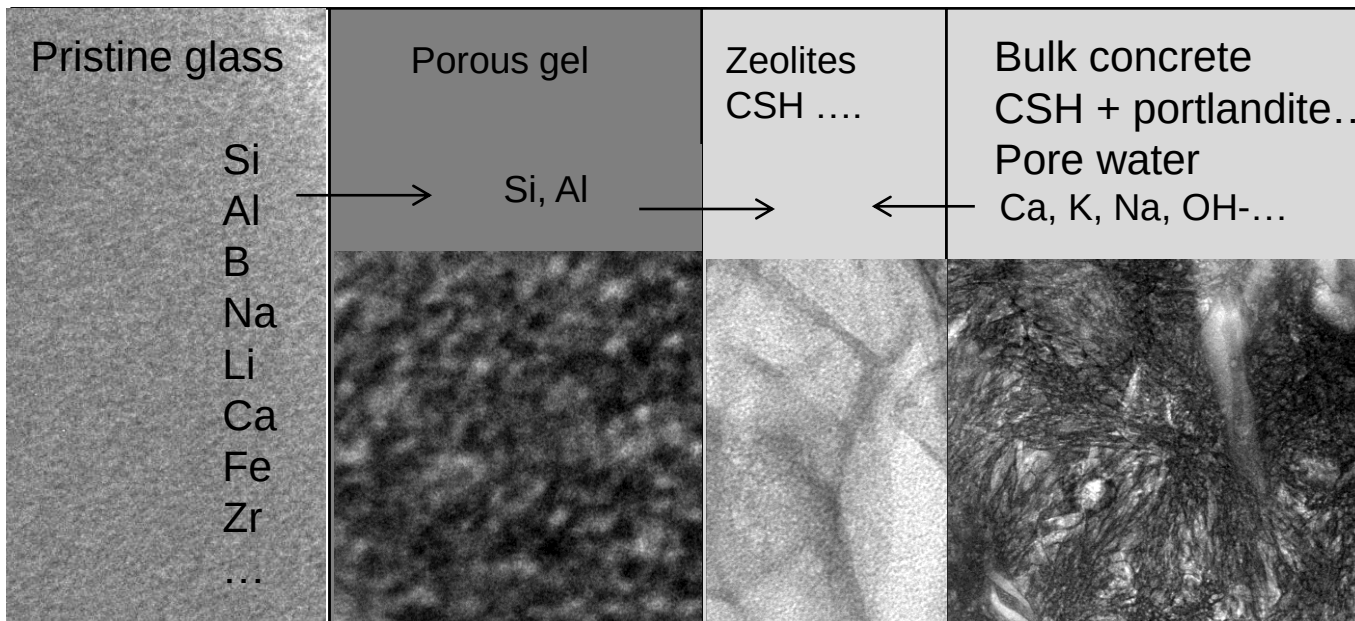
Dissolution rate of waste glass ($\text{g.m}^{-2}\text{day}^{-1}$)



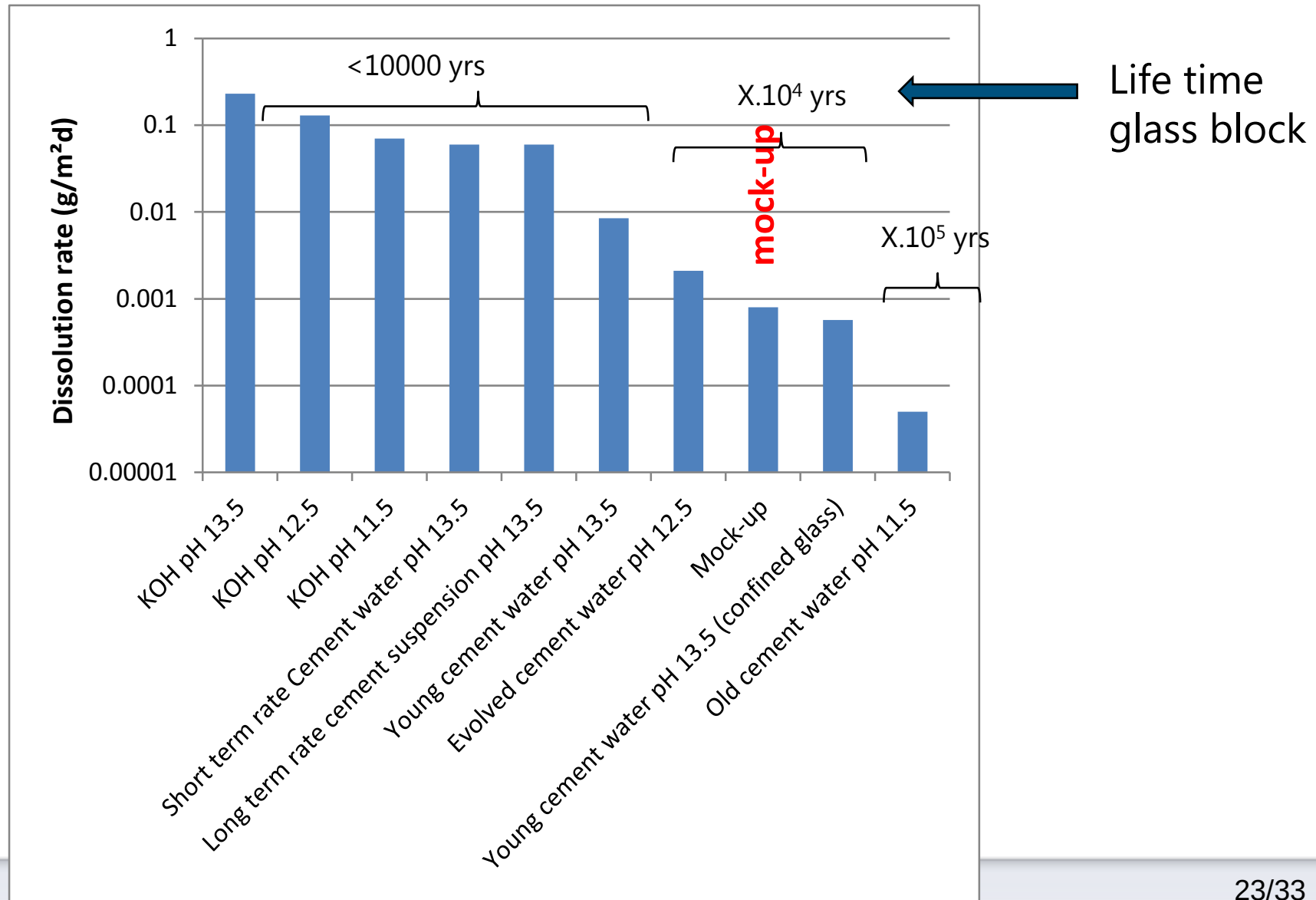
Main rate controlling mechanism and uncertainties (glass)

- 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)



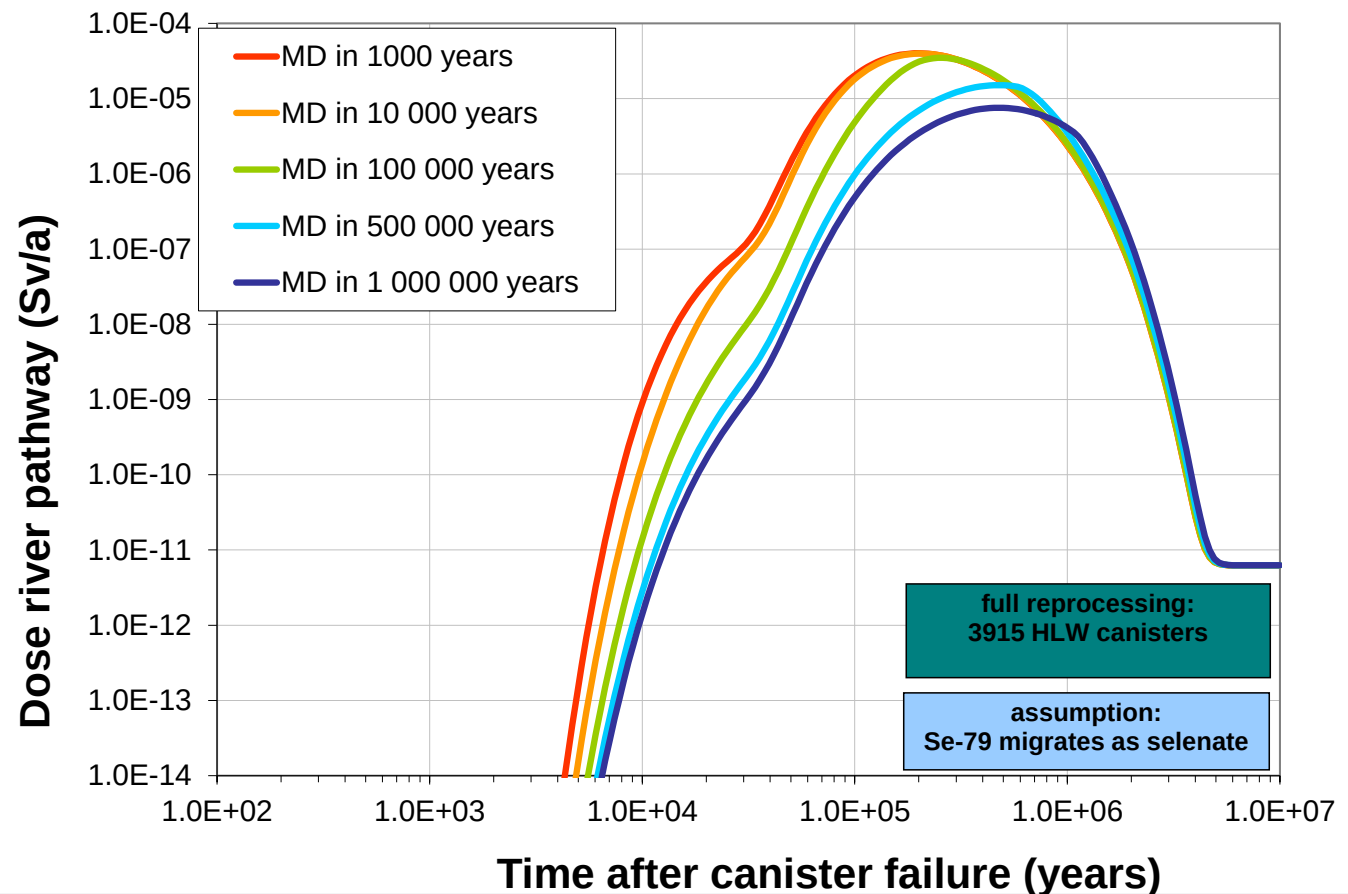
Compilation of experimental dissolution rates for reference glass SON68 in high pH/cement conditions at 30°C



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

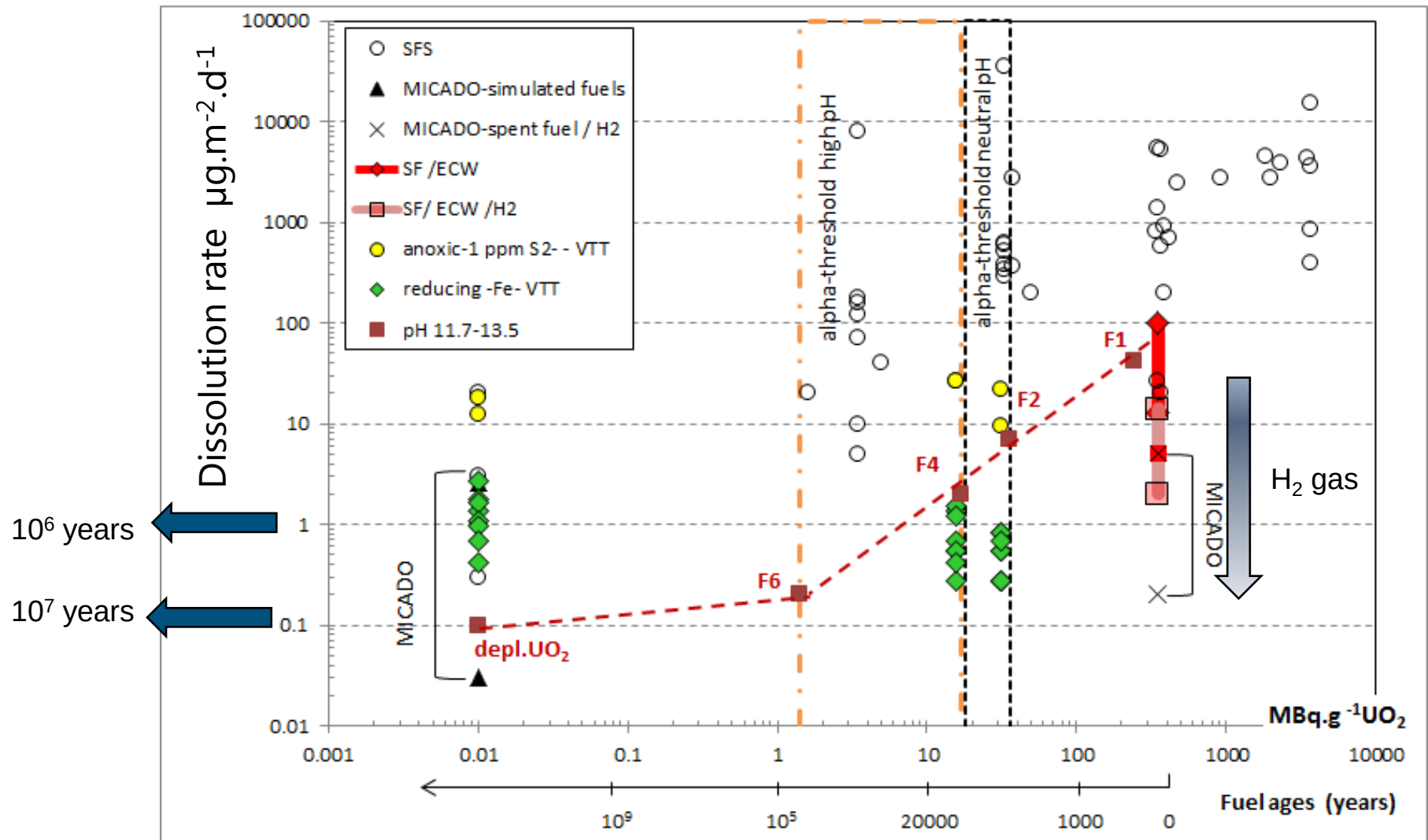


To decrease conservativeness of dissolution rate estimations

- 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

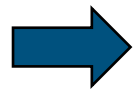
Spent fuel (UOX) matrix dissolution rate

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

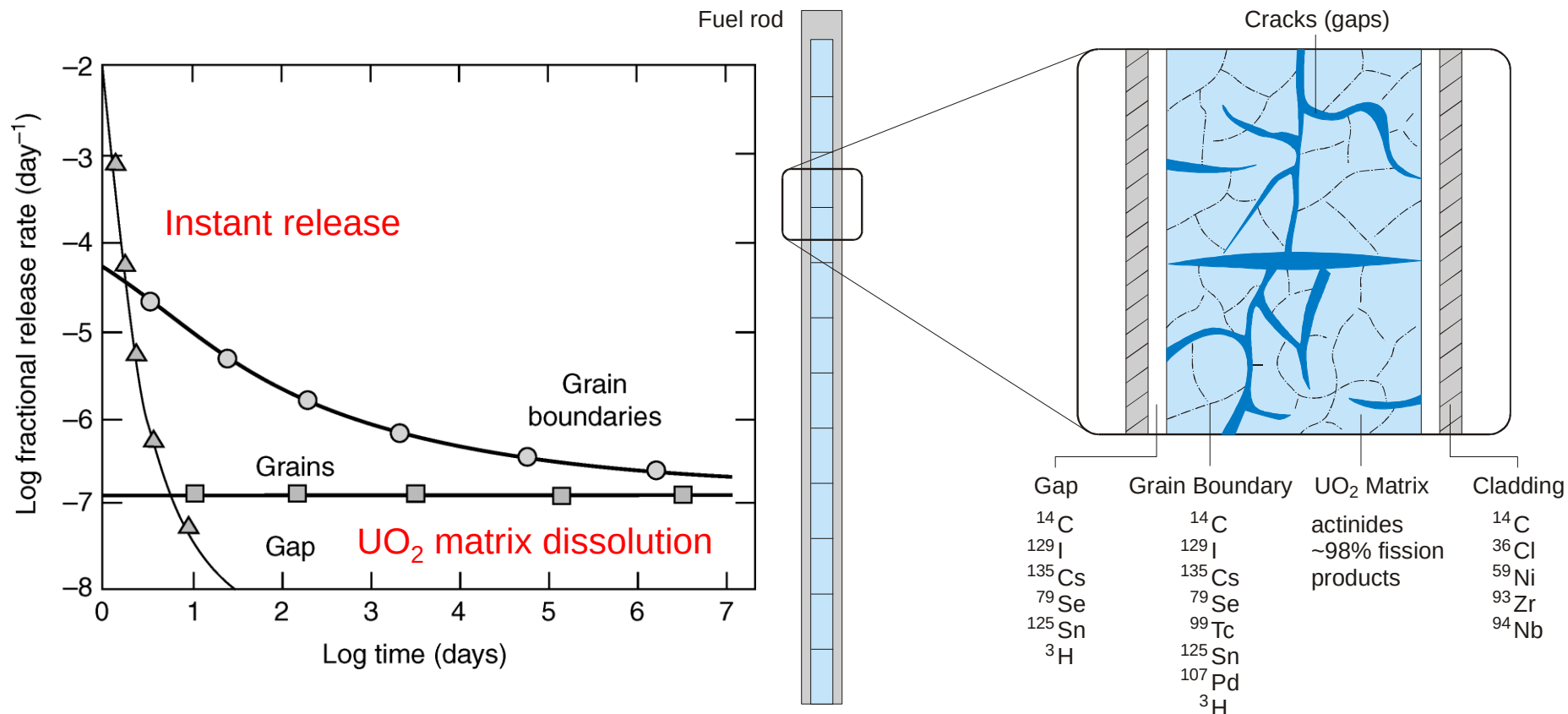
- Exact mechanisms not known
 - Radiolytical species and redox potential effects at high pH ?
 - Ca adsorption or secondary phase precipitation ?
 - Formation of colloids ?
 - Conditions under which U(VI) hydroxo-complexes play a role ?
(only for young fuel without H_2 gas ?)
 - Minimum H_2 concentration 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 $^{135-137}\text{Cs}$
 - 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 (UO₂ 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



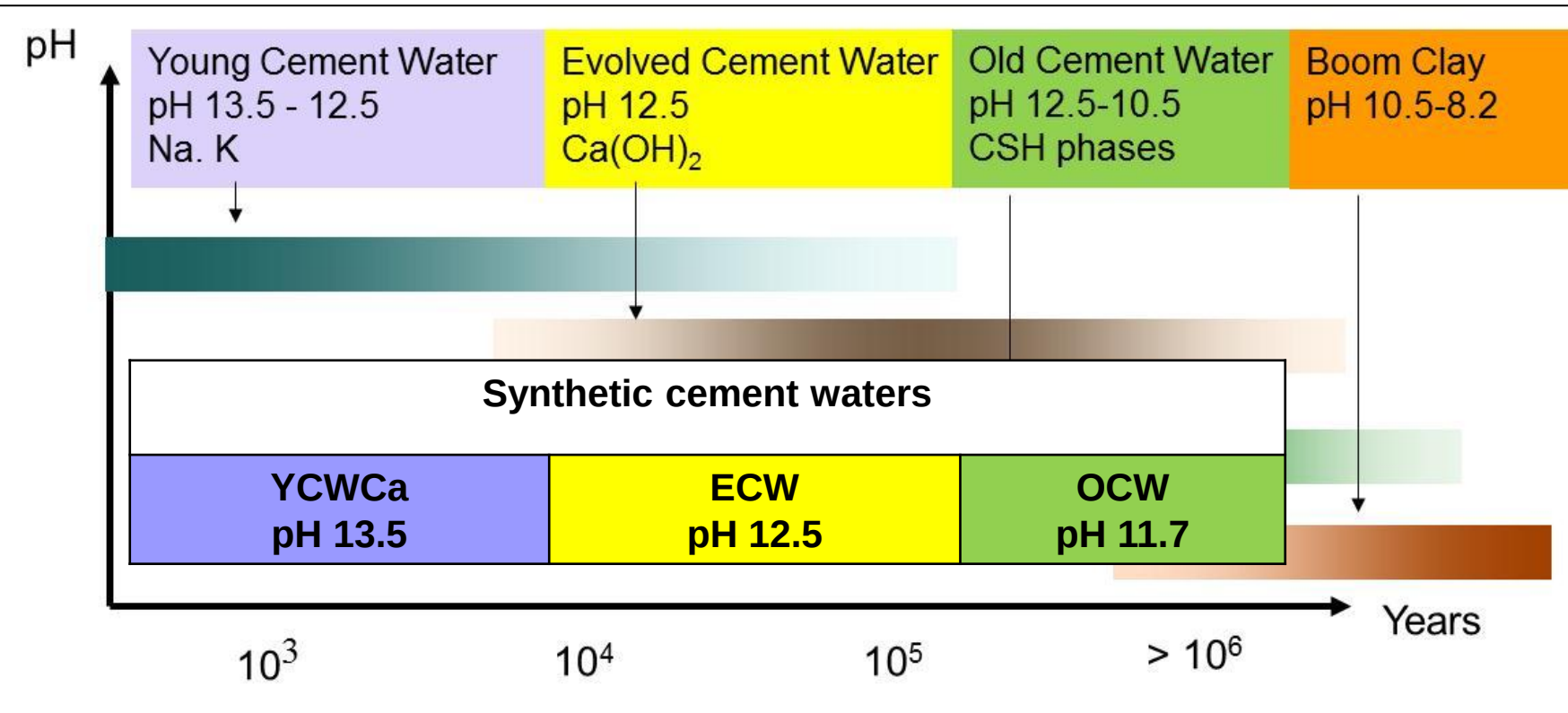


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Experimental programme to determine the stability of vitrified waste in Supercontainer conditions

K.Ferrand, K.Lemmens, S.Liu, R.Vercauter, B. Gielen

Evolution of pH concrete buffer



Average wt%	OPC (Ordinary Portland Cement)
SiO_2	21.4
MgO	2.4
$\text{Na}_2\text{O} + \text{K}_2\text{O}$	0.7
Al_2O_3	4.0
CaO	63.3
Fe_2O_3	3.3
Other	4.9

Fresh cement paste without calcite aggregates

- Ordinary Portland Cement CEM I (C42, HSR5R LA CCB)
- Ratio of water to cement = 0.4

Type of glasses

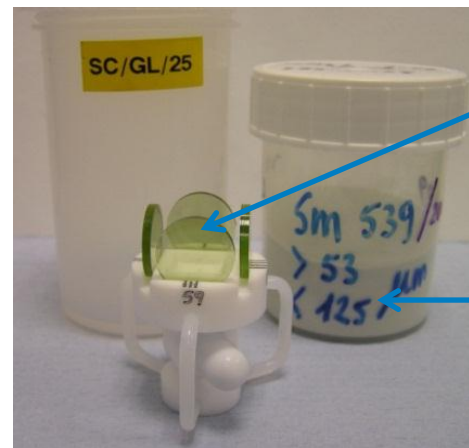
- **Inactive reference glasses** used to determine the glass alteration mechanisms and to model the glass long term behavior in the context of a deep geological repository

(wt%)	SON68 (AREVA)	SM539 (PAMELA)
SiO ₂	45.48	35.28
Al ₂ O ₃	4.91	19.83
Na ₂ O	9.86	9.21
CaO	4.04	5.05
B ₂ O ₃	14.02	25.58
Fe ₂ O ₃	2.91	0.47
ZrO ₂	2.65	0.05
Other	16.13	4.53

- **Difference in glass composition**

- **Difference in glass structure**

- **Difference in glass durability**

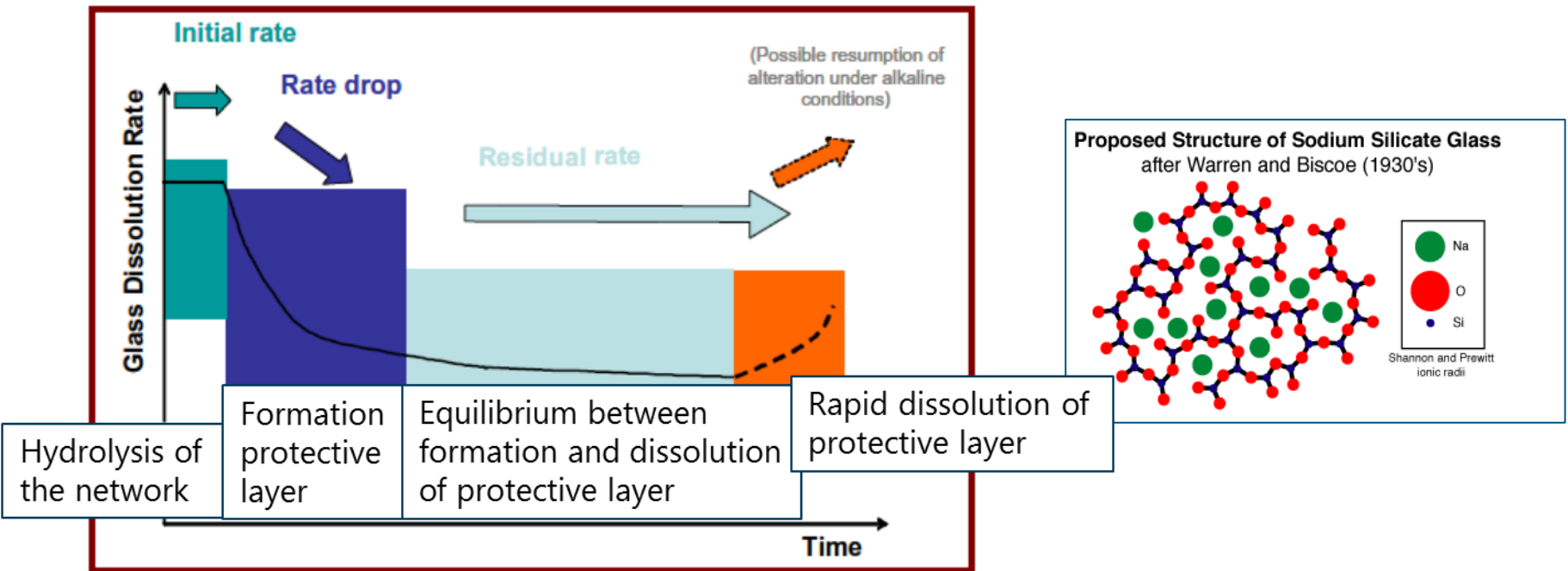


Glass monoliths

Ø 16 mm, 2 mm thickness

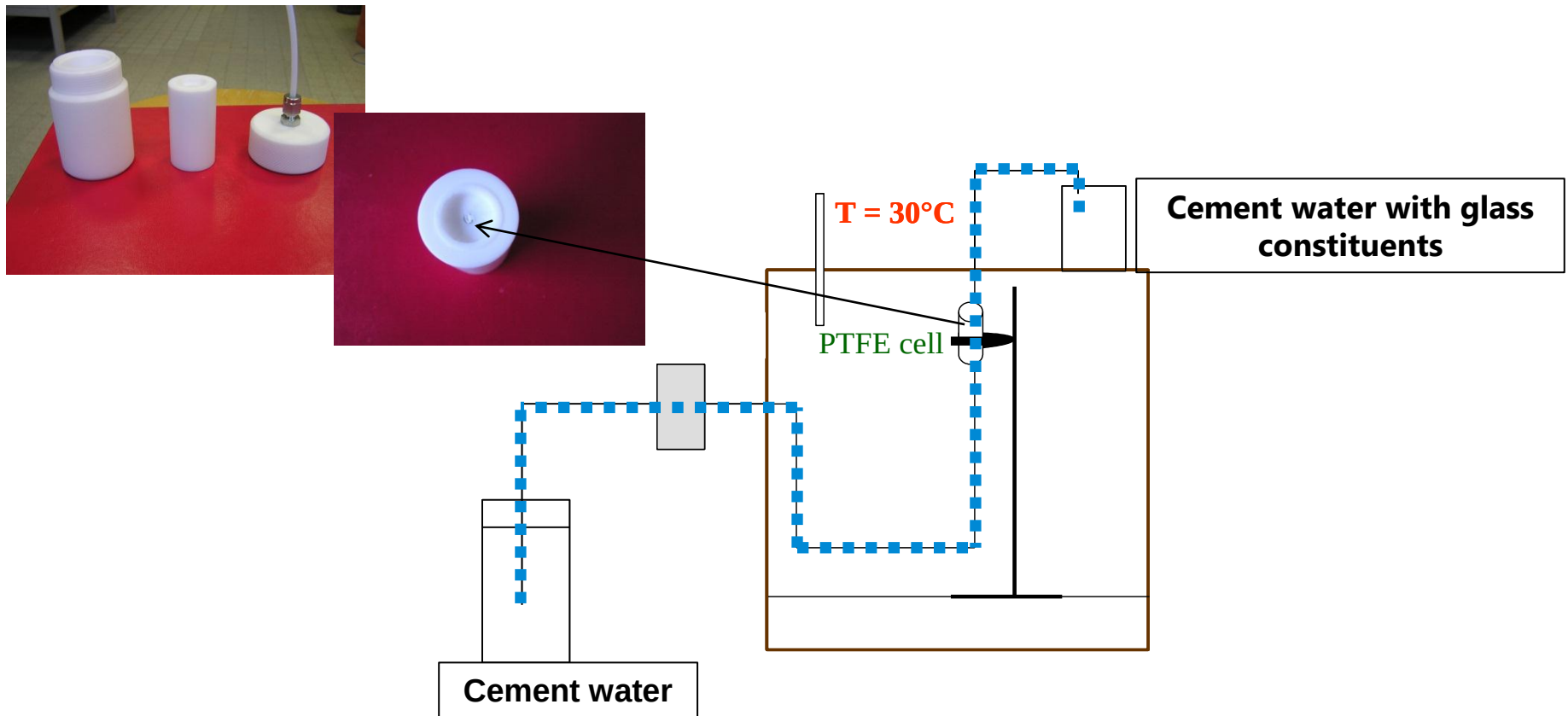
Glass powder

General glass dissolution model



Dynamic tests, static tests in cement waters in presence or without cement

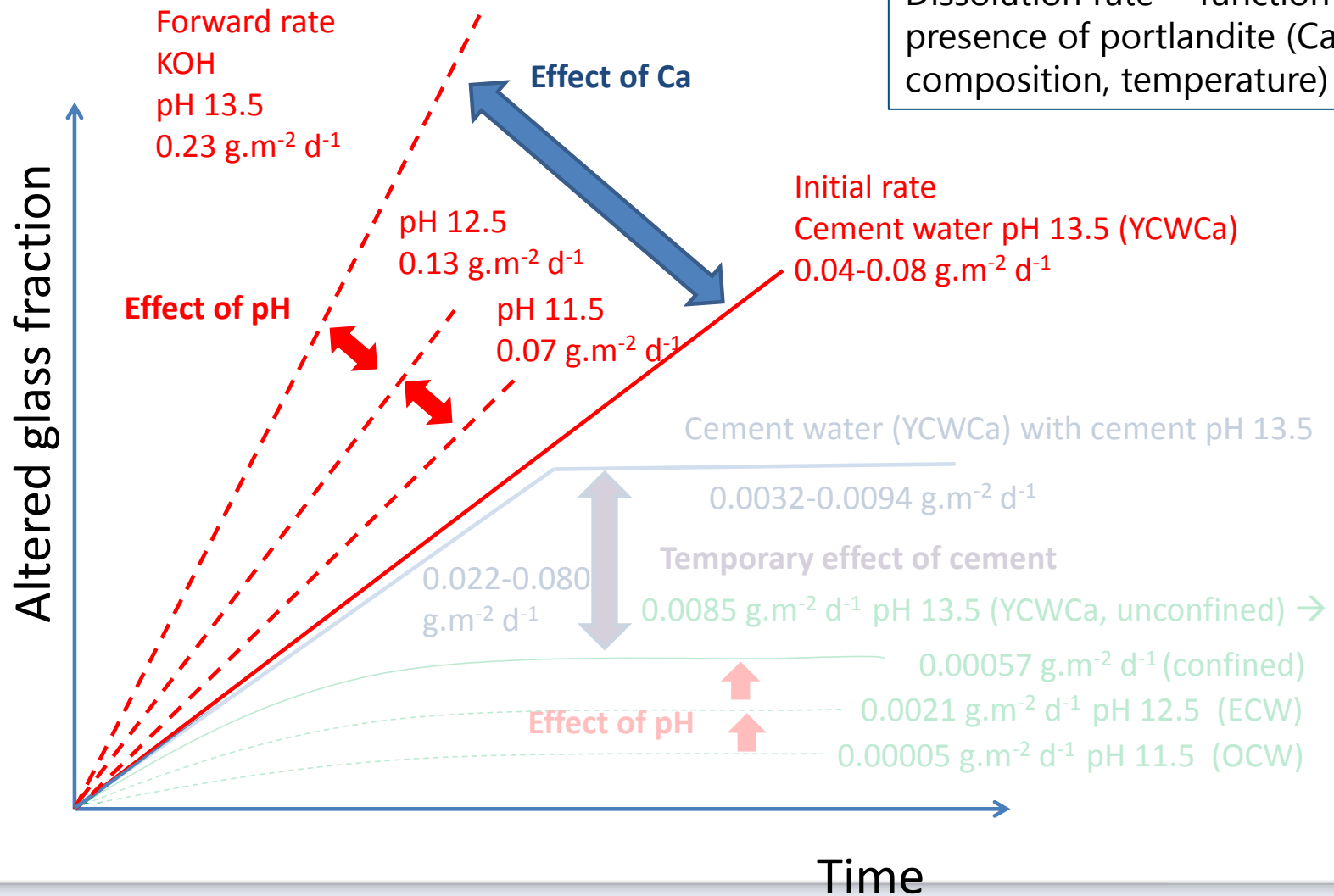
Dynamic tests: determination of the maximum dissolution rate (no precipitation of secondary phases)



