Deliverable 15.3: Training materials

Work Package 15 ConCorD

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Disclaimer

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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.

Table of content

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

- https://www.ejp-eurad.eu/publications/eurad-d151-concord-initial-sota
- Allard, T., E. Balan, G. Calas, C. Fourdrin, E. Morichon and S. Sorieul (2012). Radiation-induced defects in clay minerals: A review. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms* 277: 112-120
- Dixon, D. (2019). Review of the THMC Properties of MX-80 Bentonite, NWMO-TR-2019-07
- Enning, D. and J. Garrelfs (2014). Corrosion of iron by sulfate-reducing bacteria: new views of an old problem. *Appl Environ Microbiol* 80: 1226-1236
- King, F. (2017). 13 - Nuclear waste canister materials: Corrosion behavior and long-term performance in geological repository systems. Geological Repository Systems for Safe Disposal of Spent Nuclear Fuels and Radioactive Waste (Second Edition). M. J. Apted and J. Ahn, Woodhead Publishing: 365-408
- 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: 678-707
- Fraser King, 2017 - 13 - Nuclear waste canister materials: Corrosion behavior and long-term performance in geological repository systems - doi.org/10.1016/B978-0-08-100642-9.00013-X
- Landolt, D., A. W. Davenport, J. H. Payer and D. W. Shoesmith (2011). A Review of Materials and Corrosion Issues Regarding Canisters for Disposal of Spent Fuel and High-Level Waste in Opalinus Clay. *ChemInform* 42

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

- https://www.ejp-eurad.eu/publications/eurad-d151-concord-initial-sota
- Holdsworth, S.R., 2013. Ceramic Material Solutions for Nuclear Waste Disposal Canisters. NAGRA report NAB12-45.
- Holdsworth, S.R. 2018. Alternative coating Materials as Corrosion Barriers for SF and HLW Disposal Canisters. NAGRA report NAB18-19.
- INTERNATIONAL ATOMIC ENERGY AGENCY (2006). Development of Specifications for Radioactive Waste Packages. IAEA-TECDOC-1515. IAEA, Vienna

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

- https://www.ejp-eurad.eu/publications/eurad-d151-concord-initial-sota
- King, F. (2014). "Predicting the Lifetimes of Nuclear Waste Containers." JOM 66(3).

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- Performance Assessment for the Proposed High-Level Radioactive Waste Repository at Yucca Mountain, Nevada https://www.sciencedirect.com/journal/reliability-engineering-and-system-safety/vol/122/suppl/C
- Svensk Kärnbränslehantering, A. (2010). Corrosion calculations report for the safety assessment SR-Site. SKB TR-10-66

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

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ENVIRONMENTAL FACTORS AFFECTING THE CORROSION PROCESS

This project has received funding from the European Union's Horizon 2020 research and innovation programme 2014-2018 under grant agreement N°847593

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

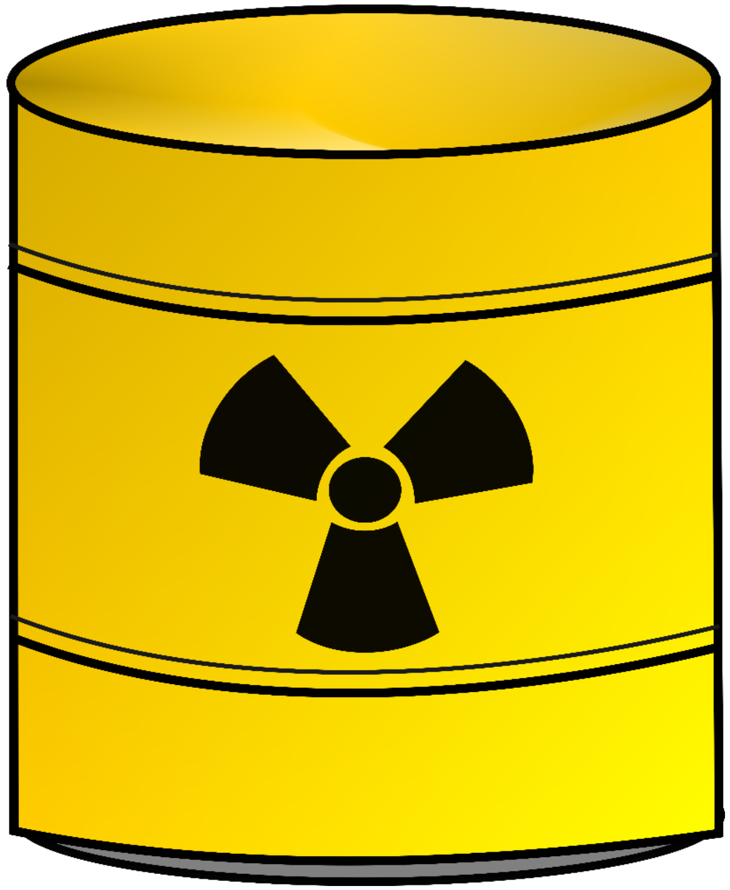
CONTENT

- 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

CONTENT

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



INTERNATIONAL ATOMIC ENERGY AGENCY, Development of Specifications for Radioactive Waste Packages, IAEA-TECDOC-1515, IAEA, Vienna (2006)

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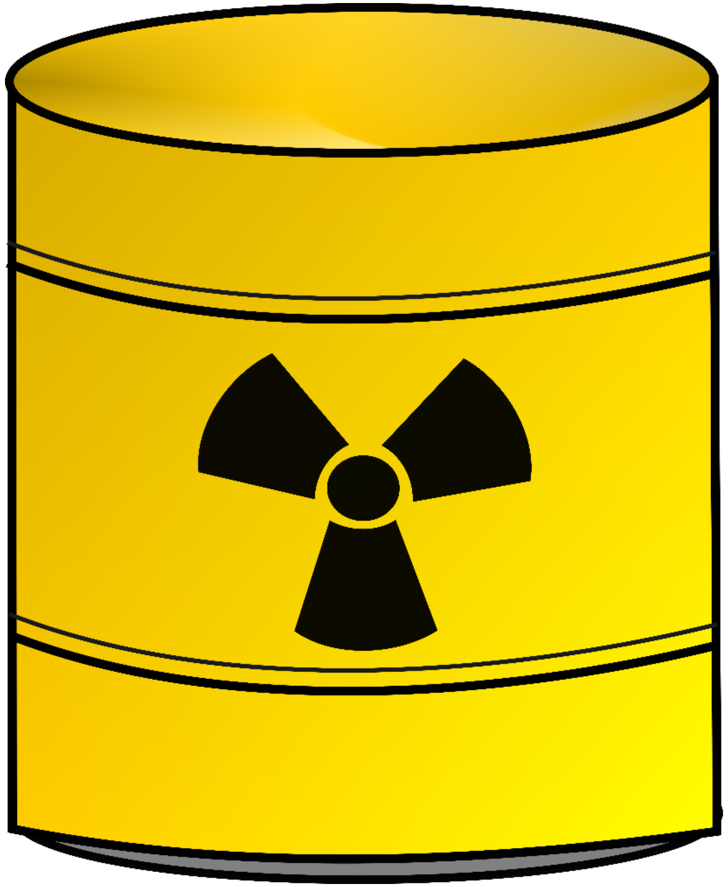

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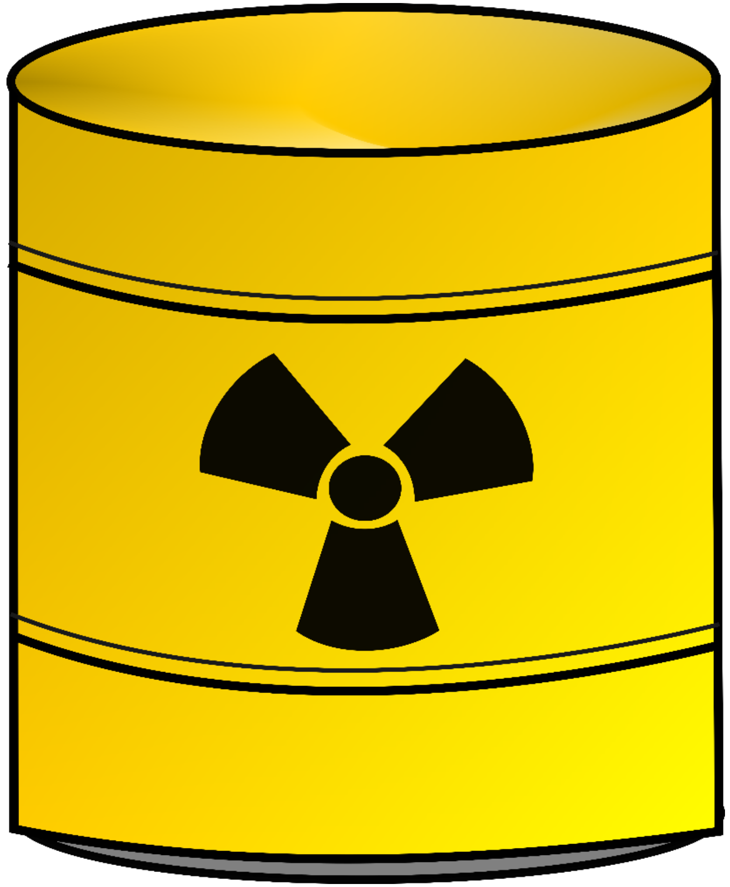
- In some cases the container also plays a role in the near field containment of the radionuclides for a certain period after closure
- Main parameters & control methods according to IAEA (2006):
  - Material itself
  - Geometric shape & dimensions
  - Design & operation of internal features
  - Lifting arrangements
  - Container internal corrosion
  - Container strength
  - Selection of surface coating & texture
  - Design & operation of closure features
  - Resistance to environmental conditions



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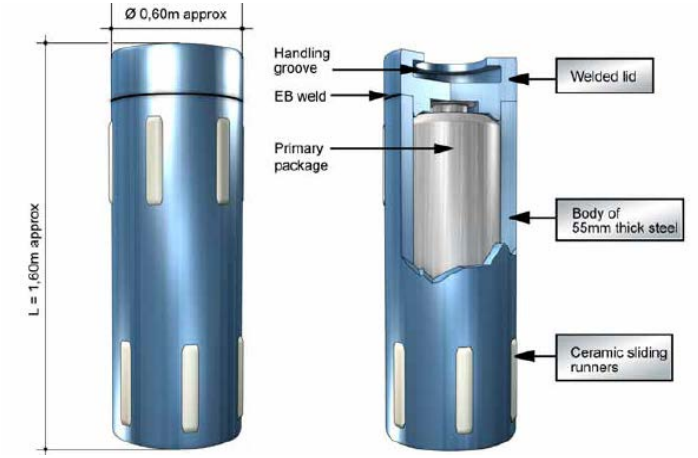
INTERNATIONAL ATOMIC ENERGY AGENCY, Development of Specifications for Radioactive Waste Packages, IAEA-TECDOC-1515, IAEA, Vienna (2006)

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

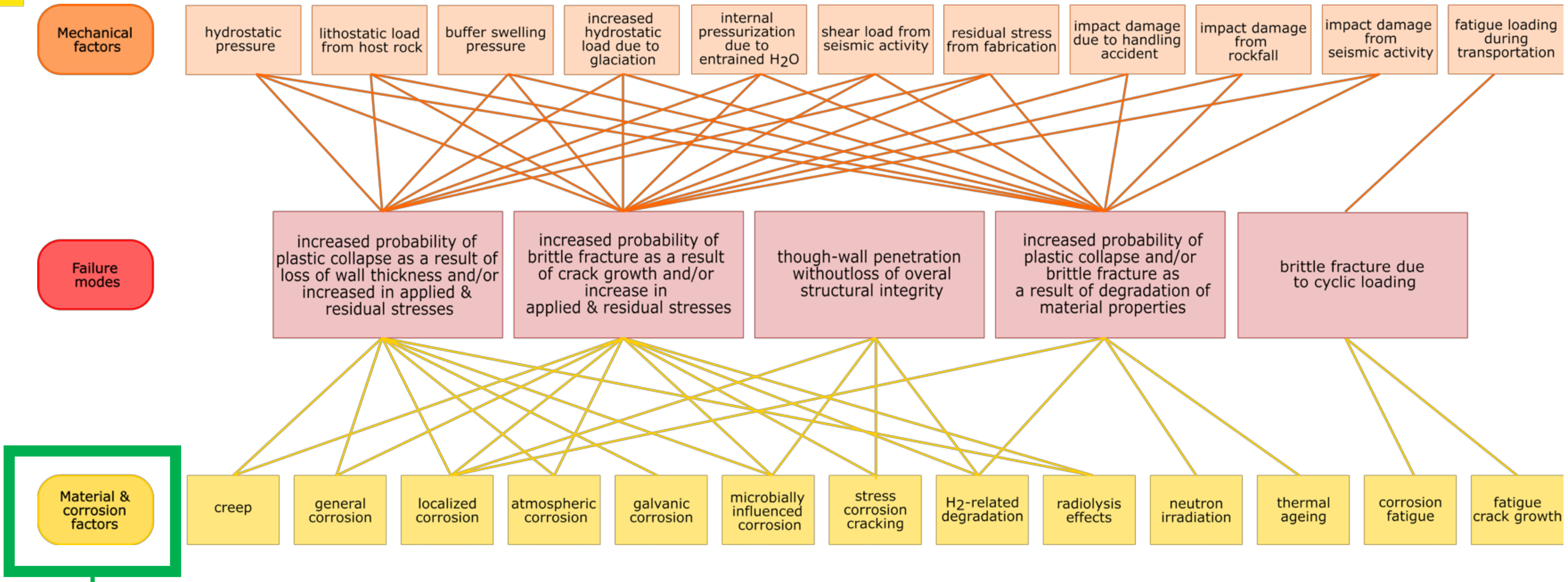
SKB/POSIVA

CANADA

DIFFERENT CONTAINER CONCEPTS & EXPECTED EXPOSURE CONDITIONS

WMO	Container concept	Estimated or target lifetime (year)	Nominal buffer dry density (g/cm^3)	Max. canister temp. (°C)	Time to full nearfield saturation (year)	Max. surface absorbed dose (Gy/h)	Expected mechanical loads (MPa)
SKB	Cu-cast Fe	$>10^6$	1.6	95	Few 10s – few 1000	0.2	15 50 (glacial)
Posiva	Cu-cast Fe	$>10^6$	1.55	95	Few 10s – few 1000	0.3	14 50 (glacial)
Andra	Carbon steel	>500	Cementitious buffer on the external face of the casing	90		10	10 Mpa (on casing)
Ondraf-Niras	Carbon steel	Several thousand	Cementitious buffer	100	5-10 to few 1000	25	8
Nagra	Carbon steel	10 000	>1.45	±120	Few centuries	0.2	22-29 max
SURAO	Carbon steel	10 000	1.4	95	100	0.3	20
NMWO	Cu-coated steel	$>10^6$	1.6	85	50-5000 ~ host rock dependent	0.8	15 45 (glacial)
NUMO	Carbon steel	> 1000	1.6	100	<1000 ~ host rock dependent	0.006-0.011	11 (hard rock)

FAILURE MODES OF CONTAINERS



Detailed knowledge of mechanisms under environmental conditions in the near-field of the container is necessary

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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

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  - Container material
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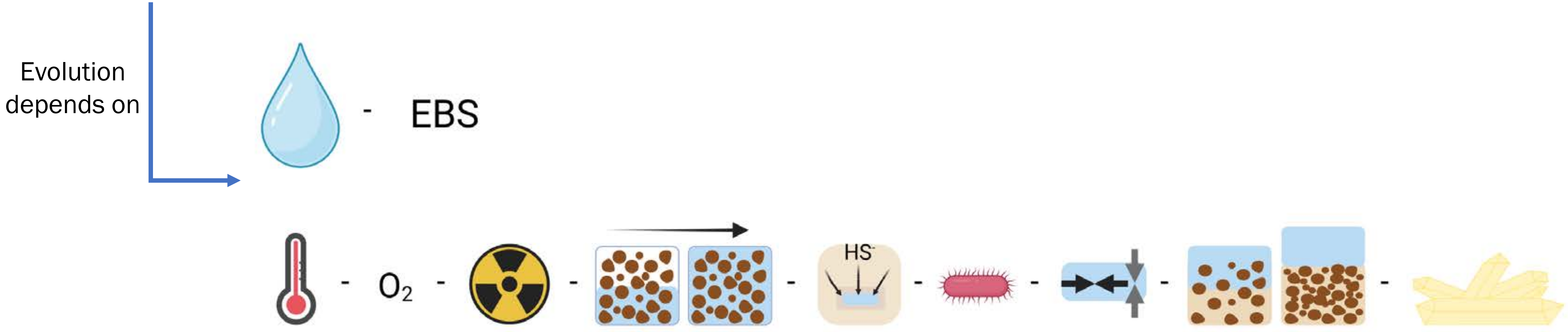

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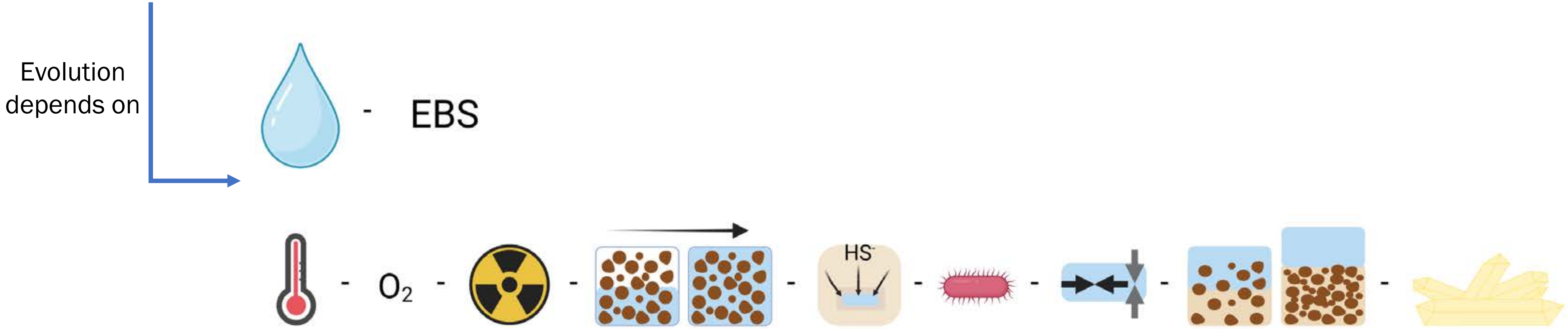

  - Constant conditions extensively studied ↔ transient conditions

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

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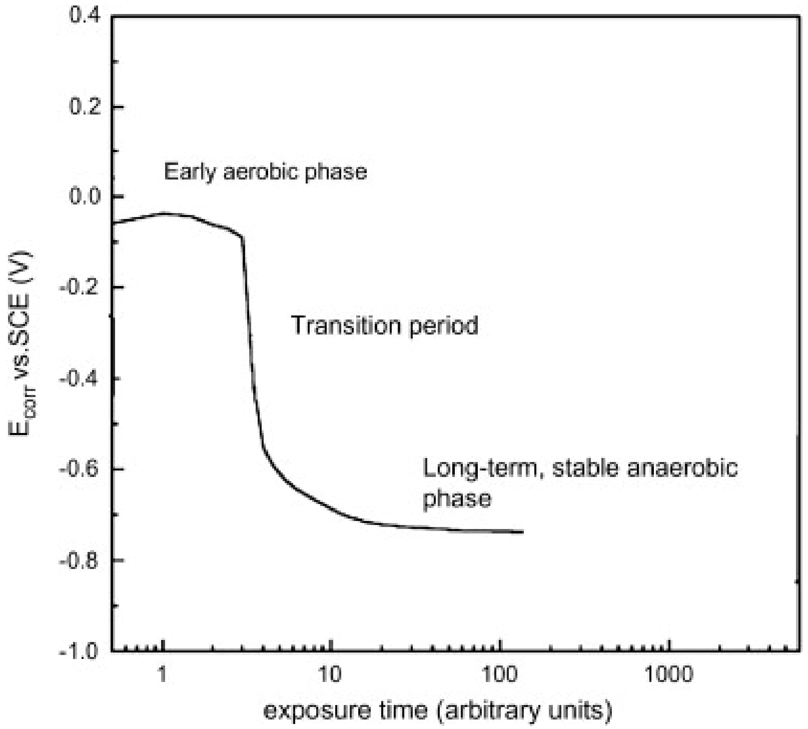

Figure from Johnson, L. and F. King (2008). "The Effect of the Evolution of Environmental Conditions on the Corrosion Evolutionary Path in a Repository for Spent Fuel and High-Level Waste in Opalinus Clay." Journal of Nuclear Materials 379(1).

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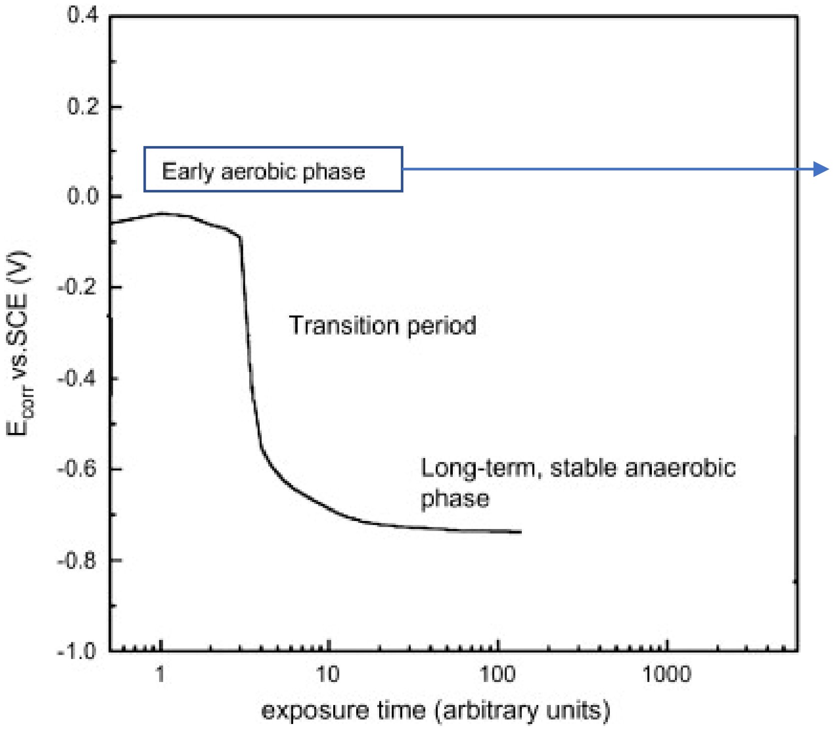

E_{CORR} is relatively noble (positive) because of the cathodic reduction of O_2 and because of the possible spatial separation of anodic and cathodic processes

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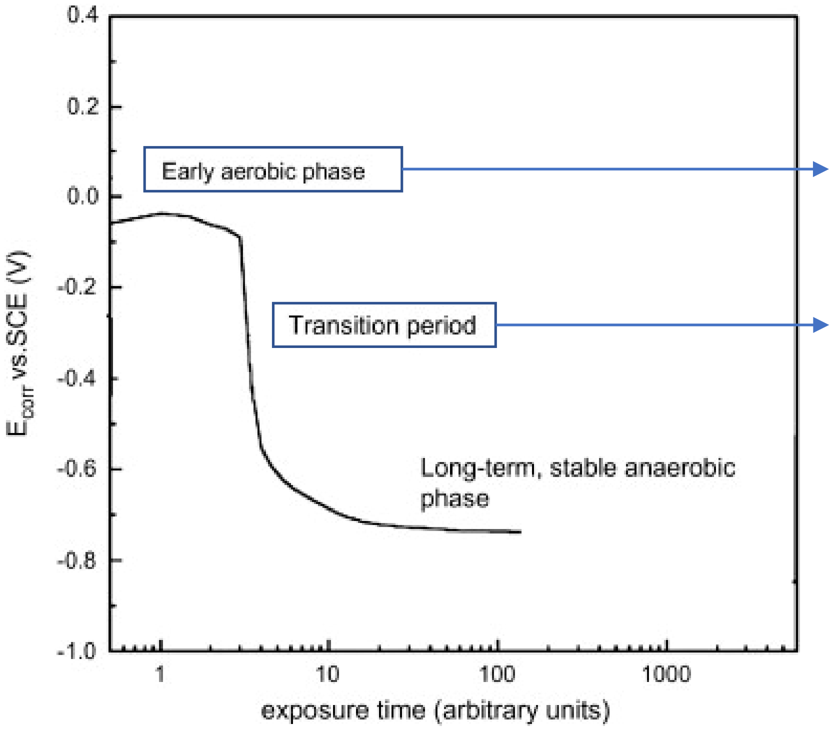

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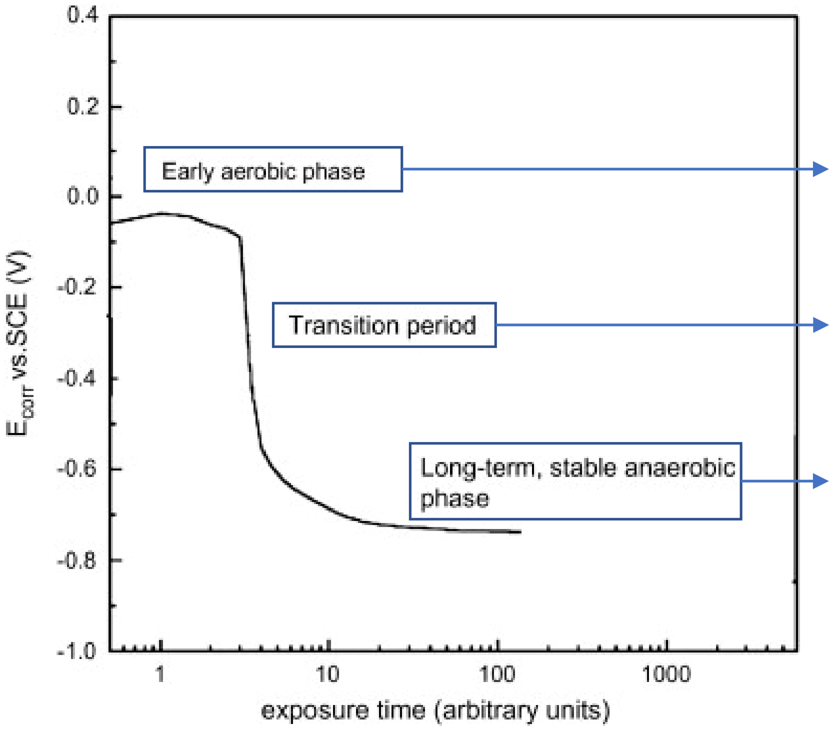

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CONTENT

- 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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- **Sources:**
  - Ambient temperature ↑ with depth
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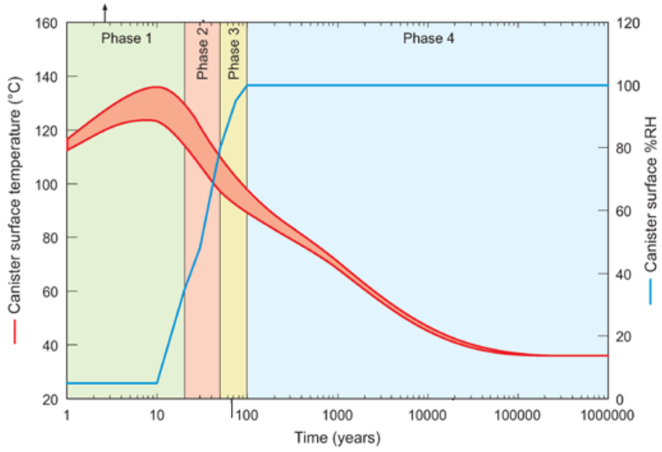
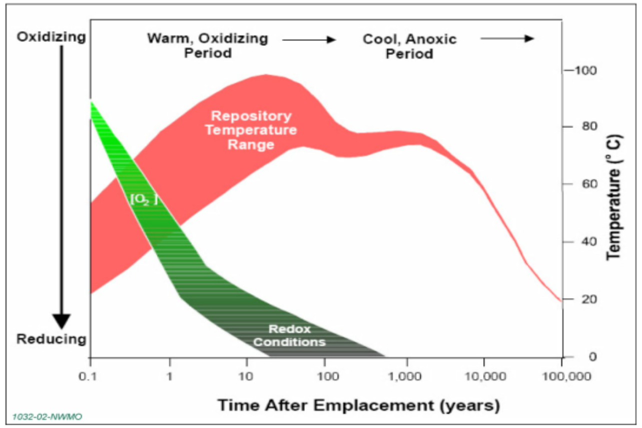
- **Longest transient but with slower changes**





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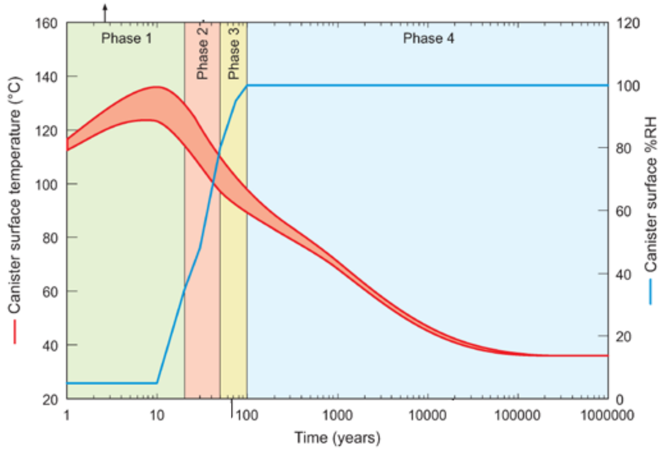
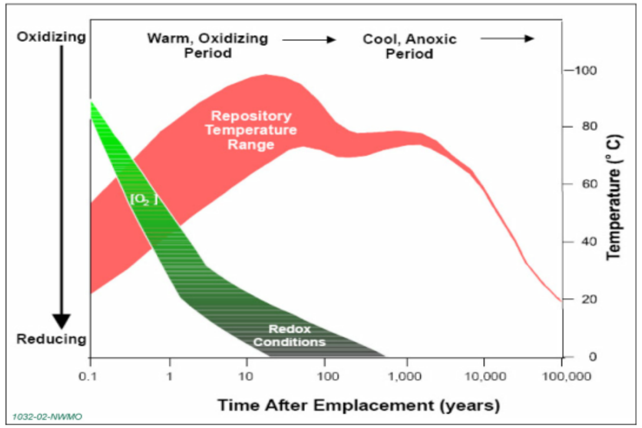
Thermal gradient between container/buffer – buffer/rock boundary





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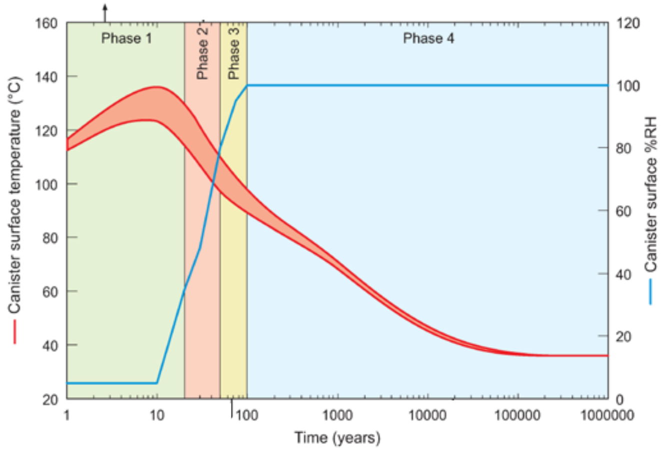

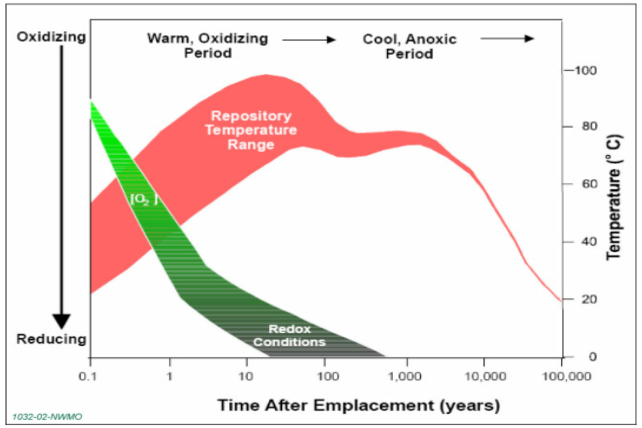

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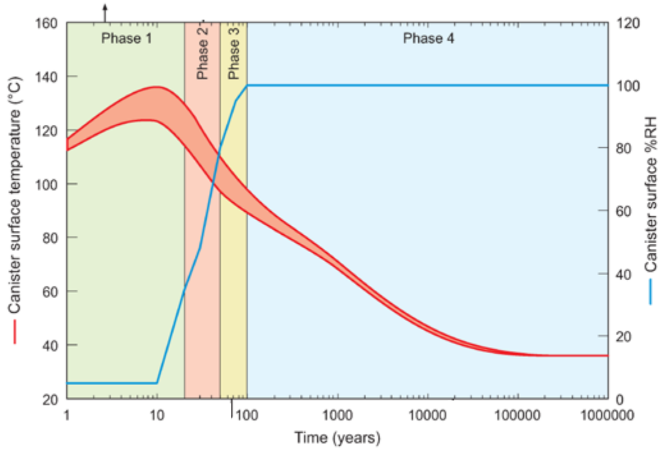
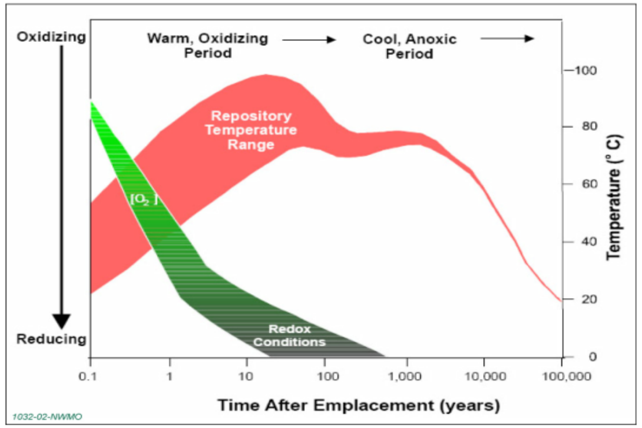
Secondary minerals can precipitate onto surfaces of primary clay minerals





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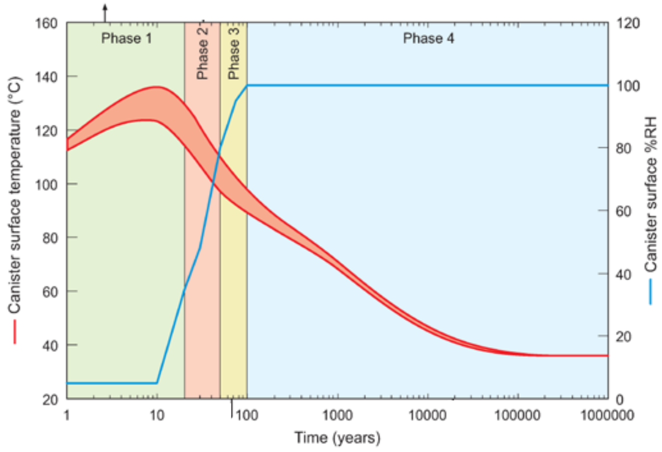

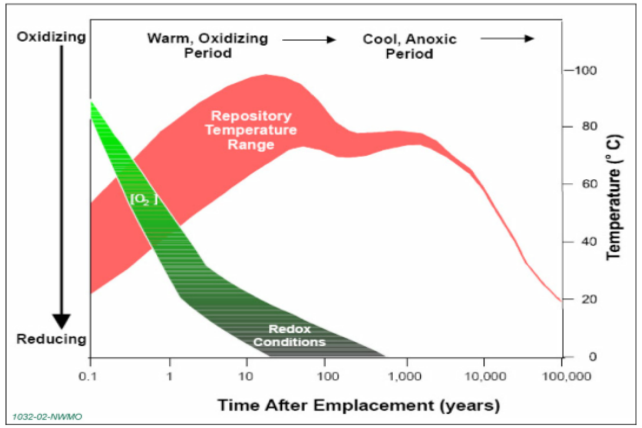

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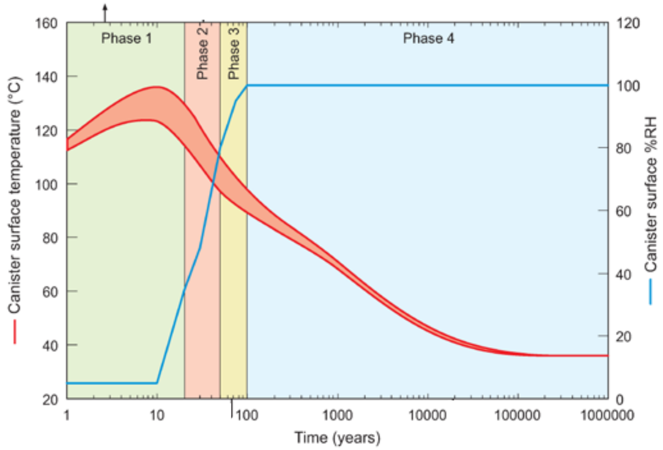
Thermal gradient between container/buffer – buffer/rock boundary

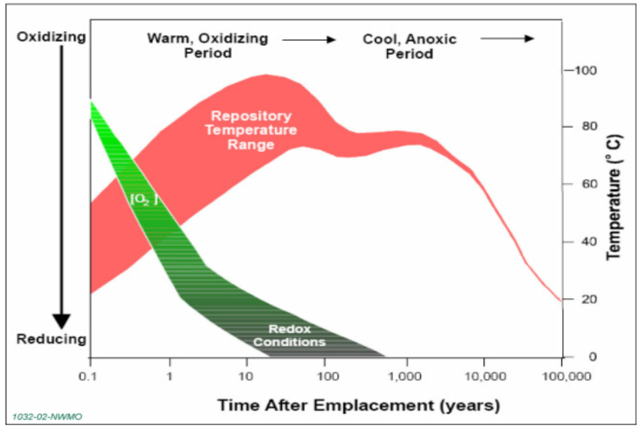
→ Concentration gradient among aqueous solutes

→ Secondary minerals can precipitate onto surfaces of primary clay minerals

→ If significant changes in mass transfer → individual clay particles cemented in secondary solids

→ Could irreversibly alter the swelling pressure & other properties of the buffer





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PORE WATER TRANSIENTS

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↳ Typically highly compacted bentonite or cementitious backfill

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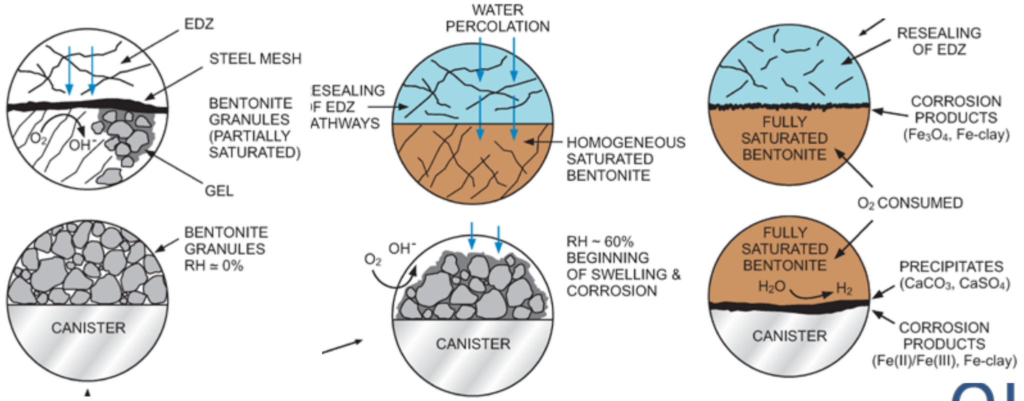
  - Dripping into open drifts
  - Deliquescence of salt contaminants



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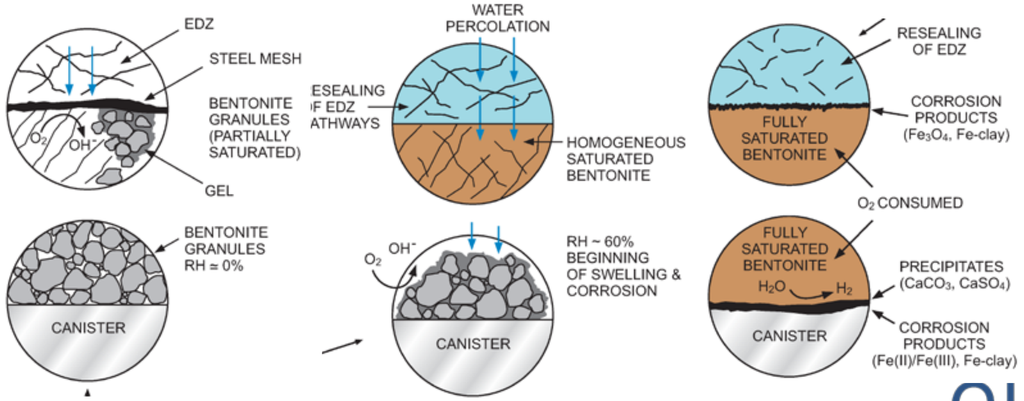

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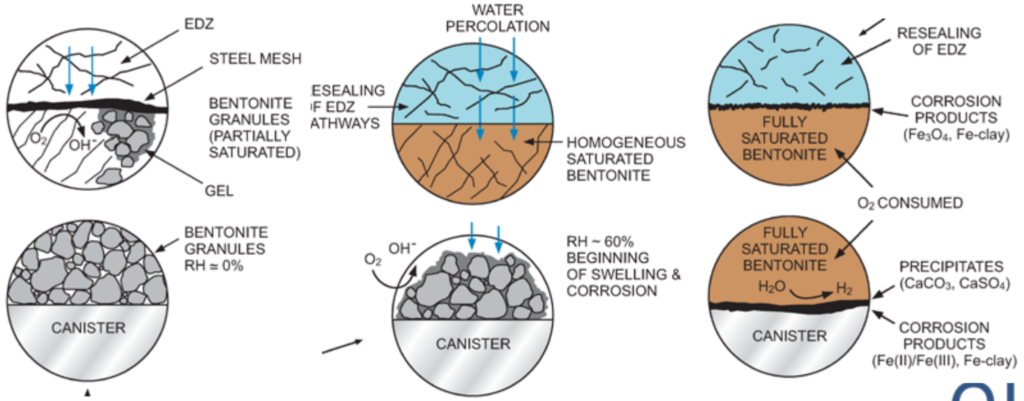
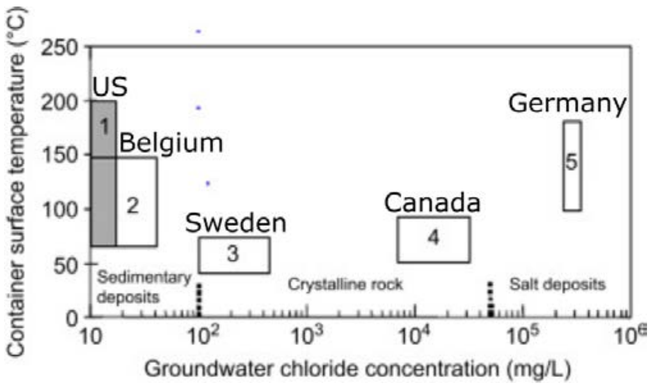
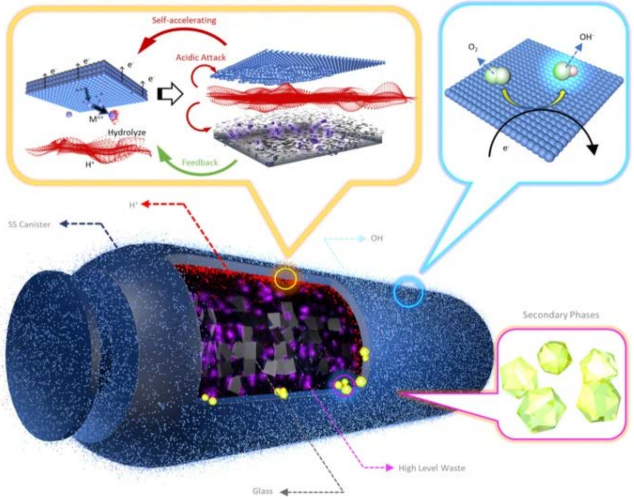
→ Non-uniform wetting of the surface



PORE WATER TRANSIENTS

- Species important for corrosion:
  - Cl^-
  - $SO_4^{2-} \rightarrow HS^-$
  - CO_3^{2-}/HCO_3^-
    - pH buffering
    - passivating certain metals (e.g. Cu or C-steel)
  - pH → alkaline pH → passivation of C-steel
  - Cations (Ca^{2+}, Mg^{2+})
    - hydrolyze to produce aggressive environments
    - promote formation of protective mineralized surface films
  - NH_4^+ stress corrosion cracking of Cu alloys





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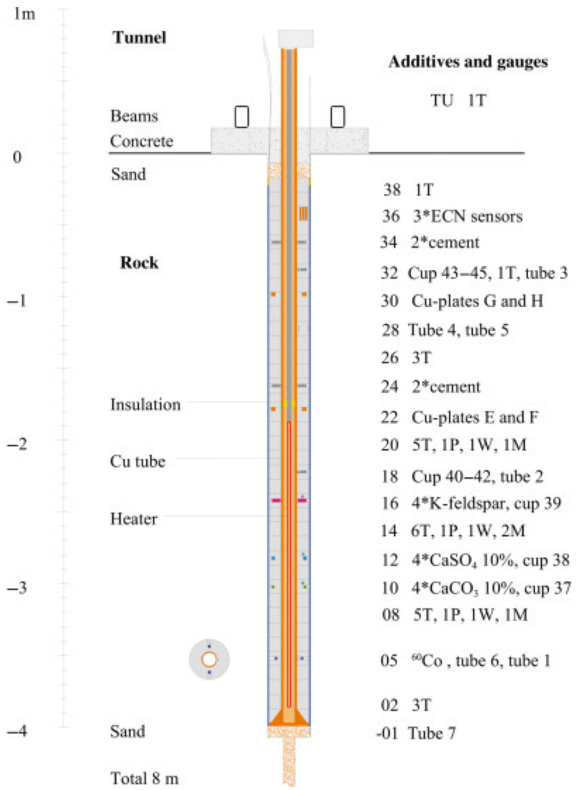
PORE WATER TRANSIENTS: EXPERIMENTAL WORK

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



Itälä A, Olin M. Chemical Evolution of Bentonite Buffer in a Final Repository of Spent Nuclear Fuel During the Thermal Phase. Nuclear Technology. 2011;174(3):342-52.

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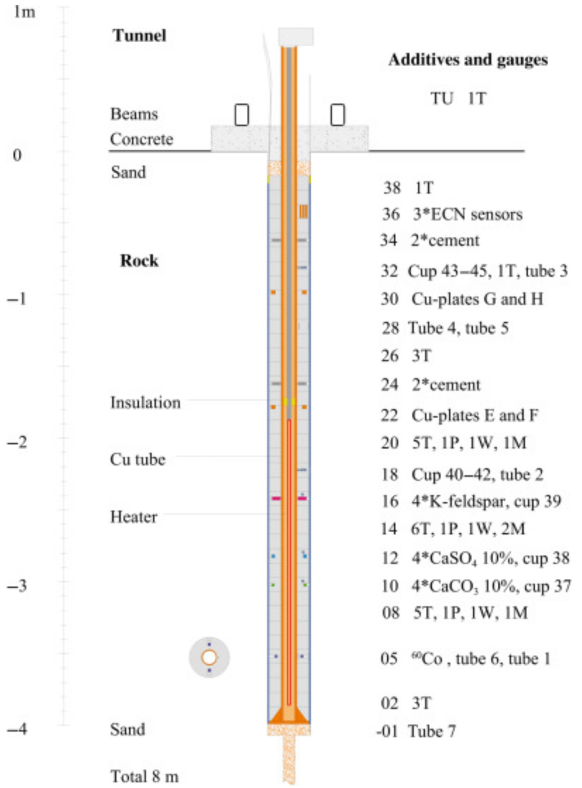
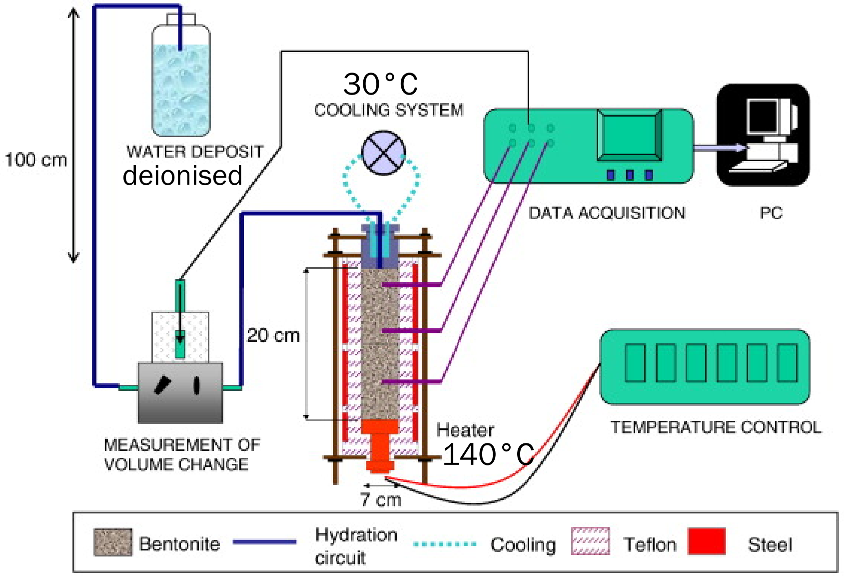


Itälä A, Olin M. Chemical Evolution of Bentonite Buffer in a Final Repository of Spent Nuclear Fuel During the Thermal Phase. Nuclear Technology. 2011;174(3):342-52.

- Influence of Ca-Mg-bentonite chemistry in contact with granitic groundwater after the thermal phase
  - [Cl$^-$] ↓ → pH ↑ → aggressive behavior ↓

Červinka, R., Vašíček, R., a kolektiv 2018. Kompletní charakterizace bentonitu. BCV 2017, SÚRAO TZ 419/2019

PORE WATER TRANSIENTS: EXPERIMENTAL WORK



- 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
  - $Na–SO_4^{2-} \longrightarrow Na–Cl$ 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

Gómez-Espina R, Villar MV. Geochemical and mineralogical changes in compacted MX-80 bentonite submitted to heat and water gradients. Applied Clay Science. 2010;47(3):400-8.

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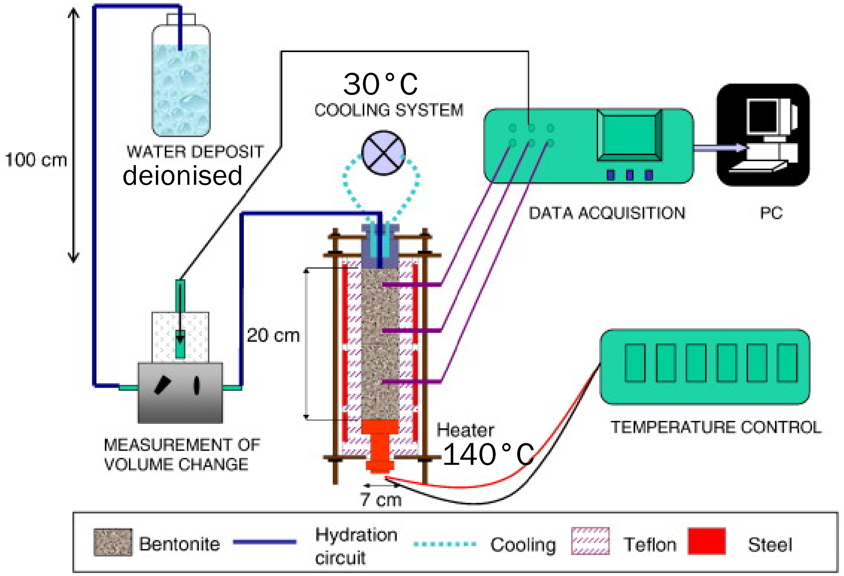

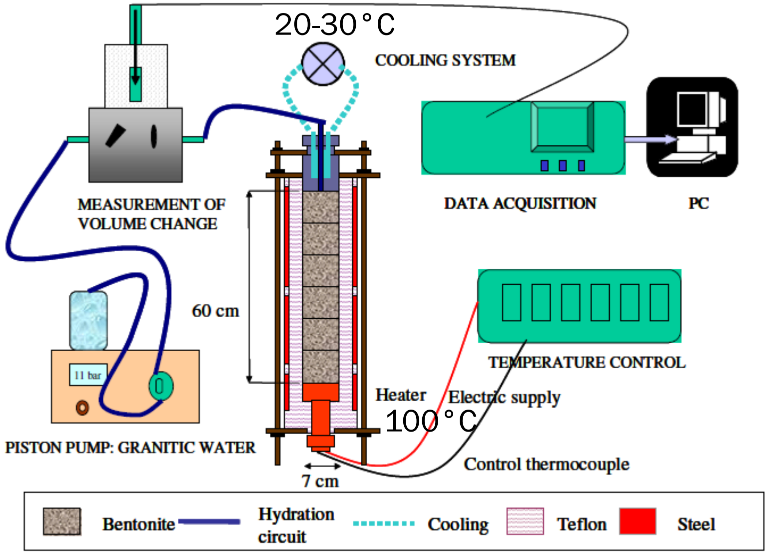

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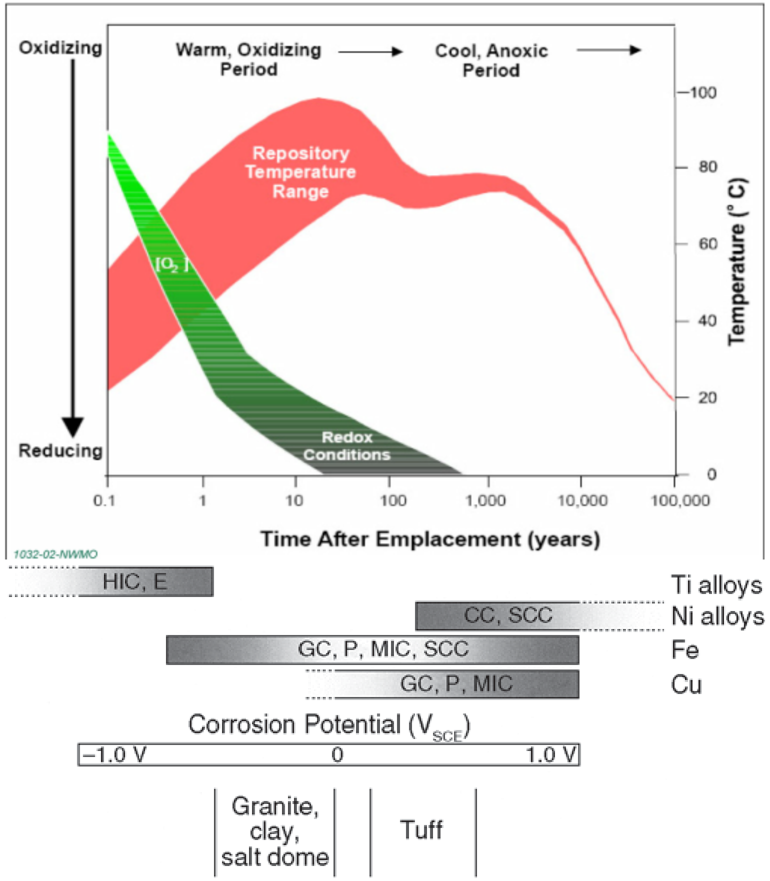
- 7.6 years, 1.64 g/cm³ dry density, initial water content 13.8%
  - Overall degree of saturation: 92 %
  - Gradient of water content & dry density along the column
  - Advection, interlayer exchange & dissolution/precipitation processes conditioned the composition of the pore water along the column
  - Exchangeable complex of smectite changed
  - $Na–SO_4^{2-} \rightarrow Na–Cl$ type near the heater
  - Physical properties not irreversibly affected

Gómez-Espina R, Villar MV. Geochemical and mineralogical changes in compacted MX-80 bentonite submitted to heat and water gradients. Applied Clay Science. 2010;47(3):400-8.
Villar, M. V., A. M. Fernández, R. Gómez, J. F. Barrenechea, F. J. Luque, P. L. Martín and J. M. Barcala (2007). State of a Bentonite Barrier after 8 Years of Heating and Hydration in the Laboratory. Materials Research Society Symposium Proceedings.

