Corrosion of disposal canisters

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Outline

- Forms of corrosion
  - Types of corrosion
  - Control by design
- Nature of the disposal environment
  - Parameters of interest
  - Evolution of the disposal environment
- Overview of corrosion behaviour of alternative canister materials
  - Copper
  - Steel/iron
  - Titanium alloys
  - Nickel alloys
- Lifetime prediction
  - General approaches
  - Typical lifetimes for each class of material

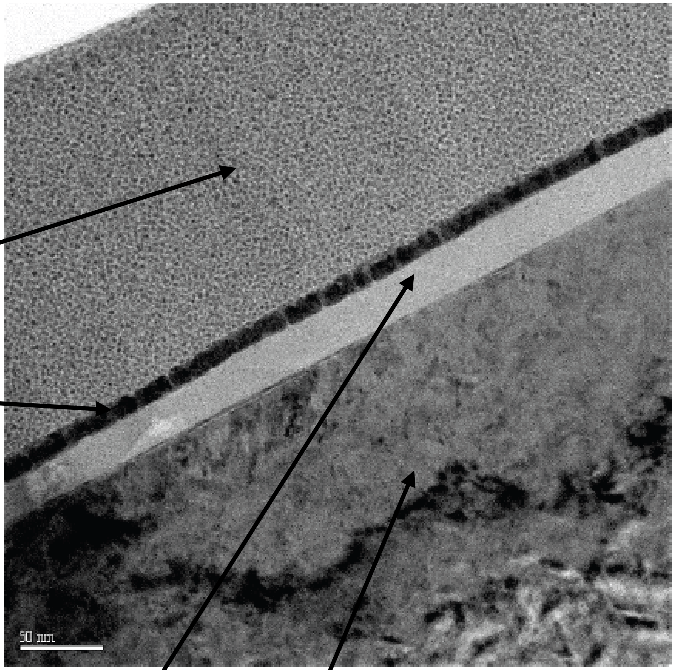
FORMS OF CORROSION

Forms of corrosion

- Introduction
  - Under disposal conditions, corrosion is primarily an electrochemical process requiring the presence of liquid water
  - The forms of corrosion that affect the canister depend on:
    - Chemical environment at the canister surface
    - Temperature
    - Applied and residual stress
  - Because the nature of the environmental conditions changes with time, so too will the corrosion behaviour of the canister
    - Not all forms of corrosion will affect the canister at all times
    - Important consideration for lifetime prediction

Corrosion processes that MAY occur (1/4)

- General (or uniform) corrosion
  - Results in loss of wall thickness
  - Requires oxidant
    - O_2, oxidizing radiolysis products, H_2O (except Cu)
  - Rate affected by:
    - Temperature, rate of mass transport, pH, (salinity)
  - Classes of alloy
    - “Active” materials (Cu, C-steel)
      - No or partially protective corrosion product layer
      - Steel/iron corrosion rate of the order of µm/yr (under anaerobic conditions)
      - Copper corrosion rate ~0.001 µm/yr (anaerobic, sulphide)
    - “Passive” materials (Ni, Ti alloys)
      - Highly protective, passive film
      - Rate of the order of nm/yr (under repository conditions)



Transmission electron micrograph of a passive film on Alloy 22: 9 months immersion in brine at 140°C

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Corrosion processes that MAY occur (2/4)

- Localised corrosion
  - Pitting
  - Crevice corrosion
- Primarily an issue for passive materials
  - Results in localised penetration
  - Requires oxidising conditions and an aggressive solution species (typically Cl^- ions)
  - Separate initiation and propagation steps
  - Probability of initiation increases with increasing T, electrochemical (corrosion) potential, [Cl^-] and decreasing pH
  - Propagation rate of the order of 10-100's μm/yr, but many alloys show a tendency to "stifle" (i.e., alloy re-passivates)
- Active materials undergo a form of surface roughening rather than deep localised penetrations

Corrosion processes that MAY occur (3/4)

- Environmentally assisted cracking
  - Stress corrosion cracking (SCC)
  - Hydrogen-related degradation
- SCC
  - Requires tensile stress and specific corrosive species
  - Results in crack growth perpendicular to maximum tensile stress
    - Penetration rates up to mm/yr
  - Most candidate canister materials susceptible in some environments (with exception of Ti alloys)
    - Question is whether that environment will be present
- Hydrogen-related degradation
  - Due to absorption of H produced during anaerobic corrosion
  - May lead to loss of ductility, reduction in toughness, blister formation, cracking, formation of brittle hydride phases
  - Only Ti alloys and carbon steel potentially affected

