Andra proposal for a future European project dealing with geochemical processes within a HLW/Spent fuel disposal cell

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Dossier 2005: feasability of an underground repository

- For both nuclear glass and spent fuel
  - Radionuclide release model defined mainly from experiments performed in pure water
    - Unsaturated period or influence of groundwater not taken into account
  - First results about the interactions between nuclear glass and corrosion products
    - Assumptions: corrosion products = magnetite/siderite

    ↳ **A first robust macroscopic approach**

- Recommendations for future R&D
  - Reduce the conservatism of radionuclide release model
  - Develop models that take into account the interactions with environment

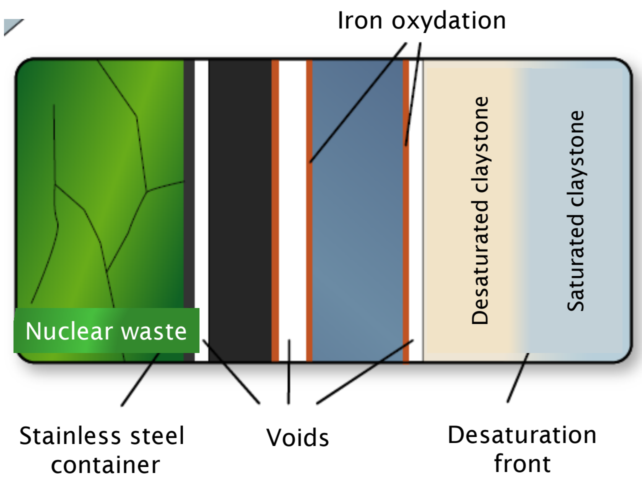
    ↳ **A better understanding of the system necessary for the optimisation process**

Towards the submission of the licence application (2017)

- Focus on interactions of nuclear waste with environment materials
  - R&D program defined from the situations expected in HL disposal cells
  - A multi-disciplinary approach : glass/spent fuel alteration, canister corrosion, evolution of clay materials
  - Long time scale: requires complementary approach
    - Experiments in surface laboratories and URL
    - Archeological analogues
    - Modeling

- R&D performed between 2006-2014:
  - Important results on long-term behaviour of nuclear waste (spent fuel and HLW glass) in repository conditions
  - Highlight some key topics that require future R&D efforts …

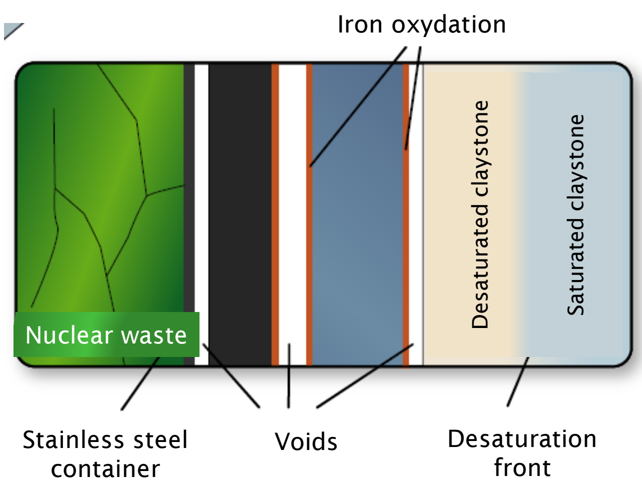
Expected situations in repository conditions
A few examples