CONTENT

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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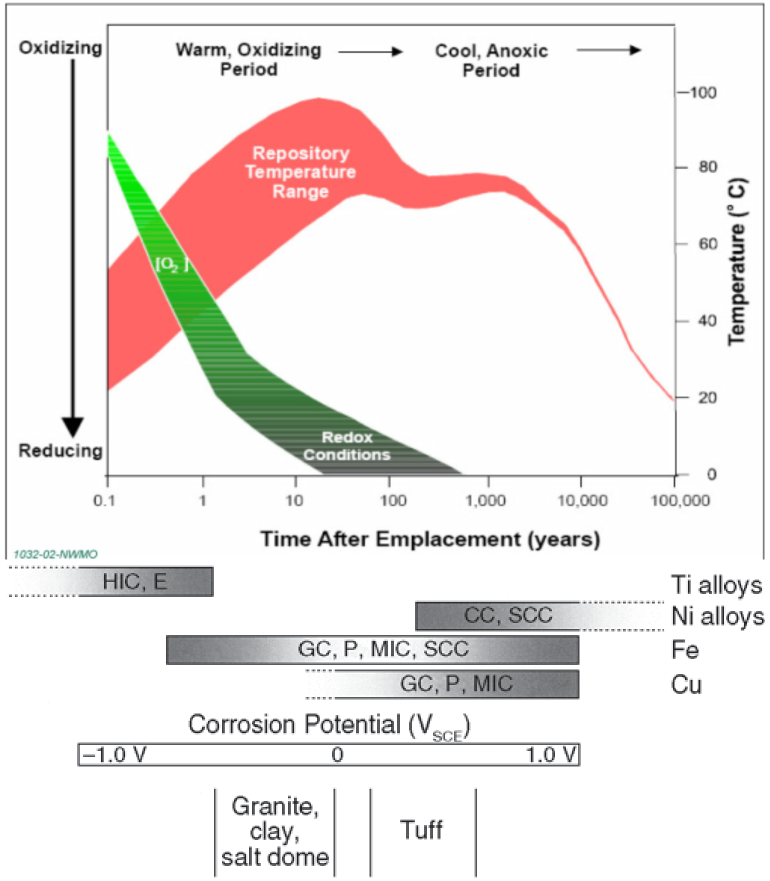

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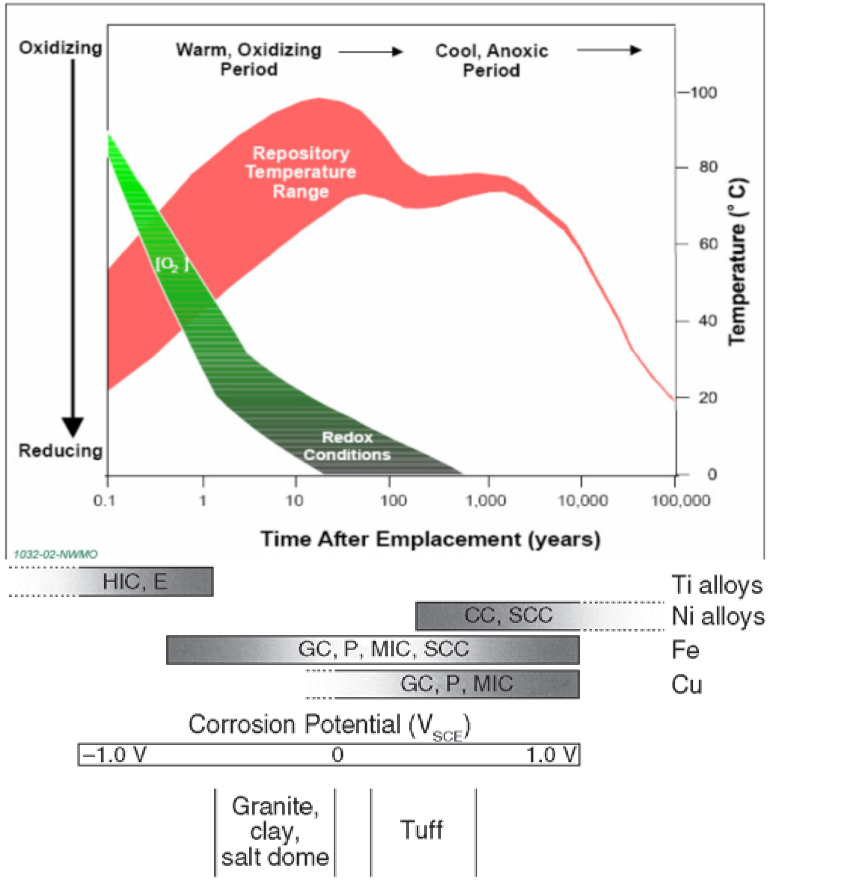

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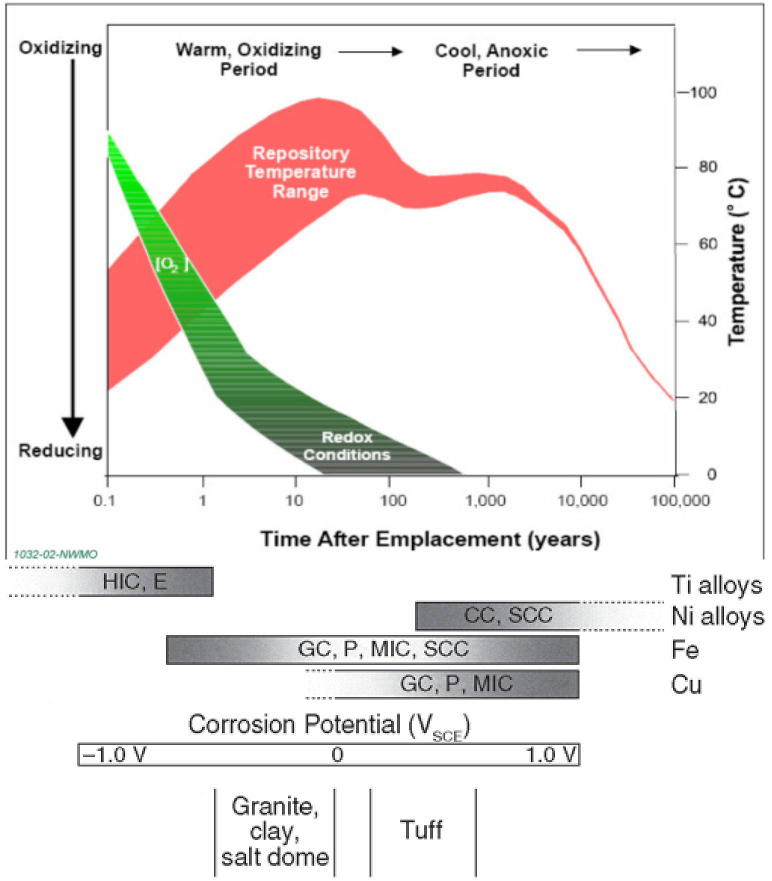
- If all the O_2 initially present reacts uniformly with the steel containers → max. corroded depth would be < 100 µm



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REDOX TRANSIENTS: EXPERIMENTAL WORK

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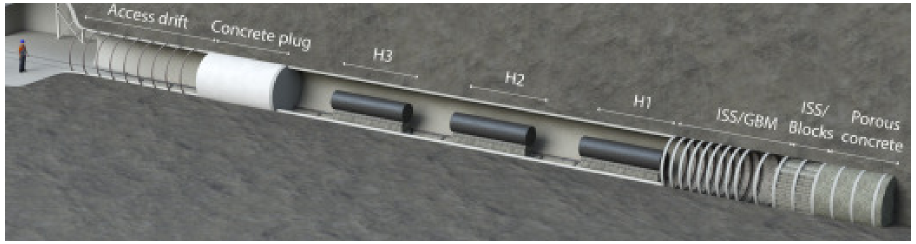
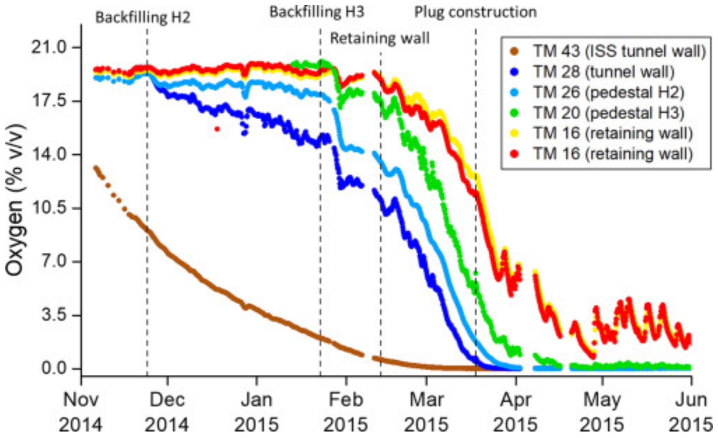
  - Very rapid O_2 consumption
    - By the bentonite buffer
    - In the EDZ





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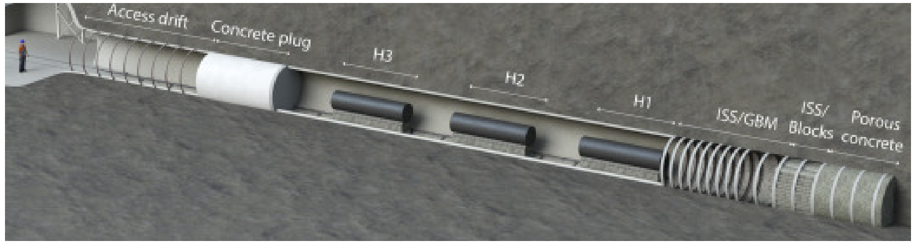

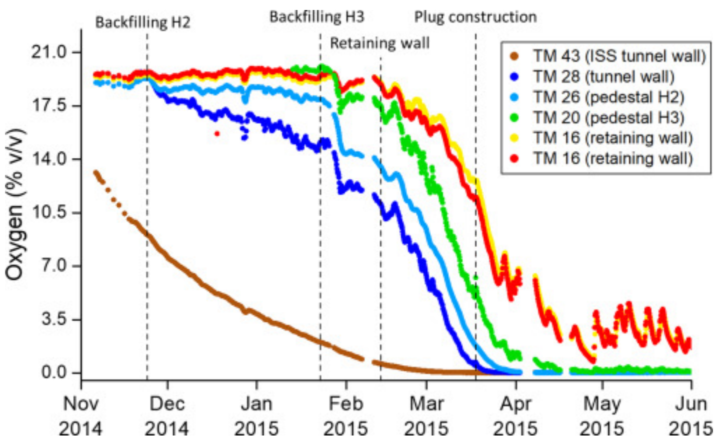

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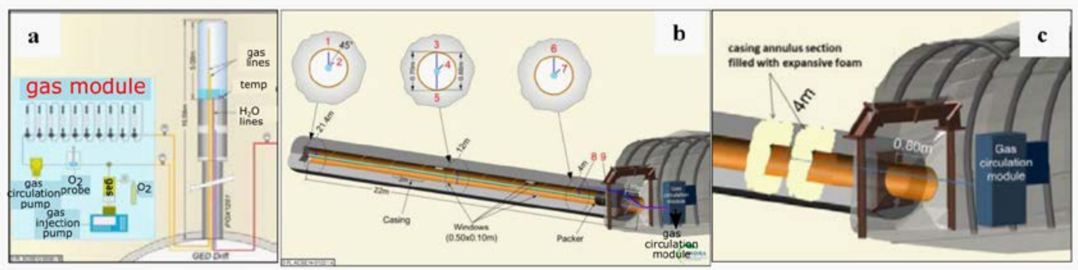
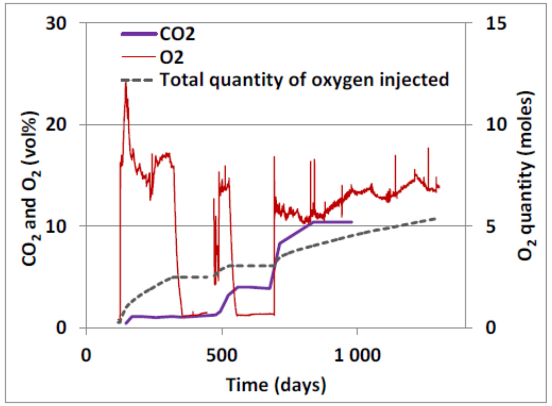
- COx argillaceous rock @ Meuse/Haute-Marne URL
  - O_2 consumption by
    - Pyrite oxidation
    - Calcite dissolution





Vinsot, A., M. Lundy and Y. Linard (2017). "O_2 Consumption and CO_2 Production at Callovian-Oxfordian Rock Surfaces." Procedia Earth and Planetary Science 17

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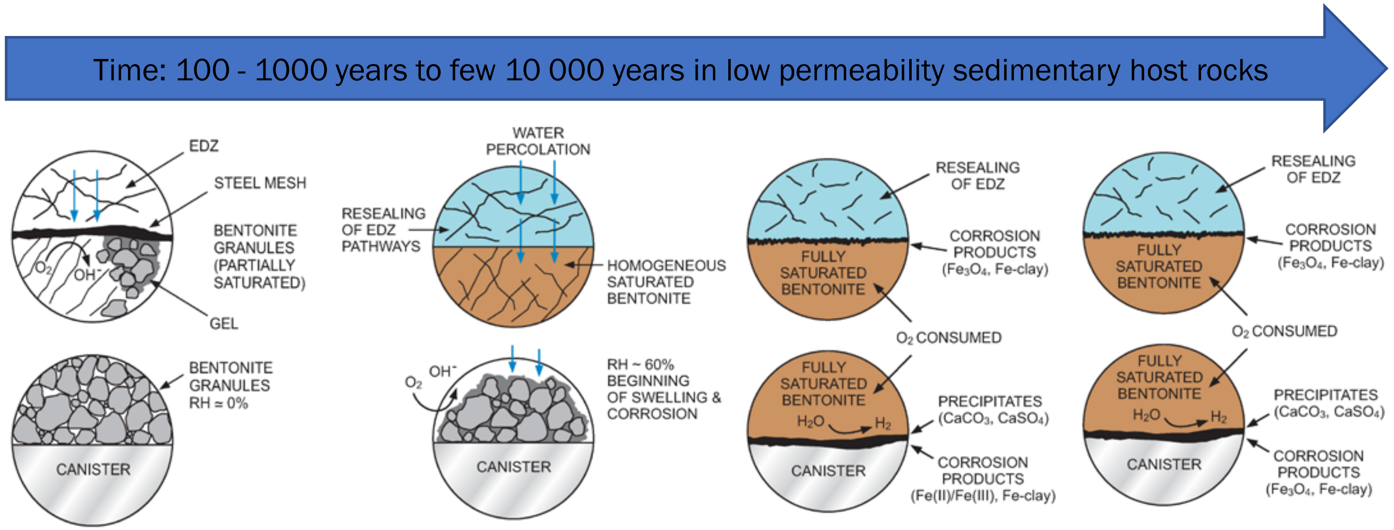
SATURATION TRANSIENTS

- When & what form of corrosion occur



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SATURATION TRANSIENTS

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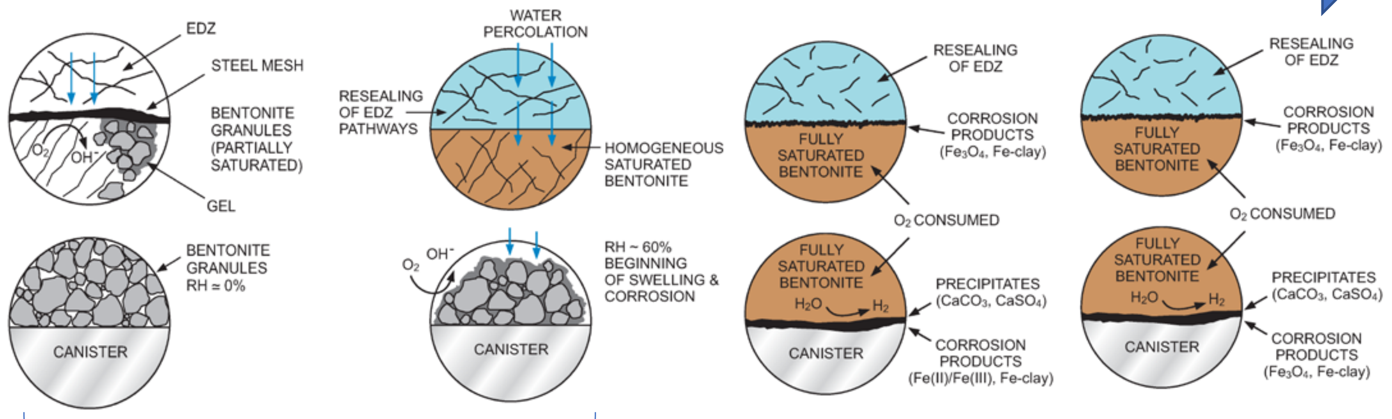
Time: 100 - 1000 years to few 10 000 years in low permeability sedimentary host rocks



- 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 ↑

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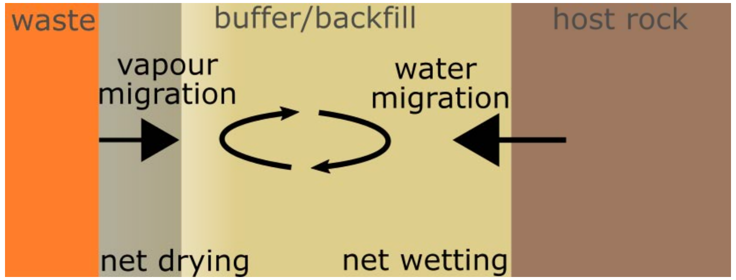

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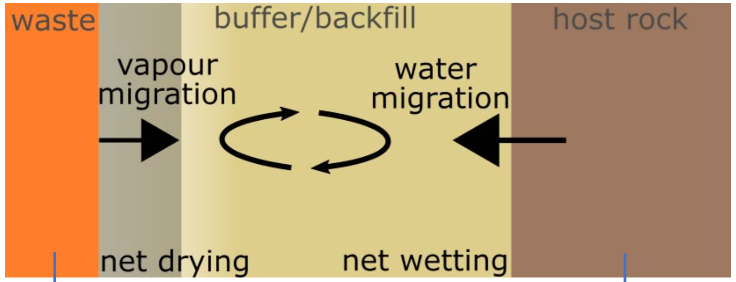

Large heat source

Low H_2O availability

Large sections of bentonite are dried + high temp inner annulus

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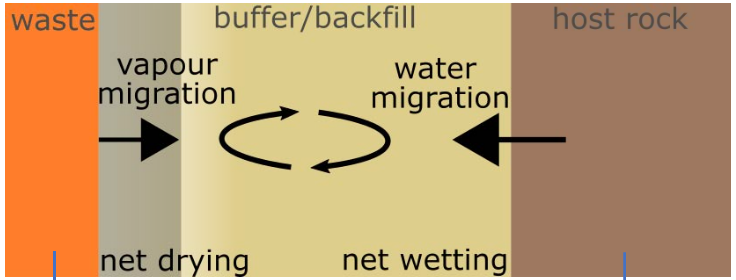

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Low H_2O availability

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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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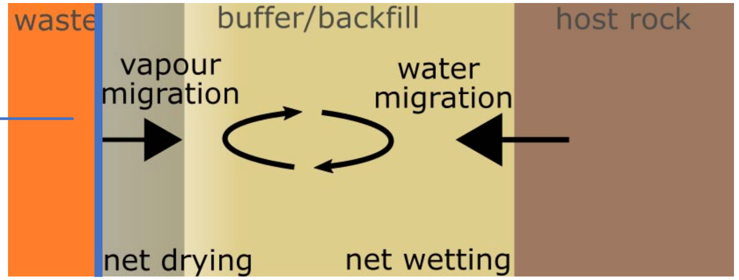
- Accumulation Cl^- & SO_4^{2-} salts
- Driving away dissolved silica

↓

- Container corrosion
- Radial variation clay density

↓

Porosity changes



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Host rock formation

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- **lithostatic pressure**

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Repository design

- 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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  - $Fe + 2H_2O \longrightarrow Fe(OH)_2 + H_2$
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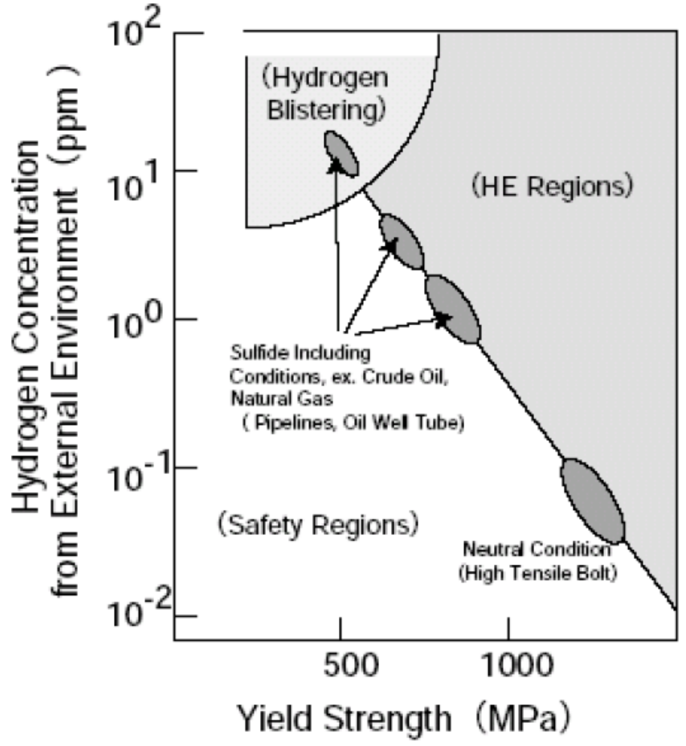

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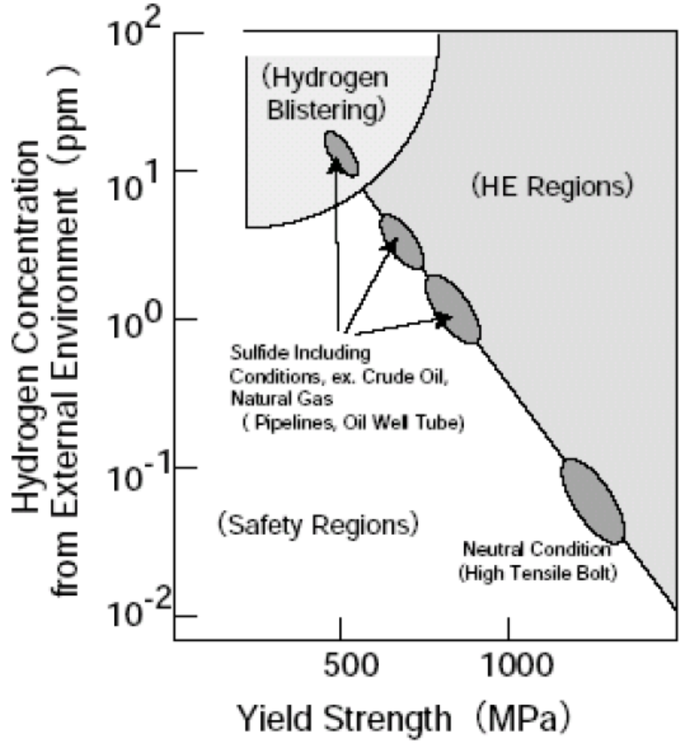
→ Use of low-strength steel container & the nature of the repository environment



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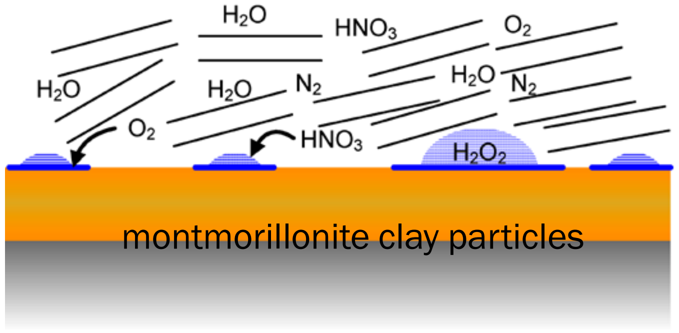
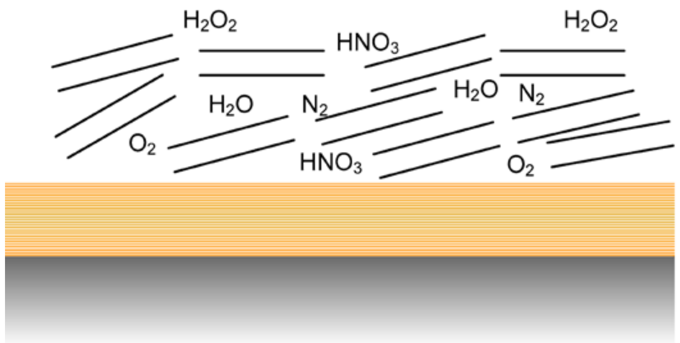
Absorption of HNO_3 formed by the radiolysis of humid air by liquid droplets on a non-uniformly wetted surface



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



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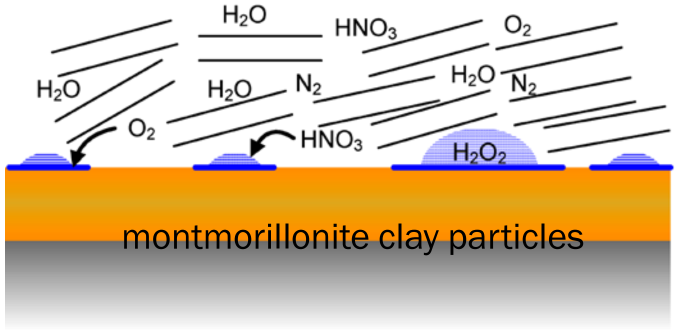

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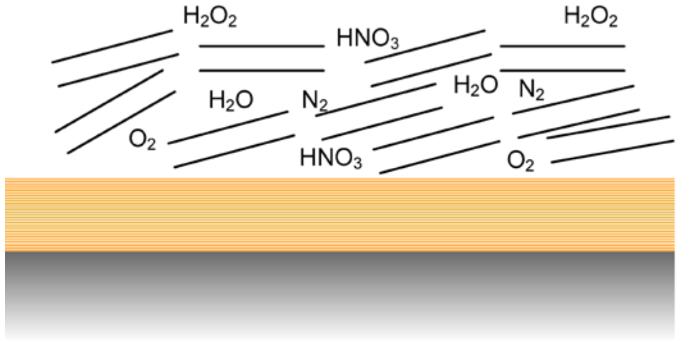
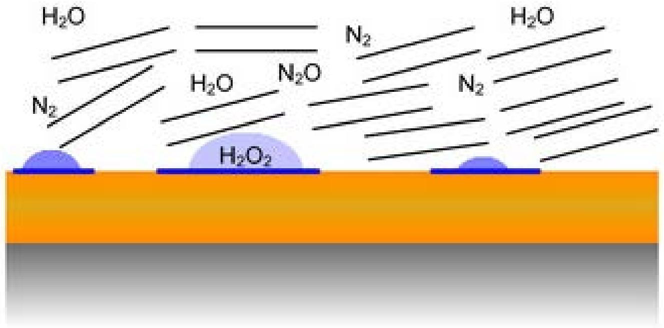
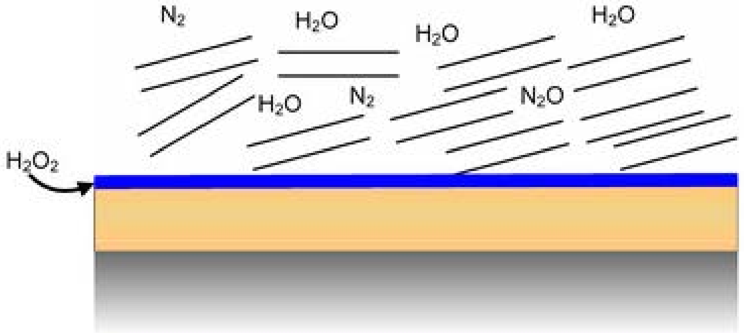


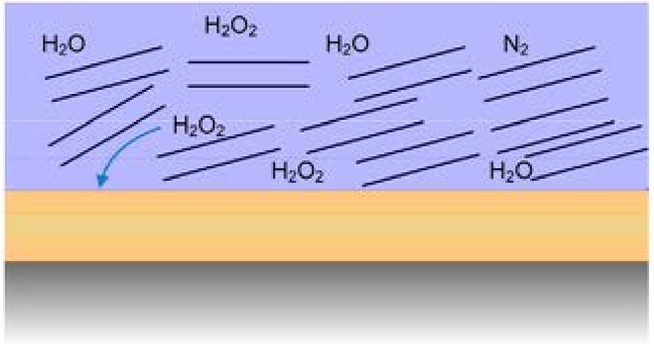
Saturated conditions



Radiolysis of **N_2-H_2O** following consumption of the initially trapped O_2 & 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 N_2-H_2O atmosphere



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

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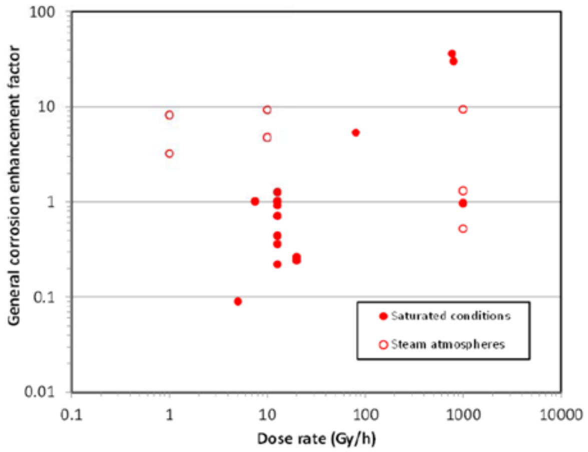

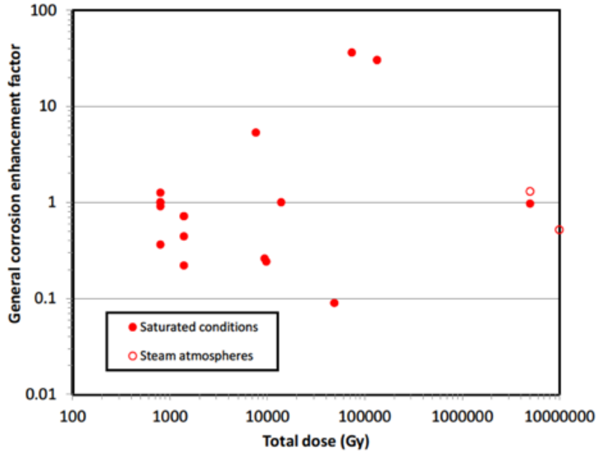

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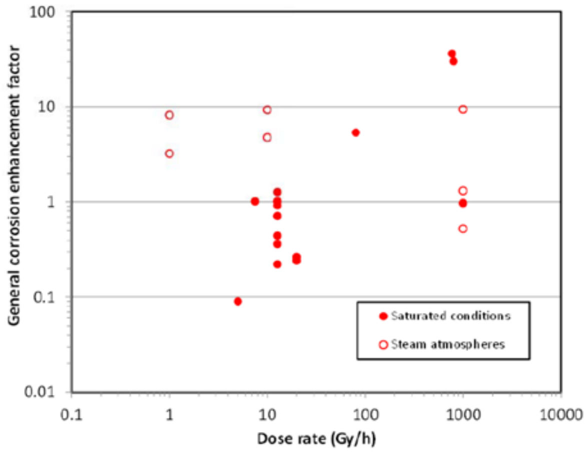
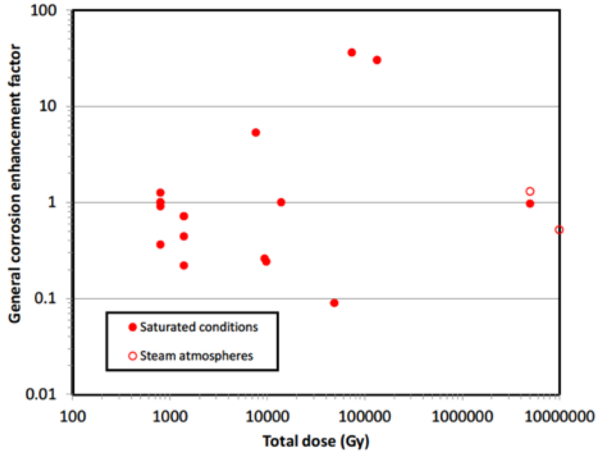
    - Unsaturated conditions ⟶ surface area copper/volume aqueous phase is high
      - affect relative influence of interfacial & homogenous processes
      - high dose rate (470-500 Gy/h) ⟶ No direct role for radiolytically produced HNO_3 in increased corrosion
      - low dose rate (0.35 Gy/h) ⟶ little impact over experimental timescales and within the measurement accuracy





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RADIOLYSIS TRANSIENTS IN THE NEAR-FIELD

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- **Radiation damage of Cu corrosion barrier negligible**

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EFFECT OF IRRADIATION ON C-STEEL CONTAINERS

- Water radiolysis products → E_{corr} ↑
- Passivating film of magnetite & hematite

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

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      - High Linear Energy Transfer (LET) radiation: molecules ↑ + radicals ↓ ↔ low LET radiation: radicals ↑
  - Buffer-container system
    - γ-irradiation + high temperature → insignificant changes of the smectite content & physical properties of MX-80 bentonite after 1 y
    - Extensive pitting corrosion

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EFFECT OF IRRADIATION ON C-STEEL CONTAINERS

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    - Except chromium & low molybdenum steels
  - Radiation at high temperature
    - 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
  - γ ↔ α

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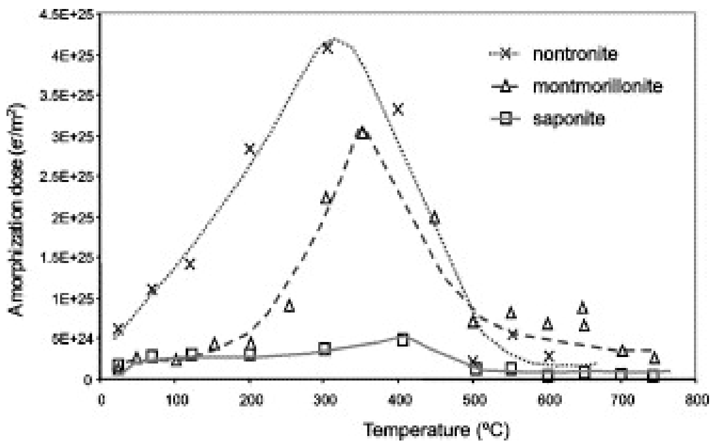

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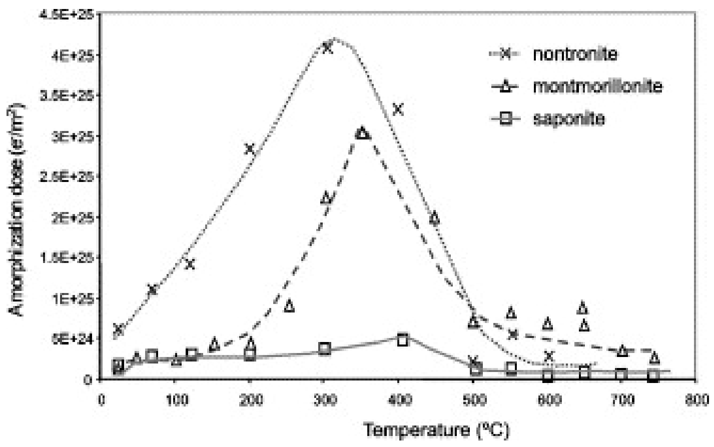

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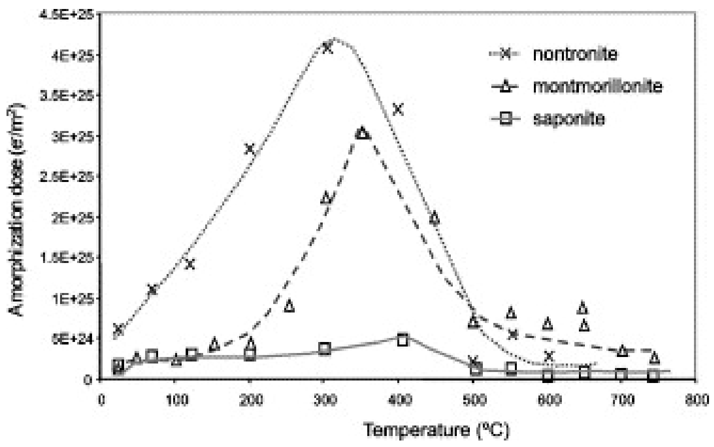

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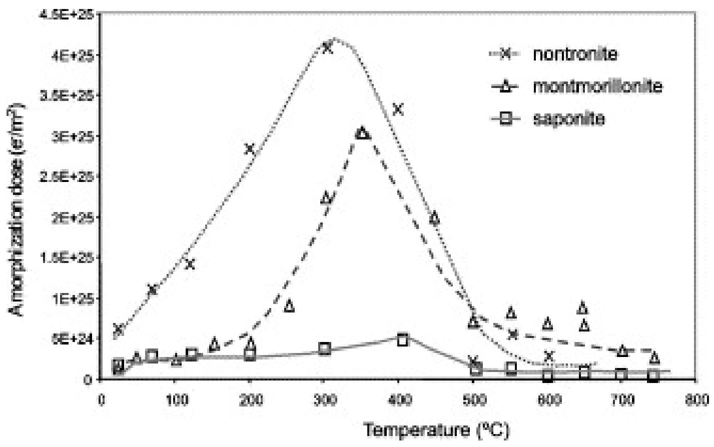
    - Structural Fe^{2+} & Fe^{3+} ⟶ influence on physical properties of the clay



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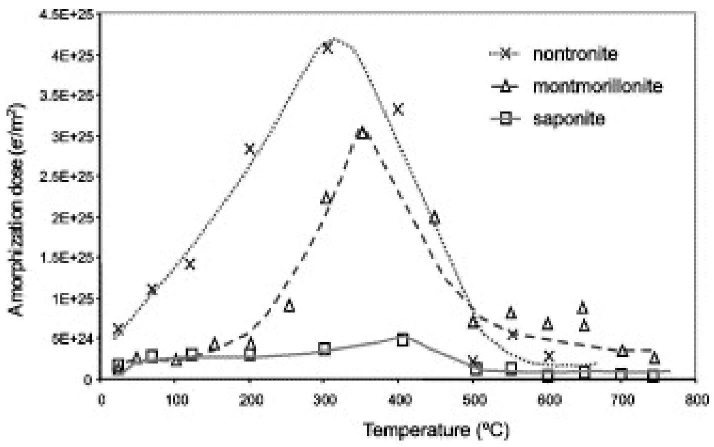
  - No deleterious effect on clay stability of a created gas phase



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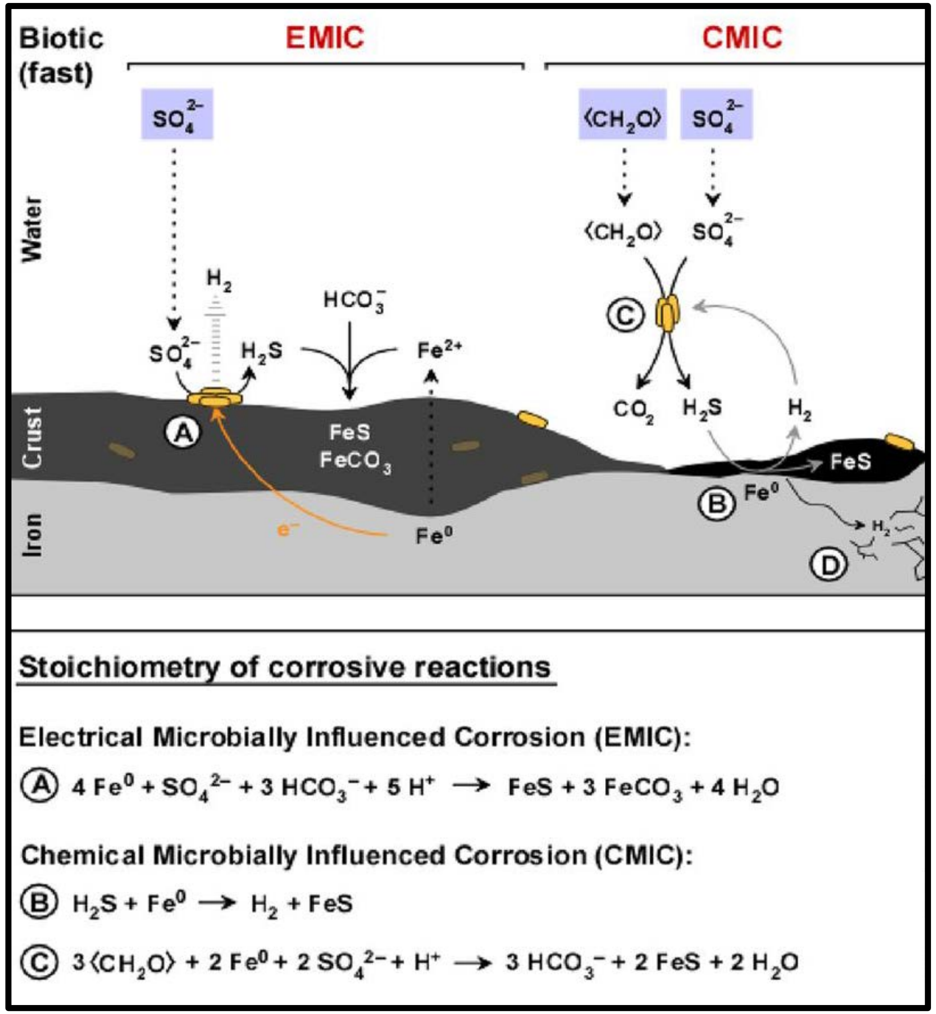
EFFECT OF IRRADIATION ON BUFFER MATERIALS

- **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

CONTENT

MICROBIAL CORROSION IN THE CONTEXT OF NUCLEAR WASTE DISPOSAL



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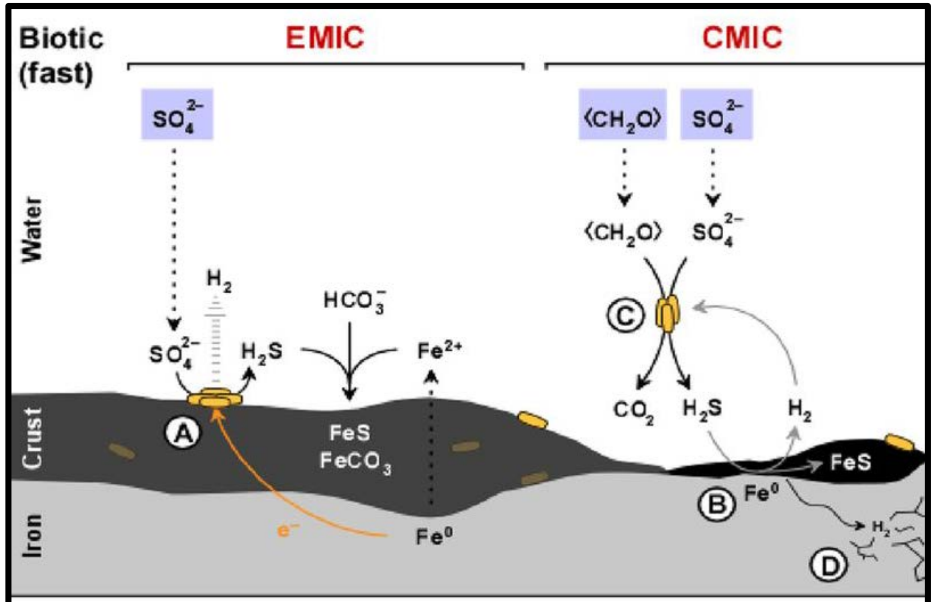

Stoichiometry of corrosive reactions

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Chemical Microbially Influenced Corrosion (CMIC):

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C $3\langle CH_2O \rangle + 2\,Fe^0 + 2\,SO_4^{2-} + H^+ \longrightarrow 3\,HCO_3^- + 2\,FeS + 2\,H_2O$

Biofilm needed

Only relevant in the absence of bentonite backfill

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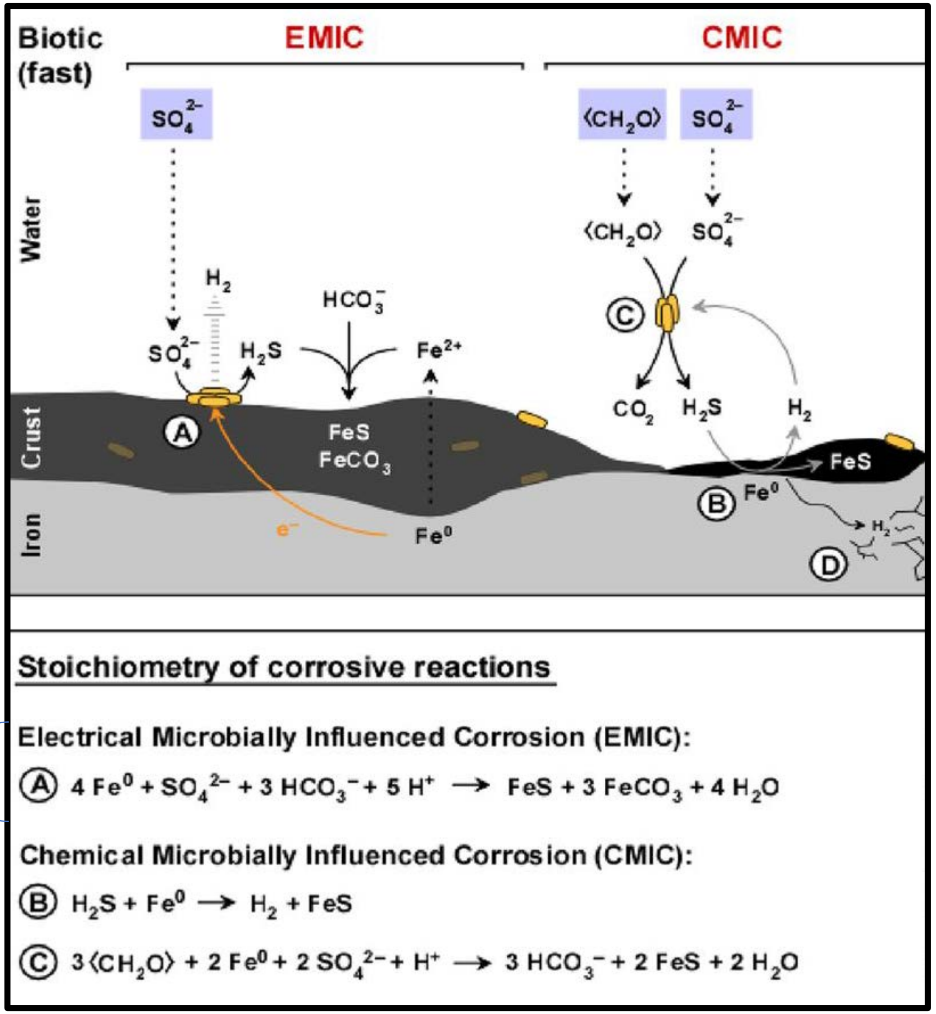

Anoxic corrosion

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

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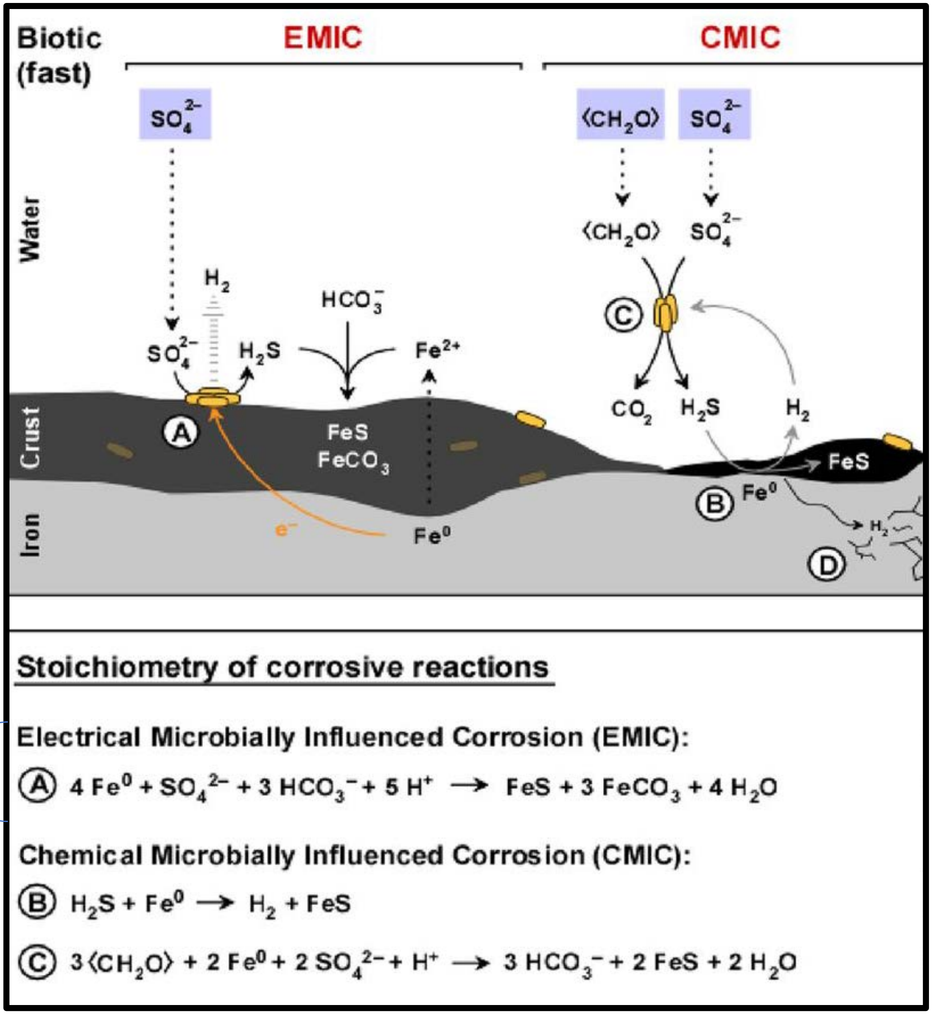

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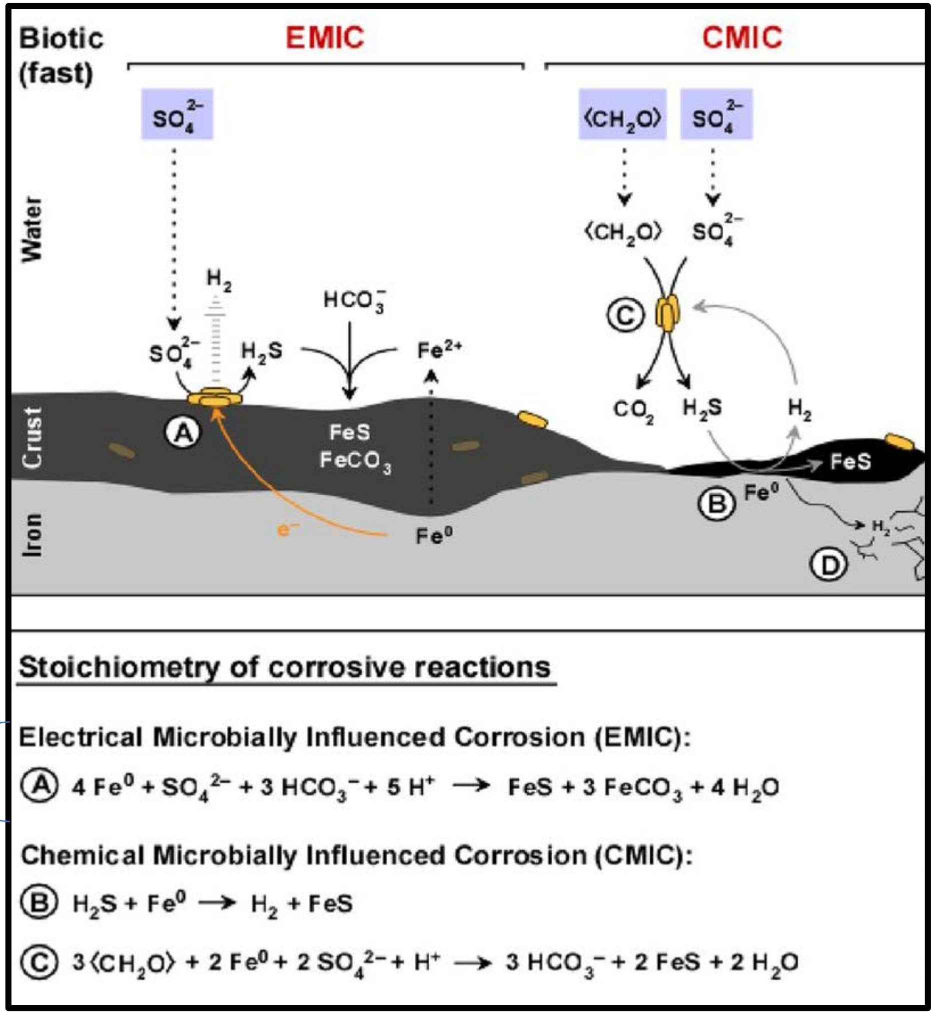

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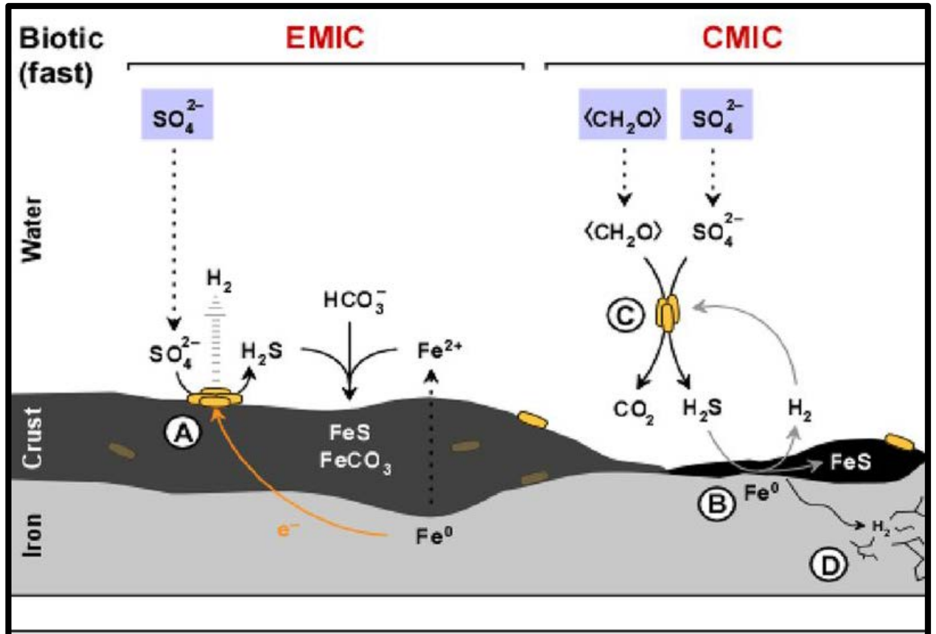

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Corrosive by-products of microbial metabolism

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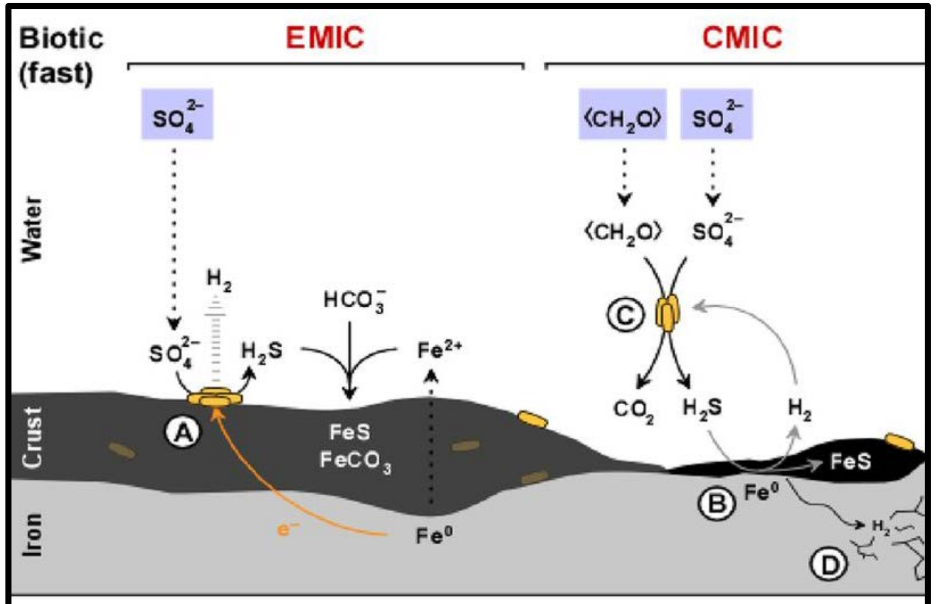

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Corrosive by-products of microbial metabolism

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

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$4\ Fe^0 + SO_4^{2-} + 3\ CO_3^{2-} + 8H^+ \longrightarrow 3\ FeCO_3 + FeS + 4\ H_2O$

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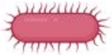
EMIC

$2\ CH_2O + SO_4^{2-} + 2H^+ \leftrightarrow H_2S + 2\ CO_2 + 2\ H_2O$ 

$4\ Fe^0 + SO_4^{2-} + 10\ H^+ \longrightarrow 4\ Fe^{2+} + H_2S + 4\ H_2O$ 

$Fe^{2+} + H_2S \leftrightarrow FeS + 2\ H^+$

$Fe^{2+} + CO \leftrightarrow FeCO_3$

$4\ Fe^0 + SO_4^{2-} + 3\ CO_3^{2-} + 8H^+ \longrightarrow 3\ FeCO_3 + \boxed{FeS} + 4\ H_2O$

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

eurad

DISSIMILATORY SULFATE REDUCTION

CMIC

$4\ H_2 + SO_4^{2-} + 2\ H^+ \leftrightarrow H_2S + 4\ H_2O$

$2\ CH_2O + SO_4^{2-} + 2H^+ \leftrightarrow H_2S + 2\ CO_2 + 2\ H_2O$

$Fe^0 + H_2S \longrightarrow FeS + H_2$

$3\ H_2 + SO_4^{2-} + Fe^0 + 2\ H^+ \longrightarrow \boxed{FeS} + 4\ H_2O$

$2\ CH_2O + SO_4^{2-} + Fe^0 + 2\ H^+ \longrightarrow \boxed{FeS} + 2\ CO_2 + H_2 + 2\ H_2O$

Protective layer

Decelerate in time, except when FeS film is disrupted

Can take place as long as a diffusion path for H_2S to the metal container exists

EMIC

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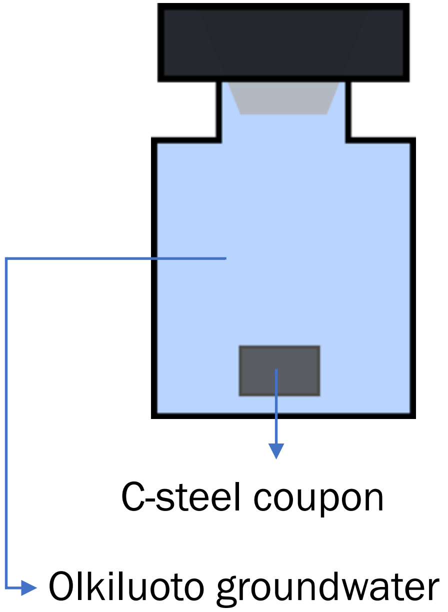
faster

Unlikely that biofilms will develop on container surfaces

$FeS \longleftrightarrow FeS + 3\ FeCO_3$

Which of the 2

MICROBIAL INDUCED CORROSION: EXPERIMENTAL WORK



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

Rajala, P., L. Carpén, M. Vepsäläinen, M. Raulio, E. Sohlberg and M. Bomberg (2015). "Microbially Induced Corrosion of Carbon Steel in Deep Groundwater Environment." Frontiers in Microbiology 6.