Corrosion processes that MAY occur (4/4)

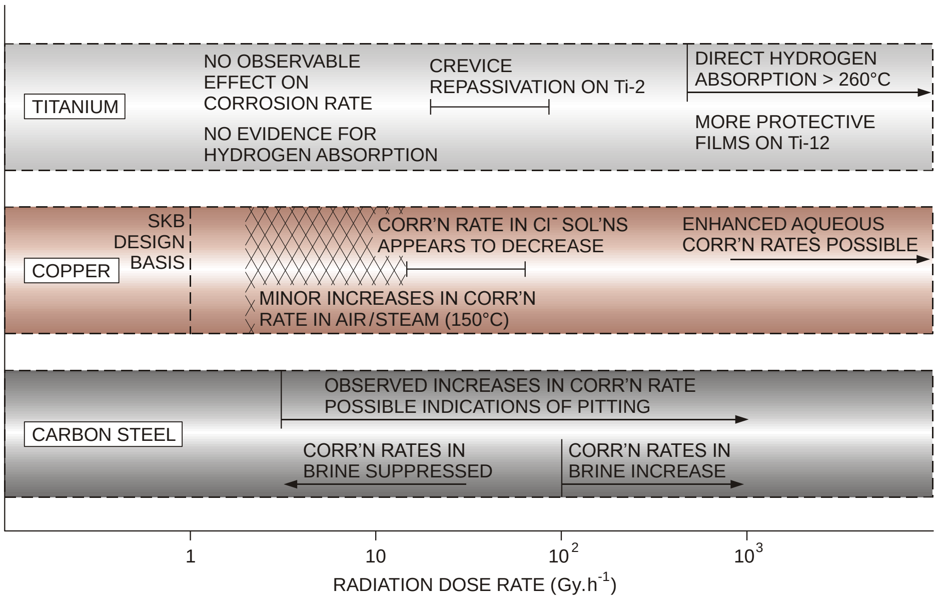
- Microbiologically influenced corrosion (MIC)
  - Microbial activity may result in:
    - Generation of corrosive metabolic by-products
      - Sulphide, organic acids, ammonia, nitrite
    - Formation of occluded localised micro-environments (biofilm)
  - In general, repository environment is inhospitable for microbial activity
    - Elevated T, high pH (concrete), limited nutrients (organic C), limited space/swelling pressure/low water activity (bentonite), radiation fields, saline ground water
  - Microbial activity suppressed by either highly compacted bentonite (low water activity/swelling pressure) or cementitious backfill (alkaline pH)
  - If near-field microbial activity is suppressed by buffer/backfill, then only concern is transport of metabolic by-products produced some distance away from canister
    - No biofilm on canister surface

Corrosion processes that are UNLIKELY to occur

- Galvanic corrosion
  - Long-range galvanic coupling between canister and other metallic components in repository is unlikely
  - May occur for dissimilar in dual-wall canisters after the outer corrosion barrier is breached
    - Effect is minor in absence of oxygen
  - Micro-galvanic effects associated with welds may be possible
- Corrosion related to cyclic mechanical loading
  - For example, corrosion fatigue
  - Canisters are not subject to cyclic loads
- High-temperature oxidation
  - Maximum canister surface temperatures of <130^{o}C too low for extensive oxidation
  - Extrapolation from rate laws determined at high temperatures suggest only nm of oxidation possible

Corrosion processes that are UNLIKELY to occur

- Radiation effects
  - Neutron fluxes too low to cause embrittlement (of steel)
  - Radiation-enhanced corrosion thresholds established
    - For thick-walled canister design, external γ-radiation field below threshold for radiation effects