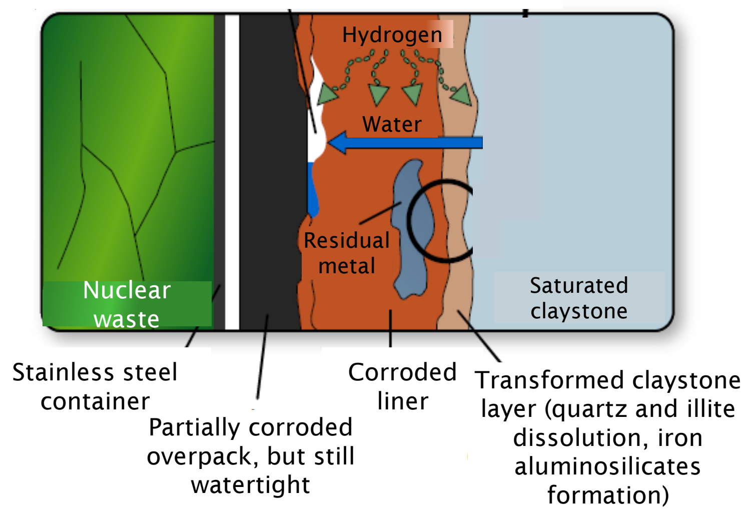


Situation 1

- *Non-saturated claystone*
- *Oxydising medium*
- *High temperature*
- *Watertight overpack*

- *Duration : ~less than 10 years*





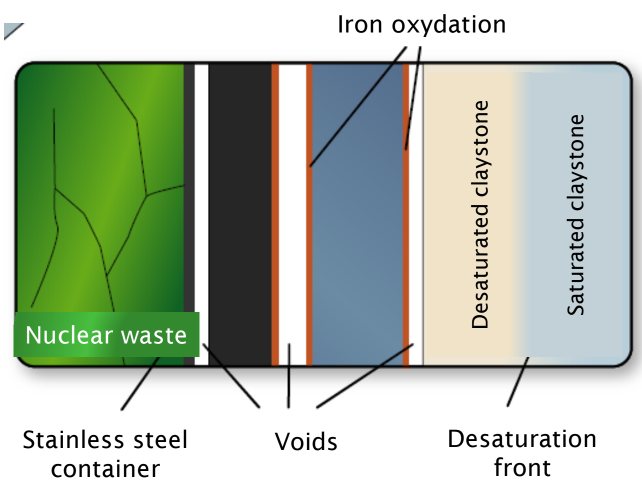
Situation 2

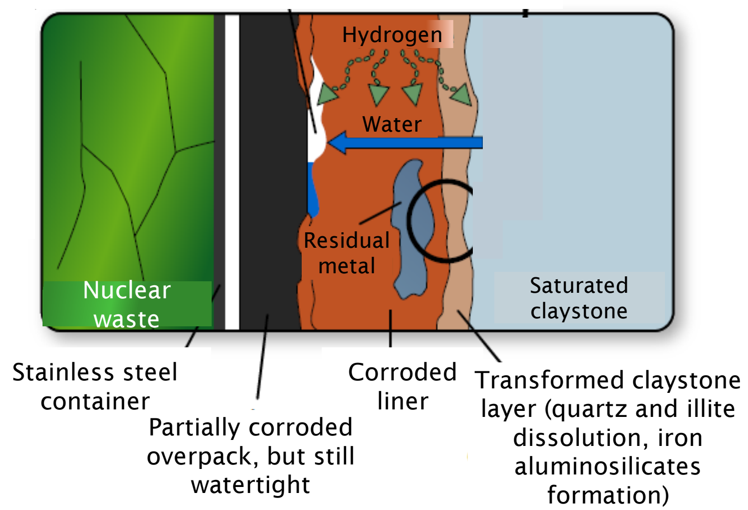
- *Saturated claystone*
- *Reduced medium*
- *Decrease of temperature*
- *Watertight overpack*