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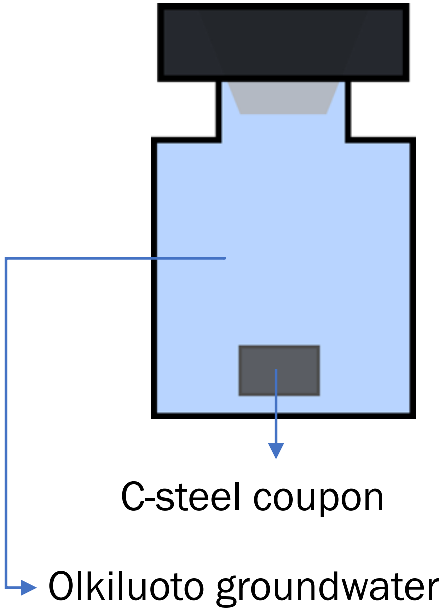
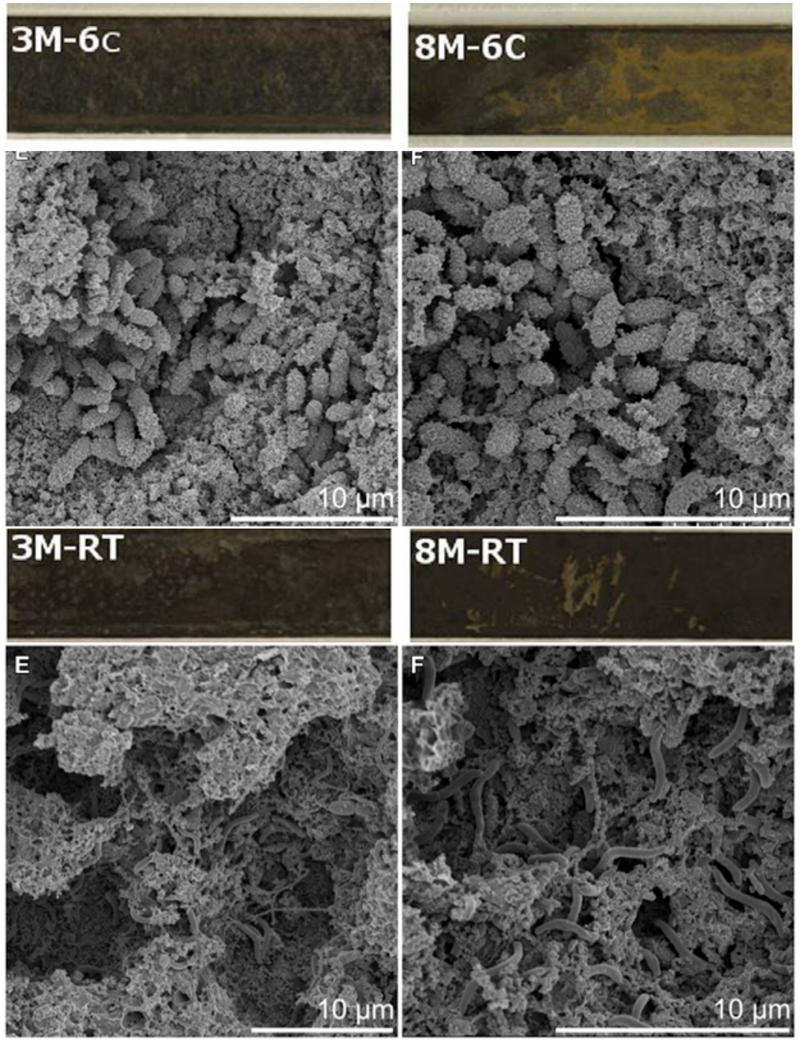


3 & 8 months at RT or 6 °C in anoxic conditions



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

Rajala, P., L. Carpén, M. Vepsäläinen, M. Raulio, E. Sohlberg and M. Bomberg (2015). "Microbially Induced Corrosion of Carbon Steel in Deep Groundwater Environment." Frontiers in Microbiology 6.

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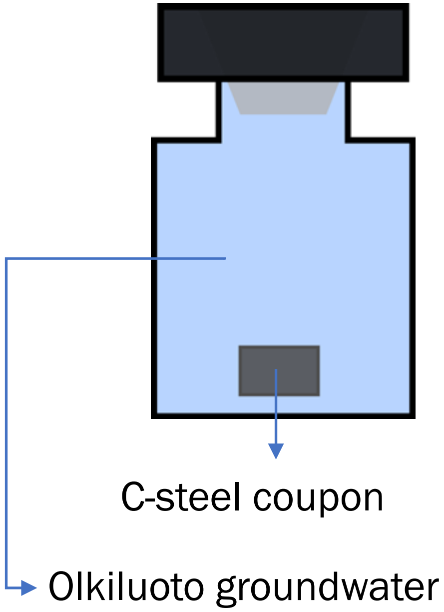

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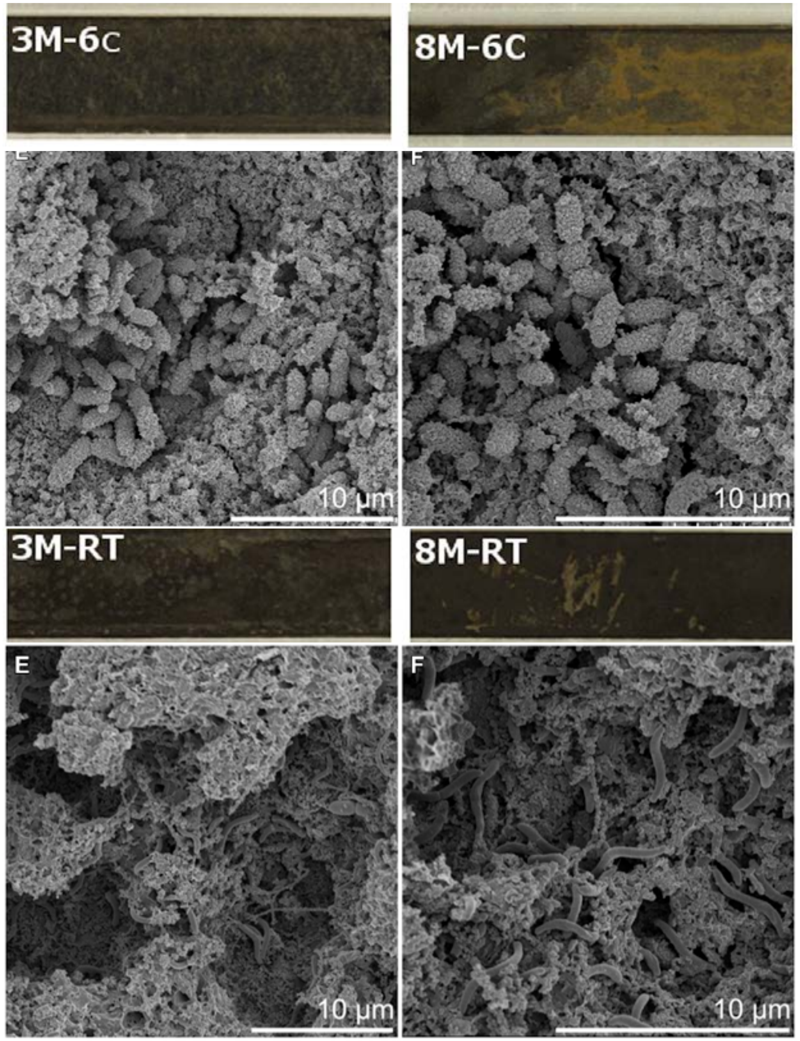

- Biofilm formation on the surface of the coupons
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- Betaproteobacteria
- Iron oxidizers
- Iron reducers
- SRB

Rajala, P., L. Carpén, M. Vepsäläinen, M. Raulio, E. Sohlberg and M. Bomberg (2015). "Microbially Induced Corrosion of Carbon Steel in Deep Groundwater Environment." Frontiers in Microbiology 6.

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

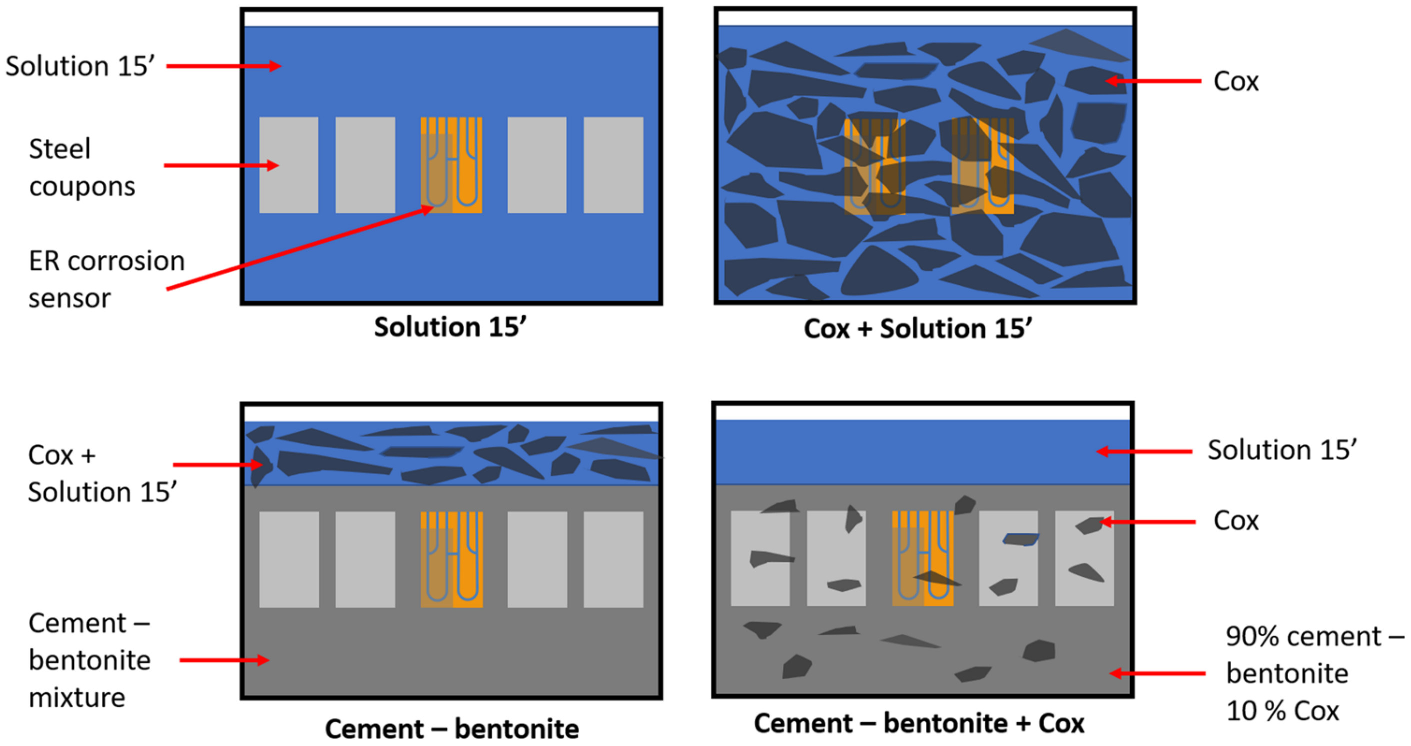
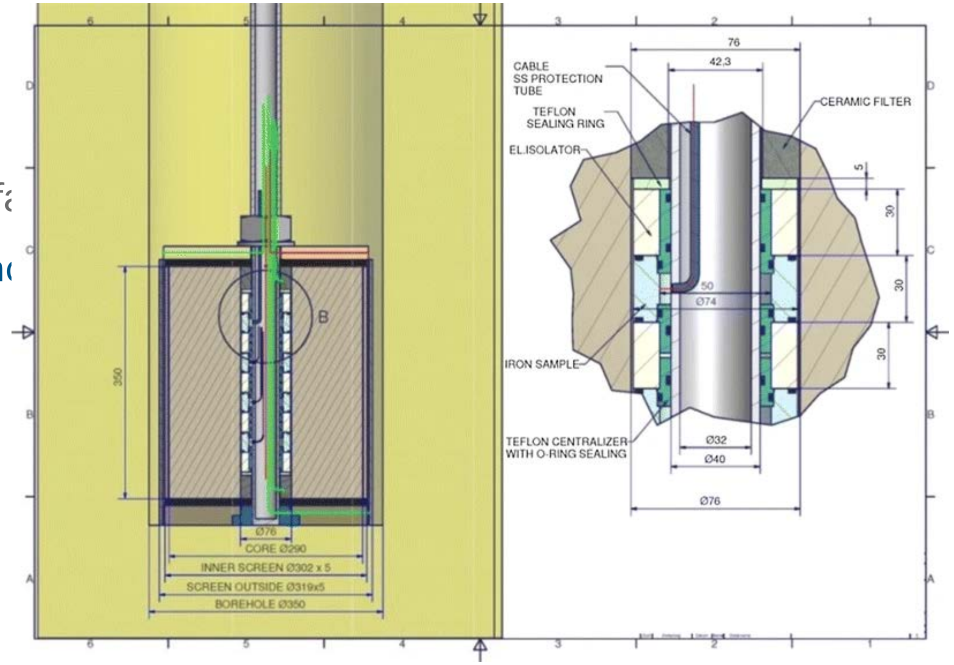


Figure from Diler, E., V. Leblanc, H. Gueuné, N. Larché, V. Deydier, Y. Linard, D. Crusset and D. Thierry (2021). "Potential Influence of Microorganisms on the Corrosion of Carbon Steel in the French High- and Intermediate-Level Long-Lived Radioactive Waste Disposal Context." Materials and Corrosion 72(1-2).

MICROBIAL INDUCED CORROSION: EXPERIMENTAL WORK

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



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  - No microbial impact on corrosion
    - No growth of SRB
      - due to persistence of O_2 in bentonite
      - bentonite is fully saturated when O_2 is depleted

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      - due to persistence of O_2 in bentonite
      - bentonite is fully saturated when O_2 is depleted
  - Indigenous bentonite community grew & persisted

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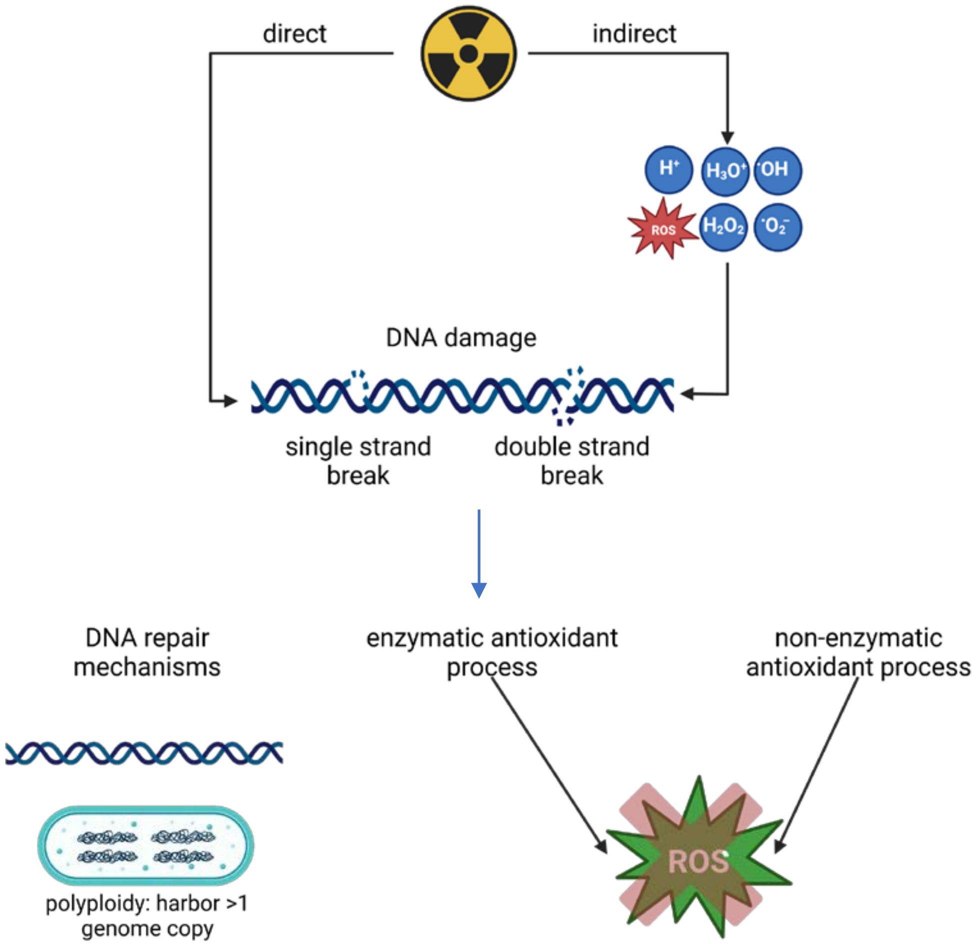
IMPACT OF IRRADIATION ON MICROBIAL VIABILITY IN THE CONTEXT OF NUCLEAR WASTE DISPOSAL



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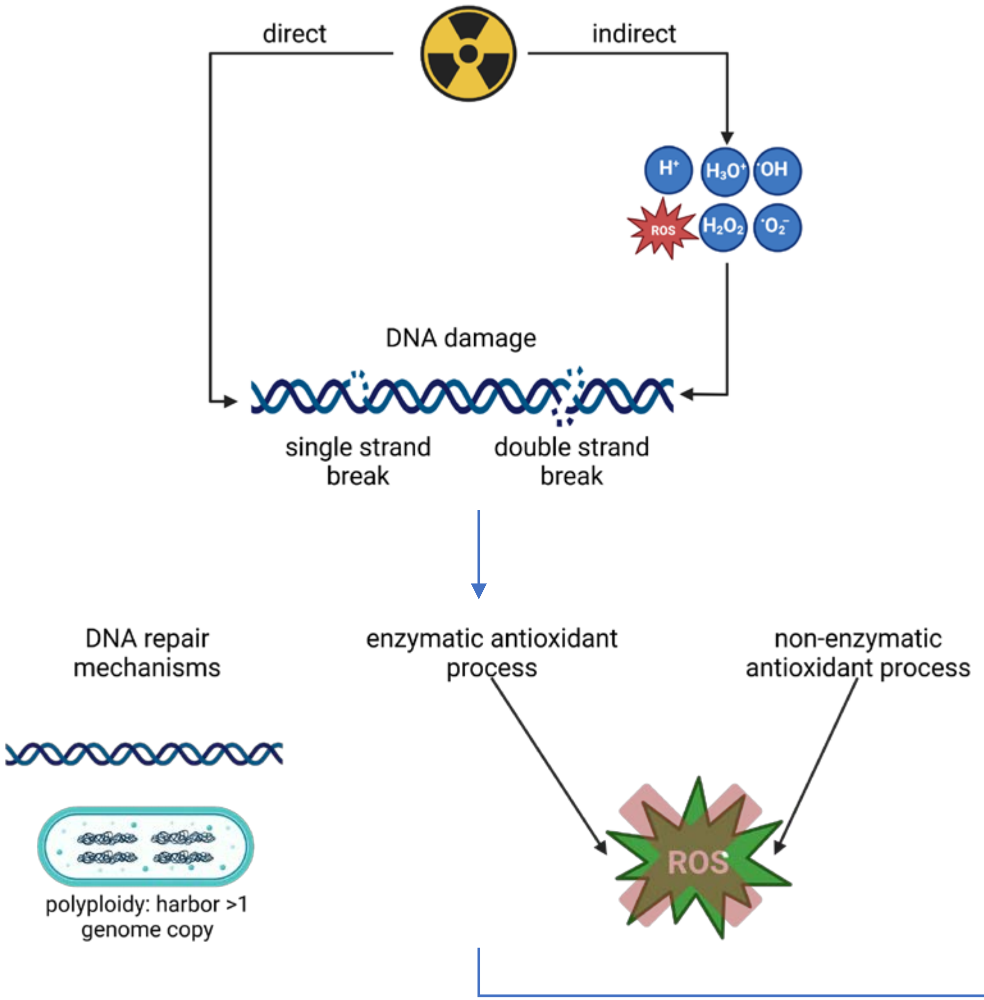

Overlaps with response to desiccation

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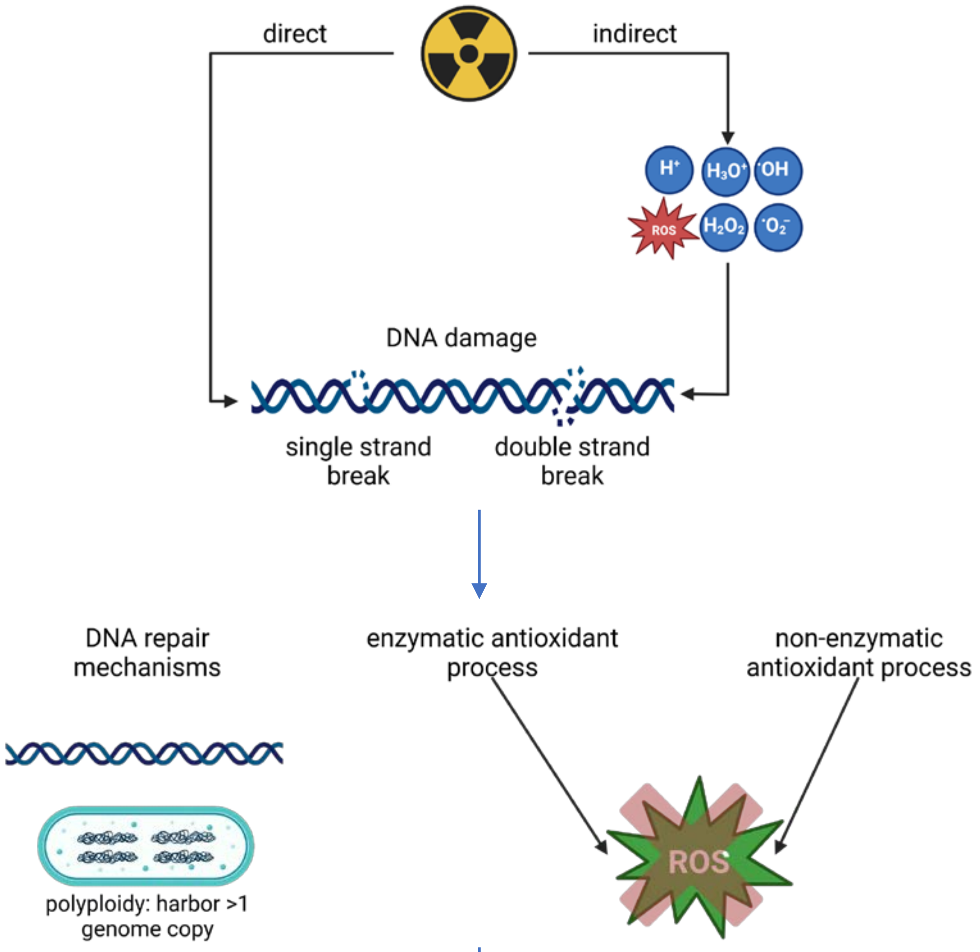

Radiation sensitivity depends on:

- Acute or chronic irradiation
- Cell concentration
- Vegetative state
- Physiological features
- Genetic features

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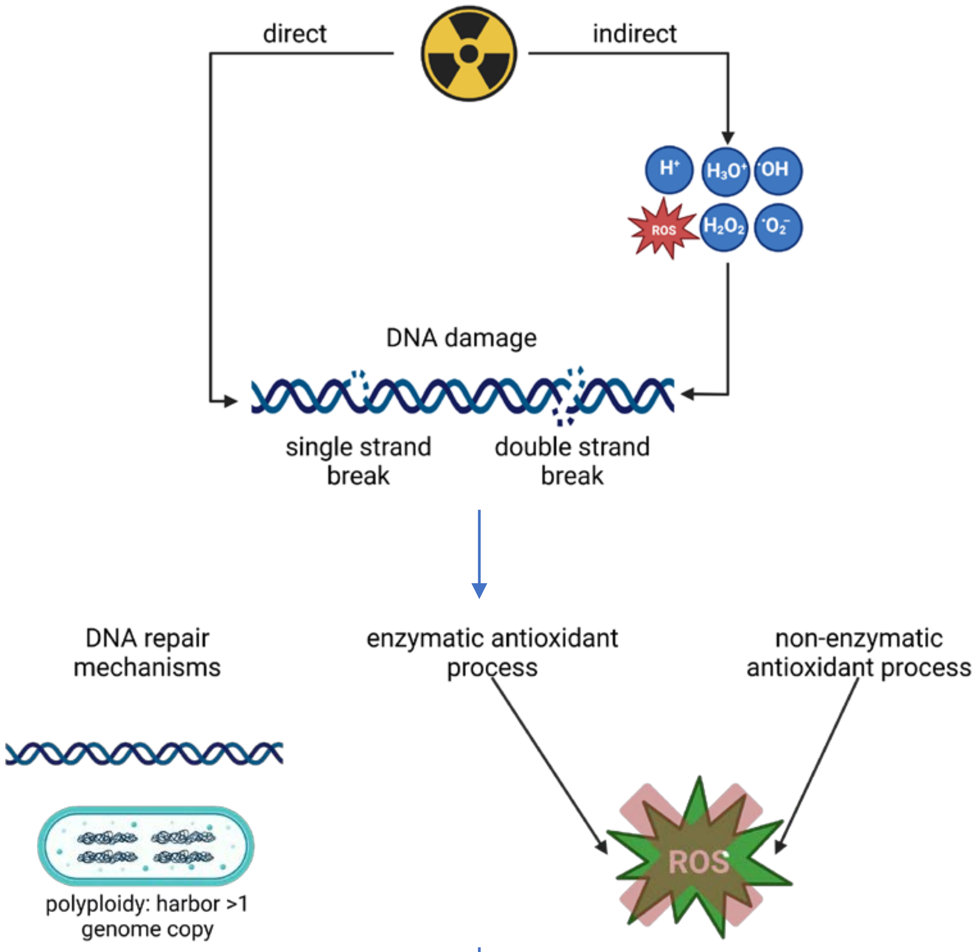

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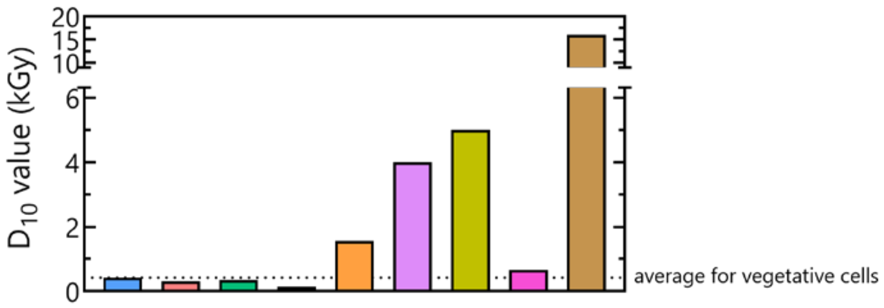
Big differences between ≠ bacteria



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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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  - BaM Bentonite + granitic porewater VITA exposed to γ-irradiation for 9 weeks at 13 Gy/h (19.6 kGy) did not completely eliminate bacteria

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  - ± 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

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  - High swelling pressure
  - Low water activity (<0.96)

Limit microbial activity

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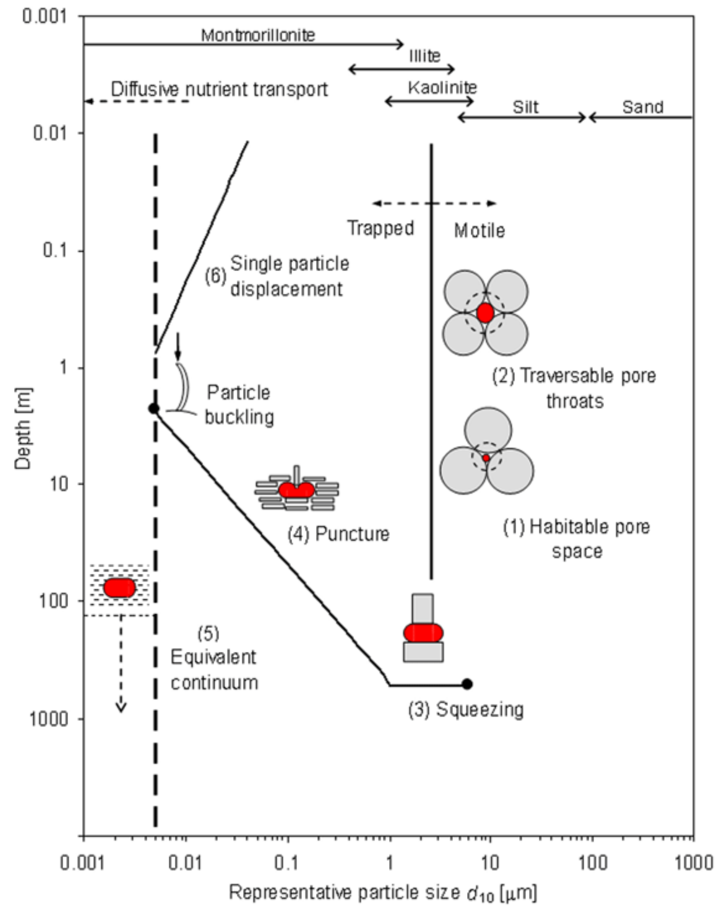
- **High swelling pressure → space limitation**
  - Direct effects
  - Indirect effects → Diffusion limited nutrient transport



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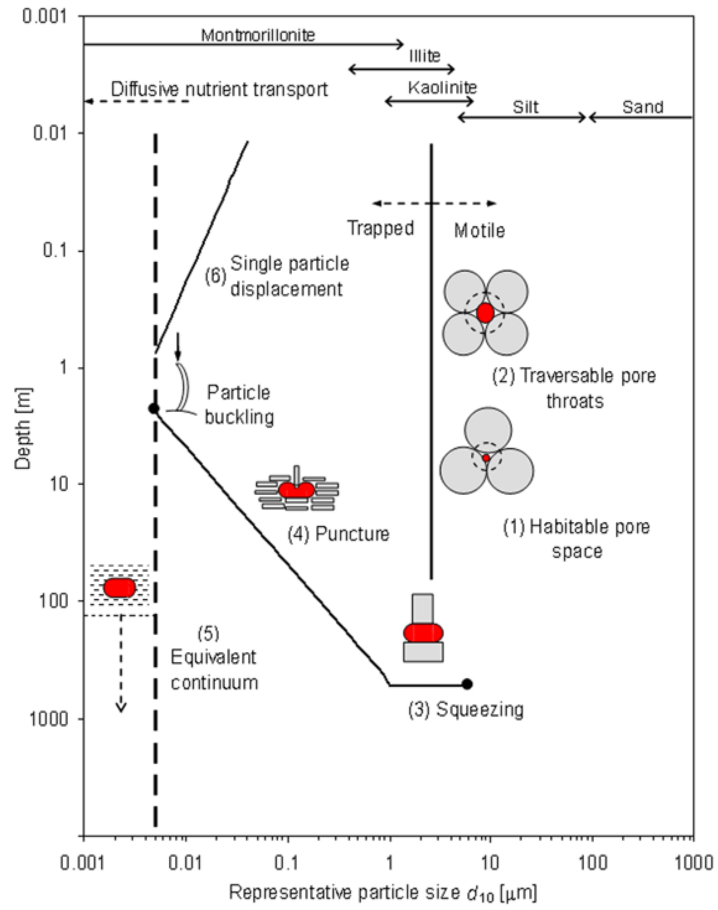
  - Uniform dry density ≥ 1600 kg/m³ → microbial activity is limited



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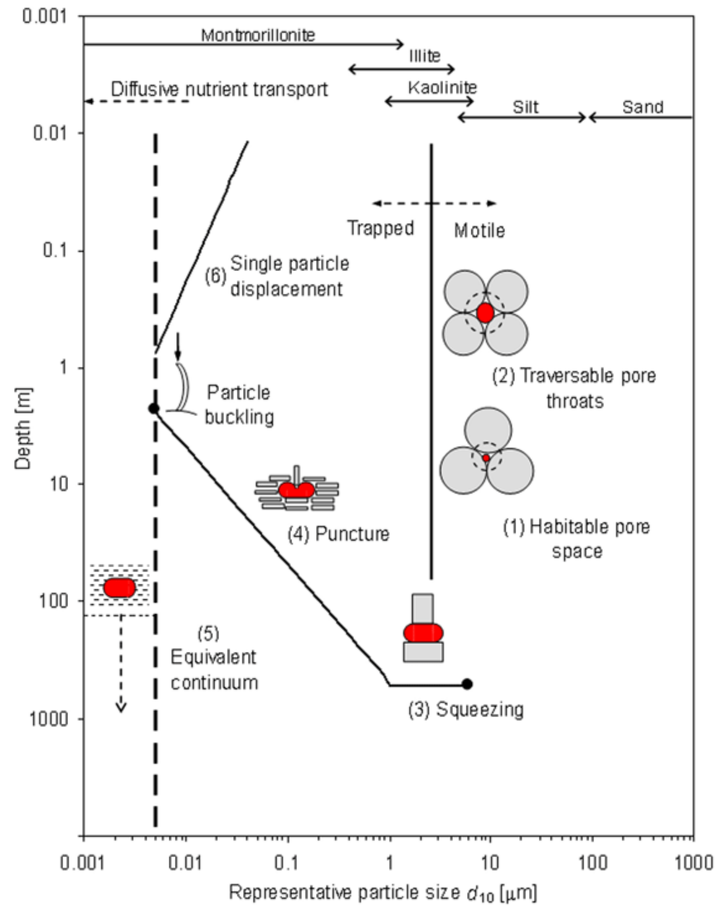
    - Fundamental basis of this limit?
    - Why is there a difference between different bentonites?



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  - Low available organic carbon mainly composed of plant-derived waxes and highly recalcitrant aromatic carbon
  - Recent analysis
    - Alkanes
    - Toluenes
    - Aromatic compounds

Biodegradable, but amount?

eurad

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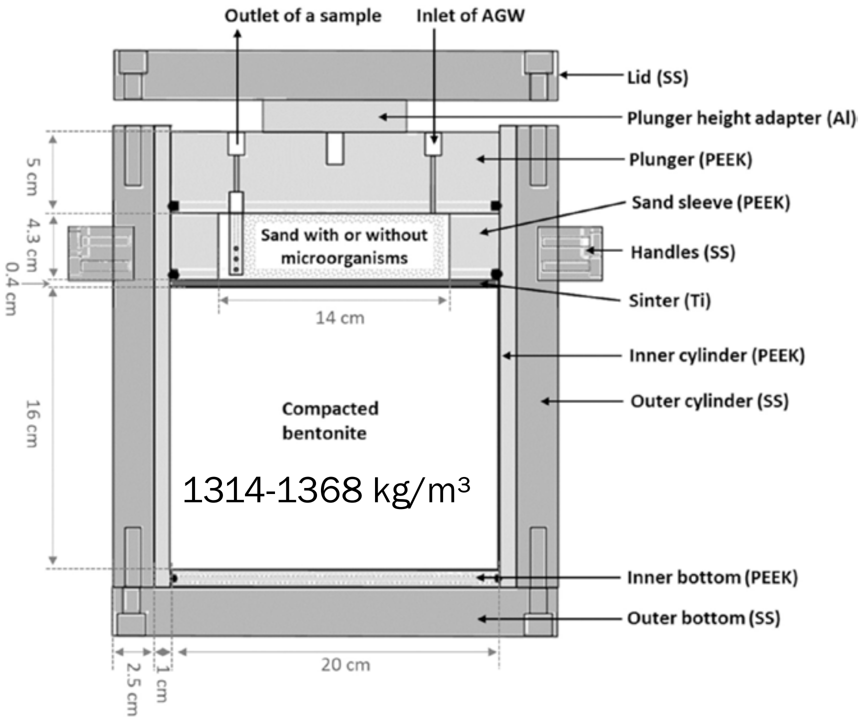
  - Organic material in compacted bentonite is able to sustain SRB
    - Wyoming, Indian & Bulgarian



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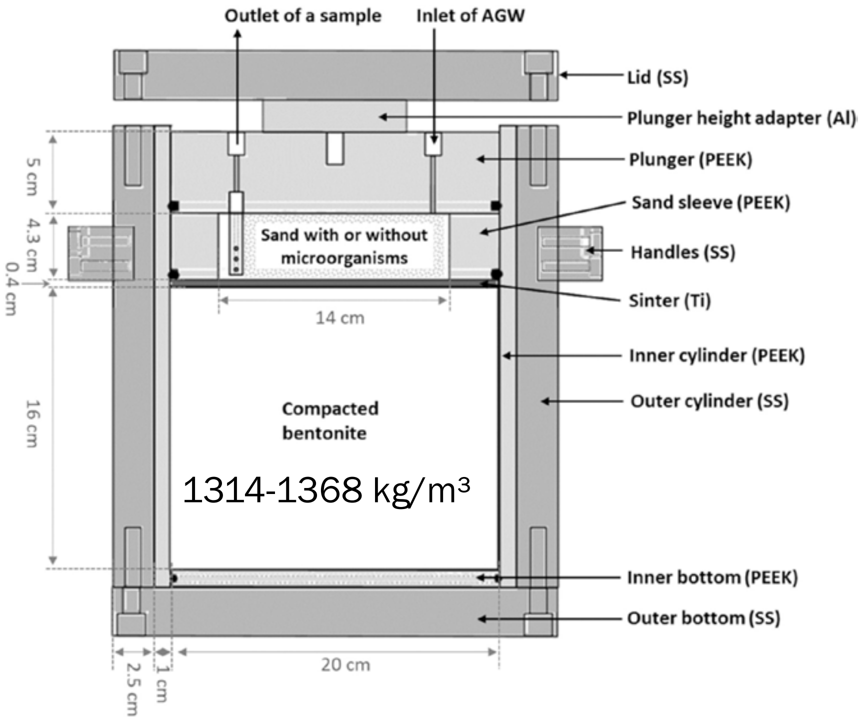
  - Organic material in compacted bentonite is able to sustain SRB
    - Wyoming, Indian & Bulgarian
  - Autotrophic growth?
    - H_2 as electron donor & CO_2 as carbon source



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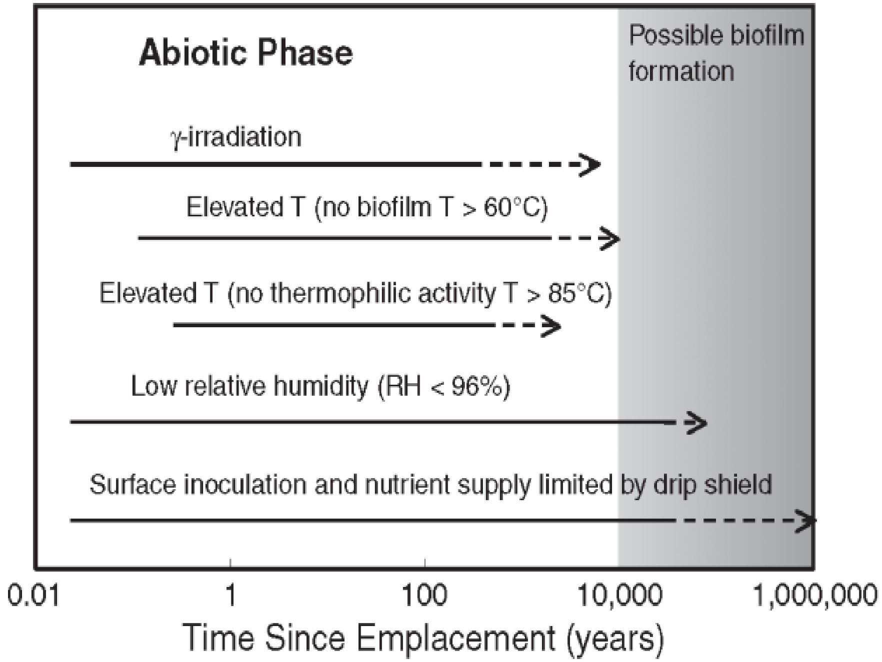
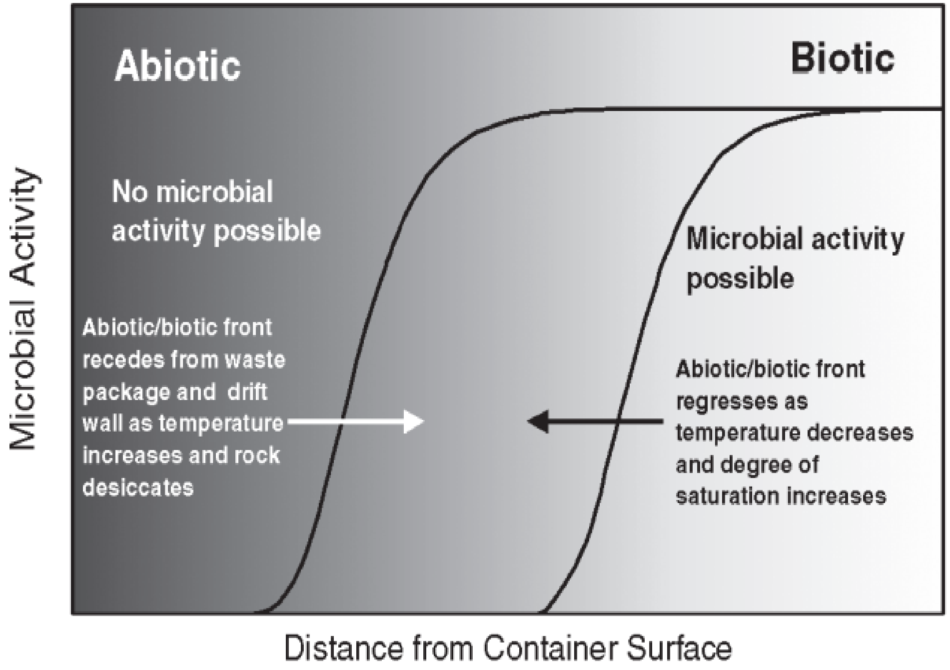
MICROBIAL TRANSIENTS

- Nuclear waste repositories are considered inhospitable for microorganisms





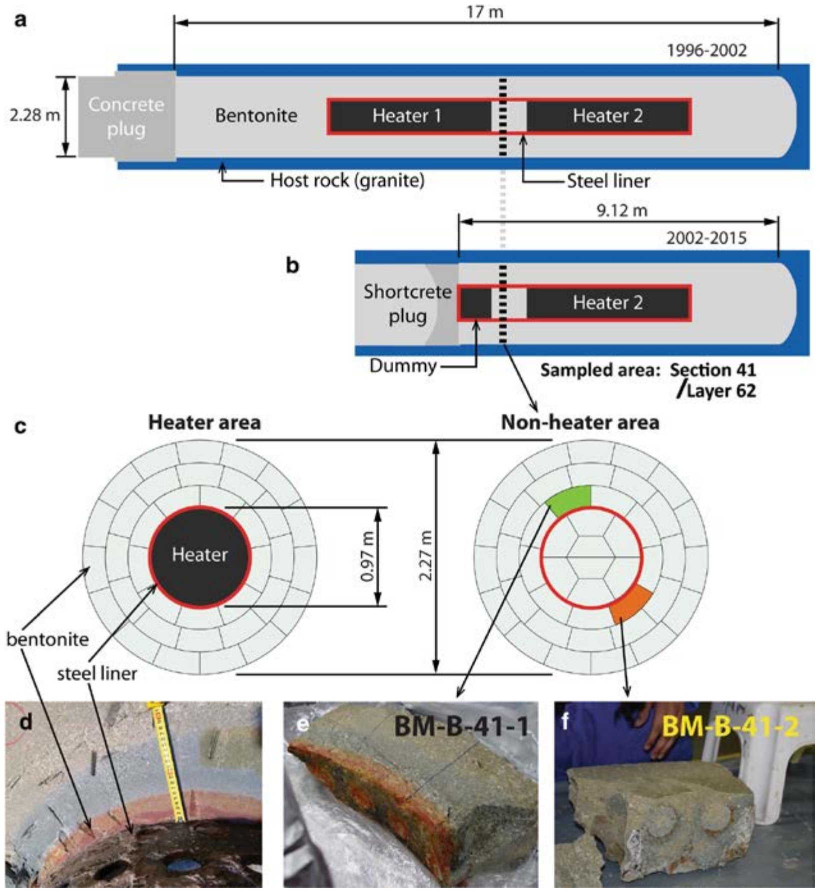
- Presence of microorganisms demonstrated in several *in situ* tests under certain conditions

Figures from King, F. (2009). "Microbiologically Influenced Corrosion of Nuclear Waste Containers." Corrosion 65(4) ; Lloyd, A. C., R. J. Schuler, J. J. Noël, D. W. Shoesmith and F. King (2004). "The Influence of Environmental Conditions and Passive Film Properties on the Mic of Engineered Barriers in the Yucca Mountain Repository." MRS Online Proceedings Library (OPL) 824.

CONTENT

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



Overall layout (a) before (1996–2002) & (b) after (2002–2015) partial dismantling. (c) Cross-sections of the heater & non-heater areas, indicating the location of the sampled blocks. (d) Corrosion-impacted bentonite block still in place at the contact with the steel liner. (e–f) Studied blocks BM-B-41-2 and BM-B-42-2

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).

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)

Figure from Fernández, A.M. 2019. Gas and water sampling from the FEBEX in situ test. Nagra Working Reports. NAB 16-13, 155 pp. NAGRA Technical Report.

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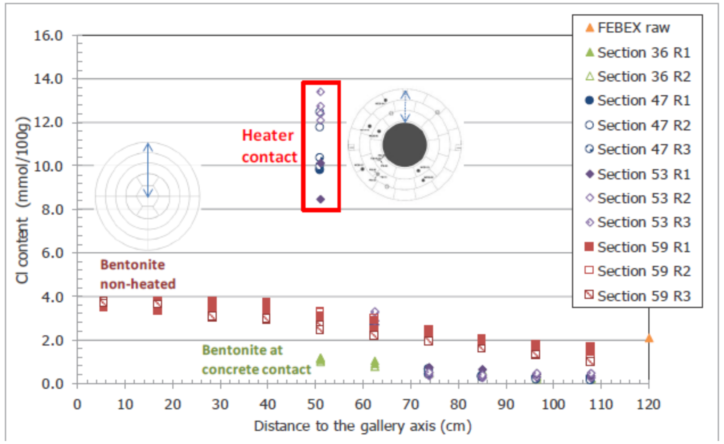
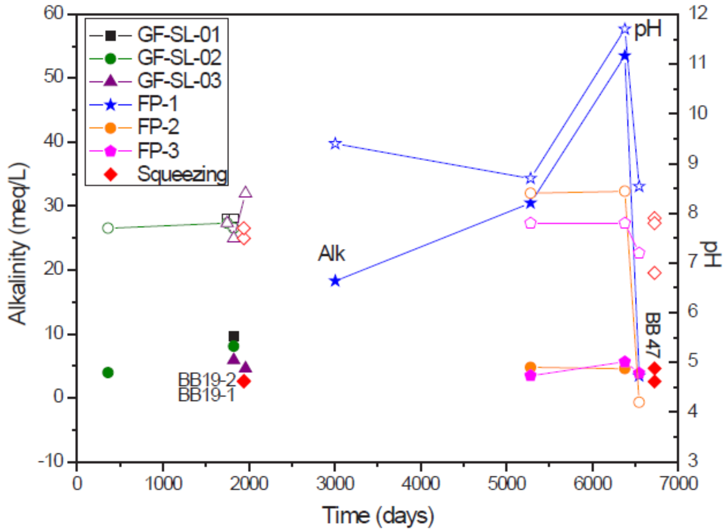
  - Cl^- accumulation at the heater → Precipitation of GR-Cl (green rusts), other chloride salts and Cl-bearing Fe^{3+} oxyhydroxide (akaganeite) observed after dismantlingthe FEBEX *in-situ* test
  - pH variations due to the thermo-hydraulic gradients in the bentonite barrier
  - Formate, acetate, oxalate only in samples near heater





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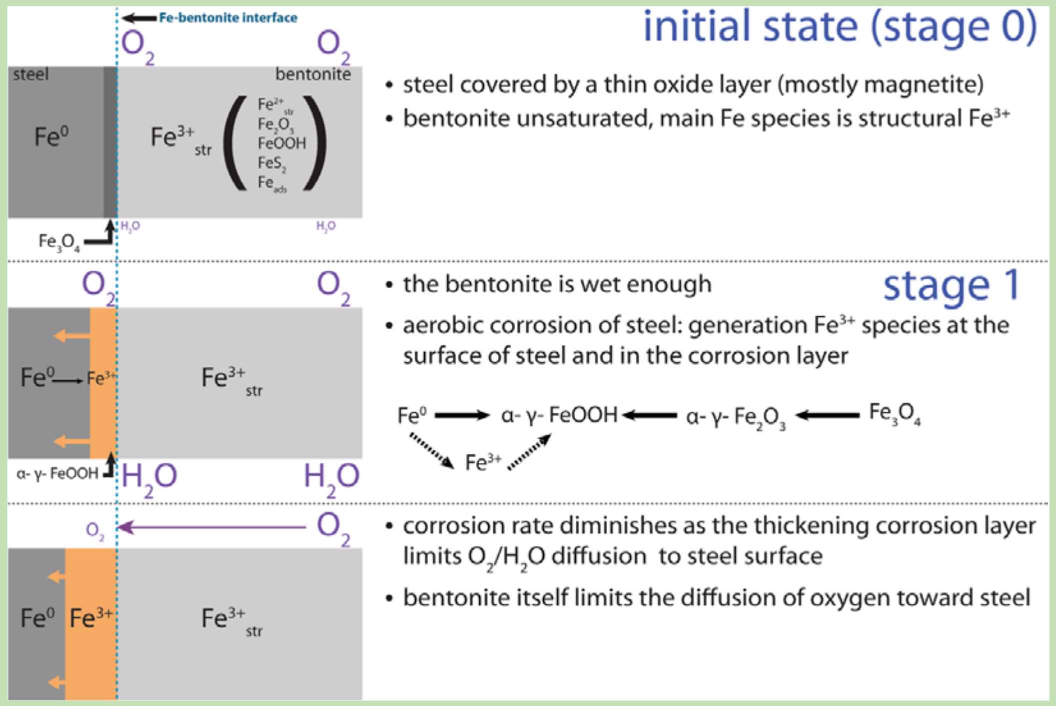

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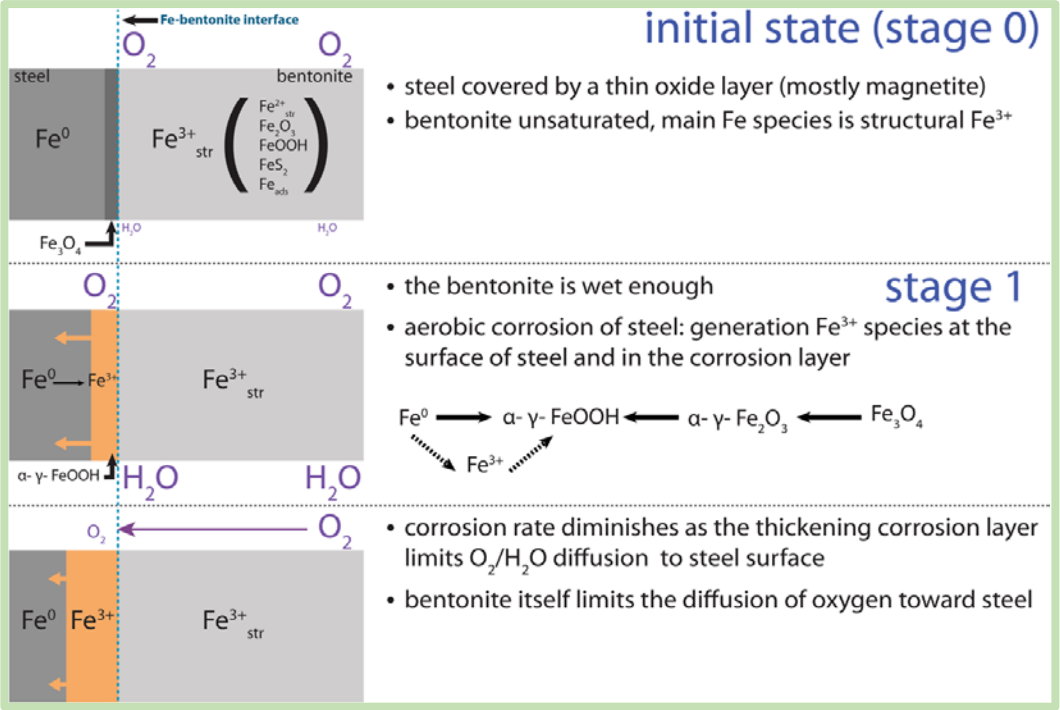


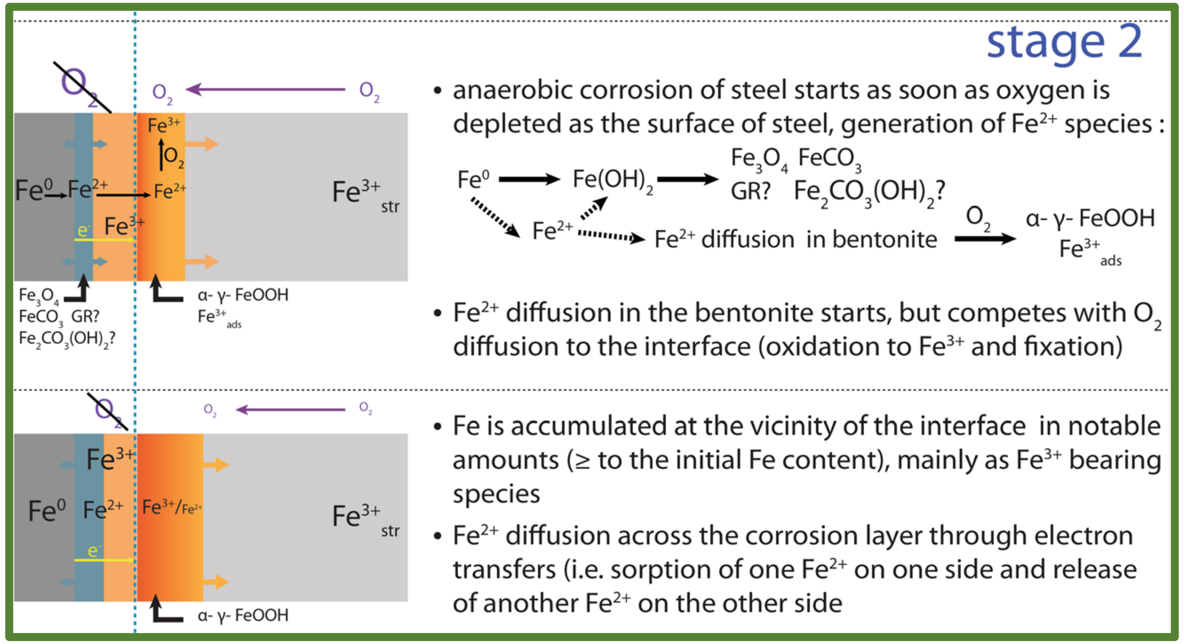
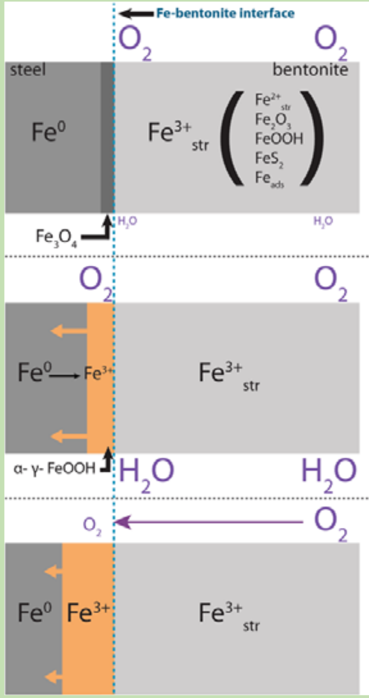


Figure from Hadi, J., P. Wersin, V. Serneels and J.-M. Greneche (2019). "Eighteen Years of Steel–Bentonite Interaction in the Febex in Situ Test at the Grimsel Test Site in Switzerland." Clays and Clay Minerals 67(2).