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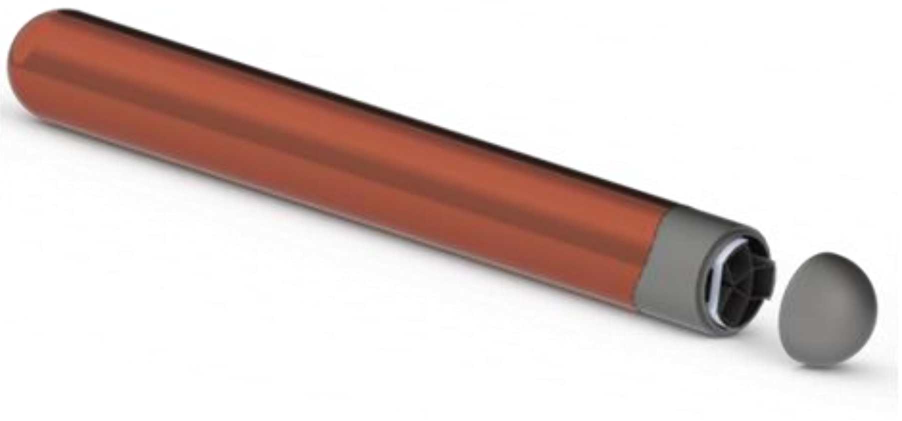
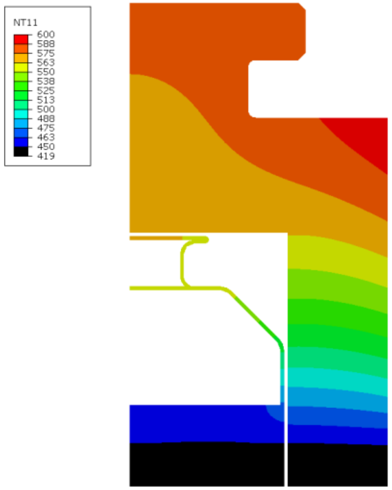
Corrosion control through design of canister

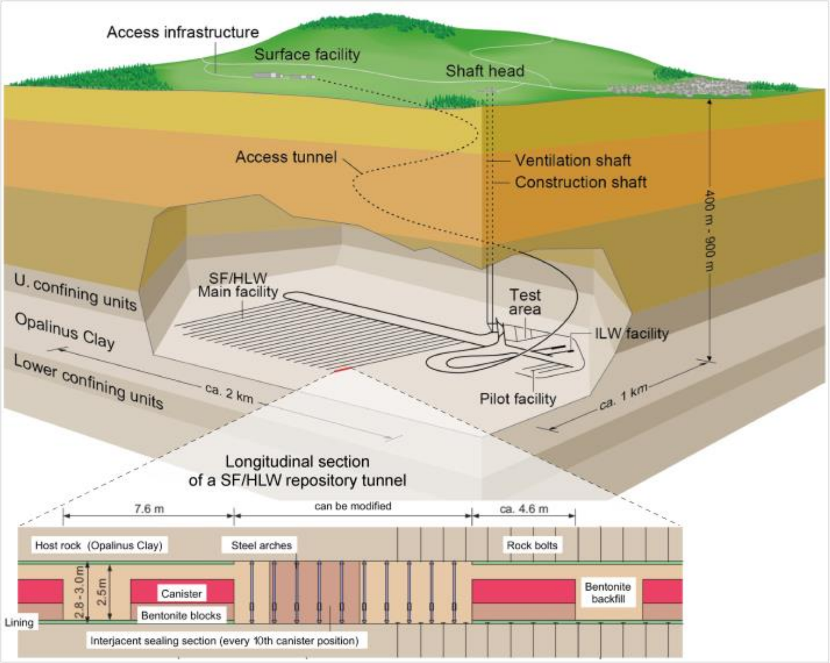
- Residual stress
  - Weld and canister design
- Radiation
  - Age of fuel
  - Design/thickness of canister wall
- SCC/creep behaviour
  - Copper-coated design
  - Proper alloy selection