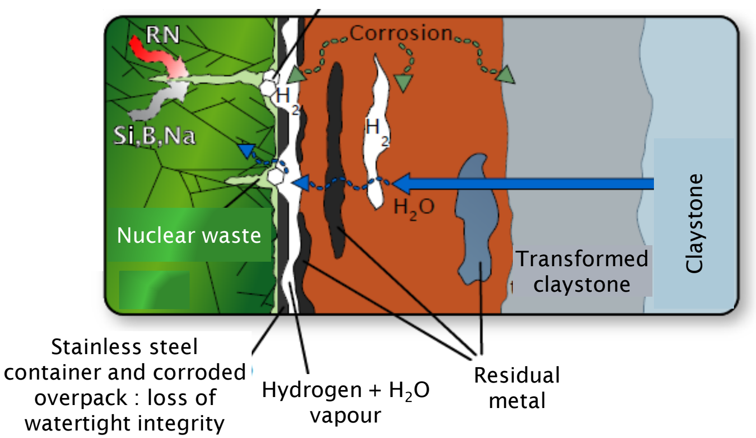
- *Duration : several thousand years*

Expected situations in repository conditions

A few examples





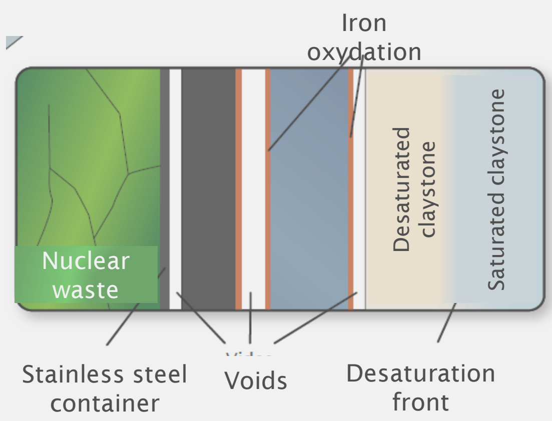


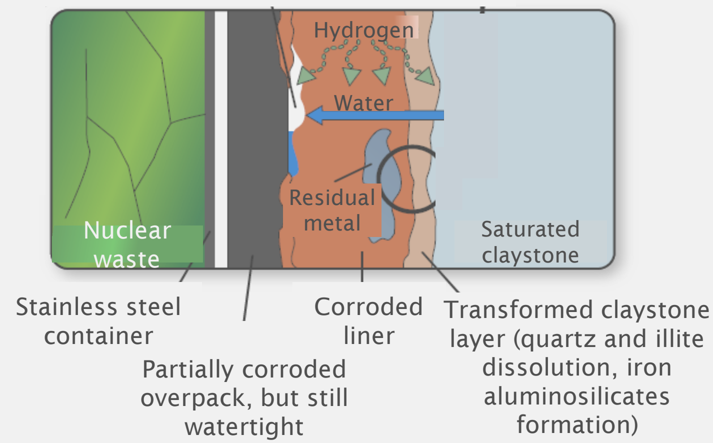
Situation 3

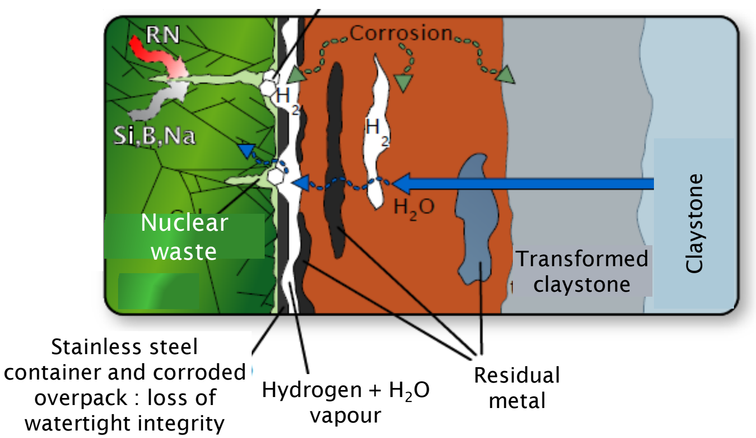
- ***Saturated claystone***
- ***Reduced medium***
- ***Low temperature***
- ***Container and overpack not watertight anymore***

- ***Duration : up to ten thousands years***

Expected situations in repository conditions
A few examples







Situation 3

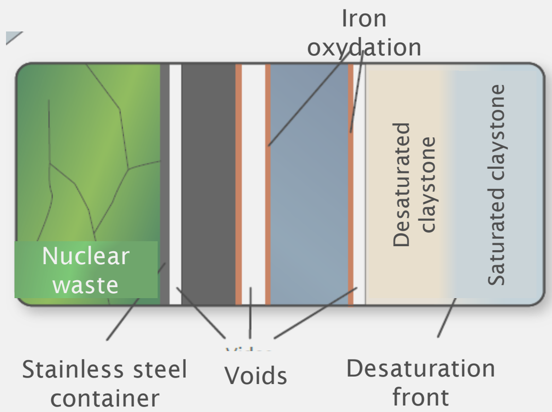
First : Overpack partially filled with water