EXAMPLE OF INTEGRATED TEST: FEBEX

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

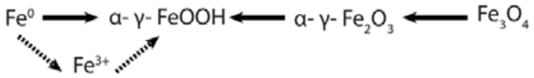


initial state (stage 0)

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

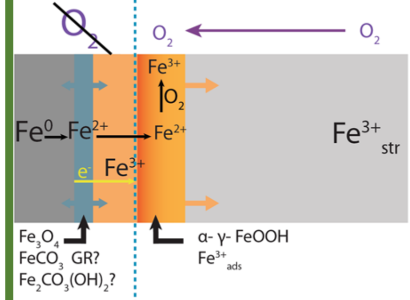
stage 1

- the bentonite is wet enough
- aerobic corrosion of steel: generation Fe^{3+} species at the surface of steel and in the corrosion layer

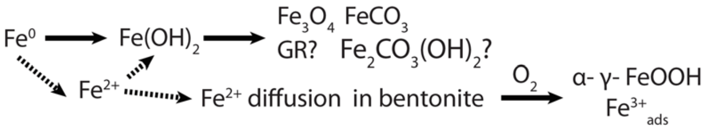


- corrosion rate diminishes as the thickening corrosion layer limits O_2/H_2O diffusion to steel surface
- bentonite itself limits the diffusion of oxygen toward steel

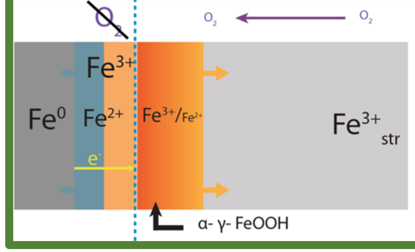
stage 2



- anaerobic corrosion of steel starts as soon as oxygen is depleted as the surface of steel, generation of Fe^{2+} species :

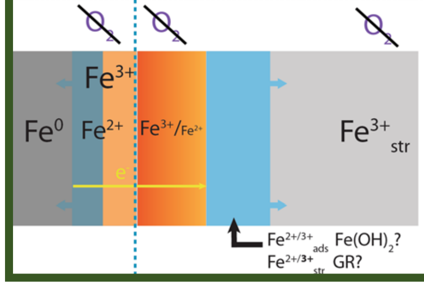


- Fe^{2+} diffusion in the bentonite starts, but competes with O_2 diffusion to the interface (oxidation to Fe^{3+} and fixation)

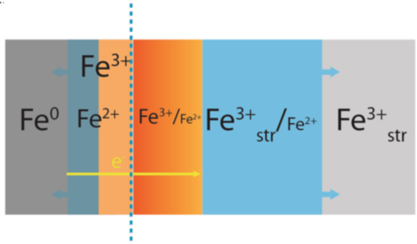


- Fe is accumulated at the vicinity of the interface in notable amounts (≥ to the initial Fe content), mainly as Fe^{3+} bearing species
- Fe^{2+} diffusion across the corrosion layer through electron transfers (i.e. sorption of one Fe^{2+} on one side and release of another Fe^{2+} on the other side

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

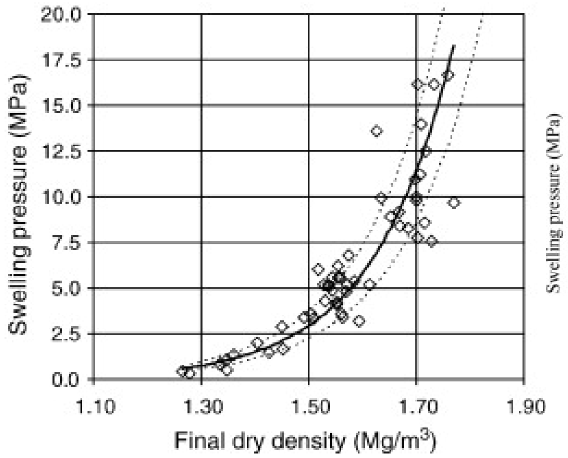


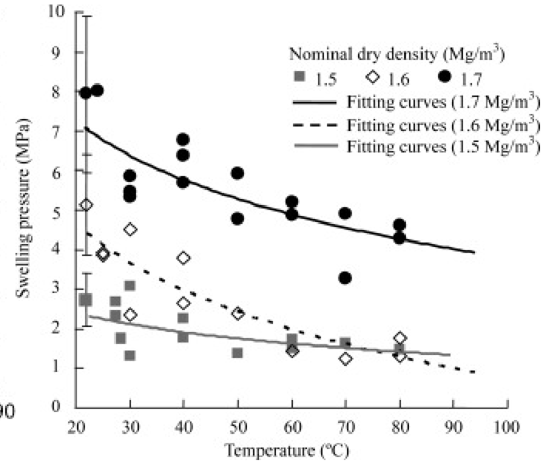
- Fe^{2+} is accumulated at the vicinity of the interface, and also further deeper in the bentonite but in lower quantities (only a small portion of initially present Fe, <10%) mainly sorbed on the clay edges
- electron transfers also possible across the zones rich in corrosion products

Figure from Hadi, J., P. Wersin, V. Serneels and J.-M. 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).

EXAMPLE OF INTEGRATED TEST: FEBEX

- Mechanical load increases with saturation
  - Depends on:
    - Dry density
    - Temperature
    - Pore water composition





Figures from Villar, M. V. and A. Lloret (2008). "Influence of Dry Density and Water Content on the Swelling of a Compacted Bentonite." Applied Clay Science 39(1);
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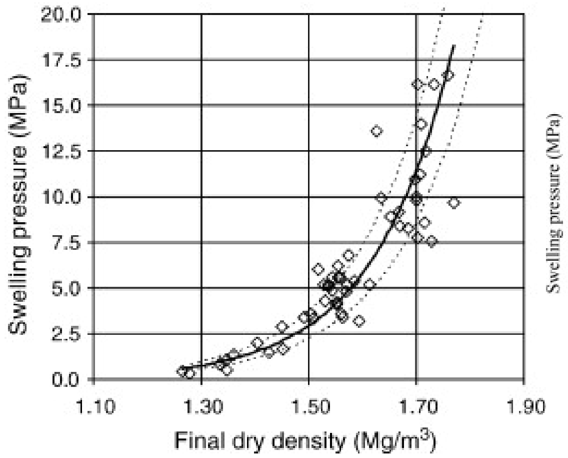
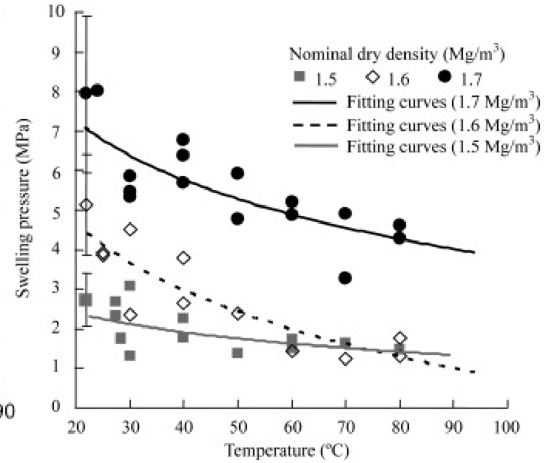
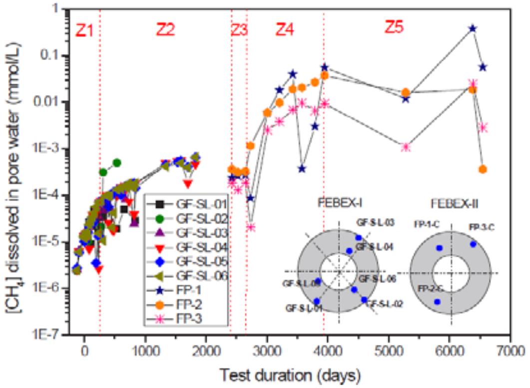
EXAMPLE OF INTEGRATED TEST: FEBEX

- Mechanical load increases with saturation
  - Depends on:
    - Dry density
    - Temperature
    - Pore water composition
- 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







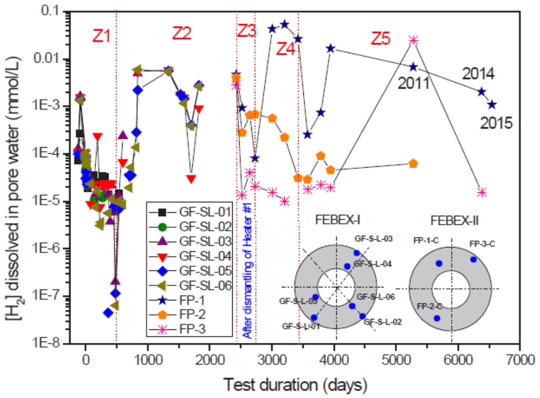


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Figure from Fernández, A.M. 2019. Gas and water sampling from the FEBEX in situ test. Nagra Working Reports. NAB 16-13, 155 pp. NAGRA Technical Report.

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

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

CONTENT

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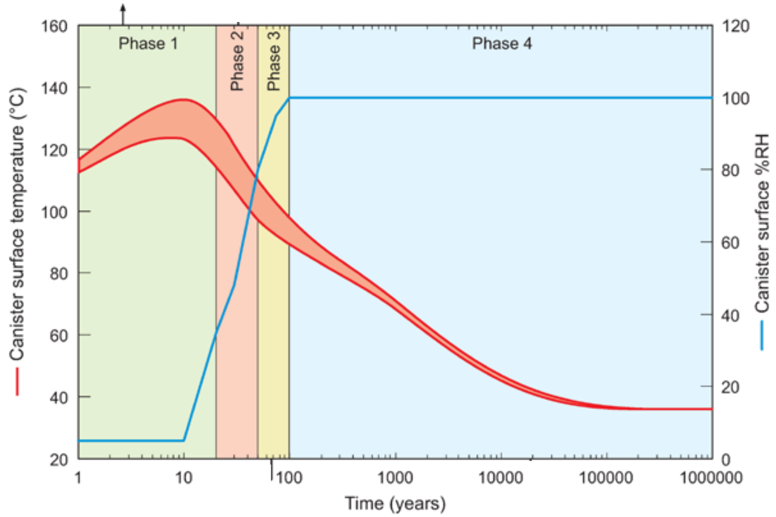
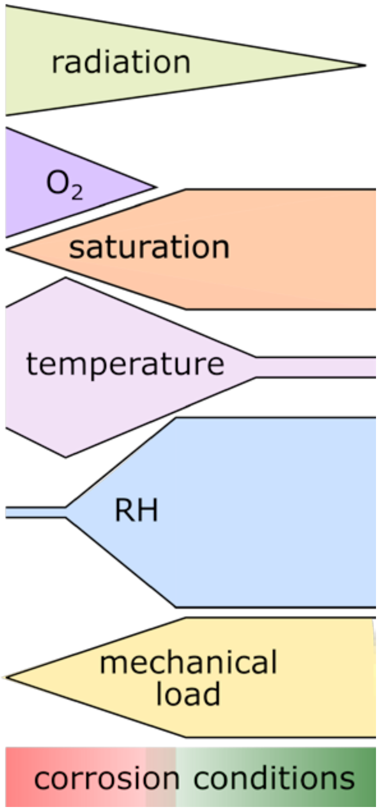
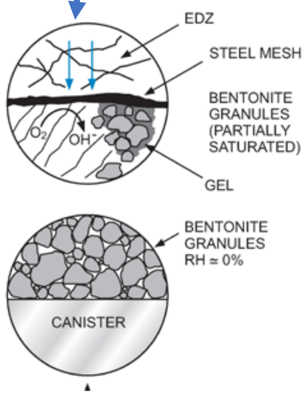
OVERVIEW: GENERIC SCHEME OF 4 IDENTIFIED PHASES & EXPECTED CORROSION PRODUCTS

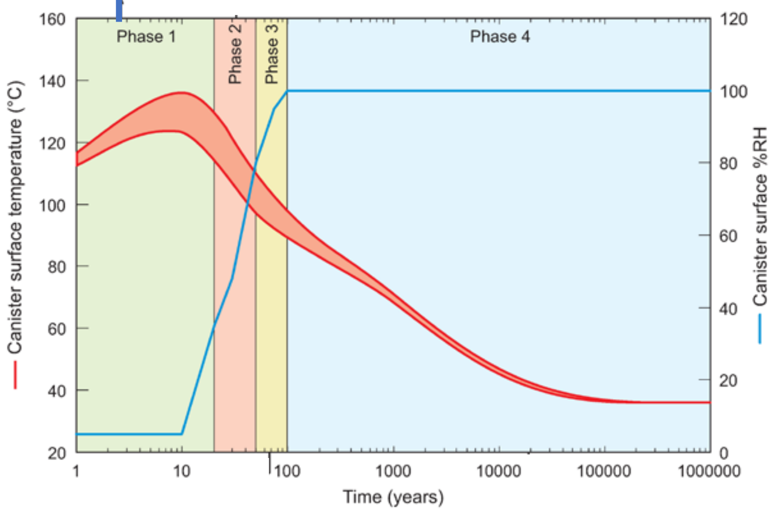




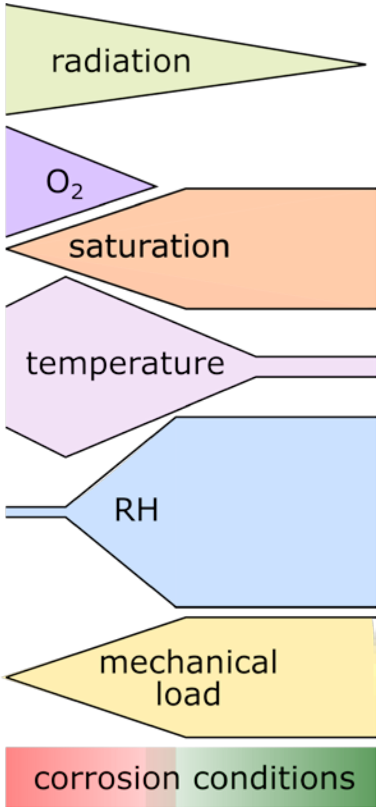
OVERVIEW: GENERIC SCHEME OF 4 IDENTIFIED PHASES & EXPECTED CORROSION PRODUCTS

1: aerobic dry





- Uniform dry oxidation ⟶ FeO_2
- Redistribution of salts ⟶ salt precipitation assisted by desiccation ⟶ swelling pressure around periphery of the tunnel



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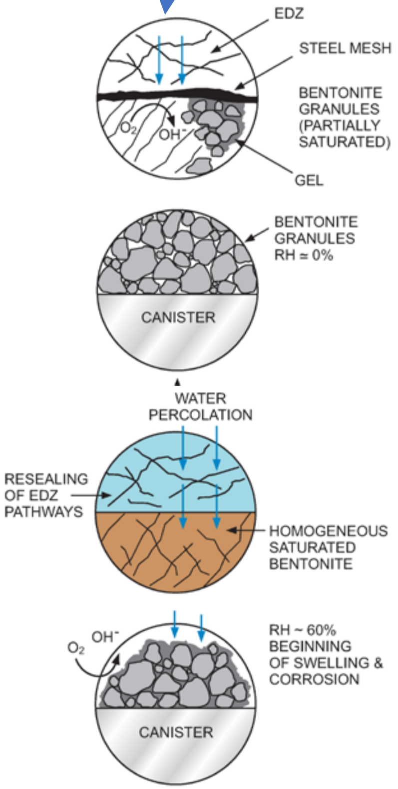
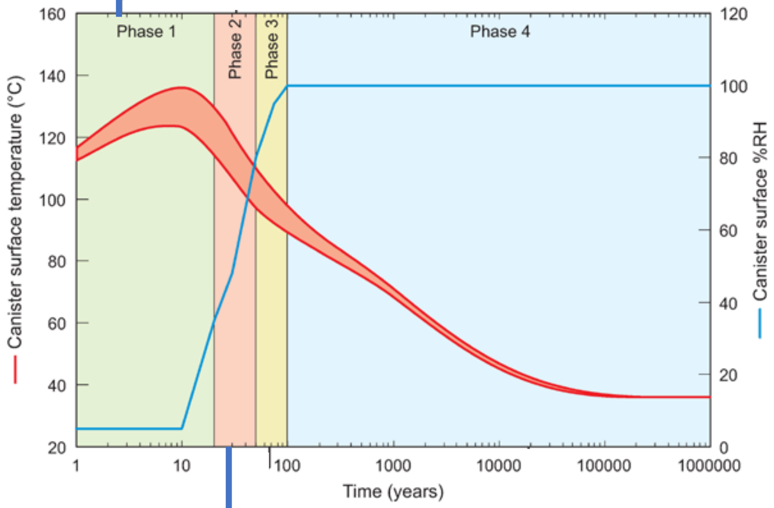
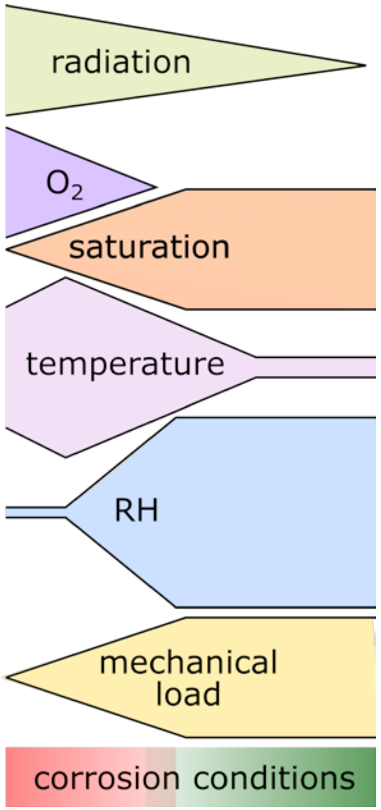




2: aerobic unsaturated

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



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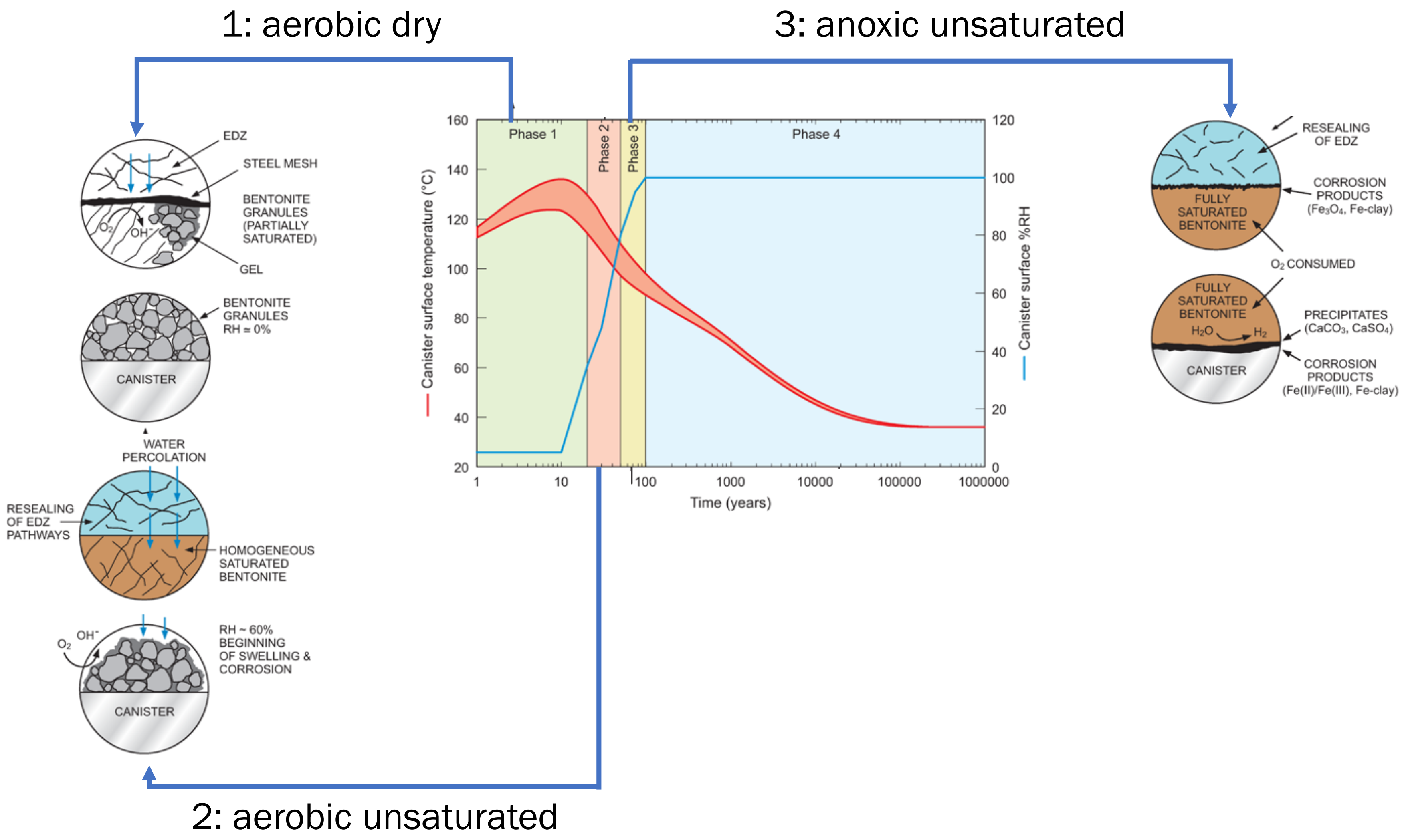

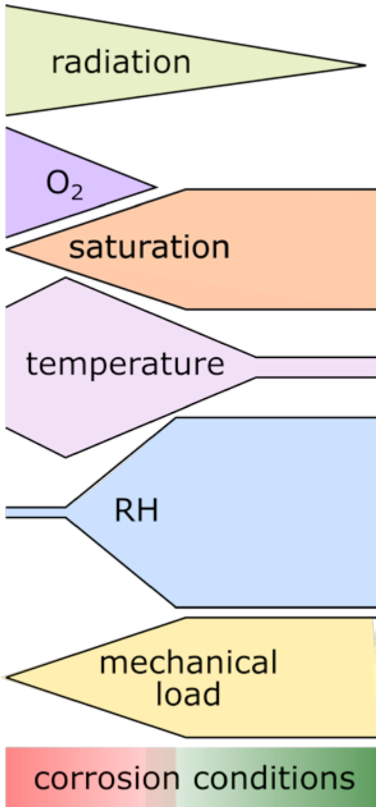

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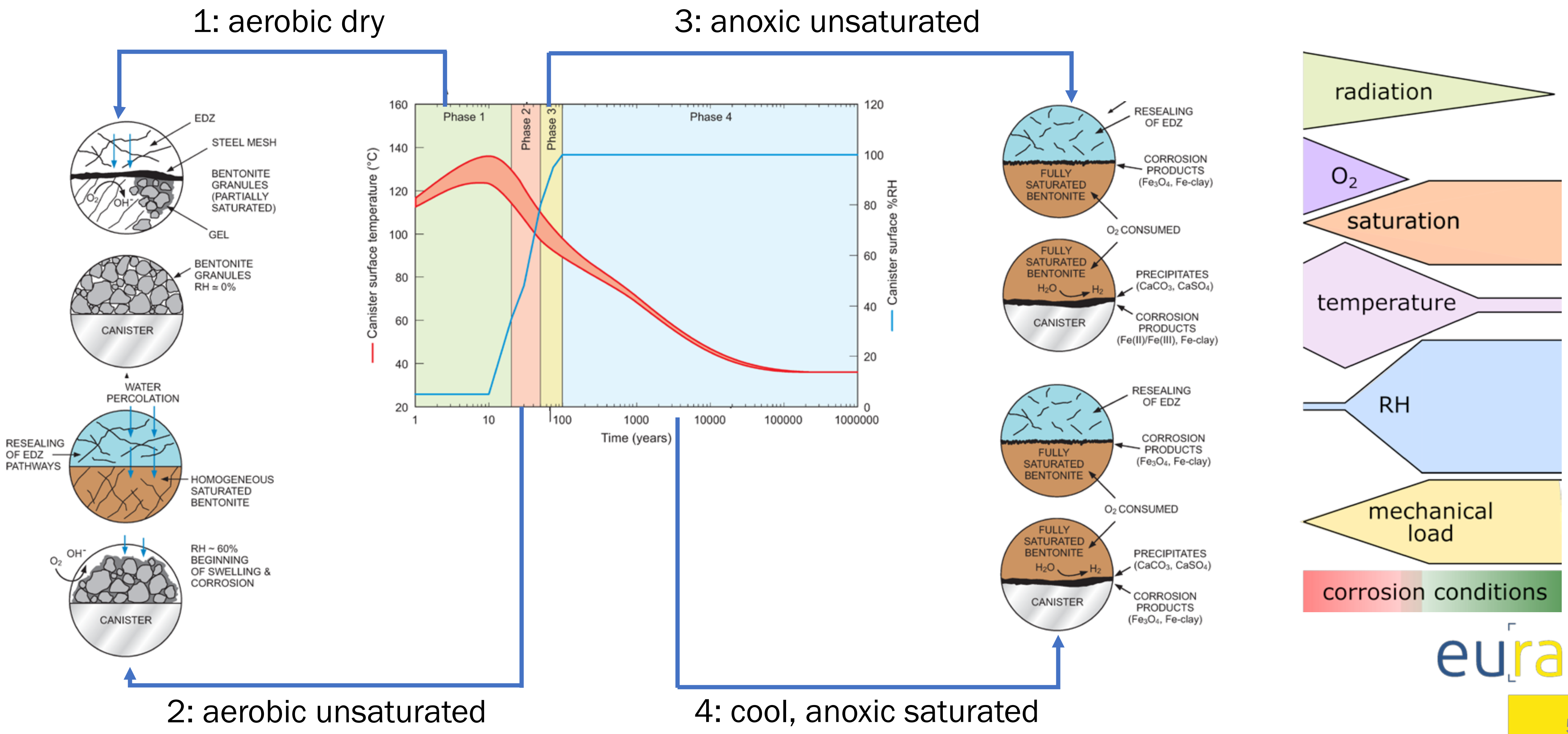

FURTHER READING

- https://www.ejp-eurad.eu/publications/eurad-d151-concord-initial-sota
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- Fraser King, 2017 - 13 - Nuclear waste canister materials: Corrosion behavior and long-term performance in geological repository systems - doi.org/10.1016/B978-0-08-100642-9.00013-X
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NOVEL MATERIAL SOLUTIONS FOR NUCLEAR WASTE DISPOSAL CONTAINER CONCEPTS

This project has received funding from the European Union's Horizon 2020 research and innovation programme 2014-2018 under grant agreement N°847593

LEARNING OUTCOMES

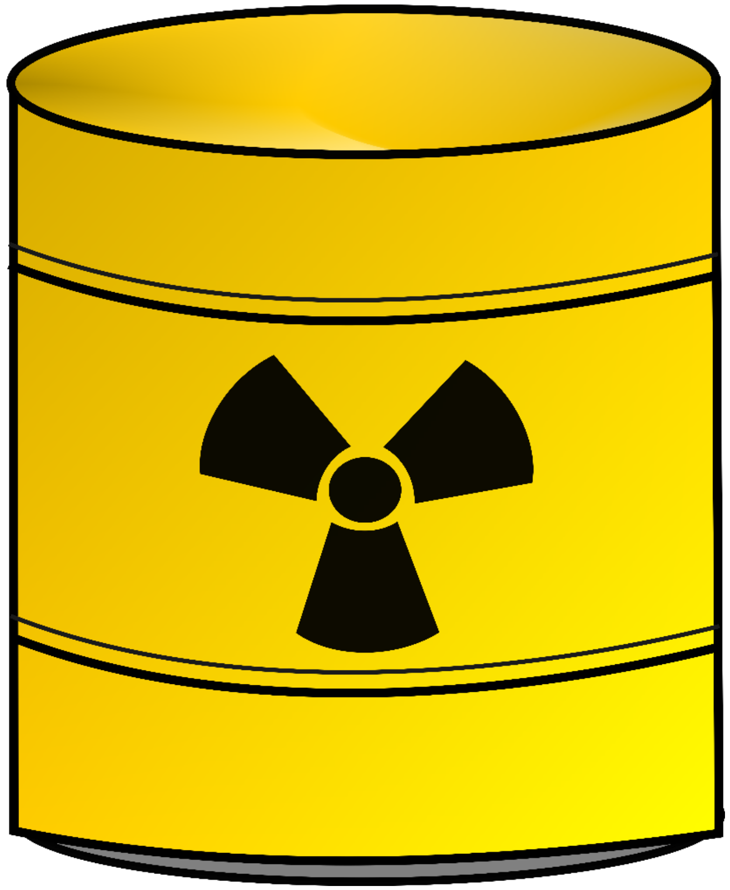
- Understand the advantages & disadvantages of the use of ceramic/metallic materials in nuclear waste disposal
- Identify the current knowledge gaps of the use of ceramic/metallic materials in nuclear waste disposal
- Give an historical overview of the use of ceramic materials in nuclear waste disposal

CONTENTS

CONTENTS

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



INTERNATIONAL ATOMIC ENERGY AGENCY, Development of Specifications for Radioactive Waste Packages, IAEA-TECDOC-1515, IAEA, Vienna (2006)

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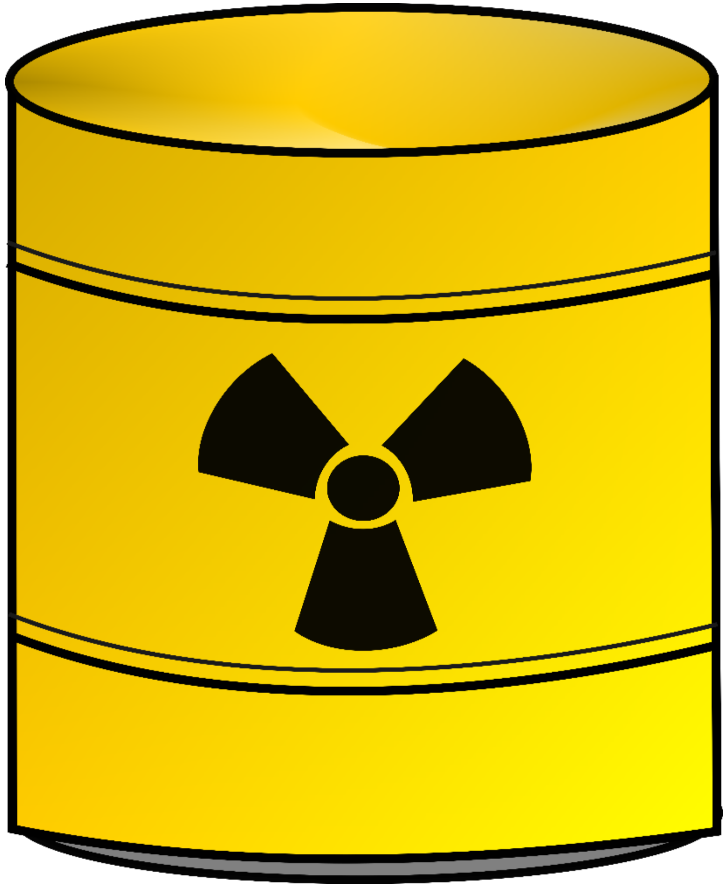
- In some cases the container also plays a role in the near field containment of the radionuclides for a certain period after closure



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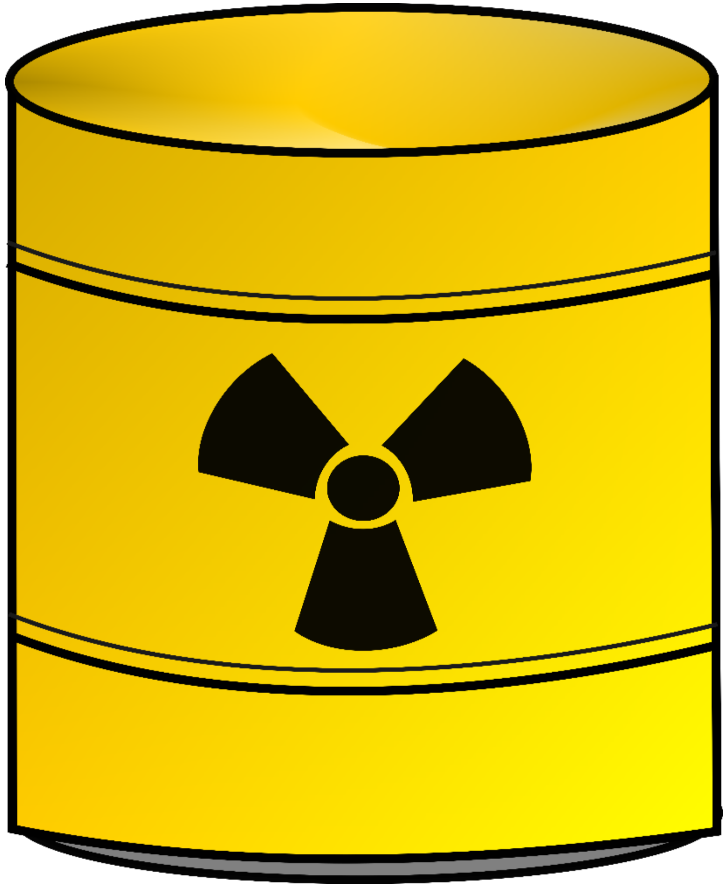
- In some cases the container also plays a role in the near field containment of the radionuclides for a certain period after closure
- Main parameters & control methods according to IAEA (2006):
  - Material itself
  - Geometric shape & dimensions
  - Design & operation of internal features
  - Lifting arrangements
  - Container internal corrosion
  - Container strength
  - Selection of surface coating & texture
  - Design & operation of closure features
  - Resistance to environmental conditions



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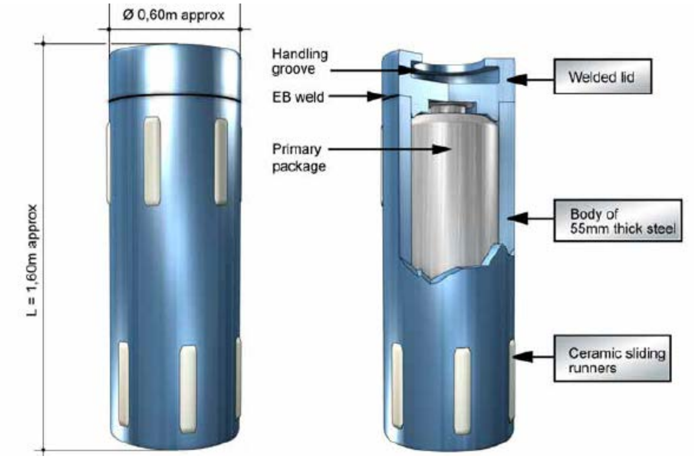
DIFFERENT TYPES OF WASTE CONTAINERS EXIST

- 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

WMO	Container concept	Estimated or target lifetime (year)	Nominal buffer dry density (g/cm³)	Max. container temp. (°C)	Time to full nearfield saturation (year)	Max. surface absorbed dose (Gy/h)	Expected mechanical loads (MPa)
SKB	Cu-cast Fe	$>10^6$	1.6	95	Few 10s – few 1000	0.2	15 50 (glacial)
Posiva	Cu-cast Fe	$>10^6$	1.55	95	Few 10s – few 1000	0.3	14 50 (glacial)
Andra	Carbon steel	>500	Cementitious buffer on the external face of the casing	90		10	10 (on casing)
Ondraf-Niras	Carbon steel	Several thousand	Cementitious buffer	100	5-10 to few 1000	25	8
Nagra	Carbon steel	10 000	>1.45	±120	Few centuries	0.2	22-29 max
SURAO	Carbon steel	10 000	1.4	95	100	0.3	20
NMWO	Cu-coated steel	$>10^6$	1.6	85	50-5000 ~ host rock	0.8	15 45 (glacial)
NUMO	Carbon steel	> 1000	1.6	100	<1000 ~ host rock	0.006-0.011	11 (hard rock)

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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_2O_3/SiO_2 VHLW container

Figure from Baroux, C. and C. Martin (2016). Summary Report of the Preliminary Feasibility Study for Ceramic Hlw Overpacks. Andra Report CG.RP.ASCM.13.0023

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  - Insufficient customer demand
- High corrosion resistance
- 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

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POTENTIAL CERAMICS CANDIDATES

- Alumina (Al_2O_3)
- Alumina in combination with silicon oxide (SiO_2)
- Silicon carbide (SiC)
- Silicon nitride (Si_3N_4)
- Partially stabilized zirconia
- Titania (TiO_2)

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- Chemical stability
- Reasonable mechanical properties
- Availability

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    - Alumina containing tetragonal zirconia → hydrothermal aging of zirconia ↓
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    - Manufacturing cost < zirconia
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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

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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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- Titanium oxide
  - Refractory < alumina
  - Sinters at lower temperatures
  - > expensive
  - Chemically inert (except high alkaline pH + soluble in H_2SO_4)
  - Sealing aid for alumina containers
  - Addition of TiO_2 → thermal gradients → cracks
- Spinel phases
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  - Alters mechanical properties

- Titanium oxide
  - Refractory < alumina
  - Sinters at lower temperatures
  - > expensive
  - Chemically inert (except high alkaline pH + soluble in H_2SO_4)
  - Sealing aid for alumina containers
  - Addition of TiO_2 → thermal gradients → cracks

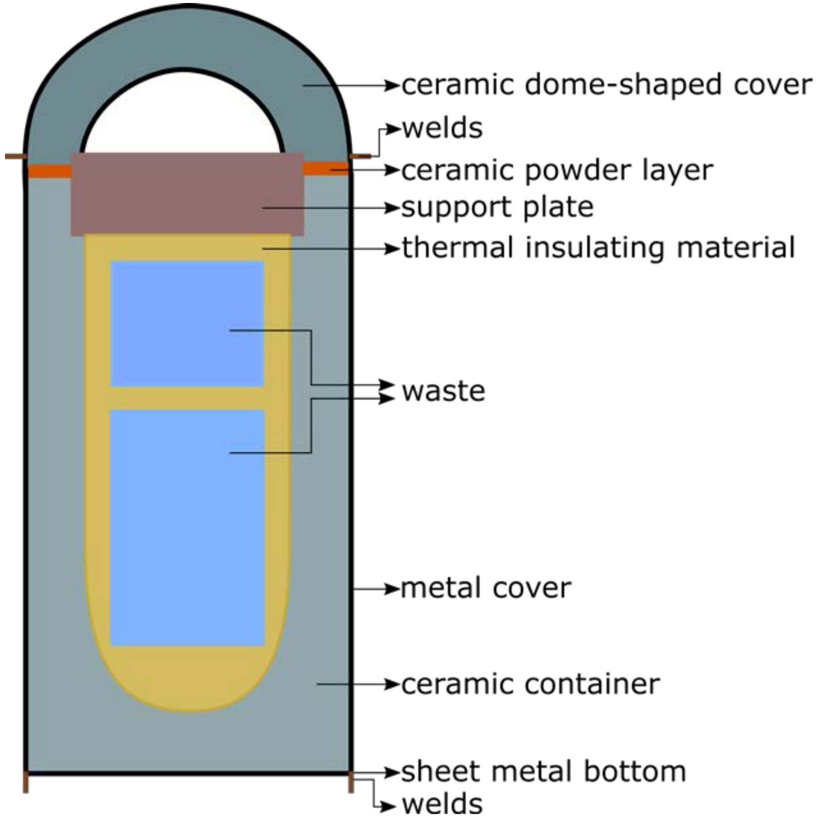
- Spinel phases
  - Properties ~ alumina
  - - phase transition during thermal spraying
  - Coatings

- Graphite
  - Porous : density 80 – 92 %
  - Can be filled by vapor deposition of SiC but expensive & time consuming

CONTENTS

ALUMINA SOLUTIONS: SKB, SWEDISH CONCEPT (1977)

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



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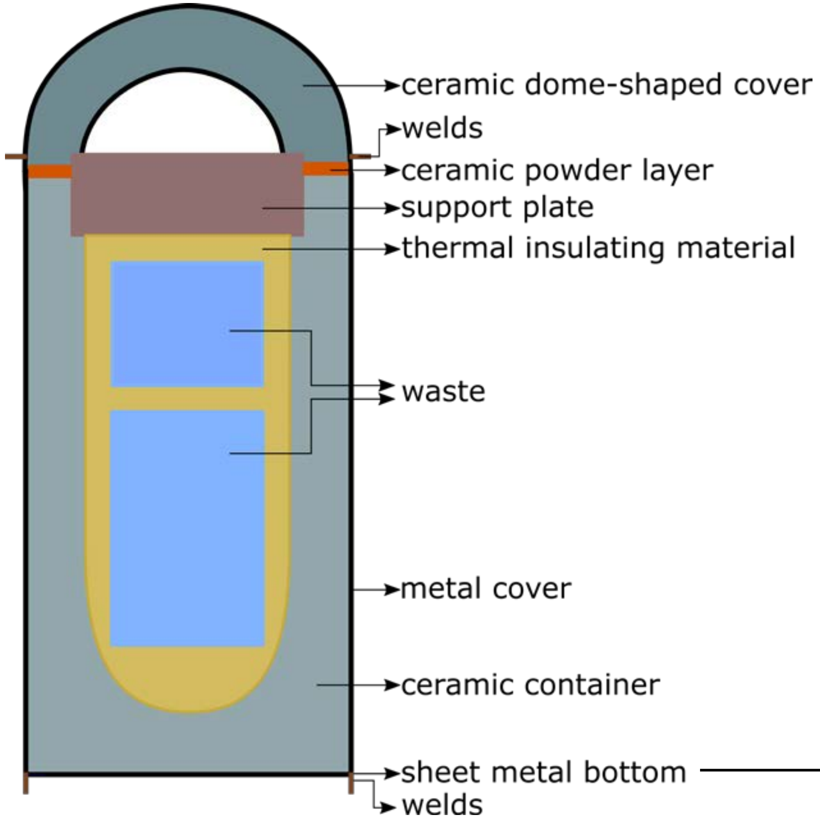

Alumina powder compacted by hot isostatic pressing (1300 °C – 1400 °C; 0.5 – 2 kbar)

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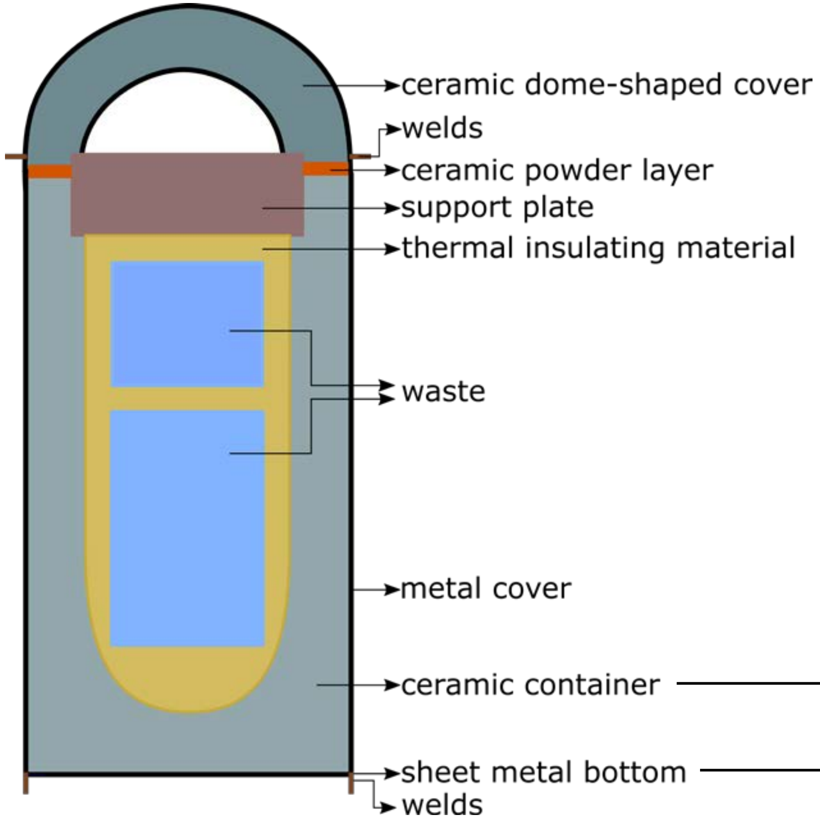

Gas-tight metal casing, joined by isostatic pressing

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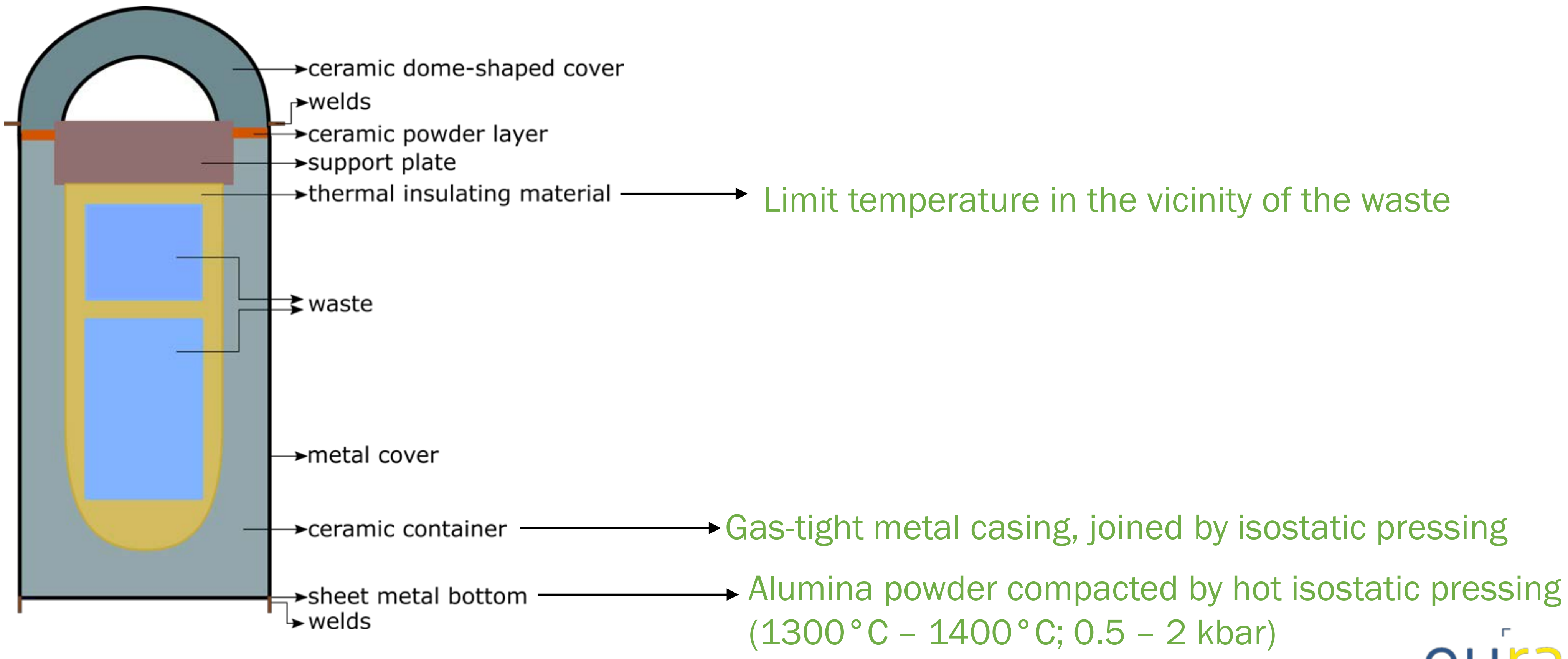

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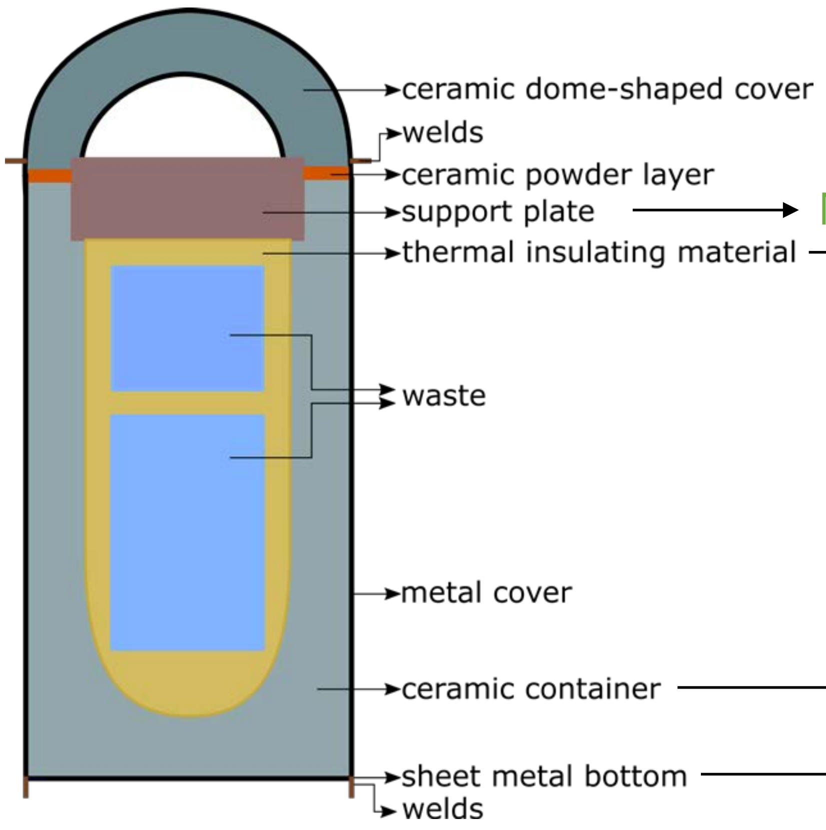

Mechanical reinforcement of sealing area

Limit temperature in the vicinity of the waste

Gas-tight metal casing, joined by isostatic pressing

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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

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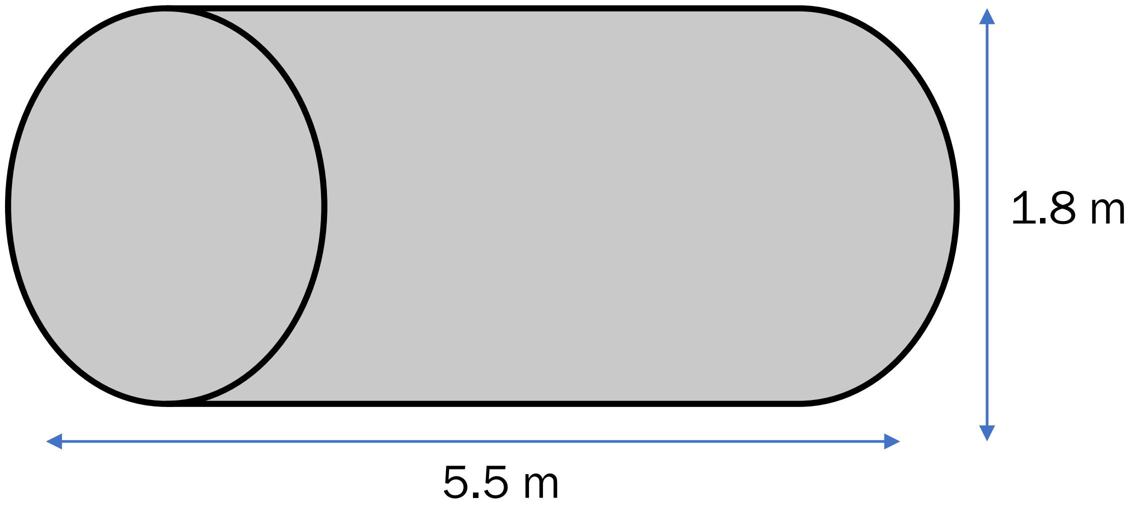
LAWRENCE LIVERMORE NATIONAL LABORATORY, USA (EARLY 1990)

- 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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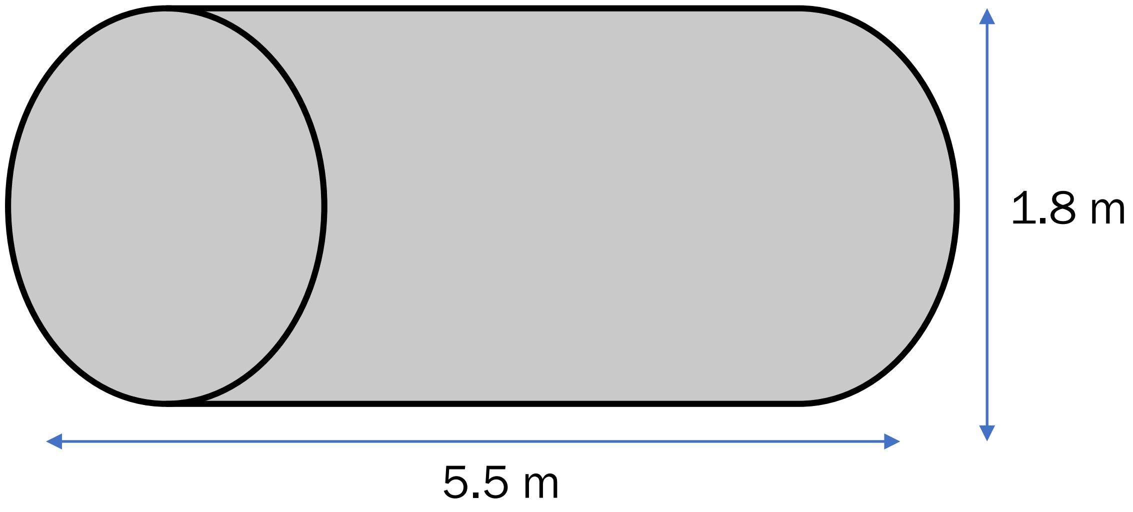
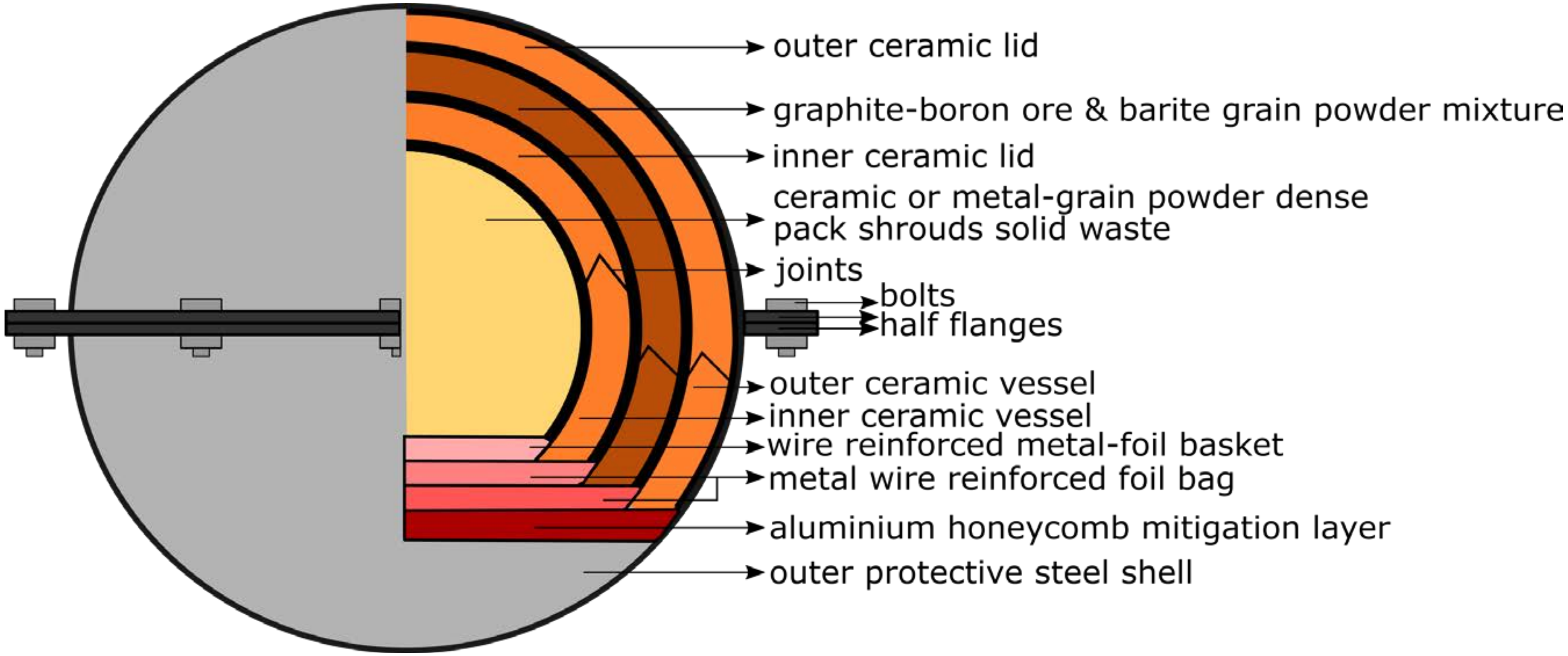


