Deliverable 15.3: Training materials

Work Package 15 ConCorD

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<thead>
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<th>Status of deliverable</th>
<th>By</th>
<th>Date</th>
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<tbody>
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Executive Summary

This report provides an overview of presentations that can be used as training materials related to the ConCorD WP. The topics and content are based on the SotA document (deliverable 15.1). The first topic gives an overview of the evolution of the environmental conditions focussed on the near-field and their impact on corrosion behaviour. More detailed information about the transient conditions, the impact of irradiation and microbial processes is provided. The second topic gives an overview of novel technological concepts for container materials and the third topic summarizes prediction tools for assessment of long-time barrier integrity and the integration of corrosion phenomena in performance assessments. The outline and learning outcomes for each of the topics is given in this report. In general, the target audience for all lectures are people that have already a basic background in corrosion but want to learn more details about a topic outside their field. For example, beginning PhD students/scientist in the field. This enables people to gain a broad basic background in studying corrosion processes related to nuclear waste disposal. A more detailed technical training or practical sessions that cover different modelling tools can be developed depending on the needs of future Training Event organizers. In principle, the slides can be used on a stand-alone basis to learn the main principles, however, more subtle information will be gained if the slides are taught by a lecturer. At the end of the project, the lectures will be updated with relevant results. The slides are attached as annexes.
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1. Introduction

Even though the feasibility and safety of established container solutions has been demonstrated, recent progress in understanding of materials and processes has shown that optimisation of container manufacturing and performance is possible. Widespread interest in repository optimisation exists and relevant projects are ongoing, e.g., WP HITEC and the HotBENT experiment in Grimsel. The systematic exploration of novel materials, while placing existing solutions in a broader context, will provide a solid state-of-the-art for the pursuit of container optimisation according to available geology, disposal concept and regulatory requirements. The testing of alternative container materials, their mechanical structural response and corrosion resistance will also bring new insights into novel technical solutions for container design.

To further increase the knowledge base and reduce remaining uncertainties, WP ConCorD aims to:

• Explore the potential of novel/advanced container materials and processes for optimisation of container performance within the engineered barrier system.

• Increase/extend the understanding of complex/coupled interfacial processes influencing container performance under repository relevant conditions, with a focus on irradiation-accelerated corrosion, microbial activity and degradation during nearfield transients, at varying scales.

• Mechanistic process understanding and development of predictive models, which will incorporate system variability and will lead to improved performance assessments addressing identified safety needs.

During and after the end of ConCorD various national programs will be able to evaluate cooperatively the long-term behaviour of container materials to such an extent as to be able to ensure confidence in the performance of engineered barriers. Such progress will particularly benefit early-stage programmes and those with a small inventory. An Expert Review Group will review and provide guidance on the scientific work performed. Emphasis will be given to issues relevant to end user needs and repository implementation, while ensuring that the generation of information is implementable and useful for performance assessment.

This document contains the content and learning outcomes of training materials developed based on the SotA (deliverable 15.1). Training materials are in the form of lectures divided over three topics related to the ConCorD project. In general, the target audience for all lectures are people that have already a basic background in corrosion but want to learn more details about a topic outside their field. For example, beginning PhD students/scientist in the field. This enables people to gain a broad basic background in studying corrosion processes related to nuclear waste disposal. A more detailed technical training or practical sessions that cover different modelling tools can be developed depending on the needs of future Training Event organizers. In principle, the slides can be used on a stand-alone basis to learn the main principles, however, more subtle information will be gained if the slides are taught by a lecturer. At the end of the project, the lectures will be updated with relevant results.

1.1 Environmental factors altering the corrosion behaviour

1.1.1 Content of the presentation

The corrosion of container materials has been extensively studied under constant conditions. However, the environment is not constant but the evolution of the chemistry of the repository environment in the period after its closure will depend mainly on two factors: the engineered barriers and the composition of groundwater. After facility closure, the thermal phase of the development of the repository is important, with a typical example being the saturation rate of the bentonite barrier leading to swelling and the development of mechanical stresses on the container. Such transients can be further influenced by attempts at repository footprint optimisation (e.g., increased container heat production). The corrosion of container materials has been usually studied under constant conditions and the translation of the
experimental result to the evolving chemical, mechanical and redox conditions of the early post-closure period needs to be verified and complemented. The different transients and their impact on the corrosion behaviour are discussed in the lectures. Two different transients, studied in the ConCorD project are discussed in more detail, namely possible effect of irradiation and of microbial activity. An example of a large in situ experiment studying several transient processes is given at the end of the presentation.

### 1.1.2 Learning outcomes

Following this presentation, people are able to:

- Understand the function of the waste container in the disposal of HLW/SF
- Sum up the different container concepts & expected exposure conditions
- Identify the different transient process in the near field environment
- Comprehend the effect of transient processes on the corrosion behavior of waste containers

### 1.1.3 Further reading


### 1.2 Novel material solutions for nuclear waste disposal container concepts

#### 1.2.1 Content of the presentation

The understanding of degradation mechanisms and resulting container durability estimates is mature and has been demonstrated for already existing disposal concepts envisaging the use of copper (e.g. Sweden, Finland, Canada) and carbon steel in a clay environment (e.g. France, Switzerland, Japan, Czech Republic). These materials are called “traditional materials” but are also the ones on which “corrosion allowance” designs are based, i.e. materials that corrode slowly and in a uniform and predictable manner. The second type of materials under consideration are the “novel materials”, which
are typically subject to very low corrosion rates. The lecture provides an overview of different "novel materials" under consideration and corrosion processes are discussed in more detail.

### 1.2.2 Learning outcomes
Following this presentation, people are able to:

- Understand the advantages & disadvantages of the use of ceramic/metallic materials in nuclear waste disposal
- Identify the current knowledge gaps of the use of ceramic/metallic materials in nuclear waste disposal
- Give an historical overview of the use of ceramic materials in nuclear waste disposal

### 1.2.3 Further reading

### 1.3 Prediction tools for assessment of long-time barrier integrity

#### 1.3.1 Content of the presentation
Development of models to predict container failure times and the development of a thorough mechanistic understanding of the corrosion processes involved have progressed significantly over the past 40 years. An overview is given of several generic corrosion modelling approaches for general corrosion and localized corrosion. For each, the assumptions, advantages and disadvantages are given. Furthermore, detailed examples of modelling processes related to copper and steel containers are provided. In a second part of the lecture, detailed information on integration of corrosion processes in performance assessments are discussed.

#### 1.3.2 Learning outcomes
Following this presentation, people are able to:

- Identify principles of different modelling approaches for several corrosion processes
- Understand advantages & disadvantages of different modelling tools
- Compare processes relevant for copper & steel containers
- Understand how corrosion processes can be integrated in performance assessments (PA)
- Get acquainted with basic modelling tools

#### 1.3.3 Further reading
EURAD Deliverable 15.3 – Training Materials

Appendix A. Environmental factors altering the corrosion behaviour
Appendix B. Novel material solutions for nuclear waste disposal container concepts
Appendix C. Prediction tools for assessment of long-time barrier integrity
References


H12 : Project to establish the scientific and technical basis for HLW disposal in Japan : second progress report on research and development for the geological disposal of HLW in Japan, Japan Nuclear Cycle Development Institute


King, F. (2011). TR-1069 Critical review of the literature on the corrosion of copper by water


Performance Assessment for the Proposed High-Level Radioactive Waste Repository at Yucca Mountain, Nevada  


Svensk Kärnbränslehantering, A. (2010) - Metodval - utvärdering av strategier och system för att ta hand om använt kärnbränsle. SKB R-10-25


ENVIRONMENTAL FACTORS AFFECTING THE CORROSION PROCESS
LEARNING OUTCOMES

• Understand the function of the waste container in the disposal of HLW/SF
• Sum up the different container concepts & expected exposure conditions
• Identify the different transient process in the near field environment
• Comprehend the effect of transient processes on the corrosion behavior of waste containers
CONTENT

• Introduction
• Thermal transients
• Pore water transients
• Redox transients
• Saturation transients
• Mechanical transients
• Transitional processes involving gas generation
• Effects of irradiation
• Effects of Microbial processes
• Example of an integrated test
• Summary
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- Example of an integrated test
- Summary
WASTE CONTAINER IS ESSENTIAL IN THE DISPOSAL OF HLW/SF

• Designed to contain, physically protect, and/or radiologically shield the waste form during the various activities involved during the period from conditioning until emplacement and closure of a disposal facility
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• Designed to contain, physically protect, and/or radiologically shield the waste form during the various activities involved during the period from conditioning until emplacement and closure of a disposal facility

• In some cases the container also plays a role in the near field containment of the radionuclides for a certain period after closure
WASTE CONTAINER IS ESSENTIAL IN THE DISPOSAL OF HLW/SF

- Designed to contain, physically protect, and/or radiologically shield the waste form during the various activities involved during the period from conditioning until emplacement and closure of a disposal facility
- In some cases the container also plays a role in the near field containment of the radionuclides for a certain period after closure
- Main parameters & control methods according to IAEA (2006):
  - Material itself
  - Geometric shape & dimensions
  - Design & operation of internal features
  - Lifting arrangements
  - Container internal corrosion
  - Container strength
  - Selection of surface coating & texture
  - Design & operation of closure features
  - Resistance to environmental conditions

DIFFERENT TYPES OF WASTE CONTAINERS EXIST

- Configuration & life time requirements depend on
  - Type of waste
  - Surrounding geological structure
  - Material used to increase canister integrity
## DIFFERENT CONTAINER CONCEPTS & EXPECTED EXPOSURE CONDITIONS

<table>
<thead>
<tr>
<th>WMO</th>
<th>Container concept</th>
<th>Estimated or target lifetime (year)</th>
<th>Nominal buffer dry density (g/cm³)</th>
<th>Max. canister temp. (°C)</th>
<th>Time to full nearfield saturation (year)</th>
<th>Max. surface absorbed dose (Gy/h)</th>
<th>Expected mechanical loads (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SKB</td>
<td>Cu-cast Fe</td>
<td>&gt;10⁶</td>
<td>1.6</td>
<td>95</td>
<td>Few 10s – few 1000</td>
<td>0.2</td>
<td>15 (glacial)</td>
</tr>
<tr>
<td>Posiva</td>
<td>Cu-cast Fe</td>
<td>&gt;10⁶</td>
<td>1.55</td>
<td>95</td>
<td>Few 10s – few 1000</td>
<td>0.3</td>
<td>14 (glacial)</td>
</tr>
<tr>
<td>Andra</td>
<td>Carbon steel</td>
<td>&gt;500</td>
<td>Cementitious buffer on the external face of the casing</td>
<td>90</td>
<td></td>
<td>10</td>
<td>10 Mpa (on casing)</td>
</tr>
<tr>
<td>Ondraf-Niras</td>
<td>Carbon steel</td>
<td>Several thousand</td>
<td>Cementitious buffer</td>
<td>100</td>
<td>5-10 to few 1000</td>
<td>25</td>
<td>8</td>
</tr>
<tr>
<td>Nagra</td>
<td>Carbon steel</td>
<td>10000</td>
<td>&gt;1.45</td>
<td>±120</td>
<td>Few centuries</td>
<td>0.2</td>
<td>22-29 max</td>
</tr>
<tr>
<td>SURAO</td>
<td>Carbon steel</td>
<td>10000</td>
<td>1.4</td>
<td>95</td>
<td>100</td>
<td>0.3</td>
<td>20</td>
</tr>
<tr>
<td>NMWO</td>
<td>Cu-coated steel</td>
<td>&gt;10⁶</td>
<td>1.6</td>
<td>85</td>
<td>50-5000 ~ host rock dependent</td>
<td>0.8</td>
<td>15 (glacial)</td>
</tr>
<tr>
<td>NUMO</td>
<td>Carbon steel</td>
<td>&gt;1000</td>
<td>1.6</td>
<td>100</td>
<td>&lt;1000 ~ host rock dependent</td>
<td>0.006-0.011</td>
<td>11 (hard rock)</td>
</tr>
</tbody>
</table>
Detailed knowledge of mechanisms under environmental conditions in the near-field of the container is necessary.

