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

Christelle Martin

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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
Introduction

Andra’s strategy

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

*Expected situations in repository conditions*

A few examples

**Situation 1**

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

- Duration: ~less than 10 years
Expected situations in repository conditions

A few examples

Iron oxidation

- Stainless steel container
- Voids
- Desaturation front
- Saturated claystone

Situation 2

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

- Duration: several thousand years
Expected situations in repository conditions
A few examples

Iron oxydation

Saturated claystone
Desaturation front
Voids
Stainless steel container

Situation 3
• Saturated claystone
• Reduced medium
• Low temperature
• Container and overpack not watertight anymore
• Duration: up to ten thousands years

Transformed claystone layer (quartz and illite dissolution, iron aluminosilicates formation)

Stainless steel container
Corroded liner
Partially corroded overpack, but still watertight

Nuclear waste
Residual metal
Hydrogen + H2O vapour

Stainless steel container and corroded overpack: loss of watertight integrity

Nuclear waste
Residual metal
Hydrogen + H2O vapour
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

- Iron oxidation
- Stainless steel container
- Nuclear waste
- Voids
- Desaturation front
- Saturated claystone
- Residual metal
- Water
- Hydrogen

Then: Overpack filled with water

Stainless steel container and corroded overpack: loss of watertight integrity

Transformed claystone layer (quartz and illite dissolution, iron aluminosilicates formation)

Hydrogen + H₂O vapour

Stainless steel container

Corroded liner

Transformed claystone

Saturated claystone

Residual metal

Nuclear waste

Claystone

RN, Si, B, N

Residual metal

Hydrogen + H₂O vapour

Saturated claystone

Transformed claystone

Claystone

RN, Si, B, N

Water

H₂O (complete resaturation)

Stainless steel container and corroded overpack: loss of watertight integrity
GW composition (50 °C, mg/L) and calculated pH

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Na</th>
<th>K</th>
<th>Ca</th>
<th>Mg</th>
<th>Cl⁻</th>
<th>SO₄²⁻</th>
<th>CO₃²⁻</th>
<th>pH₅₀°C</th>
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<td>10</td>
<td>966</td>
<td>39</td>
<td>397</td>
<td>100</td>
<td>1453</td>
<td>1345</td>
<td>232</td>
<td>6,7</td>
</tr>
</tbody>
</table>

If \( \text{pH}_{90°C} > 7 \) or \( \text{pH}_{50°C} > 8,3-8,4 \):
Rate drop delayed
\( r_{R\ SON68\ (GW)} > r_{R\ SON68\ (DW)} \)

\( \Rightarrow \) precipitation of magnesium silicates
\( \Rightarrow \) silica consumption
Expected situations in repository conditions

Influence of groundwater on nuclear glass

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

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S/V = 3,3 cm⁻¹
T = 90 °C

As long as Mg is available, otherwise
\( r_R \text{ SON68 (GW)} \rightarrow r_R \text{ SON68 (DW)} \)

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 $\text{Fe}_{1-x}\text{Ca}_x\text{CO}_3$, chukanovite $\text{Fe}_2\text{(OH)}_2\text{CO}_3 + (\text{Fe},\text{Mg})$ 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

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<th>iron</th>
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<td>porous inert membrane</td>
<td>[50^\circ C \text{ anoxic media}]</td>
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synthetic solution at thermodynamic equilibrium with COx clay

Alteration layer $\sim 3 - 4 \mu m$

$=$ Gel $\sim 1.5 - 2 \mu m + (\text{Fe, Mg})$silicates

RE precipitates (P, Ca, La, Ce, Nd)

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Alteration layer $\sim 10 - 15 \mu m$

Iron powder $\sim 250 \mu m$  $\sim 1 \text{ mm}$  $\sim 2.5 \text{ mm}$
Expected situations in repository conditions

*Interactions with iron/corrosion products*

**Glass dissolution in presence of iron**

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**Spent fuel ($\alpha$-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)O₂ 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 under the influence of different physico-chemical parameters

- Waste dissolution (and RN release)
- Iron corrosion
- Mineralogical transformations

- Thermal (temperature evolution)
- Water conditions (dry/wet conditions, unsaturated/saturated medium)
- Chemical (evolution of redox conditions, water chemistry...)
- Mechanical
- Radiological (influence of water radiolysis...)
Main parameters associated to the glass and CP:
- \( r_w, r_0, r_R, \tau_w, \tau_0, \tau_R \) (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
Radionuclide release models highly dependant on environment parameters
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 corrosion, glass alteration, spent fuel dissolution)

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