Highlights difficulty of manufacturing large ceramic parts

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

- Onion-like system



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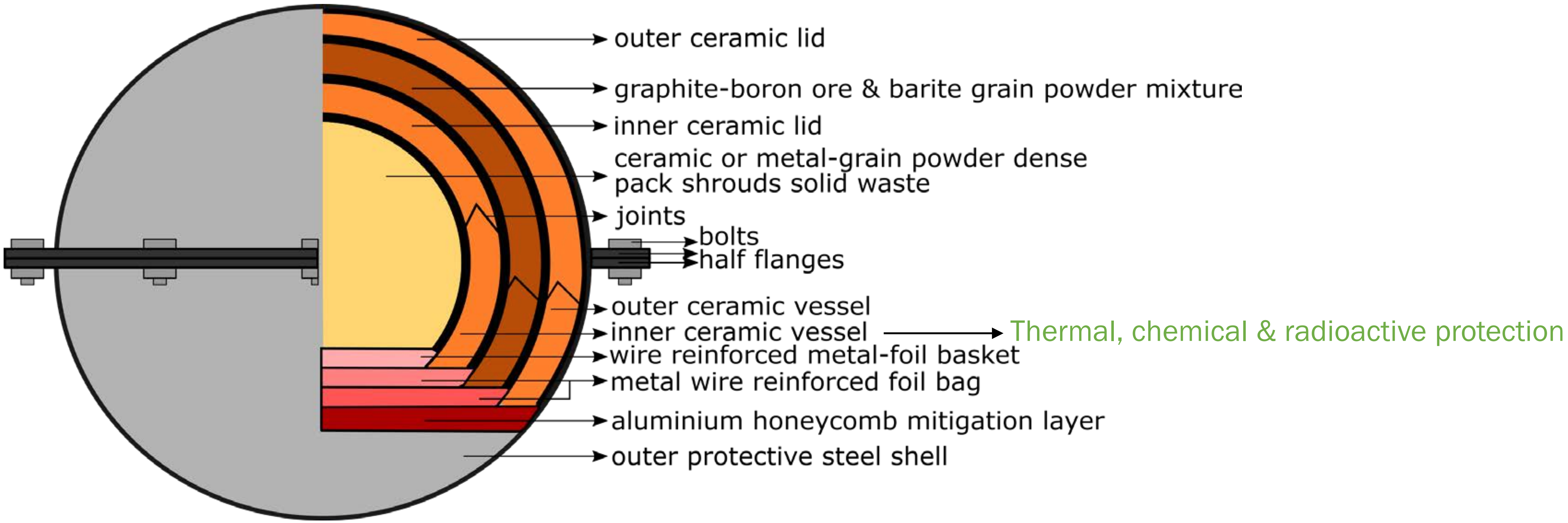

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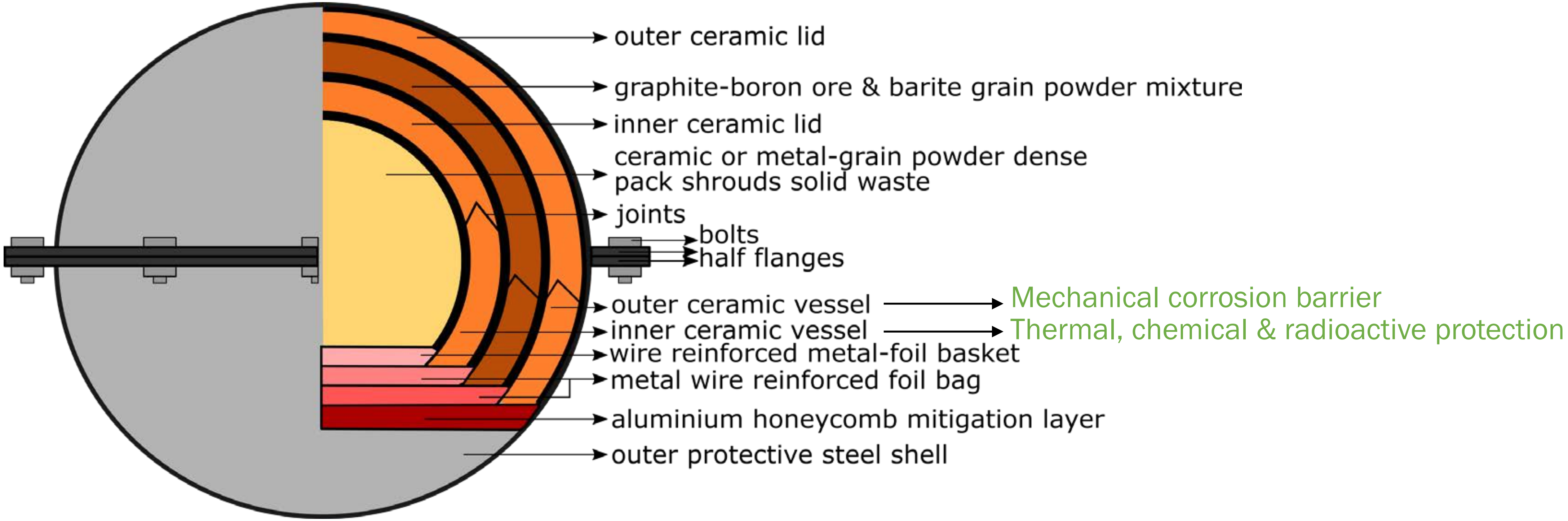

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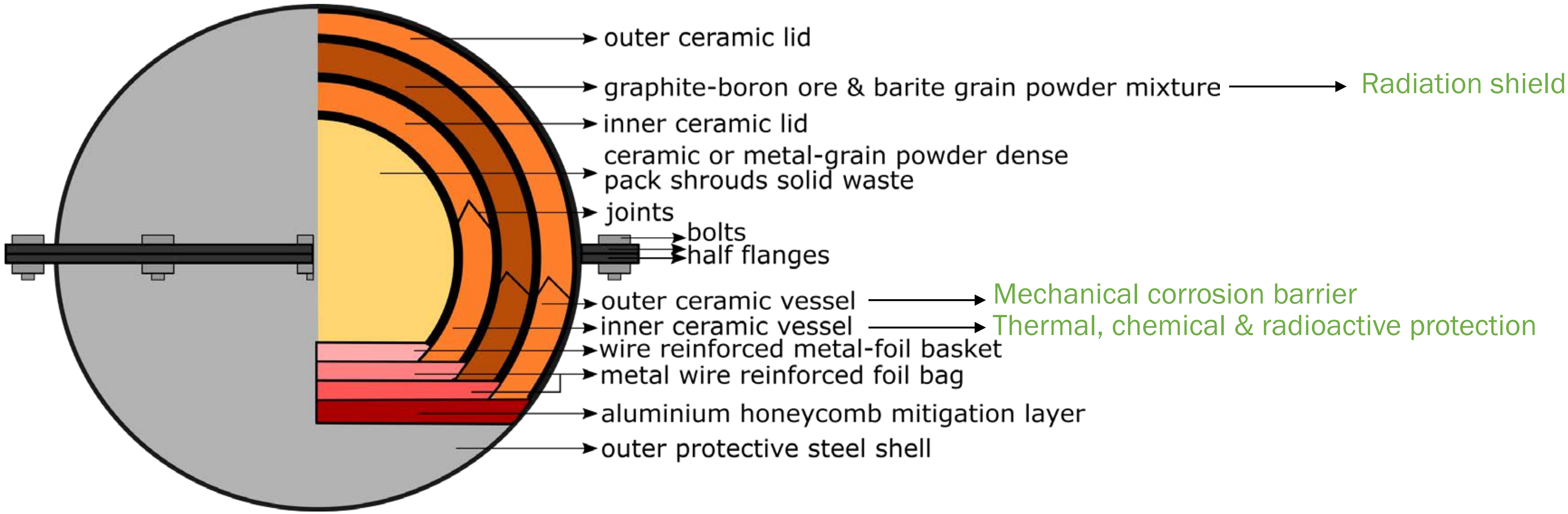

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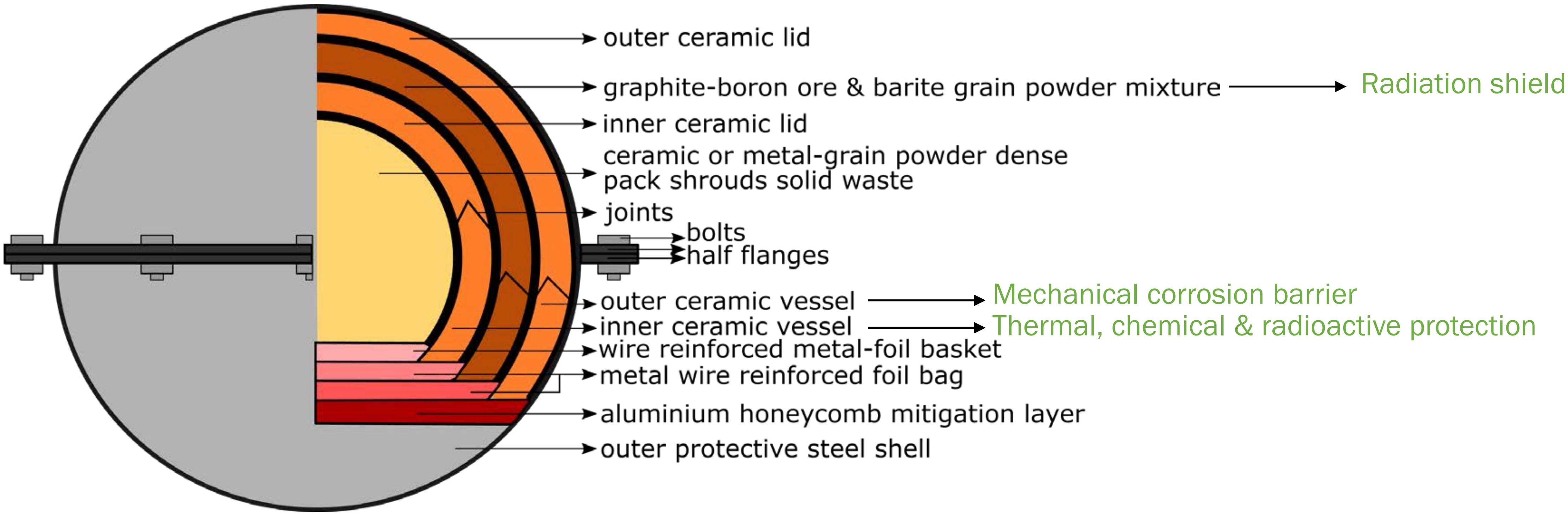
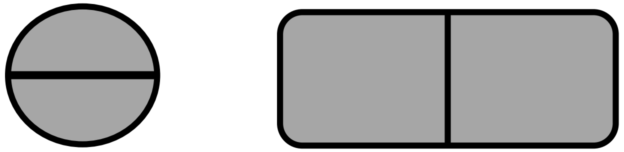


- Depending on the size of the waste



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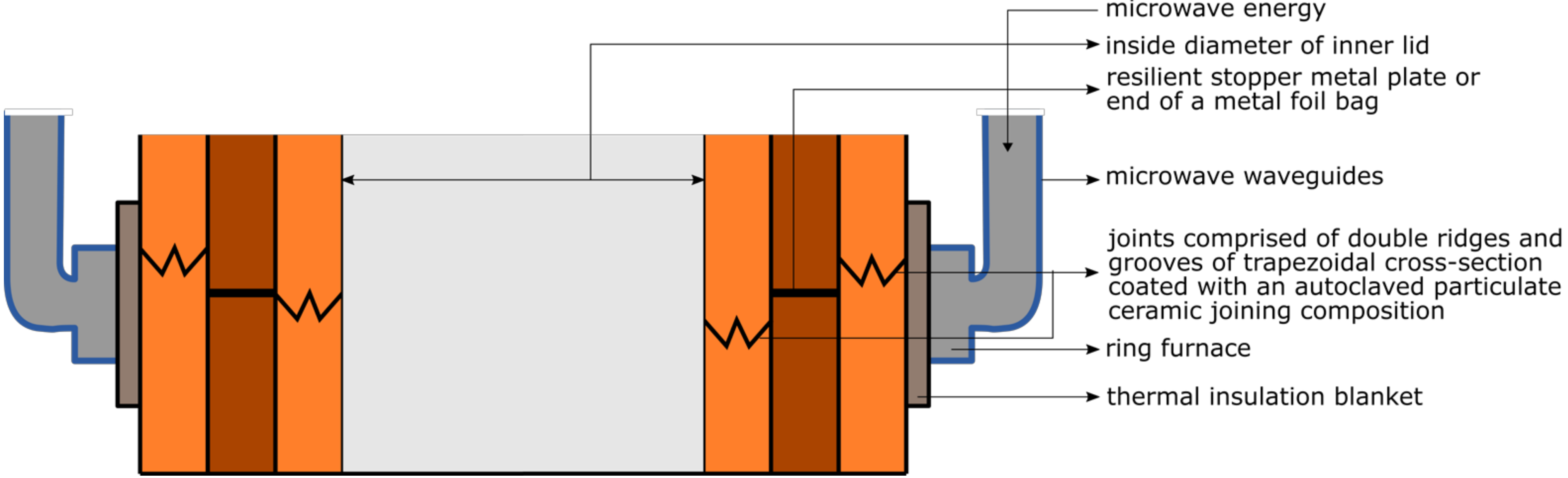

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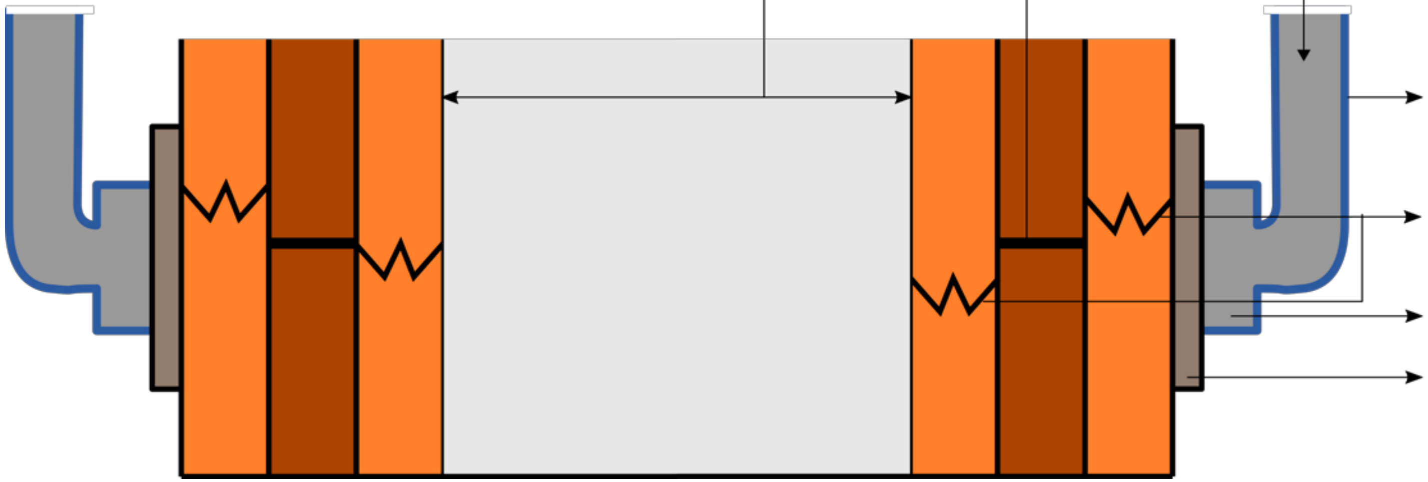
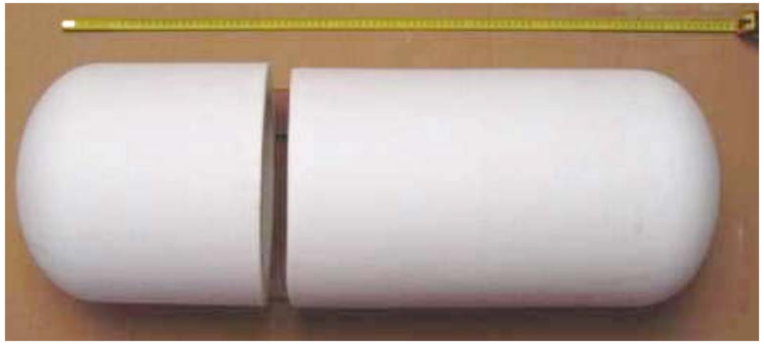


- Addition of ceramic fibers
  - Mechanical reinforcement of the container
  - Favor the thermal treatment of the material
  - Increase radiological properties of the container

Figure adapted from Rockhvarger, A.E., Khizh, A.B. 1998. Large size, thick-walled ceramic containers. NUCON SYSTEMS INC, Patent WO9844834

ALUMINA SOLUTIONS: ANDRA, FRANCE (2007-2009)

- **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



half-scale model of Al_2O_3/SiO_2 VHLW container

Lid: thickness at scale, ~4 cm

Figure from Baroux, C. and C. Martin (2016). Summary Report of the Preliminary Feasibility Study for Ceramic Hlw Overpacks. Andra Report CG.RP.ASCM.13.0023

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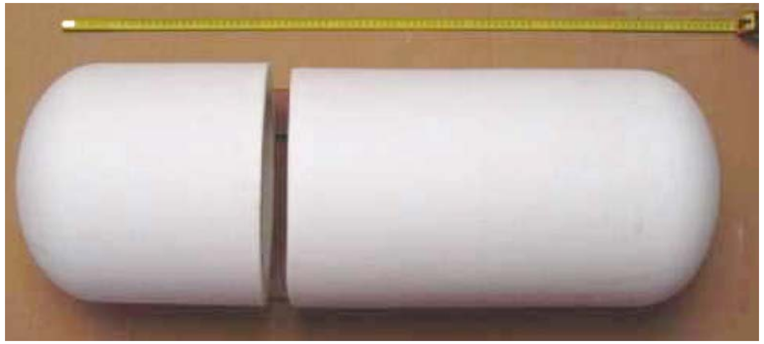
  - Adapted design of a container for HLW
  - Adapted casting, drying & sintering processes
- **Closure of the system?**
  - Focus on the sealing technology
  - Two major constraints to preserve the containment properties of the glass matrix
    - Max surface temperature of the ceramic container of 600-700°C
    - Heating technology localized to the closure area
  - Microwaves & interaction of ceramic materials to assemble ceramic parts



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- 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
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  - Verify the viability of the process
- **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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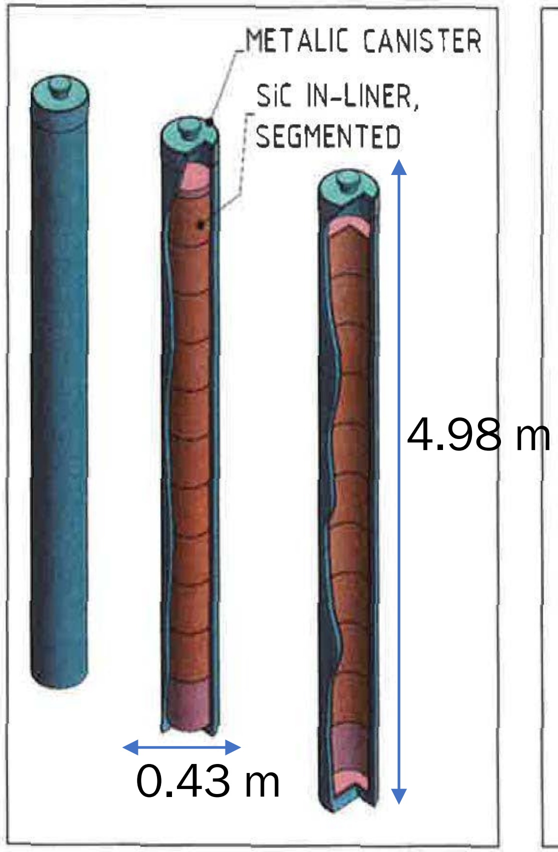
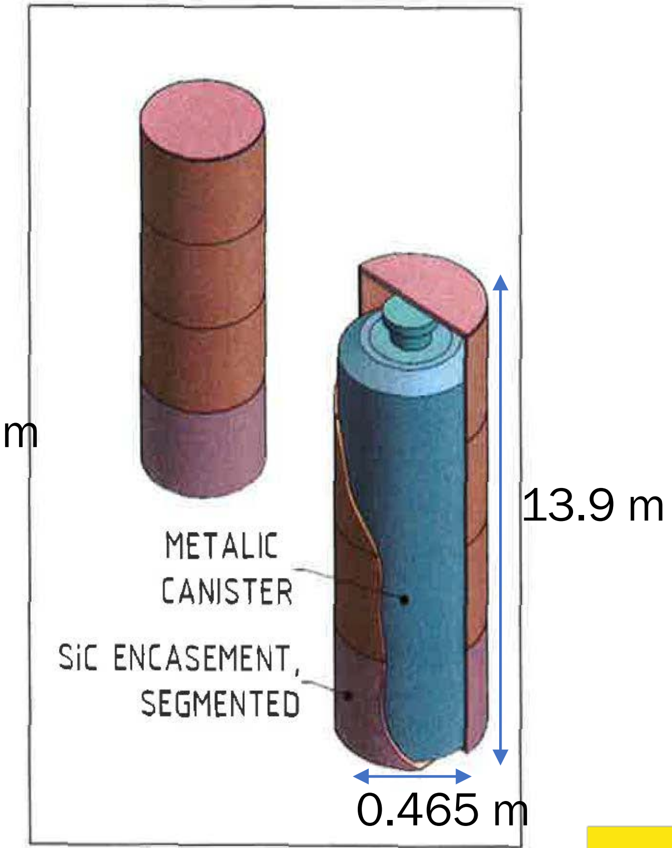


SSiC encasement for SF



SSiC encasement for VHLW

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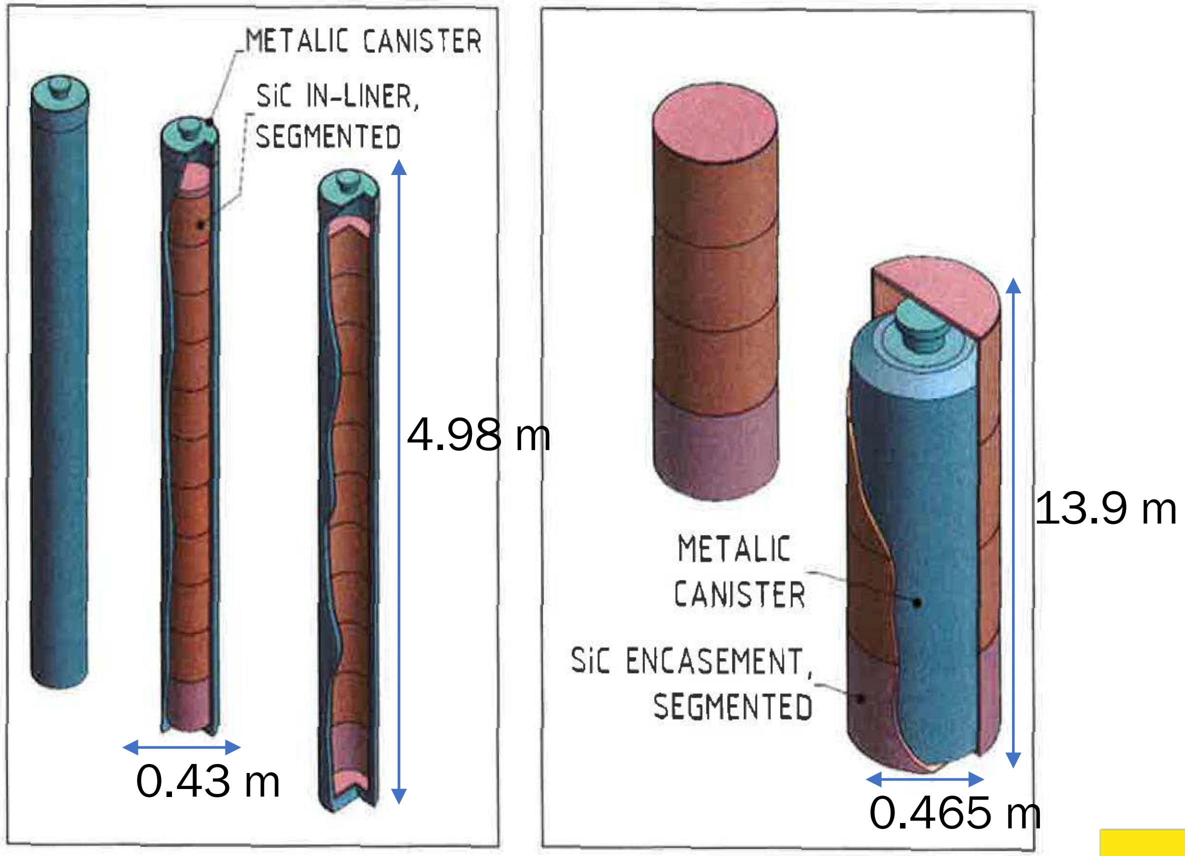

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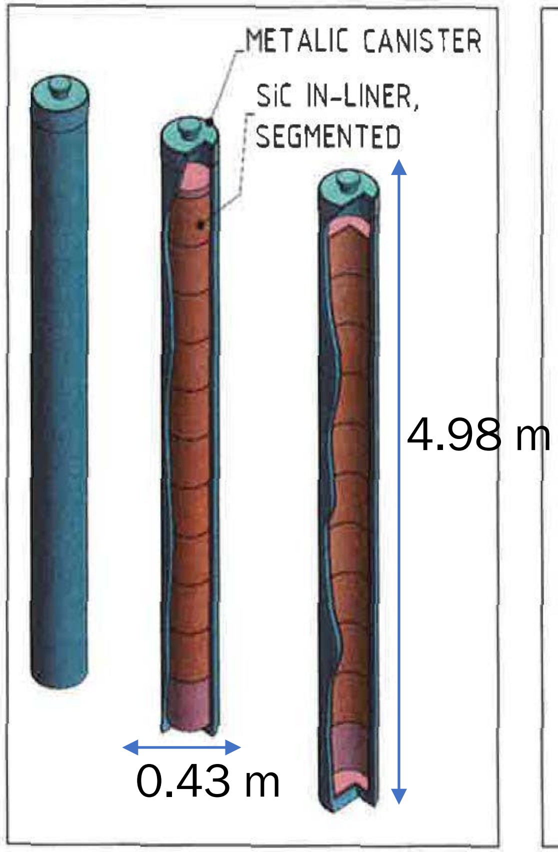

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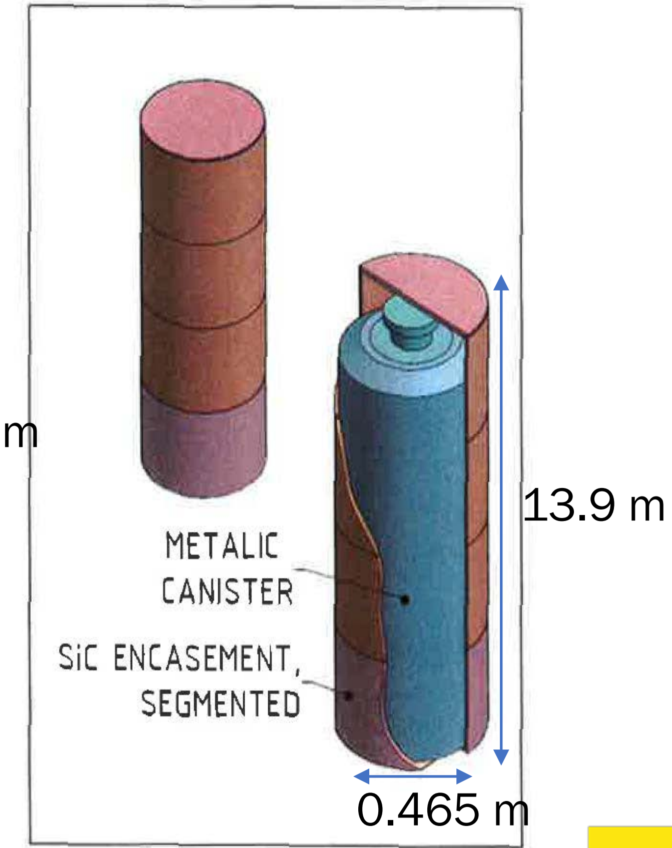

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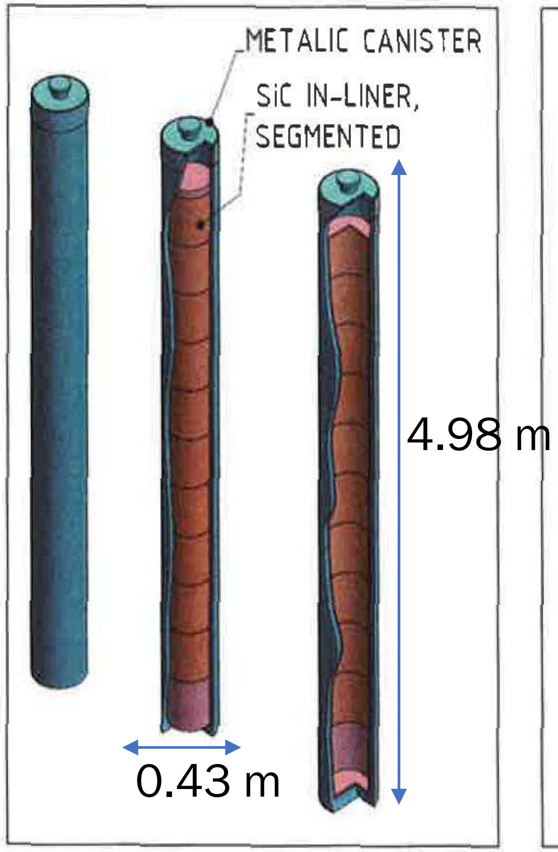

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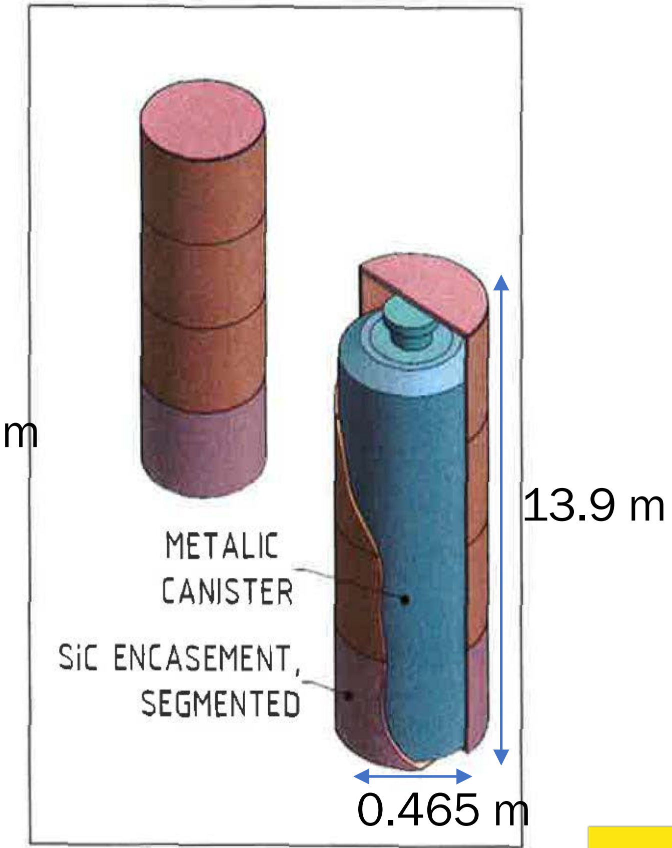

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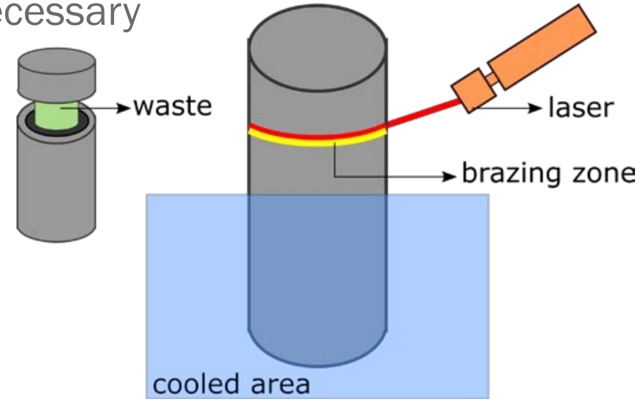

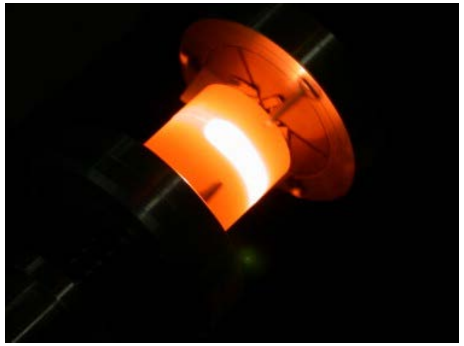

Joining process of SiC-capsule

SiC compact

Knorr, J., W. Lippmann, A. M. Reinecke, R. Wolf, A. Kerber and A. Wolter (2008). "Sic Encapsulation of (V)Htr Components and Waste by Laser Beam Joining of Ceramics." Nuclear Engineering and Design 238(11).

SILICON CARBIDE CONCEPT

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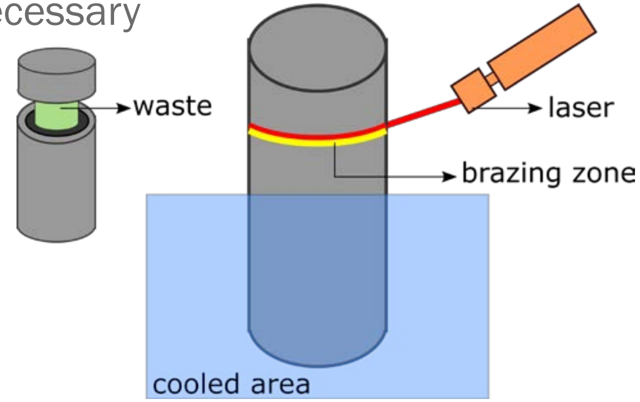

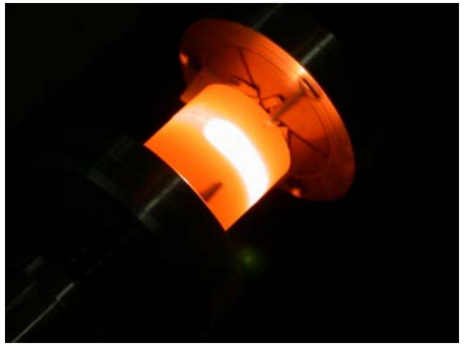

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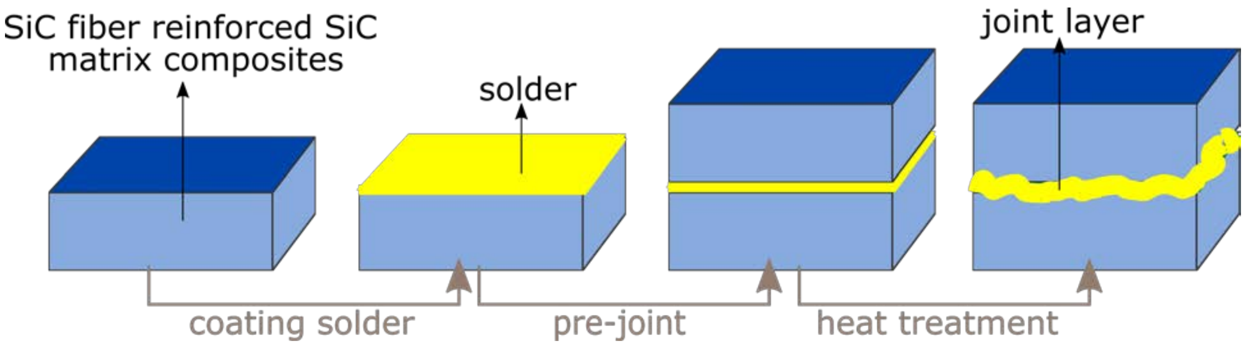

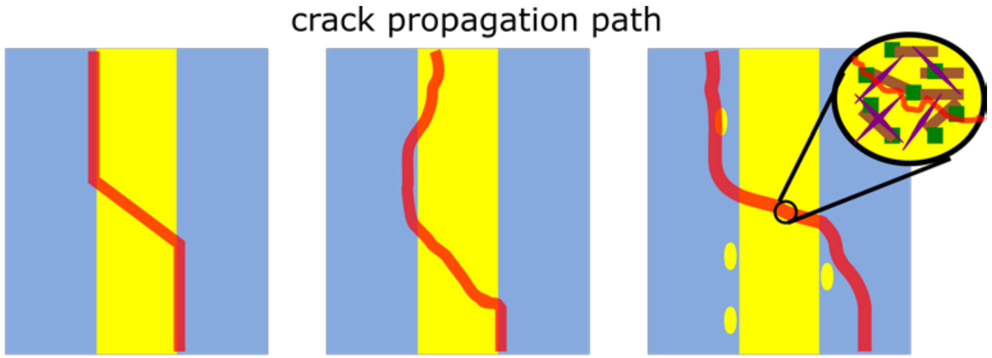

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Figures based on Wang, L., S. Fan, H. Sun, B. Ji, B. Zheng, J. Deng, L. Zhang and L. Cheng (2020). "Pressure-Less Joining of Sicf/Sic Composites by Y_2O_3–Al_2O_3–SiO_2 Glass: Microstructure and Properties." Ceramics International 46(17).

CONTENTS

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CERAMIC COATINGS

- Prevent access of bentonite and/or clay pore waters to the substrate via cracking or leaching over a period of ≥ 10000 years

Figure redrawn from Faraji, G., H. S. Kim and H. T. Kashi (2018). Introduction. Severe Plastic Deformation. G. Faraji, H. S. Kim and H. T. Kashi, Elsevier

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- **Very low porosity**
- **Damage tolerance**
- **Methods needs to be developed for**
    - Covering the lid-to-container weld
    - Coating repair

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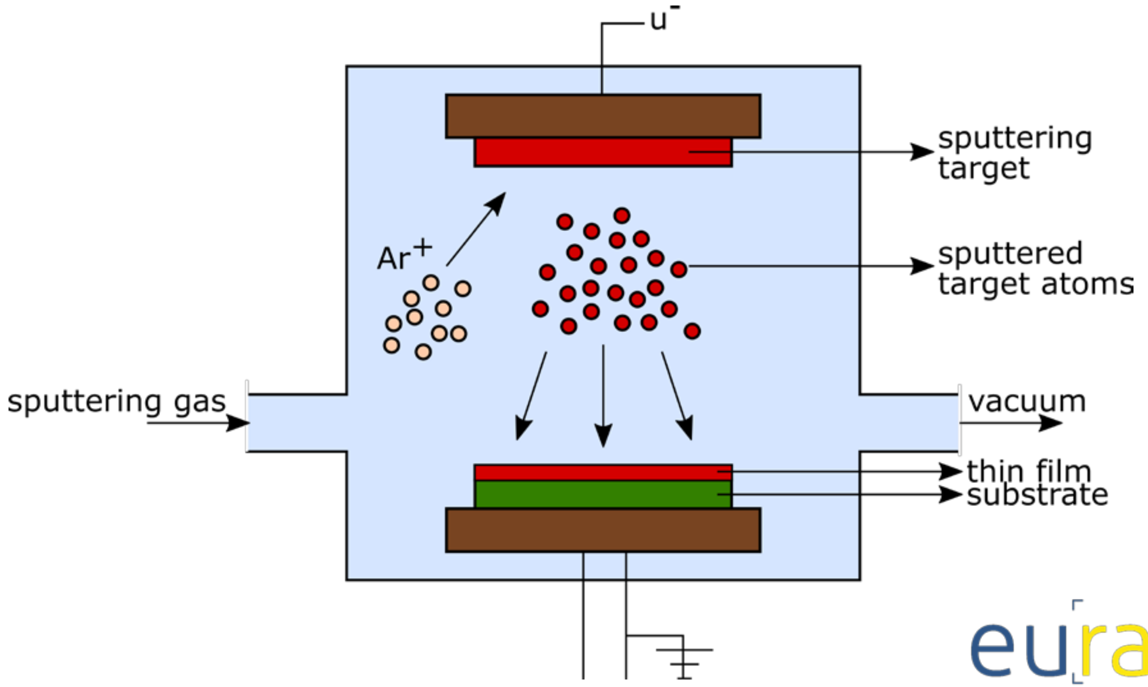
- Physical vapor deposition



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- Titanium nitrides & carbides

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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 $MgCa_2Zn_1Gd_3$ effectively protected this alloy from corrosion in Ringer's solution at 37 °C

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- 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

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CERAMIC COATINGS: CHROMIUM NITRIDE COATINGS

CERAMIC COATINGS: CHROMIUM NITRIDE COATINGS

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- Excellent wear resistance
- High corrosion resistance

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CERAMIC COATINGS: CHROMIUM NITRIDE COATINGS

- High hardness
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- High corrosion resistance
- Corrosion resistance of 2-4 μm thick Zry-4 alloy CrN > TiAIN > AICrN
- CrN coating (7 μm) on cobalt based alloy in high temperature and high-pressure water with γ-rays of 100 Gy/h by ^{60}Co source irradiation during testing

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

CERAMIC COATINGS: CHROMIUM NITRIDE COATINGS

- High hardness
- Excellent wear resistance
- High corrosion resistance
- Corrosion resistance of 2-4 µm thick Zry-4 alloy CrN > TiAlN > AlCrN
- CrN coating (7 µm) on cobalt based alloy in high temperature and high-pressure water with γ-rays of 100 Gy/h by ^{60}Co source irradiation during testing
- Chromium nitride coatings are promising for corrosion protection of the carbon steel
- Additional studies are needed on long-term corrosion processes under relevant geological disposal conditions

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

CONTENTS

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

Material	+	-	e.g. Countries	Remark
Low alloyed steel	• Cost • Fabrication • Mechanical strength • Radiation shielding	• Corrosion resistance < copper but low • SCC	France, Japan, Switzerland	Carbon steel
Stainless steel	Corrosion resistance (passive film)	• Localized corrosion • Some classes SCC	UK, Spain, Japan, USA	Focus on austenitic alloys
Titanium	Corrosion resistance	• Crevice corrosion in O_2 phase • HIC	Canada, Belgium, Japan	Alloys with Pd or Ru could avoid crevice corrosion
Nickel alloys	• Corrosion resistance • Mechanical properties in high-temp applications • Fabrication	• Localized corrosion in certain environments • Uncertainties associated with MIC	Germany, Belgium, USA, Argentina	Ni-Cr-Mo or Ni-Fe-Cr-Mo
Copper	• Corrosion resistance • Mechanical properties	cost	UK, Japan, Sweden, Finland, Canada, Switzerland	Fi, Sw: O_2 free, phosphorous doped copper; J, Ca,Swi: relatively pure cold spray & electrodeposited copper
Lead	• Cost • Radiation shielding	• Corrosion behavior? • Mechanical strength? • Environmental aspects?	Argentina, Brazil, Russia	Not considered

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METALLIC COATINGS

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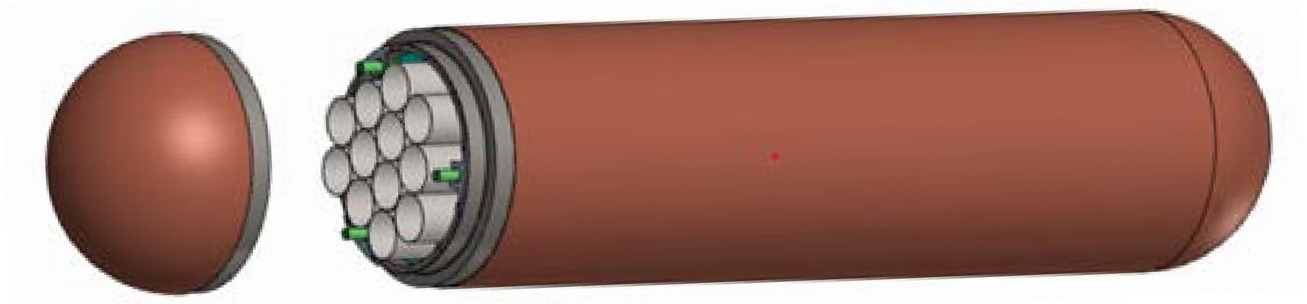
- Dual-wall container with copper coating:
    - Copper layer is directly on the steel vessel → no gap between layers → no fabrication issues
    - ↔ standard design → gap between outer copper layer and cast iron insert can introduce creep & SCC of the copper shell
    - Welding joint could be covered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

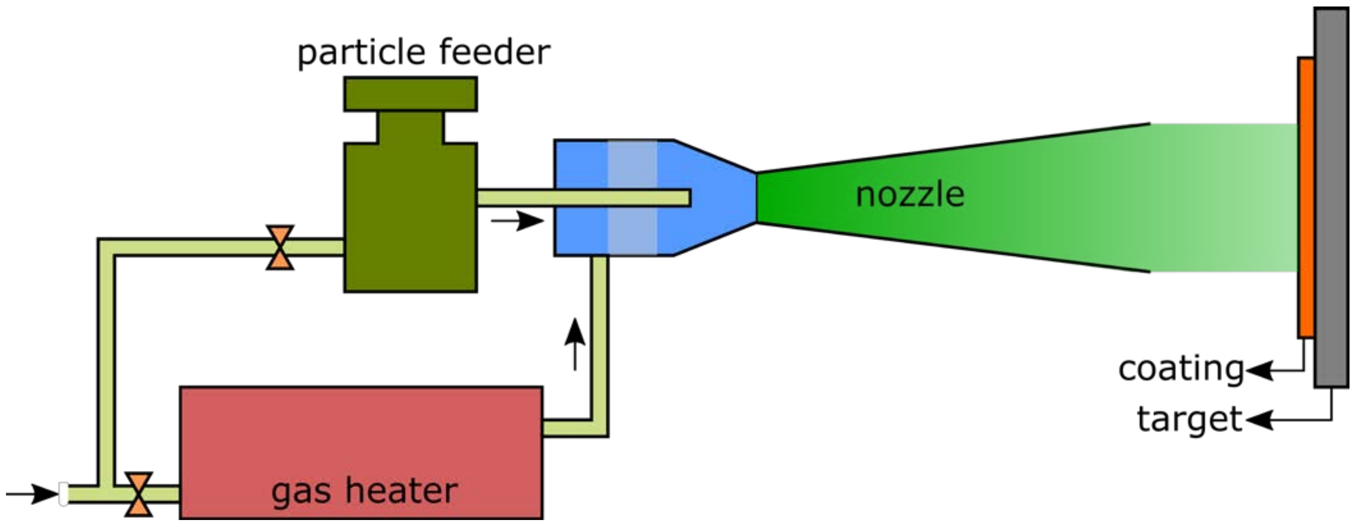


Figure adapted from Alkhimov, A. P., V. F. Kosarev, S. V. Klinkov, A. A. Sova, G. V. Trubacheev and V. N. Zaikovsky (2012). "Conical Separation Zone Formation at Impingement of Supersonic Jet on Obstacle under Cold Spraying." Thermophysics and Aeromechanics 19(2).

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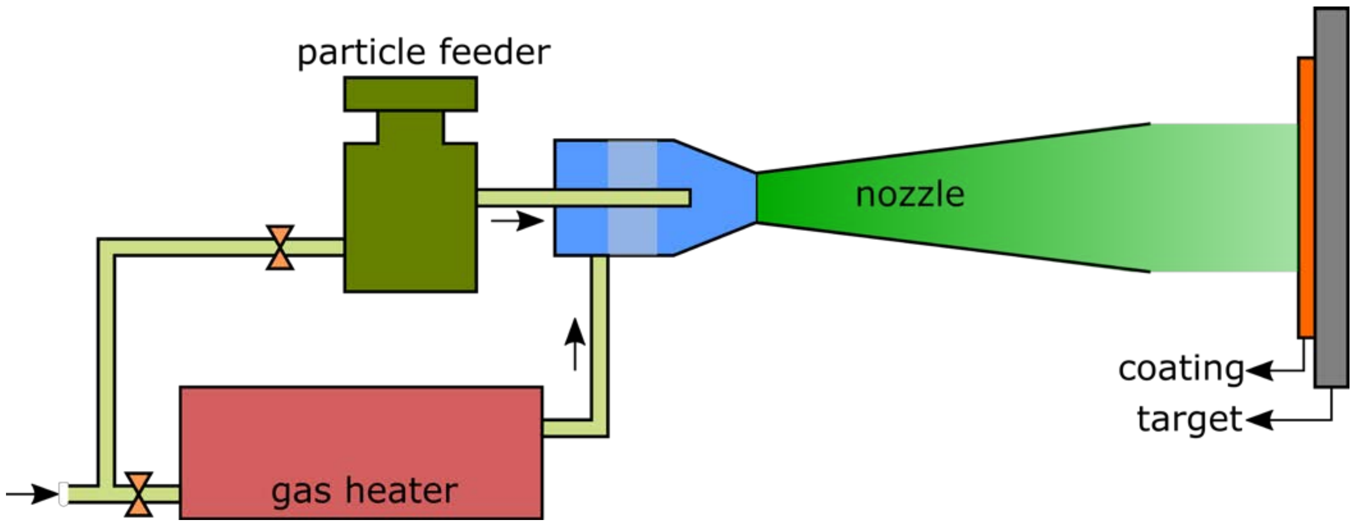
- Quality of the coating depends on:
  - Nozzle displacement
  - Carrier gas type & velocity



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  - 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
- Holdsworth, S.R., (2013). Ceramic Material Solutions for Nuclear Waste Disposal containers. NAGRA report NAB12-45.
- Holdsworth, S.R., (2014). Feasibility evaluation study of candidate container solutions for the disposal of spent nuclear fuel and high-level waste-A status review. NAGRA report NAB14-90.
- Holdsworth, S.R. (2018). Alternative coating Materials as Corrosion Barriers for SF and HLW Disposal containers. NAGRA report NAB18-19.
- INTERNATIONAL ATOMIC ENERGY AGENCY (2006). Development of Specifications for Radioactive Waste Packages. IAEA-TECDOC-1515. IAEA, Vienna

PREDICTION TOOLS FOR ASSESSMENT OF LONG-TIME BARRIER INTEGRITY

This project has received funding from the European Union's Horizon 2020 research and innovation programme 2014-2018 under grant agreement N°847593

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
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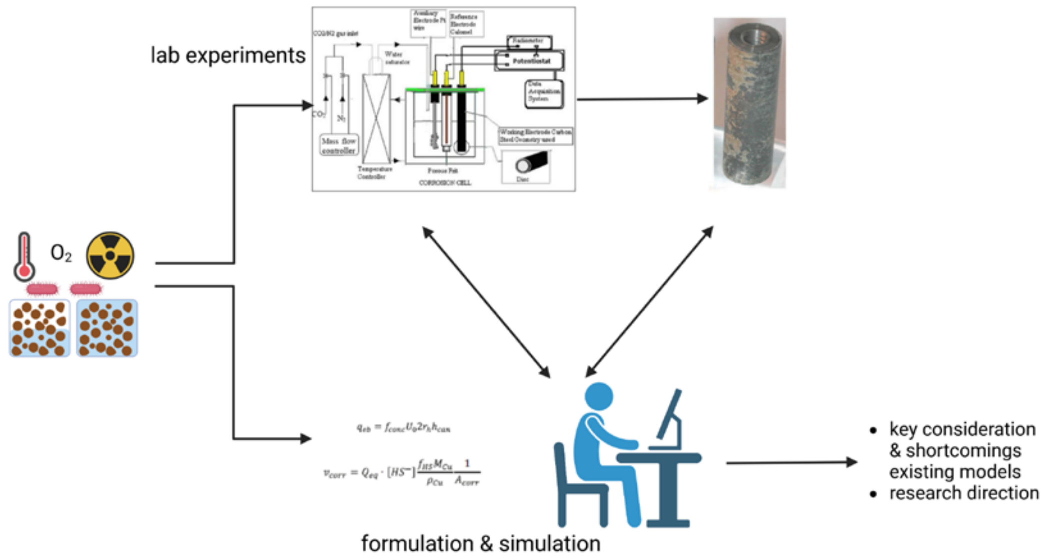
MODELLING CORROSION PROCESSES AIMS

- 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



GENERIC CORROSION MODELLING APPROACHES: GENERAL CORROSION

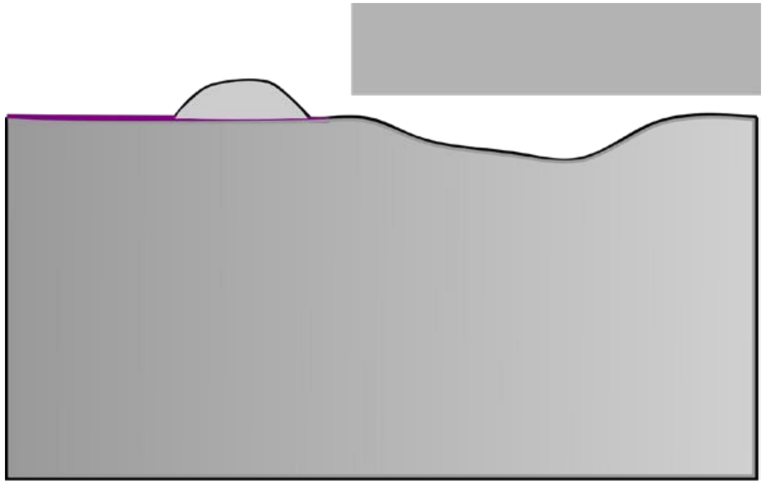
Method	Principle	Assumptions	Remarks
Empirical extrapolation	Extrapolate corrosion rate short-term lab exp. to long-term corrosion rates	• Stable environmental conditions • No step changes in corrosion mechanisms	• Built-in conservatism • Useful to consider validation with archaeological analogues
Mass balance	With O_2 → amount of O_2 after closure determines extent of corrosion Without O_2 → anaerobic corrosion		Anaerobic corrosion → corrosion rate is not determined by the total available mass of the cathodic reactant
Mass transport	Corrosion rate determined by rate of supply of the corrodent	• Correct calculation of the mass transport • Reactant is irreversibly consumed in the corrosion reaction	Also the mass transport of corrosion products could be limiting
Reactive transport modeling (e.g. PhreeqcRM, Geochemist Workbench)	Use of available software systems to perform equilibrium & kinetic reaction calculations for reactive transport simulators		• May require a lot of input data • Can be mathematically complex • Once developed, very useful

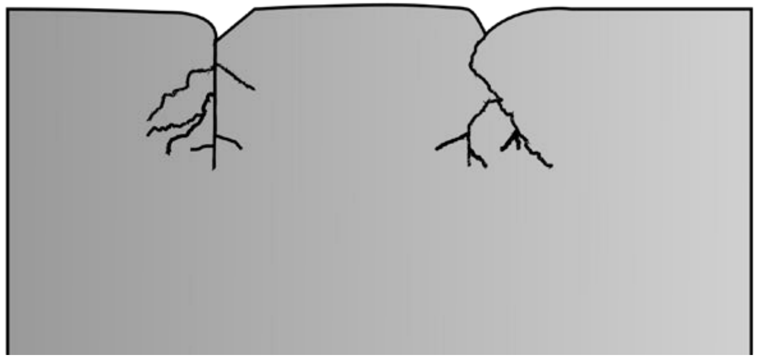
GENERIC CORROSION MODELLING APPROACHES: LOCALIZED CORROSION

Method	Principle	Remarks	Disadvantages
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. $P = kt^n$		
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	• No prediction of localized corrosion rates or penetration depth over time • Large database necessary

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

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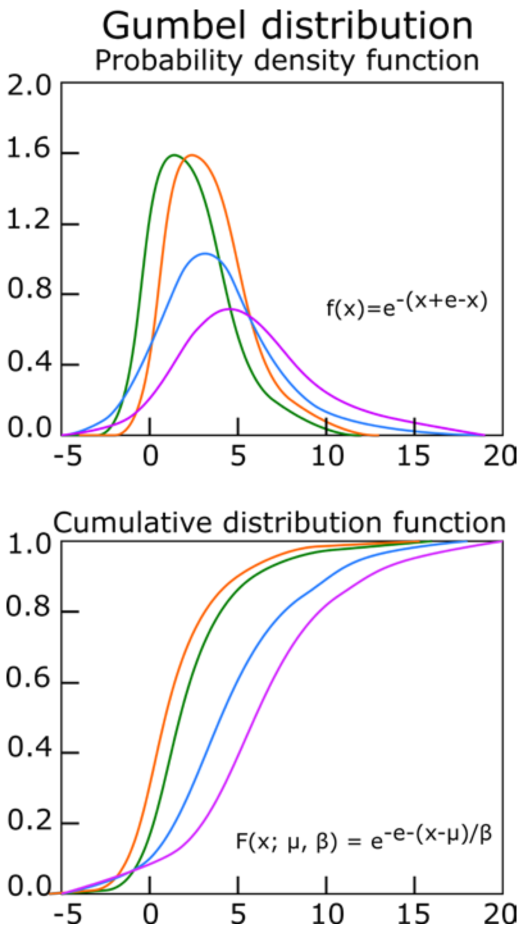
- Extreme value statistics
  - Extrapolation from small test coupons or inspection sites to real structures
  - Pitting corrosion → max pit depth over time
  - Very conservative



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

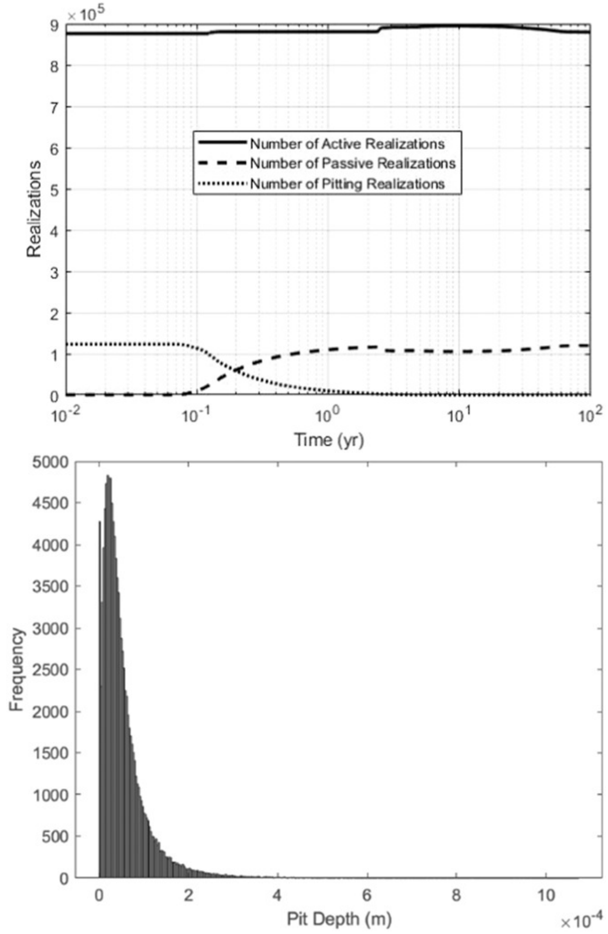

Figure from Briggs, S., C. Lilja and F. King (2021). "Probabilistic Model for Pitting of Copper Canisters." Materials and Corrosion 72(1-2).