High flow rate → maximum dissolution rate
Function of pH and composition of cement water

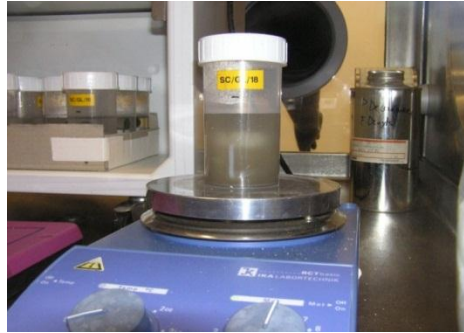
Dynamic dissolution rates (red lines on the graph)

SON68, 30°C



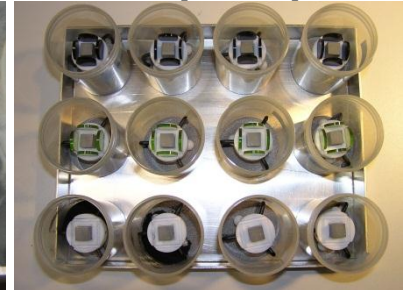
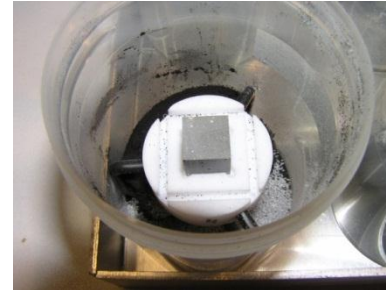
Static tests under Ar atmosphere and magnetic stirring (no refreshment of the solution)

Cementitious waters (30°C, 70°C)



- YCWCa (pH 13.5), ECW (pH 12.5) or OCW (pH 11.7)
- glass powder + glass monoliths
- **[B] in solution good dissolution indicator**

Presence of cement (30°C)



- YCWCa (pH 13.5)
- glass powder + glass monoliths
- Different ratios of cement to glass powders
- **B sorption on cement**
 - **Rates from the mass loss of the monoliths**
 - **Rates from [Li]_{solution}**



For both type of tests:

- pH, [element] by ICP-AES (MS)
- Solid analyses: OM, SEM, XRD

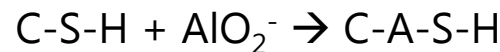


OPC triggers glass dissolution at the maximum rate

- **Abundant OPC:** dissolution rate close to the maximum rate

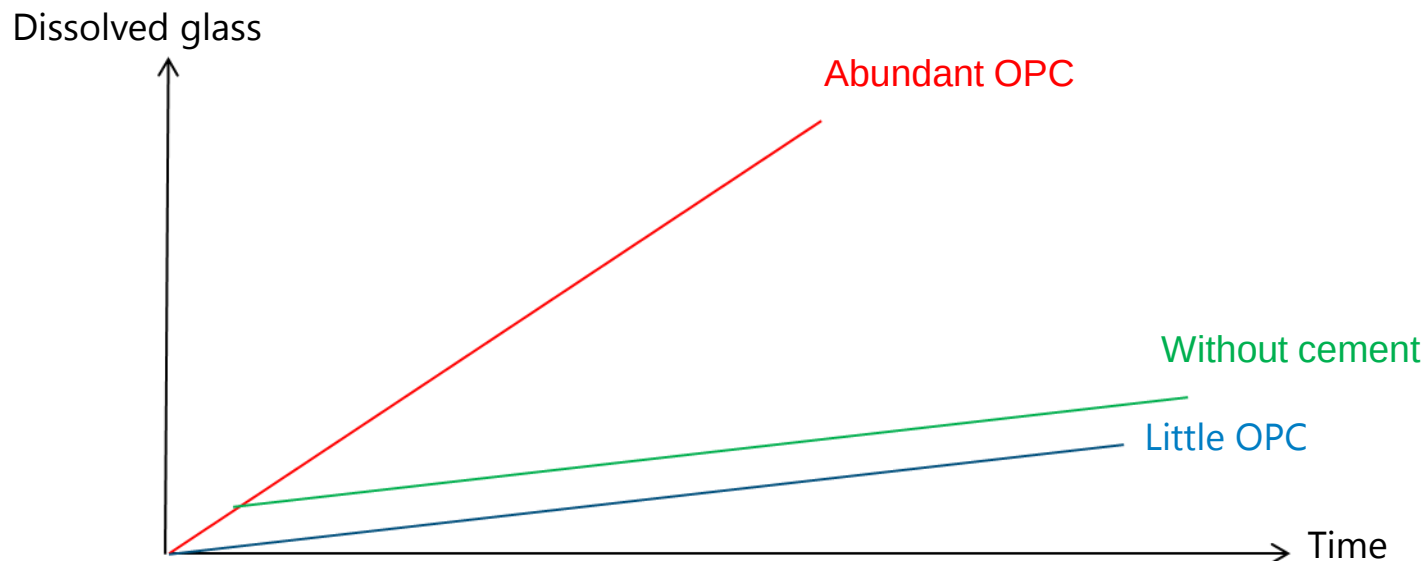


Calcium Silicate Hydrate



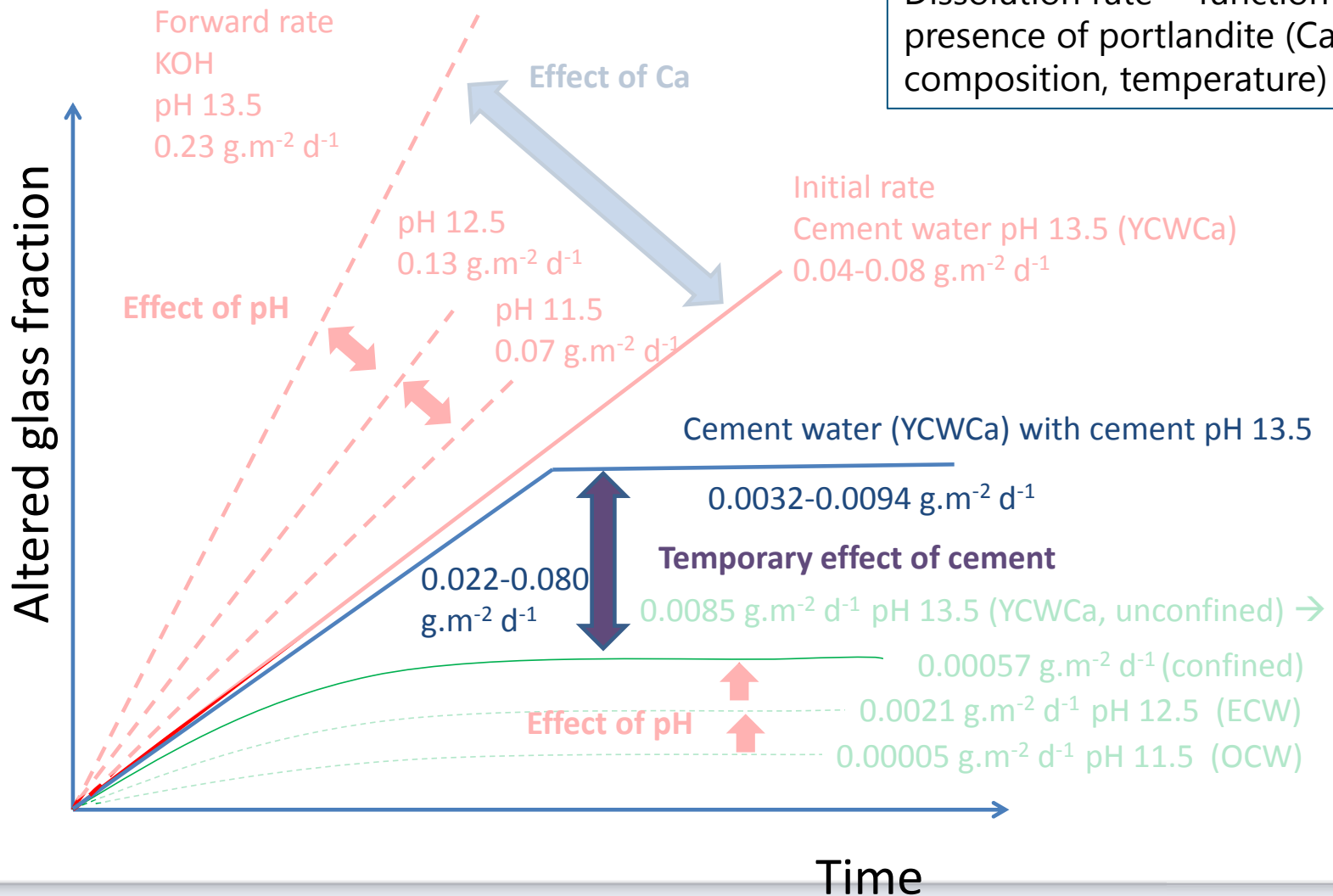
Calcium Aluminum Silicate Hydrate

- **Little OPC:** dissolution rate lower than the maximum rate, portlandite rapidly consumed and rate similar as **without cement**



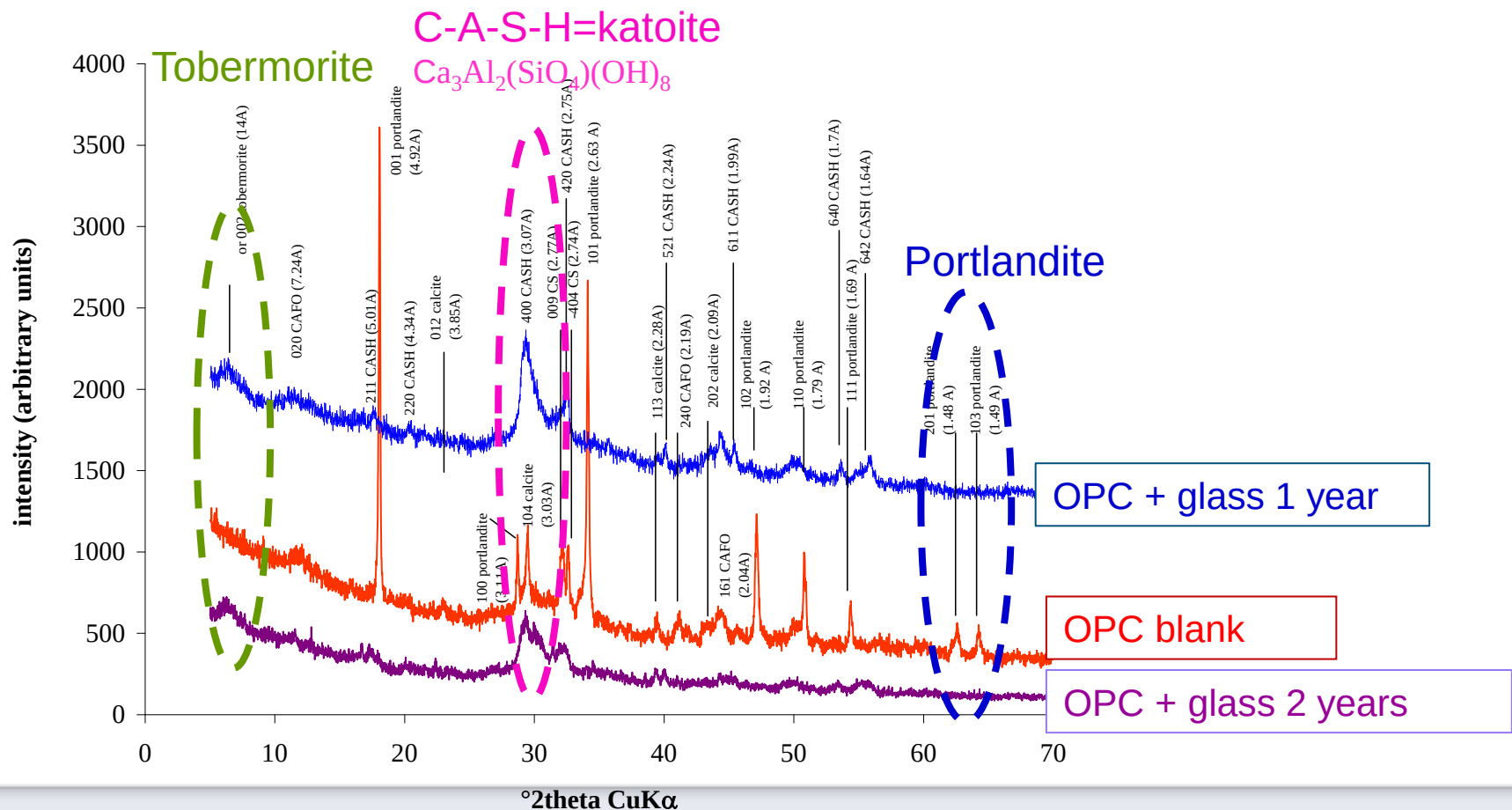
Static dissolution rates (blue lines on the graph)

SON68, 30°C



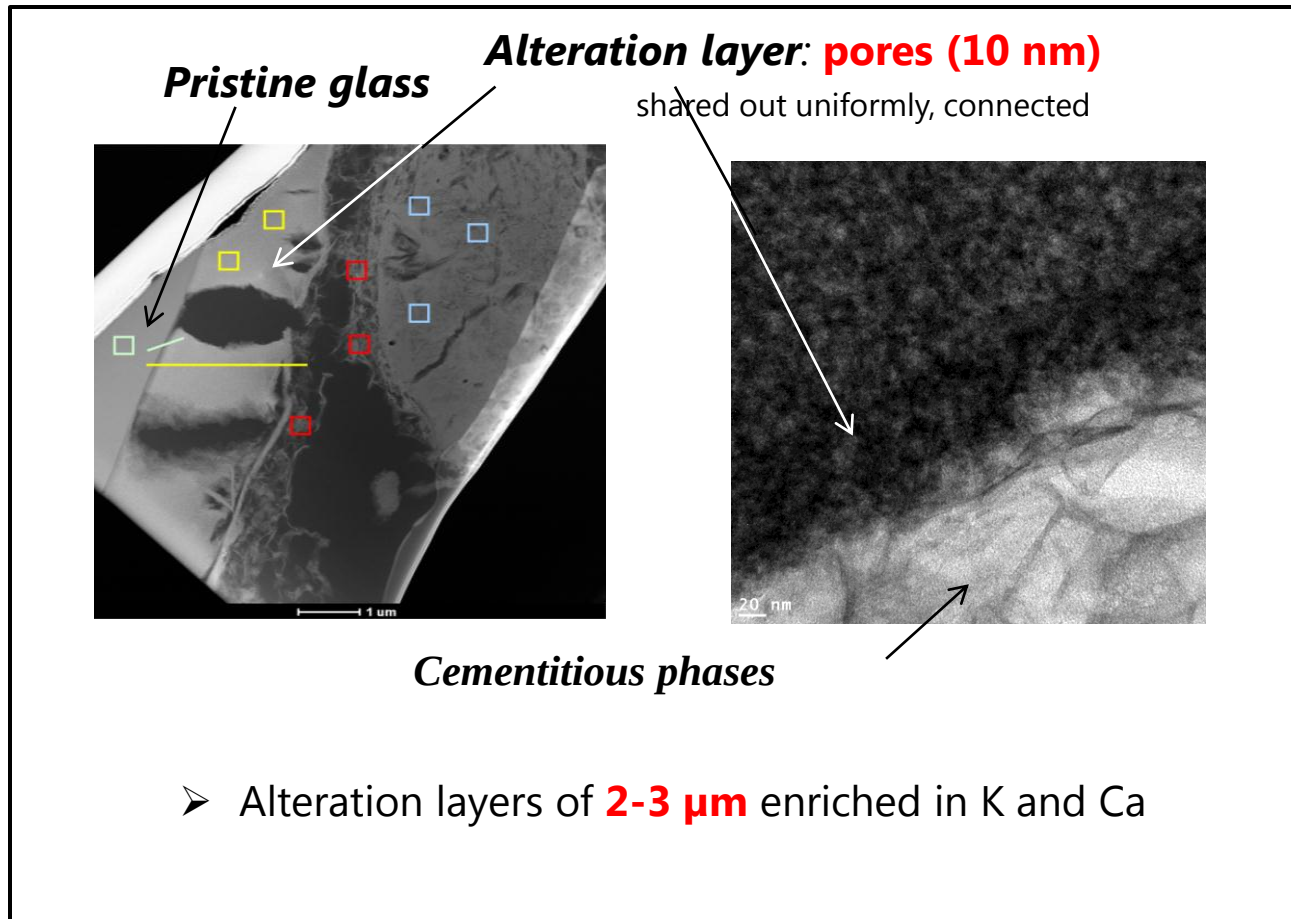
XRD analysis reveals reactions between glass and concrete

- appearance of **tobermorite** and **C-A-S-H** phases
- disappearance of **portlandite** → transformation into C-S-H



SON68 with cement at 30°C: porous, Ca-rich alteration layer

HRTEM micrographs of SON68 glass powder in contact with OPC after 713 days

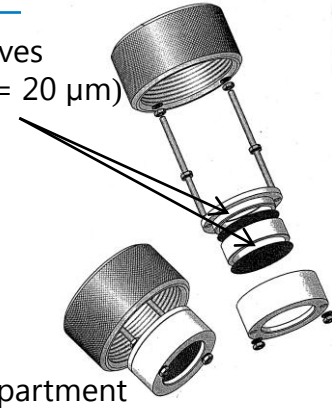


Static tests with confined glass powder: dissolution rate in the internal cracks



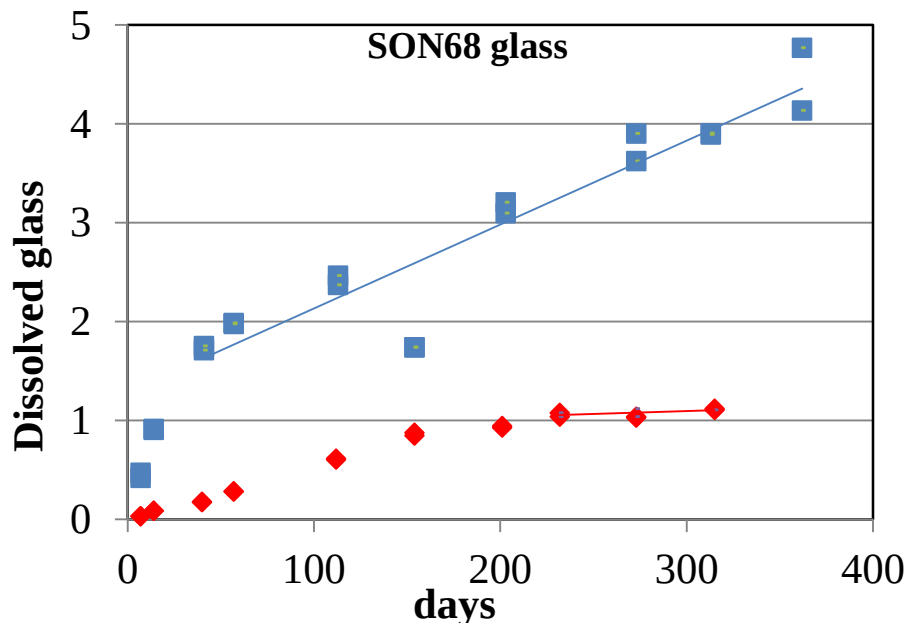
- Glass powder enclosed between sieves ('Confined')

Stainless steel sieves
($\emptyset = 3$ cm mesh = $20\text{ }\mu\text{m}$)

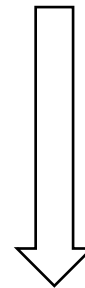


Teflon[®] compartment

Confinement: rate suppressing effect due to slow transport in confined solution and favorable effect of build-up of dissolved matrix constituents



Unconfined glass



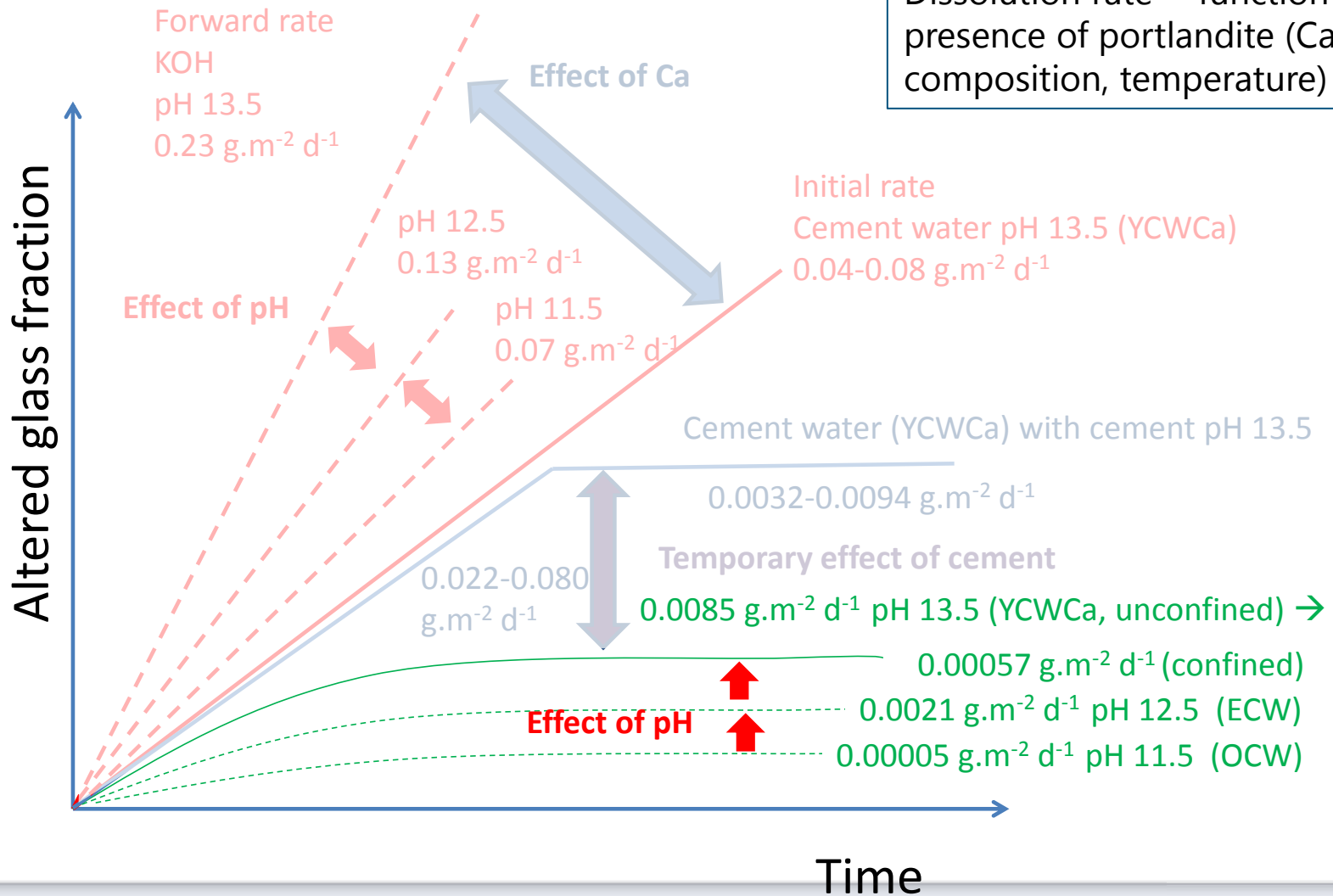
Confined glass

Glass alteration rate 14 times lower

Static dissolution rates for confined glass

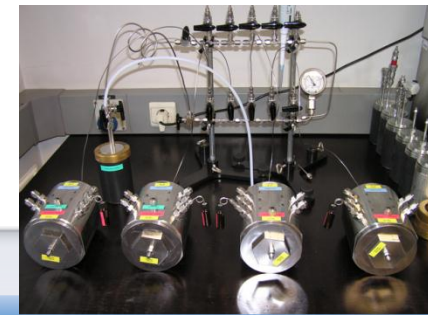
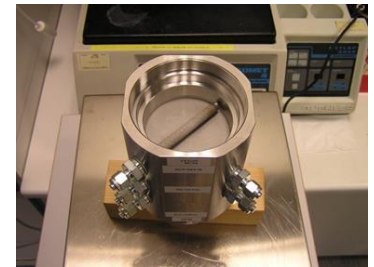
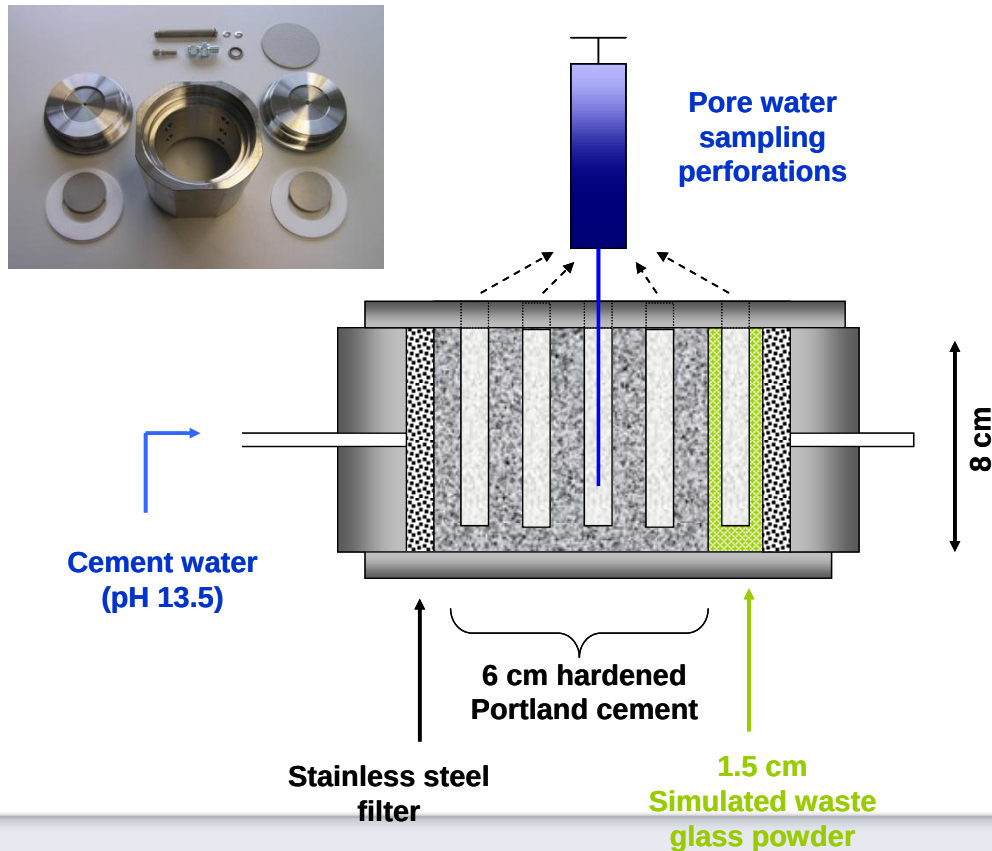
SON68, 30°C

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



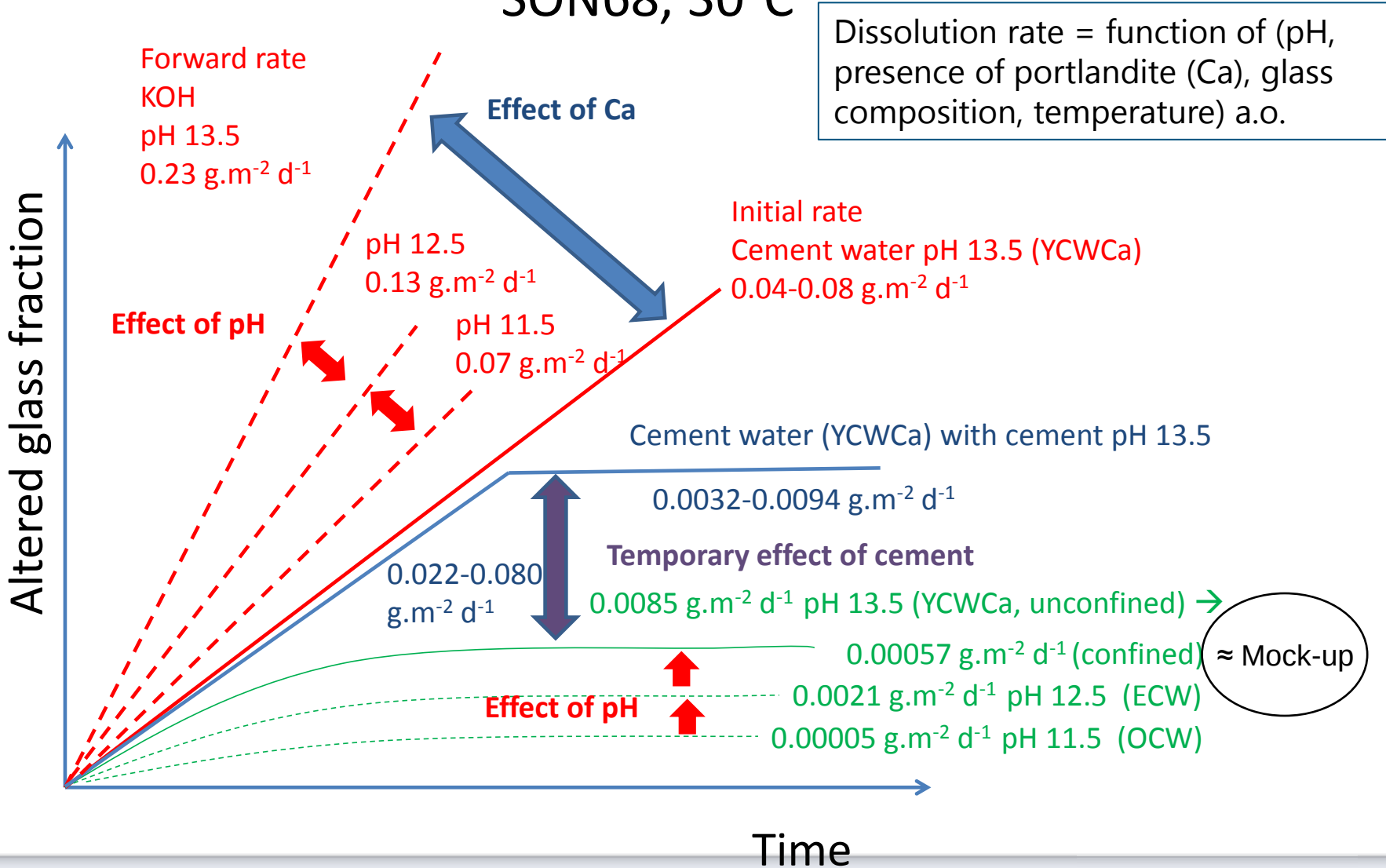
More realistic tests: mock-up tests

- Take into account the distance between the concrete and the glass



Static dissolution rate for mock-up

SON68, 30°C



Geochemical modelling using PHREEQC code

Geochemical modelling complementary to laboratory tests and necessary to build-up a glass dissolution model at the long term

- Tests in cementitious waters at pH 13.5 and at pH 12.5 (30°C / 70°C)
- Tests at pH 13.5 in presence of cement at 30°C