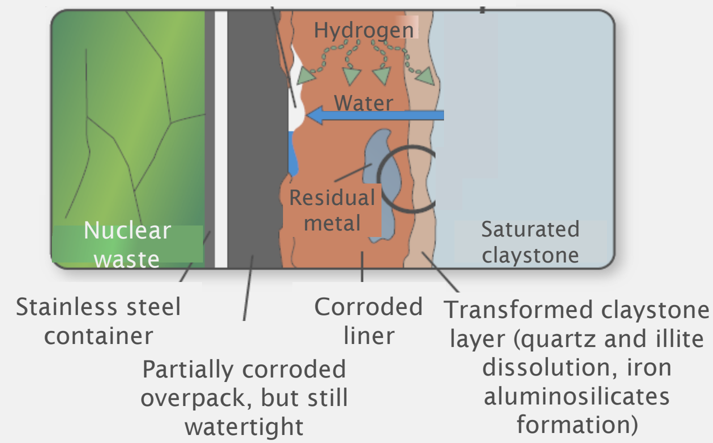
Hydration of nuclear waste depending on resaturation kinetics

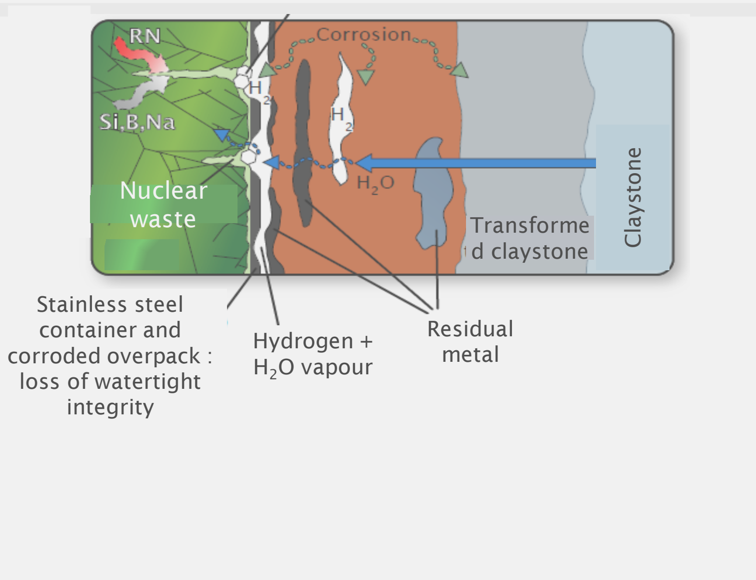
- For long resaturation time, fraction of hydrated waste could be significant
- First results available for some nuclear glasses
- What about spent fuel?