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
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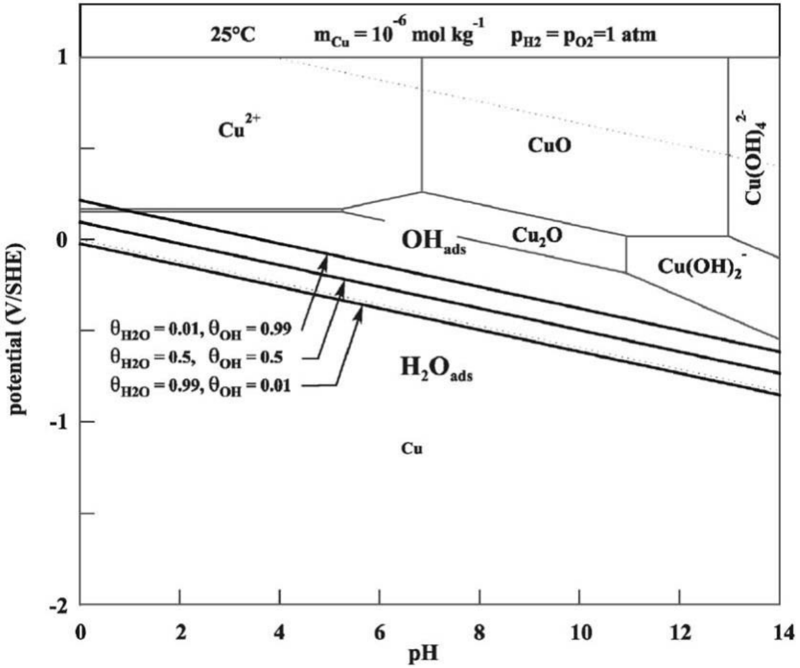
- Pourbaix diagrams
  - Potential – pH stability diagrams

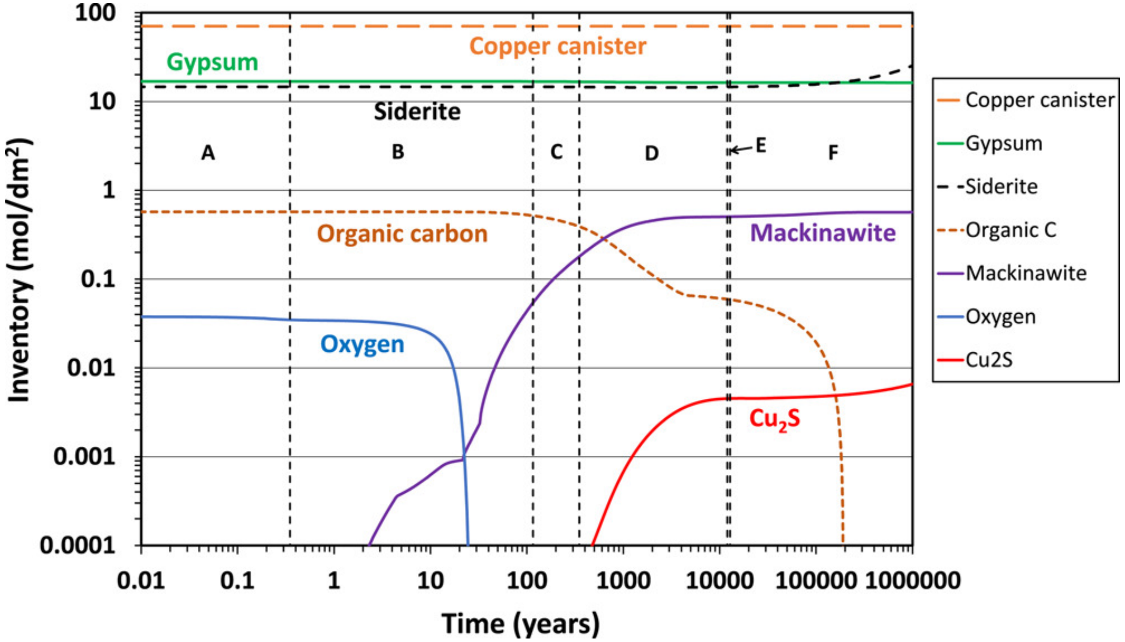


Pourbaix diagram for the Cu–H_2O system at 25°C including the regions of stability of $Cu(OH)_{ADS}$ for various surface coverages θ

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



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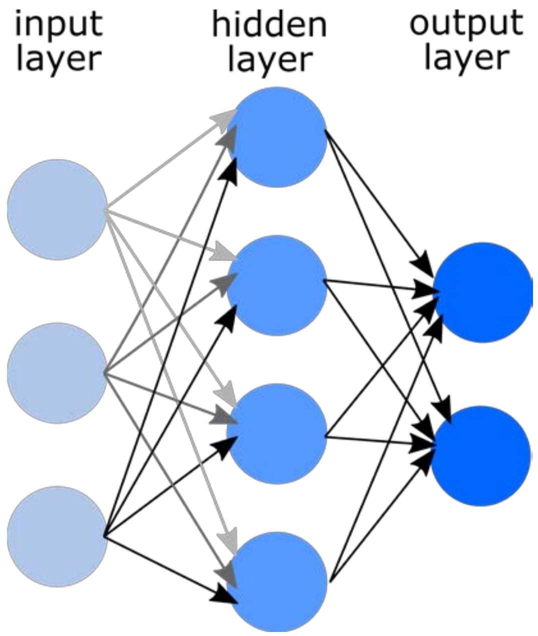
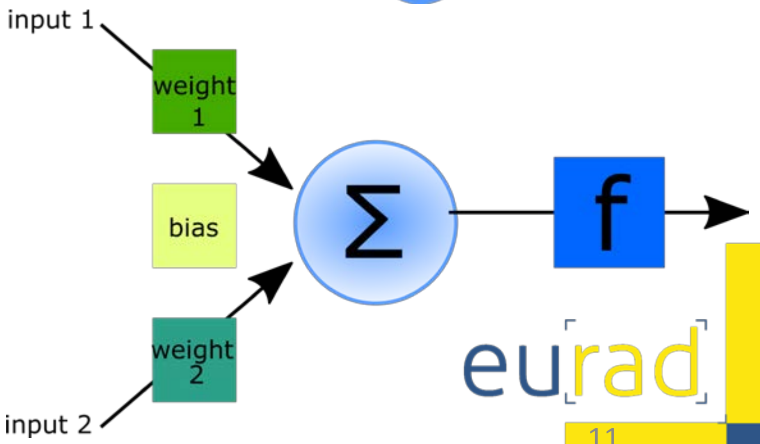
- Principle:
  - Set up series of artificial neurons in a layered structure ~ brain





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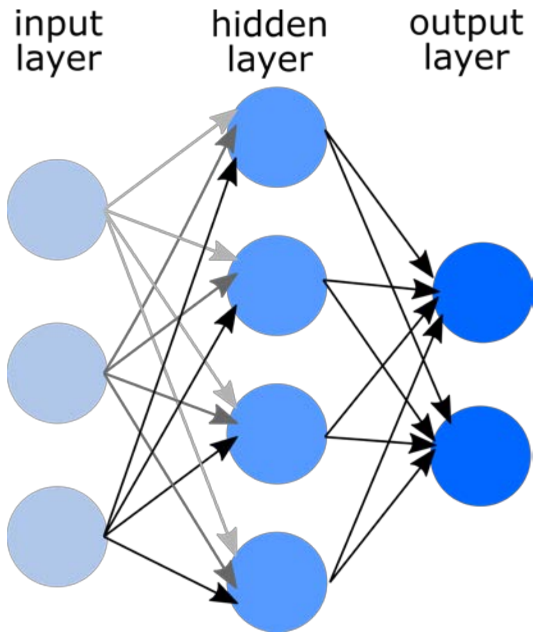

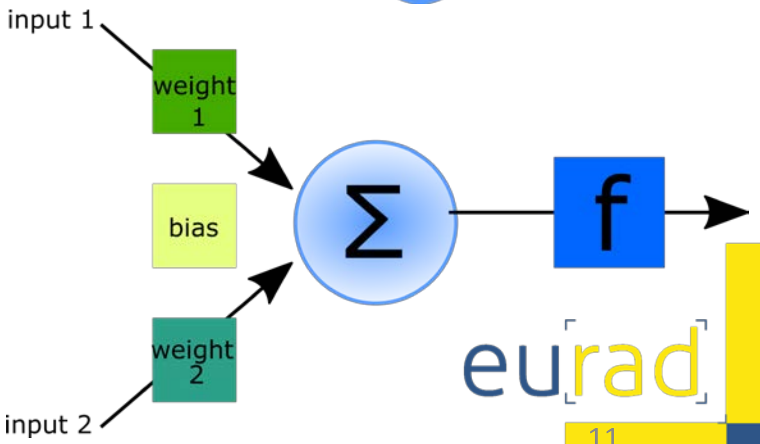

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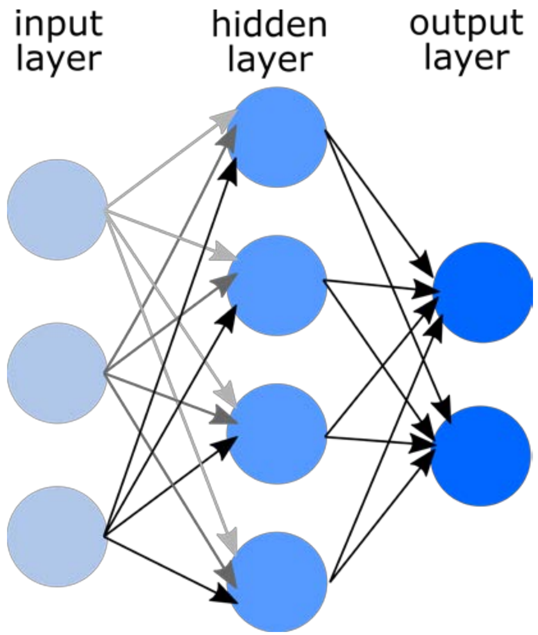
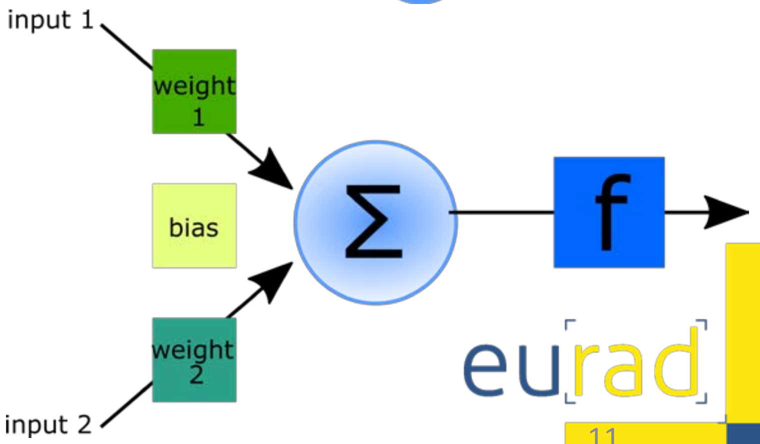
- Software is commercially available





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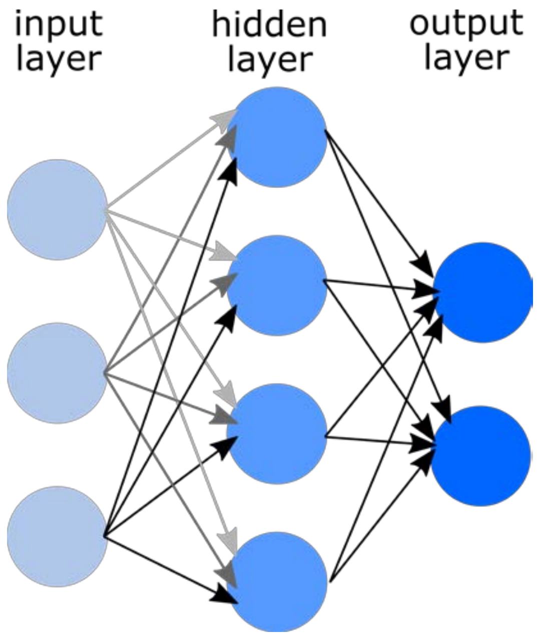
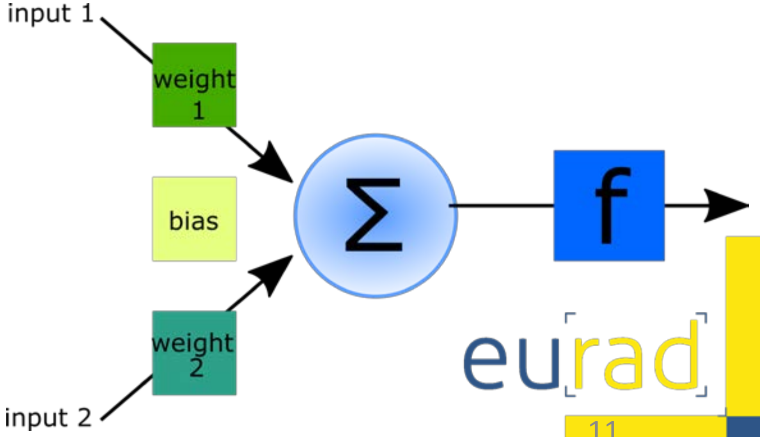
- Large data set needed





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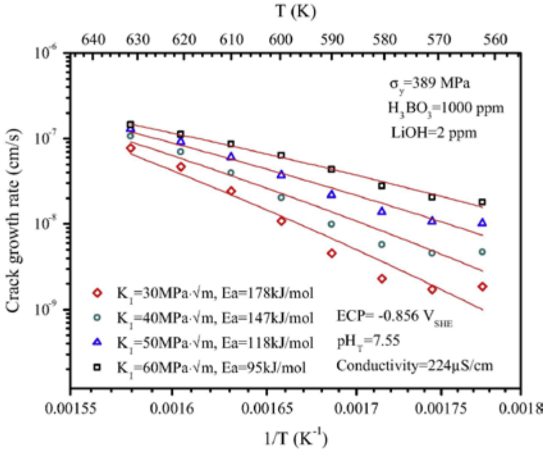
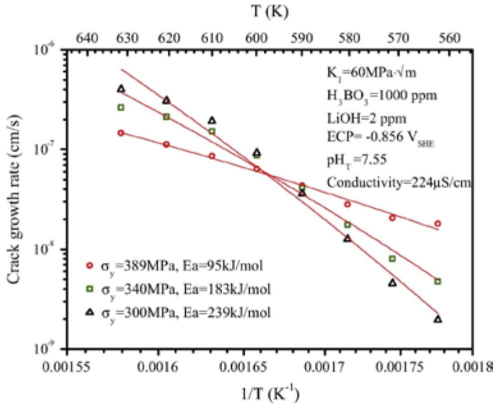
  - To predict time of failure as a function of multiple variables

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



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ARTIFICIAL INTELLIGENCE: NEURAL NETWORKS

- **When can it be used?**
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  - To analyze data from monitoring sensors
  - To predict time of failure as a function of multiple variables
- **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

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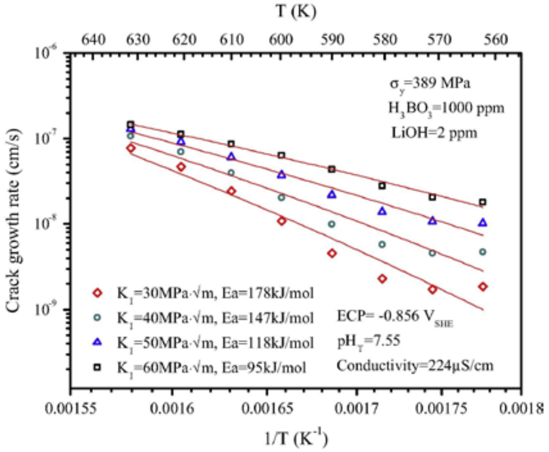

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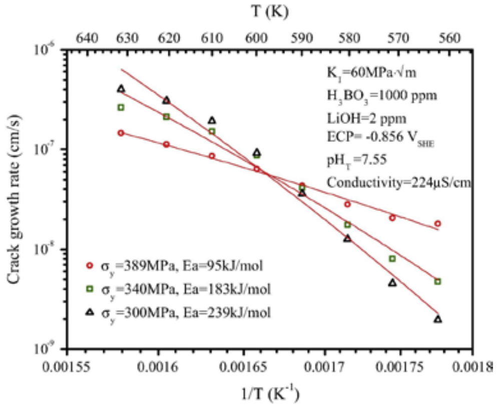

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MODELLING CORROSION PROCESSES CHALLENGES

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  - Large scale, *in situ* tests under realistic repository conditions

Landscape of the excavated area of the Oda Castle remains

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➡ Generate sound mechanistic understanding of the underlying corrosion processes

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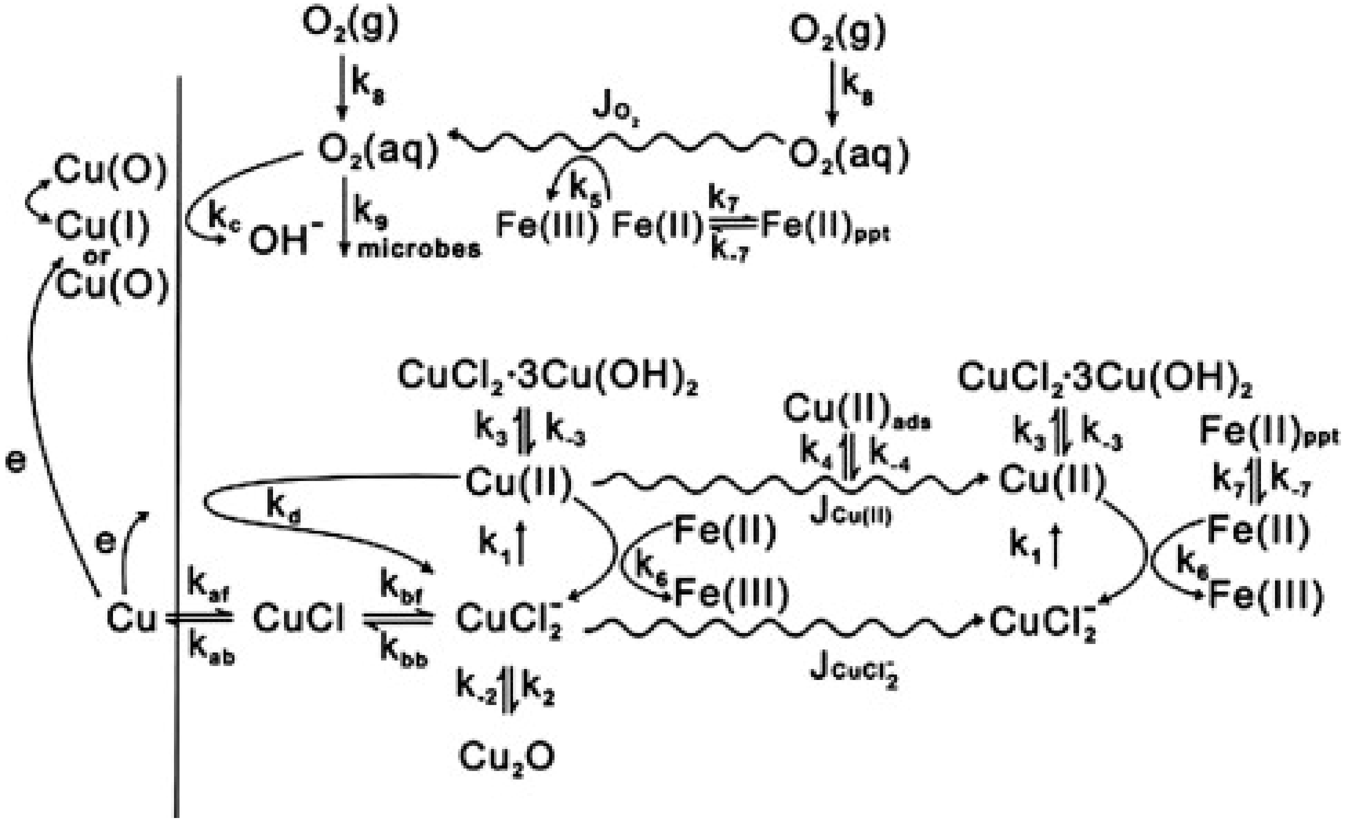

j: diffusive fluxes
k: rate constants

Figures from King, F., M. Kolar and P. Maak (2008). "Reactive-Transport Model for the Prediction of the Uniform Corrosion Behaviour of Copper Used Fuel Containers." Journal of Nuclear Materials 379(1).
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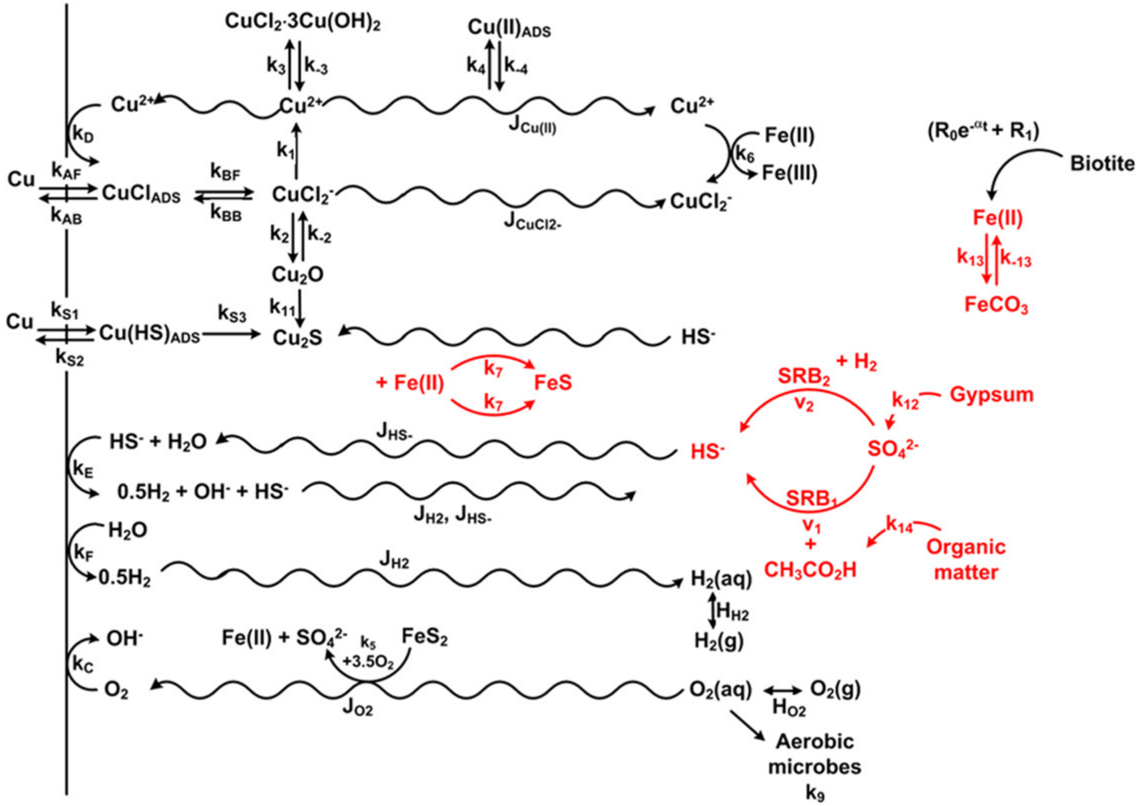
COPPER CONTAINER CORROSION

- Copper corrosion model (CCM)
  - Uniform copper corrosion focusing on Cl^- and O_2 transport-controlled corrosion
  - Has been progressively updated, e.g. copper sulfide model (CSM)



microbial sulfate reduction in red

j: diffusive fluxes
k: rate constants

Figures from King, F., M. Kolar and P. Maak (2008). "Reactive-Transport Model for the Prediction of the Uniform Corrosion Behaviour of Copper Used Fuel Containers." Journal of Nuclear Materials 379(1).
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).

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5. Simplified multi-porosity model
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VALIDATION OF THE MODELS WITH $^{36}Cl^-$ IN THE BHA VAULT OF THE SFL REPOSITORY (SE)

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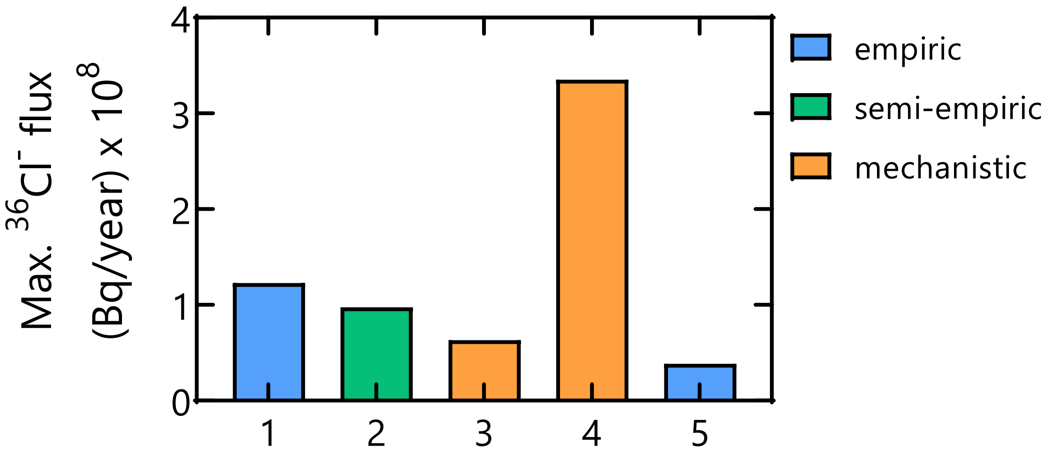

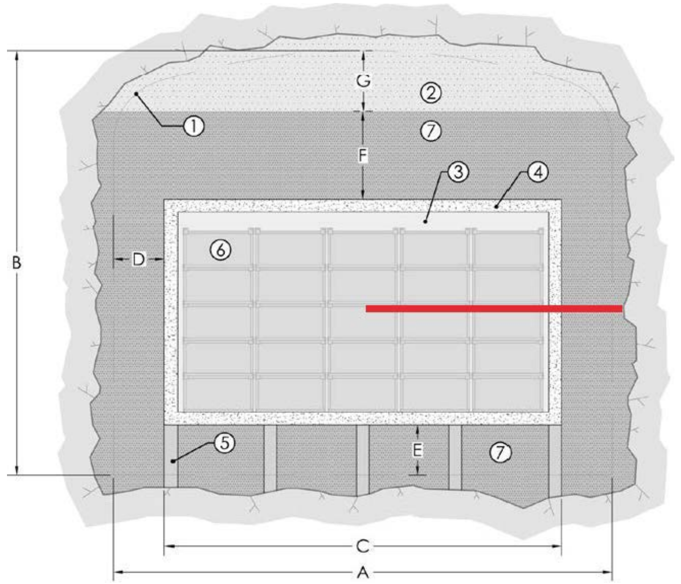

Position of the 2D studied domain (in red) referred to the 2D cross-sectional view of the BHA vault. 1) Theoretical tunnel contour. 2) Bentonite pellets. 3) Grout. 4) Concrete structure for the operating period (0.5 meter). 5) Granite pillars. 6) Waste containers. 7) Bentonite blocks. Approximate dimensions: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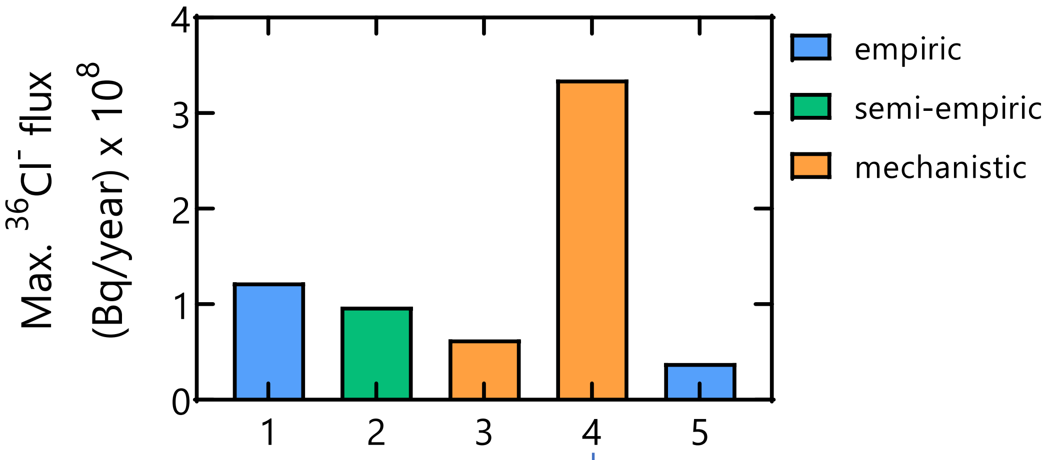
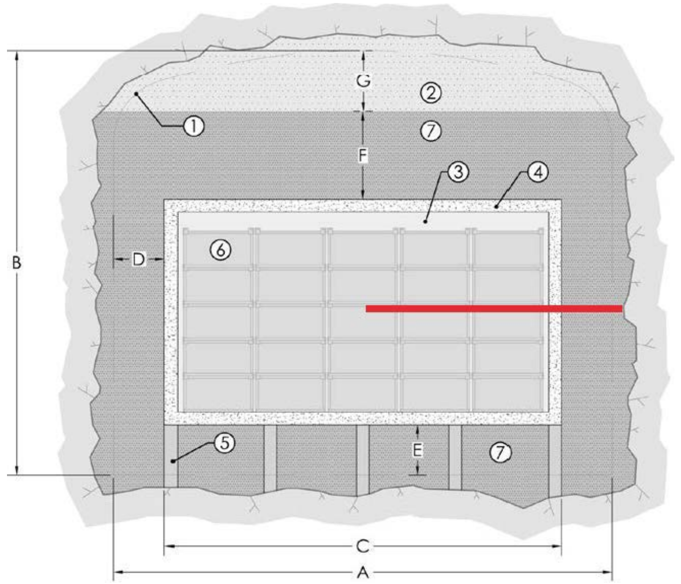


Lack of detailed description of several necessary parameters

overestimation



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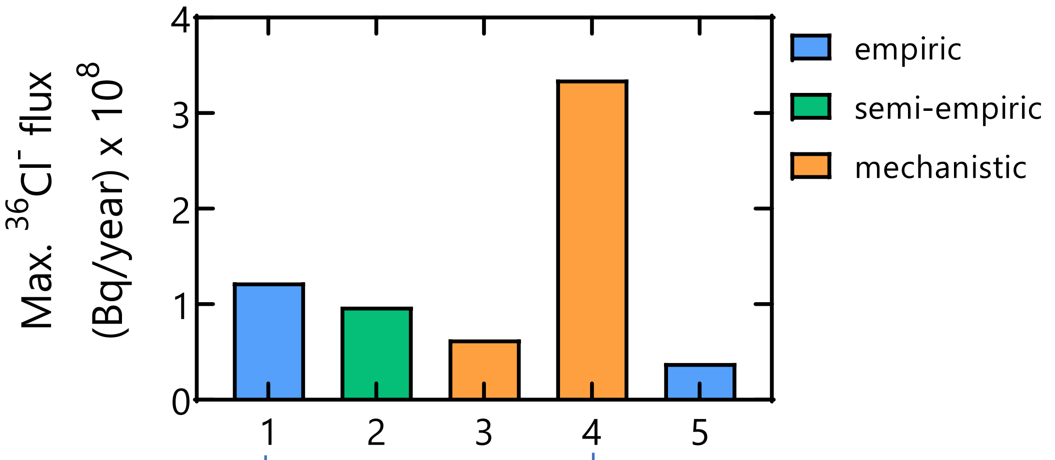

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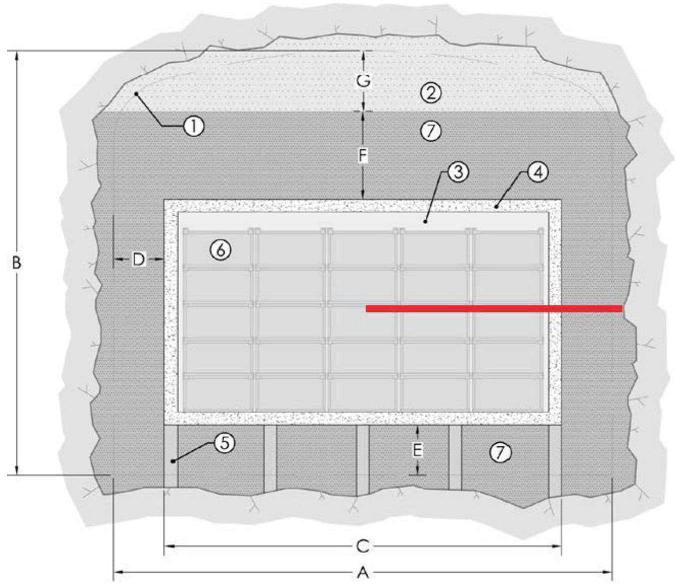

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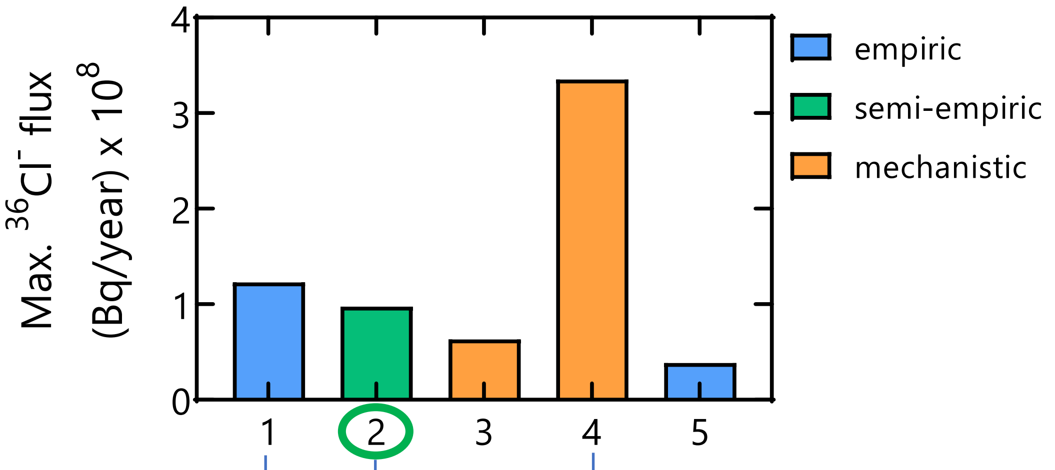

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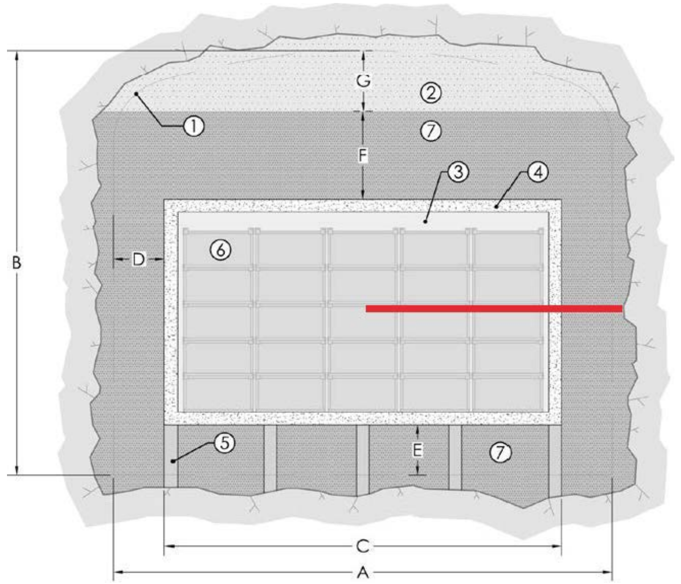

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- Copper corrosion in container of KBS-3V repository
  - Dual continuum approaches:
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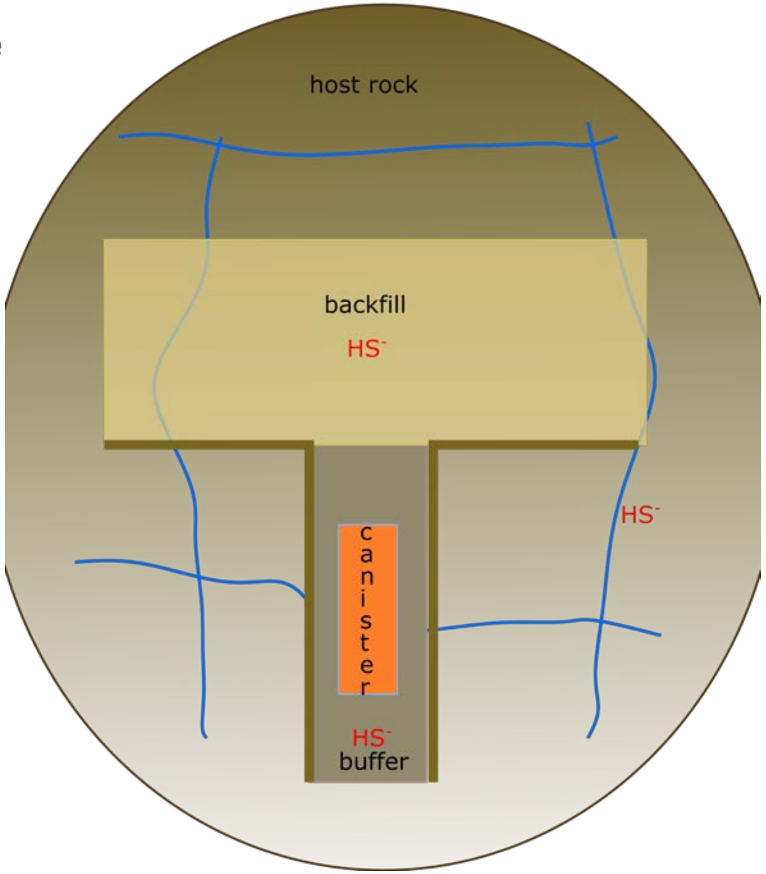
MODELLING OF SULFIDE FLUXES

- Sulfide: main corroding agent for copper containers in anoxic phase



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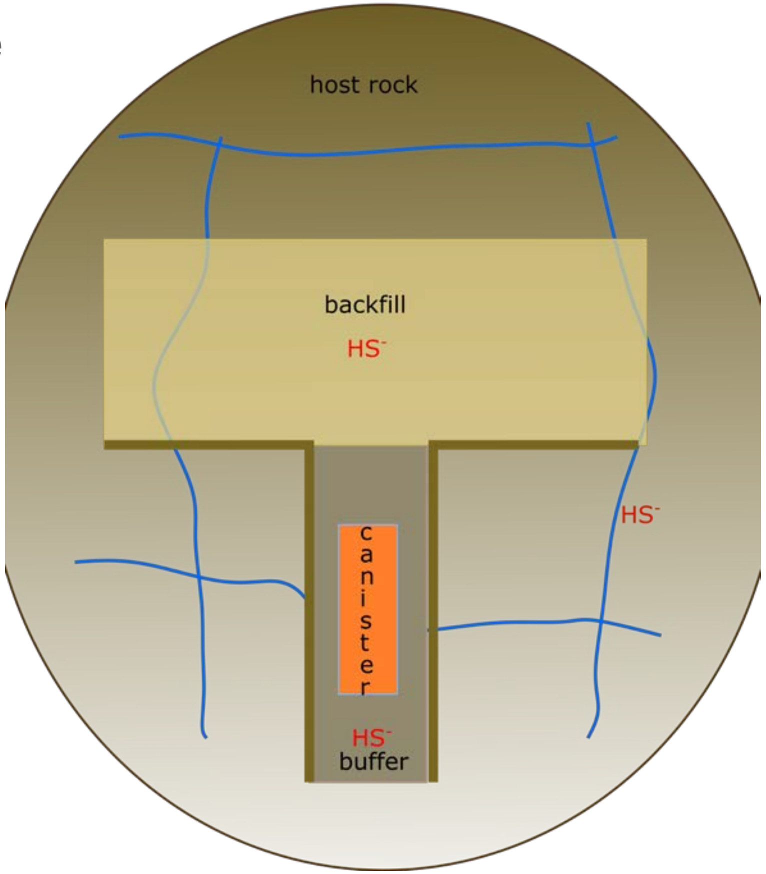

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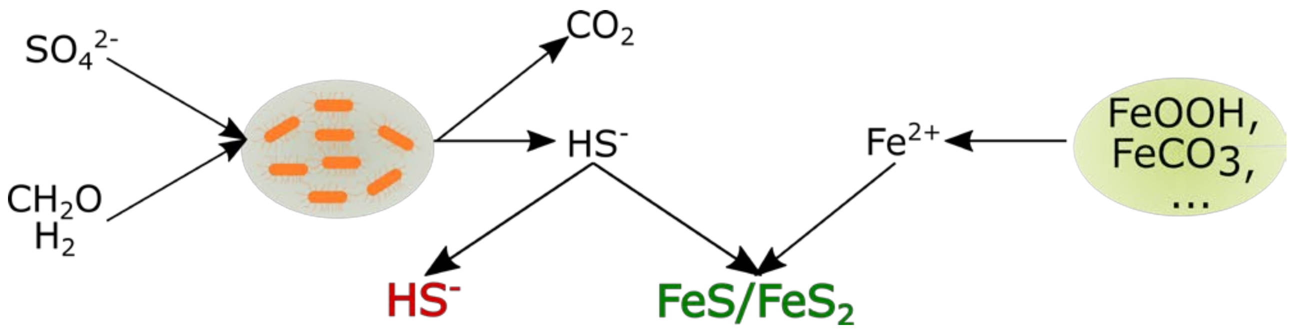

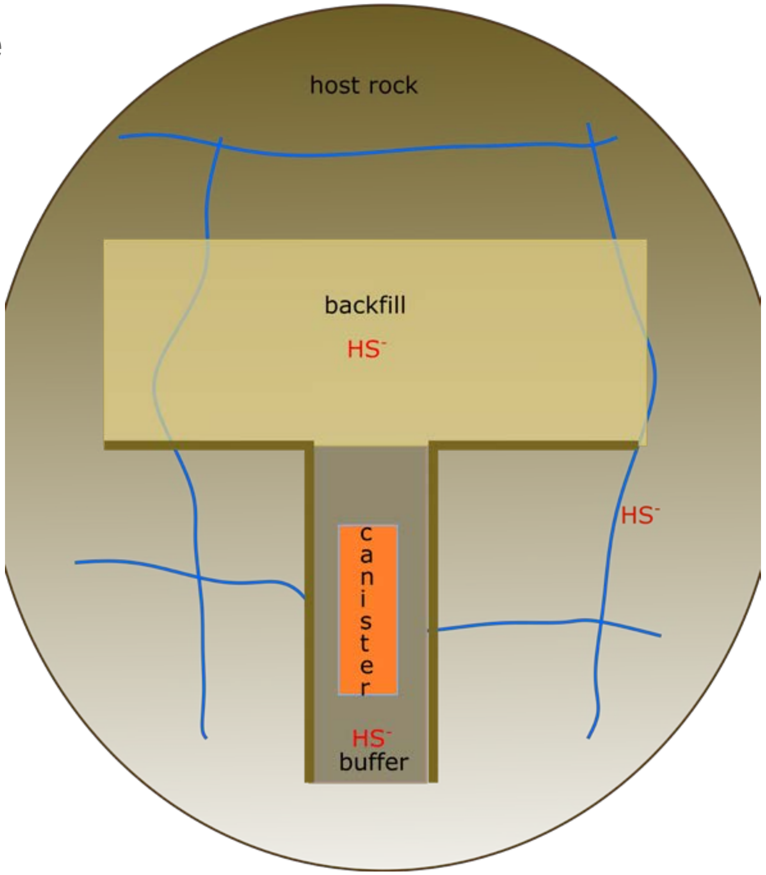

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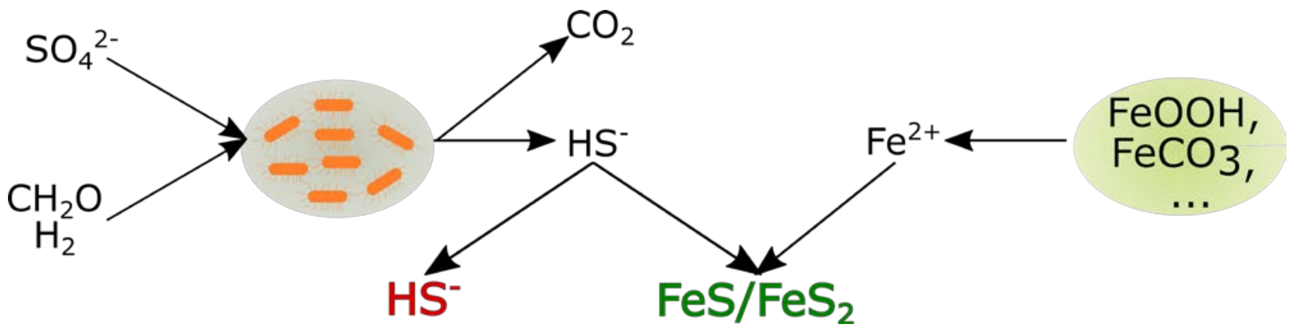

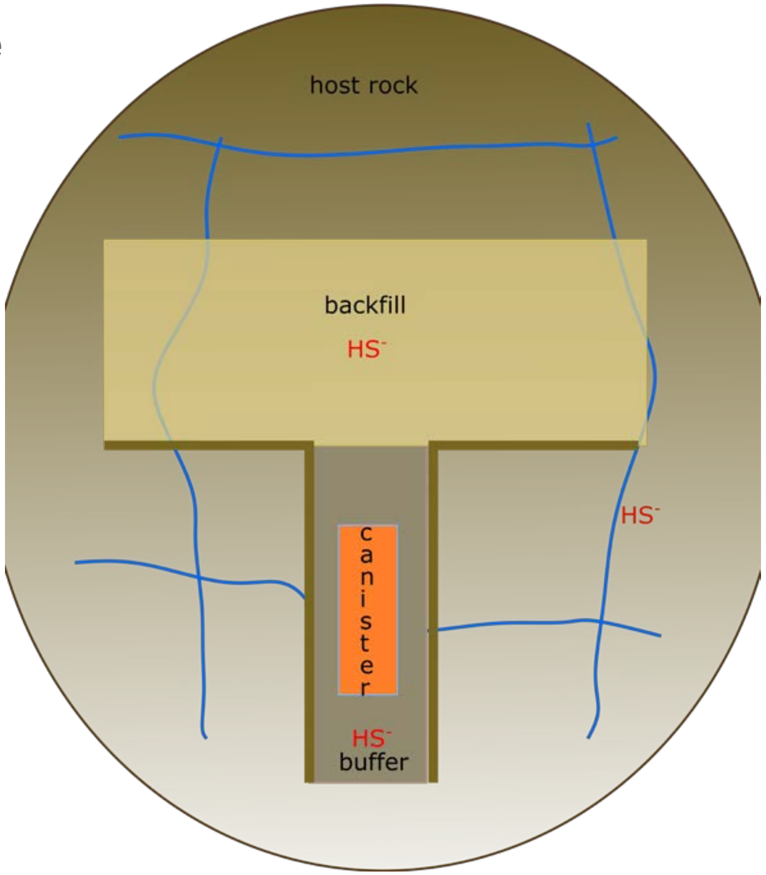

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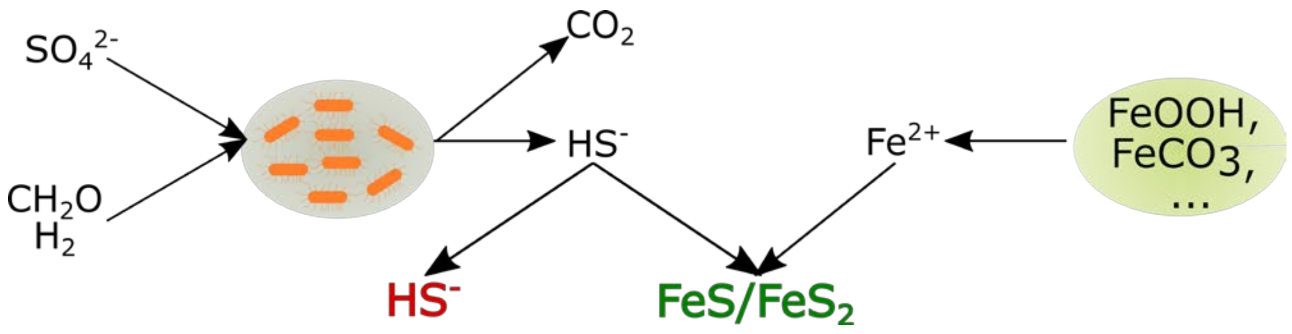

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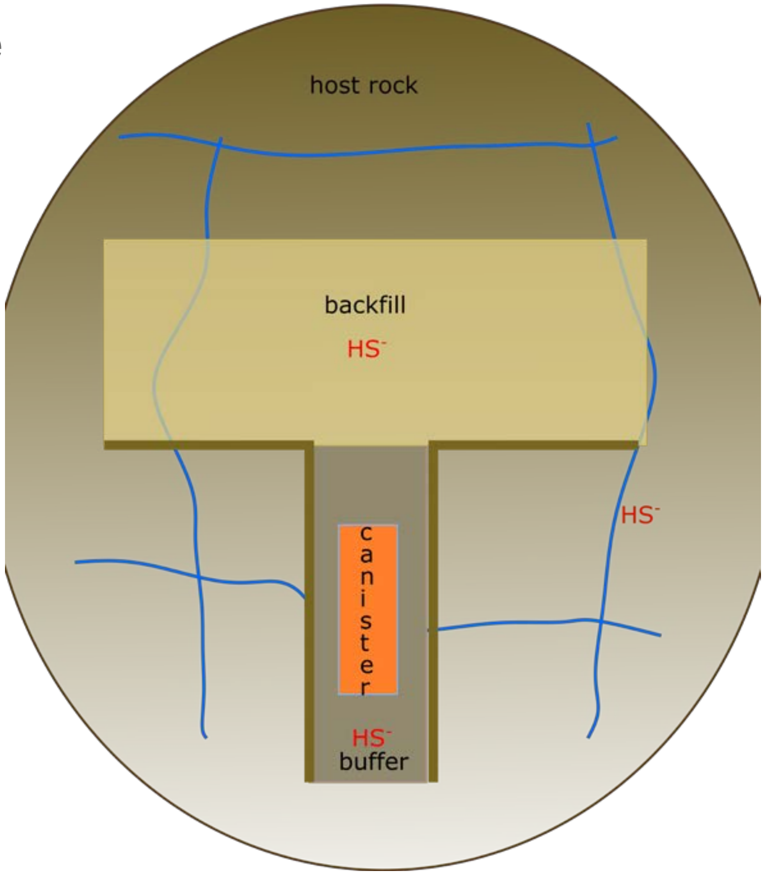

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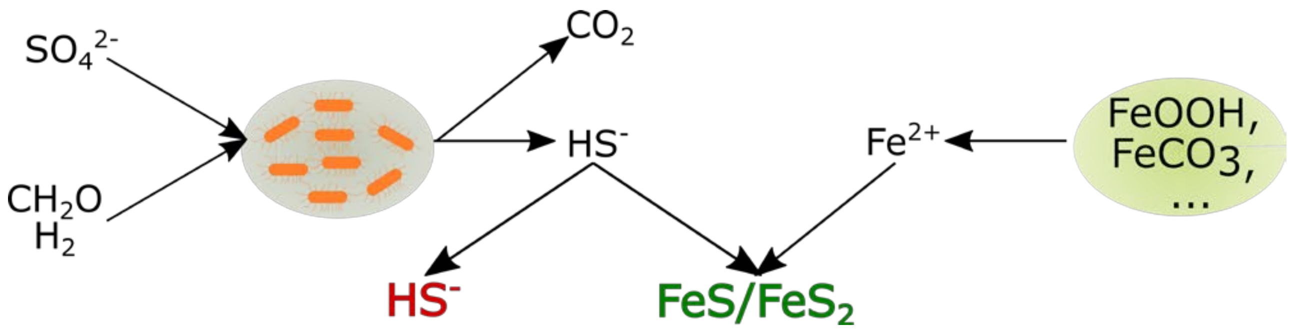

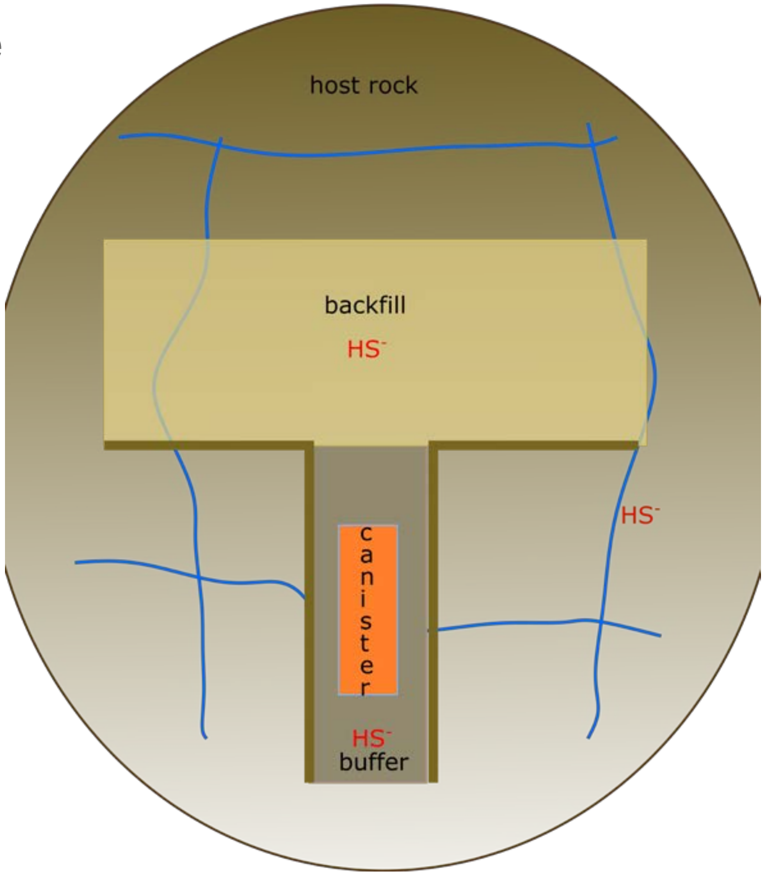

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→ Possible when relevant sulfide sources together with limited iron availability