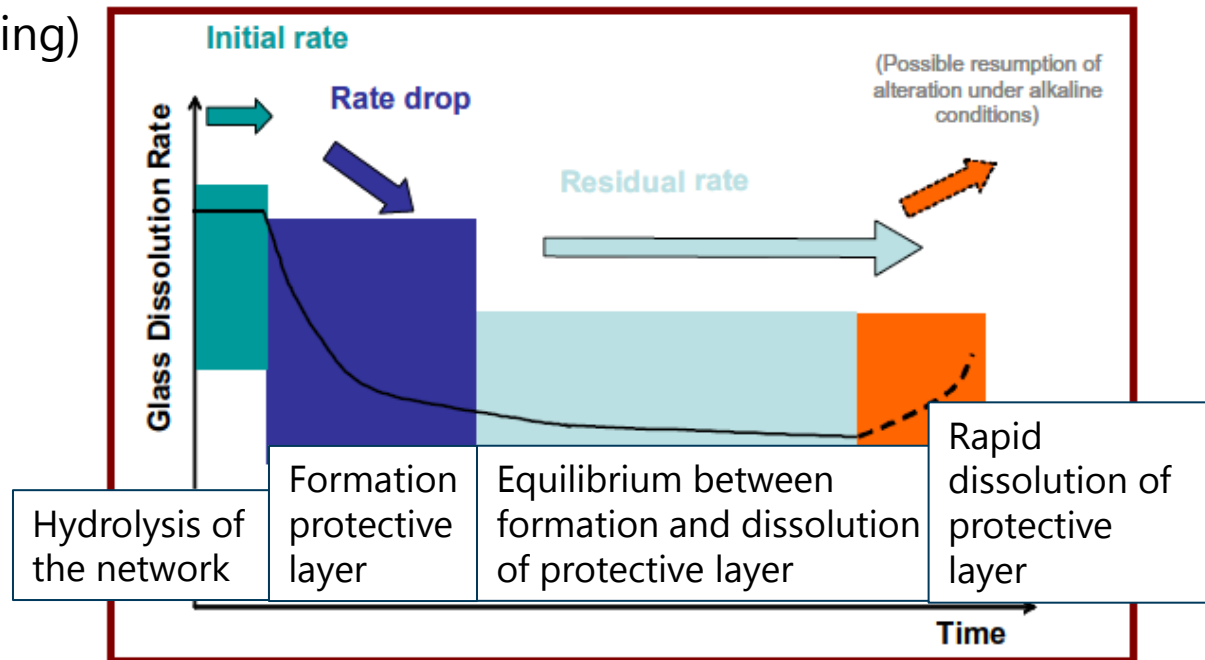
STUDIECENTRUM VOOR KERNENERGIE
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Geochemical modeling of the dissolution of SON68 glass in hyper-alkaline solution

S.Liu, K.Ferrand, K.Lemmens

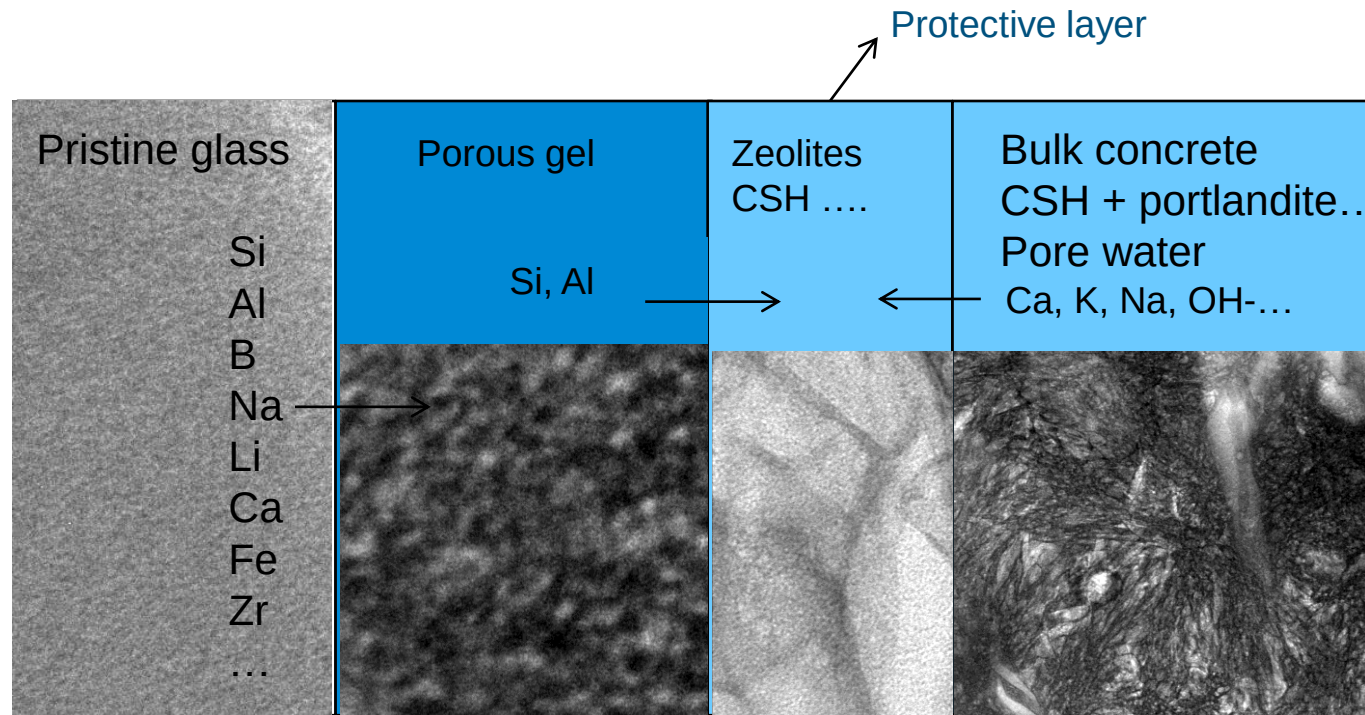
Glass alteration in Young Cement Water (YCWCa, pH 13.5)

- High pH, alkalis and ionic strength (≈ 0.5 M in YCWCa, up to 1 M one year after glass alteration)
- Possible precipitation of secondary phases, such as C-S-H and zeolites
 - C-(A)-S-H (driving force)
 - Diffusion barrier (limiting)
 - Zeolites (resumption)



Why geochemical modeling ?

- Understand chemical/kinetical/transport processes triggering the glass alteration



Pristine Glass  Solution

(for illustration only, not representative of the real scale)

Factors affecting glass dissolution in general

- pH (high pH, nucleophilic attack of siloxane bonds)
- Temperature
- Glass composition (the higher the alkali content in the glass, the faster the glass dissolves)
- Al in the solution (inhibitory)
- Ca in the solution (inhibitory or promotional)
- Mg in the solution (similar to Ca)
- Silicon saturation in the solution (chemical affinity)
- Precipitation on the surface of the glass (protection)
- Zeolite formation (resumption)

Glass dissolution rate = $f(\text{Alkali}, \text{pH}, \text{Al}, \text{Ca}, \text{Mg}, \text{Si}, \text{zeolite}, \text{C}-(\text{A})-\text{S}-\text{H}, \dots)$

Glass dissolution model

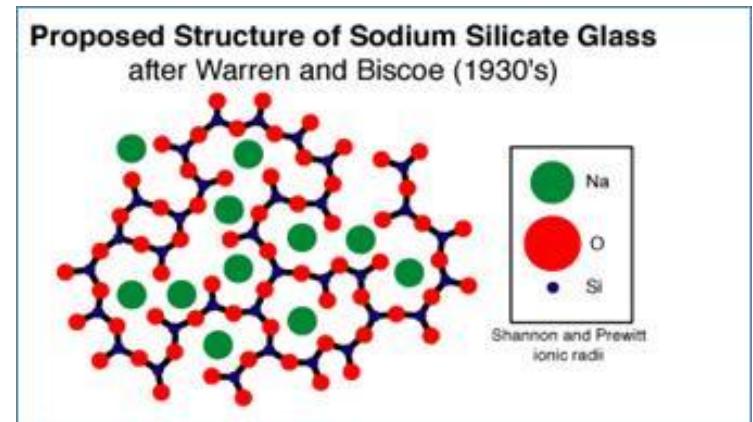
- Dissolution controlled by reaction affinity

$$r = r_0 \left(1 - \frac{[H_4SiO_4]}{[H_4SiO_4]_{sat}} \right)$$

Approaches zero rate at saturation

→ Forward dissolution: (dissolution of network)

$$rate = f(T, pH, k^+, \dots)$$



- Dissolution controlled by transport through the alteration layer
 - 1) Alteration products form a barrier to the transport from both sides
 - 2) The barrier is formed as hydrated glass species (Si-OH, Al-OH, Zr-OH...) that react together and with other species to form a new amorphous material

→ Diffusion: (for network modifier Li, Na... and B)

$$rate = f(D, t, T, pH, \dots)$$

Tests with glass in cement water without cement

Alkali Silica Reaction controlled dissolution

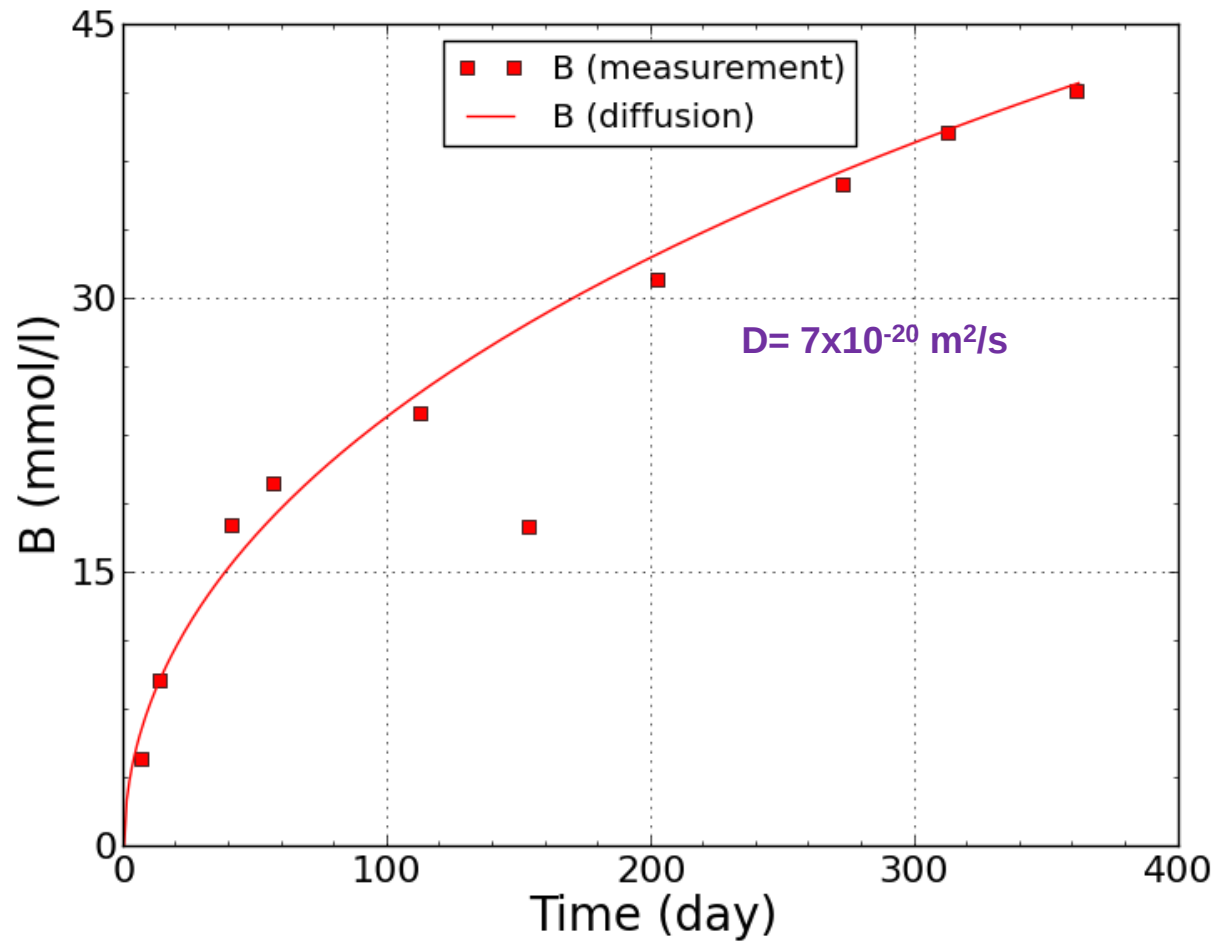
- Alkali Silica Reaction (ASR)



- The gel is amorphous and difficult to characterize. C-S-H (low Ca/Si) and zeolites have been reported in literatures.
- Diffusion of water/glass constituents through Alkali Silica gel

Tests with glass SON68 in cement water without cement

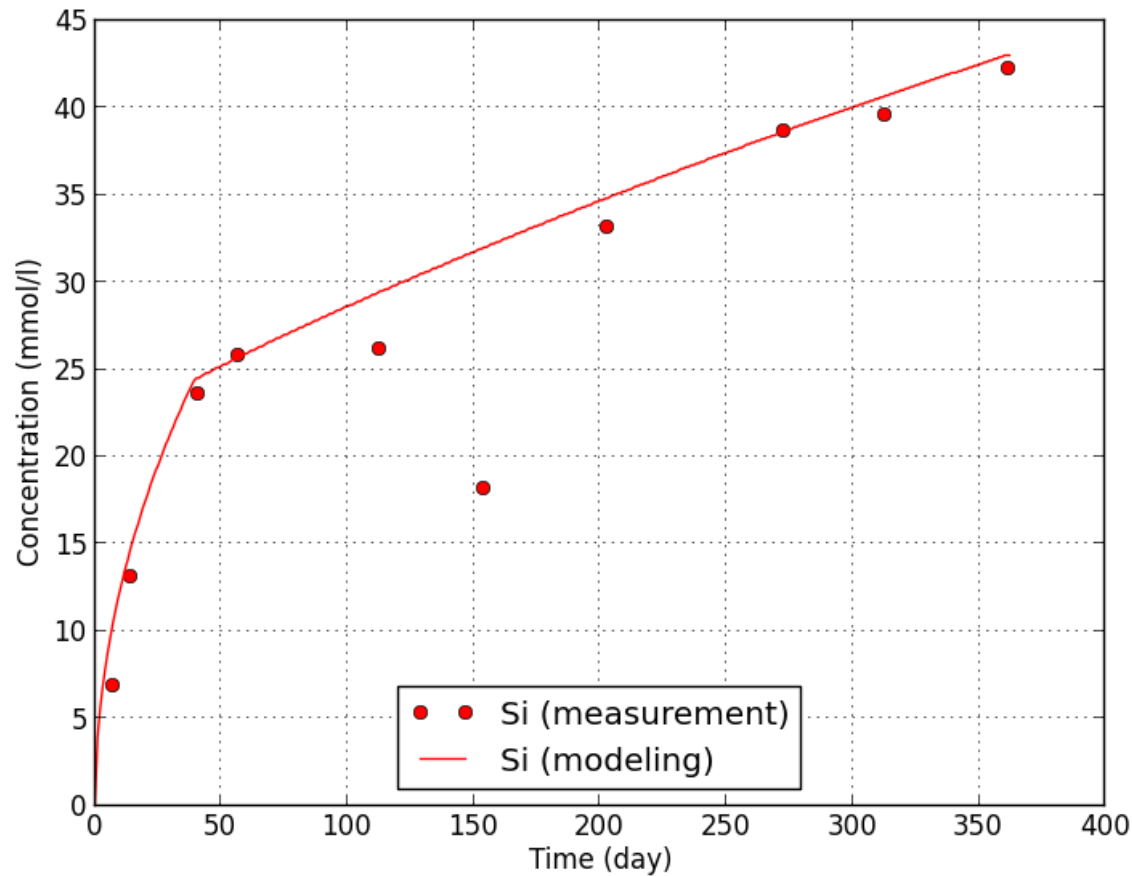
Boron release controlled by diffusion through ASR gel at 30 °C



Boron is used as a dissolution indicator

Tests with glass SON68 in cement water without cement

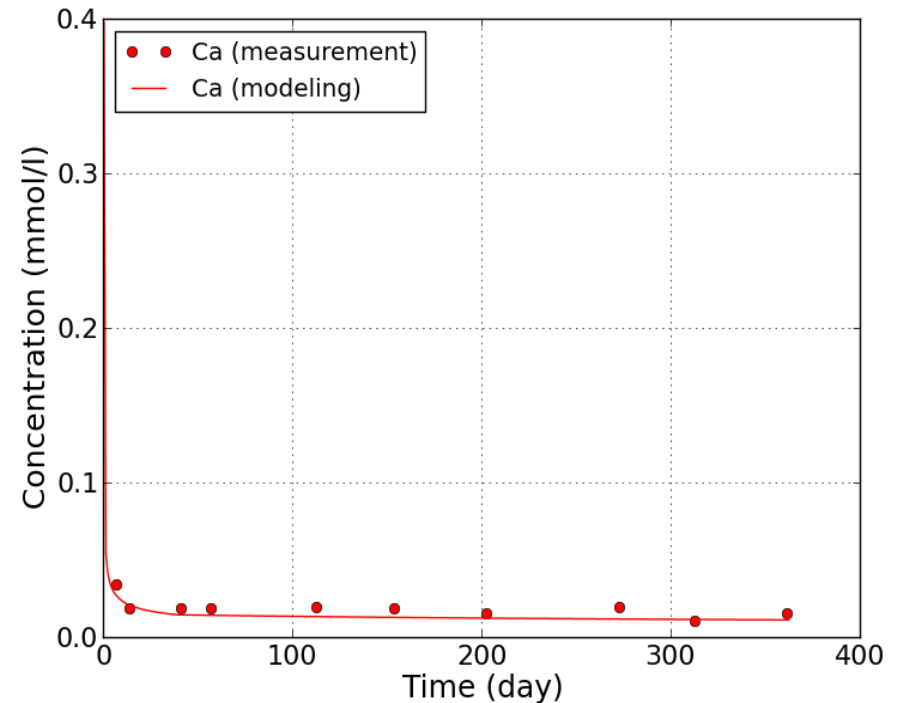
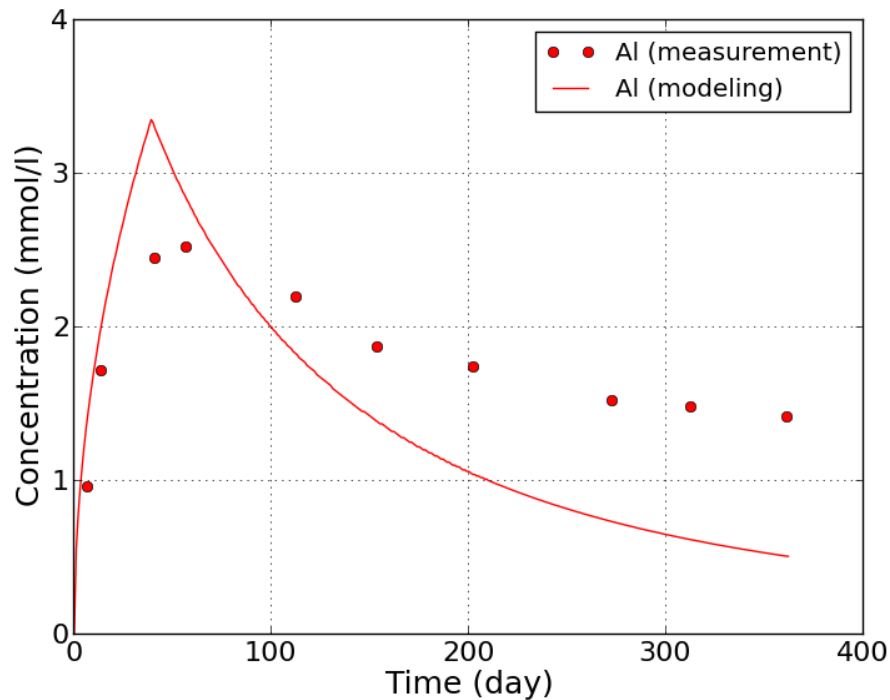
Silicon release controlled by formation of ASR gel at 30 °C



Assuming k-feldspar and Foshagite in equilibrium with the solution

Tests with glass SON68 in cement water without cement

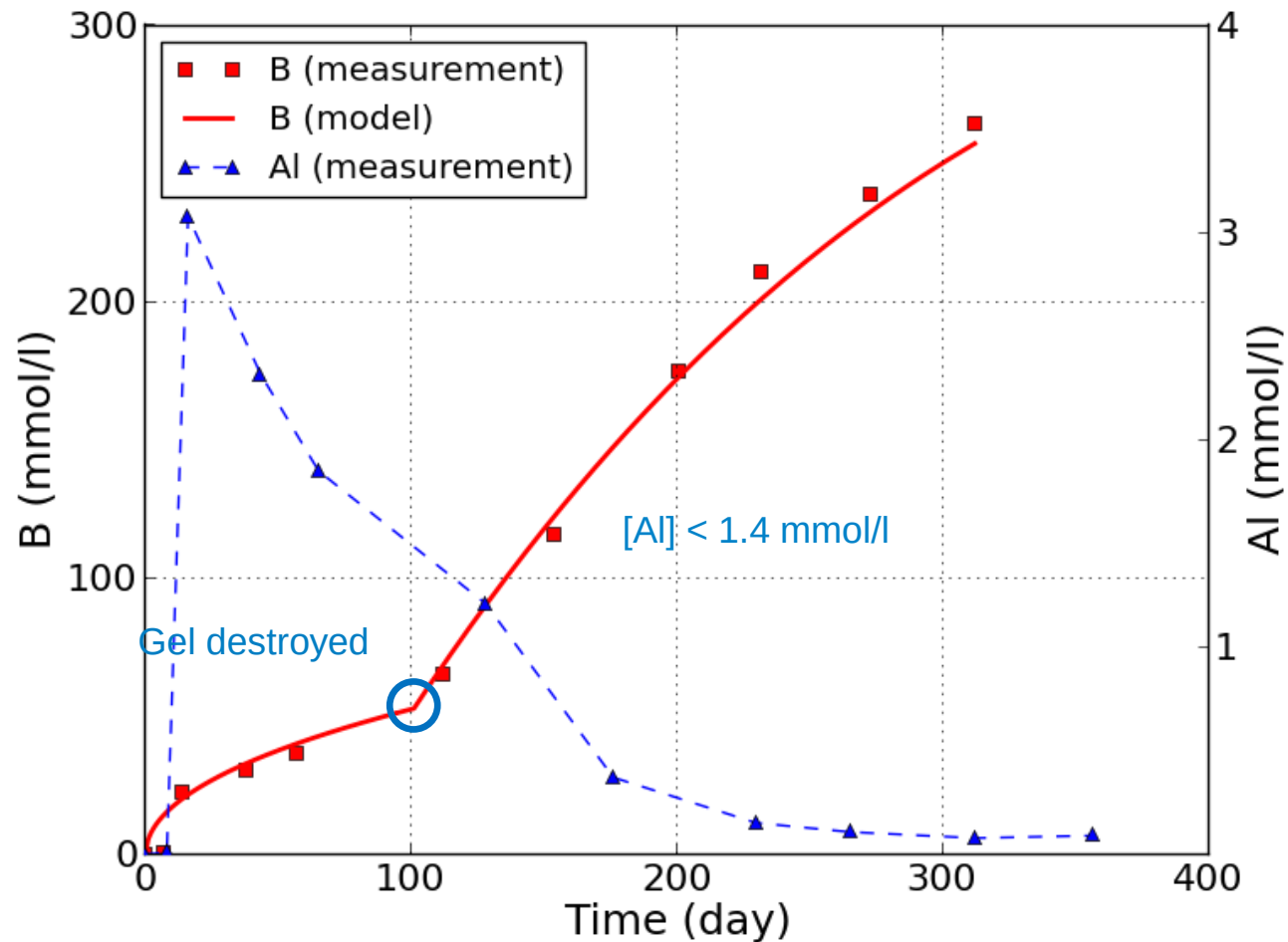
Al and Ca involved in the formation of ASR gel at 30 °C



Assuming k-feldspar and Foshagite in equilibrium with the solution

Tests with glass SON68 in cement water without cement:

Formation of zeolites can explain corrosion resumption at 70°C

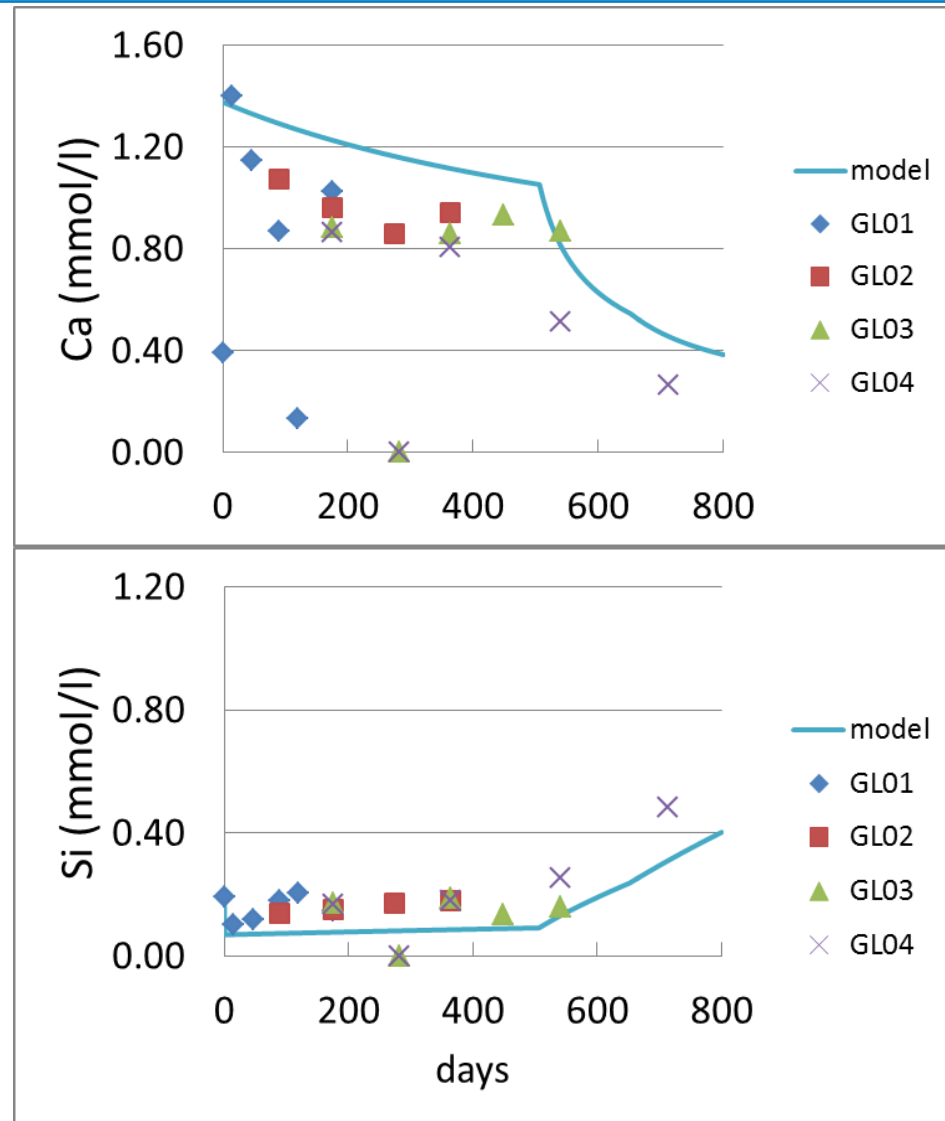


Higher temperature is in favor of zeolite formation.

Tests with glass SON68 and cement at 30°C

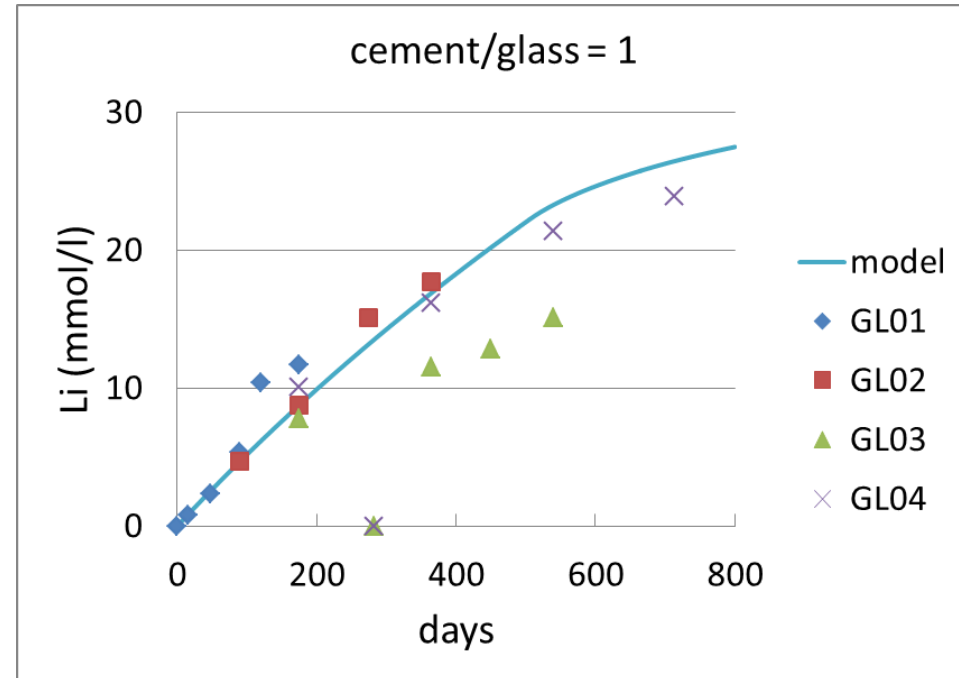
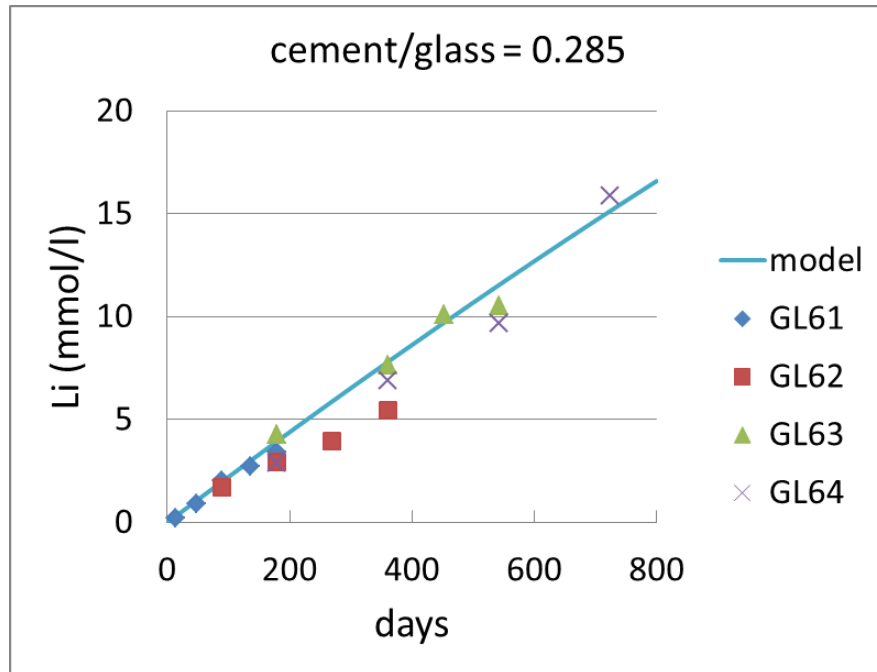
Equilibrium with C-S-H solid solution can explain the Ca and Si evolution

C-S-H is modeled as a solid solution of Jennite ($\text{Ca/Si} \approx 1.67$) and Tobermorite ($\text{Ca/Si} \approx 0.83$)



Tests with glass SON68 and cement at 30°C

The model can also explain the effect of the amount of cement



Due to Boron sorption onto cement, Lithium is used as the dissolution indicator

Conclusions

- The geochemical model is able to explain the observed glass dissolution behavior with and without cement
 - In the presence of cement powders, pozzolanic reaction is the main driving force for glass alteration with the formation of C-S-H phases. As long as portlandite is present, the glass dissolves at a higher rate than without portlandite at the same pH.
 - Without cement powders, alkali-silica reaction is the main reaction controlling glass alteration with formation of ASR gel (amorphous), and diffusion through the ASR gel limits glass alteration.