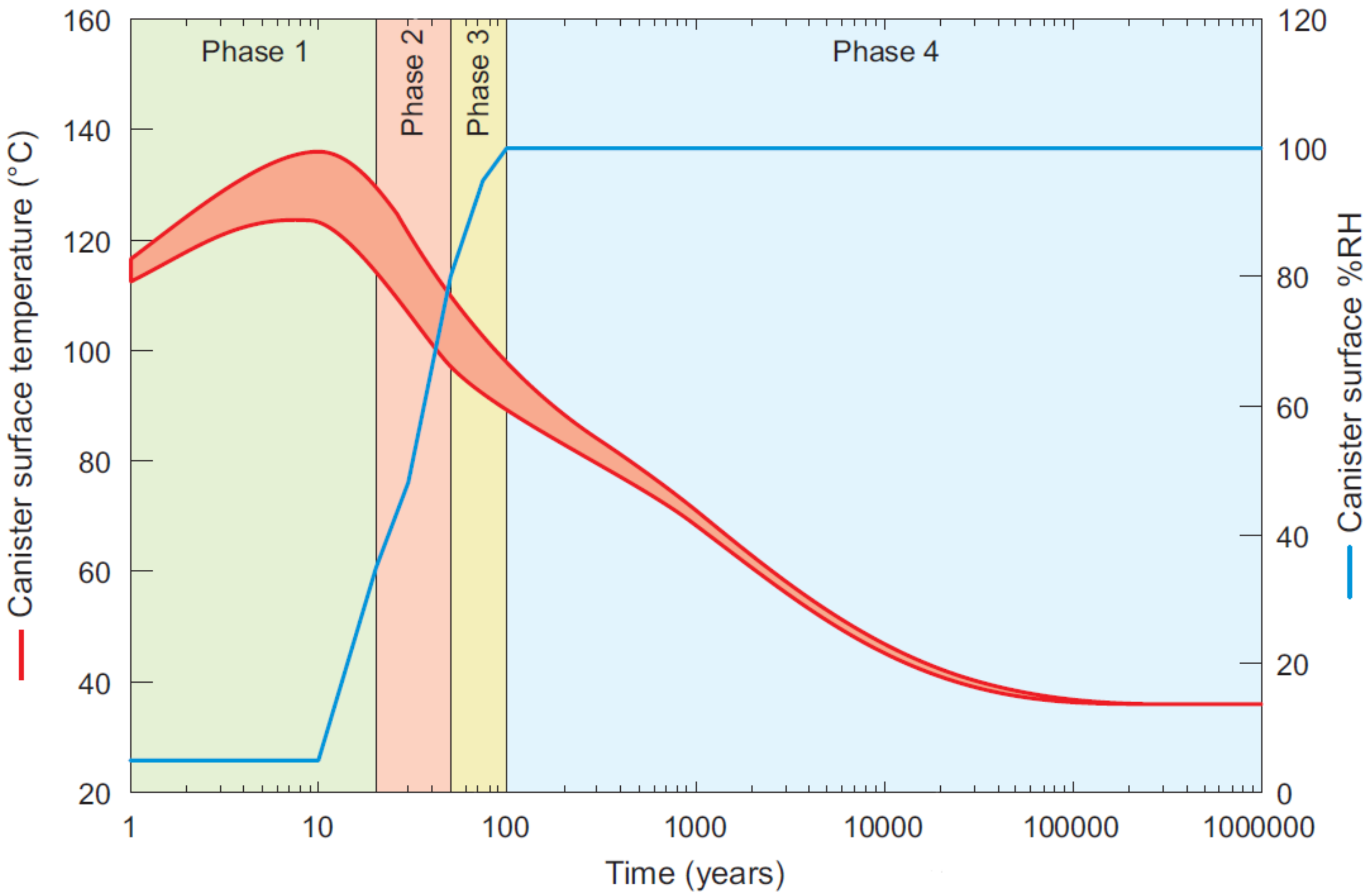
Corrosion control through design of repository environment

- Control over temperature
  - Age of fuel
  - Canister spacing/waste loading
- Limited mass transport
  - Highly compacted bentonite
- Suppression of microbial activity
  - Highly compacted bentonite
  - Cementitious backfill

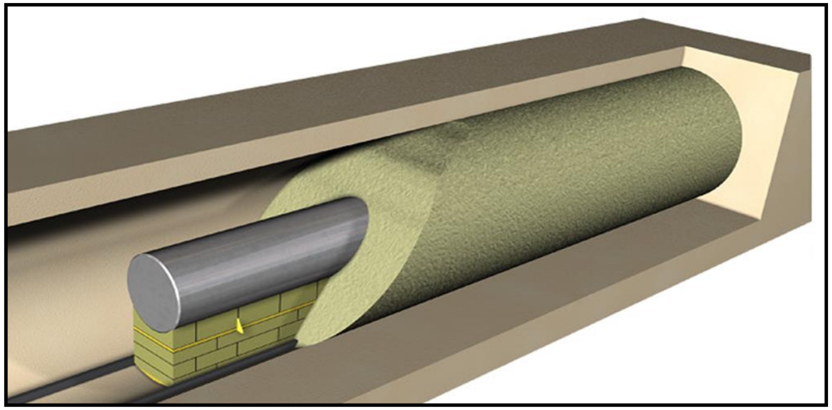


NATURE OF THE DISPOSAL ENVIRONMENT

Temperature and degree of saturation



The amount of oxidant is limited



Oxygen

- Approx 140 mol O_2 per canister
  - Equivalent to ~110 μm as Fe(II)
  - Much of this O_2 will be consumed by processes other than canister corrosion
- Recent evidence from FE experiment at Mont Terri suggests this will occur over period of weeks-months