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- Gaseous H_2S
  - Can be transported in during unsaturated period
  - Highly corrosive also in dry atmospheres

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- Evolution in time:
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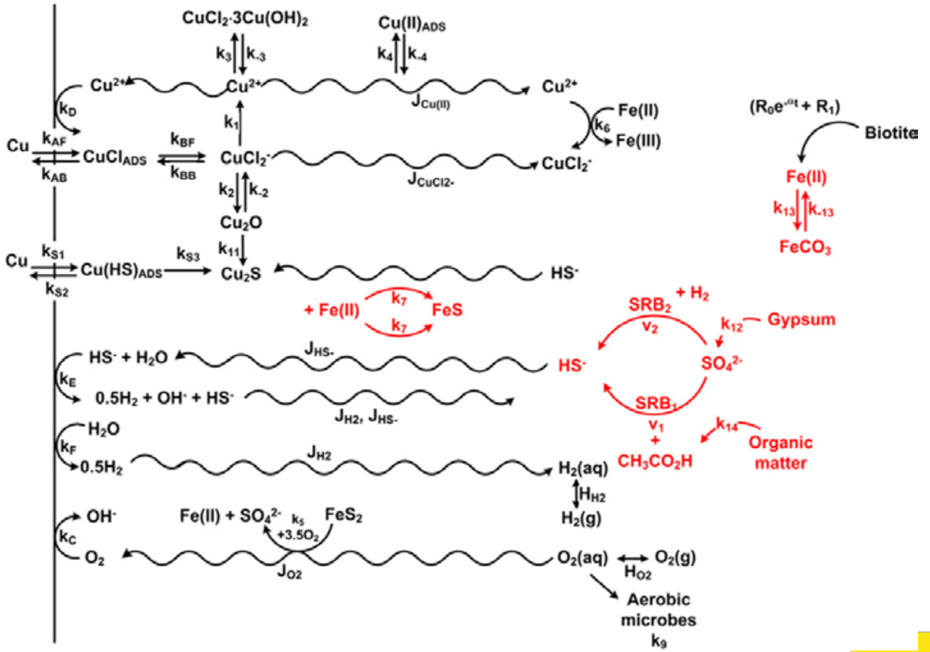

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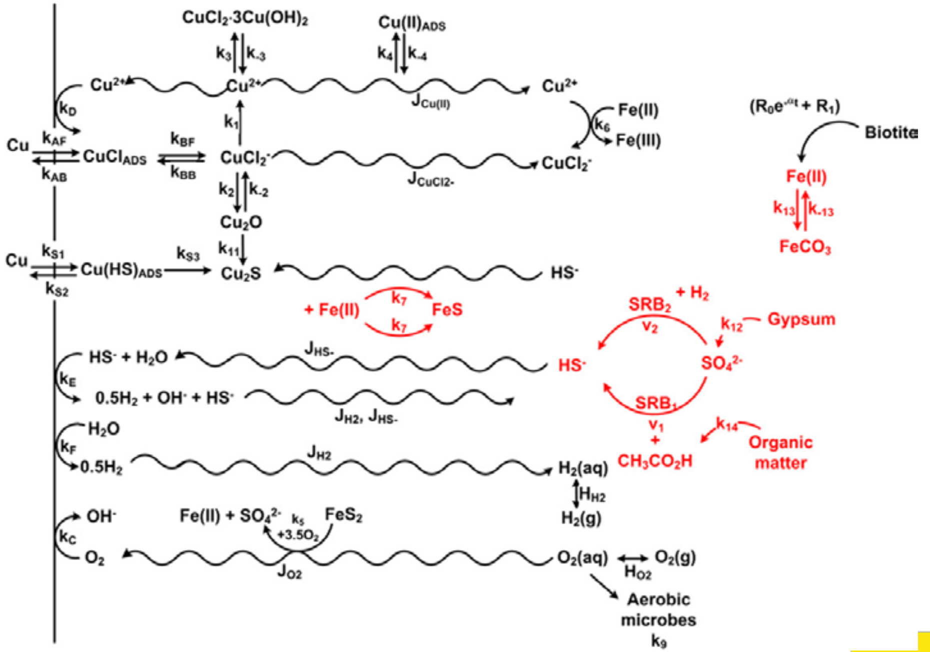
  - 2021 3D reactive transport sulfide model → kinetic Monod model for SRB
    - Max rate constant 5×10^{-5} and 10^{-4} mol sulphide/L water



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    - Initially present in backfill & rock layers
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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
    - $Fe^{3+} + HS^- \longrightarrow S + \text{polysulfides} + Fe^{2+} \longrightarrow FeS$

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- Radiolysis → molecular & radical oxidants/reductants with concentration dependent on:
  - Type of radiation
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https://www.mcpa-software.com

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  - Reactive transport models in bentonite
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  - Modelling irradiation-induced corrosion
- Steel-bentonite models
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  - Transport properties

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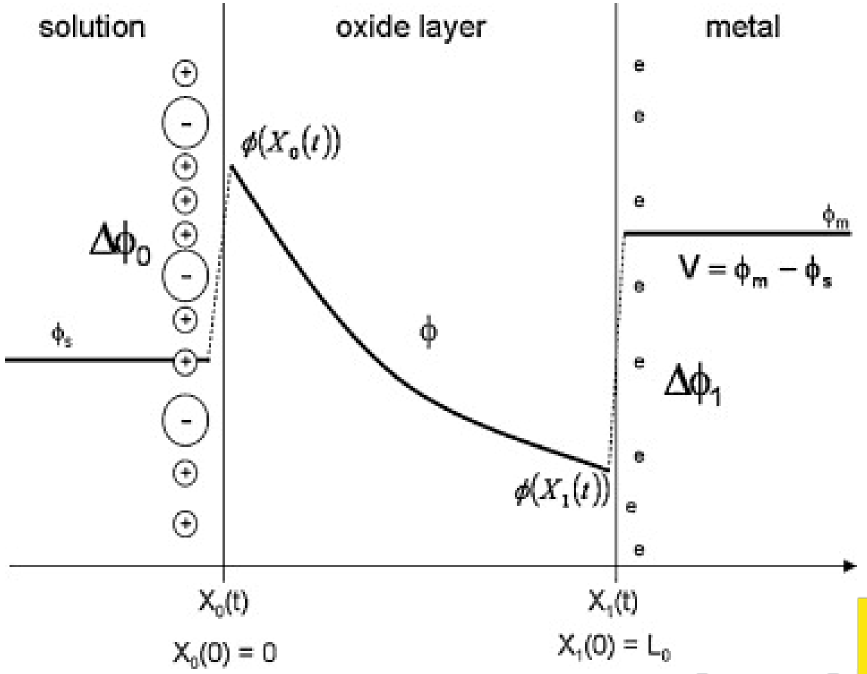

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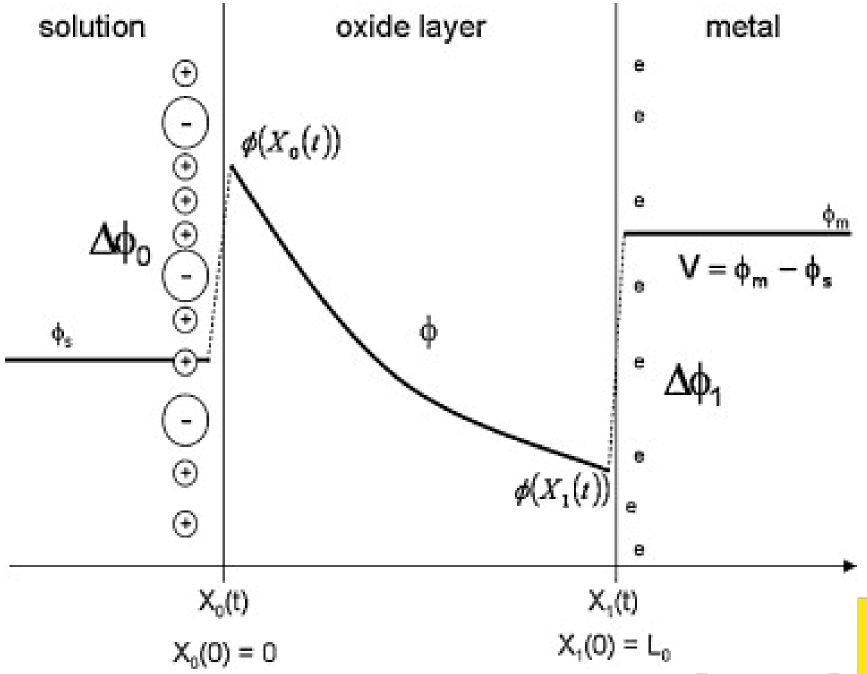

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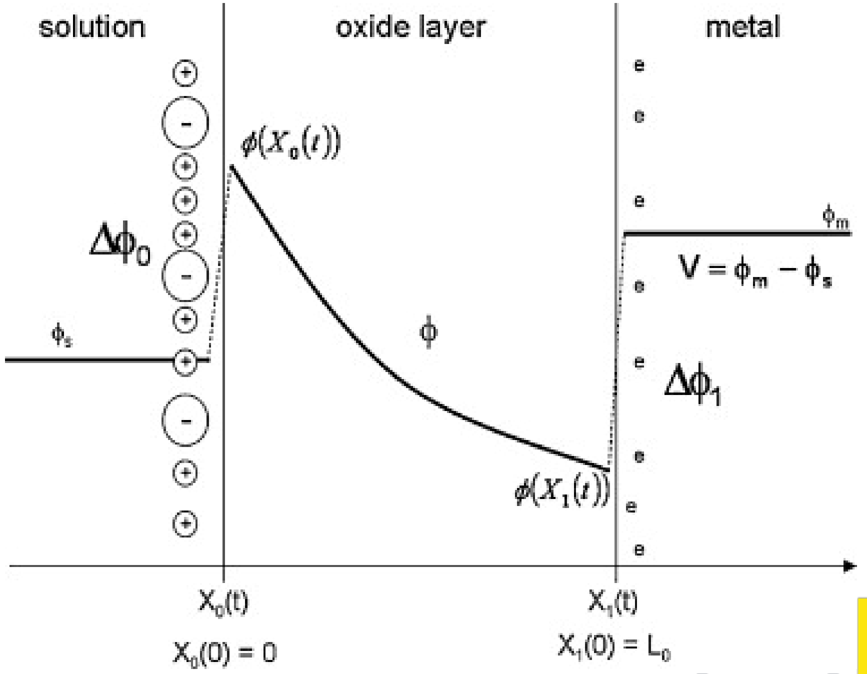
  - Estimate lifetime of the carbon steel overpack & pressure increase from H_2



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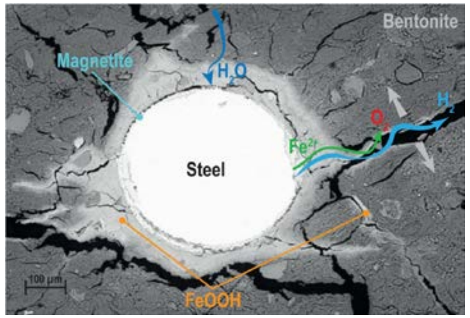
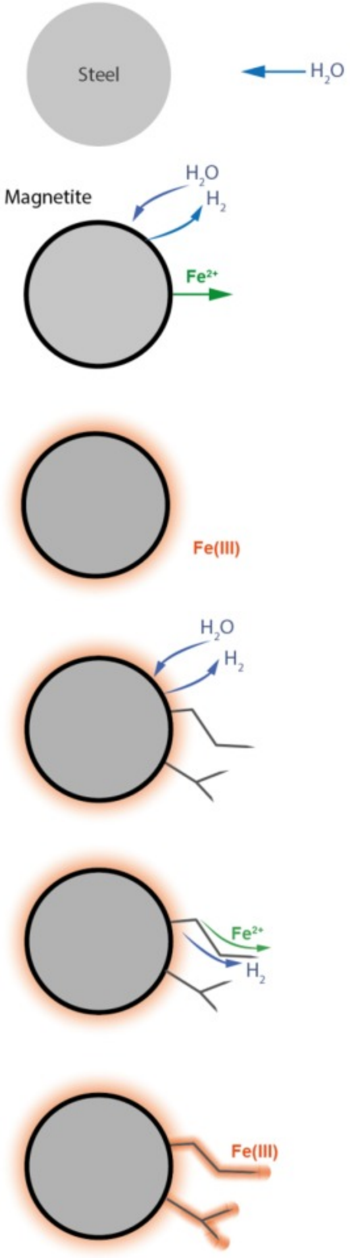
- DPCM in CALIPSO
  - Coupled with geochemistry-transport code, Kirmat
    - Realistic representation of corrosion of iron & alteration clay
- Two-phase modelling
  - Consumption of H_2O by corrosion >> diffusion of H_2O through bentonite → shrinkage micro-fractures in bentonite acting as preferential 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 Fe^{2+} ions. The cathodic reaction is the reduction of H_2O producing H_2. Fe^{2+} diffuses into the bentonite resulting in an iron enriched zone.

Fe^{2+} is oxidized by residual O_2 leading to precipitation of red Fe(III) corrosion products. The magnetite remains unaffected because the O_2 is not mobile.

The high rate of water consumption and H_2 production leads to local dessication and shrinkage microfractures because the hydraulic conductivity of saturated bentonite is low.

Fe^{2+} and H_2 continuously produced by corrosion preferentially diffuse along the shrinkage microfractures into the bentonite.

Fe^{2+} reacts with residual O_2 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).

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COMPARISON OF MAIN ASSUMPTIONS & RESULTS OF EXISTING MODELLING EXERCISES AT DISPOSAL SCALE AT FE-MX80 BENTONITE INTERFACE

T (°C)	Simulation time (years)	Corrosion rate	Assumptions	Main secondary minerals	Max. perturbation extent	Relevant results
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 ⟶ 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 ≠ 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	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 ⟶ limited the diffusion aqueous corrosion products toward the bentonite barrier ⟶ porosity ↓ & mineralogical transformation in the bentonite zone close to the bentonite/steel overpack interface.

COMPARISON OF MAIN ASSUMPTIONS & RESULTS OF EXISTING MODELLING EXERCISES AT DISPOSAL SCALE AT FE-FEBEX & FE-BENTONITE INTERFACE

T (ºC)	Simulation time (years)	Corrosion rate	Assumptions	Main secondary minerals	Max. perturbation extent	Relevant results
25	300.000	Constant (0.2 µm/y)	• 1D and 2D model • No reactivity for clay minerals • Use of cation exchange & surface complexation	Siderite Goethite	7 cm	• Magnetite precipitation (no clogging) ⟶ bentonite porosity ↓ • Proton surface complexation is highly effective in buffering pH in bentonite
25	300.000	Constant (0.1 µm/y) & ¢ (max. 0.7 µm/y)	• 1D model • Use of cation exchange & 3 types of sorption sites in the bentonite • Kinetically-controlled container corrosion & magnetite precipitation		-	• Kinetically-controlled container corrosion ⟶ significant ↓ in the corrosion rate • [dissolved Fe] computed with kinetic magnetite precipitation is < [obtained at equilibrium]
≠	1.000.000	Constant (2 µm/y) & ¢	• 1D model • Use of cation exchange & 3 types of sorption sites in the bentonite • Kinetically-controlled container corrosion & magnetite precipitation • Smectite dissolution is considered	Analcime Cronstedtite	7 cm	• Magnetite precipitation ⟶ bentonite porosity ↓ near the container (7 cm thickness of the zone of reduced porosity at 1 Ma) • Thickness: < 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 & analcime precipitation ⟶ thickness ↓ 3 cm
≠	1.000.000	Constant (2 µm/y)	• 1D model • Use of cation exchange and 3 types of sorption sites in the bentonite. • Smectite dissolution is considered	Gypsum Sepiolite	1 cm	• Pore clogging at the container-bentonite interface • Narrow alteration zones • Limited smectite dissolution after 1 Ma
70	100.000	Constant (1 µm/y) & ¢ (M2)	• Model 1: fixed steel corrosion rate • Model 2: diffusion-limited corrosion rate • Model 3: corrosion cell approach	M1: Berthierine Fe-saponite Greenalite M2 and M3: Berthierine	2 cm	• Extent & nature of the alteration predicted by the models sensitive to model conceptualization • M1 and M2: - M3: Magnetite Siderite

CONTENT

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INTEGRATION OF CORROSION PHENOMENA IN PERFORMANCE ASSESSMENTS

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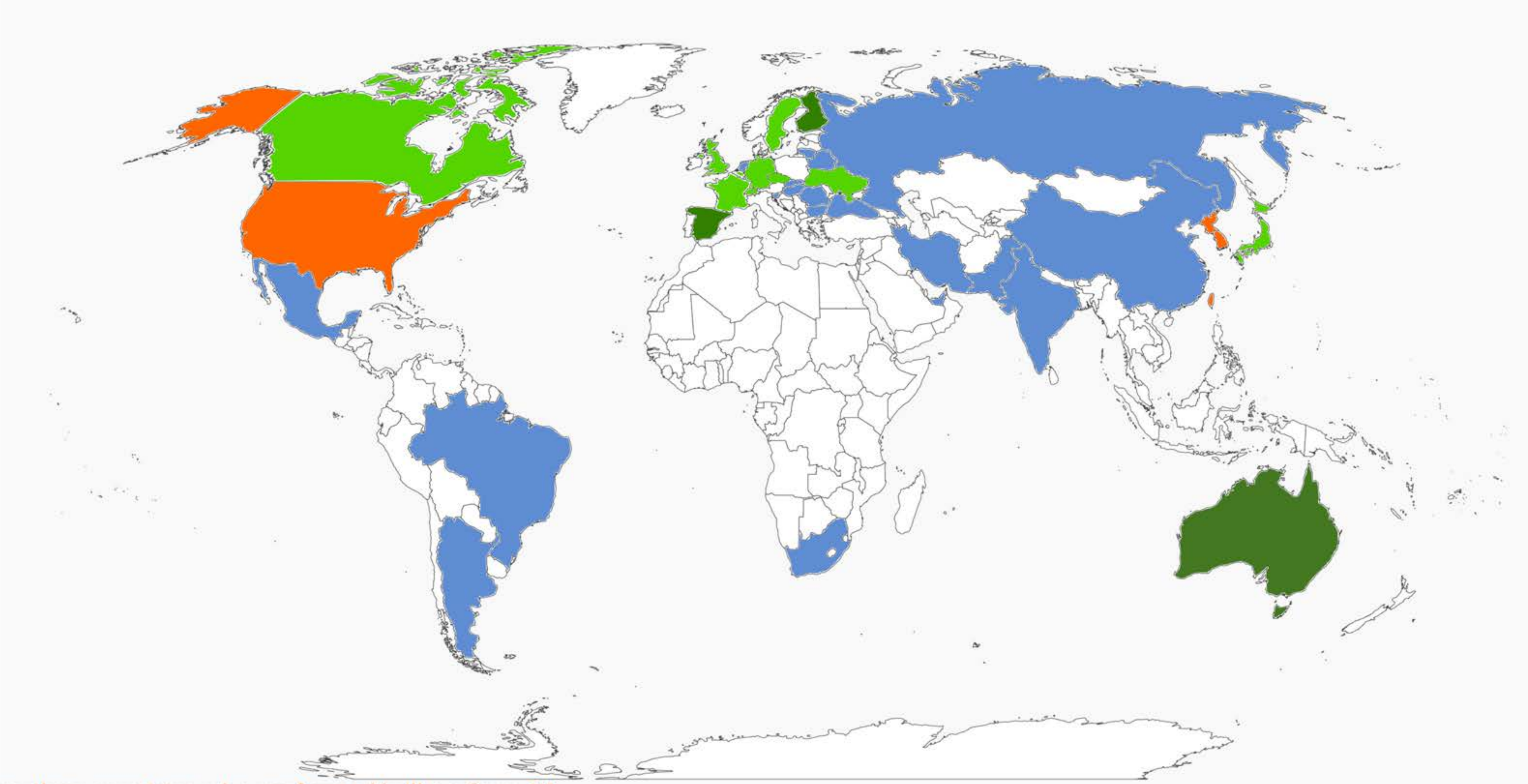
- No standardized prescriptive approach to include corrosion in PA → specific to each concept & environmental conditions
- General guidance of safety assessment provided by IAEA

COUNTRIES OPERATING NUCLEAR POWER PLANTS (36) & PROGRESS IN PA



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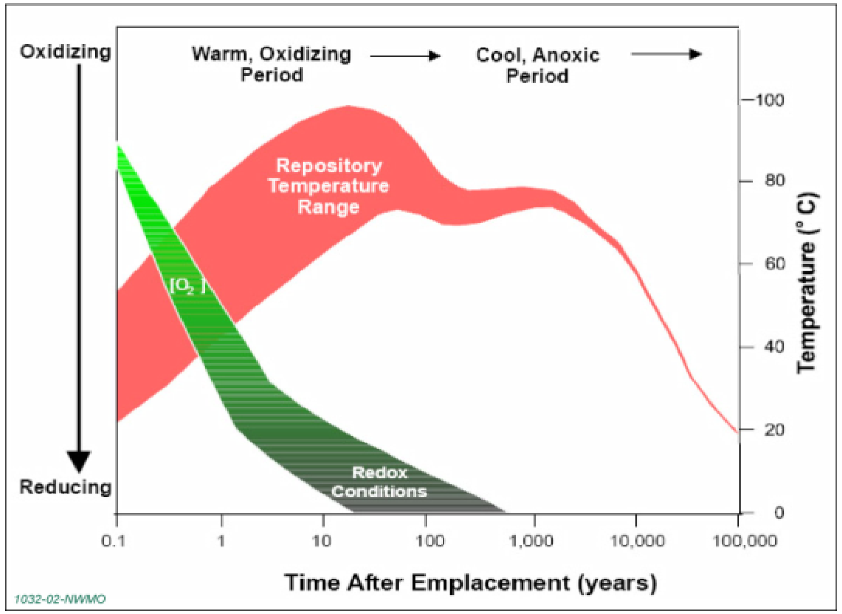

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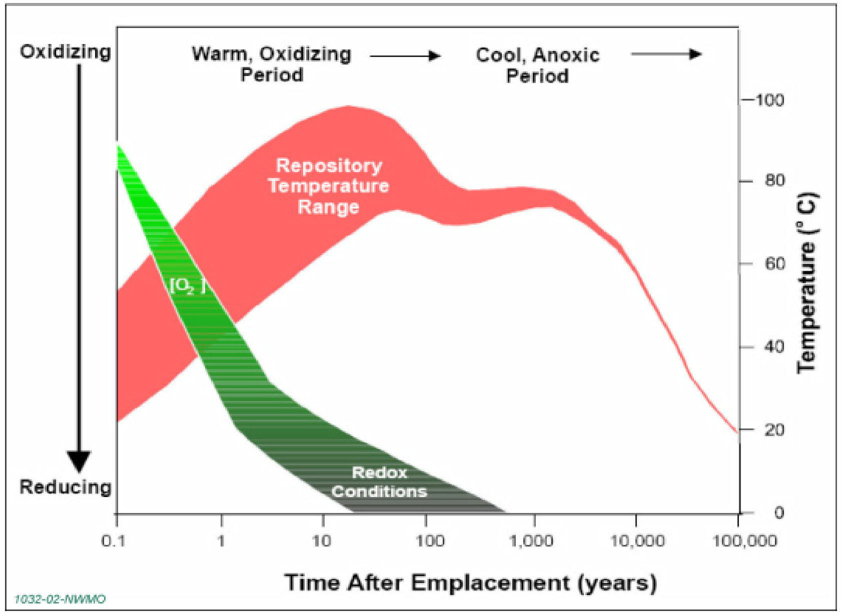

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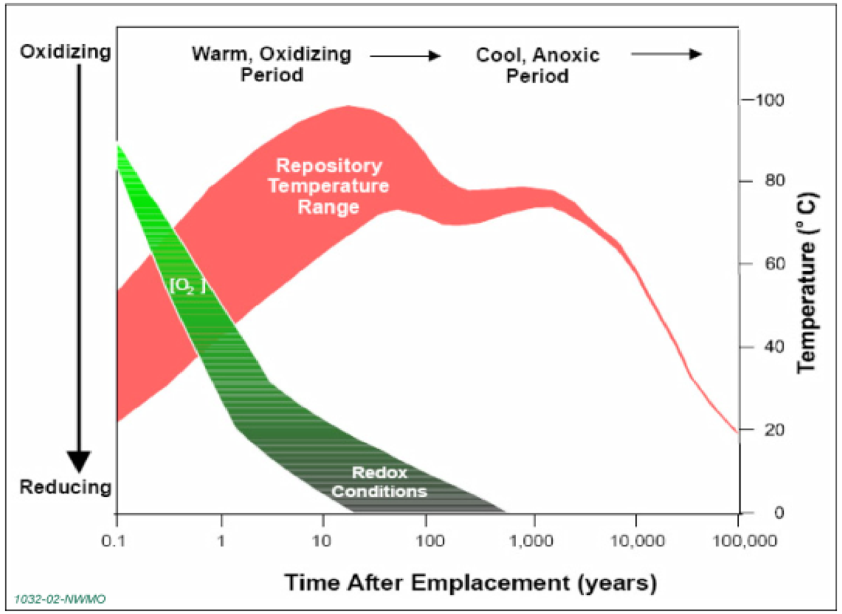

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- Copper-based waste container ↔ iron-based container

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    - 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

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PA FOR COPPER-BASED CONTAINER CORROSION

- O_2-free copper → Sweden, Finland, Switzerland, Canada

Furthest developed concept:
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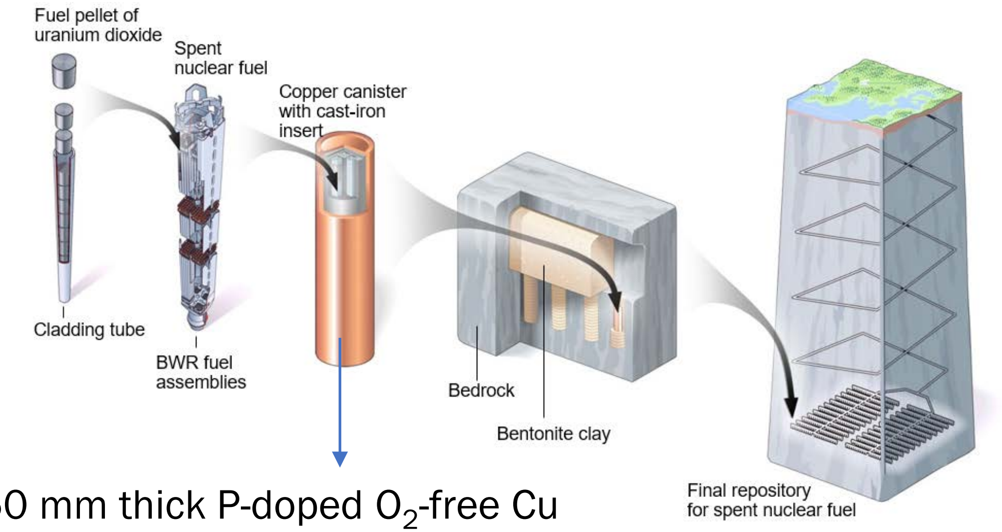

50 mm thick P-doped O_2-free Cu

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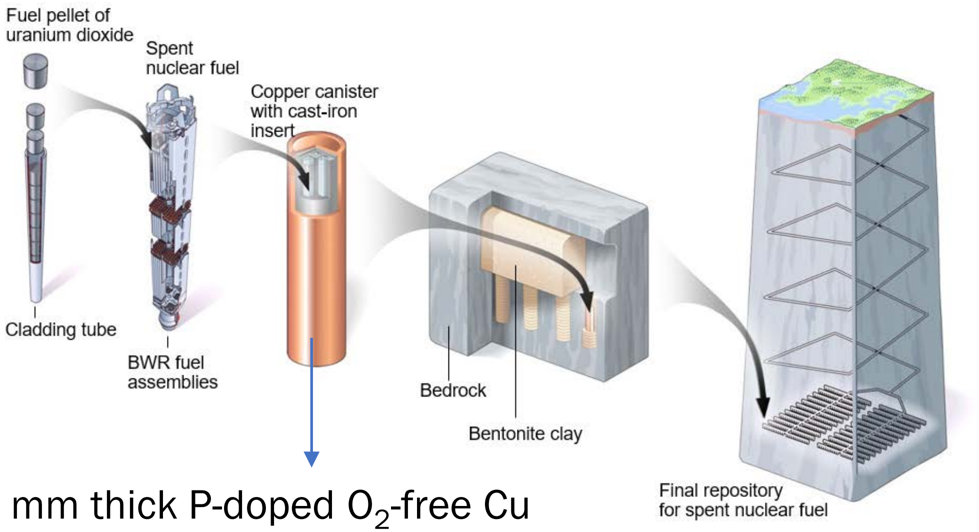

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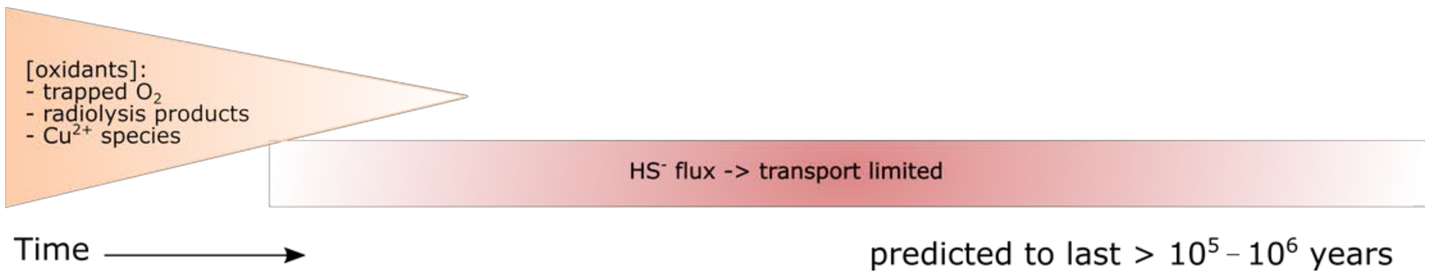
- Cu is not expected to passivate prediction lifetime based on general corrosion with moderate uniformity



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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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- Pessimistically bounded by assuming that:
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    - production of copper oxide surface film

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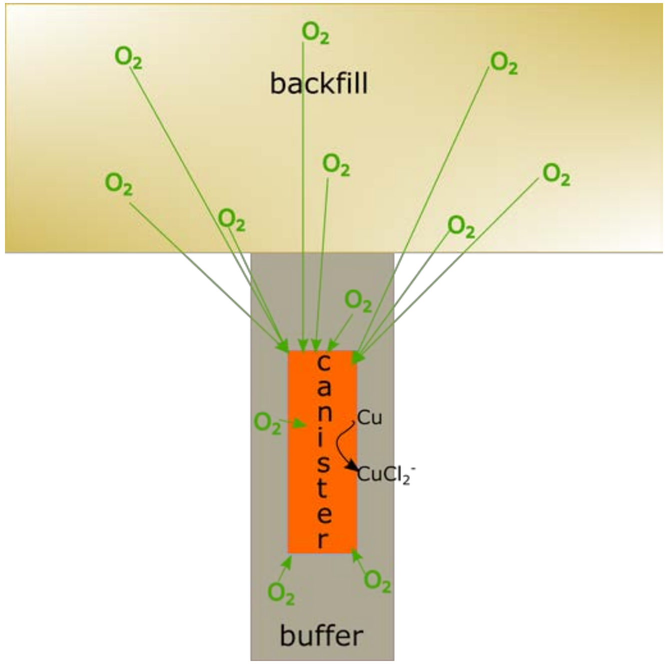
- Unsaturated phase: including any corrosion before emplacement in the buffer and within the buffer before groundwater re-saturation occurs
- Evaluated in KBS-3 environment
- Temp 50 °C → relative humidity < critical value of 50-70% ↔ dry air → corrosion rate ↑ with temp: 10s of nm/year if 50-150°C
- ~ measurements Äspo Hard Rock Lab : < 0.1 µm at 75°C
- Pessimistically bounded by assuming that:
  - atmospheric corrosion < 1 µm
  - production of copper oxide surface film

→ Extent of corrosion expected to be negligible

Final repository
for spent nuclear fuel

GENERAL CORROSION

- All oxygen in voids reaches container → highly conservative



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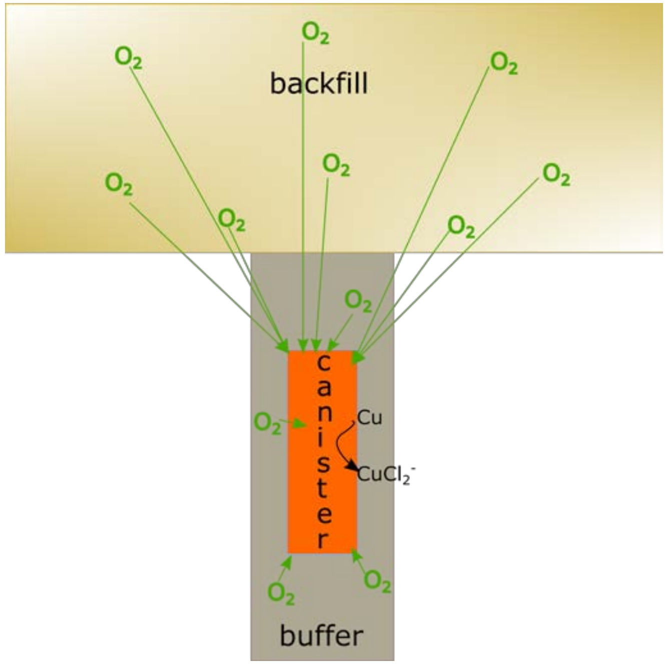
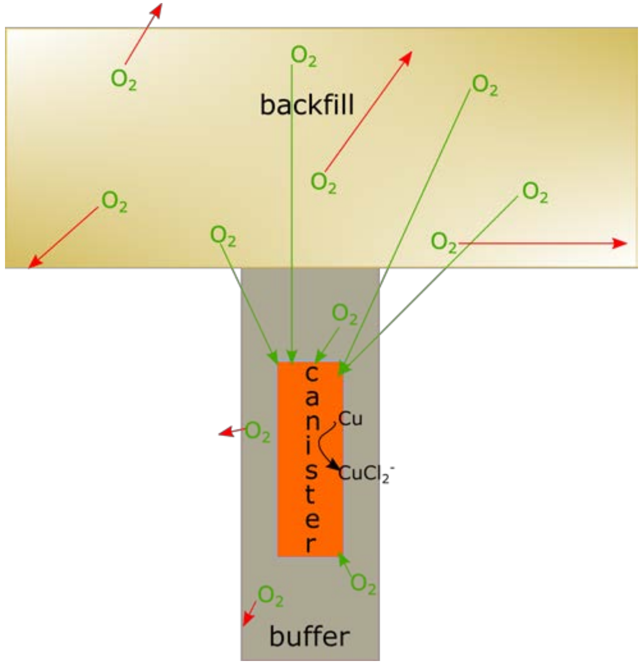


KBS-3 design: 50 % reaches surface → corrosion loss of 17 μm (max. 36 μm)



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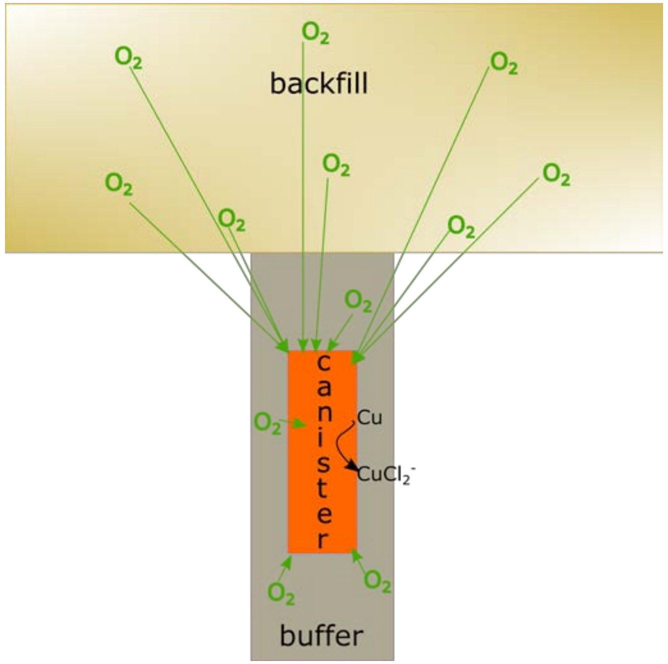

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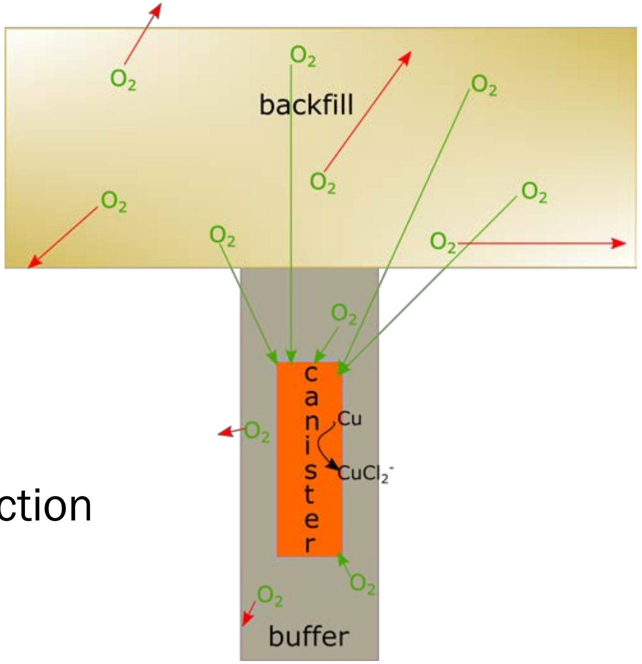

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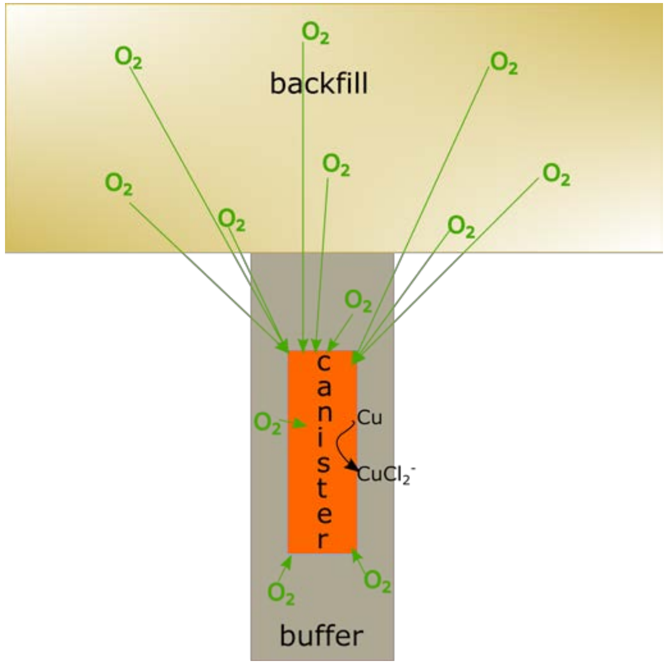

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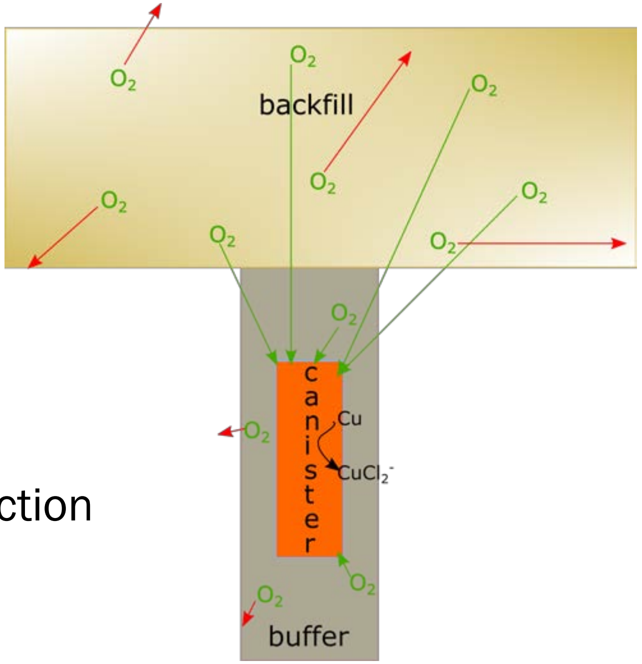

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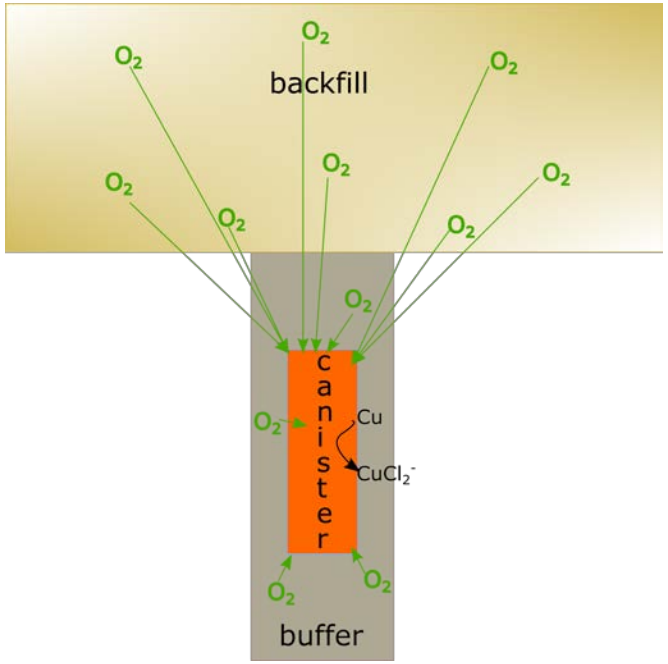

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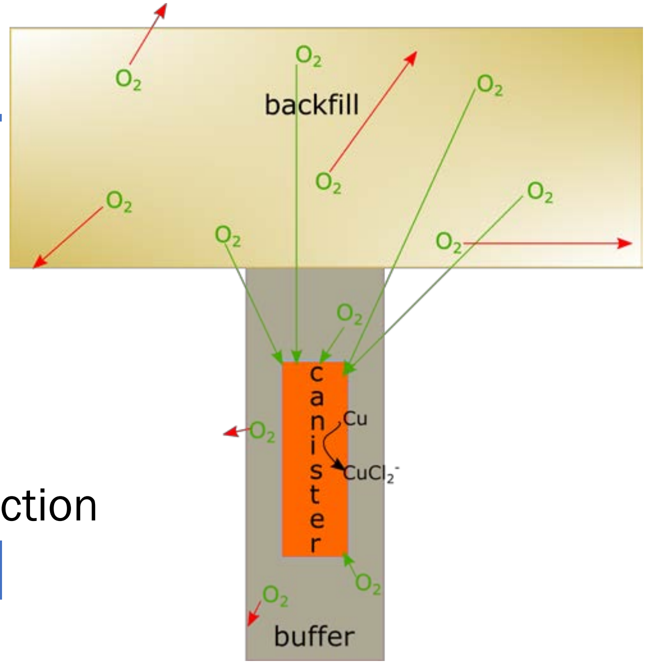

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Corrosion loss 106 µm = **123 µm total loss**

GENERAL CORROSION

- Swiss concept

Host rock	Repository depth (m)	Repository Temp (°C)	Hydrostatic pressure	Lithostatic pressure	Bentonite saturation time	Bentonite swelling pressure	Salinity Cl (mol/l)
Opalinus Clay	450-850	Ambient 30-45 Max. ~ 160	4.5-8.5 MPa	15-22 MPa + glacial: 5 MPa	>100 years	2-4 MPa	Typ. 0.1 Max. 0.3

Johnson, L.H., King, F. 2003. Canister Options for the Disposal of Spent Fuel. Technical report 02-11, National Cooperative for the Disposal of Radioactive Waste, Wettingen, Switzerland.

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- Mass transport approach for trapped O_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

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GENERAL CORROSION

- - O_2
- Reactive transport modelling

e.g.

$$2\,Cu(s) + HS^- + OH^- \rightarrow Cu_2S(s) + H_2O + e^-$$
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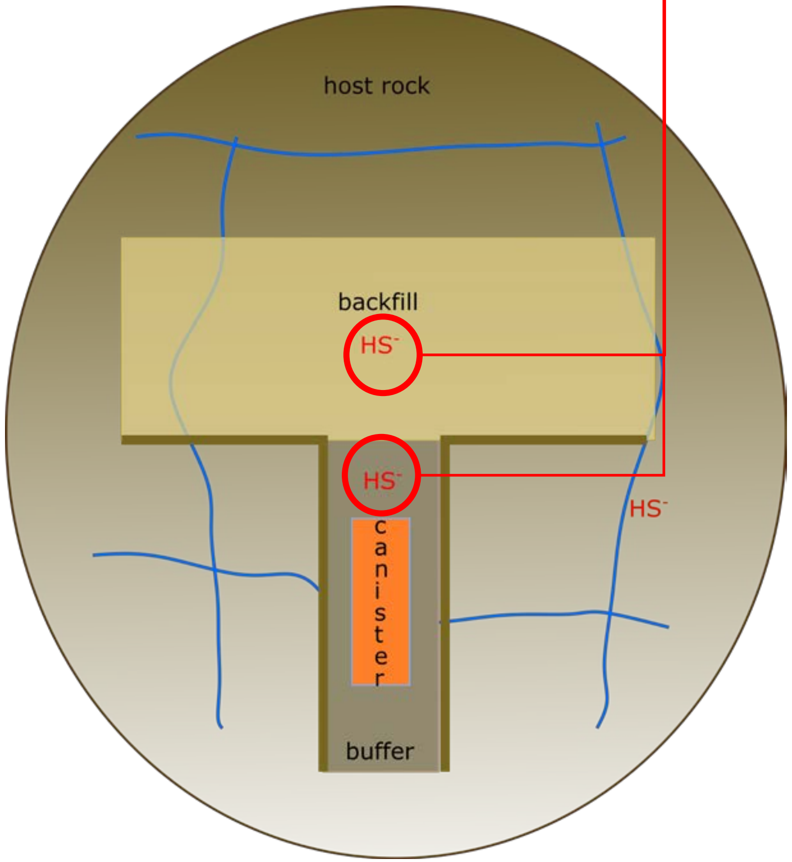

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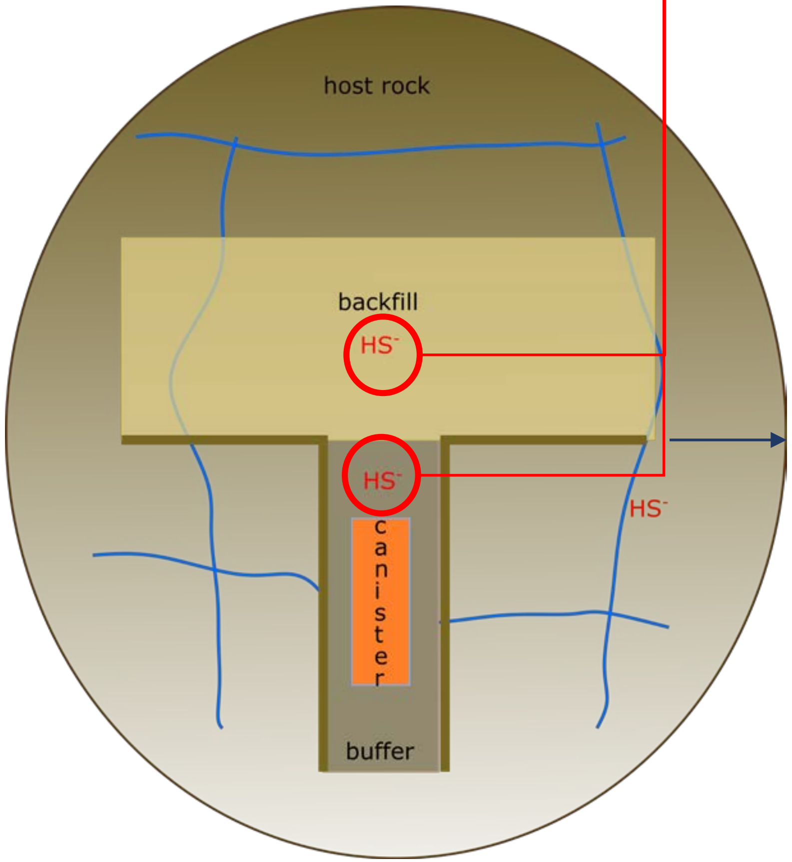

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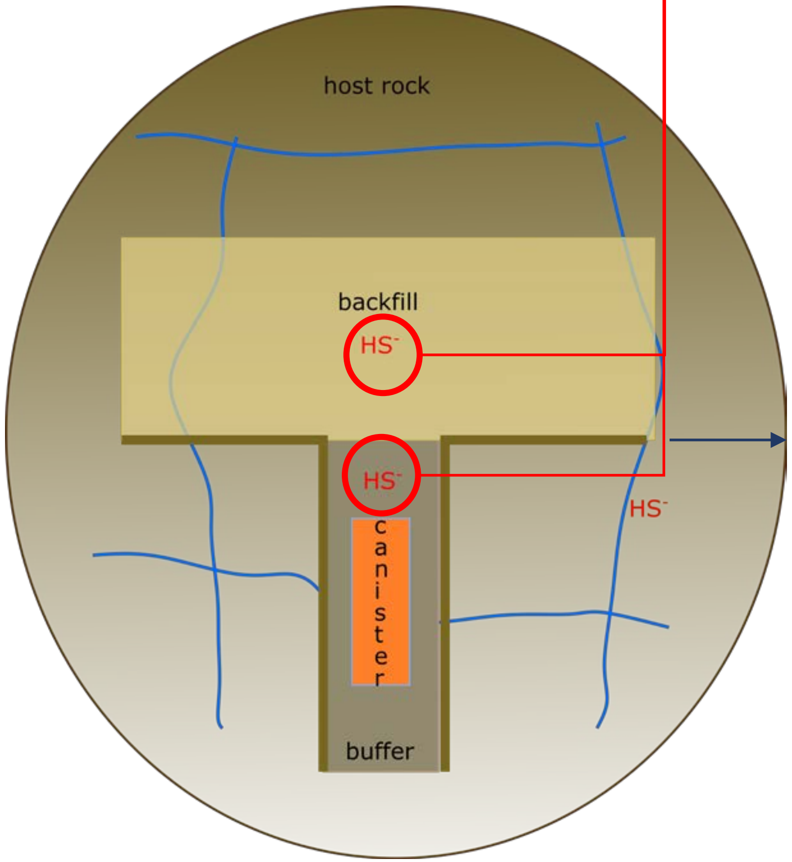

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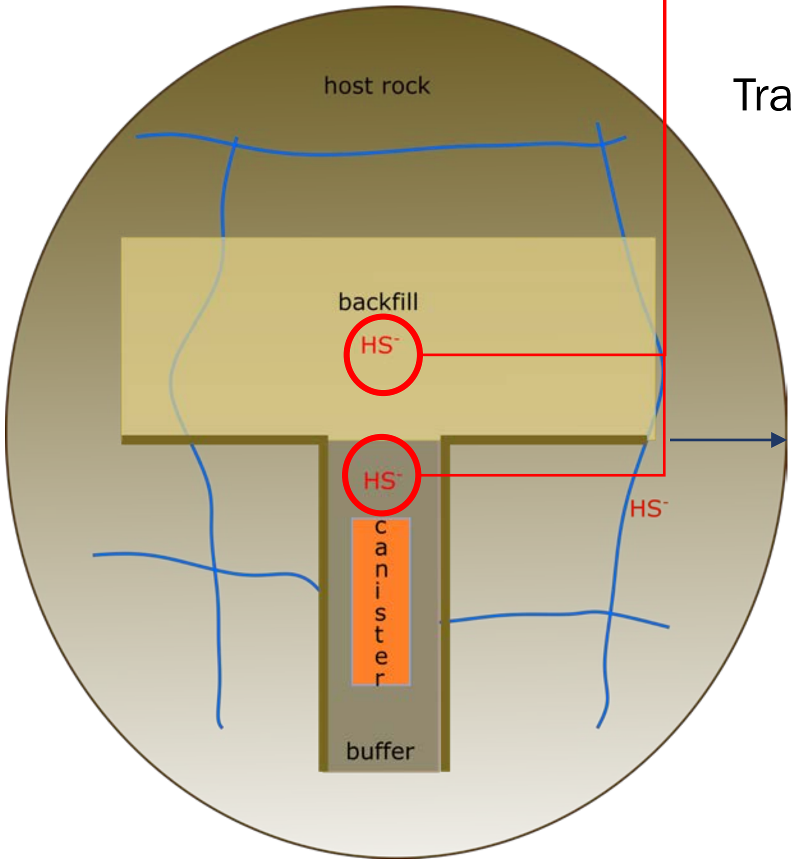

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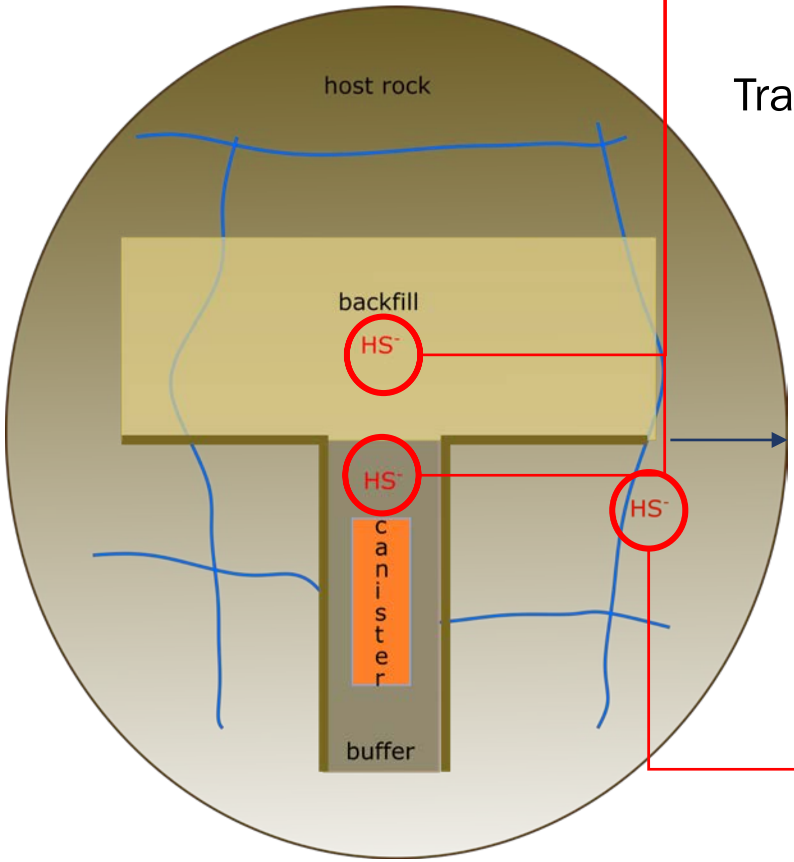

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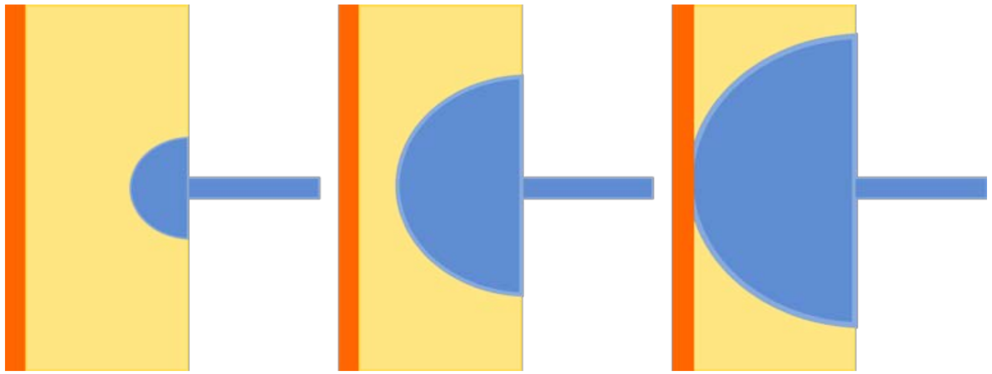
Corrosion of copper by HS- transport in groundwater
evaluated by mass transport limitation
Equilibrium $[HS^-]$ determined by source & sink