But

- It is difficult to characterize secondary phases.
 - Transport through cement/glass alteration layers cannot yet be modeled
- Simulations of more complicated longer term evolution not yet possible

- ONDRAF/NIRAS
- Technicians: R.Vercauter, B.Gielen
- XRD: M.Honty
- ToF-SIMS: L.Dupuy
- HRTEM: S.Depierre
- ICP: G.Verpoucke
- Discussion: M.Aertsens, L.Wang, S.Salah, D.Jacques, P.V Iseghem



STUDIECENTRUM VOOR KERNENERGIE
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CORALUS: an integrated *in situ* test on the corrosion of alpha-active (SON68) HLW glass

E. Valcke, S. Smets, S. Labat, P. Boven, B. Gielen, W. Verwimp, R. Vercauter,
K. Lemmens, K. Ferrand, M. Aertsens, and P. Van Iseghem

Belgian Nuclear Research Centre, SCK•CEN elie.valcke@sckcen.be

N. Godon, P. Jollivet, J.P. Mestre, G. Parisot, M. Bojat, J.M. Boubals,
and X. Deschanel

CEA-Valrhô nicole.godon@cea.fr

The objective of CORALUS was/is to study the behaviour of the SON68 glass type in realistic disposal conditions

- ❑ CORALUS = 4 *in situ* test tubes + complementary laboratory tests + modelling predictions (CEA Lixiver 2 model)
- ❑ SON68 = generic glass composition for R7T7 vitrified HLW (La Hague, Fr.)
- ❑ The *in situ* tests integrate non-radioactive and highly alpha-active SON68 glass samples, 3 different backfill materials at swelling pressure of 2 MPa, alpha-beta-gamma-radiation (from glass and ^{60}Co sources), heating, and contact with host clay formation, ...
- ❑ ... and allow to study a.o.:
 - glass dissolution in contact with dense clay
 - combined effect of γ -irradiation and temperature
 - effect of alpha activity
- ❑ Results to be compared with results of CORALUS and other surface laboratory experiments, and with modelling predictions

CORALUS: an international collaboration project



❑ SCK•CEN, Mol, Belgium (co-ordinator, *in situ* test, glass)



❑ CEA-Valrhô, France (glass samples, lab tests, modelling)



❑ GRS, Braunschweig, Germany (gas analysis)

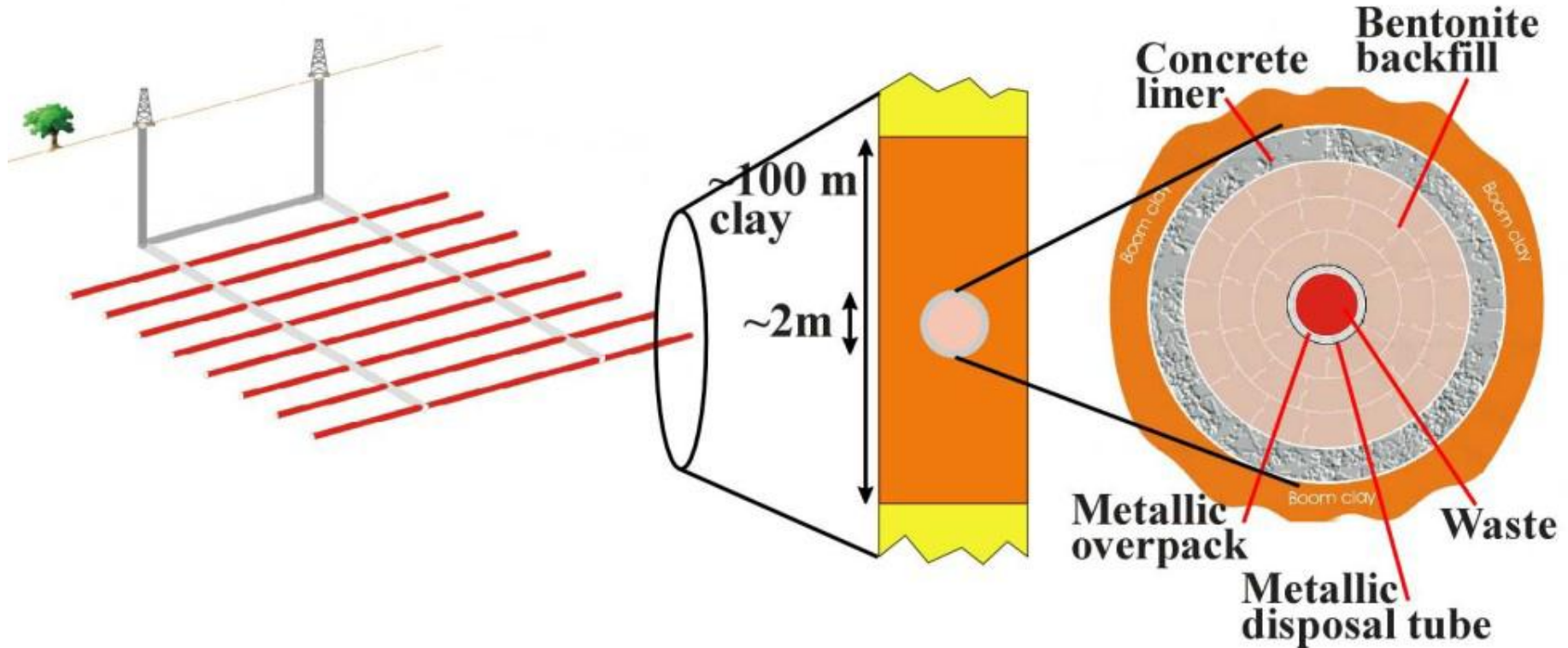


❑ EC Contracts FI4W-CT96-0035 (1997-2000)
FI5W-CT2000-00011 (2000-2004)



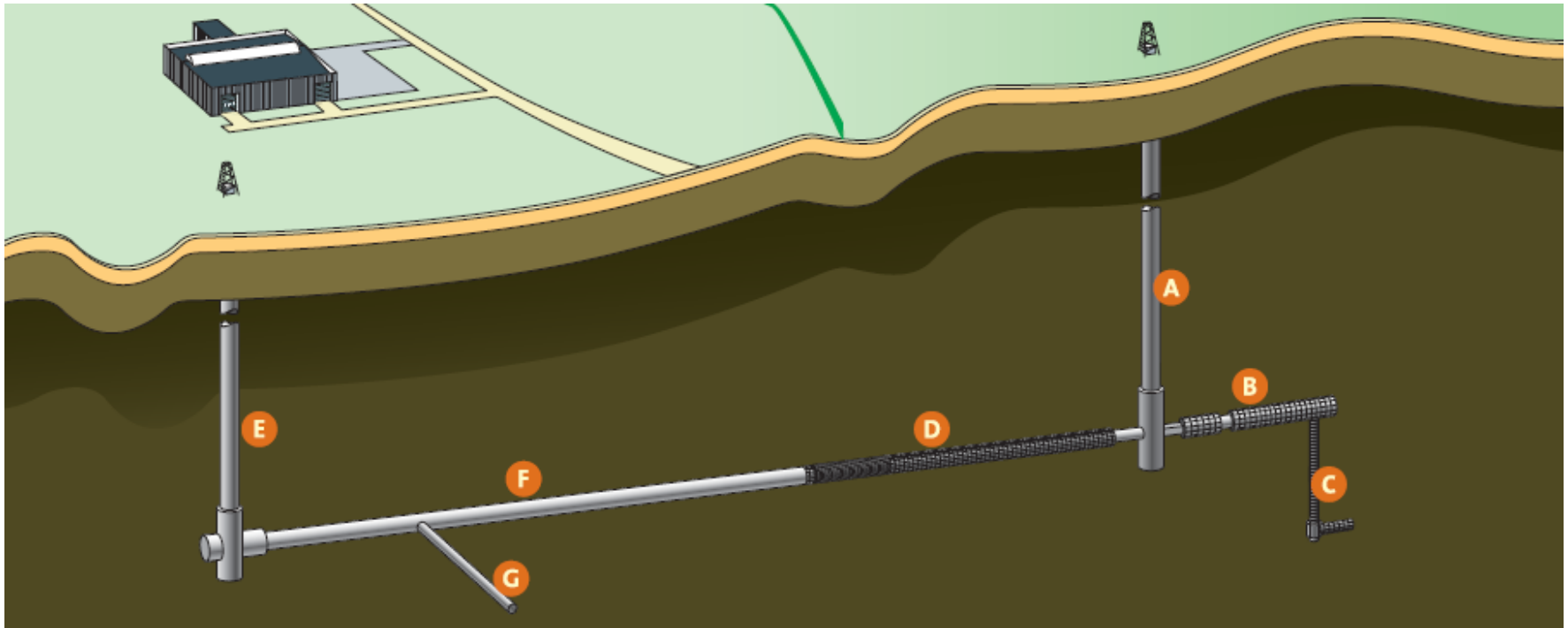
❑ N/O Contracts CCHO-98/332 (2000-2003)
CCHO-2004-2470 (2004-2008)
CCHO-2009-00940000 (2009-2014)

The clay-based disposal concept for heat-emitting waste was originally developed for disposal in granite



Schematic view of the SAFIR2 engineered barrier system for geological disposal of vitrified high-level waste in Boom Clay. (Figure 10 in RD&D plan of ONDRAF/NIRAS)

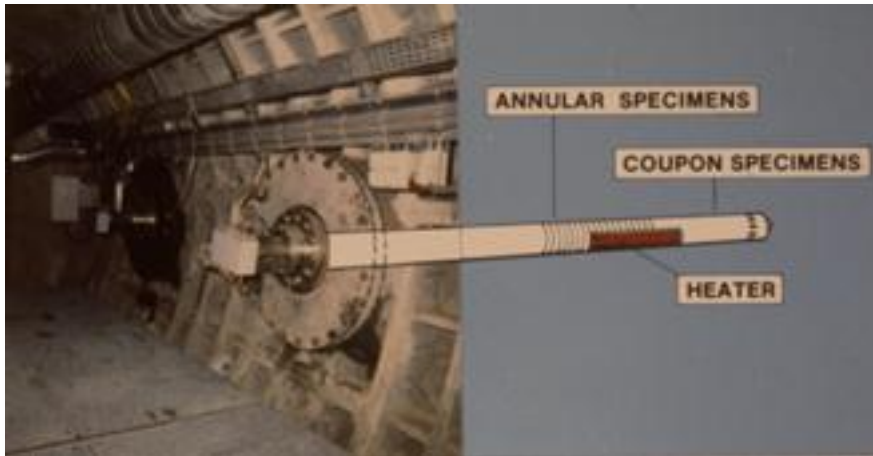
The first part of the URF–HADES was constructed in the 1980's



- A** 1980–1982: construction 1st shaft
- B** 1983–1984: construction 1st gallery (URL)
- C** 1984: construction exp. shaft & gallery
- D** 1987: construction 2nd gallery (Test Drift)

- E** 1997–1999: construction 2nd shaft
- F** 2001–2002: construction connecting gallery
- G** 2006–2007: construction Praclay gallery

The design of the first series of *in situ* corrosion experiments was relatively simple



- ❑ Each *in situ* corrosion experiment consisted of a long stainless steel (SS) carrier tube (5 to 7m) to ensure that the experiments were performed in the undisturbed clay
- ❑ The specimens were placed either on the outside or on a support tube on the inside of the SS carrier tube

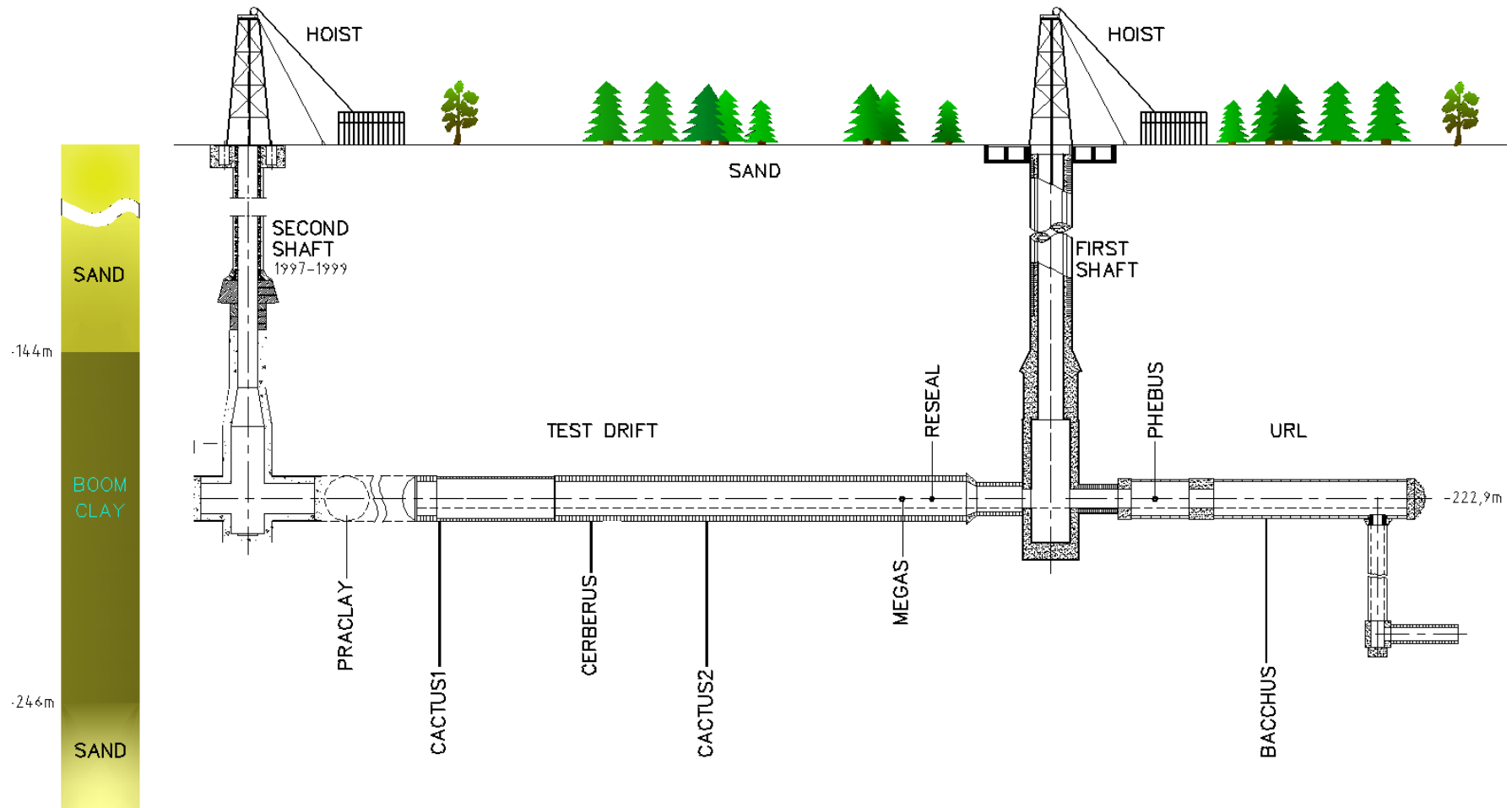


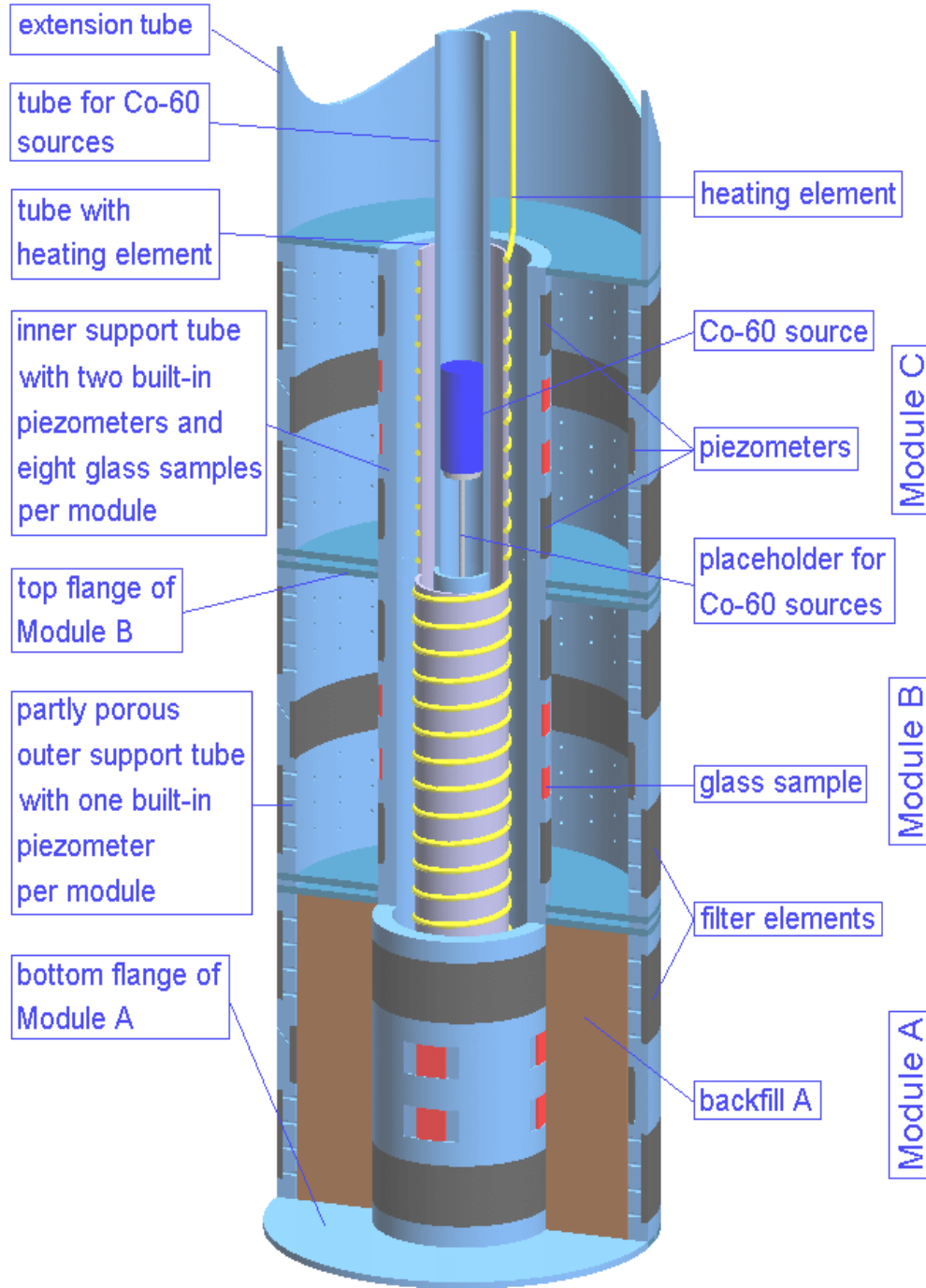
view of a *type I* corrosion test tube during installation in the underground research facility



view of a *type III* corrosion test tube (outer porous concrete tube + inner support tube)

Selection of other *in situ* experiments in HADES





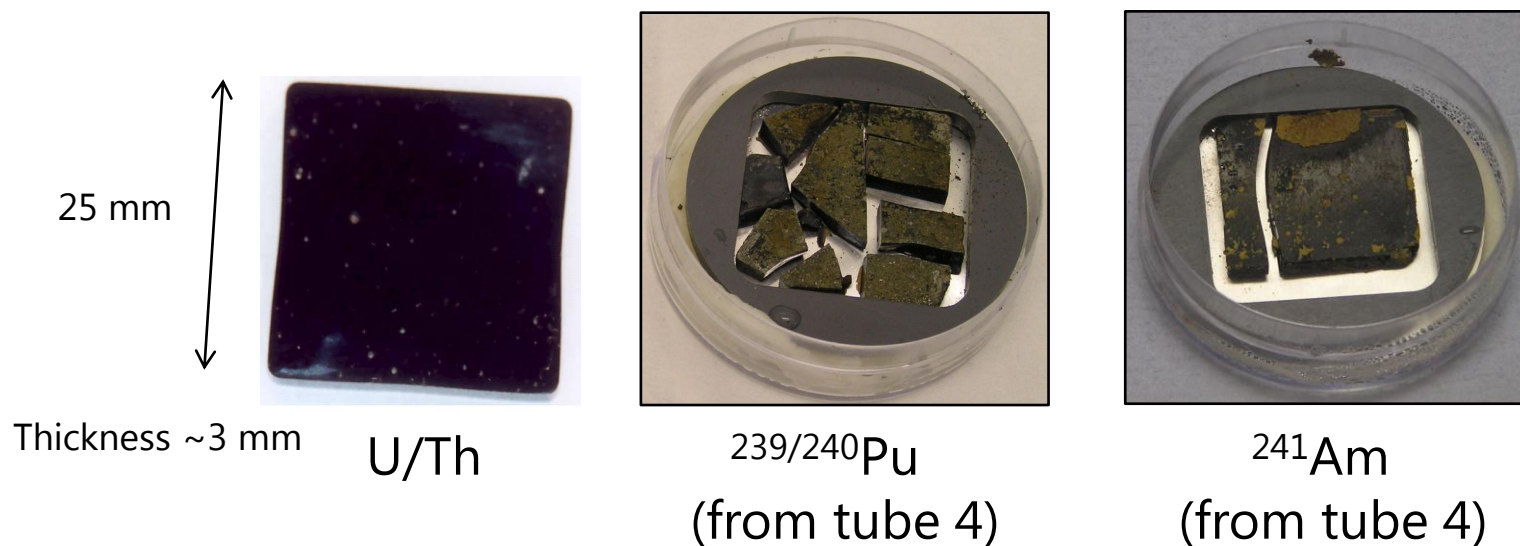
Modular test tube

for integrated testing of waste form behaviour

Radioactive SON68 glass samples are doped with ~0.85 wt% of actinide oxide

	Fraction of actinide oxide	Alpha activity (MBq per g glass; 01.05.2000)
U/Th	0.06 wt% UO_2 + 0.33 wt% ThO_2	negligible
^{237}Np	0.96 wt% NpO_2	0.22
$^{239/240}\text{Pu}$	0.85 wt% PuO_2	27
^{241}Am	0.85 wt% Am_2O_3	1000

Nominal alpha activity of freshly produced R7T7 vitrified waste: ~500 MBq per g glass.



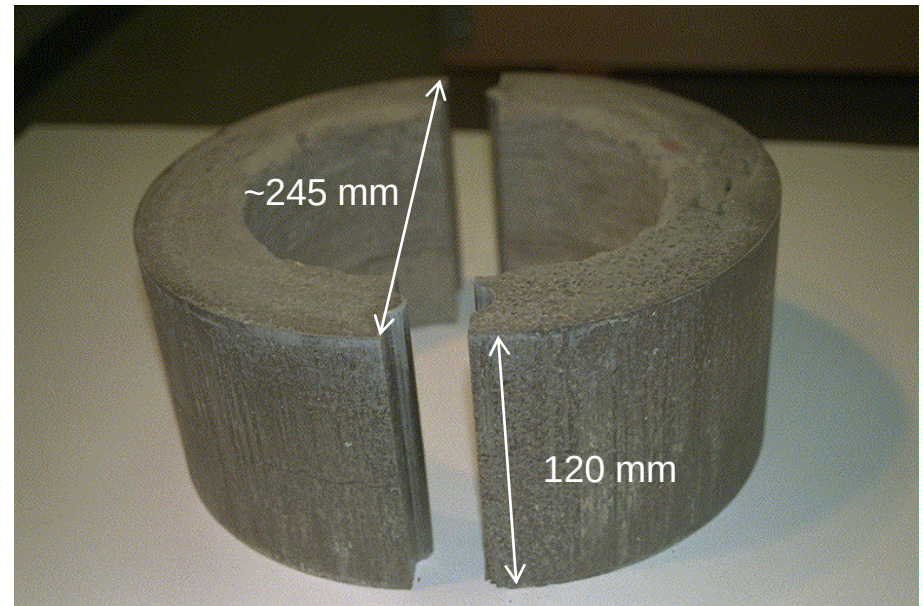
Backfill materials were placed as pre-compacted half-cylindrical blocks

Mod.	Backfill material	Dry density block	Reduced dry density
A	Crushed dried Boom Clay	2.17	1.88
B	Ca-bentonite (FoCa) + sand + graphite (65/30/5 wt%)	2.17	1.88
C	Ca-bentonite (FoCa) + powdered glass frit (95/5 wt%)	1.88	1.62

Densities in kg/dm³

Target swelling pressure = 2 MPa

2 of the 4 half-cylindrical blocks for module B of large test tube



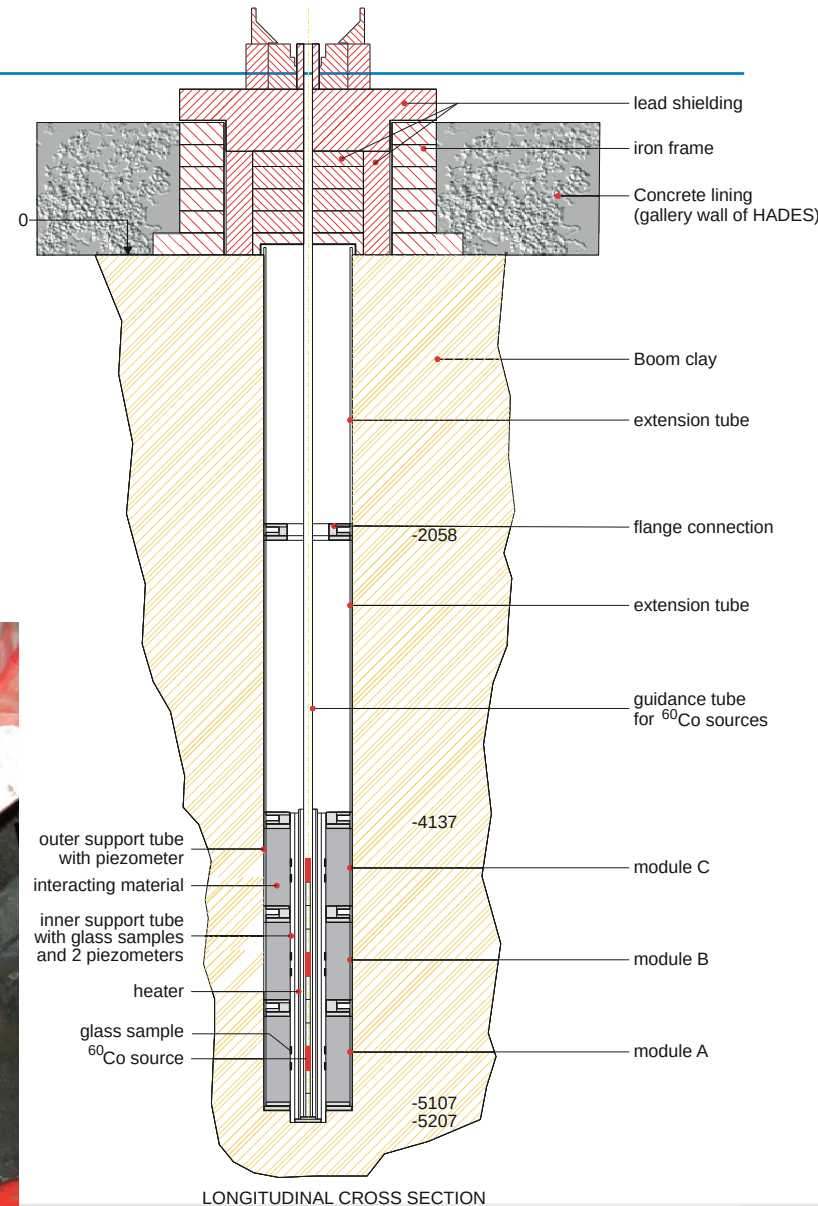
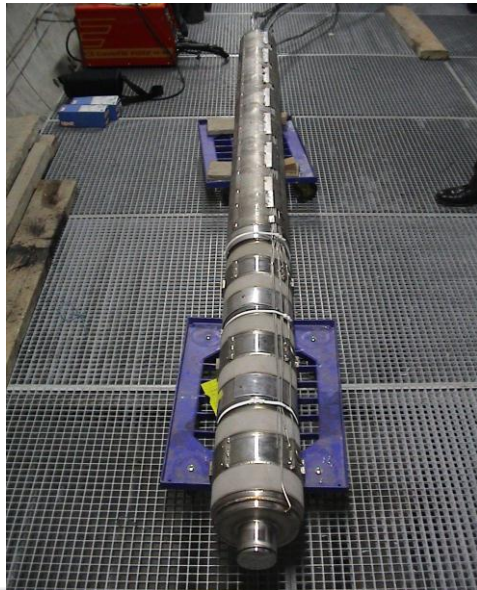
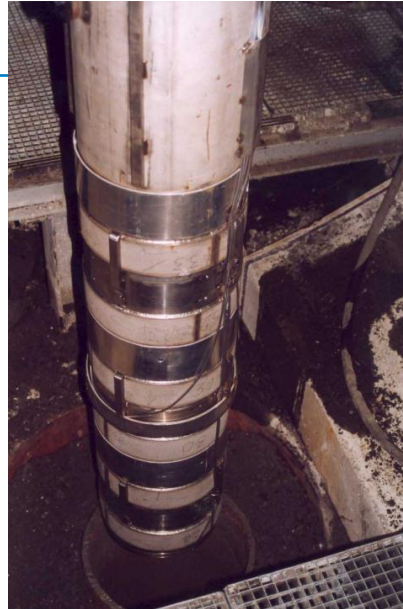
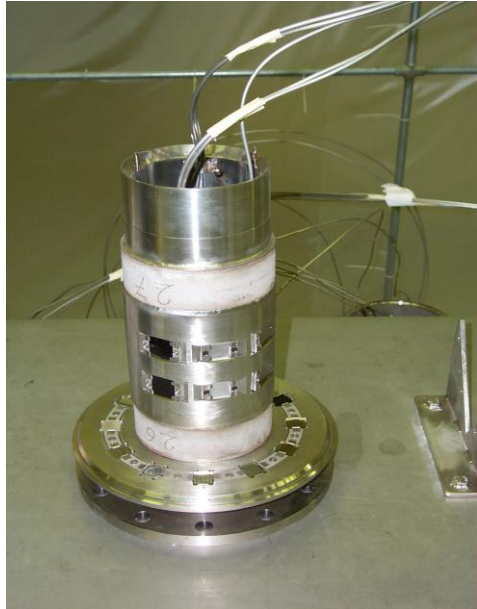
Two scenario's: normal evolution and early failure

30 °C = reference temperature in repository >500 years after disposal

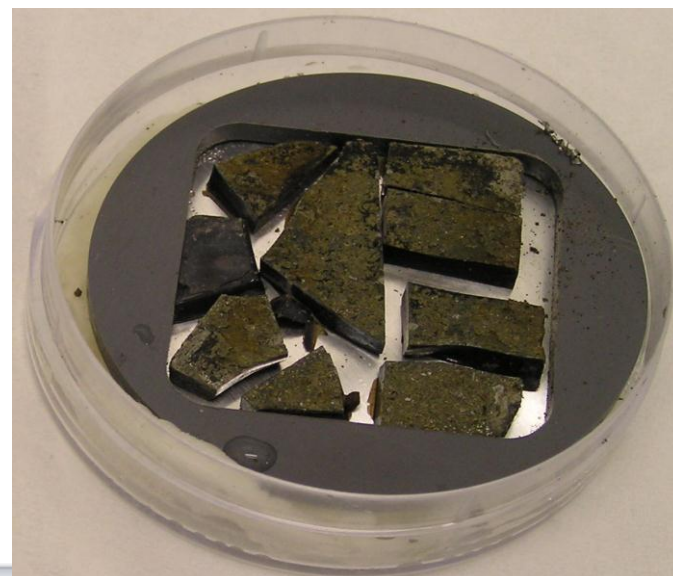
	Temp.	⁶⁰ Co	Installed	Operation	Duration
Tube 2	30 °C	No	2000	⇒2004	3.3 yr
Tube 5	30 °C	No	2003	⇒2025	22 yr
Tube 3	90 °C	Yes	2001	⇒2004	1.2 yr
Tube 4	90 °C	Yes	2001	⇒2009	6.5 yr

⁶⁰Co sources = γ dose rate of ~130 to ~40 Gy/h
90 °C + ~100 Gy/h = ~110 years after HLW production

Assembly and installation



Retrieval and dismantling



Mass loss of the SON68 glass samples corresponds with results from other tests

Mass loss rate (g/m ² .day)	Test tube 2 (30 °C, 3.3 y)	Test tube 3 (90 °C, ⁶⁰ Co, 1.2 y)
Module A	0.009 (U/Th)	No data (U/Th)
"	0.014 (Am)	0.3 (Am)
Module B	0.008 (U/Th)	No data
Module C	(~0)	No data

0.01 g/m².day = ~1.3 µm/y; 0.3 g/m².day = ~40 µm/y. All glass samples of test tube 4 were broken.