Figure based on King, F., Sanderson, D., Watson, S. 2016. Durability of High-Level Waste and Spent Fuel Disposal Containers – an overview of the combined effect of chemical and mechanical degradation mechanisms. AMEC Report 17697/TR/03
CORROSION UNDER ENVIRONMENTAL TRANSIENTS

- Corrosion behavior depends on:
  - Container material
  - Environmental conditions
Corrosion behavior depends on:

- Container material
- Environmental conditions

Evolution depends on:

- EBS
- O₂
- Radiation
- Phase change
CORROSION UNDER ENVIRONMENTAL TRANSIENTS

- Corrosion behavior depends on:
  - Container material
  - Environmental conditions

- Constant conditions extensively studied ↔ transient conditions
CORROSION UNDER ENVIRONMENTAL TRANSIENTS

- Corrosion evolutionary path (CEP) → time-dependent corrosion behavior of the container
  - Closely tied to the evolution of environmental conditions
  - Corrosion potential ($E_{corr}$) is a useful indicator
CORROSION UNDER ENVIRONMENTAL TRANSIENTS

- Corrosion evolutionary path (CEP) \(\rightarrow\) time-dependent corrosion behavior of the container
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  - Corrosion potential \((E_{\text{corr}})\) is a useful indicator
    - Example: Evolution in sealed repository containing a limited amount of entrapped \(\text{O}_2\).

Corrosion under environmental transients

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$E_{\text{CORR}}$ is relatively noble (positive) because of the cathodic reduction of $O_2$ and because of the possible spatial separation of anodic and cathodic processes.

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Fe(III) corrosion products formed during the aerobic phase are reductively dissolved to Fe(II) species.

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Fe(III) corrosion products formed during the aerobic phase are reductively dissolved to Fe(II) species.

Relative rates of Fe dissolution and the reduction of $H_2O$, resulting in $E_{\text{CORR}}$ values close to the $H_2/H_2O$ equilibrium.

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• Transitional processes involving gas generation
• Effects of irradiation
• Effects of Microbial processes
• Example of an integrated test
• Summary
THERMAL TRANSIENT

• Sources:
  • Ambient temperature ↑ with depth
  • Waste

• Longest transient but with slower changes
THERMAL TRANSIENT

• **Sources:**
  - Ambient temperature ↑ with depth
  - Waste

• Longest transient but with slower changes

  Thermal gradient between container_buffer – buffer/rock boundary

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Concentration gradient among aqueous solutes

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  Concentration gradient among aqueous solutes

  Secondary minerals can precipitate onto surfaces of primary clay minerals

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If significant changes in mass transfer → individual clay particles cemented in secondary solids
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Could irreversibly alter the swelling pressure & other properties of the buffer

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PORE WATER TRANSIENTS

- Corrosion $\rightarrow$ contact of water with container surface
- Chemistry is modified by backfill/groundwater interactions

Typically highly compacted bentonite or cementitious backfill
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  - Deliquescence of salt contaminants
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  • Episodic fracture flow
  • Dripping into open drifts
  • Deliquescence of salt contaminants
    • Temp & RH depends on type of salt deposit
  $\Rightarrow$ Non-uniform wetting of the surface
PORE WATER TRANSIENTS

• Species important for corrosion:
  • Cl⁻
  • $\text{SO}_4^{2-} \rightarrow \text{HS}^-$
  • $\text{CO}_3^{2-}/\text{HCO}_3^-$
    • pH buffering
    • passivating certain metals (e.g. Cu or C-steel)
  • pH → alkaline pH → passivation of C-steel
  • Cations (Ca²⁺, Mg²⁺)
    • hydrolyze to produce aggressive environments
    • promote formation of protective mineralized surface films
  • $\text{NH}_4^+$ stress corrosion cracking of Cu alloys

PORE WATER TRANSIENTS: EXPERIMENTAL WORK

- 10 year modelling of chemistry of MX-80 during saturation and heating (up to 130 °C)
  - pH ↓ with saturation

PORE WATER TRANSIENTS: EXPERIMENTAL WORK

• 10 year modelling of chemistry of MX-80 during saturation and heating (up to 130 °C)
  • pH ↓ with saturation

• Influence of Ca-Mg-bentonite chemistry in contact with granitic groundwater after the thermal phase
  • $[\text{Cl}^-] \downarrow \rightarrow \text{pH} \uparrow \rightarrow$ aggressive behavior ↓


• 496 days, 1.72 g/cm³ dry density, initial water content 16%
  • No water penetration into the column beyond the area where > 100°C
  • Advection, interlayer exchange & dissolution/precipitation processes conditioned the composition of the pore water along the column
  • Na–SO₄²⁻ → Na–Cl type near the heater
  • Changes in cation content could be explained by changes in smectite interlayer & mineral phases equilibrium
  • No significant alteration of smectite or other mineral phases of the bentonite

PORE WATER TRANSIENTS: EXPERIMENTAL WORK

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  - No significant alteration of smectite or other mineral phases of the bentonite

- 7.6 years, 1.64 g/cm³ dry density, initial water content 13.8%
  - Overall degree of saturation: 92 %
  - Gradient of water content & dry density along the column
  - Advection, interlayer exchange & dissolution/precipitation processes conditioned the composition of the pore water along the column
  - Exchangeable complex of smectite changed
  - Na–SO₄²⁻ → Na–Cl type near the heater
  - Physical properties not irreversibly affected

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**REDOX TRANSIENTS**

- Most important species undergoing redox reactions contain:
  - C, Fe, S, N species (gases + dissolved components + solids + components associated with solids by ion exchange)


Anticipated corrosion behavior of various materials as a function of redox conditions (expressed as a corrosion potential): P—pitting; MIC—microbially-induced corrosion; SCC—stress corrosion cracking; CC—crevice corrosion; HIC—hydrogen-induced cracking; GC—general corrosion; E—embrittlement.
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  - C, Fe, S, N species (gases + dissolved components + solids + components associated with solids by ion exchange)
  - Determined by $O_2$
    - $O_2$ trapped in pore space
    - Oxidizing species produced by the radiolysis of water (↓ in absence of $O_2$)

---


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REDOX TRANSIENTS

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- Determined by O\(_2\)
  - O\(_2\) trapped in pore space
  - Oxidizing species produced by the radiolysis of water (↓ in absence of O\(_2\))
  - Consumed by:
    - Diffusion in the surrounding rock
    - Reaction with mineral phases in buffer & backfill materials
    - Corrosion
    - Microbial activity

- O\(_2\) consumption in time predictions vary from a few year to a few centuries

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  - C, Fe, S, N species (gases + dissolved components + solids + components associated with solids by ion exchange)
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  - $O_2$ trapped in pore space
  - Oxidizing species produced by the radiolysis of water (absence of $O_2$)
- Consumed by:
  - Diffusion in the surrounding rock
  - Reaction with mineral phases in buffer & backfill materials
  - Corrosion
  - Microbial activity
- $O_2$ consumption in time predictions vary from a few years to a few centuries
- If all the $O_2$ initially present reacts uniformly with the steel containers $\rightarrow$ max. corroded depth would be $< 100 \mu m$

REDOX TRANSIENTS: EXPERIMENTAL WORK

- FE-G experiment @ Mont Terri
  - Very rapid $O_2$ consumption
    - By the bentonite buffer
    - In the EDZ

REDOX TRANSIENTS: EXPERIMENTAL WORK

• FE-G experiment @ Mont Terri
  • Very rapid $O_2$ consumption
    • By the bentonite buffer
    • In the EDZ

• COx argillaceous rock @ Meuse/Haute-Marne URL
  • $O_2$ consumption by
    • Pyrite oxidation
    • Calcite dissolution


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SATURATION TRANSIENTS

• When & what form of corrosion occur

Time: 100 - 1000 years to few 10 000 years in low permeability sedimentary host rocks

SATURATION TRANSIENTS

• When & what form of corrosion occur

Time: 100 - 1000 years to few 10 000 years in low permeability sedimentary host rocks

• Localized corrosion due to deliquescence of salts
• Non-uniform wetting
• Rate of supply of gaseous reactants higher ↔ rate of removal dissolved corrosion products ↓ → formation of protective film ↑
SATURATION TRANSIENTS

- Re-saturation rate controlled by intrinsic permeability & water saturation of surrounding rock
SATURATION TRANSIENTS

• Re-saturation rate controlled by intrinsic permeability & water saturation of surrounding rock

• Thermal load → acceleration of generation & diffusion H$_2$O vapor

Figure based on Wilson, J., Savage, D., Bond, A., Watson, S., Pusch, R., Bennett, D. 2011. Bentonite. A Review of key properties, processes and issues for consideration in the UK context. Quintesa report QRS-1378ZG-1
SATURATION TRANSIENTS

- Re-saturation rate controlled by intrinsic permeability & water saturation of surrounding rock
- Thermal load → acceleration of generation & diffusion H₂O vapor

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Large heat source
Low H₂O availability

Large sections of bentonite are dried + high temp inner annulus

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Large heat source → Low H₂O availability

→ Large sections of bentonite are dried + high temp inner annulus
→ Intense desiccation in warmest part microstructural collapse
→ Expandability & self-healing capacity of affected part of the buffer can be permanently damaged

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- Thermal load $\rightarrow$ acceleration of generation & diffusion $\text{H}_2\text{O}$ vapor

- Accumulation $\text{Cl}^-$ & $\text{SO}_4^{2-}$ salts
- Driving away dissolved silica
  - Container corrosion
  - Radial variation clay density
  - Porosity changes

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• Summary
MECHANICAL TRANSIENTS

- Exposure to residual & applied stresses $\rightarrow$ environmentally assisted cracking
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20-50 MPa

Repository design

Host rock formation
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Self-supporting rock:
- swelling pressure of highly compacted bentonite backfill
- hydrostatic pressure after saturation
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• hydrostatic pressure
• lithostatic pressure
MECHANICAL TRANSIENTS

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Host rock formation

- Thick-walled container designs
- In some designs: internal pressurization due to the diffusion of hydrogen produced by anaerobic corrosion through the wall of a carbon steel container

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TRANSITIONAL PROCESSES INVOLVING GAS GENERATION

- Anaerobic corrosion of C-steel:
  - \( \text{Fe} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + \text{H}_2 \)
  - \( 3\text{Fe(OH)}_2 \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} + \text{H}_2 \)

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Use of low-strength steel container & the nature of the repository environment
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Absorption of $\text{HNO}_3$ formed by the radiolysis of humid air by liquid droplets on a non-uniformly wetted surface

Radiolysis of humid air during a period when the container surface is dry

Absorption of HNO₃ formed by the radiolysis of humid air by liquid droplets on a non-uniformly wetted surface

Radiolysis of humid air during a period when the container surface is dry

Saturated conditions

Radiolysis of N₂H₂O following consumption of the initially trapped O₂ & radiolysis of liquid droplets following re-wetting of the container surface

Radiolysis of a thin surface water layer following complete wetting of the surface, with continued radiolysis of a humid N₂-H₂O atmosphere

Radiolysis of a bulk aqueous phase following complete saturation of the buffer box

EFFECT OF IRRADIATION ON THE CORROSION OF COPPER CONTAINERS

• Dose rate ↔ total dose → impact on
  • design of experiments
  • interpretation of results
  • how to make long-term predictions
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Figure from King, F. and M. Behazin (2021). "A Review of the Effect of Irradiation on the Corrosion of Copper-Coated Used Fuel Containers." Corrosion and Materials Degradation 2(4).
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    • Unsaturated conditions → surface area copper/volume aqueous phase is high
      • affect relative influence of interfacial & homogenous processes
      • high dose rate (470-500 Gy/h) → No direct role for radiolytically produced HNO₃ in increased corrosion
      • low dose rate (0.35 Gy/h) → little impact over experimental timescales and within the measurement accuracy

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RADIOLYSIS TRANSIENTS IN THE NEAR-FIELD

• Effects of γ-irradiation on the corrosion behavior of Cu container
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- Radiation damage of Cu corrosion barrier negligible
EFFECT OF IRRADIATION ON C-STEEL CONTAINERS

- Water radiolysis products $\rightarrow E_{\text{corr}} \uparrow$
- Passivating film of magnetite & hematite
EFFECT OF IRRADIATION ON C-STEEL CONTAINERS

• Water radiolysis products $\rightarrow E_{corr}$ ↑

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• Factors that can have an impact on corrosion behavior under irradiation
  • Water & vapor hydration:
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    • Max. corrosion rate observed for RH of 45 % ↔ 95 % without irradiation
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  - Change the radiolysis products
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• Irradiation source
  • Change the radiolysis products
    • High Linear Energy Transfer (LET) radiation: molecules $\uparrow$ + radicals $\downarrow$ ↔ low LET radiation: radicals $\uparrow$
  • Buffer-container system
    • $\gamma$-irradiation + high temperature $\rightarrow$ insignificant changes of the smectite content & physical properties of MX-80 bentonite after 1 y
    • Extensive pitting corrosion