Expected situations in repository conditions

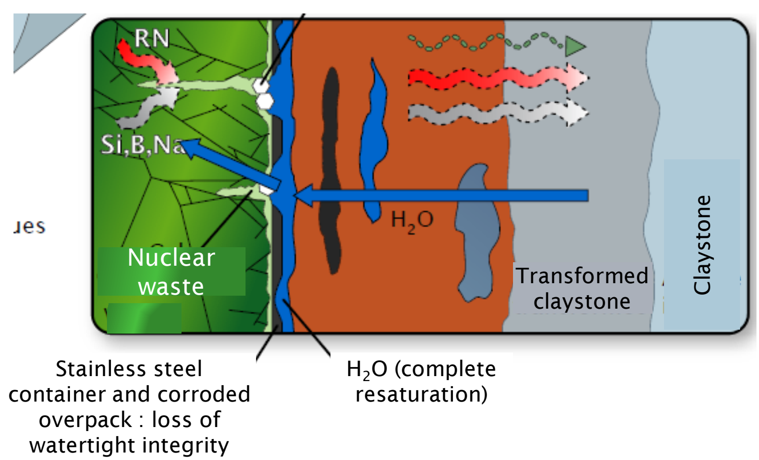
A few examples





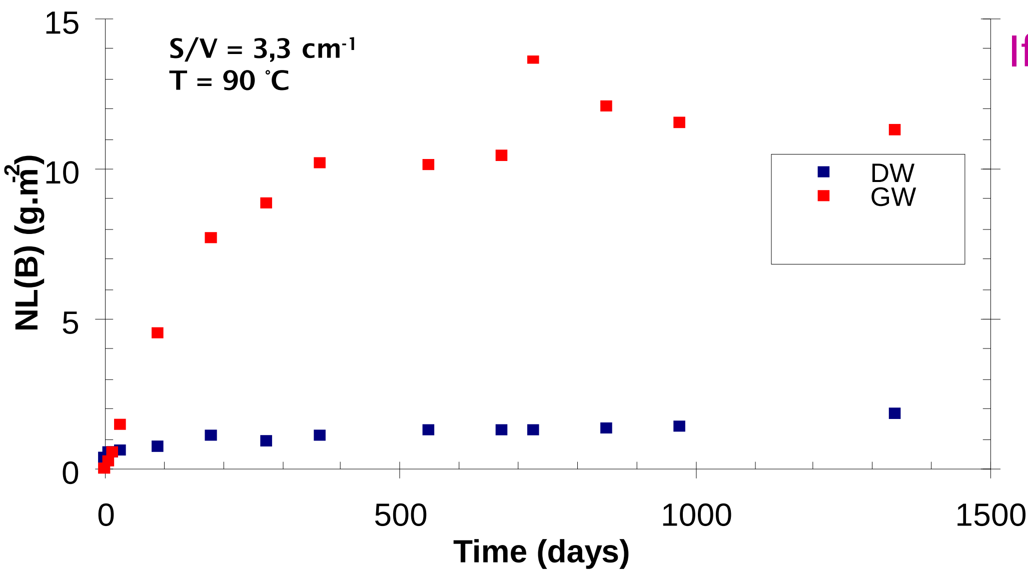


Then : Overpack filled with water



GW composition (50 ˚C, mg/L) and calculated pH

Si	Na	K	Ca	Mg	Cl^-	SO_4^{2-}	CO_3^{2-}	$pH_{50°C}$
10	966	39	397	100	1453	1345	232	6,7



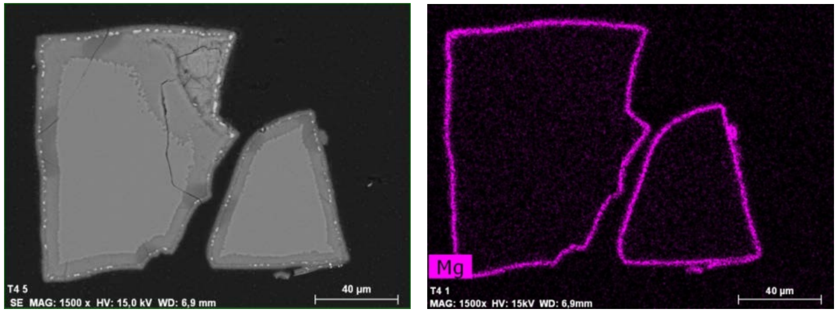
If $pH_{90˚C}$ > 7 or $pH_{50˚C}$ > 8,3-8,4:

Rate drop delayed

$r_{R\ SON68}$ (GW) > $r_{R\ SON68}$ (DW)