GENERAL CORROSION

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

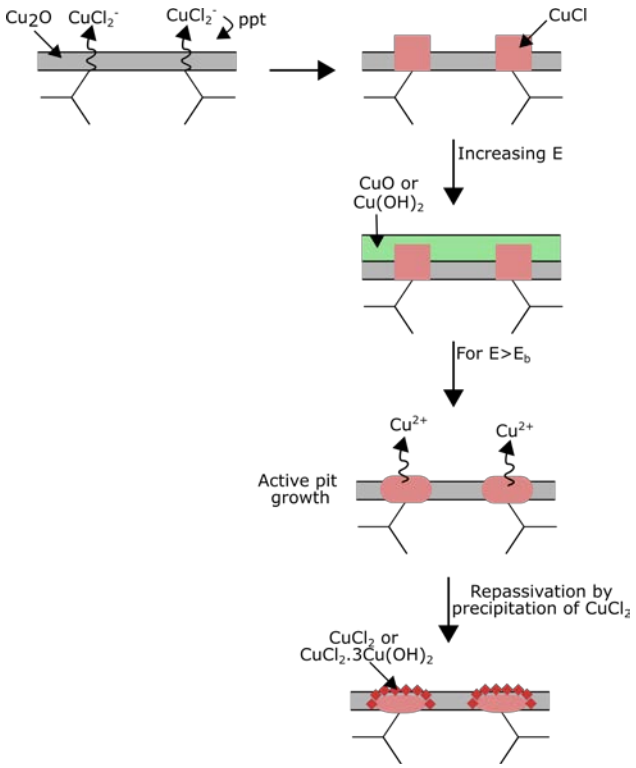


Intact buffer	Partially eroded buffer	
	Most pessimistic assumptions: • $[HS^-]$ 0.12 mM • flow rate ≥ 0.161 m/s	Failure (> 47mm) could occur in 10^5 years
$[HS^-]$ 0.01 mM → < 0.001 μm/year	More realistic assumptions: • $[HS^-]$ 0.01 mM • High flow rate 0.251 m/s	Failure after 850 000 years

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



Figures redrawn from King, F., L. Ahonen, C. Taxen, U. Vuorinen and L. Werme (2001). Copper Corrosion under Expected Conditions in a Deep Geologic Repository. Sweden

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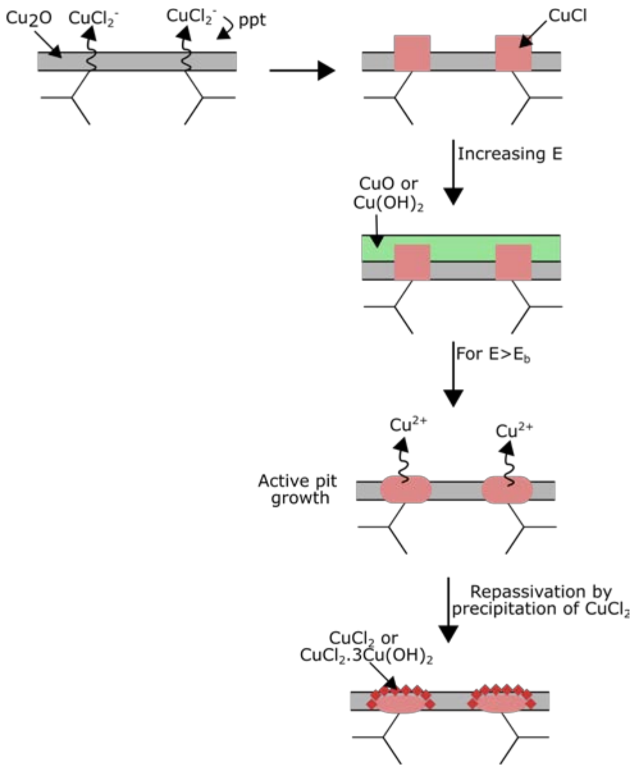
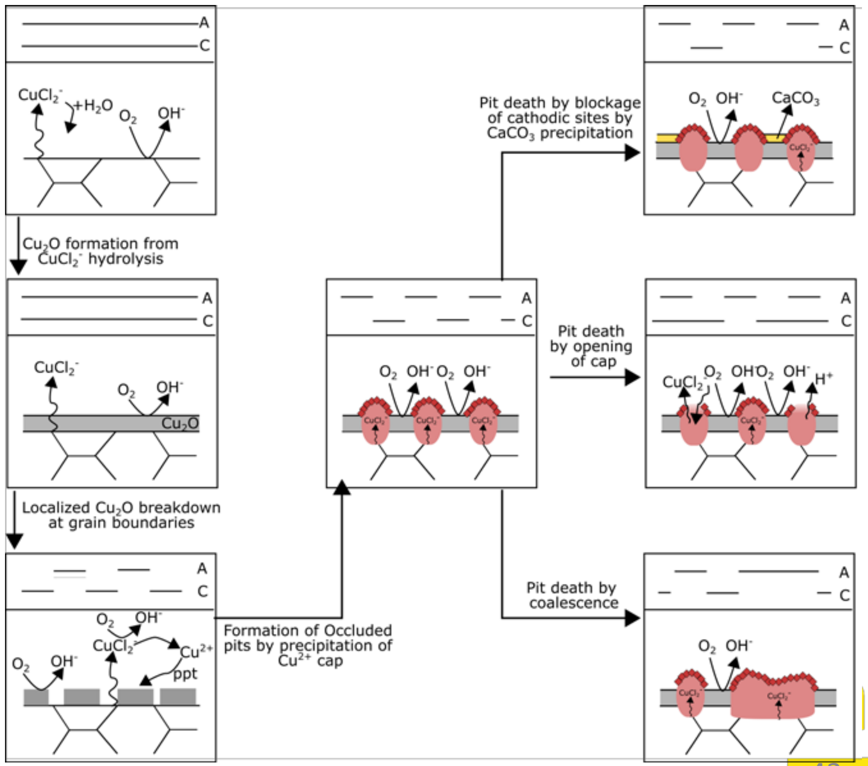


- Under-deposit corrosion → form of crevice corrosion
  - underneath precipitated surface film that acts as selective ion exchange membrane to create permanent anodic region



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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

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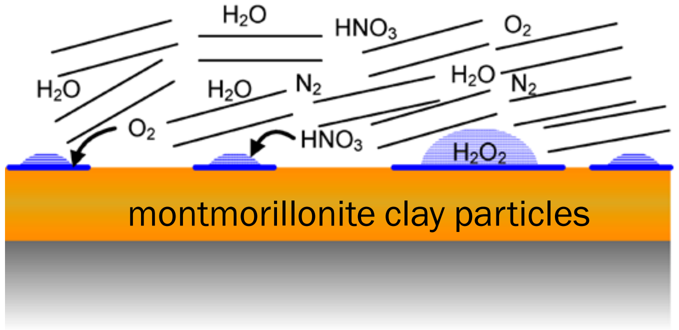
- **Extreme-value statistical analysis**
  - $F(x) = \exp[-\exp(-ax + b)]$

    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

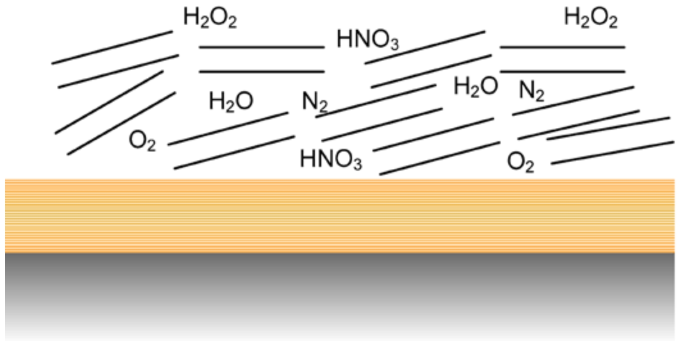
RADIATION ASSISTED CORROSION

- Radiolysis transients in the near-field

Absorption of 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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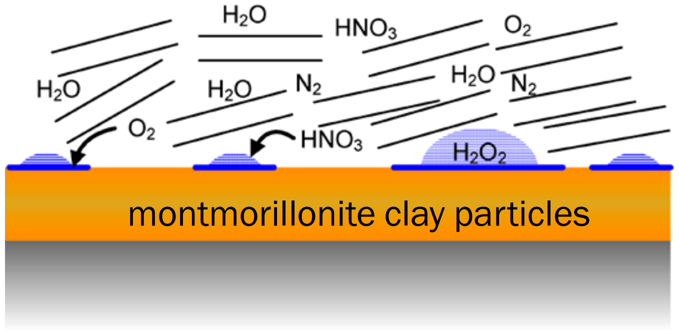

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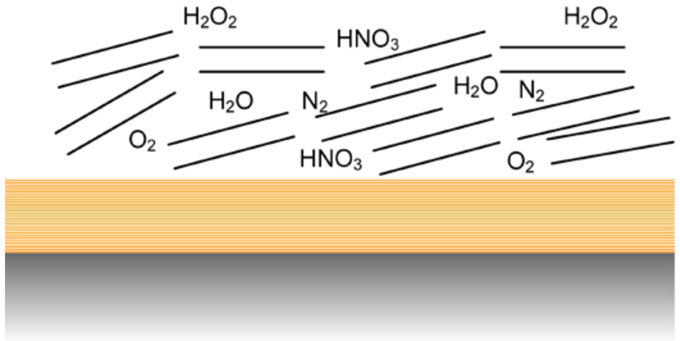
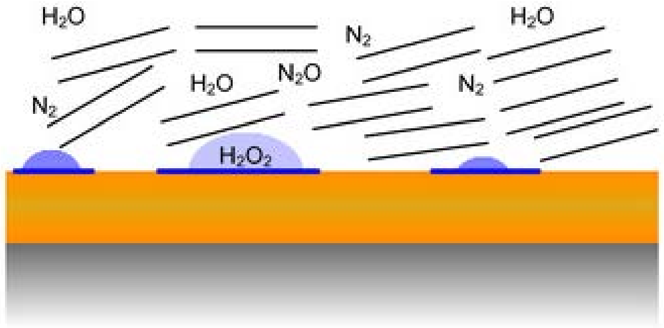
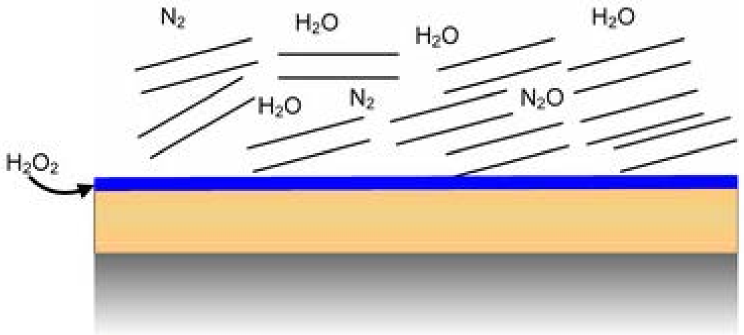


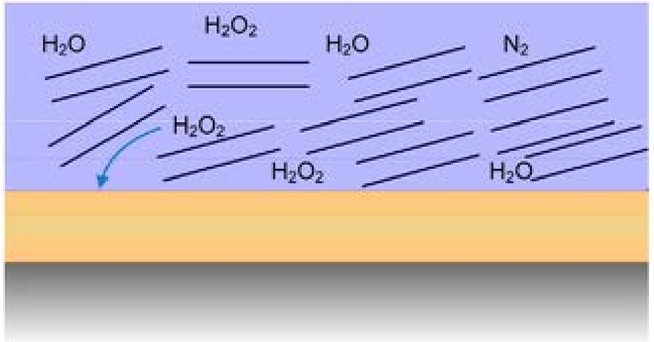
Saturated conditions



Radiolysis of **N_2-H_2O** following consumption of the initially trapped O_2 & 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 N_2-H_2O atmosphere



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

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).

CALCULATION METHODS RADIATION ASSISTED CORROSION

- **Mass balance of radiolytic produced oxidants**
  - Unsaturated conditions:
    - calculation radiolytic yield/volume
    - assume oxidants produced will react

    Bounding value

  - Used to calculate HNO_3 from γ-radiation in container buffer gap in KBS-3 concept
    - $HNO_3 = (G \times V \times \rho \times D_0/A_v) \times (T/\ln 2) \times (1 - e^{-\ln 2 \cdot t/T})$
    - 0.015 mol HNO_3 & corrosion depth < 7 nm
  - Saturated conditions:
    - Radiolysis of $H_2O \rightarrow H_2$ + 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 Fe^{2+} → 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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  - No corrosion enhancement

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MICROBIOLOGICALLY INFLUENCED CORROSION

- 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

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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

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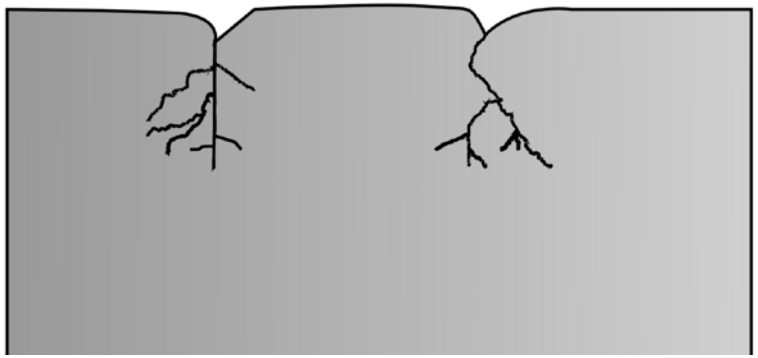
ENVIRONMENTAL - ASSISTED CRACKING

- Stress corrosion cracking
  - Stress + aggressive ions + oxidizing ions ⟶ unlikely
  - No mechanistic arguments
  - Experimentally validated by mixed-potential modelling of E_{corr} of copper
    - E_{corr} & surface pH ⟶ 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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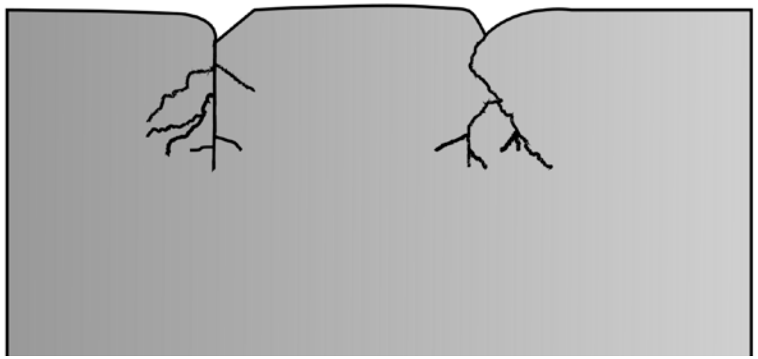

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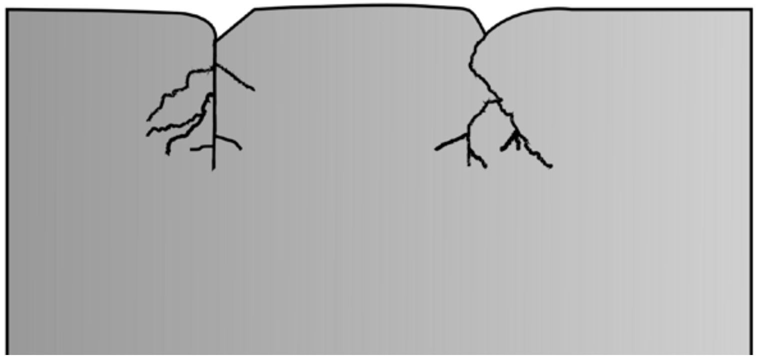
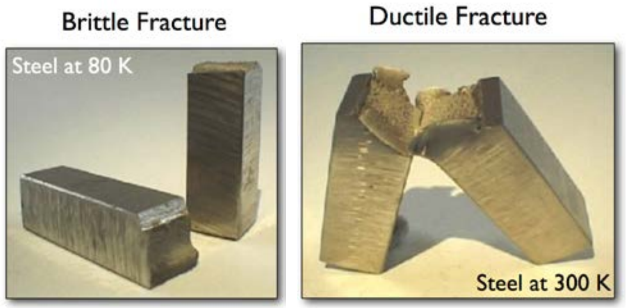
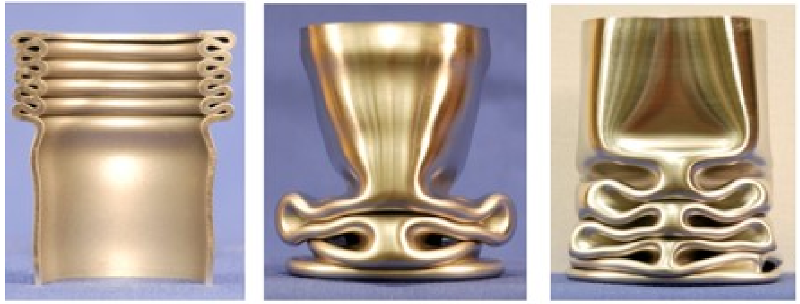


➡ Reasoned arguments for non-susceptibility

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
    - O_2-free P-doped copper → higher creep ductility





MECHANICAL & MATERIAL-RELATED FACTORS LEADING TO CONTAINER FAILURE & THEIR RELATIONSHIP TO VARIOUS FAILURE MODES

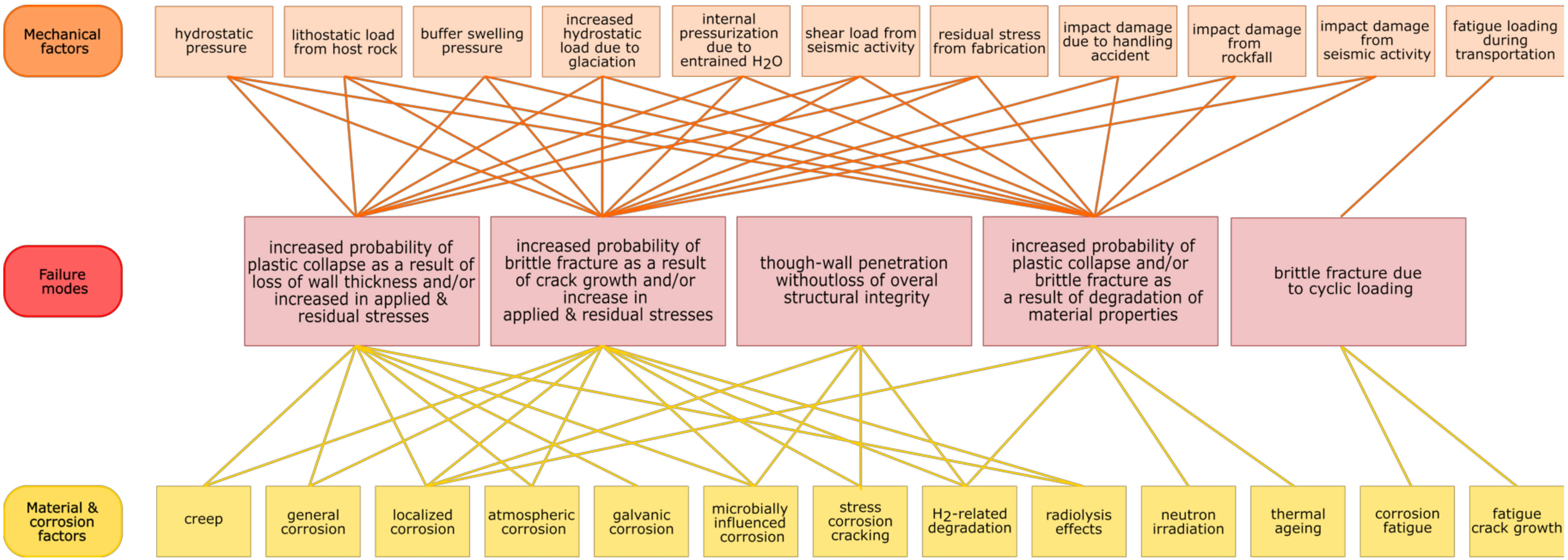
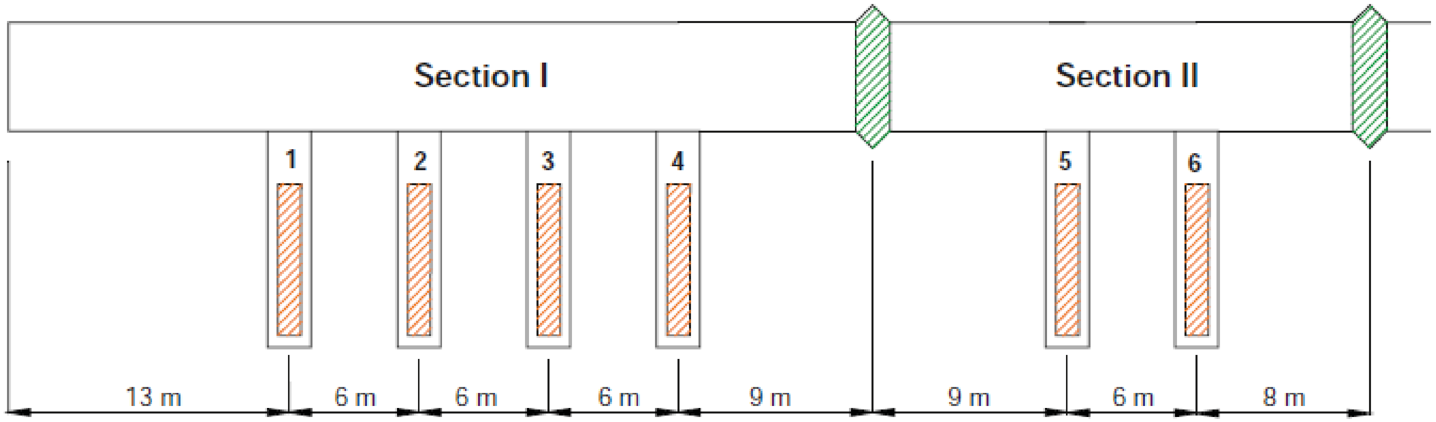


Figure based on King, F., Sanderson, D., Watson, S. 2016. Durability of High-Level Waste and Spent Fuel Disposal Containers – an overview of the combined effect of chemical and mechanical degradation mechanisms. AMEC Report 17697/TR/03

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



Svemar, C., Johannesson, L-E., Grahm, Svensson, D. 2016. Opening and retrieval of outer section of Prototype Repository at Äspö Hard Rock Laboratory. Svensk Kärnbränslehantering AB, Stockholm. TR-13-22

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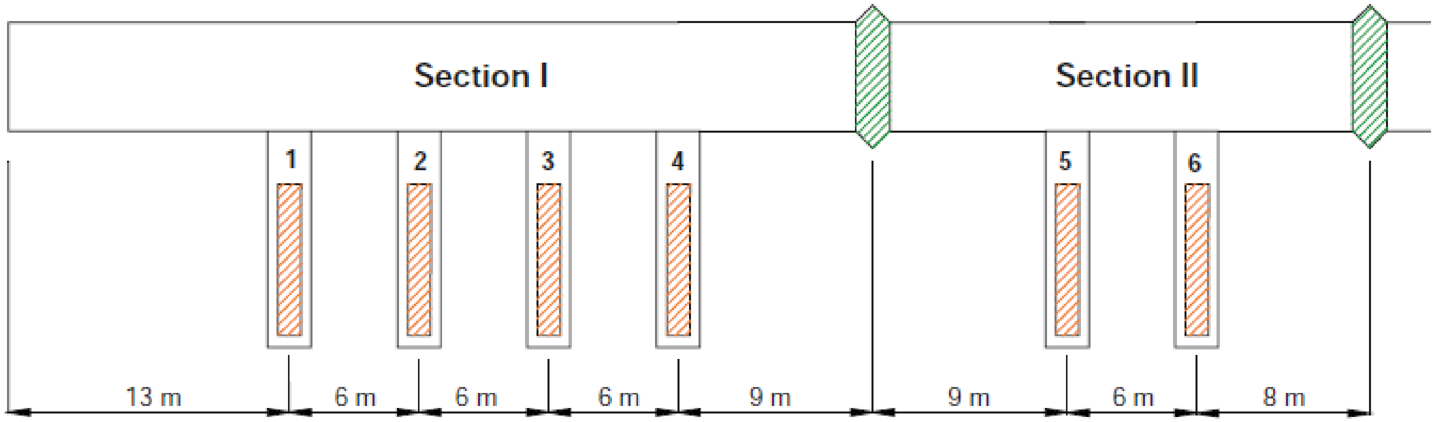

- Shift to anaerobic conditions
- Low level of corrosion
- No microbial activity in bentonite buffer, low amount in backfill

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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 → 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”

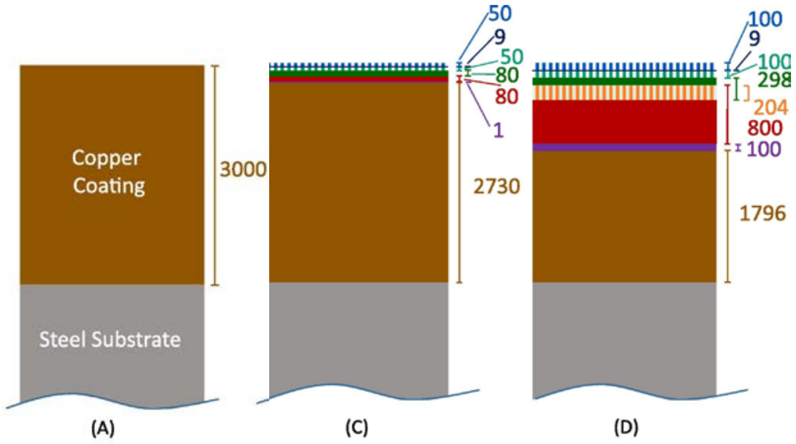

Illustration of cross sections for the Canadian used fuel container with relevant dimensions in μm for (A) the as-manufactured container; Maximum corrosion damage from non-uniform radiation-induced (light blue), radiation-induced (blue), non-uniform oxic (light green), oxic corrosion (green), sulphide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

Figure from Hall, D. S., M. Behazin, W. Jeffrey Binns and P. G. Keech (2021). "An Evaluation of Corrosion Processes Affecting Copper-Coated Nuclear Waste Containers in a Deep Geological Repository." Progress in Materials Science 118.

SUMMARY OF APPROACHES FOR CORROSION IN PA FOR COPPER CONTAINERS

<table>
<tr><th>Mode of corrosion</th><th>Canada</th><th>Finland</th><th>Sweden</th><th>Switzerland</th><th>UK</th></tr>
<tr><td>Oxidic general corrosion</td><td colspan="5">Mass balance within corrosion allowance</td></tr>
<tr><td>Radiolysis-induced corrosion</td><td colspan="5">Excluded or Mass balance within corrosion allowance</td></tr>
<tr><td>Sulfide-induced anaerobic corrosion</td><td colspan="5">Mass transport controlled – key factor driving corrosion allowance</td></tr>
<tr><td>MIC before saturation</td><td></td><td colspan="2">Excluded by reasoned argument</td><td colspan="2"></td></tr>
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<tr><td>Pitting</td><td>Fixed corrosion allowance to account for surface roughening</td><td></td><td>Fixed corrosion allowance to account for surface roughening</td><td colspan="2"></td></tr>
</table>

CONTENT

PA FOR IRON-BASED ALLOY CONTAINER CORROSION

- Low strength, low carbon alloys but ≠ among countries
- Belgium, France, Japan, Switzerland and UK

French design

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buffer destabilization

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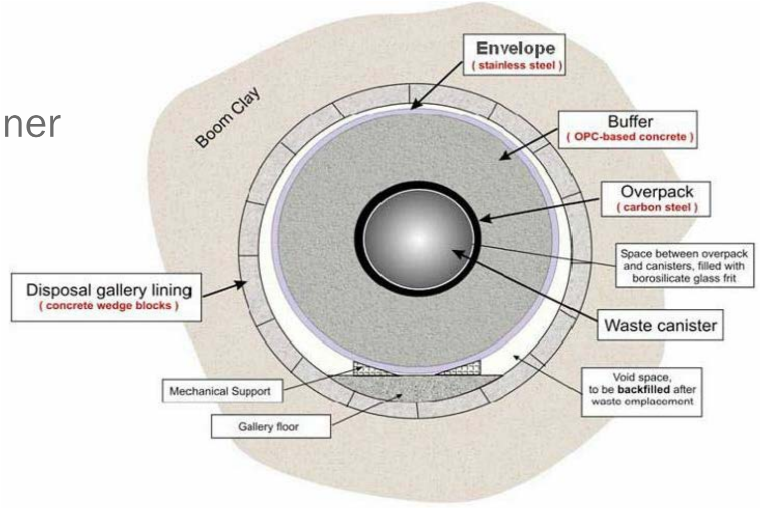
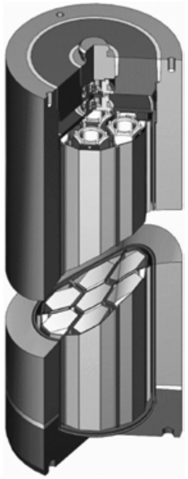
LIFETIME CONTAINERS IN DIFFERENT CONCEPTS

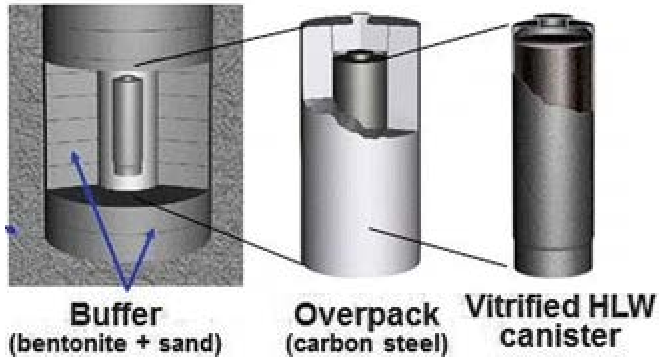
- Belgium:
  - Supercontainer
  - 5000 years



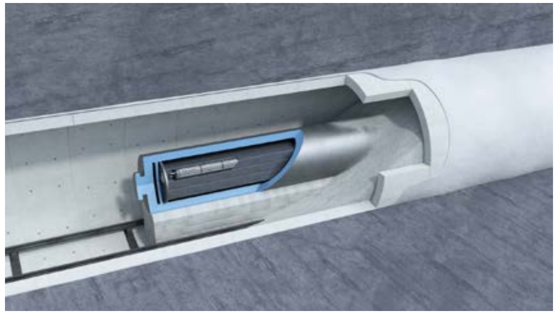
- Czech Republic
  - Double walled:
    - inner stainless steel layer
    - outer carbon steel layer
  - 10000 years



- Japan
  - Double walled
  - 1000 year



- Switzerland
  - 10000 year

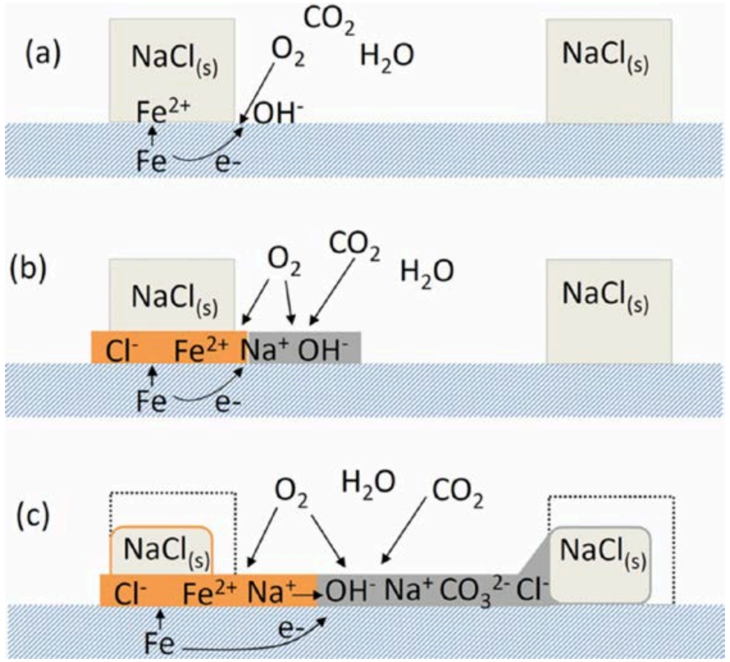


Pospiskova, I., D. Dobrev, M. Kouril, J. Stoulil, D. Novikova, P. Kotnour and O. Matal (2017). "Czech National Programme and Disposal Canister Concept." Corrosion Engineering, Science and Technology 52(sup1).
Yamaji, K. (2015). Issues of Hlw Disposal in Japan. Nuclear Back-End and Transmutation Technology for Waste Disposal: Beyond the Fukushima Accident. K. Nakajima. Tokyo, Springer Japan
Weetjens, E., Marivoet, J., Govaerts, J. 2012. Conceptual model description of the reference case, External Report SCK•CEN-ER-215. Niras / Ondraf.
www.nagra.ch

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



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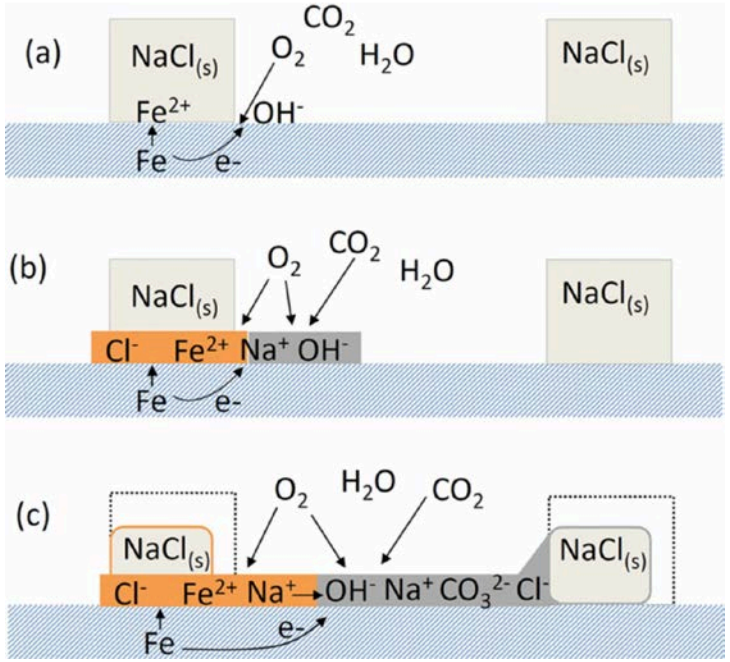

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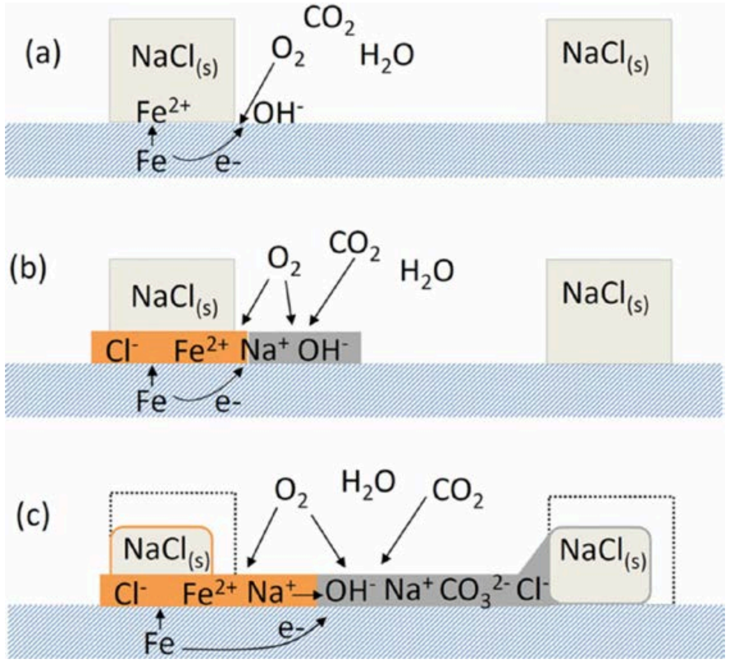

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- Fe (hydr)oxides → not expected to directly significantly undermine the integrity of the containers in environments of limited corrosivity
- Impact of layer of rust?

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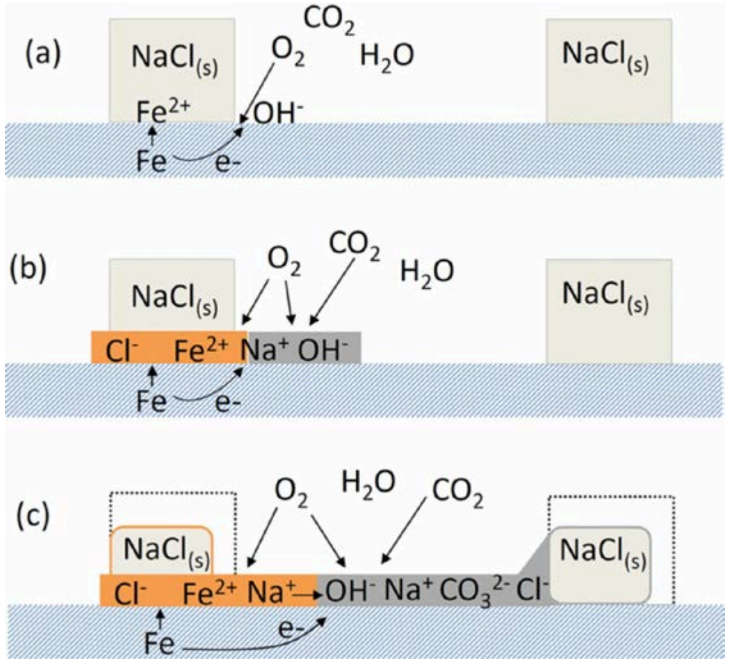

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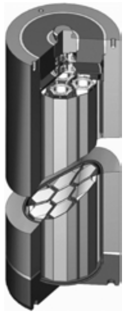

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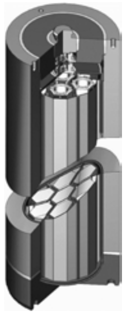

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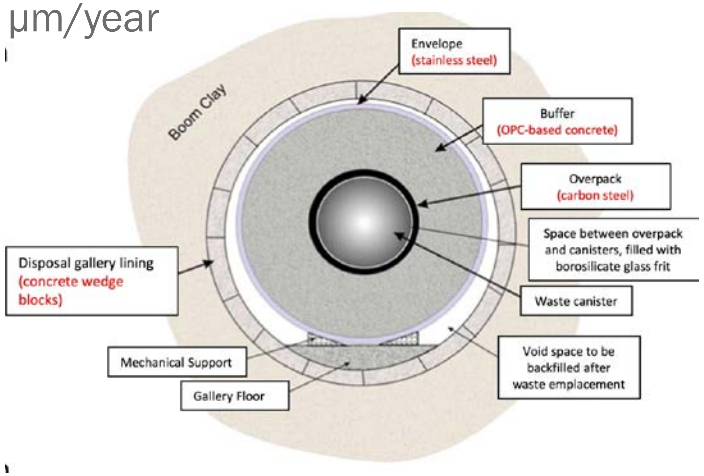

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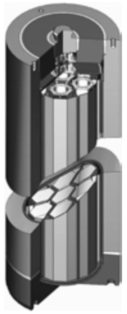

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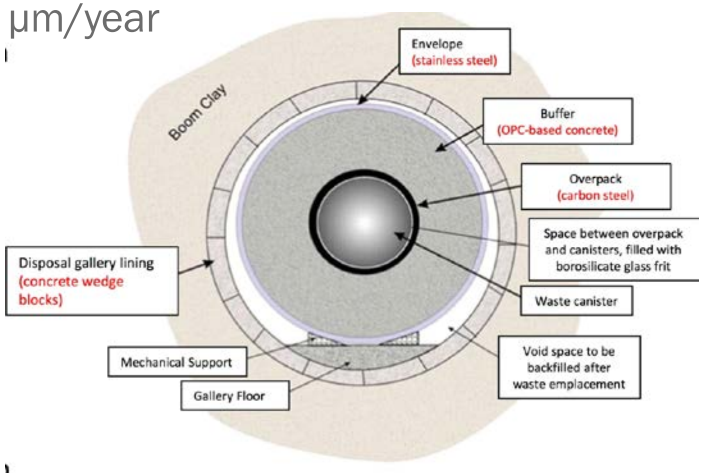
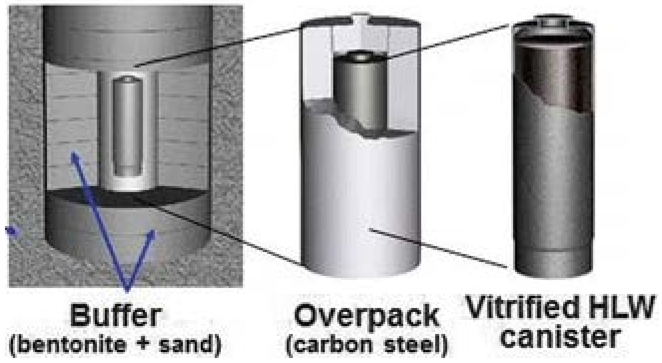


- Japan
  - Lab tests:
    - corrosion rates dropped after 1 year
    - linear for several years at 2 μm/year
    - 2 mm over 1000 year but pitting factor of 3 → 6 mm corrosion allowance



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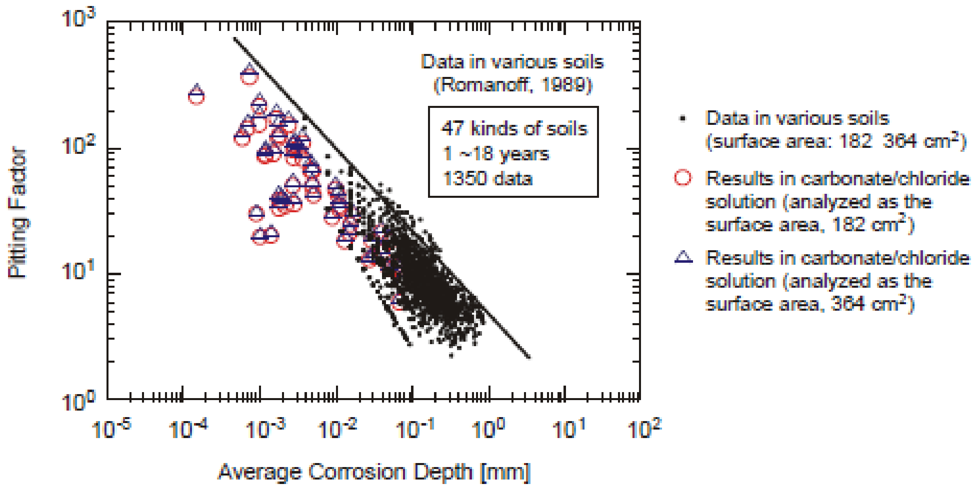

H12 : Project to Establish the Scientific and Technical Basis for Hlw Disposal in Japan : Second Progress Report on Research and Development for the Geological Disposal of Hlw in Japan, Japan Nuclear Cycle Development Institute.

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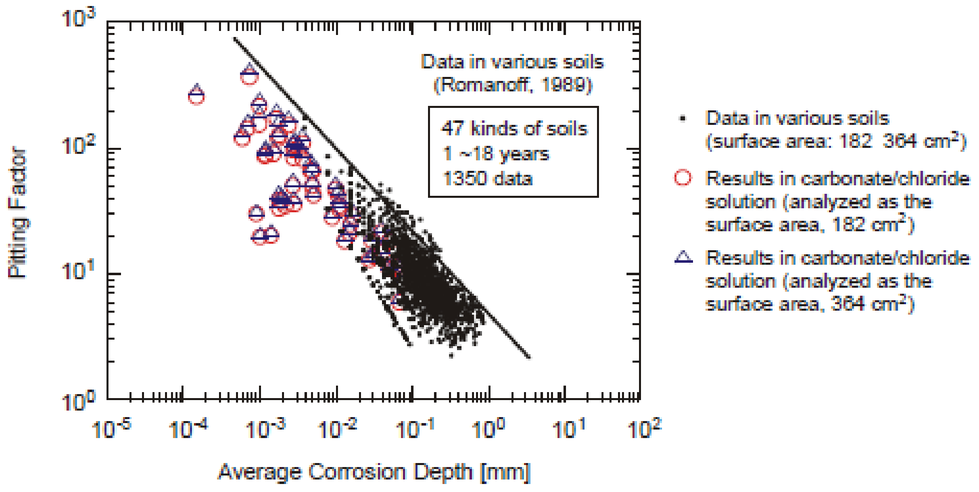

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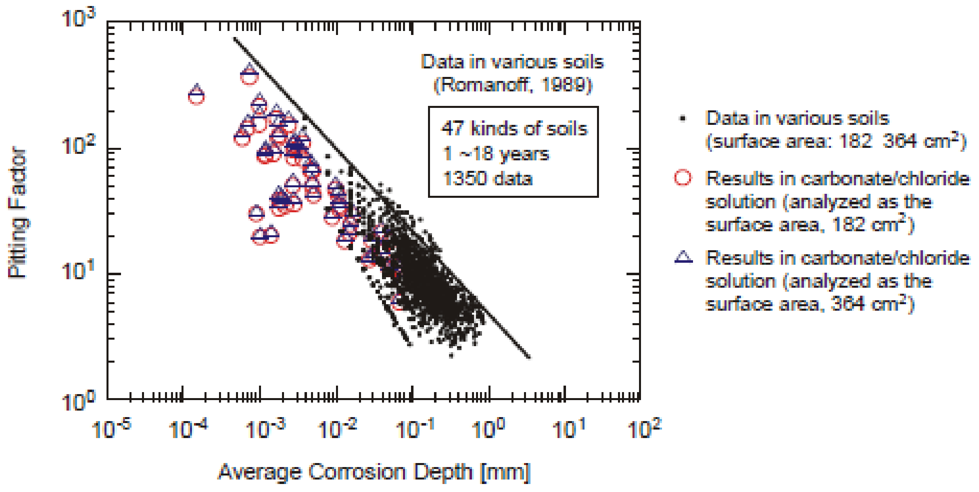

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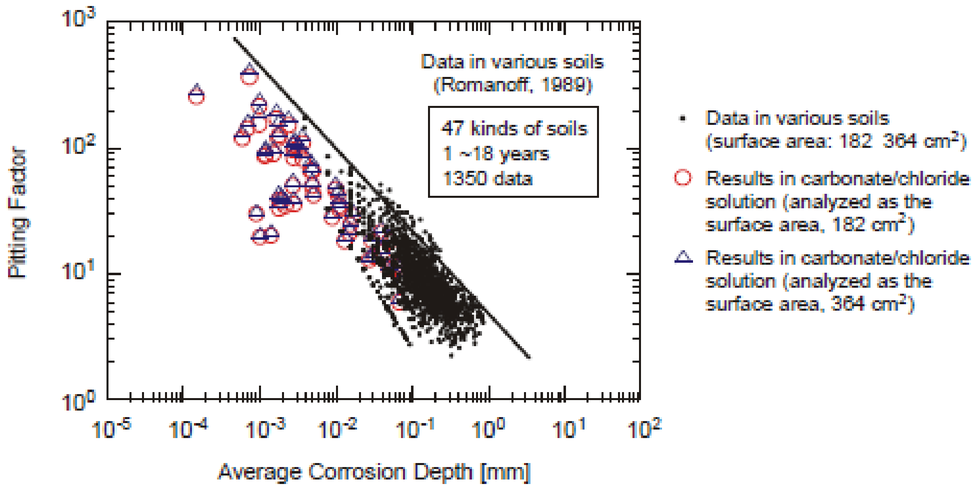

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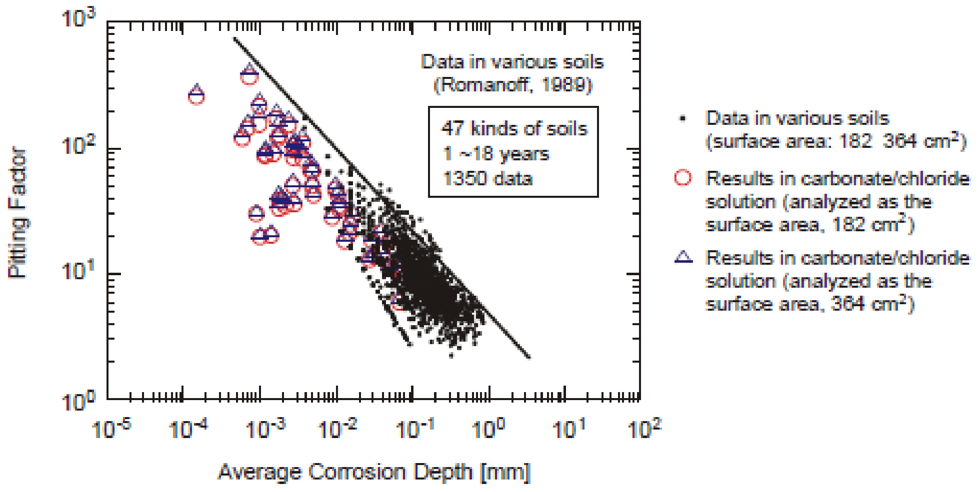

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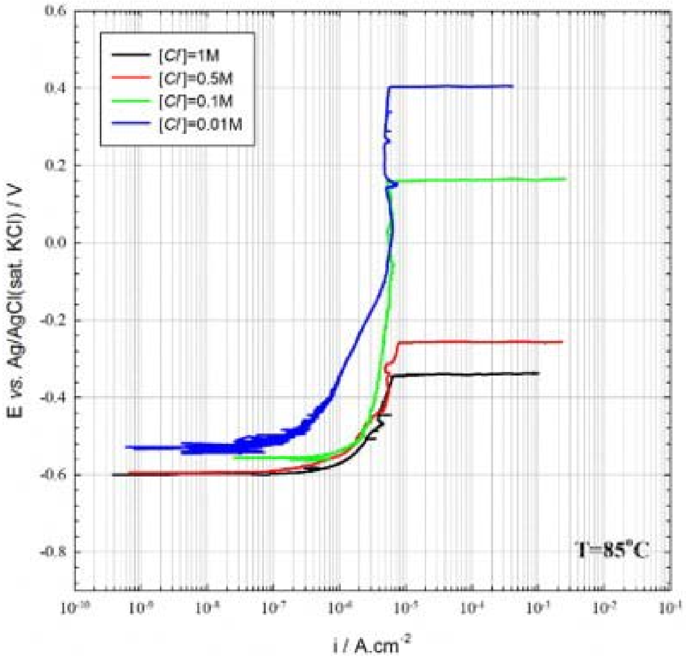
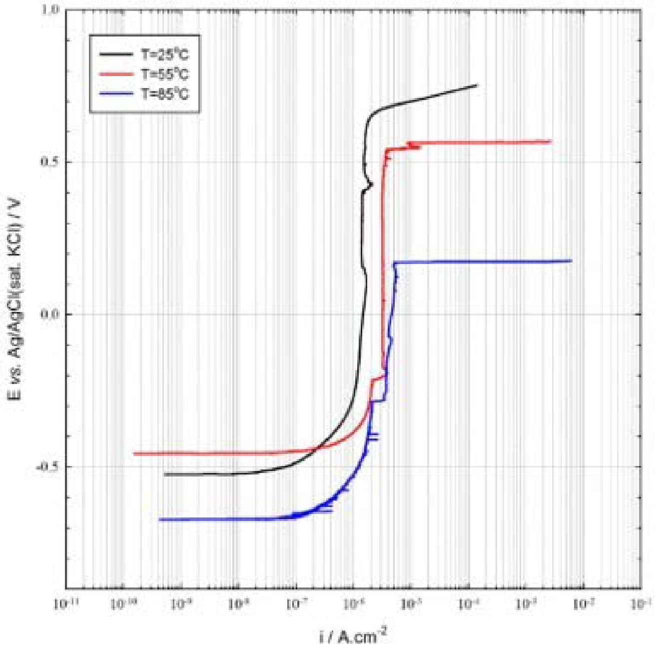
- Belgian supercontainer
  - Risk if magnetite film break down
  - Examined using electrochemical measurements
    - Dependency on [Cl-]
    - Dependency on temp





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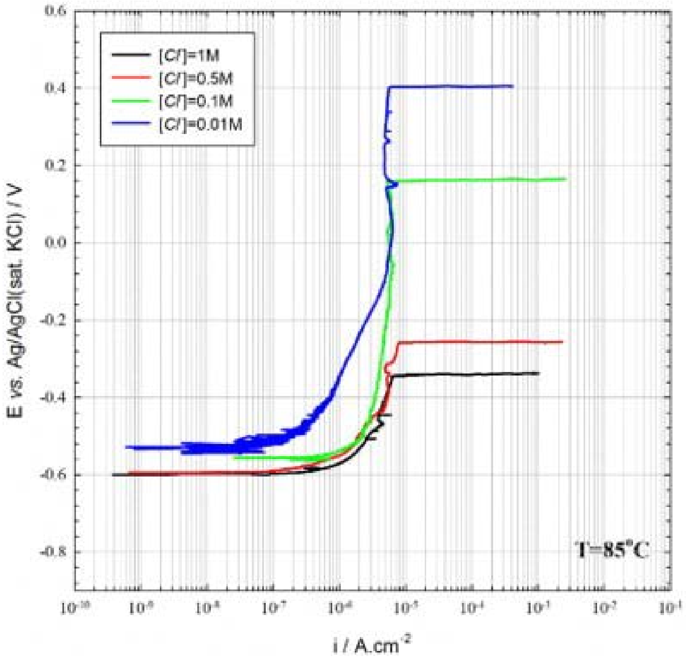
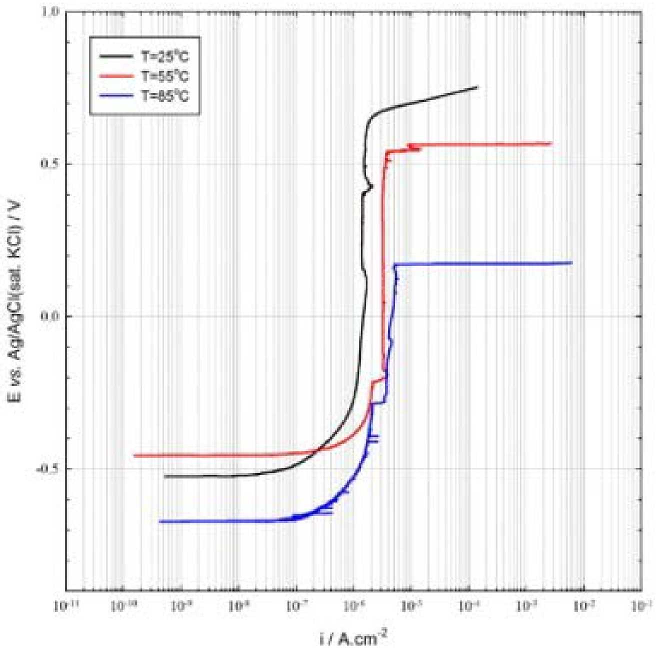
Most aggressive conditions (1 M Cl, 85 °C): lowest potential ± 200 mV





Kursten, B., D. D. Macdonald, N. R. Smart and R. Gaggiano (2017). "Corrosion Issues of Carbon Steel Radioactive Waste Packages Exposed to Cementitious Materials with Respect to the Belgian Supercontainer Concept." Corrosion Engineering, Science and Technology 52(sup1).

RADIATION-ASSISTED CORROSION

- Unsaturated ↔ saturated phase : HNO_3 ↔ H_2O_2
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- Unsaturated ↔ saturated phase : HNO_3 ↔ H_2O_2
- Additional oxidation of steel by radiolysis products is small compared to general corrosion loss by H_2O oxidation
- Long-term corrosion tests Andra:
  - 80 Gy/h → increase corrosion rate
  - 20 Gy/h → no effect

  External surface dose rate < 10 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

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MICROBIOLOGICALLY INFLUENCED CORROSION

- High bentonite density/high pH expected to inhibit microbial activity → SRB only in far field
- Steel corrosion loss due to HS^- flux << general anaerobic corrosion from H_2O oxidation
    - Experiment in Opalinus Clay: 0.02 mm over 1000 years ↔ 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 HCO_3^-/CO_3^{-2} at pH 6 and pH 10-11 ↔ pH bentonite porewater pH 7.3
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- **Japan:**
  - Heat treatment on bulk material & welds eliminate or reduces tensile residual stresses
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SCC UNLIKELY TO OCCUR

PREDICTION OF CONTAINER LIFETIMES & IMPLICATIONS FOR PA

- Conservative approaches:
  - expected lifetime 1000-10000 year (<< copper)
  - >> corrosion:
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Mode of corrosion	France	Belgium	Switzerland	Japan	UK	Czech republic
Anaerobic general corrosion	Empirical corrosion rate		Empirical corrosion rate and pitting factor		Empirical corrosion rate	
Radiolysis-induced corrosion	Limit dose rate to 10 Gy hr^{-1}.	No effect for dose rate of 25 Gy hr^{-1}.	Design requirement (<1 Gy hr^{-1})	Limit dose rate to 3 Gy hr^{-1}		
Localised corrosion		Reasoned argument based on passivity of surface film	Depth-dependent pitting factor	Mass balance and extreme value statistical analysis		
SCC	Specify resistant material		Exclude by reasoned argument			
MIC			Corrosion allowance based on mass transport	Excluded by reasoned argument – negligible rate		

FURTHER READING

- https://www.ejp-eurad.eu/publications/eurad-d151-concord-initial-sota
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- Nagra. (2002). Demonstration of disposal feasibility for spent fuel, vitrified high-level waste and long-lived intermediate-level waste. Nagra Report NTB 02-05.
- Performance Assessment for the Proposed High-Level Radioactive Waste Repository at Yucca Mountain, Nevada https://www.sciencedirect.com/journal/reliability-engineering-and-system-safety/vol/122/suppl/C