EFFECT OF IRRADIATION ON C-STEEL CONTAINERS

• Factors with limited or no impact on corrosion behavior under irradiation
  • Steel composition & microstructure
    • Except chromium & low molybdenum steels
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  • Steel composition & microstructure
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    • Determines amount of corrosion products & oxide layer thickness
  • Total dose & dose rate
    • Limited in time, corrosion rates often evolve toward those in unirradiated conditions
    • Quite high doses rates (kGy/h) range are necessary to show corrosion enhancement
EFFECT OF IRRADIATION ON BUFFER MATERIALS

• Intact container ↔ container failure
  • $\gamma \leftrightarrow \alpha$
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  - Electron beam of 200 keV → amorphization dose depends on type of clay but requires extremely high doses, many orders of magnitude higher than possible in the repository
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  • Radiation decreases temp. at which dehydroxylation occurs

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  • No deleterious effect on clay stability of a created gas phase

EFFECT OF IRRADIATION ON BUFFER MATERIALS

• Influence of radiation source efficiency to induce amorphization
  • Heavy ions → atomic displacements & collision cascades → origin of extended defects & amorphization
  • Ionizing radiation → thermally unstable electronic point defects

• Influence of dose rate & total dose
  • Very high doses are needed to induce changes, vastly in excess of what is possible in a repository
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Anodic corrosion

Anode: $M^0 \leftrightarrow M^{2+} + 2e^- \ (M= Fe \ or \ Cu)$

Cathode: $2H_2O + 2e^- \leftrightarrow H_2 + 2OH^-$

Biofilm needed

Only relevant in the absence of bentonite backfill

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consumed by microorganisms

cathodic depolarization

Corrosive by-products of microbial metabolism

Sulfide oxidation
Manganese oxidation
Iron oxidation
Sulfate reduction
Iron reduction
Production acidic compounds

Biofilm needed

Only relevant in the absence of bentonite backfill

DISSIMILATORY SULFATE REDUCTION

CMIC

\[ 4 \text{H}_2 + \text{SO}_4^{2-} + 2 \text{H}^+ \leftrightarrow \text{H}_2\text{S} + 4 \text{H}_2\text{O} \]

\[ 2 \text{CH}_2\text{O} + \text{SO}_4^{2-} + 2\text{H}^+ \leftrightarrow \text{H}_2\text{S} + 2 \text{CO}_2 + 2 \text{H}_2\text{O} \]

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Fe⁰ + H₂S → FeS + H₂

3 H₂ + SO₄²⁻ + Fe⁰ + 2 H⁺ → FeS + 4 H₂O

2 CH₂O + SO₄²⁻ + Fe⁰ + 2 H⁺ → FeS + 2 CO₂ + H₂ + 2 H₂O

Protective layer
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Protective layer

Decelerate in time, except when FeS film is disrupted

Can take place as long as a diffusion path for H$_2$S to the metal container exists
DISSIMILATORY SULFATE REDUCTION

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\]

\[
3 \text{H}_2 + \text{SO}_4^{2-} + \text{Fe}^0 + 2 \text{H}^+ \rightarrow \text{FeS} + 4 \text{H}_2\text{O}
\]

\[
2 \text{CH}_2\text{O} + \text{SO}_4^{2-} + \text{Fe}^0 + 2 \text{H}^+ \rightarrow \text{FeS} + 2 \text{CO}_2 + \text{H}_2 + 2 \text{H}_2\text{O}
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EMIC

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\[
4 \text{Fe}^0 + \text{SO}_4^{2-} + 10 \text{H}^+ \rightarrow 4 \text{Fe}^{2+} + \text{H}_2\text{S} + 4 \text{H}_2\text{O}
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\text{Fe}^{2+} + \text{H}_2\text{S} \leftrightarrow \text{FeS} + 2 \text{H}^+
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\[
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Protective layer

Decelerate in time, except when FeS film is disrupted

Can take place as long as a diffusion path for H2S to the metal container exists
DISSIMILATORY SULFATE REDUCTION

**CMIC**

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Protective layer

Decelerate in time, except when FeS film is disrupted

Can take place as long as a diffusion path for H$_2$S to the metal container exists

No protective layer: conductivity of FeS crust allows the extraction of e$^-$ from metallic iron & their transport through the FeS faster

Unlikely that biofilms will develop on container surfaces
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Which of the 2
MICROBIAL INDUCED CORROSION: EXPERIMENTAL WORK


C-steel coupon

Olkiluoto groundwater

3 & 8 months at RT or 6°C in anoxic conditions
MICROBIAL INDUCED CORROSION: EXPERIMENTAL WORK

- Biofilm formation on the surface of the coupons
- Pitting corrosion

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3 & 8 months at RT or 6°C in anoxic conditions

MICROBIAL INDUCED CORROSION: EXPERIMENTAL WORK

- Biofilm formation on the surface of the coupons
- Pitting corrosion
- Betaproteobacteria
- Iron oxidizers
- Iron reducers
- SRB

C-steel coupon

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3 & 8 months at RT or 6°C in anoxic conditions

MICROBIAL INDUCED CORROSION: EXPERIMENTAL WORK

• 47 days incubation
  • Strong corrosion in exp. with solution representative of the Callovo-Oxfordian (Cox) rock formation (=solution 15') where microorganisms were added
  • Cement-bentonite → decrease in corrosion
  • Embedding clay rock in cement/bentonite mix further decreased corrosion
  • Microbial community dominated by Firmicutes, including SRB
  • But SRB activity is inhibited by alkaline conditions

MICROBIAL INDUCED CORROSION: EXPERIMENTAL WORK

- IC experiment @ Mont Terri
  - Dismantled after 7 years
  - Several layers of corrosion products on metal surface/clay interface:
    - magnetite, goethite, lepidocrocite, akageneite, chukanovite, and siderite
    - Fe sulfide at various oxidation states & elemental S
    - Original surface replaced by FeS $\rightarrow$ MIC

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• IC-A experiment @ Mont Terri (still ongoing)
  • C-steel coupons in MX-80 with different dry density
  • No microbial impact on corrosion
    • No growth of SRB
      • due to persistence of O₂ in bentonite
      • bentonite is fully saturated when O₂ is depleted

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      • due to persistence of O₂ in bentonite
      • bentonite is fully saturated when O₂ is depleted
  • Indigenous bentonite community grew & persisted

IMPACT OF IRRADIATION ON MICROBIAL VIABILITY IN THE CONTEXT OF NUCLEAR WASTE DISPOSAL

- Direct irradiation
- Indirect irradiation

DNA damage
- Single strand break
- Double strand break

DNA repair mechanisms

- Enzymatic antioxidant process
- Non-enzymatic antioxidant process

polyplody: harbor >1 genome copy

ROS (Reactive Oxygen Species)
IMPACT OF IRRADIATION ON MICROBIAL VIABILITY IN THE CONTEXT OF NUCLEAR WASTE DISPOSAL

Overlaps with response to desiccation
Radiation sensitivity depends on:
- Acute or chronic irradiation
- Cell concentration
- Vegetative state
- Physiological features
- Genetic features

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Big differences between ≠ bacteria

Overlaps with response to desiccation
IMPACT OF IRRADIATION ON MICROBIAL VIABILITY

• Contaminated sites (e.g. Chernobyl, Hanford) harbor microbial community

• Chronic low dose exposure ↔ acute high dose rate
  • Soil biota exposed to 1h γ-irradiation every week during 6 weeks
    • 0.1 kGy/h/week
    • 1 kGy/h/week
    • 3 kGy/h/week

  Bacterial diversity ↓ ↔ fungi & algae diversity ↑

  Changes in community composition → potential radiation-tolerant groups were identified
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- Sediment exposed to $\gamma$-irradiation for 8 weeks was not restrictive for microbial processes
  - 0.5 Gy/h → 0.6 kGy
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- BaM Bentonite + granitic porewater VITA exposed to $\gamma$-irradiation for 9 weeks at 13 Gy/h (19.6 kGy) did not completely eliminate bacteria
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• 25 kGy for routine sterilization procedures of foodstuff & medical application
• ± 50 kGy to sterilize bentonite
• > 70 kGy might be needed to eliminate radiation resistant bacteria from soil
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SKB-3 concept (0.055 Gy/h) → 145 years before it is reached
INHIBITION OF MICROBIAL ACTIVITY AND GROWTH BY BENTONITE

- Uncompacted bentonite harbors diverse microbial community, including SRB
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• Compacted bentonite
  • High swelling pressure
  • Low water activity (<0.96) — Limit microbial activity
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    - Direct effects
    - Indirect effects → Diffusion limited nutrient transport

Figure from Rebata-Landa, V. and J. C. Santamarina (2006). “Mechanical Limits to Microbial Activity in Deep Sediments.” Geochemistry, Geophysics, Geosystems 7(11).
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• Depend on dry density
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  - Uniform dry density ≥ 1600 kg/m³ → microbial activity is limited
    - Fundamental basis of this limit?
    - Why is there a difference between different bentonites?

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INHIBITION OF MICROBIAL ACTIVITY AND GROWTH BY BENTONITE

• Nutrient limited environment
  • Low available organic carbon mainly composed of plant-derived waxes and highly recalcitrant aromatic carbon
  • Recent analysis
    • Alkanes
    • Toluene
    • Aromatic compounds

Biodegradable, but amount?
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    • Alkanes
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    • Aromatic compounds
  • Organic material in compacted bentonite is able to sustain SRB
    • Wyoming, Indian & Bulgarian
  • Autotrophic growth?
    • H₂ as electron donor & CO₂ as carbon source

Biodegradable, but amount?

1314-1368 kg/m³

MICROBIAL TRANSIENTS

- Nuclear waste repositories are considered inhospitable for microorganisms

- Presence of microorganisms demonstrated in several *in situ* tests under certain conditions

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• Introduction
• Thermal transients
• Pore water transients
• Redox transients
• Saturation transients
• Mechanical transients
• Transitional processes involving gas generation
• Effects of irradiation
• Effects of Microbial processes

• Example of an integrated test
• Summary
**EXAMPLE OF INTEGRATED TEST: FEBEX**

- **Full-scale Engineered Barriers Experiment**
  - *In situ* test @ Grimsel Test site in Switzerland
  - Mock-up test @ CIEMAT in Spain
  - Laboratory tests to complement large-scale tests

- **Thermal-hydrologic effects**
  - Thermal expansion of pore water
  - Geochemical conditions & corrosion products
  - Geomechanical properties & stress-state

---

EXAMPLE OF INTEGRATED TEST: FEBEX

- Pore water transients
  - Chemical composition of the pore water evolved with time as a function of hydration of the bentonite, which was affected by
    - temperature
    - the geochemical processes in the bentonite–water system
  - Comparison of chloride content data after dismantling of Heater #1 (5 years of experiment, open symbols) and Heater #2 (18 years of experiment, filled symbols)

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  - Comparison of chloride content data after dismantling of Heater #1 (5 years of experiment, open symbols) and Heater #2 (18 years of experiment, filled symbols)
  - Cl⁻ accumulation at the heater → Precipitation of GR-Cl (green rusts), other chloride salts and Cl⁻-bearing Fe³⁺ oxyhydroxide (akaganeite) observed after dismantling the FEBEX *in-situ* test
  - pH variations due to the thermo-hydraulic gradients in the bentonite barrier
  - Formate, acetate, oxalate only in samples near heater

EXAMPLE OF INTEGRATED TEST: FEBEX

- Redox transients: Proposed Fe diffusion mechanism at the steel-bentonite interface

  **initial state (stage 0)**
  - steel covered by a thin oxide layer (mostly magnetite)
  - bentonite unsaturated, main Fe species is structural Fe$^{3+}$

  **stage 1**
  - the bentonite is wet enough
  - aerobic corrosion of steel: generation Fe$^{3+}$ species at the surface of steel and in the corrosion layer
  - corrosion rate diminishes as the thickening corrosion layer limits O$_2$/H$_2$O diffusion to steel surface
  - bentonite itself limits the diffusion of oxygen toward steel

---

Figure from Hadi, J., P. Wersin, V. Serneels and J.-M. Greneche (2019). *Eighteen Years of Steel–Bentonite Interaction in the Febex In Situ Test at the Grimsel Test Site in Switzerland.* Clays and Clay Minerals 67(2).
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  **stage 2**