❑ Very few data, and high uncertainty:

➤ clay adhering on cleaned glass sample; loss of small fragments of glass ?

❑ Values rather in lower range of results of other tests with dense clay:

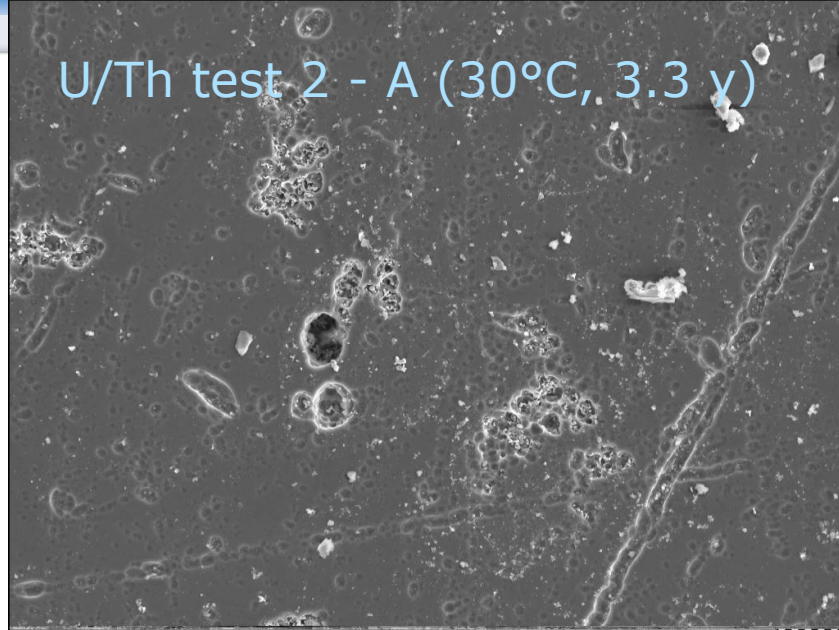
➤ Surface lab tests: 0.01 g/m².day (30 °C)

0.3–0.5 g/m².day (90 °C)

➤ *In situ* tests: 0.4–0.8 g/m².day (90 °C; no ⁶⁰Co; first *in situ* tests)

0.3 g/m².day (80–85 °C; ⁶⁰Co: CERBERUS)

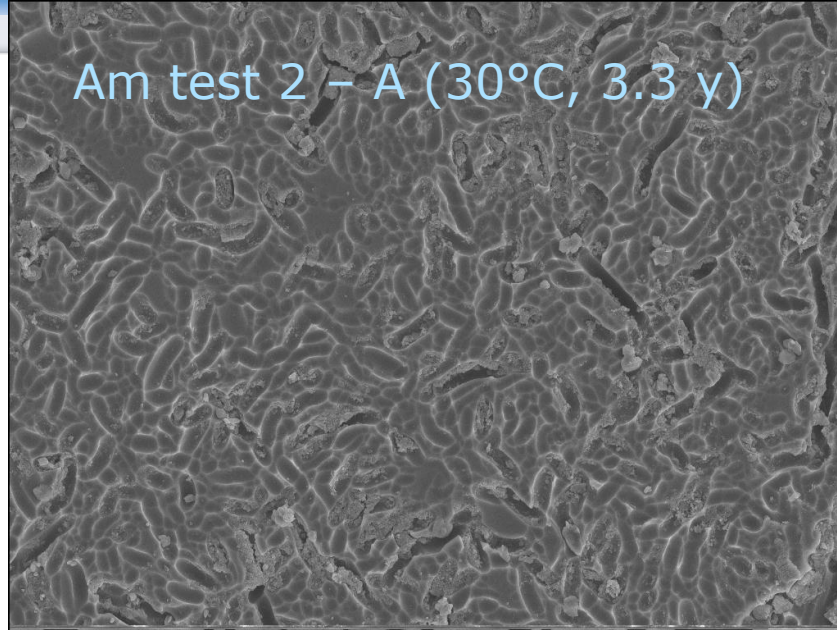
U/Th test 2 - A (30°C, 3.3 y)



Date : 2004/10/6
15KV WD13mm
File : 6857.tif
Mag500X

10µm

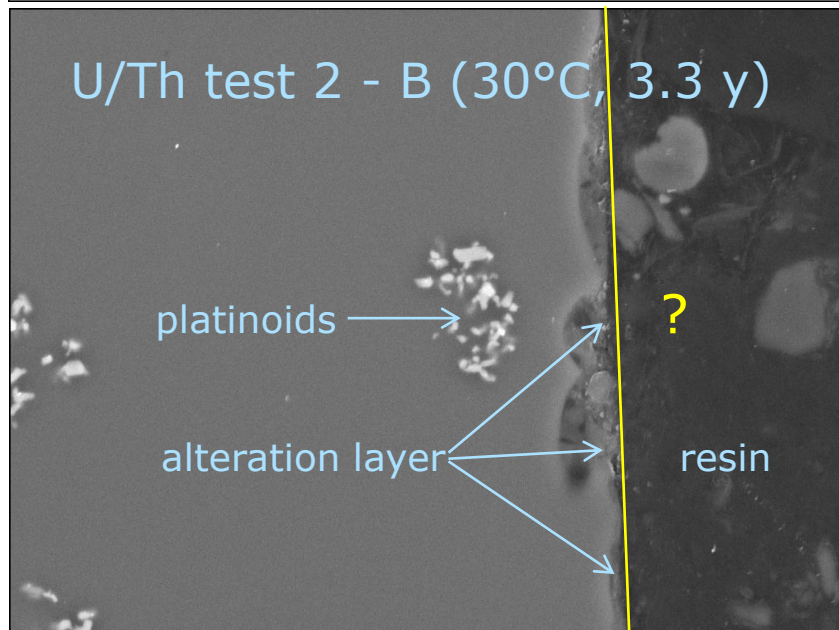
Am test 2 - A (30°C, 3.3 y)



Date : 2004/11/5
15KV WD13mm
File : 7148.tif
Mag500X

10µm

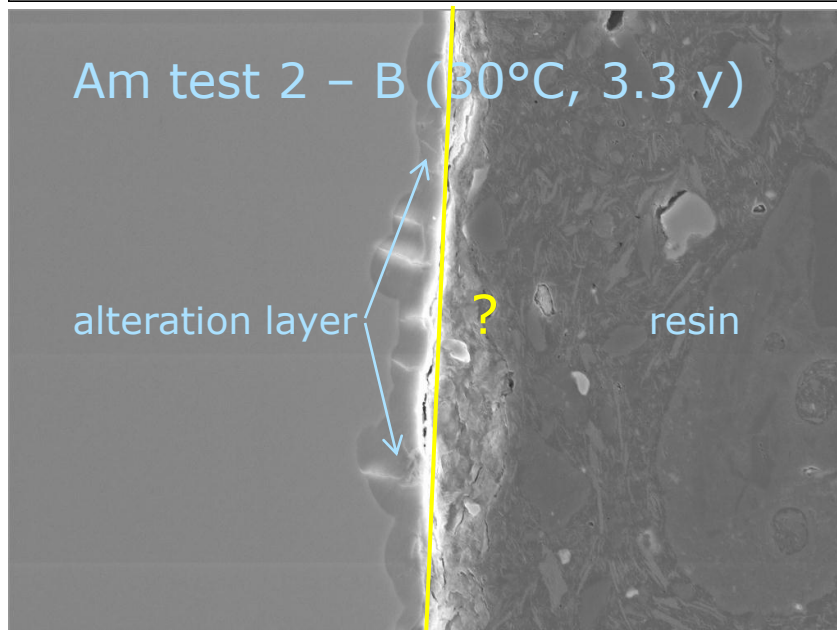
U/Th test 2 - B (30°C, 3.3 y)



Date : 2004/10/8
15KV WD13mm
File : 6897.tif
Mag2500X

10µm

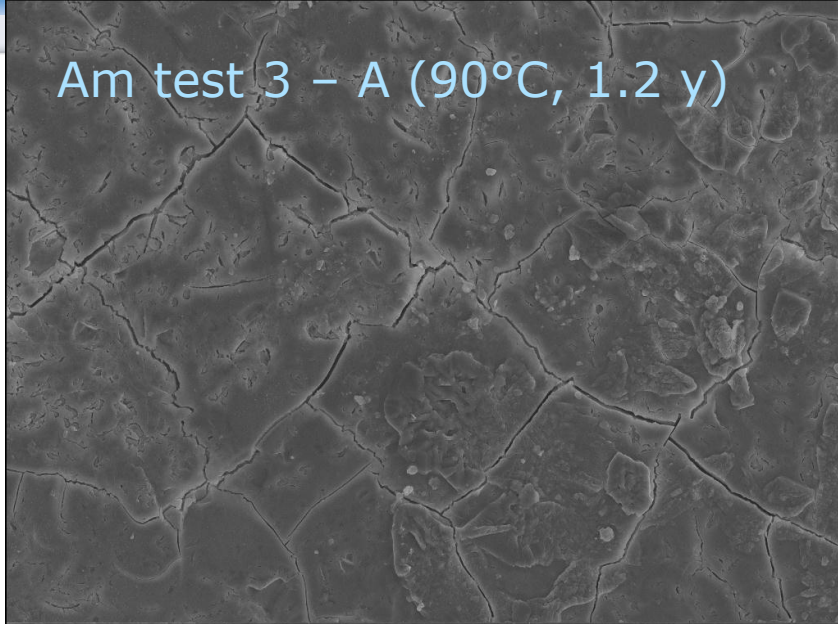
Am test 2 - B (30°C, 3.3 y)



Date : 2005/5/4
15KV WD14mm
File : 7771.tif
Mag1000X

10µm

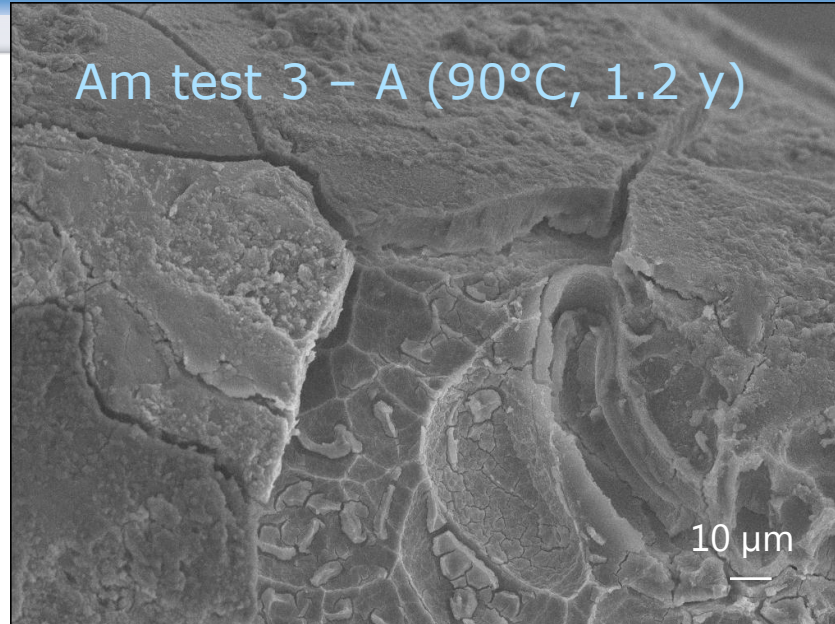
Am test 3 – A (90°C, 1.2 y)



Date : 2004/11/5
15KV WD13mm
File : 7164.tif
Mag500X

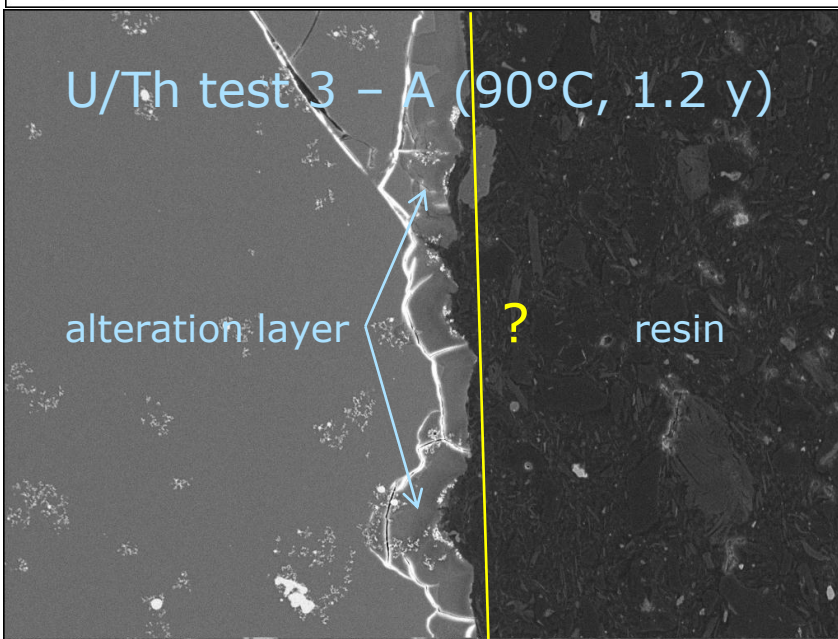
10µm

Am test 3 – A (90°C, 1.2 y)



10 µm

U/Th test 3 – A (90°C, 1.2 y)



alteration layer

?

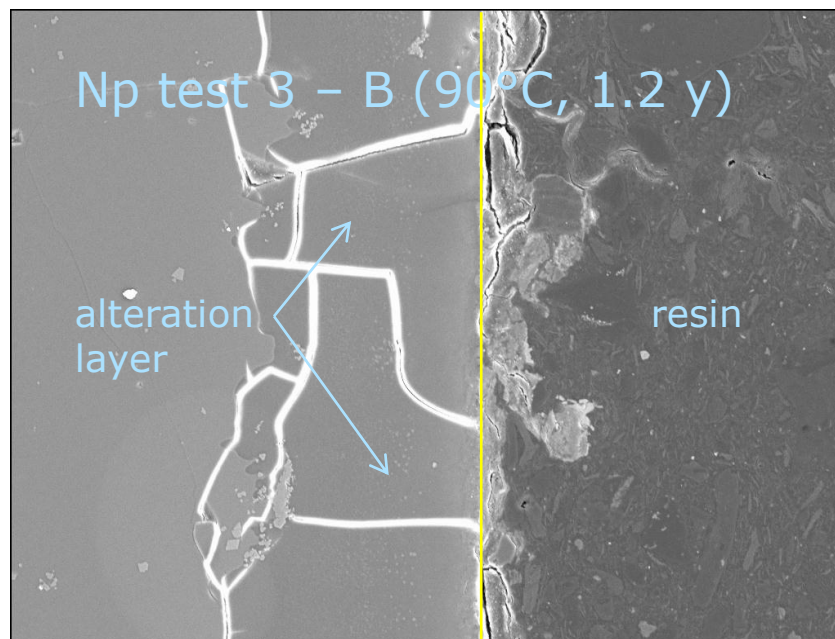
resin



Date : 2004/10/8
15KV WD13mm
File : 6891.tif
Mag250X

100µm

Np test 3 – B (90°C, 1.2 y)



alteration
layer

resin



Date : 2005/5/4
15KV WD13mm
File : 7539.tif
Mag300X

100µm

Average thickness of alteration layers (μm):
tendency to thicker layers with increasing alpha activity

	Tube 2 (30 °C, 3.3 y)			Tube 3 (90 °C, ^{60}Co , 1.2 y)		
	A (DBC)	B (BSG)	C (BGF)	A (DBC)	B (BSG)	C (BGF)
U/Th	1.5	2.3	0.2	25	20	2.5
Np	3.7	3.5	<0.5	35	80*	2.6
Pu	3.5	3.0	<0.5	40	50	2.8
Am	6.0	4.0	<0.5	45	50	Lost

- ❑ Interpretation hampered by partial loss of alteration layer
=> important uncertainty

* Np in module B tube 3: alteration layer intact (very likely only poor contact with clay)

- ❑ Based on the mass loss, the maximum thickness of the missing layer is:
(for several reasons, the real thickness is lower)
 - ~4 μm (U/Th) to ~6 μm (Am) at 30°C
 - ~30 μm (U/Th) to 45 μm (Am) at 90°C

- ❑ Analyses of glass samples of tube 4 still ongoing

Discussion on glass alteration (1/3)

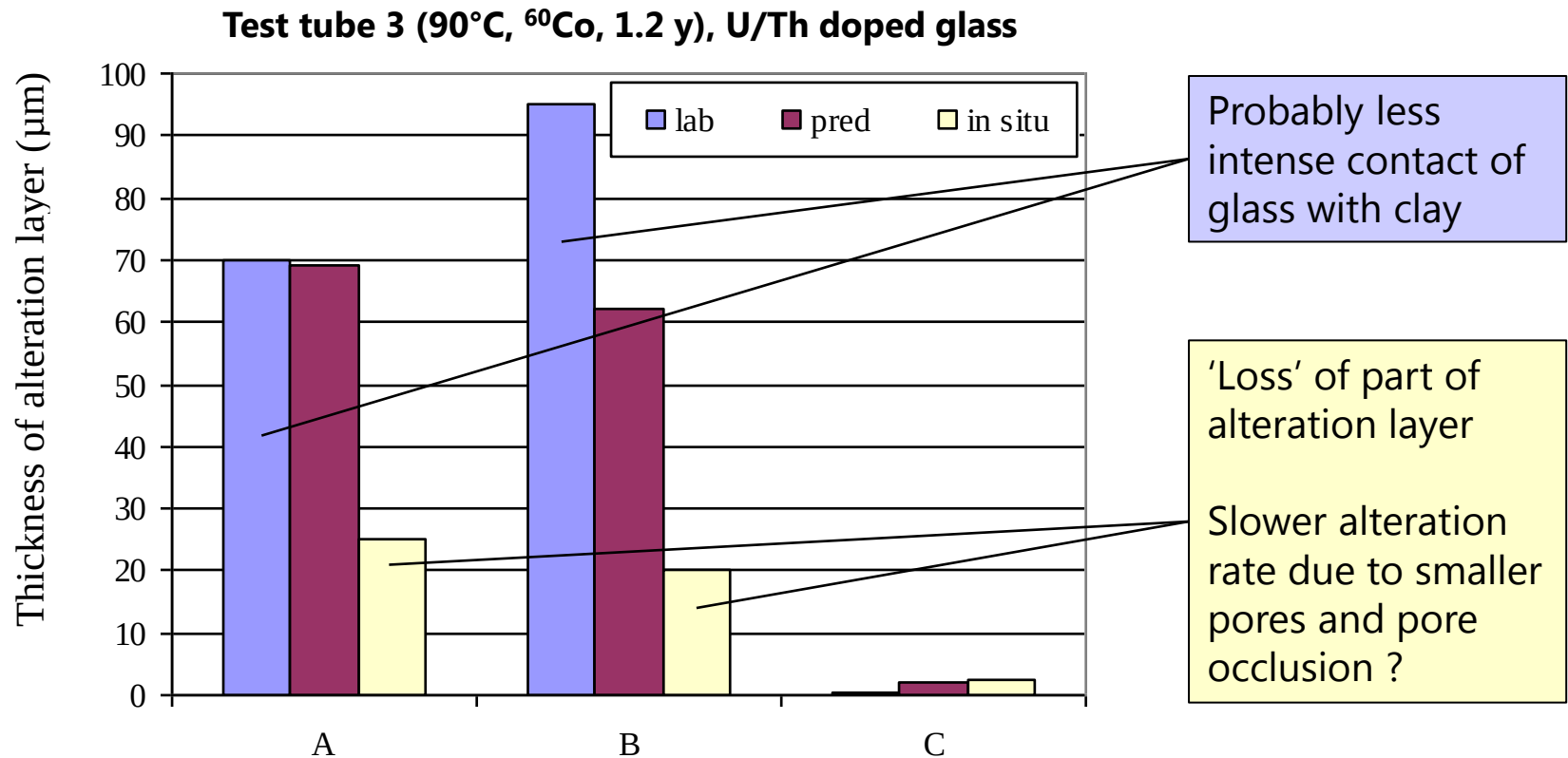
- ❑ Mass losses in lower range of measured values (uncertainty!)
 - Lower pH ?
 - Alteration slowed down by smaller porosity of highly compacted backfill and by pore occlusion ?
- ❑ Tendency to higher mass loss as alpha activity increases (uncertainty!)
 - Already reported in literature (for glass alteration in water) for beta/gamma
 - It takes more time before the lower long-term dissolution rate is reached, because more time is needed before effective protective layer is formed
 - Our data suggest a similar effect of alpha radiation on glass alteration in contact with dense clay

Discussion on glass alteration (2/3)

- ❑ Part of the alteration layer has 'disappeared', by sorption of its constitutive elements on the clay, by secondary phase formation, by intrusion of gel into clay, and/or by cleaning of samples
 - Rough estimate of thickness of missing layer on basis of mass loss
 - Higher loss as alpha activity increases (~mass loss) ?
 - Can explain the lower mass losses (occlusion of pores in contacting clay)
- ❑ Thicker alteration layers as alpha activity increases
 - In literature, importance of beta/gamma is stressed
 - Our data suggest a similar effect of alpha radiation on glass alteration in contact with dense clay
- ❑ Alpha activity of Am-doped glass is unrealistically high; that of Pu-doped glass only realistic for early failure scenario.

Discussion on glass alteration (3/3)

- 'Fairly good' agreement between results of *in situ* tests, surface laboratory tests (by CEA), and modeling predictions (CEA, Lixiver 2)



- Expected effect of temperature and addition of powdered glass frit

Pro's and con's of *in situ* testing

- ❑ 'Realistic' data => important added value (validation, demonstration)
 - No corrosion products; no 'history' (alteration clay, pore occlusion, ...)
 - Highly active samples hamper dismantling and sample treatment and analysis, which contributes to higher uncertainty
- ❑ Expensive and long-lasting
 - Cost and complexity increase with degree of integration
 - => international collaboration !
- ❑ Small experimental matrix
 - Limited set of results
 - Test cases should be well focused
- ❑ Results = overall result of many coupled processes
 - => good knowledge of underlying processes needed
 - Detailed analytical programme

- ❑ Properly executed integrated *in situ* test
=> 'realistic' data => important added value
- ❑ CORALUS data confirm results of lab experiments and modelling predictions on SON68 glass corrosion
 - Effect of temperature
 - Effect of addition of powdered glass frit (<—> dried Boom Clay)
 - Consumption of alteration layer, congruent and incongruent alteration, influx of K^+ and Mg^{2+} , gel layer and diffusion layer, ...
 - Effect of dense clay ?
 - (Small) effect of α -activity on thickness of alteration layer ?
- ❑ = validation and small-scale demonstration test for clay-based design
- ❑ + contribute to our general understanding of SON68 glass behaviour
(=> interpretation of tests at high pH, discussion with other glass experts, ...)

CORALUS: an SCK•CEN collaboration project

- ❑ W&D-RDW: co-ordinator, *in situ* test, glass
- ❑ W&D-RDD: backfill (RESEAL project), radionuclide migration
- ❑ IPA-PAS: scoping calculations, follow-up
- ❑ HWP: design, manufacturing, assembly, dismantling
- ❑ LHMA: assembly and dismantling; analysis of altered glass samples
- ❑ EURIDICE: installation, follow-up, retrieval
- ❑ RCA + LRM: measurement of activity of clay slices
- ❑ IDPBW
- ❑ ...

⇒ THANK YOU !

Acknowledgements

This project was co-funded by the European Commission, and was and still is being funded by and performed in close collaboration with ONDRAF/NIRAS, the Belgian Agency for the Management of Radioactive Waste and Fissile Materials, as part of its programme on the geological disposal of high-level and intermediate-level long-lived radioactive waste.

Installation and operation of the test tubes



- ❑ Installation of test tubes in Boom Clay through URF HADES
- ❑ Gap between tube and Boom Clay daily flushed with Ar until convergence of the clay, to minimise clay oxidation
- ❑ Saturation of the pre-compacted backfill materials proceeded very slowly
 - 'Small' tubes (without ^{60}Co sources): ~6 months (35 mm backfill)
 - 'Large' tubes (with ^{60}Co sources): > 1.5 years (53 mm backfill)
 - ⇒ During this period, glass samples were in contact with a clay slurry (at ~20 °C)
- ❑ Low effective permeability to water: $\sim 5 \times 10^{-19} \text{ m}^2$ (tube 2)

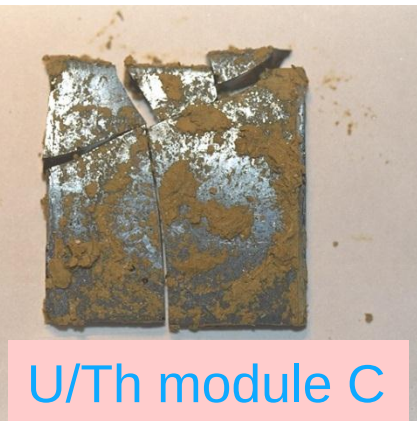
Characterisation of the piezometer solutions

- ❑ First solutions: up to 0.25 Bq/l ^{241}Am (tube 2)
 - = before full saturation of backfill (voids)
- ❑ Later: < D.L. of total alpha measurement ($\sim 0.3\text{-}0.5$ Bq /l)
- ❑ Composition of solutions fingerprinted by oxidised Boom Clay (Na_2SO_4 and $\text{Na}^+\text{-Ca}^{2+}$ ion exchange), by Ca-bentonite ($\text{Na}^+\text{-Ca}^{2+}$ ion exchange), and powdered glass frit (Si, B)
- ❑ CO_2 the major dissolved gas, 3-5 times higher at 90°C in module A (thermal degradation of Boom Clay organic matter) and module B (reaction of graphite ?)
- ❑ pH lower in tubes 3 and 4 (90°C), especially modules A (dried Boom Clay) and B (Ca-bentonite + sand + graphite)
 - Related to higher dissolved CO_2 concentration
- ❑ Analytical results = indicative
 - Real interstitial solution probably somewhat different

pH and redox values in piezometer solutions (on line measurement, FTC)

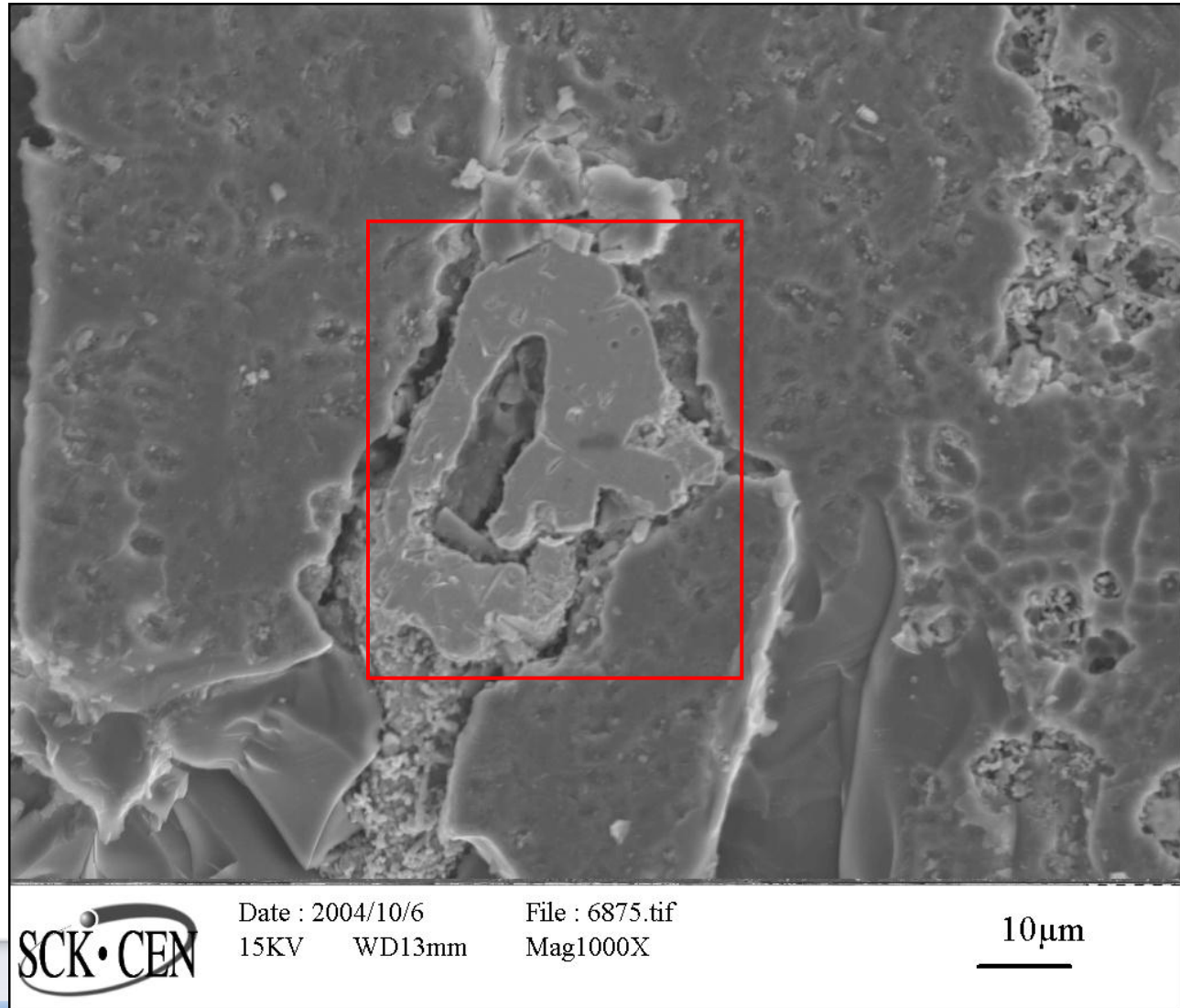
	pH		E _h	
	Tubes 3+4 (90°C, ⁶⁰ Co)	Tube 2 (30°C)	Tube 3+4 (90°C, ⁶⁰ Co)	Tube 2 (30°C)
A (Boom Clay)	6.5 – 6.5	7.9 – 7.4	-40 – -80	-340 – -350
B (bent. + sand + graphite)	6.0 – 5.5	7.3 – 7.3	0 – -80	-310 – -170
C (bent. + glass frit)	6.7 – 6.7	6.8 – 7.3	-80 – -80	-200 – -240

Observations during dismantling of test tubes

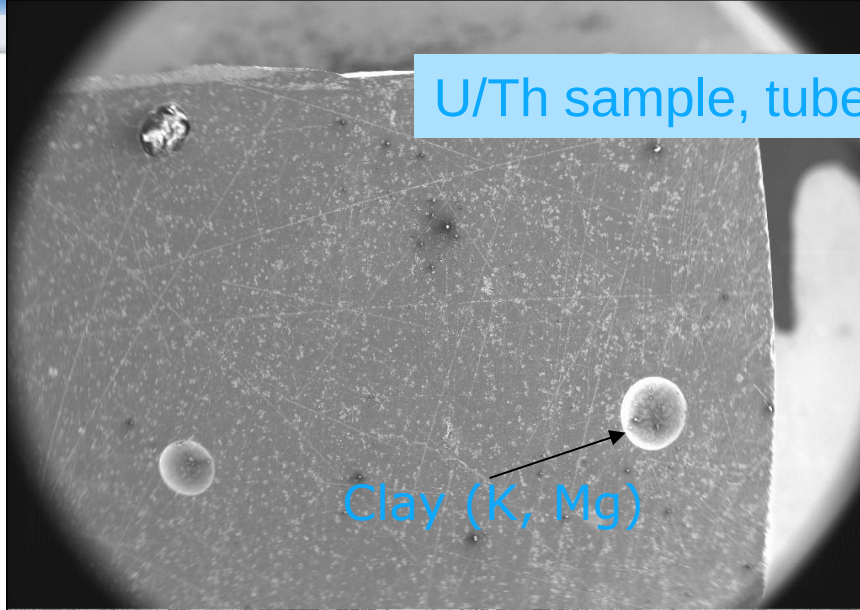


- ❑ Ca-bentonite backfills of tubes 3 and 4 (mod. B and C):
 - Fell apart in original pre-compacted bricks
 - very high density, with lower water content
- ❑ Clay cores up to glass surface
 - These samples were not used for surface analyses
- ❑ ~65 % (tube 2), ~90 % (tubes 3 + 4) of the glass samples were broken
- ❑ Clay adhering on glass samples