⇨precipitation of magnesium silicates

⇨silica consumption



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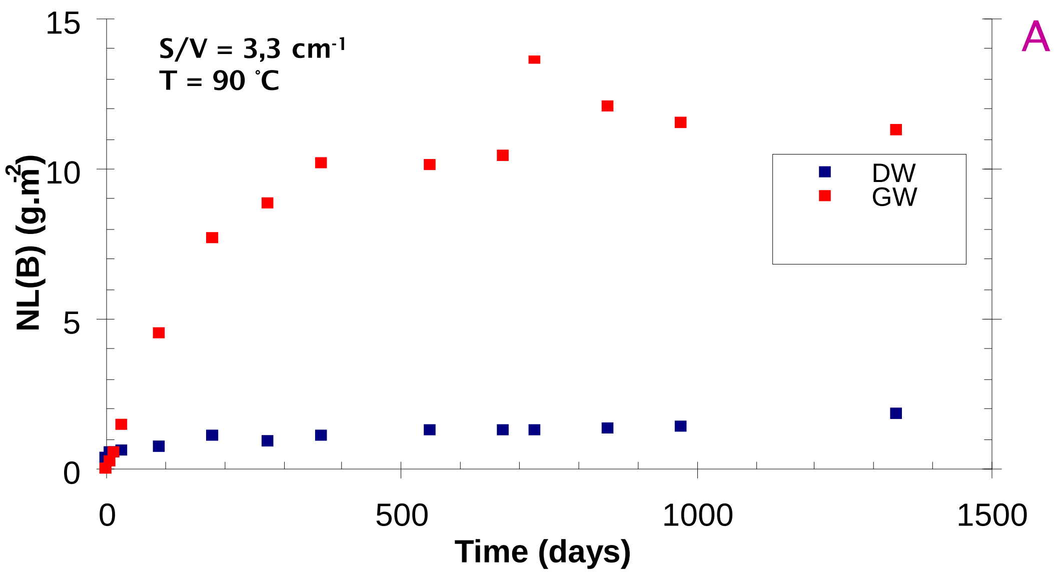
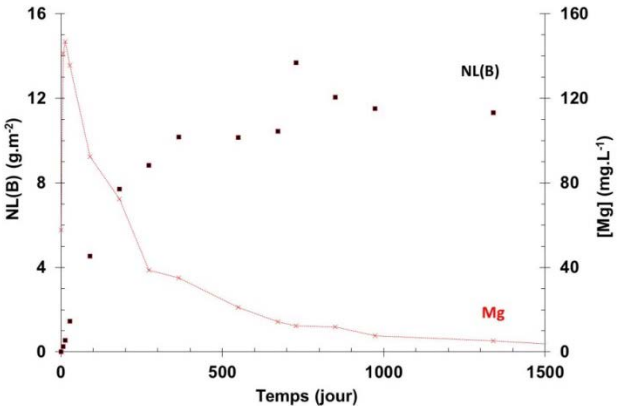


As long as Mg is available, otherwise $r_{R\ SON68}$ (GW) → $r_{R\ SON68}$ (DW)

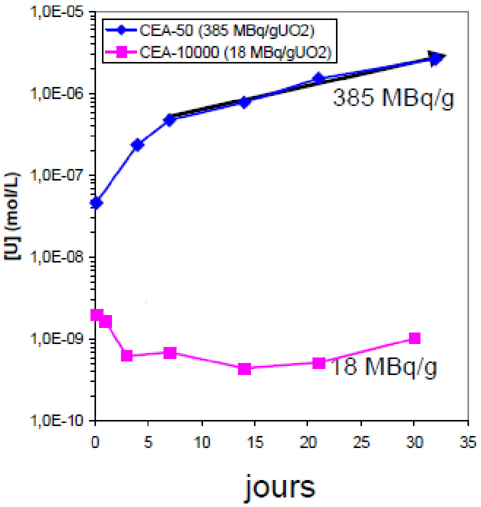


- **Highly dependant on chemistry-transport coupling:**
  - **Mg flux**
  - **pH locally at the glass surface resulting from glass alteration, iron corrosion processes)**

Expected situations in repository conditions
Influence of groundwater on spent fuel

R&D 2006-2015

- 2007: first experiments in carbonated water: Threshold effect depending on the alpha activity
  - ⇨ radiolytic dissolution / solubility control
- Hydrogen effect