  - anaerobic corrosion of steel starts as soon as oxygen is depleted as the surface of steel, generation of Fe$^{2+}$ species:
    - \( \text{Fe}^{0} \rightarrow \text{Fe(OH)}_{2} \rightarrow \text{FeCO}_{3} \rightarrow \text{Fe}_{2} \text{CO}_{3} (\text{OH})_{2} \rightarrow \alpha-\gamma \text{-FeOOH} \)
    - Fe$^{2+}$ diffusion in bentonite starts, but competes with O$_2$ diffusion to the interface (oxidation to Fe$^{3+}$ and fixation)
    - Fe$^{2+}$ is accumulated at the vicinity of the interface in notable amounts (≥ to the initial Fe content), mainly as Fe$^{3+}$ bearing species
    - Fe$^{2+}$ diffusion across the corrosion layer through electron transfers (i.e. sorption of one Fe$^{2+}$ on one side and release of another Fe$^{2+}$ on the other side)

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- Fe$^{2+}$ → Fe$^{3+}$
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 stage 2

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  - Fe$^{2+}$ diffusion in the bentonite starts, but competes with O$_2$ diffusion to the interface (oxidation to Fe$^{3+}$ and fixation)

 stage 3

- Oxygen has been completely depleted
- Fe$^{2+}$ diffusion in the corrosion product free zone of the bentonite (blue) is now only controlled by ion exchange, edge sorption and to a lesser extent sorption/electron exchange with structural iron
- Fe$^{3+}$ is accumulated at the vicinity of the interface, and also further deeper in the bentonite but in lower quantities (only a small portion of initially present Fe$_0$ < 10%) mainly sorbed on the clay edges
- electron transfers also possible across the zones rich in corrosion products

Figure from Hadi, J., P. Wersin, V. Serneels and J.-M. Grenache (2019). *Eighteen Years of Steel–Bentonite Interaction in the Febex in Situ Test at the Grimsel Test Site in Switzerland.* Clays and Clay Minerals 67(2).
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- Mechanical load increases with saturation
  - Depends on:
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    - Temperature
    - Pore water composition

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  - Depends on:
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- Gas generation
  - Corrosion of metallic compounds
    - Consumes $O_2$, $H_2O$ and $CO_2$
    - Produces $H_2$
  - Degradation organic compounds
    - Consumes $O_2$
    - Produces $H_2$, $CO_2$, $CO$ & $CH_4$

EXAMPLE OF INTEGRATED TEST: FEBEX

- Microbial community
  - very few or no cultivable cells from the sections around & adjacent to the heater
    - Temp.: 84 - 99 °C
    - dry densities: 1.6 - 1.7 g/cm³
  - significantly higher number of cultivable cells on different media: SRB, NRB and IRB
    - Temp 20-30 °C
    - dry density 1.4-1.5 g/cm³
    - the water content >20%
  - Viable ↔ activity
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OVERVIEW: GENERIC SCHEME OF 4 IDENTIFIED PHASES & EXPECTED CORROSION PRODUCTS
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1: aerobic dry

- Uniform dry oxidation $\rightarrow$ FeO$_2$
- Redistribution of salts $\rightarrow$ salt precipitation assisted by desiccation $\rightarrow$ swelling pressure around periphery of the tunnel
OVERVIEW: GENERIC SCHEME OF 4 IDENTIFIED PHASES & EXPECTED CORROSION PRODUCTS

1: aerobic dry

- RH reaches critical value for formation of thin films of moisture on metal surface → start aqueous corrosion

2: aerobic unsaturated
OVERVIEW: GENERIC SCHEME OF 4 IDENTIFIED PHASES & EXPECTED CORROSION PRODUCTS

1: aerobic dry

2: aerobic unsaturated

3: anoxic unsaturated
OVERVIEW: GENERIC SCHEME OF 4 IDENTIFIED PHASES & EXPECTED CORROSION PRODUCTS

1: aerobic dry
2: aerobic unsaturated
3: anoxic unsaturated
4: cool, anoxic saturated
FURTHER READING

NOVEL MATERIAL SOLUTIONS FOR NUCLEAR WASTE DISPOSAL CONTAINER CONCEPTS
LEARNING OUTCOMES

• Understand the advantages & disadvantages of the use of ceramic/metallic materials in nuclear waste disposal

• Identify the current knowledge gaps of the use of ceramic/metallic materials in nuclear waste disposal

• Give an historical overview of the use of ceramic materials in nuclear waste disposal
CONTENTS

• Introduction

• Alumina solutions: historical overview
  • SKB, Swedish concept
  • Lawrence Livermore National Laboratory, USA
  • BNL/Nucon, USA
  • Andra, France

• Silicon carbide concept

• Ceramic coatings
  • Titanium oxide
  • Chromium nitride

• Metallic containers

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WASTE CONTAINER IS ESSENTIAL IN THE DISPOSAL OF HLW/SF

- Designed to contain, physically protect, and/or radiologically shield the waste form during the various activities involved during the period from conditioning until emplacement and closure of a disposal facility.
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- In some cases the container also plays a role in the near field containment of the radionuclides for a certain period after closure.
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- In some cases the container also plays a role in the near field containment of the radionuclides for a certain period after closure

- Main parameters & control methods according to IAEA (2006):
  - Material itself
  - Geometric shape & dimensions
  - Design & operation of internal features
  - Lifting arrangements
  - Container internal corrosion
  - Container strength
  - Selection of surface coating & texture
  - Design & operation of closure features
  - Resistance to environmental conditions
DIFFERENT TYPES OF WASTE CONTAINERS EXIST

- Configuration & life time requirements depend on
  - Type of waste
  - Surrounding geological structure
  - Material used to increase canister integrity

NAGRA

ANDRA

SKB/POSIVA

CANADA
# DIFFERENT CONTAINER CONCEPTS & EXPECTED EXPOSURE CONDITIONS

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<thead>
<tr>
<th>WMO</th>
<th>Container concept</th>
<th>Estimated or target lifetime (year)</th>
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Although studied very well, they also have some disadvantages → study alternative materials
CERAMIC MATERIALS & COATINGS

- First interest in the 1970s >> early 2000s
  - Insufficient motivation to invest in the research
  - Insufficient customer demand

half-scale model of Al$_2$O$_3$/SiO$_2$ VHLW container

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• Lack of gas generation

• Variable compressive strength

• Variable hardness

• Low tensile strength

• Low toughness (except in form of composites)

• Manufacturing challenges:
  • Efficient handling of very large lumps in the green state just after shaping
  • Achieving adequate density with section thicknesses of 50 mm
  • R&D is needed to obtain effective sealing of thick ceramics
    • Funding is limited to the nuclear waste disposal community
POTENTIAL CERAMICS CANDIDATES

• Alumina (Al$_2$O$_3$)
• Alumina in combination with silicon oxide (SiO$_2$)
• Silicon carbide (SiC)
• Silicon nitride (Si$_3$N$_4$)
• Partially stabilized zirconia
• Titania (TiO$_2$)
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- Chemical stability
- Reasonable mechanical properties
- Availability
EXISTING MATERIALS & PROCESSES

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  • Chemically inert
  • Good mechanical strength
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  - Zirconia toughened alumina → mechanical properties ↑
  - Alumina containing tetragonal zirconia → hydrothermal aging of zirconia ↓
  - Mechanical properties > alumina
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• **Silicon carbide**
  - Light, tough, refractory material
  - Chemically resistant in acid & alkaline environments
  - Industrially produced at some scale but porous
  - Possible corrosion in geological environments
EXISTING MATERIALS & PROCESSES

• Silicate materials

  • Interest in
    • Silica
    • Mullite
    • Forsterite
    • Cordierite

    High level of glassy phase
    • Facilitates densification
    • Chemical resistance ↓
    • Alters mechanical properties
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  - Sinters at lower temperatures
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  - Addition of TiO₂ → thermal gradients → cracks
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- Graphite
  - Porous : density 80 – 92 %
  - Can be filled by vapor deposition of SiC but expensive & time consuming
CONTENTS

• Introduction

• Alumina solutions: historical overview
  • SKB, Swedish concept
  • Lawrence Livermore National Laboratory, USA
  • BNL/Nucon, USA
  • Andra, France

• Silicon carbide concept

• Ceramic coatings
  • Titanium oxide
  • Chromium nitride

• Metallic containers

• Metallic coatings

• Outlook
ALUMINA SOLUTIONS: SKB, SWEDISH CONCEPT (1977)

- Waste can be stored in a single cavity or in multiple separated ones

Figure adapted from Larker, H. (1980). Method of Containing Spent Nuclear Fuel or High-Level Nuclear Fuel Waste, United States
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- Alumina powder compacted by hot isostatic pressing (1300°C – 1400°C; 0.5 – 2 kbar)
- Gas-tight metal casing, joined by isostatic pressing
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**Diagram Description**
- Ceramic dome-shaped cover
- Welds
- Ceramic powder layer
- Support plate
- Thermal insulating material
- Waste
- Metal cover
- Ceramic container
- Sheet metal bottom
- Welds

**Mechanical reinforcement of sealing area**
**Limit temperature in the vicinity of the waste**
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ALUMINA SOLUTIONS: LAWRENCE LIVERMORE NATIONAL LABORATORY, USA (EARLY 1990)

• Specifications:
  • Cylindrical containers placed nose to nose in horizontal tunnels
  • No transport function
  • Storage of spent fuel assemblies or vitrified waste
  • Identifiable & retrievable for 50 years
  • Leak proof for 300-1000 years
  • Closure system feasible remotely in a hot cell without thermal damage to the waste package

• Two exploratory routes:
  • Solid ceramic containers
  • Composite containers: metal structure + ceramic coating/liner

https://en.wikipedia.org/wiki/Yucca_Mountain_nuclear_waste_repository
• **Selection criteria**

  - Good tensile strength and impact resistance of the material
  - High toughness material
  - Dense material with no open pores or cracks
  - Joint or weld areas must have the same properties as the body material
  - Good chemical resistance of the material in the storage environment
  - Sufficient thermal conductivity to remove heat from the waste
  - Use of conventional processes requiring only minor adaptations
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Highlights difficulty of manufacturing large ceramic parts
**ALUMINA SOLUTIONS: BNL/NUCON, USA (LATE 1990)**

- Onion-like system

Figure adapted from Rockhvarger, A.E., Khizh, A.B. 1998. Large size, thick-walled ceramic containers. NUCON SYSTEMS INC, Patent WO9844834
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![Diagram of onion-like system with layers labeled as follows:
- outer ceramic lid
- graphite-boron ore & barite grain powder mixture
- inner ceramic lid
- ceramic or metal-grain powder dense pack shrouds solid waste
- joints
- bolts
- half flanges
- outer ceramic vessel
- inner ceramic vessel
- wire reinforced metal-foil basket
- metal wire reinforced foil bag
- aluminium honeycomb mitigation layer
- outer protective steel shell

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• Onion-like system

ALUMINA SOLUTIONS: BNL/NUCON, USA (LATE 1990)

- Radiation shield
- Mechanical corrosion barrier
- Thermal, chemical & radioactive protection

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- Depending on the size of the waste

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Watertight sealing of ceramic containers made of MgAl$_2$O$_4$ using microwave process

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- Addition of ceramic fibers
  - Mechanical reinforcement of the container
  - Favor the thermal treatment of the material
  - Increase radiological properties of the container

• Development & characterization of alumino-silicate ceramics >> conventional silicate ceramics
  • Suitable chemical durability → thickness reduction of ~ 3 – 4 mm over 1000 years
  • Adapted design of a container for HLW
  • Adapted casting, drying & sintering processes


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• Closure of the system?
  • Focus on the sealing technology
  • Two major constraints to preserve the containment properties of the glass matrix
    • Max surface temperature of the ceramic container of 600-700 °C
    • Heating technology localized to the closure area
  • Microwaves & interaction of ceramic materials to assemble ceramic parts

Figure from Baroux, C. and C. Martin (2016), Summary Report of the Preliminary Feasibility Study for Ceramic Hiw Overpacks, Andra Report CG.RP.ASCM.13.0023
ALUMINA SOLUTIONS: ANDRA, FRANCE (2007-ONGOING)