Pd/Th/U inclusion in pore
(U/Th glass, tube 2, module B)



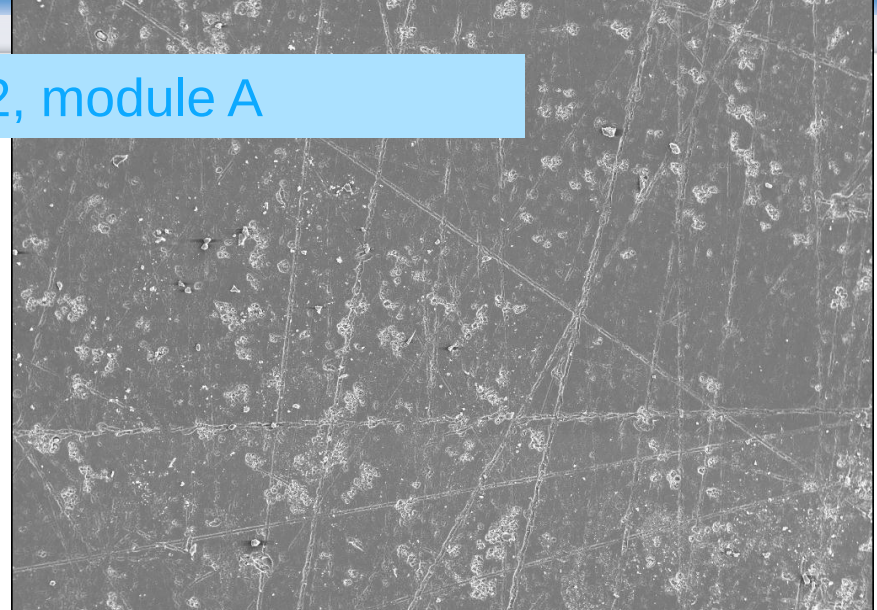
U/Th sample, tube 2, module A



SCK·CEN

Date : 2004/10/6
15KV WD13mm
File : 6854.tif
Mag20X

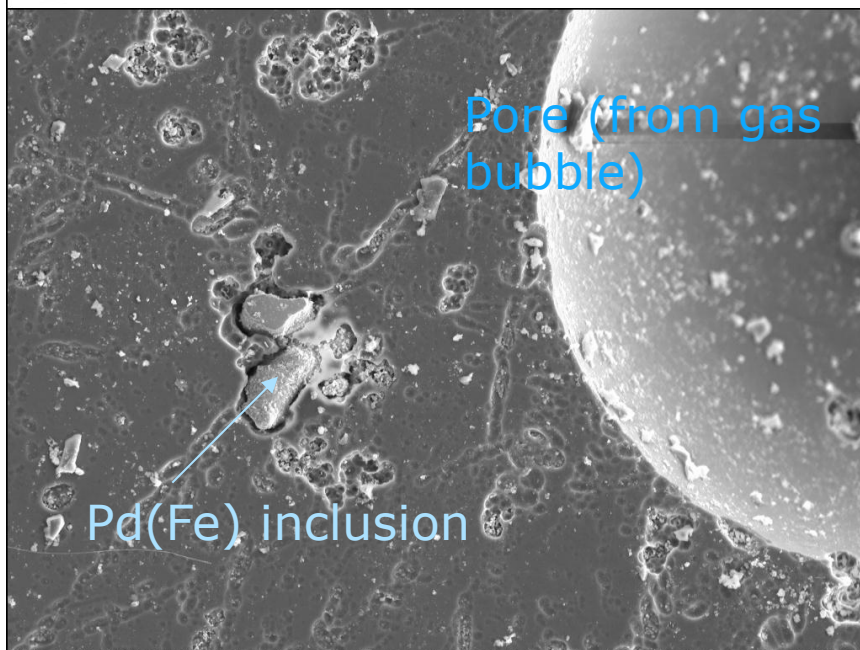
1mm



SCK·CEN

Date : 2004/10/6
15KV WD13mm
File : 6855.tif
Mag100X

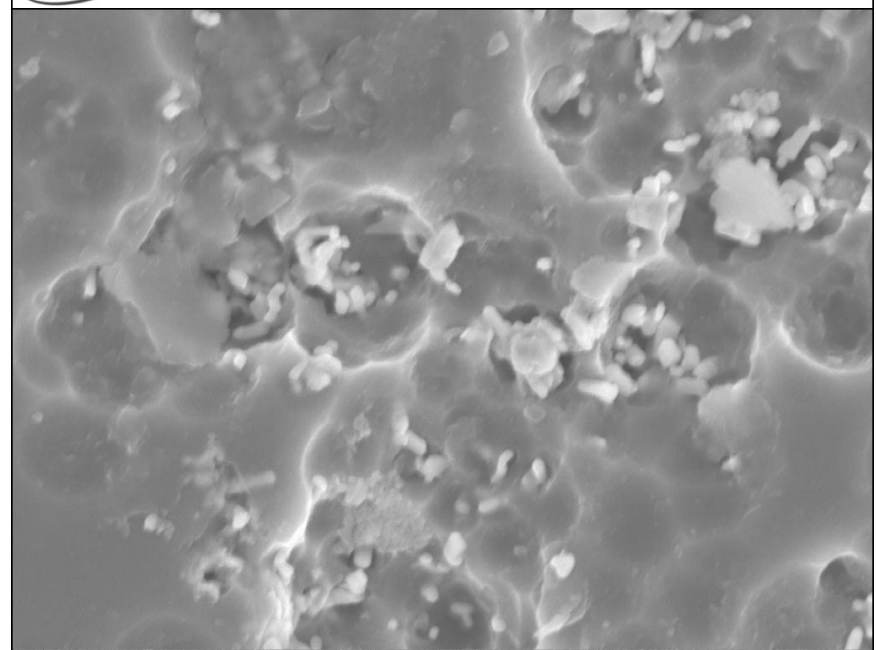
100μm



SCK·CEN

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15KV WD13mm
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Mag500X

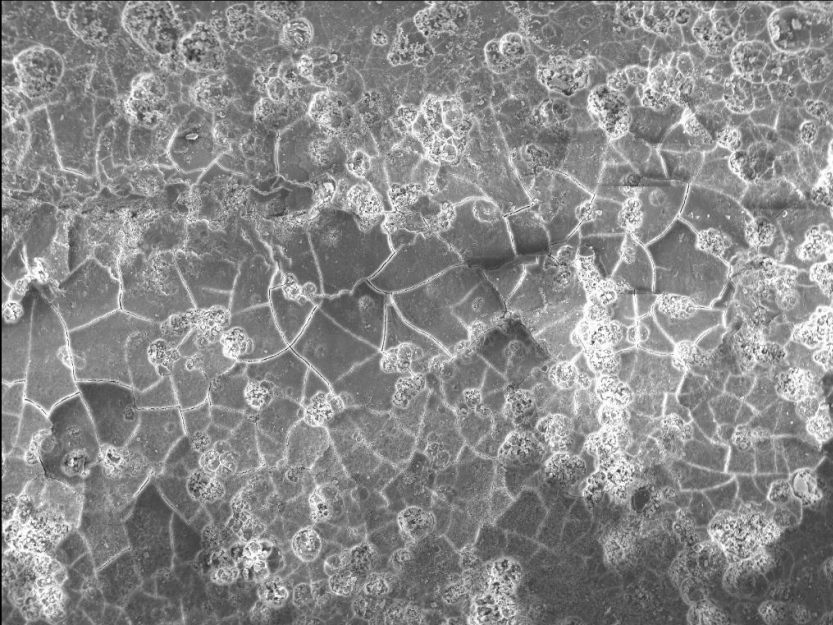
10μm



SCK·CEN

Date : 2004/10/6
15KV WD13mm
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Mag5000X

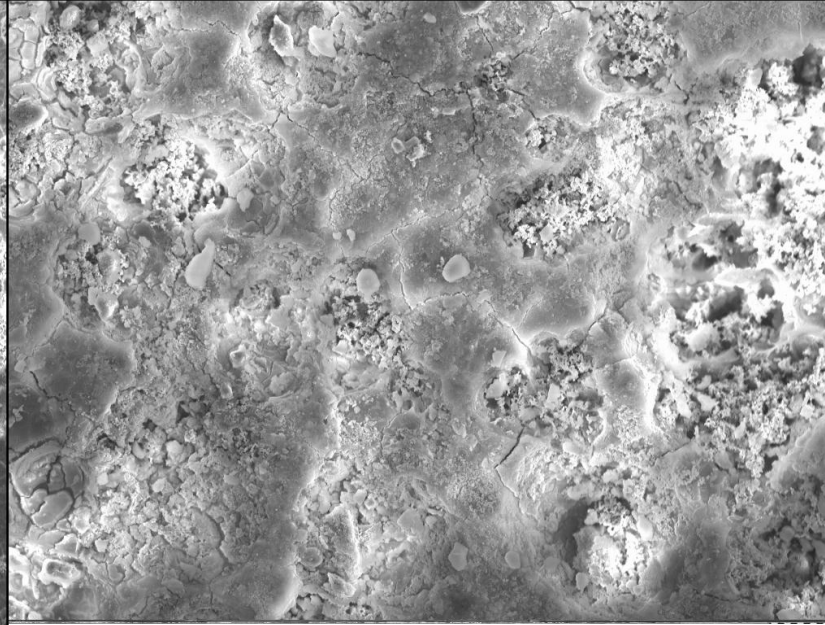
1μm



SCK·CEN

Date : 2004/10/6
15KV WD13mmFile : 6862.tif
Mag100X

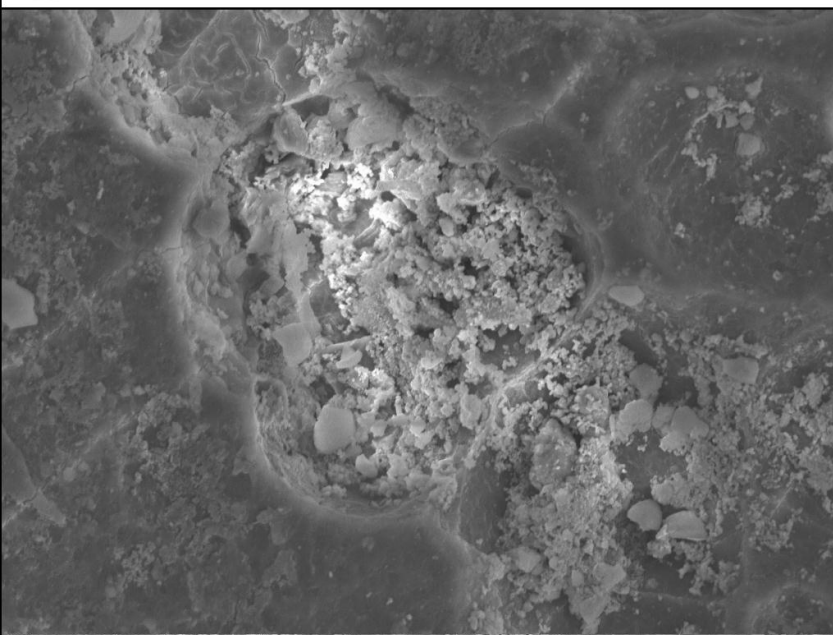
100µm



SCK·CEN

Date : 2004/10/6
15KV WD13mmFile : 6863.tif
Mag500X

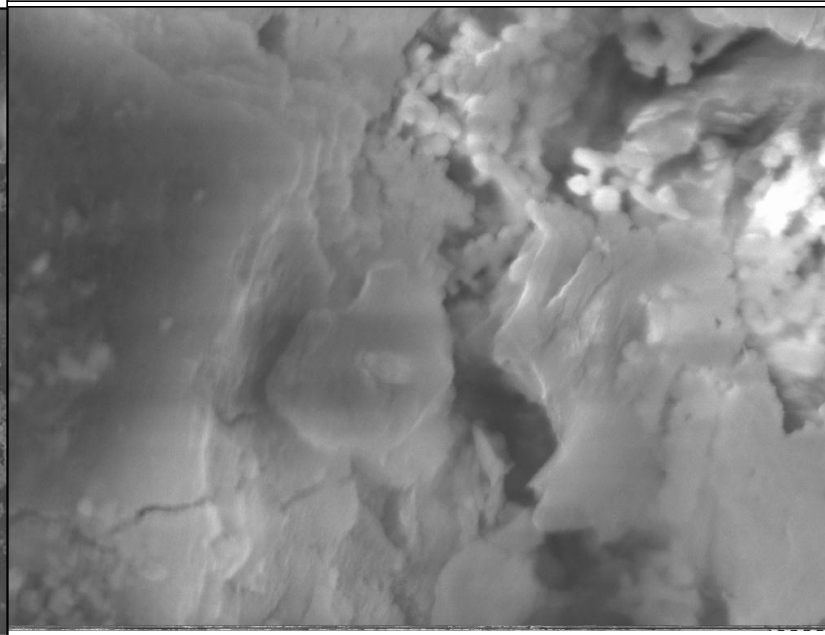
10µm



SCK·CEN

Date : 2004/10/6
15KV WD13mmFile : 6870.tif
Mag1000X

1µm

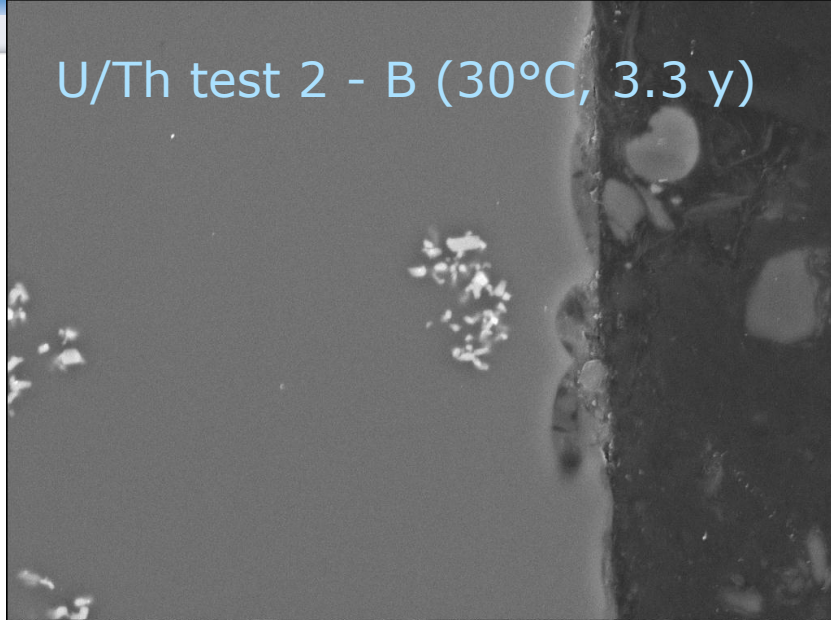


SCK·CEN

Date : 2004/10/6
15KV WD13mmFile : 6871.tif
Mag5000X

1µm

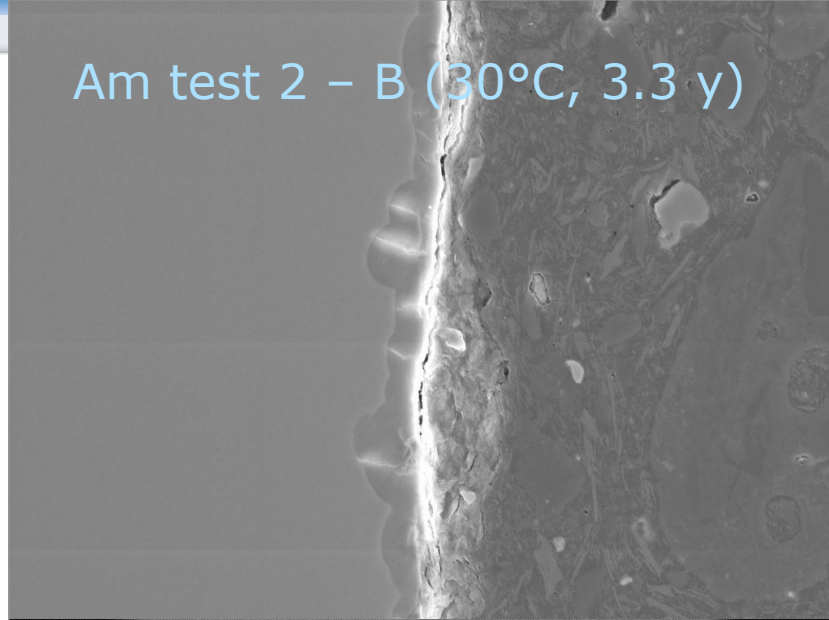
U/Th test 2 - B (30°C, 3.3 y)



Date : 2004/10/8
15KV WD13mm
File : 6897.tif
Mag2500X

10μm

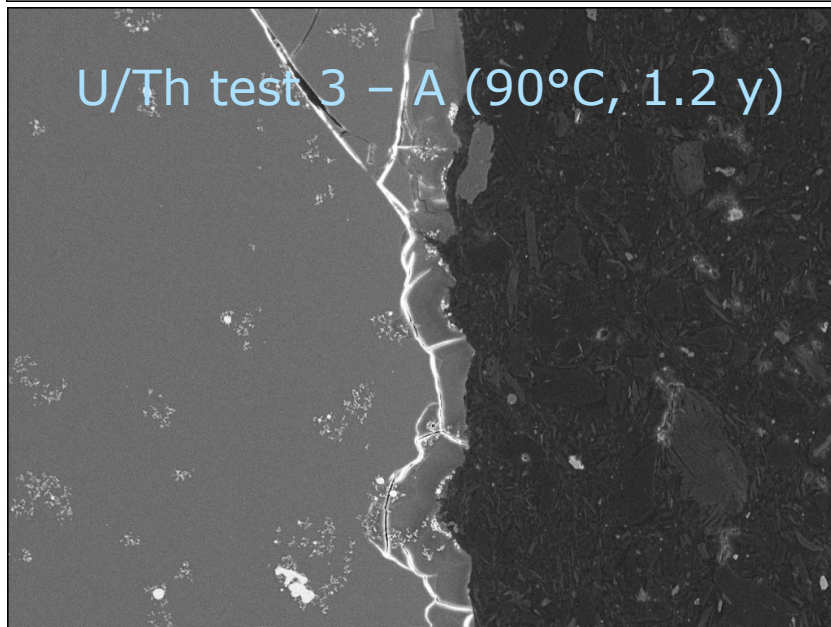
Am test 2 - B (30°C, 3.3 y)



Date : 2005/5/4
15KV WD14mm
File : 7771.tif
Mag1000X

10μm

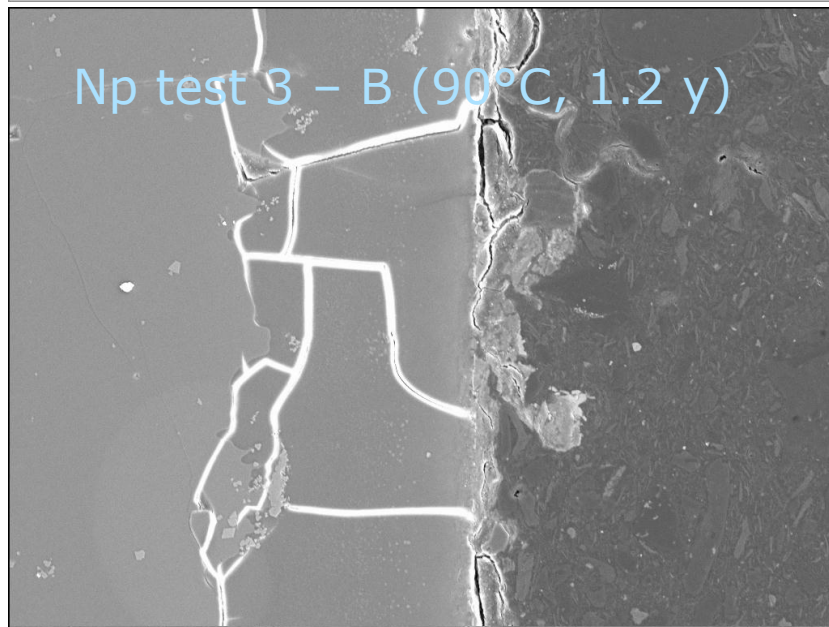
U/Th test 3 - A (90°C, 1.2 y)



Date : 2004/10/8
15KV WD13mm
File : 6891.tif
Mag250X

100μm

Np test 3 - B (90°C, 1.2 y)

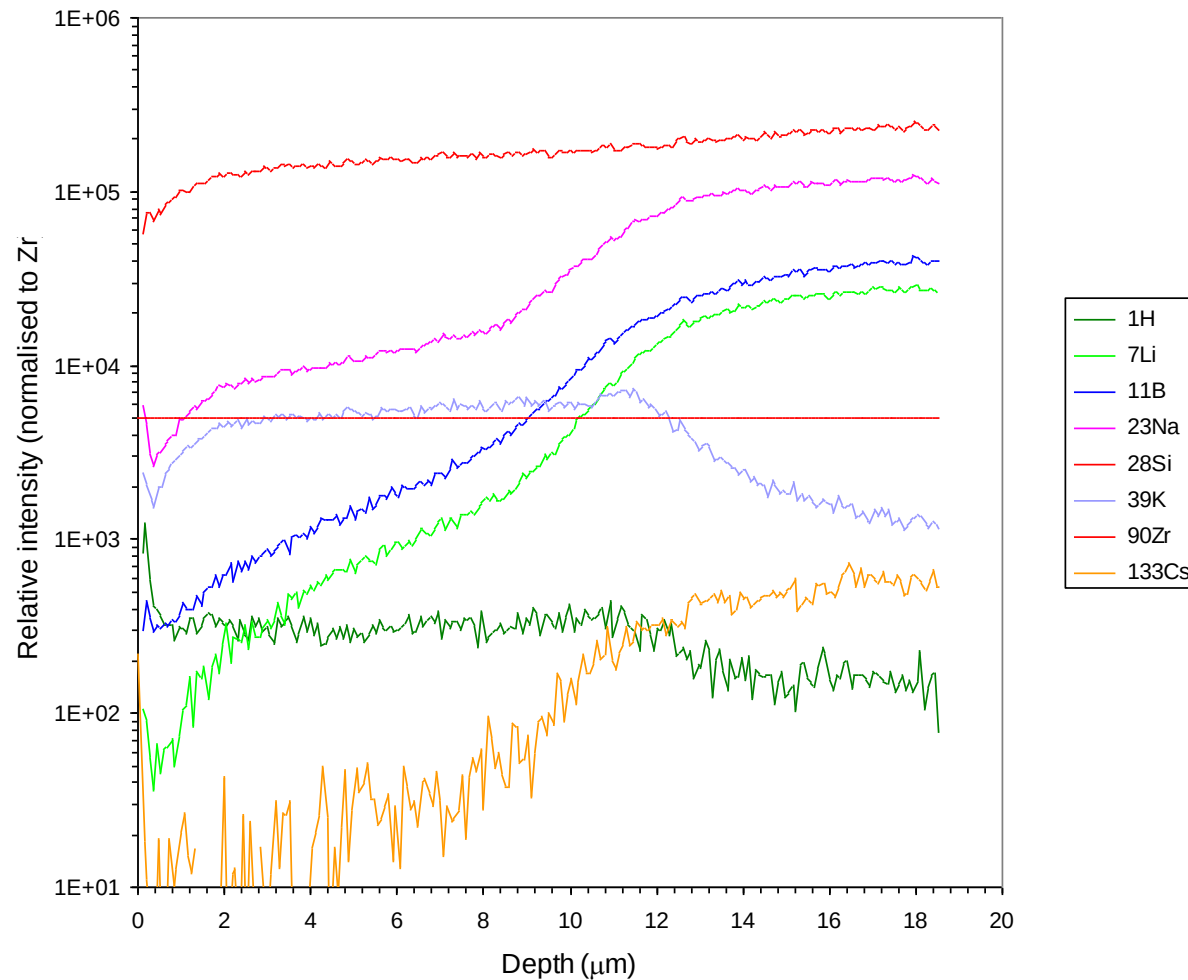


Date : 2005/5/4
15KV WD13mm
File : 7539.tif
Mag300X

100μm

Results of SIMS analyses are in line with results from surface laboratory experiments

Tube 3, Module A, U/Th



Average thickness of alteration layers (μm): tendency to thicker layers with increasing alpha activity

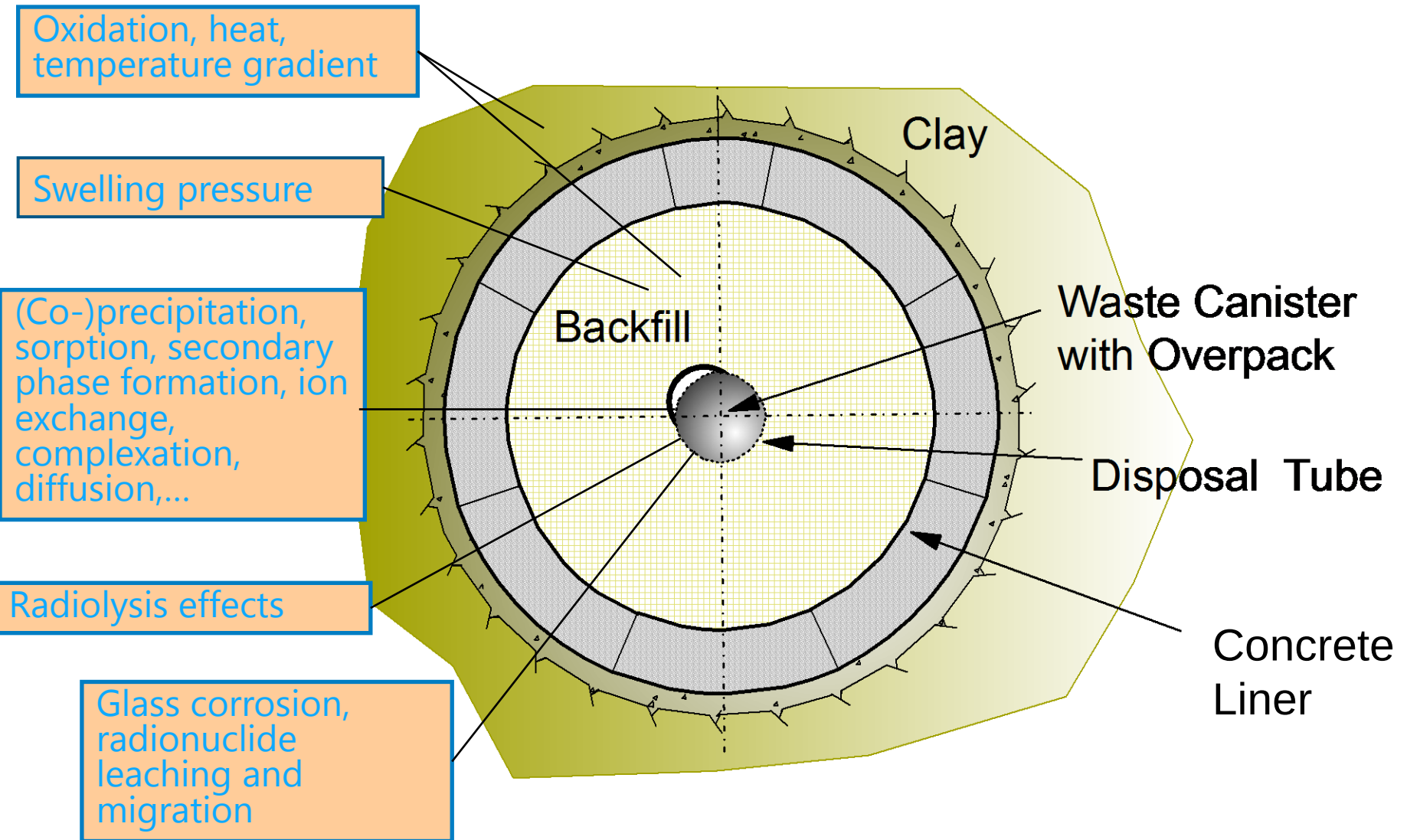
	Tube 2 (30 °C, no ^{60}Co , 3.3 years)			Tube 3 (90 °C, ^{60}Co , 1.3 years)		
	Module A (DBC)	Module B (BSG)	Mod. C (BGF)	Module A (DBC)	Module B (BSG)	Module C (BGF)
U/Th	$0.5 < 1.5 \pm 0.5 < 5$	$0.5 < 2.3 \pm 0.3 < 5$	0.2 ± 0.1	$10 < 25 \pm 3 < 55$	$15 < 20 \pm 5 < 50$	$1 < 2.5 \pm 0.5 < 5$
Np	$3 < 3.7 \pm 0.3 < 6$	$2 < 3.5 \pm 0.5 < 10$	< 0.5	$30 < 35 \pm 3 < 50$	$55 < 80 \pm 10 < 130$	$1 < 2.6 \pm 0.5 < 5$
Pu	$3 < 3.5 \pm 0.5 < 12$	$2 < 3.0 \pm 1 < 12$	< 0.5	$30 < 40 \pm 10 < 50$	$45 < 50 \pm 5 < 55$	$2.3 < 2.8 \pm 0.5 < 3.3$
Am	$5 < 6 \pm 0.5 < 12$	$3 < 4.0 \pm 1 < 15$	< 0.5	$40 < 45 \pm 3 < 55$	$45 < 50 \pm 10 < 90$	gel layer lost

- ❑ Interpretation hampered by partial loss of alteration layer (intrusion in clay, treatment of glass samples) => important uncertainty.

* Np in module B tube 3: alteration layer intact (contact with clay ?)

- ❑ Analyses of glass samples of tube 4 still ongoing.