- Development of a new model based on an electrochemical approach
  - Still on going work difficult to achieve a complete model
  - But recent results: according to the lifetime of the container, radiolytic contribution for MOX fuel, not for UOX fuel

Future R&D

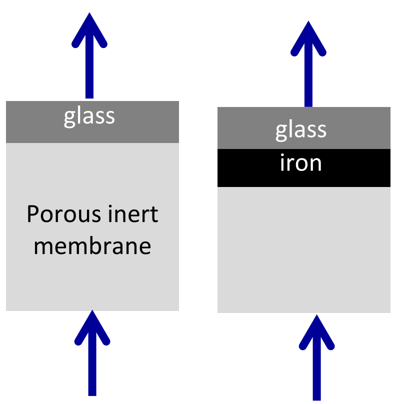
- Effect of temperature
- Improvement of a model based only on solubility control (alteration tracer?)

Expected situations in repository conditions

Interactions with iron/corrosion products

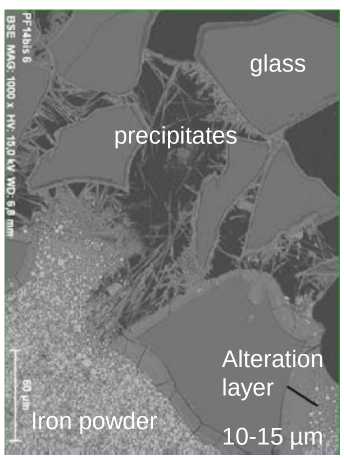
Glass dissolution in presence of iron

- Interest: formation of corrosion products in situ
  - Magnetite, siderite $Fe_{1-x}Ca_xCO_3$, chukanovite $Fe_2(OH)_2CO_3$ + (Fe,Mg) silicates…
- Different experiments:
  - iron powder mixed with glass powder or with glass monoliths: influence of grain size and reactive surface
  - iron powder in contact with glass powder:
    - **Reactivity at the interface**
    - **Nature and morphology of the alteration products depend on the iron flow and the glass-iron distance**

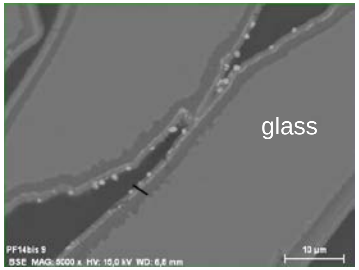


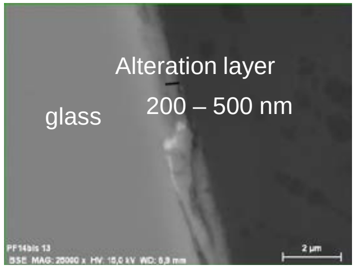
50°C anoxic media

synthetic solution at thermodynamic equilibrium with COx clay



Alteration layer ~ 3 – 4 µm
= Gel ~ 1.5 - 2 µm + (Fe, Mg)silicates
RE precipitates (P, Ca, La, Ce, Nd)





Iron powder —— 250 µm —— 1 mm —— 2.5 mm →

Expected situations in repository conditions
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    - ↳ **Reactivity at the interface**
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Spent fuel (α-doped UOX/irradiated MOX) dissolution in presence of iron

- On-going work (PhD Melina Odorowski, Spent Fuel Workshop 2014)
- Both experimental and modeling approach
- Strong influence of alpha/gamma irradiation on iron oxydation
- Very low U concentrations but U is not an alteration tracer

↳ **Need of modeling by coupling waste alteration / iron corrosion and waste/iron interactions**

Conclusions

How to describe what happens in a spent fuel / nuclear glass disposal cell ?