- It is possible to:
  - Improve the quality of the ceramic/glass sealing interface via a two-stage enameling process:
    - Firing in a conventional furnace → sealing the enameled parts by microwave heat treatment
  - Confirm that the selected and tested glasses have processing temperatures compatible with the constraints imposed by the presence of the primary package
  - Confirm the feasibility of sealing by microwave heating
  - Improve the quality of the joints for heating under minimal load
  - Verify the viability of the process
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• Considerations for the design & testing of a first prototype
  • Production of a prototype furnace for testing the annular shapes of test bodies and the localized heating of these parts
  • Understanding the resistance of the ceramic to the thermal gradients resulting from localized heating
  • Improve the coupling with the microwaves
  • Optimization of the compositions of sealing glasses to reinforce their mechanical and leaching resistance
SILICON CARBIDE CONCEPT

• Until recently only possible to manufacture large pieces out of:
  • Silicon impregnated silicon carbide
  • Recrystallized silicon carbide
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• R&D under geological disposal conditions is needed

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• Outlook
SILICON CARBIDE CONCEPT

- Interconnecting SiC segments:
  - Laser joining method → no pretreatment necessary

Joining process of SiC-capsule

SiC compact

SILICON CARBIDE CONCEPT

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  Laser joining diagram:
  - Laser
  - Waste
  - Brazing zone
  - Cooled area
  - SiC fiber reinforced SiC matrix composites
  - Coating solder
  - Pre-joint
  - Heat treatment
  - Crack propagation path

  Joint layer

  brazed at 1300°C

  1350°C

  1400°C


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  • Inherent brittleness
  • Mismatch of the thermal expansion coefficient with the underlying steel
  • Requirement for relatively large thickness
  • Very low porosity
  • Damage tolerance
• Methods needs to be developed for
  • Covering the lid-to-container weld
  • Coating repair

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- Physical vapor deposition

CERAMIC COATINGS: TITANIUM OXIDE-BASED COATINGS

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• Coating thickness of 12 µm:
  • Slower corrosion correlated with coating porosity ↓
  • Corrosion current density decreased by 2.5-3 orders of magnitude

• TiO$_2$ films deposited on MgCa$_2$Zn$_1$Gd$_3$ effectively protected this alloy from corrosion in Ringer’s solution at 37 °C
CERAMIC COATINGS: TITANIUM OXIDE-BASED COATINGS

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  • Slower corrosion correlated with coating porosity ↓
  • Corrosion current density decreased by 2.5-3 orders of magnitude

• TiO$_2$ films deposited on MgCa$_2$Zn$_1$Gd$_3$ effectively protected this alloy from corrosion in Ringer’s solution at 37 °C

• Titanium oxide coatings deposited by PVD methods are promising for corrosion protection of the low carbon steel containers

• Additional studies are needed on long-term corrosion processes under relevant geological disposal conditions

CERAMIC COATINGS: CHROMIUM NITRIDE COATINGS
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• High hardness
• Excellent wear resistance
• High corrosion resistance
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CONTENTS

• Introduction

• Alumina solutions: historical overview
  • SKB, Swedish concept
  • Lawrence Livermore National Laboratory, USA
  • BNL/Nucon, USA
  • Andra, France

• Silicon carbide concept

• Ceramic coatings
  • Titanium oxide
  • Chromium nitride

• Metallic containers

• Metallic coatings

• Outlook
# METALLIC CONTAINERS: OVERVIEW OF CURRENT CONCEPTS AND PLANNED INNOVATIONS FOR STORAGE CONTAINERS

<table>
<thead>
<tr>
<th>Material</th>
<th>+</th>
<th>-</th>
<th>e.g. Countries</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low alloyed steel</td>
<td>• Cost</td>
<td>• Corrosion resistance &lt; copper but low</td>
<td>France, Japan, Switzerland</td>
<td>Carbon steel</td>
</tr>
<tr>
<td></td>
<td>• Fabrication</td>
<td>• SCC</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Mechanical strength</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Radiation shielding</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stainless steel</td>
<td>Corrosion resistance (passive film)</td>
<td>• Localized corrosion</td>
<td>UK, Spain, Japan, USA</td>
<td>Focus on austenitic alloys</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Some classes SCC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Titanium</td>
<td>Corrosion resistance</td>
<td>• Crevice corrosion in O₂ phase</td>
<td>Canada, Belgium, Japan</td>
<td>Alloys with Pd or Ru could avoid crevice corrosion</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• HIC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nickel alloys</td>
<td>• Corrosion resistance</td>
<td>• Localized corrosion in certain</td>
<td>Germany, Belgium, USA,</td>
<td>Ni-Cr-Mo or Ni-Fe-Cr-Mo</td>
</tr>
<tr>
<td></td>
<td></td>
<td>environments</td>
<td>Argentina</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Mechanical properties in high-temp</td>
<td>• Uncertainties associated with MIC</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>applications</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Fabrication</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>• Corrosion resistance</td>
<td>cost</td>
<td>UK, Japan, Sweden, Finland, Canada, Switzerland</td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Mechanical properties</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>• Cost</td>
<td>• Corrosion behavior?</td>
<td>Argentina, Brazil, Russia</td>
<td>Not considered</td>
</tr>
<tr>
<td></td>
<td>• Radiation shielding</td>
<td>• Mechanical strength?</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Environmental aspects?</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

METALLIC COATINGS

• Titanium, chromium & copper

• Open questions:
  • Required thickness to exclude through porosity
  • Effect of through defects and irradiation on corrosion resistance
METALLIC COATINGS

• Titanium, chromium & copper

• Open questions:
  • Required thickness to exclude through porosity
  • Effect of through defects and irradiation on corrosion resistance

• Dual-wall container with copper coating:
  • Copper layer is directly on the steel vessel → no gap between layers → no fabrication issues
  • ↔ standard design → gap between outer copper layer and cast iron insert can introduce creep & SCC of the copper shell
  • Welding joint could be covered after welding steel cover

Canadian design of dual wall-container
COPPER DEPOSITION PROCESSES

- **Electrodeposition**
  - To coat 95% of the container

- **Cold gas dynamic spray**
  - To coat the region of the closure weld
  - Production of metal deposits
  - Metal-ceramic coatings:
    - Corrosion resistance ↑
    - Mechanical properties ↑
    - Wear resistance ↑

Figure adapted from Alkhimov, A. P., V. F. Kosarev, S. V. Klinkov, A. A. Sova, G. V. Trubacheev and V. N. Zaikovsky (2012). "Conical Separation Zone Formation at Impingement of Supersonic Jet on Obstacle under Cold Spraying." Thermophysics and Aeromechanics 19(2).
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    • Corrosion resistance ↑
    • Mechanical properties ↑
    • Wear resistance ↑

• Quality of the coating depends on:
  • Nozzle displacement
  • Carrier gas type & velocity

Figure adapted from Alkhimov, A. P., V. F. Kosarev, S. V. Klinkov, A. A. Sova, G. V. Trubacheev and V. N. Zaikovsky (2012). "Conical Separation Zone Formation at Impingement of Supersonic Jet on Obstacle under Cold Spraying." Thermophysics and Aeromechanics 19(2).
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OUTLOOK

• Each concept has advantages & disadvantages
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• Diversity of the envisaged solutions leads to a large variability of experiments needed
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  • Ceramics
    • Production of large-scale pieces
    • Optimization of the sintering process
    • Optimization of the sealing process
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    • How do they behave in relevant geological disposal conditions?
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    - Optimization of the sealing process
  - Alternative copper grades (DLP, XLP or HCP copper)
    - How do they behave in relevant geological disposal conditions?
  - Coatings
    - Damage resistance
    - Long-term corrosion data & archaeological analogues do not exist
    - Development new metal/ceramic coatings
FURTHER READING

• https://www.ejp-eurad.eu/publications/eurad-d151-concord-initial-sota


PREDICTION TOOLS FOR ASSESSMENT OF LONG-TIME BARRIER INTEGRITY
LEARNING OUTCOMES

• Identify principles of different modelling approaches for several corrosion processes
• Understand advantages & disadvantages of different modelling tools
• Compare processes relevant for copper & steel containers
• Understand how corrosion processes can be integrated in performance assessments (PA)
• Get acquainted with basic modelling tools
CONTENT

• Introduction

• Copper container corrosion
  • Reactive transport models in bentonite
  • Modeling sulfide fluxes
  • Modelling irradiation-induced corrosion

• Steel-bentonite models
  • Integration of corrosion phenomena in performance assessments
  • Performance assessments for copper-based canister corrosion
  • Performance assessments for iron-based alloy canister corrosion
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MODELLING CORROSION PROCESSES AIMS

• Predict the durability of the disposal container

• Provide a key input into performance assessments

• Consolidate & demonstrate scientific understanding of the processes involved in the evolution of the disposal container

• Underpin the treatment of container durability PAs
<table>
<thead>
<tr>
<th>Method</th>
<th>Principle</th>
<th>Assumptions</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical extrapolation</td>
<td>Extrapolate corrosion rate short-term lab exp. to long-term corrosion rates</td>
<td>• Stable environmental conditions</td>
<td>• Built-in conservatism</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• No step changes in corrosion mechanisms</td>
<td>• Useful to consider validation with archaeological analogues</td>
</tr>
<tr>
<td>Mass balance</td>
<td>With O₂ → amount of O₂ after closure determines extent of corrosion</td>
<td></td>
<td>Anaerobic corrosion → corrosion rate is not determined by the total</td>
</tr>
<tr>
<td></td>
<td>Without O₂ → anaerobic corrosion</td>
<td></td>
<td>available mass of the cathodic reactant</td>
</tr>
<tr>
<td>Mass transport</td>
<td>Corrosion rate determined by rate of supply of the corrodent</td>
<td>• Correct calculation of the mass transport</td>
<td>Also the mass transport of corrosion products could be limiting</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Reactant is irreversibly consumed in the corrosion reaction</td>
<td></td>
</tr>
<tr>
<td>Reactive transport</td>
<td>Use of available software systems to perform equilibrium &amp; kinetic reaction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>modeling (e.g. PhreeqcRM, Geochemist Workbench)</td>
<td>calculations for reactive transport simulators</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## GENERIC CORROSION MODELLING APPROACHES: LOCALIZED CORROSION

<table>
<thead>
<tr>
<th>Method</th>
<th>Principle</th>
<th>Remarks</th>
<th>Disadvantages</th>
</tr>
</thead>
</table>
| **Pitting factors**           | Max. loss of thickness on a surface/average loss of thickness on the same surface | • For surfaces that exhibit true corrosion pits or uneven/patchy general corrosion  
• Can be measured over the short-term | Long-term data estimated using archaeological analogues → direct applicability?                      |
| **Empirical roughening factor** | Provide a topographical model of a corroded surface not necessarily based on mechanistic understanding | Assume the production of a given surface profile that deviates from the mean line of the surface within a predefined constraint | Not suitable for true corrosion pitting of passive materials                                      |
| **Empirical localized corrosion growth rate** | Measure pit depths ∼ time → develop growth rate curve → develop model e.g. $P = kt^n$ | Reasonable accuracy over comparatively long-time scales if transient conditions are well-known | No prediction of localized corrosion rates or penetration depth over time  
• Large database necessary                                                                 |
| **Electrochemical prediction** | Comparison of the free corrosion potential with the critical potential for localized corrosion | Reasonable accuracy over comparatively long-time scales if transient conditions are well-known |  
  

MODELLING CHEMISTRY WITHIN SITES OF LOCALIZED CORROSION

- Models to predict the chemistry within cracks and crevices
- To understand fundamental processes within sites of localized corrosion
- No reliable predictions of growth rates
- Defining & justifying the size of the coupled cathode
STATISTICAL APPROACHES

- To analyze experimental results from pitting corrosion studies
- To analyze inspection results to estimate corrosion rates
STATISTICAL APPROACHES

- To analyze experimental results from pitting corrosion studies
- To analyze inspection results to estimate corrosion rates
- Extreme value statistics
  - Extrapolation from small test coupons or inspection sites to real structures
  - Pitting corrosion → max pit depth over time
  - Very conservative
STATISTICAL APPROACHES

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• To analyze inspection results to estimate corrosion rates

• Extreme value statistics
  • Extrapolation from small test coupons or inspection sites to real structures
  • Pitting corrosion → max pit depth over time
  • Very conservative

• Probabilistic assessment of pitting corrosion of copper containers based on:
  • Consideration of breakdown & repassivation potentials for pitting of copper
  • Predicted evolution of the environment
  • Combined with machine learning techniques

Figure from Briggs, S., C. Lilja and F. King (2021). "Probabilistic Model for Pitting of Copper Canisters." Materials and Corrosion 72(1-2).
THERMODYNAMIC MODELLING OF ENVIRONMENTAL CHEMISTRY