Integration allows coupled processes to occur, and therefore requires sufficient degree of understanding





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

Experimental programme to determine the stability of spent fuel in Supercontainer conditions

C. Cachoir, T. Mennecart, K. Lemmens, B. Gielen, R. Vercauter

Belgian Nuclear Research Centre, SCK•CEN

19th Exchange Meeting Euridice, May 6th 2014

Evaluation of Spent Fuel behaviour in Supercontainer conditions

Programme in close cooperation with,
and with financial support of
NIRAS/ONDRAF

Tests with **depleted**
UO₂ and **Pu-doped**
UO₂

SCK•CEN (Belgium)

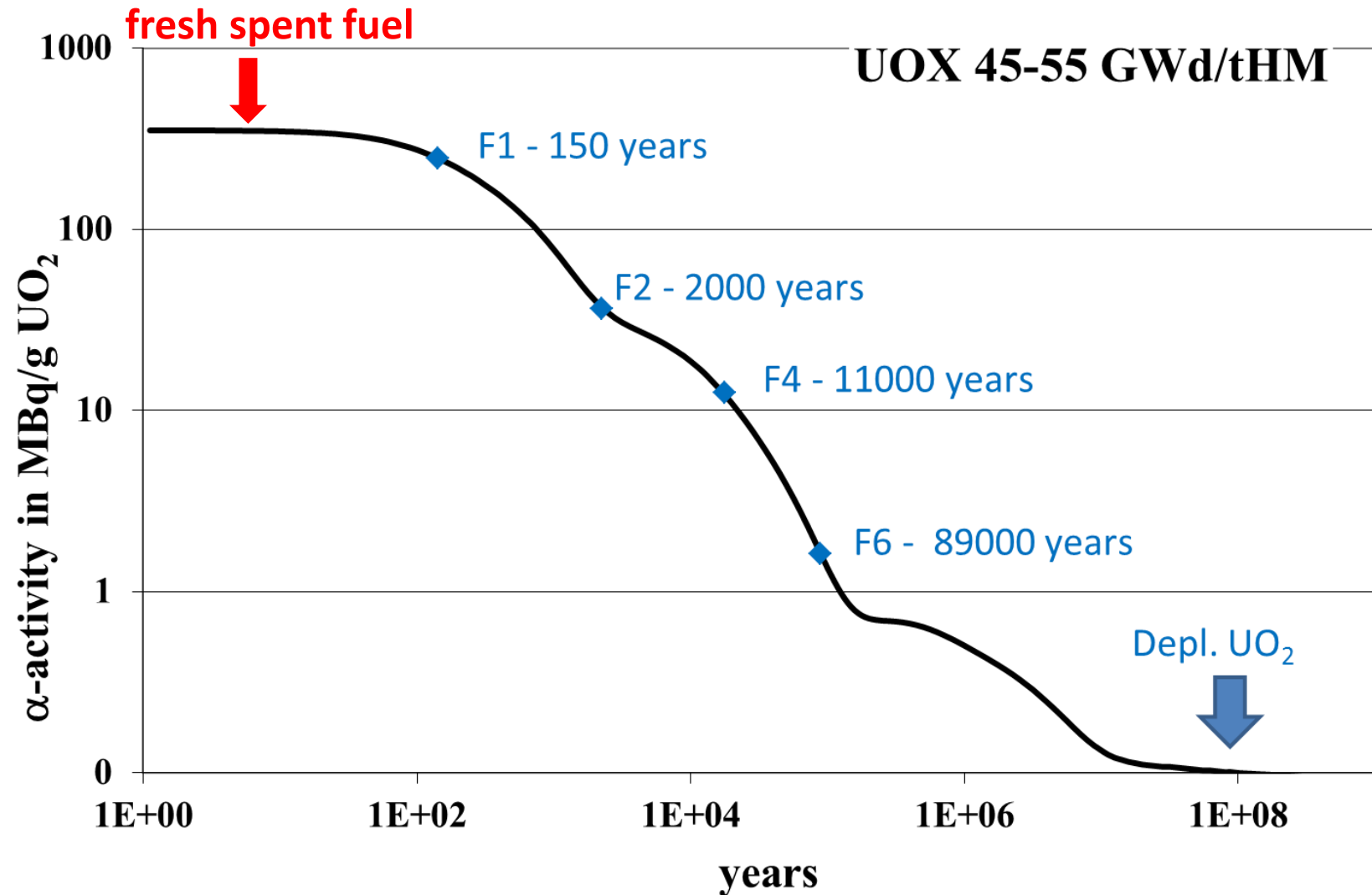
Tests with **real**
spent fuel and **H₂**
overpressure

KIT-INE (Germany)

Literature

Pu doped UO_2 batches as UOX fuels after 150 to 89000 years

Depleted UO_2 as a very old spent fuel



Cement waters with different pH and [Ca]

**Young Cement water
with Ca**

YCWCa

pH 13.5
140 mM NaOH
0.65 mM Ca(OH)_2
330 mM KOH

**Young Cement water
with less Ca**

YCW

pH 13.5
140 mM NaOH
0.038 mM Ca(OH)_2
330 mM KOH

Old Cement water

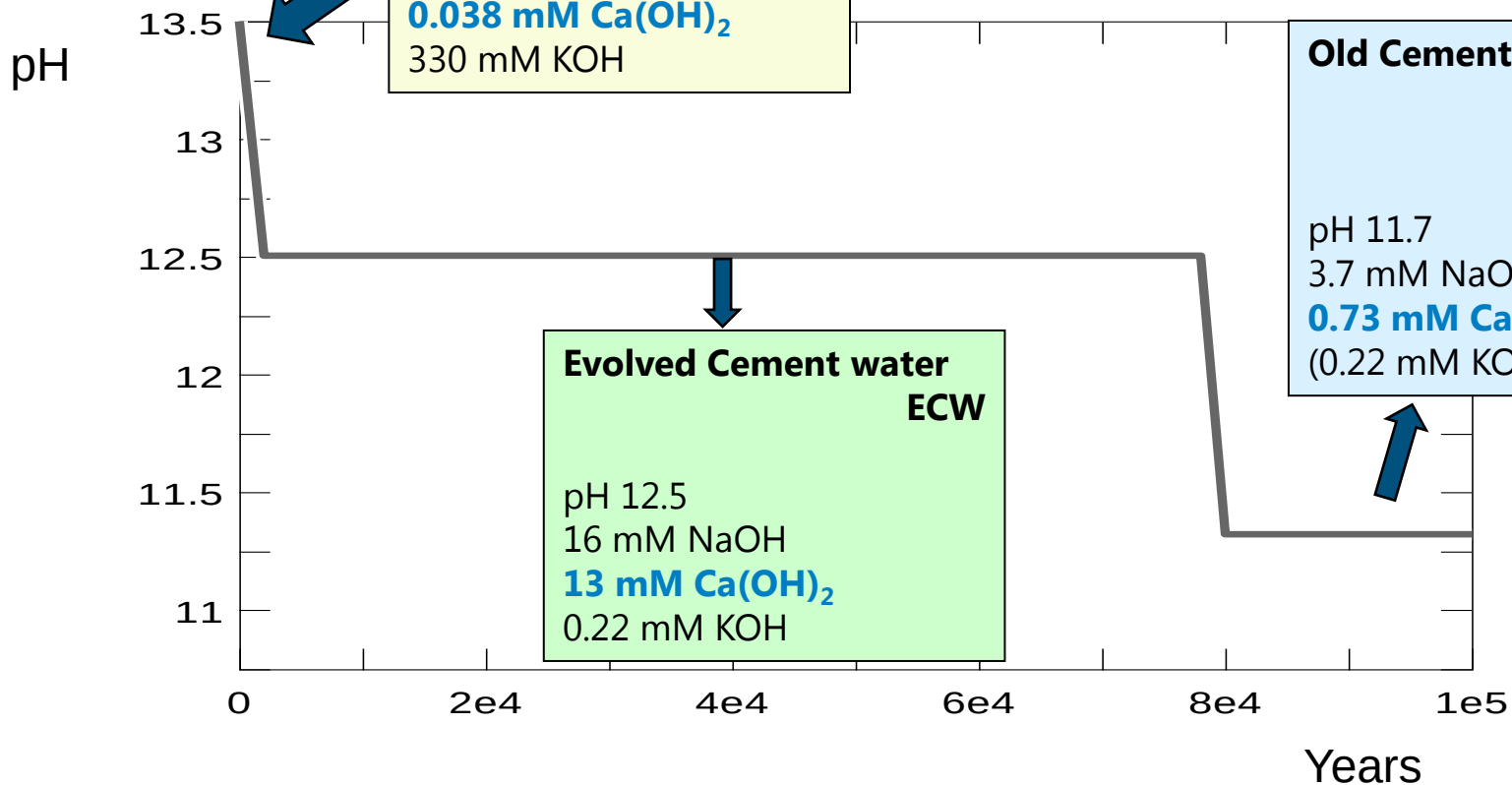
OCW

pH 11.7
3.7 mM NaOH
0.73 mM Ca(OH)_2
(0.22 mM KOH)

Evolved Cement water

ECW

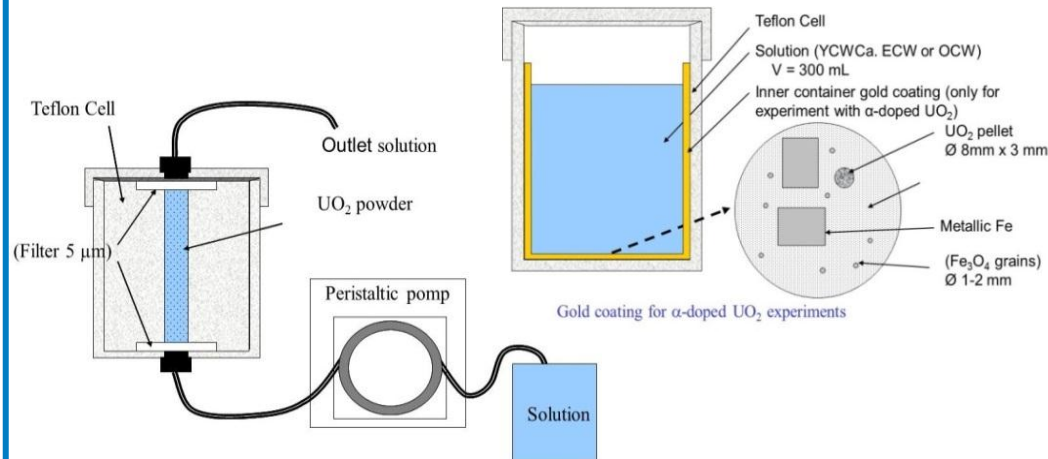
pH 12.5
16 mM NaOH
13 mM Ca(OH)_2
0.22 mM KOH



Measurement of stability of UO_2 / spent fuel matrix

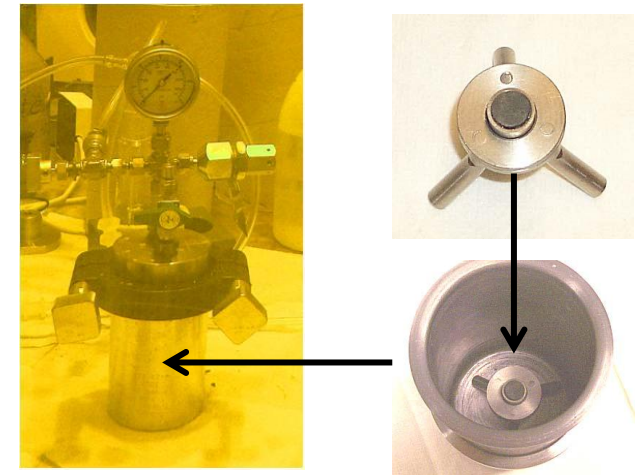
Matrix solubility and dissolution rate

Depleted UO_2 and Pu-doped UO_2



- Static tests for UO_2 solubility
- Dynamic tests for determination of UO_2 dissolution rate
- Powder / pellet
- pH 11.7, 12.5 and 13.5
- Without H_2
- Inert atmosphere (no O_2)

Real spent fuel (KIT-INE)

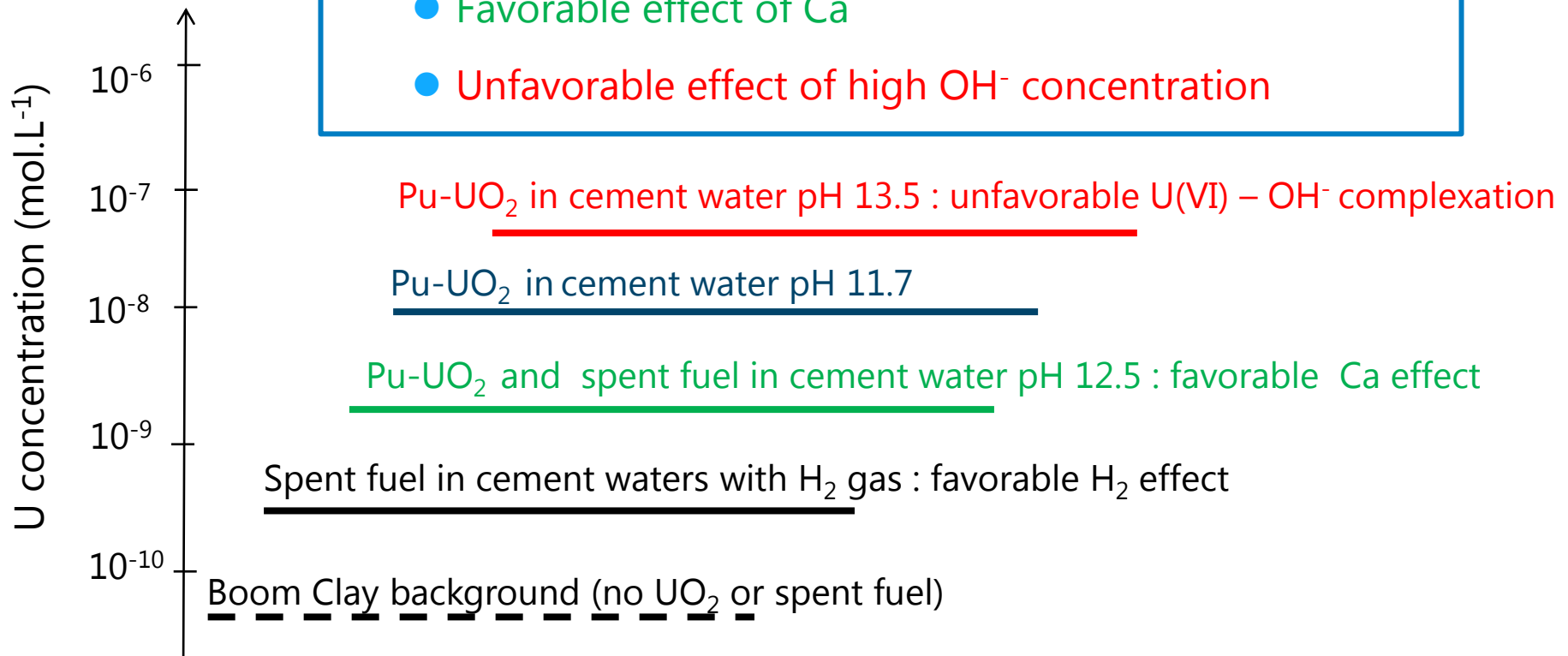


- Static tests for determination of fresh spent fuel dissolution rate
- Cladded and decladded fragments
- pH 12.5 and 13.5
- With(out) H_2 (1 bar, 3.2 bar)
- Inert atmosphere (no O_2)

Effect of high pH on UO_2 solubility

Effect of cement water on solubility of UO_2 matrix

- Presence of spent fuel will cause minor increase of U concentrations, thanks to H_2 effect
- Higher U concentrations in absence of H_2
 - Favorable effect of Ca
 - Unfavorable effect of high OH^- concentration



Effect of high pH on UO_2 matrix dissolution rate

pH 13.5 is reference pH

- Assessment of *in situ* behavior of spent fuel will be based on extrapolation of behavior observed in most penalizing conditions, selected as reference conditions
- pH range “11.7-13.5” did not influence the dissolution rate

Most tests done with cement water of pH 13.5 as

- it is the most extreme condition
- it may occur *in situ* for a long time
- it removes better U(VI) from the surface
- it is relatively stable

Determination of fuel matrix dissolution rate

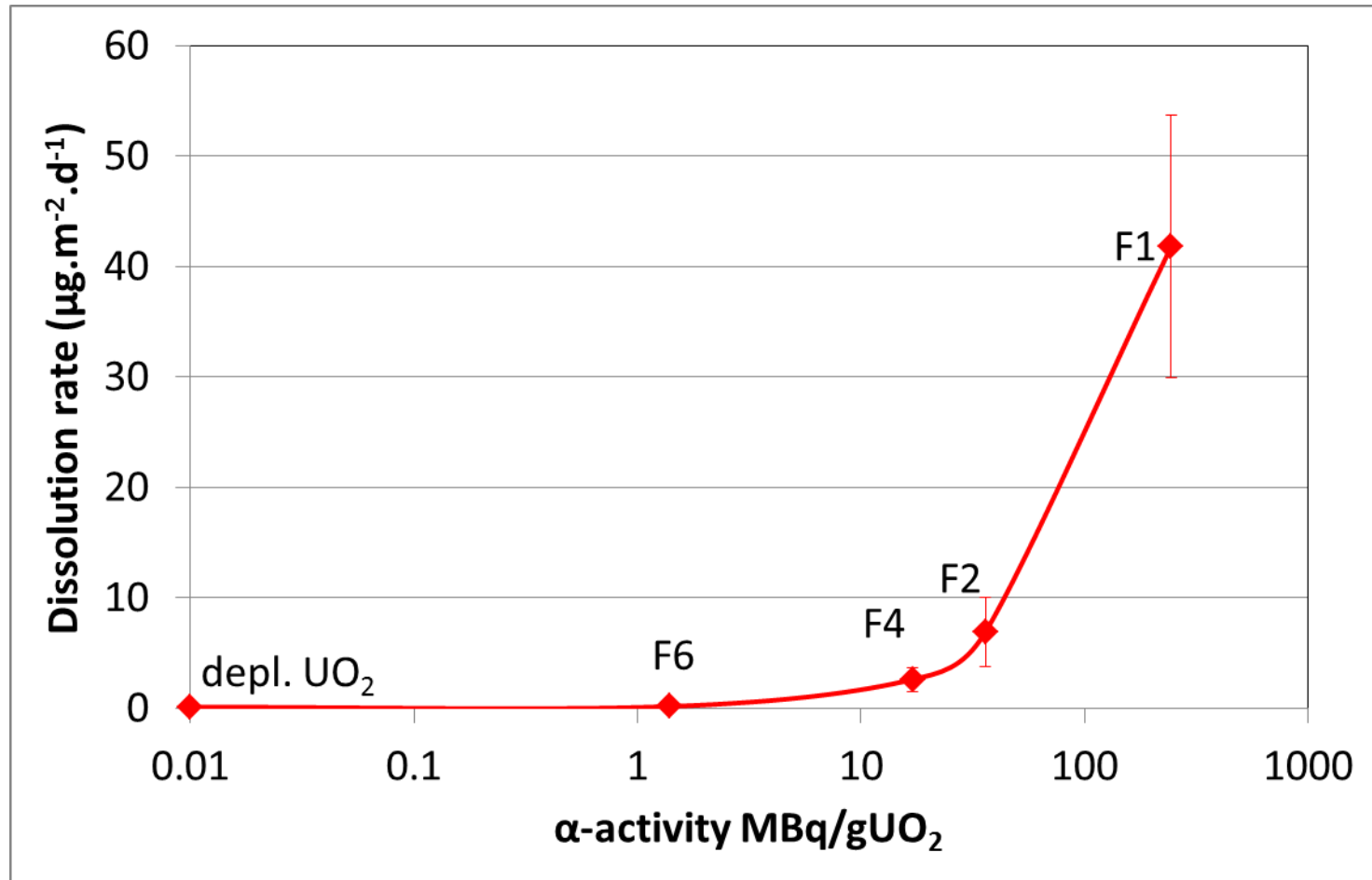
For depleted UO_2 and Pu-doped UO_2

- Based on evolution of uranium concentration in solution
- UO_2 surface area much larger than expected *in situ*
- In absence of H_2 gas $\rightarrow$ rates higher than expected *in situ* with H_2 gas

For fresh spent fuel

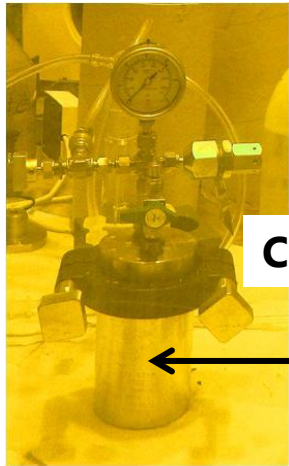
- Based on evolution of strontium concentration in solution
- Realistic surface area
- Influence of H_2 overpressure $\rightarrow$ lower rates, expected *in situ*
- Comparison with static and dynamic dissolution rates of depleted and Pu-doped UO_2
 - Estimation of surface area (SA)
 - Realistic SA = $10 \text{ cm}^2 \cdot \text{g}^{-1}$
 - Max SA = $80 \text{ cm}^2 \cdot \text{g}^{-1}$

Increase of UO_2 dissolution rate with α -activity of Pu doped UO_2 in absence of H_2

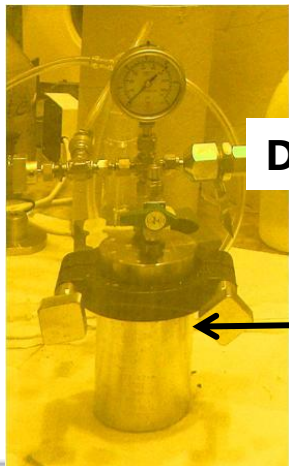
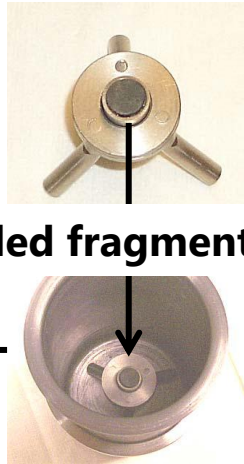


H₂ suppresses the radiolytical dissolution of real spent fuel at high pH

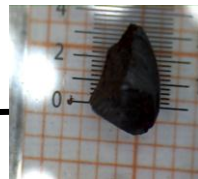
ECW- pH 12.5



Cladded fragment



Decladded fragment



	No H ₂	H ₂ 1 bar	H ₂ 3.2 bar
Rate (d ⁻¹)	10 ⁻⁷	10 ⁻⁷	1.4 x 10 ⁻⁸

Minimum [H₂] required ?

Sr release from the gap
between fuel and cladding

	H ₂ 3.2 bar
Rate (d ⁻¹)	~ 0

Dissolution rates at high pH similar as at neutral pH

Dissolution rate range ($\mu\text{g.m}^{-2}.\text{d}^{-1}$)	Neutral pH	pH 13.5
UO₂	0.03 – 20	0.1 – 1
Simulated fuel	0.3 – 26	0.16 – 41
Spent fuel / H₂	0.2 – 5	0 – 14

- Soluble U(IV) is not affected by high pH
- Soluble U(VI) increases with pH due to the formation of hydroxo-complexes
- Possible favorable effect of Ca
- Dissolution rate at high pH is similar to the dissolution rate at more neutral pH
- Suppressing effect of H_2 on dissolution of real spent fuel exists also at high pH, but the required minimum $[H_2]$ is not yet known

→ No indications for fuel destabilization in Supercontainer conditions, but confirmation by complementary research necessary



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

Experimental programme to determine the stability of spent fuel in Supercontainer conditions

Instant Release from Spent Fuel

Mennecart Th., Cachoir C., Lemmens K., Gielen B., Vercauter R.

Belgian Nuclear Research Centre, SCK-CEN

Thierry.mennecart@sckcen.be

Instant Release Fraction (IRF)

The IRF is the **fraction of safety relevant Radionuclides (RN)**, located in the fuel microstructures (cladding, gap, grain boundaries, rim) and **potentially released quickly from spent fuel** rods at the **time of canister breaching**. It is expressed in % of total inventory of the fuel.

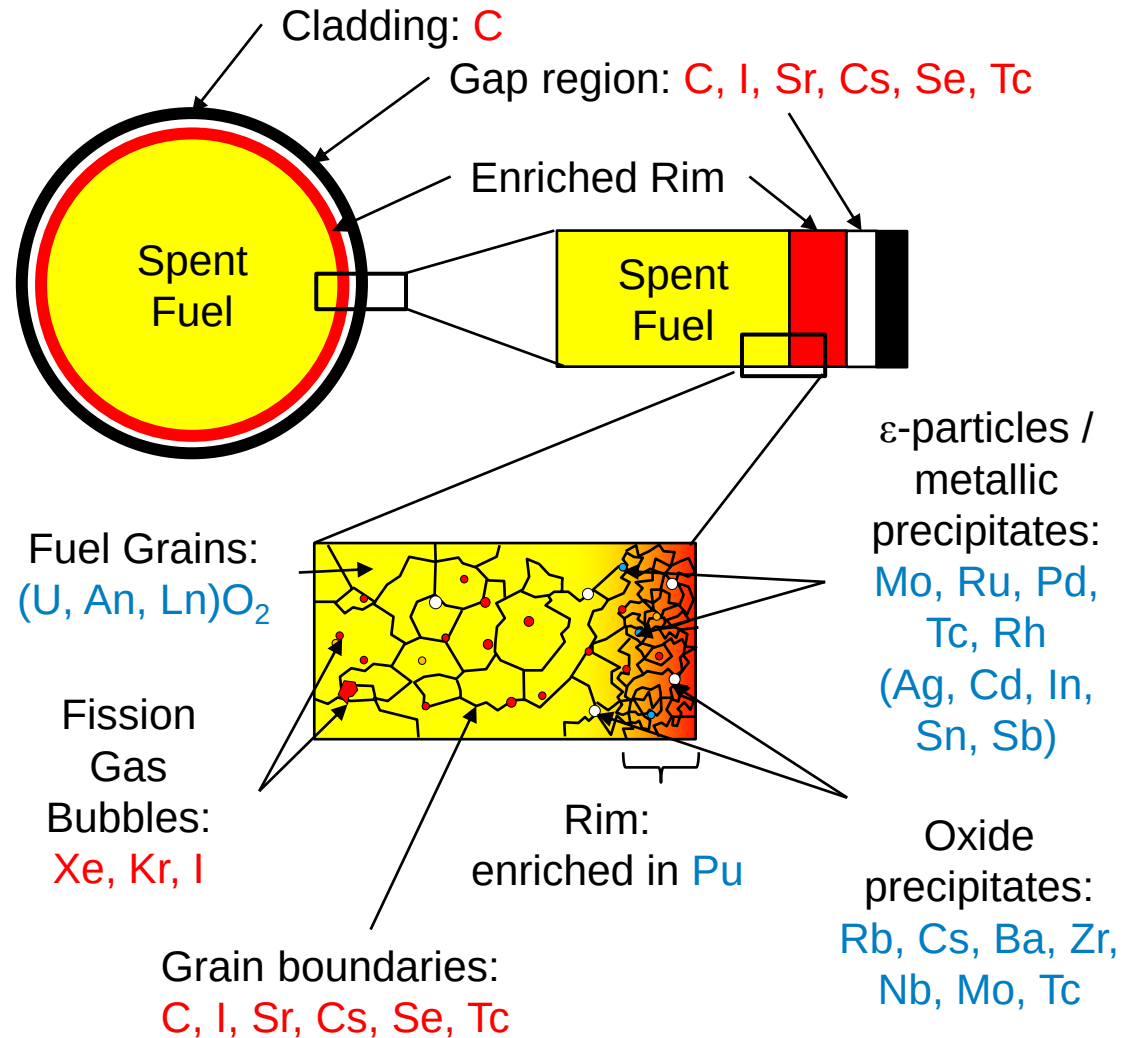
- IRF depends on
 - RN distribution within the Spent Fuel
 - Evolution of the μ -structure before/after canister breaching

$$IRF(t) = IRF(t_0) + F(t)$$

- Burnup (released energy in GWd/tHM)
 - Irradiation history
- Uranium oxide fuel (UOX) $\neq$ Mixed oxide fuel (MOX)
- Relatively independent of the disposal design

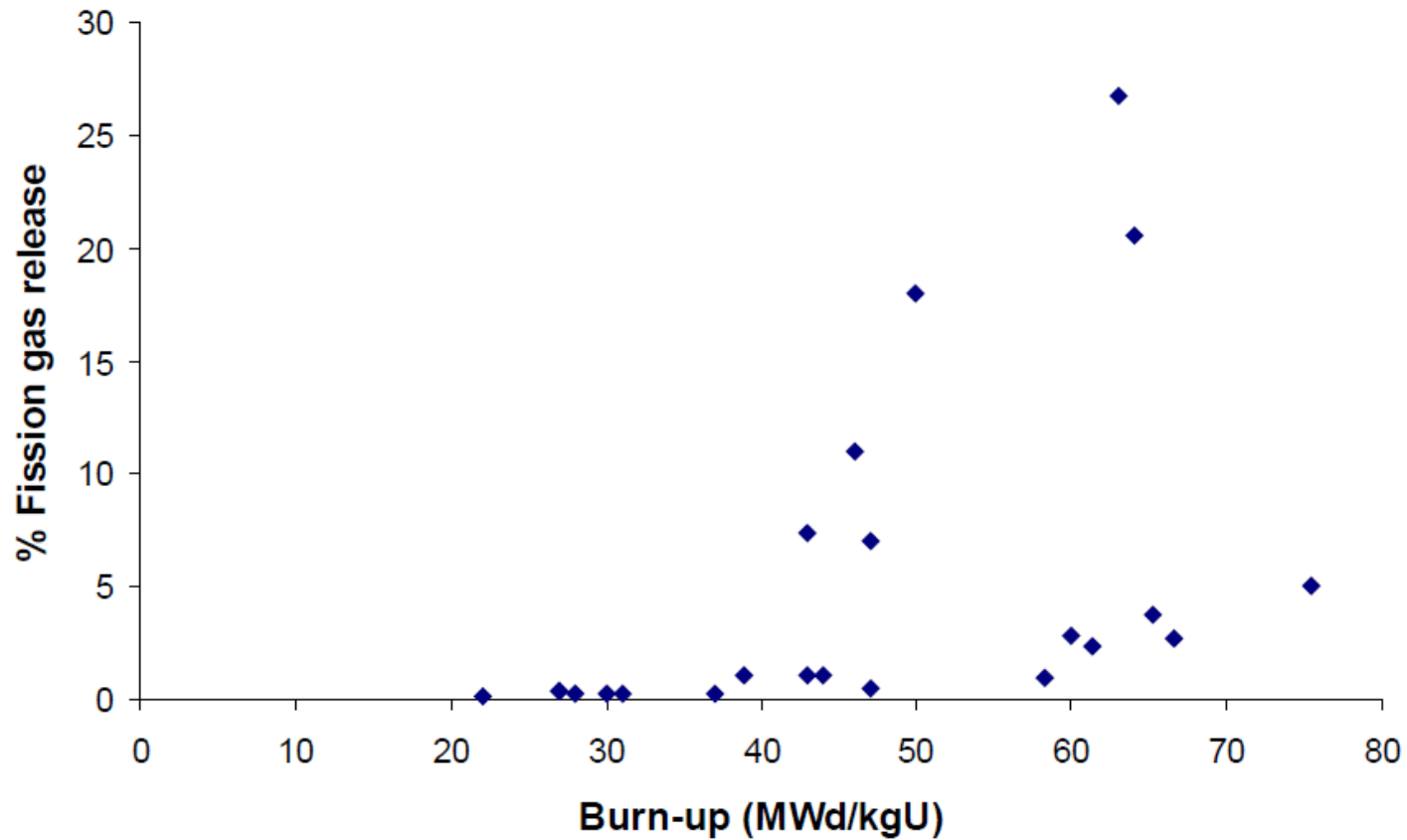
Structures prone to IRF

- Gap between fuel and cladding
At high burnup, access to water limited
- Open cracks in the fuel
- Grain boundaries (GB)
- For $BU > 40 \text{ GWd/tHM}$, rim appears with
 - $BU_{\text{rim}} = 1.33 \times BU_{\text{average}}$
 - Pores of the rim
 - The grains of the rim

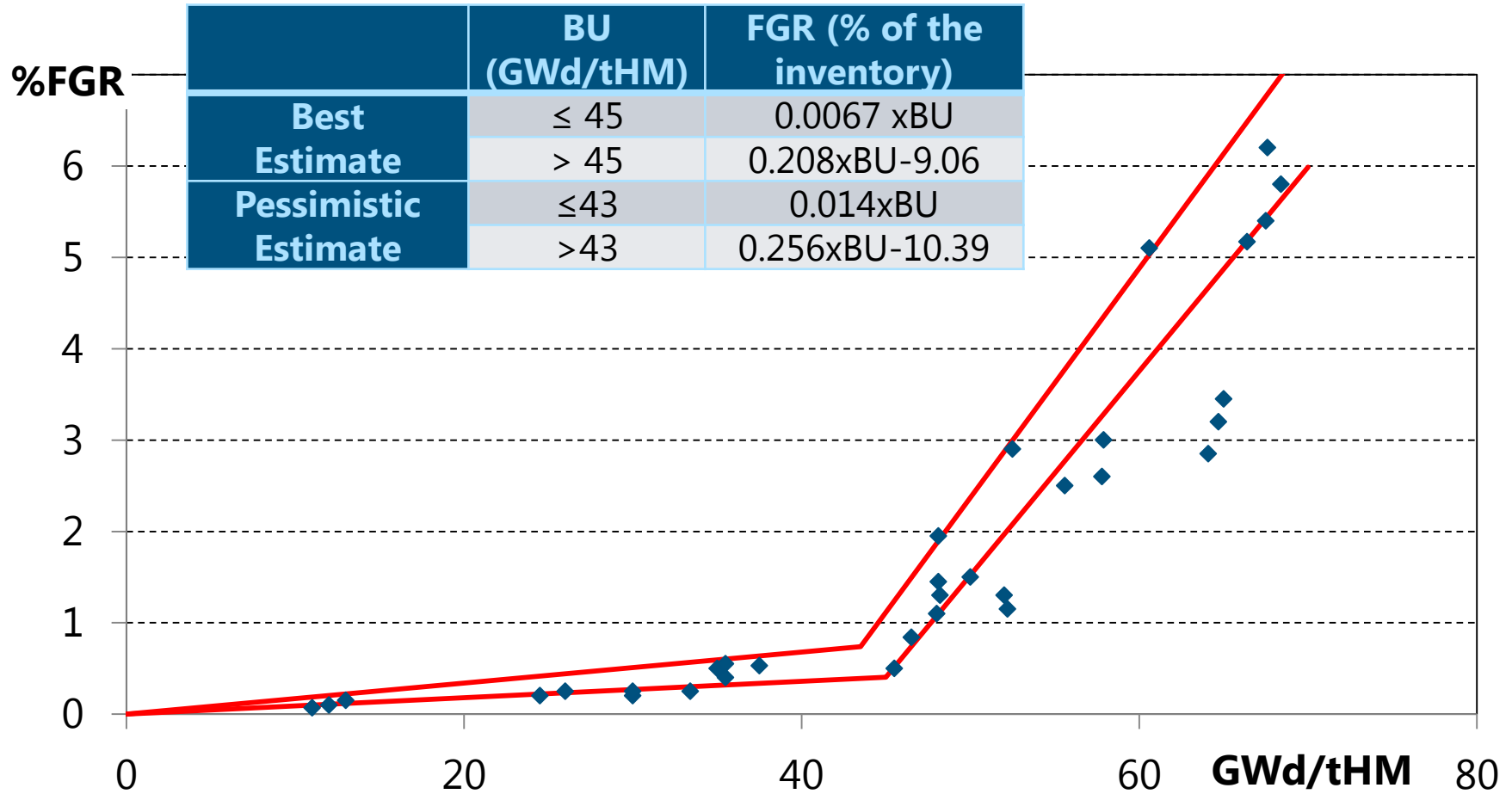


(Nearly instantaneous release upon contact with water)
(Slower release rate)