- Identification and understanding of chemical processes
  - Glass alteration, IRF, (U, Pu)O_2 dissolution, iron corrosion …
- Strong interactions/feedback between chemical processes in the disposal cell
  - Importance of the reactivity at interfaces between different materials in a system that evolve with time

3 processes

Waste dissolution
(and RN release)

↕ (interactions)

Iron corrosion

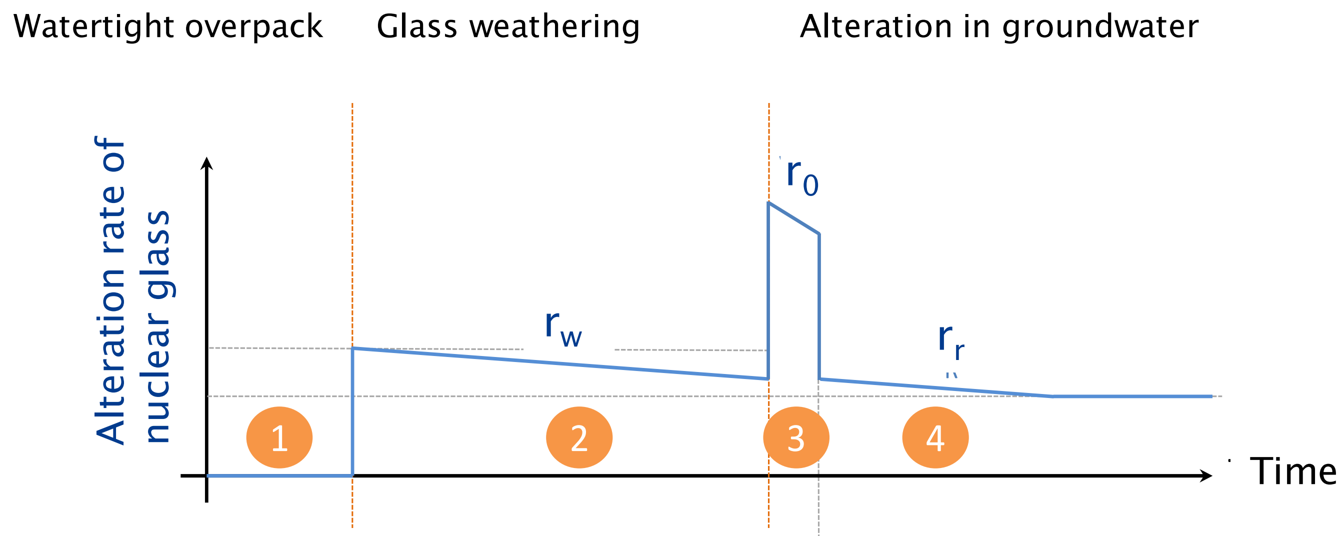
↕ (interactions)

Mineralogical transformations

under the influence of different physico-chemical parameters

- Thermal (temperature evolution)
- Water conditions (dry/wet conditions, unsaturated/saturated medium)
- Chemical (evolution of redox conditions, water chemistry…)
- Mechanical
- Radiological (influence of water radiolysis…)

Conclusions
Radionuclide release models highly dependant on environment parameters



- Main parameters associated to the glass and CP:
  - r_w, r_0, r_R, τ_w, τ_0, τ_R (cracking ratio)
  - iron fraction that leads to CP formation
  - nature of CP (Mg silicates, Fe silicates, Si/Fe ratio)
  - silicon sorption capacity
- Other parameters depending on the environment
  - Temperature evolution
  - Water conditions:
    - » *Duration of resaturation*
  - Corrosion
    - » *Quantity of corroded metal until the watertightness loss (→ quantity of CP)*
    - » *Time necessary to corrode the residual metal after the watertightness loss (metal corrosion + glass alteration → iron silicates formation)*

Conclusions

For a more realistic description of a disposal cell

A model that take into account the interactions with environment requires :

- Multi-disciplinary R&D approach, not only focused on waste

- Both experimental and modeling approach
  - Comparative modeling (HYTEC, CRUNCH, PHREEQC)
  - Modeling of lab experiments and repository conditions (disposal cell)
  - Improvement of coupling (iron corrosion, glass alteration, spent fuel dissolution)

- Up-scaling approach from lab experiments to disposal cell
  - Lab experiments, URL experiments
  - Studied sample: powder, monoliths, model (1: X scale)
  - Improvement of coupling (iron c ... ation, spent fuel dissolution)

Model of broken overpack with a rod of SON68 glass altered in a claystone brick