• To predict the conditions under which a given metal may react with a given environment leading to the formation of dissolved ions or solid reaction products

• To predict properties of a system in equilibrium or how equilibrium is reached

• No corrosion rate
THERMODYNAMIC MODELLING OF ENVIRONMENTAL CHEMISTRY

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• No corrosion rate

• Pourbaix diagrams
  • Potential – pH stability diagrams

Pourbaix diagram for the Cu–H₂O system at 25°C including the regions of stability of Cu(OH)₅⁺ for various surface coverages θ

Figure from King, F. (2011). Tr-1069 Critical Review of the Literature on the Corrosion of Copper by Water.
**Reactive Transport Models**

- Estimate max. amount of corrosion
- Species of interest & transport-related factors:
  - Sources
  - Sinks
- Assumptions:
  - Zero-concentration boundary condition
  - Gradual accumulation over time

Figure from King, F., M. Kolář, I. Puigdomenech, P. Pitkänen and C. Lilja (2021). “Modeling Microbial Sulfate Reduction and the Consequences for Corrosion of Copper Canisters.” Materials and Corrosion 72(1-2).
ARTIFICIAL INTELLIGENCE: NEURAL NETWORKS

• Principle:
  • Set up series of artificial neurons in a layered structure ~ brain

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• If several variables control the behavior of the system in a non-linear manner

• Software is commercially available

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- If several variables control the behavior of the system in a non-linear manner

- Software is commercially available

- No physical understanding of the processes & mechanisms

- Large data set needed
ARTIFICIAL INTELLIGENCE: NEURAL NETWORKS

• When can it be used?
  • To map out the regions of stability and environmental conditions
  • To analyze data from monitoring sensors
  • To predict time of failure as a function of multiple variables

Effect of temperature on crack growth rate in Alloy 600 in PWR primary coolant as a function of stress intensity factor for different values of yield strength.

ARTIFICIAL INTELLIGENCE: NEURAL NETWORKS

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  • To map out the regions of stability and environmental conditions
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• Program of experimental research needed to generate data under disposal conditions:
  • Measurement of breakdown or pitting potentials using electrochemical techniques
  • Measurement of electrochemical noise
  • Execution of a matrix of experiments to map out conditions that lead to corrosion as a function of key variables

Effect of temperature on crack growth rate in Alloy 600 in PWR primary coolant as a function of stress intensity factor for different values of yield strength

MODELLING CORROSION PROCESSES CHALLENGES

• Numerous methods exist for making long-term predictions
  • ‘Simple’ extrapolation of empirical corrosion rates ↔ sophisticated numerical models

References:
MODELLING CORROSION PROCESSES CHALLENGES

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• Justification of extremely long-term predictions
  • How much confidence do we have in the estimated container lifetime?
  • How robust is the prediction?

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- Confidence building by:
  - Simplification of performance through repository design
  - Development of alternative models
  - For some container materials, the study of archaeological and natural analogs
  - Large scale, in situ tests under realistic repository conditions

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Generate sound mechanistic understanding of the underlying corrosion processes
• Introduction

• **Copper container corrosion**
  • Reactive transport models in bentonite
  • Modeling sulfide fluxes
  • Modelling irradiation-induced corrosion

• **Steel-bentonite models**

• **Integration of corrosion phenomena in performance assessments**

• **Performance assessments for copper-based canister corrosion**

• **Performance assessments for iron-based alloy canister corrosion**
COPPER CONTAINER CORROSION

- Copper corrosion model (CCM)
  - Uniform copper corrosion focusing on Cl⁻ and O₂ transport-controlled corrosion


j: diffusive fluxes
k: rate constants
COPPER CONTAINER CORROSION

- Copper corrosion model (CCM)
  - Uniform copper corrosion focusing on Cl⁻ and O₂ transport-controlled corrosion
  - Has been progressively updated, e.g. copper sulfide model (CSM)

COPPER CONTAINER CORROSION: REACTIVE TRANSPORT MODELS IN BENTONITE

• Limited mass transport rate in compacted bentonite → corrosion influenced by diffusion coefficient of dissolved species
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  1. Table of values of available porosity, effective diffusivity & distribution coefficients for 38 elements & oxidation states
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     • Electrical double layer: size is coupled with ionic strength of pore water (computationally demanding)
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  5. Simplified multi-porosity model
     • Effective diffusion coefficient as a function of bentonite dry density & ionic strength
     • Interlayer porosity is devoid of anions
VALIDATION OF THE MODELS WITH $^{36}\text{Cl}$ IN THE BHA VAULT OF THE SFL REPOSITORY (SE)

- Implemented in Comsol Multiphysics version 5.3

![Graph showing Max. $^{36}\text{Cl}$ flux (Bq/year) x 10^8]

- Position of the 2D studied domain (in red) referred to the 2D cross-sectional view of the BHA vault.
  1) Theoretical tunnel contour.
  2) Bentonite pellets.
  3) Grout.
  4) Concrete structure for the operating period (0.5 meter).
  5) Granite pillars.
  6) Waste containers.
  7) Bentonite blocks. Approximate dimensions: 
     - A = 20.6 m, B = 18.5 m, C = 16 m, D = 2.3 m, E = 2.4 m, F = 4 m, G = 3.7 m.

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![Graph showing Max. $^{36}\text{Cl}$ flux (Bq/year) x 10^8 for empiric, semi-empiric, and mechanistic categories.]

Lack of detailed description of several necessary parameters

overestimation

Position of the 2D studied domain (in red) referred to the 2D cross-sectional view of the BHA vault. 1) Theoretical tunnel contour. 2) Bentonite pellets. 3) Grout. 4) Concrete structure for the operating period (0.5 meter). 5) Granite pillars. 6) Waste containers. 7) Bentonite blocks. Approximate dimensions: $A = 20.6 \text{ m}$, $B = 18.5 \text{ m}$, $C = 16 \text{ m}$, $D = 2.3 \text{ m}$, $E = 2.4 \text{ m}$, $F = 4 \text{ m}$, $G = 3.7 \text{ m}$.

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<thead>
<tr>
<th>Max. $^{36}$Cl$^-$ flux (Bq/year) $\times 10^8$</th>
<th>empiric</th>
<th>semi-empiric</th>
<th>mechanistic</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.5</td>
<td>2</td>
<td>3.5</td>
</tr>
<tr>
<td>2</td>
<td>1.4</td>
<td>2.5</td>
<td>3</td>
</tr>
<tr>
<td>3</td>
<td>1.3</td>
<td>2.4</td>
<td>3.2</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>2.1</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>1.2</td>
<td>2.3</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Lack of detailed description of several necessary parameters

Most reliable because parameters obtained specifically for chloride diffusion through bentonite.

But not sensitive to the ionic strength of background solution

Position of the 2D studied domain (in red) referred to the 2D cross-sectional view of the BHA vault. 1) Theoretical tunnel contour. 2) Bentonite pellets. 3) Grout. 4) Concrete structure for the operating period (0.5 meter). 5) Granite pillars. 6) Waste containers. 7) Bentonite blocks. Approximate dimensions:

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- $G = 3.7$ m

VALIDATION OF THE MODELS WITH $^{36}$Cl IN THE BHA VAULT OF THE SFL REPOSITORY (SE)

- Implemented in Comsol Multiphysics version 5.3

![Graph showing empirical, semi-empirical, and mechanistic models for $^{36}$Cl flux]

Position of the 2D studied domain (in red) referred to the 2D cross-sectional view of the BHA vault. 1) Theoretical tunnel contour. 2) Bentonite pellets. 3) Grout. 4) Concrete structure for the operating period (0.5 meter). 5) Granite pillars. 6) Waste containers. 7) Bentonite blocks. Approximate dimensions: $A = 20.6$ m, $B = 18.5$ m, $C = 16$ m, $D = 2.3$ m, $E = 2.4$ m, $F = 4$ m, $G = 3.7$ m.

Lack of detailed description of several necessary parameters

Most reliable because parameters obtained specifically for chloride diffusion through bentonite.

But not sensitive to the ionic strength of background solution

If ionic strength differs significantly from the base Case value of value used here

COPPER CONTAINER CORROSION: REACTIVE TRANSPORT MODELS IN BENTONITE

• Copper corrosion in container of KBS-3V repository
  • Dual continuum approaches:
    • Reactive transport modelling iCP framework: interface coupling Comsol Multiphysics & PhreeqC
    • Adapted PFLOTRAN: Nernst-Planck equation accounting for immobile charge & Donnan equilibrium → allowed a coupled transport simulation of all components while preserving different diffusivities depending on their charge & concentration of the electrolyte
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Possible when relevant sulfide sources together with limited iron availability

MODELLING OF SULFIDE FLUXES IN THE EARLY TRANSIENT STAGE (2 PHASE FLOW)

• Geochemistry & thermal & hydrological conditions should be considered

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- Gaseous $\text{H}_2\text{S}$
  - Can be transported in during unsaturated period
  - Highly corrosive also in dry atmospheres
MODELLING OF MICROBIAL SULFIDE PRODUCTION

• Evolution in time:
  • 2006 assumed that in the initial phase:
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  • 2021 3D reactive transport sulfide model → kinetic Monod model for SRB
    • Max rate constant $5 \times 10^{-5}$ and $10^{-4}$ mol sulphide/L water
MODELLING THE INTERACTION OF SULFIDE WITH FE-BEARING MINERAL PHASE

• Extreme low solubility of pyrite → rate constant for anaerobic dissolution of pyrite excluded from CSM
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  • Biotite (K(Mg₀.₆₋₁.₈Fe²⁺₂.₄₋₁.₂)(Si₃Al)O₁₀(OH,F)₂):
    • Initially present in backfill & rock layers
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  • Pyrite (FeS₂):
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• 3D reactive transport model for safety case of the spent fuel repository in Olkiluoto (Finland):
  - Main sources are ferric (oxyhydr)oxides
    - Fe$^{3+}$ + HS$^-$ $\rightarrow$ S + polysulfides + Fe$^{2+}$ $\rightarrow$ FeS

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https://www.mcpa-software.com
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  • full set of chemical reactions describing radiation chemistry of water + reaction of Cu oxidized by O₂
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    • Catalytic decomposition of radiolytically produced H₂O₂ on the oxide surface

• FACSIMILE → modelling complex reaction kinetics (https://www.mcpa-software.com)

Account for the observed corrosion in the experiment
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• Comsol Multiphysics $\rightarrow$ complete set of kinetic reactions dealing with recombination of H$_2$O radiolysis species

Account for the observed corrosion in the experiment.
• Introduction

• Copper container corrosion
  • Reactive transport models in bentonite
  • Modeling sulfide fluxes
  • Modelling irradiation-induced corrosion

• **Steel-bentonite models**
  • Integration of corrosion phenomena in performance assessments
  • Performance assessments for copper-based canister corrosion
  • Performance assessments for iron-based alloy canister corrosion
STEEL – BENTONITE MODELS

• Focused on the geochemical aspects of bentonite alteration
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• Most recent models include
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  • Modifications of mineral properties
  • Transport properties
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  - Corrosion rate
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  - Porosity clogging is considered in some simulations under different assumptions
  - Complete inhibition of the corrosion process has never been observed
STEEL – BENTONITE MODELS

• Hydrogen has been ignored in current simulations
  • Catalyst for chemical reduction of aqueous sulfate but thermal sulfate reduction by $\text{H}_2$ is inconsequential at the temperatures and pressures in the repository
  • Damage EBS structures
  • Transport of gaseous radionuclides to the biosphere
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  - Numerical code implemented in CALIPSO
  - 2 interfaces bound the oxide layer
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  - Estimate lifetime of the carbon steel overpack & pressure increase from H$_2$

STEEL – BENTONITE MODELS

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  • Coupled with geochemistry-transport code, Kirmat
    • Realistic representation of corrosion of iron & alteration clay
STEEL – BENTONITE MODELS

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  • Coupled with geochemistry-transport code, Kirmat
    • Realistic representation of corrosion of iron & alteration clay
• Two-phase modelling
  • Consumption of H₂O by corrosion >> diffusion of H₂O through bentonite → shrinkage micro-fractures in bentonite acting as preferential pathways for corrosion products

During saturation water diffuses through the bentonite towards the steel surface.

The anaerobic corrosion of iron leads to the production of magnetite and Fe²⁺ ions. The cathodic reaction is the reduction of H₂O producing H₂. Fe²⁺ diffuses into the bentonite resulting in an iron enriched zone.