Fission gas release increases with burnup



Fission gas release increases with burnup



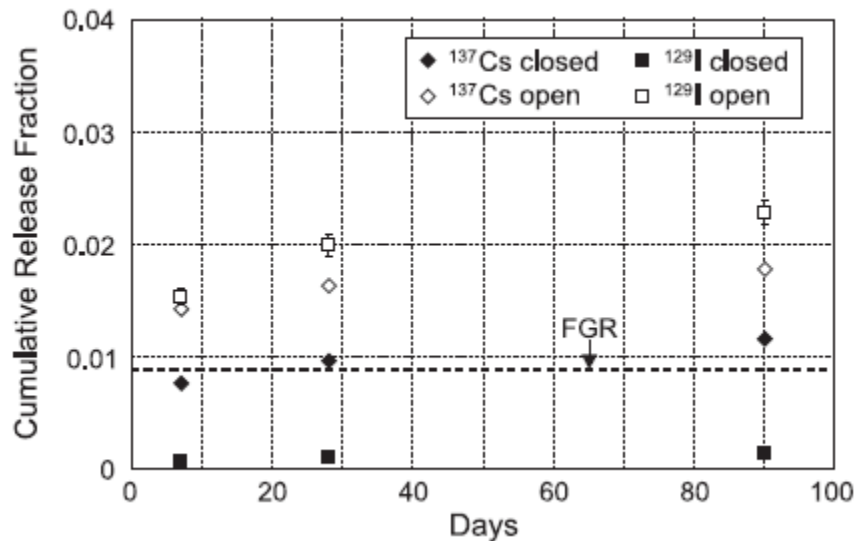
Leaching experiments: Cs release can be larger or smaller than FGR

Experiments were carried out using

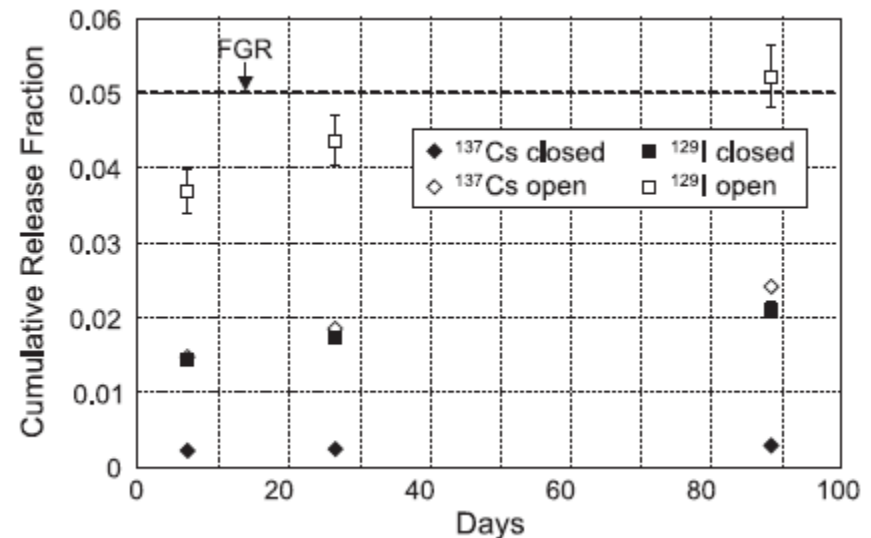
- Rod segment: clad segment (fuel + cladding)
- Fragment: pieces of SNF without cladding
- Powder: no cladding

Fraction of Inventory in the Aqueous Phase

$$FIAP_i = \frac{m_{i,solution}}{m_{i,SNF}}$$



Ringhals 3 PWR fuel (58.2 GWd/tHM)

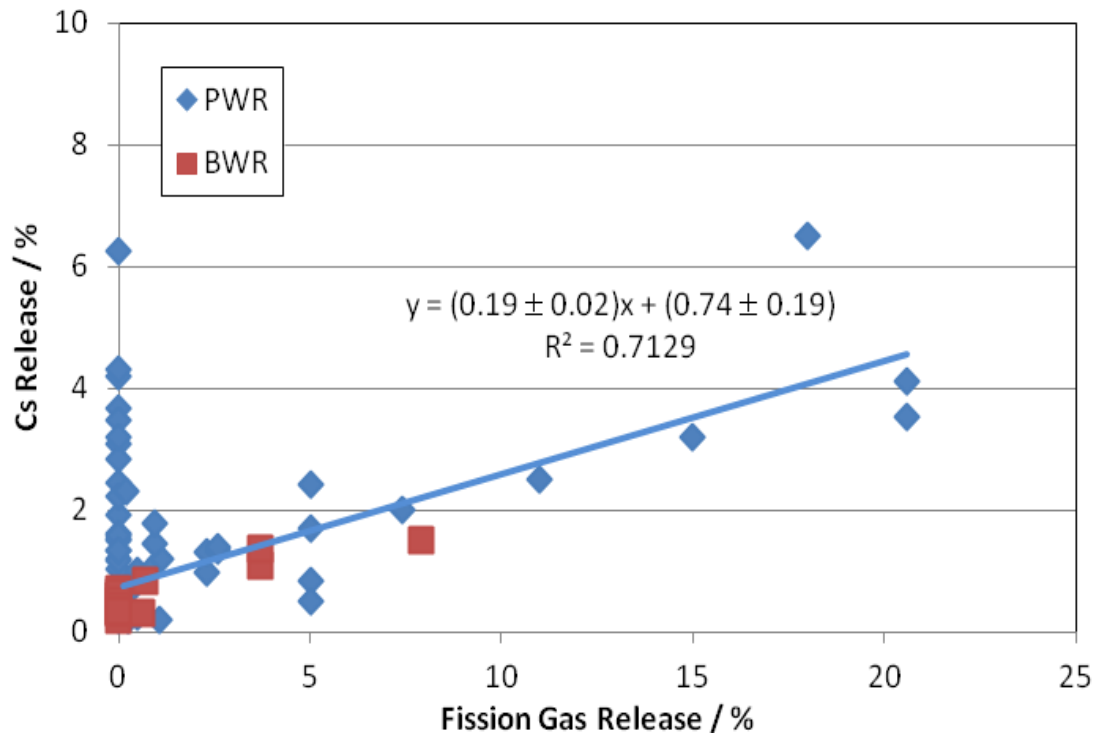


North Anna PWR fuel (75.4 GWd/tHM)

The Cs release can be estimated well from the correlation with FGR

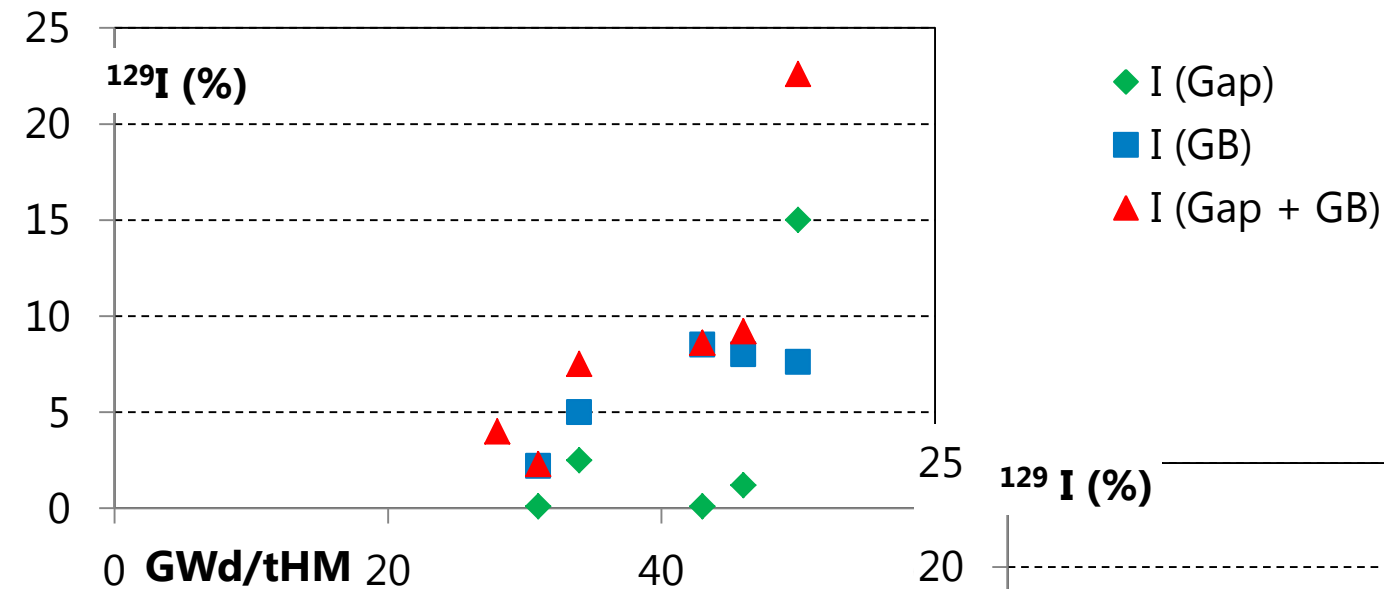
Instant Release Fraction

$$IRF_i = FIAP_i - FIAP_U$$

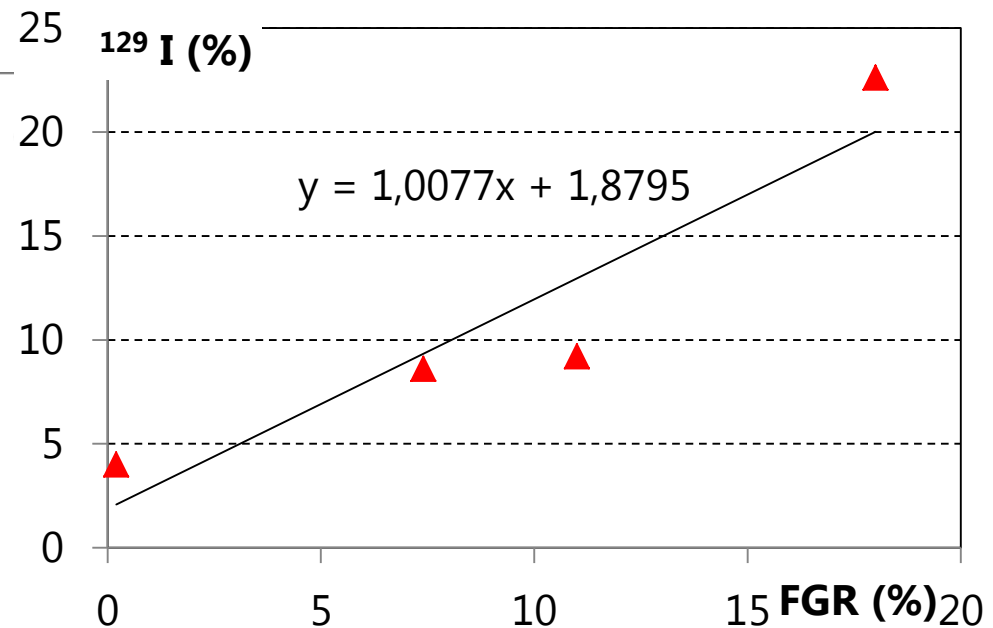


Cs is released more slowly than FG

^{129}I and FGR: same behaviour



- Good correlation between the release of the ^{129}I and the FGR
- Quite similar diffusion coefficient



Input for performance assessment

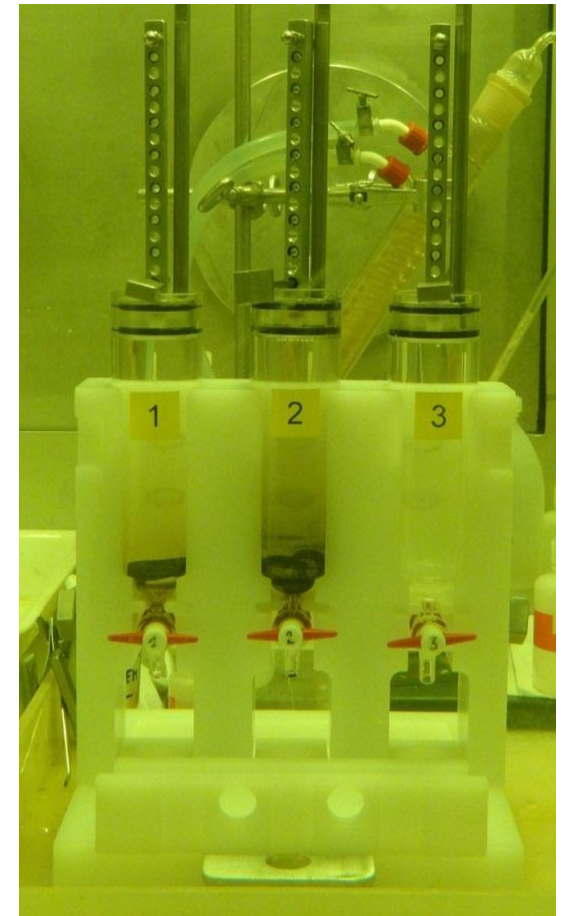
Selection criteria	Full Range (Min)	Restricted range (Min)	Restricted range (Max)	Full Range (Max)
Gap	x	x	x	x
Readily accessible grain boundaries	x	x	x	x
Best estimate rim thickness: pore (and grain boundary) inventory			x	
Pessimistic rim thickness: pore (and grain boundary) inventory				x
Pessimistic rim thickness: grain inventory				x

	Full Range (Min)	Restricted range (Min)	Restricted range (Max)	Full Range (Max)	Best Estimate
Fission gas	2	2	4	6	2
¹⁴ C	10	10	15	15	
³⁶ Cl	15	10	15	15	
⁹⁰ Sr, ⁴¹ Ca	1	1	3	4	1
⁹⁹ Tc, ¹⁰⁷ Pd	0.1	0.1	3	4	0.1
¹²⁹ I	2	2	4	6	2
¹³⁵ Cs	2	2	4	6	2

IRF (% of inventory)
at 50 GWd/tHM



Fast / Instant Release of Safety Relevant Radionuclides from Spent Nuclear Fuel



- Characterization of the samples
 - Data fabrication,
 - History of the irradiation
- Optical measurement
- Burnup – total inventory
- Leaching experiment: sampling of solution:
 - Release of the radionuclides
 $\text{U, Pu, } ^{93}\text{Zr, } ^{129}\text{I, } ^{134}\text{Cs, } ^{135}\text{Cs, } ^{137}\text{Cs, } ^{99}\text{Tc, } ^{107}\text{Pd, } ^{126}\text{Sn, } ^{59}\text{Ni, } ^{94}\text{Nb, } ^{137}\text{Cs, } ^{14}\text{C, } ^{36}\text{Cl, } ^{63}\text{Ni, } ^{90}\text{Sr}$
 - Dissolution rate (air atmosphere)
 - Instant Release Fraction (IRF)

Concluding remarks

- Most of the data come from irradiated fuel < 50 GWd/tHM
- Only few data for High Burnup and MOX: need more measurements
 - Difficult and expensive to measure (hot cell)
 - Representative fuels
 - Released data must be approved by fuel owners
- Focus experiments on finding relationship between fuel characteristics and IRF
 - Estimation of IRF by calculations - Correlation between some radioisotopes and %FGR
- The burnup alone cannot be used as a single parameter to characterize the SNF, also the history of irradiation (linear power, number of cycles,...)
- ...

Thanks to...



... And to you for your attention

R. Vercauter
The RCA & LRM teams





ONDRAF/NIRAS

Some concluding remarks

R. Gens, M. Van Geet / Dpt. LT RD&D

Belgian Agency for Radioactive Waste and Enriched Fissile Materials



Spent Fuel

- Spent fuel behaviour & dissolution rate
 - Key step: $\text{U IV} \rightarrow \text{U VI}$
 - Oxidative dissolution driven by radiolysis
 - Same radiolytic yields at neutral and high pH
 - Very similar behaviour in cementitious environment and neutral/slightly alkaline media (in terms of dissolution rates) $\Rightarrow$ we can rely on existing databases
 - Data coherent with other programs
 - Alpha threshold is environment dependent
 - No Eh poisoning capacity associated to the concrete buffer(CEM I)

Spent Fuel

- **H₂ inhibits UO₂ dissolution (very low residual rates)**
 - Detailed mechanisms still raising questions
- **In presence of hydrogen and/or below alpha threshold**
 - Dissolution mainly controlled by chemical equilibriums (solubility, diffusion/sorption)
 - SA: not a key parameter for non oxidative dissolution
 - Lifetime: millions of years

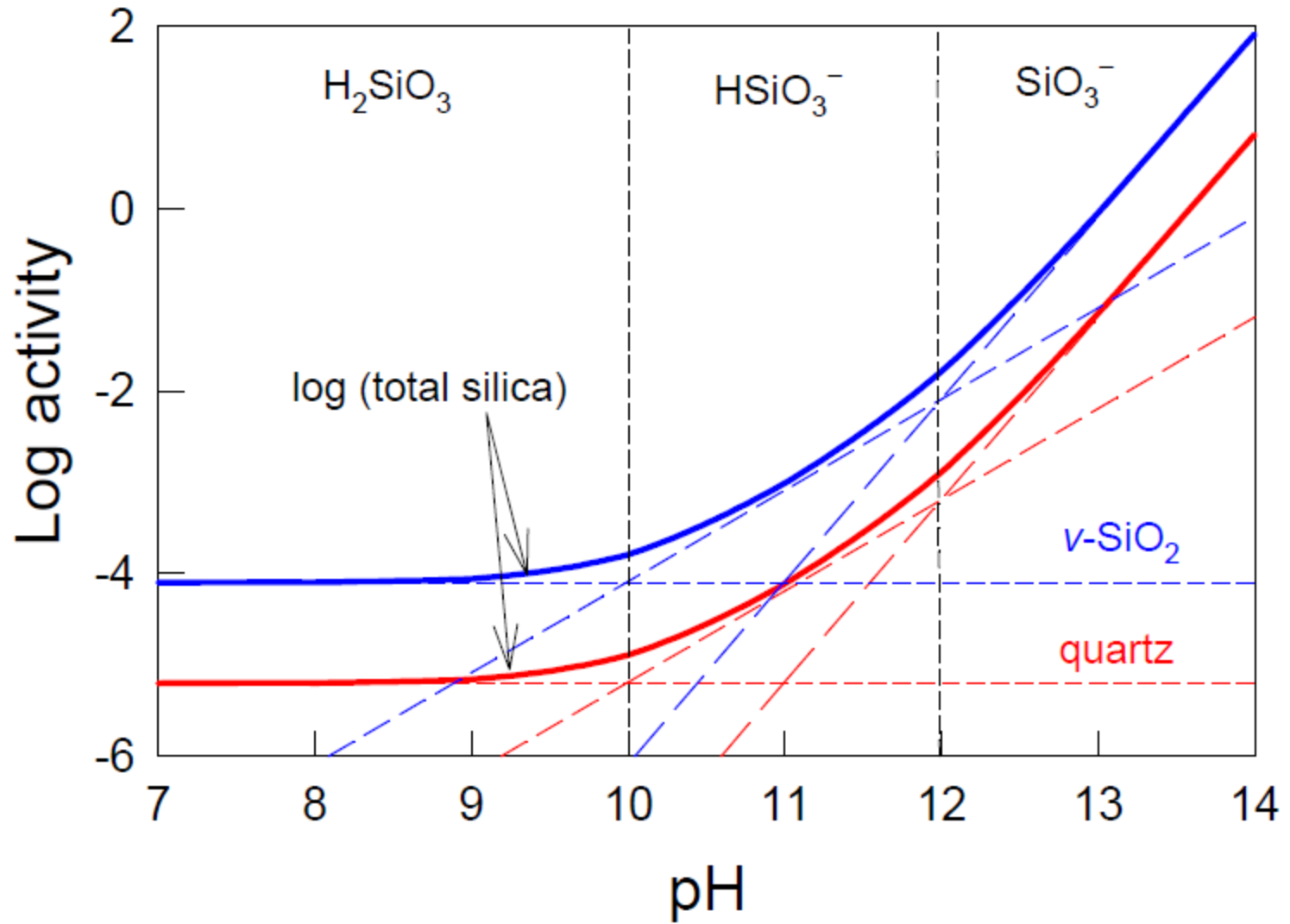
Spent Fuel

- **Future program will focus on the following topics**
 - Need additional evidences, datasets for confidence building (robustness)
 - New pgm with real spent fuels under preparation in close collaboration with and between KIT & SCK•CEN
 - Decrease uncertainty on alpha threshold in cementitious environment (→ related to overpack lifetime & early canister failure scenario)
 - Tests at low hydrogen partial pressures (passive corrosion of steel overpack & insert)
 - Data needed for alpha doped materials (with ϵ particles?)
 - IRF
 - Few data for high burn up UOX and MOX fuels
 - Follow up of international & national programs
 - Participation to EC First Nuclides Project

Glass

- **Same fundamental dissolution mechanisms as in neutral – slightly alkaline media**
 - But different kinetic regimes/controlling steps
 - High initial dissolution rate
- **At high pH: main dissolution drivers**
 - Attack of silica network (Si-O-Si bridges broken)
 - Formation of A-S-H/C-S-H
 - Resumption of alteration as a result of secondary phase formation (zeolites)

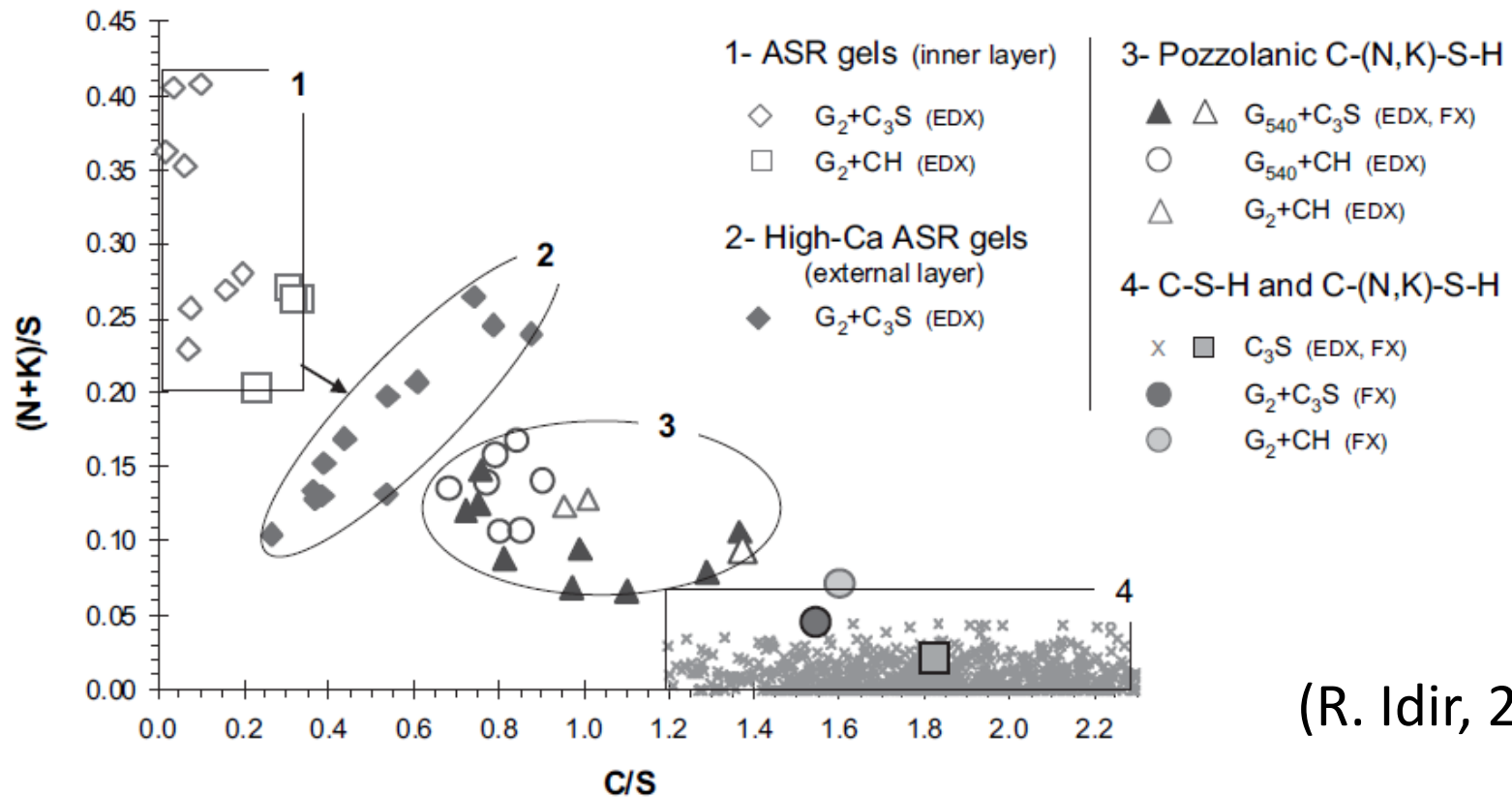
Glass



Glass

- **Cement industry: many relevant publications (different goals)**
 - R&D on ASR mechanisms (glass used as reactive “aggregate”)
 - Main potential application: as SCM in concrete (ASR $\Leftrightarrow$ Pozzolanic reaction)
- **SCM (BFS, FA, glass) & Radioactive vitrified waste**
 - Similar reaction path (to some extent)

Glass



(R. Idir, 2011)

Reaction path in line with Ichikawa mechanistic model
(T. Ichikawa, 2007)

Glass

- Future R&D: long-term dissolution rate evolution

N-S-H (ASR) $\Leftrightarrow$ C-S-H $\Leftrightarrow$ Zeolites $\Leftrightarrow$
Recondensation (protective layer)



Coupled transport

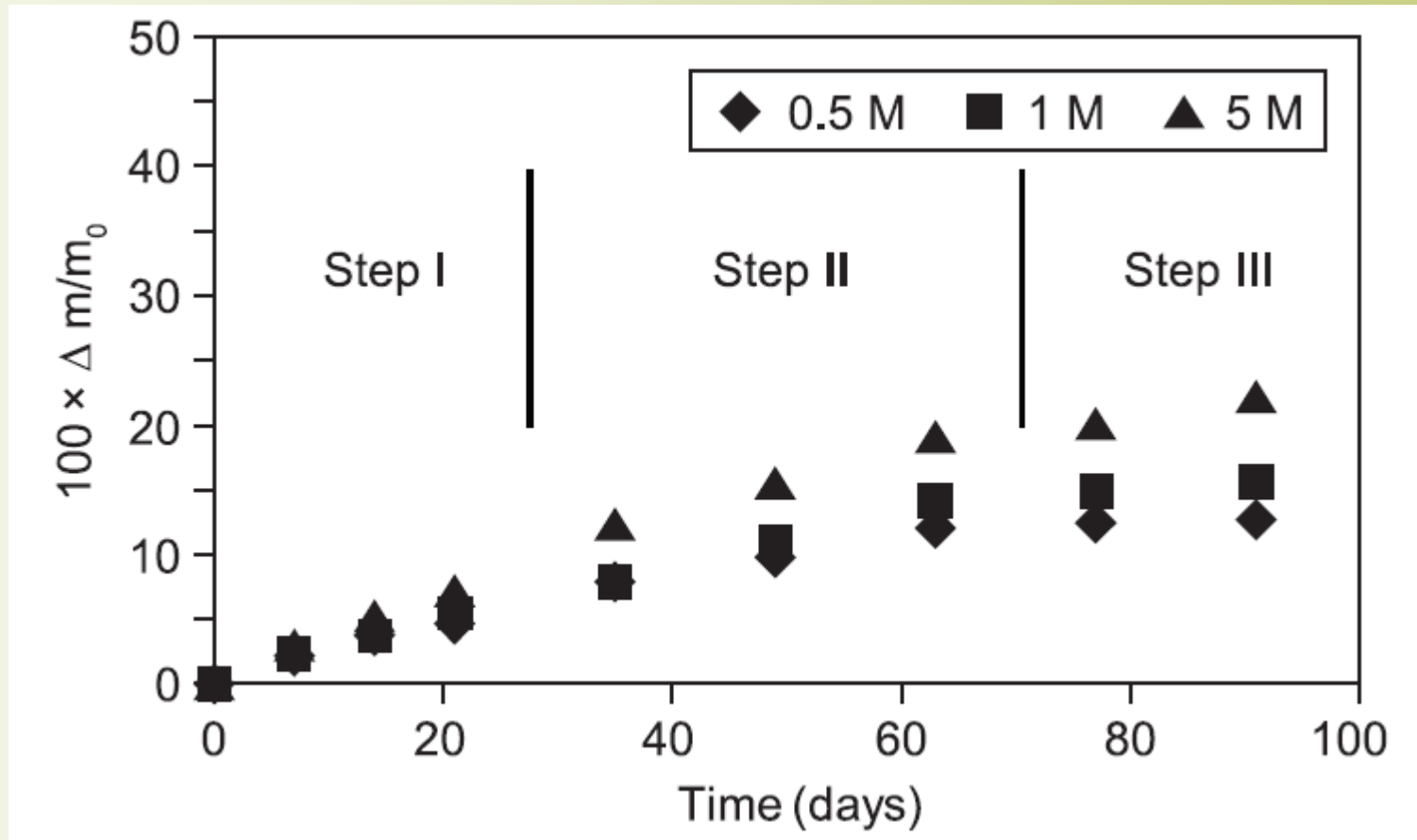
Glass

- **Experimental data and expected prevailing repository conditions (confined conditions, no renewal) suggest that the dissolution rate should decrease**
 - Confined tests (SCK●CEN): lower rates
 - Glass rods in mortar: lower ASR rate for uncracked samples (Song, 2008)
 - Already observed with Al metal in cement (“quasi” passivation)
 - Transport constrains (diffusion controlled)
 - Percolation tests (SCK●CEN): $V_{Fin} \ll V_{int}$
- **Filler material in the overpack: reactive silica to fix the alkalis** (prevent ASR, R. Takata, 2004)
- **Overpack lifetime > concrete stage 1 (alkalis leached out?)**

Glass

- **Formation of a protective layer on the long term (C-S-H and/or zeolites) ?**
 - Clogging of the fractures (decrease of SA)?
 - “Cementation” observed with glass powder (SCK•CEN, CEA)
 - Dense zeolite phases observed (CEA)
- **Experimental and modeling pgm needed**
- **Objectives: to provide multiple lines of evidence ($V_{LT} \ll V_{int}$)**
 - No use in PA for SFC 1
 - Safety reserve
 - Secondary phase formation: complex processes depending on many parameters (M. Fournier *et al*, 2014)
 - Kinetic & TDB: data missing
 - Multiple interfaces + evolving conditions
 - Concrete buffer/Filler/Overpack/Filler(?)/Canister/glass

Glass



(S. Kouassi *et al.*, 2010)

Glass

- **Concrete $\Leftrightarrow$ Clay**
 - No ideal design optimizing the durability and performance of all EBS components
- **Clay**
 - LT tests (SCK•CEN): no leveling off after 10 years
 - Fe-Glass interaction: could keep high initial dissolution rate during some (long?) transient (G. de Combarieu *et al*, 2011)
- **Confinement phase (overpack + glass)**
 - SAFIR 2 (clay): $\sim 75\,000$ years
 - Supercontainer (concrete): $\sim 100\,000$ years (at least)

General conclusions

- **10 years ago: change of design (Supercontainer, concrete buffer)**
 - Challenging situation: only very few relevant data available (very limited interest in other countries)
- **10 years later: significant progress + international collaboration**
 - Significant progress in the development of the scientific assessment basis (databases, mechanistic understanding)
 - Spent fuel: bridges between Belgian and other national pgm (no different behaviour in concrete)
 - R&D performed by KIT & SCK
 - Expert Panel review (on an yearly basis)
 - Glass
 - Studies performed in France (CSD-B) and UK (Magnox glass)
 - Scientific collaboration with AREVA, CEA, ANDRA, Subatech

General conclusions

- **Coralus**
 - Highly valuable technical & scientific outcomes
 - REX: relevant input for potential future *in situ* pgm (Supercontainer Design)
- **Future R&D**
 - Knowledge gaps and priorities well identified (see RD&D plan)
 - Will take place in the frame of international collaborations