Fe²⁺ is oxidized by residual O₂ leading to precipitation of red Fe(III) corrosion products. The magnetite remains unaffected because the O₂ is not mobile.

The high rate of water consumption and H₂ production leads to local dessication and shrinkage microfractures because the hydraulic conductivity of saturated bentonite is low.

Fe²⁺ and H₂ continuously produced by corrosion preferentially diffuse along the shrinkage microfractures into the bentonite.

Fe²⁺ reacts with residual O₂ at the walls of the microfractures and precipitates as Fe(III). As the corrosion product layer grows the corrosion rate decreases and the bentonite resaturates. The microfractures cannot re-seal because their walls are coated with Fe(III).
## COMPARISON OF MAIN ASSUMPTIONS & RESULTS OF EXISTING MODELLING EXERCISES AT DISPOSAL SCALE AT FE-MX80 BENTONITE INTERFACE

<table>
<thead>
<tr>
<th>$T$ ($^\circ$C)</th>
<th>Simulation time (years)</th>
<th>Corrosion rate</th>
<th>Assumptions</th>
<th>Main secondary minerals</th>
<th>Max. perturbation extent</th>
<th>Relevant results</th>
</tr>
</thead>
</table>
| 50             | 10,000                  | Constant (4.3 μm/y) | • 1D diffusive model  
• Porosity feedback effect | Cronstedtite  
Berthierine | 5 cm | Porosity clogging after 5,000 years |
| 100            | 500,000                 | Constant (1 μm/y) | • 1D model (Test case D0)  
• Porosity update  
• Clay reactions are considered  
• Use of cation exchange and surface complexation | Cronstedtite  
Berthierine | Few cm | Interaction of Fe with bentonite spatially limited for very long times $\rightarrow$ Fe clay re-precipitation & diffusional limitation |
| -              | 1,000,000               | Constant (~2 μm/y) | • Time-dependent variation of reactive surface areas for the Fe-bearing minerals  
• The sequence of the alteration of the clay by Fe-rich fluids may proceed via an Ostwald step sequence | Cronstedtite  
Berthierine | - | • Secondary minerals evolution $\neq$ predicted by the fixed surface area model  
• Sequence of precipitation: magnetite-
cronstedtite-berthierine-chlorite |
| 100            | 100,000                 | Decreases from 5 to 0.2 μm/y | • Porosity update  
• Clay reactions are considered | Fe-chlorite  
Fe-saponite  
Berthierine | 15 cm | Porosity clogging after 100,000 years |
| 100            | 10,000                  | Decreases from 5 to 0.2 μm/y | • Porosity update  
• Clay reactions are considered  
• - & + influence of the reactive surface areas of the primary minerals | Greenalite  
Fe-saponite  
Fe-chlorite  
Berthierine | 10 cm | Large surface area primary clay minerals provides a significant porosity ↓ in the zone in contact with the steel overpack $\rightarrow$ limited the diffusion aqueous corrosion products toward the bentonite barrier $\rightarrow$ porosity ↓ & mineralogical transformation in the bentonite zone close to the bentonite/steel overpack interface. |
<table>
<thead>
<tr>
<th>T (ºC)</th>
<th>Simulation time (years)</th>
<th>Corrosion rate</th>
<th>Assumptions</th>
<th>Main secondary minerals</th>
<th>Max. perturbation extent</th>
<th>Relevant results</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>300.000</td>
<td>Constant (0.2 μm/y)</td>
<td>• 1D and 2D model • No reactivity for clay minerals • Use of cation exchange &amp; surface complexation</td>
<td>Siderite Goethite</td>
<td>7 cm</td>
<td>• Magnetite precipitation (no clogging) → bentonite porosity ↓ • Proton surface complexation is highly effective in buffering pH in bentonite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Constant (0.1 μm/y) &amp; $\phi$ (max. 0.7 μm/y)</td>
<td>• 1D model • Use of cation exchange &amp; 3 types of sorption sites in the bentonite • Kinetically-controlled container corrosion &amp; magnetite precipitation</td>
<td>-</td>
<td>-</td>
<td>• Kinetically-controlled container corrosion → significant ↓ in the corrosion rate • [dissolved Fe] computed with kinetic magnetite precipitation is &lt; [obtained at equilibrium]</td>
</tr>
<tr>
<td>≠ 1.000.000</td>
<td>Constant (2 μm/y) &amp; $\phi$</td>
<td>• 1D model • Use of cation exchange &amp; 3 types of sorption sites in the bentonite • Kinetically-controlled container corrosion &amp; magnetite precipitation • Smectite dissolution is considered</td>
<td>Analcime Cronstedtite</td>
<td>7 cm</td>
<td>• Magnetite precipitation → bentonite porosity ↓ near the container (7 cm thickness of the zone of reduced porosity at 1 Ma) • Thickness: &lt; 5 cm for a corrosion rate of 5 μm/year - 12 cm for a rate of 0.5 mm/year. • Corrosion rate ~ chemical conditions → thickness ↑ when Smectite dissolution &amp; analcime precipitation → thickness ↓ 3 cm</td>
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<td>Gypsum Sepiolite</td>
<td>1 cm</td>
<td>• Pore clogging at the container-bentonite interface • Narrow alteration zones • Limited smectite dissolution after 1 Ma</td>
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<tr>
<td>70</td>
<td>100.000</td>
<td>Constant (1 μm/y) &amp; $\phi$ (M2)</td>
<td>• Model 1: fixed steel corrosion rate • Model 2: diffusion-limited corrosion rate • Model 3: corrosion cell approach</td>
<td>M1: Berthierine Fe-saponite Greenalite M2 and M3: Berthierine</td>
<td>2 cm</td>
<td>• Extent &amp; nature of the alteration predicted by the models sensitive to model conceptualization • M1 and M2: - M3: Magnetite Siderite</td>
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• Introduction

• Copper container corrosion
  • Reactive transport models in bentonite
  • Modeling sulfide fluxes
  • Modelling irradiation-induced corrosion

• Steel-bentonite models
  • Integration of corrosion phenomena in performance assessments
  • Performance assessments for copper-based canister corrosion
  • Performance assessments for iron-based alloy canister corrosion
INTEGRATION OF CORROSION PHENOMENA IN PERFORMANCE ASSESSMENTS

• Definition according to NRC in US:

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• No standardized prescriptive approach to include corrosion in PA → specific to each concept & environmental conditions

• General guidance of safety assessment provided by IAEA
COUNTRIES OPERATING NUCLEAR POWER PLANTS (36) & PROGRESS IN PA

- nuclear countries who performed/will perform PA
- nuclear countries who performed/will perform PA with WMO involved in ConCorD
- nuclear countries who plan deep geological disposal but didn't do PA
INTEGRATION OF CORROSION PHENOMENA IN PERFORMANCE ASSESSMENTS

• Variation between different disposal concepts but in general:

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• Variation between different disposal concepts but in general:
  
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  • Copper-based waste container ↔ iron-based container

CONTENT

• Introduction
• Copper container corrosion
• Steel-bentonite models
• Integration of corrosion phenomena in performance assessments

• Performance assessments for copper-based canister corrosion
  • Corrosion in unsaturated conditions
  • General corrosion
  • Localised corrosion
  • Radiation assisted corrosion
  • Microbially influenced corrosion
  • Environmental-assisted cracking
  • Mechanical degradation & combined corrosion-mechanical effects
  • In-situ testing of copper spent fuel canisters
  • Prediction of canister lifetimes and implications for PA

• Performance assessments for iron-based alloy canister corrosion
PA FOR COPPER-BASED CONTAINER CORROSION

- O₂-free copper → Sweden, Finland, Switzerland, Canada

Furthest developed concept: KBS-3 concept considered in Sweden & Finland

50 mm thick P-doped O₂-free Cu

Figure from SKB (2010) - Metodval - utvärdering av strategier och system för att ta hand om använt kärnbränsle. SKB. R-10-25
PA FOR COPPER-BASED CONTAINER CORROSION

- O$_2$-free copper → Sweden, Finland, Switzerland, Canada

Furthest developed concept: KBS-3 concept considered in Sweden & Finland

- Cu is not expected to passivate prediction lifetime based on general corrosion with moderate uniformity

50 mm thick P-doped O$_2$-free Cu

[oxidants]:
- trapped O$_2$
- radiolysis products
- Cu$^{2+}$ species

Time

predicted to last > 10$^5$ - 10$^6$ years
PA FOR COPPER-BASED CONTAINER CORROSION

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• Types of corrosion that need to be considered in PA:
  • Corrosion under unsaturated conditions
  • General corrosion
  • Localized corrosion
  • Microbial influenced corrosion
  • Environmentally assisted cracking
CORROSION IN UNSATURATED CONDITIONS

• Unsaturated phase: including any corrosion before emplacement in the buffer and within the buffer before groundwater re-saturation occurs

• Evaluated in KBS-3 environment

• Temp 50 °C → relative humidity < critical value of 50-70% ↔ dry air → corrosion rate ↑ with temp: 10s of nm/year if 50-150°C

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Extent of corrosion expected to be negligible
GENERAL CORROSION

• All oxygen in voids reaches container → highly conservative
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- KBS-3 design: 50% reaches surface → corrosion loss of 17 µm (max. 36 µm)
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Corrosion loss 106 µm = 123 µm total loss
GENERAL CORROSION

- Swiss concept

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• Conservative calculation for corrosion from trapped O\textsubscript{2} : 70 µm

• Mass transport approach for trapped O\textsubscript{2}
  • Cautious and sufficient (conservative)
  • Can be used in relevant scenarios including:
    • Deliberately or inadvertently unsealed tunnels during the GDF operational period
    • Access of glacial-melt water

GENERAL CORROSION

• - O$_2$

• Reactive transport modelling

\[
2 \text{Cu(s)} + \text{HS}^- + \text{OH}^- \rightarrow \text{Cu}_2\text{S}(s) + \text{H}_2\text{O} + e^- \\
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Corrosion of copper by HS$^-$ transport in groundwater evaluated by mass transport limitation
Equilibrium [HS$^-]$ determined by source & sink
GENERAL CORROSION

- Effect of buffer erosion from rock fracture on HS⁻ transport → mass transport modelling

<table>
<thead>
<tr>
<th>Intact buffer</th>
<th>Partially eroded buffer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Most pessimistic assumptions:</td>
</tr>
<tr>
<td></td>
<td>• [HS⁻] 0.12 mM</td>
</tr>
<tr>
<td></td>
<td>• flow rate ≥ 0.161 m/s</td>
</tr>
<tr>
<td></td>
<td>Failure (&gt; 47mm) could occur in 10⁵ years</td>
</tr>
<tr>
<td>[HS⁻] 0.01 mM</td>
<td>&lt; 0.001 µm/year</td>
</tr>
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<td>• [HS⁻] 0.01 mM</td>
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<td>• High flow rate 0.251 m/s</td>
</tr>
<tr>
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<td>Failure after 850 000 years</td>
</tr>
</tbody>
</table>

Figure redrawn from SKB 2010. Corrosion calculations report for the Safety Assessment SR-site. SKB Technical report TR-10-66, SKB.
LOCALIZED CORROSION

- Pitting corrosion → non-uniformal general corrosion
  - Only in aerobic early post closure phase

LOCALIZED CORROSION

- Pitting corrosion → non-uniform general corrosion
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- Under-deposit corrosion → form of crevice corrosion
  - underneath precipitated surface film that acts as selective ion exchange membrane to create permanent anodic region

CALCULATION METHODS OF LOCALIZED CORROSION IN PA

- Empirical pitting factor
  - Pitting factors from bronze-age artifacts i.e. 3000 years: 2-5
  - Pitting factors from 50-80 year buried lightening conductor plates: 0-5

→ Pessimistic pitting factor of 5 for buried copper containers

→ Overly conservative due to shift to more general corrosion → expected to decrease in time
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- **Extreme-value statistical analysis**
  - \( F(x) = \exp [-\exp (-ax + b)] \)

  KBS-3 design:
  - \( 10^6 \) chance of a pit exceeding 7.5 mm after \( 10^6 \) years
  - \( 10^6 \) chance of a pit exceeding 5 mm after just 10 years

  - Copper will not passivate under repository conditions → not meaningful to use
RADIATION ASSISTED CORROSION

- Radiolysis transients in the near-field

Absorption of $\text{HNO}_3$ formed by the radiolysis of humid air by liquid droplets on a non-uniformly wetted surface

Radiolysis of humid air during a period when the container surface is dry

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Radiolysis of a thin surface water layer following complete wetting of the surface, with continued radiolysis of a humid N$_2$-H$_2$O atmosphere

Radiolysis of a bulk aqueous phase following complete saturation of the buffer box

CALCULATION METHODS RADIATION ASSISTED CORROSION

• Mass balance of radiolytic produced oxidants
  • Unsaturated conditions:
    • calculation radiolytic yield/volume
    • assume oxidants produced will react
      → Used to calculate HNO₃ from γ-radiation in container buffer gap in KBS-3 concept
        • HNO₃ = \((G \times V \times ρ \times D_{0}/A_{v}) \times (T/\ln 2) \times (1−e^{−\ln 2 \cdot t/T})\)
        • 0.015 mol HNO₃ & corrosion depth < 7 nm
  • Saturated conditions:
    • Radiolysis of H₂O → H₂ + oxidants that can cause corrosion → assumptions:
      • volume around container where all oxidants reach surface
      • Moles of oxidants produced/moles of metals corroded uniformly fixed
    • KBS-3 concept: volume 5 mm and Cu is oxidized as efficiently as dissolved Fe²⁺ → 14 µm
RADIATION ASSISTED CORROSION

- Reasoned argument for exclusion
  - < 10 Gy/h → no or inhibiting effect
  - > 10 Gy/h → no consensus. No consistent effect of increasing cumulative dose
  - Mechanistic impact → dose rate is key factor influencing corrosion rate
  - Surface dose rate 0.055 Gy/h (KBS-3) – 1 Gy/h (Canadian design)
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• Mass transport
  • Pessimistically bounded by the supply of nutrients, i.e. organic matter
    • Assumptions 1D diffusion calculation for HS⁻ transport
      • [HS⁻] in backfill maintained at 0.1 mM
      • Diffusivity set as that for uncharged species
      • Corrosion on lid & topmost 10% of the container height
    • Canadian system corrosion allowance of 1 mm if buffer remains intact

• Corrosion depth of 2 mm
MICROBIOLOGICALLY INFLUENCED CORROSION

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• Reasoned arguments for exclusion
  • Swedish SR-Site & Finish safety case
    • High density of compacted bentonite
      • Low water activity
      • High swelling pressure
      • Lack of physical space
ENVIROMENTAL - ASSISTED CRACKING

• Stress corrosion cracking
  • Stress + aggressive ions + oxidizing ions → unlikely
  • No mechanistic arguments
  • Experimentally validated by mixed-potential modelling of $E_{\text{corr}}$ of copper
    • $E_{\text{corr}}$ & surface pH $\rightarrow$ CuO$_2$/CuO surface film not thermodynamically stable
  • Not considered in Canadian concept
    • pH & corrosion potential far from range in which SCC is feasible
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    • HS$^-$ transport sufficiently slow $\rightarrow$ corrosion transport-limited
    
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Reasoned arguments for non-susceptibility
MECHANICAL DEGRADATION & COMBINED CORROSION - MECHANICAL EFFECTS

• Modes of mechanical degradation
  • Fracture
    • brittle fracture → caused by some form of embrittlement
    • ductile fracture → cup & cone dimpled fracture structure
  • Plastic deformation
    • metal overloaded past its yield strength
    • avoided by container design i.e. wall thickness
  • Creep
    • Slow deformation under influence of an applied static load below the yield stress
    • O₂-free P-doped copper → higher creep ductility
MECHANICAL & MATERIAL-RELATED FACTORS LEADING TO CONTAINER FAILURE & THEIR RELATIONSHIP TO VARIOUS FAILURE MODES

Figure based on King, F., Sanderson, D., Watson, S. 2016. Durability of High-Level Waste and Spent Fuel Disposal Containers – an overview of the combined effect of chemical and mechanical degradation mechanisms. AMEC Report 17697/TR/03
IN-SITU TESTING OF COPPER SPENT FUEL CONTAINERS

• Prototype Repository Experiment
  • Simulate conditions in KBS-3 repository
    • 6 full-sized dual-shell copper containers within vertical deposition holes in contact with bentonite
    • containers heated

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    • 6 full-sized dual-shell copper containers within vertical deposition holes in contact with bentonite
    • containers heated
  • Shift to anaerobic conditions
  • Low level of corrosion
  • No microbial activity in bentonite buffer, low amount in backfill
PREDICTION OF CONTAINER LIFETIMES & IMPLICATIONS FOR PA

• KBS-3 concept
  • Max. corrosion loss by each mechanism over period of $10^6$ year
  • Absence erosion/corrosion scenarios $\rightarrow$ no process > few mm
  • Sum is expected to be overestimate of the true expected corrosion loss
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- **Canadian system**
  - Expected corrosion 0.27 mm over $10^6$ year (conservative max. of 1.02 mm)
    - Assuming fixed [HS] of 0.1 ppm at bentonite-rock interface for “expected value” and 1 ppm for “max value”

Illustration of cross sections for the Canadian used fuel container with relevant dimensions in μm for (A) the as-manufactured container; Maximum corrosion damage from non-uniform radiation-induced (light blue), radiation-induced (blue), non-uniform oxic (light green), oxic corrosion (green), sulphide corrosion (red), anoxic (purple), (C) current analysis, and (D) extreme upper bound.

### SUMMARY OF APPROACHES FOR CORROSION IN PA FOR COPPER CONTAINERS

<table>
<thead>
<tr>
<th>Mode of corrosion</th>
<th>Canada</th>
<th>Finland</th>
<th>Sweden</th>
<th>Switzerland</th>
<th>UK</th>
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<tbody>
<tr>
<td>Oxidic general corrosion</td>
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<td>Mass balance within corrosion allowance</td>
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<td>Radiolysis-induced corrosion</td>
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<td>Excluded or Mass balance within corrosion allowance</td>
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<td>Sulfide-induced anaerobic corrosion</td>
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<td>Mass transport controlled – key factor driving corrosion allowance</td>
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<td>MIC before saturation</td>
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<td>Excluded by reasoned argument</td>
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<td>SCC</td>
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<td>Excluded by reasoned argument</td>
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<tr>
<td>Pitting</td>
<td></td>
<td>Fixed corrosion allowance to account for surface roughening</td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>
• Introduction
• Copper container corrosion
• Steel-bentonite models
• Integration of corrosion phenomena in performance assessments
• Performance assessments for copper-based canister corrosion

• Performance assessments for iron-based alloy canister corrosion
  • Atmospheric corrosion
  • General corrosion
  • Localised corrosion
  • Radiation assisted corrosion
  • Microbially influenced corrosion
  • Environmental-assisted cracking
  • Weld corrosion
  • Prediction of canister lifetimes and implications for PA
PA FOR IRON-BASED ALLOY CONTAINER CORROSION

- Low strength, low carbon alloys but ≠ among countries
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$\rightarrow H_2$

buffer destabilization

French design

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LIFETIME CONTAINERS IN DIFFERENT CONCEPTS

- **Belgium:**
  - Supercontainer
  - 5000 years

- **Japan:**
  - Double walled
  - 1000 year

- **Czech Republic:**
  - Double walled:
    - inner stainless steel layer
    - outer carbon steel layer
  - 10000 years

- **Switzerland:**
  - 10000 year
ATMOSPHERIC CORROSION

• Dependent on the relative humidity
  • < 60 % RH → extremely slow
  • salts deposits

Schematic interpretation of the development of corrosion chemistry associated with NaCl crystals on a mild steel substrate below 76% RH

Upon initiation of corrosion (a), discrete chemistries develop at the anodic (orange) and cathodic (gray) sites (b), the extent to which is dependent on time and humidity level. At higher RH and longer times (c), puddles of catholyte develop on the surface that can substantially dissolve the NaCl crystals.

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- Fe (hydr)oxides → not expected to directly significantly undermine the integrity of the containers in environments of limited corrosivity
- Impact of layer of rust?

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UNIFORM GENERAL CORROSION

- Long-term anoxic conditions
- $\pm 1 \mu m/\text{year} \sim$ natural analogues $0.1 \mu m/\text{year}$
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  • outer carbon steel container:
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Japan
• Lab tests:
  • corrosion rates dropped after 1 year
  • linear for several years at 2 µm/year
  • 2 mm over 1000 year but pitting factor of 3 → 6 mm corrosion allowance
LOCALIZED CORROSION

• Only considered feasible in early oxic period
• Long-term field burial tests: pitting factors $100 \rightarrow 10$
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LOCALIZED CORROSION

• Belgian supercontainer
  • Risk if magnetite film break down
  • Examined using electrochemical measurements
    • Dependency on [Cl⁻]
    • Dependency on temp
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    - Dependency on [Cl-]
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Most aggressive conditions (1 M Cl, 85°C): lowest potential ± 200 mV
RADIATION-ASSISTED CORROSION

• Unsaturated ↔ saturated phase: $\text{HNO}_3 \leftrightarrow \text{H}_2\text{O}_2$

• Additional oxidation of steel by radiolysis products is small compared to general corrosion loss by $\text{H}_2\text{O}$ oxidation
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• Long-term corrosion tests Andra:
  • \( 80 \text{ Gy/h} \) → increase corrosion rate
  • \( 20 \text{ Gy/h} \) → no effect

  \[ \text{External surface dose rate} < 10 \text{ Gy/h} \]

• Swiss concept
  • Wall thickness container 14 cm → radiation shielding dose rate ±0.2 Gy/h

• Czech concept
  • 0.3 Gy/h

• Japanese concept
  • 80 mm shielding allowance → surface dose rate << 3 Gy/h

• Belgian concept
  • No effect on anaerobic corrosion rate up to 25 Gy/h
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NEGLIGIBLE EFFECT OF RADIOLYSIS
MICROBIOLOGICALLY INFLUENCED CORROSION

• High bentonite density/high pH expected to inhibit microbial activity $\rightarrow$ SRB only in far field

• Steel corrosion loss due to HS$^-$/flux $<<$ general anaerobic corrosion from $\text{H}_2\text{O}$ oxidation
  • Experiment in Opalinus Clay: 0.02 mm over 1000 years $\leftrightarrow$ 1 mm
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WELD CORROSION

• Japanese concept
  • additional 3 mm corrosion allowance for welded regions → undetected welding defect up to 3 mm depth
  • preferential weld corrosion mitigated by Ni doping on weld material
ENVIRONMENTAL ASSISTED CRACKING

- **Switzerland:**
  - SCC occurs in \( \text{HCO}_3^-/\text{CO}_3^{2-} \) at pH 6 and pH 10-11 ↔ pH bentonite porewater pH 7.3
  - Crack initiates → stifle due to absence of cyclic loading

- **Japan:**
  - Heat treatment on bulk material & welds eliminate or reduces tensile residual stresses

- **Belgium**
  - Slow strain testing at 140°C with [HS] up to 15.6 mM fraction properties of plain carbon steel ~ in argon
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SCC UNLIKELY TO OCCUR
PREDICTION OF CONTAINER LIFETIMES & IMPLICATIONS FOR PA

- Conservative approaches:
  - expected lifetime 1000-10000 year (<< copper)
  - >> corrosion:
    - 0.1 µm/year cementitious alkaline conditions
    - 1-2 µm/year in bentonite
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<th>UK</th>
<th>Czech republic</th>
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<tr>
<td>Anaerobic general</td>
<td>Empirical corrosion rate</td>
<td>Empirical corrosion rate and pitting factor</td>
<td>Empirical corrosion rate</td>
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<td>corrosion</td>
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<tr>
<td>Radiolysis-induced</td>
<td>Limit dose rate to</td>
<td>No effect for dose</td>
<td>Design requirement</td>
<td>Limit dose rate to</td>
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<tr>
<td>corrosion</td>
<td>10 Gy hr⁻¹</td>
<td>rate of 25 Gy hr⁻¹</td>
<td>(&lt;1 Gy hr⁻¹)</td>
<td>3 Gy hr⁻¹</td>
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<td>Localised corrosion</td>
<td>Reasoned argument based on</td>
<td>Reasoned argument based on passivity</td>
<td>Depth-dependent pitting factor</td>
<td>Mass balance and extreme value statistical analysis</td>
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<td>passivity of surface film</td>
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<td>Corrosion allowance based on mass transport</td>
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<td>Excluded by reasoned argument – negligible rate</td>
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FURTHER READING

• https://www.ejp-eurad.eu/publications/eurad-d151-concord-initial-sota