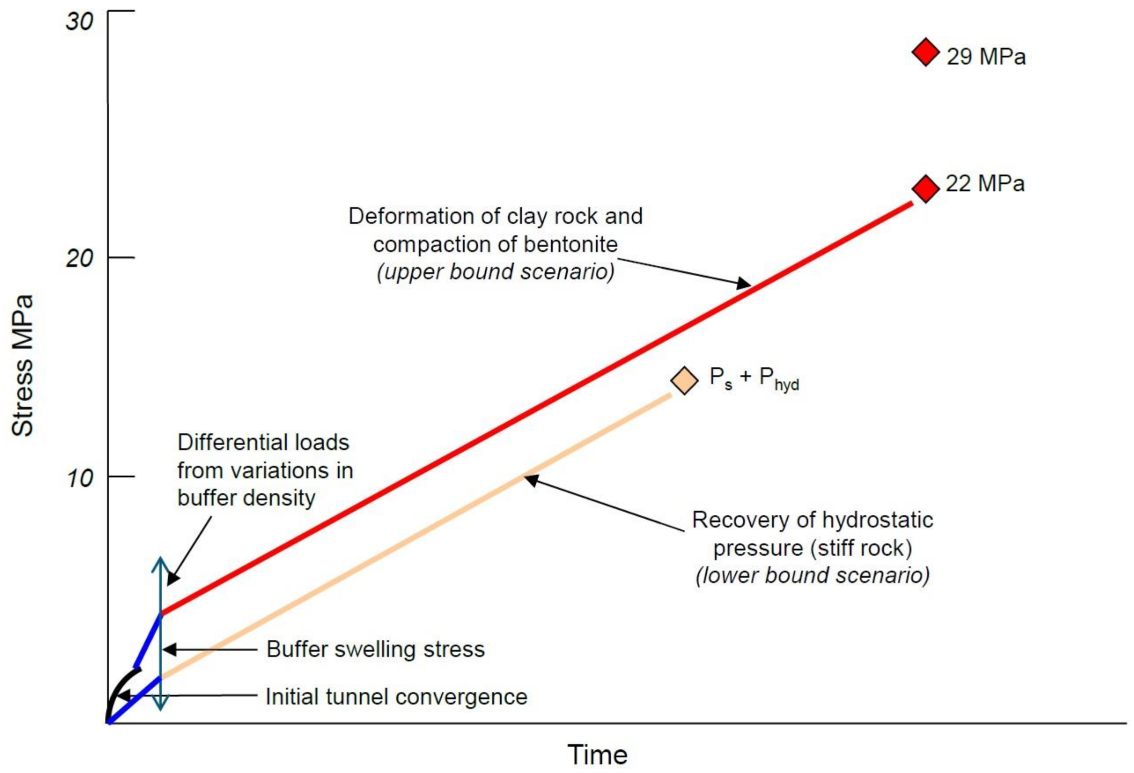
- The amount of available oxidant is limited
  - **Oxygen**
    - Equivalent to 10's-100's μm general corrosion
    - Also results in limited period of localized corrosion/SCC
  - **Water (not oxidant for Cu)**
    - Unlimited supply(?), but tends to support general corrosion only
  - **Radiolysis products**
    - Insignificant for the typical thick-walled canister designs

Porewater composition and evolution

			Maximum expected variation	
	Opalinus Clay reference water	Bentonite[1] reference water	Bentonite[1] low pH	Bentonite[1] high pH
pH log pCO_2[bar]	7.24 -2.2	7.25 -2.2	6.90 -1.5	7.89 -3.5
Ionic strength [eq/L]	2.28×10^{-1}	3.23×10^{-1}	3.65×10^{-1}	2.63×10^{-1}
CO_3	2.70×10^{-3}	2.83×10^{-3}	6.99×10^{-3}	5.86×10^{-4}
Na	1.69×10^{-1}	2.74×10^{-1}	2.91×10^{-1}	2.49×10^{-1}
Ca	1.05×10^{-2}	1.32×10^{-2}	1.33×10^{-2}	1.34×10^{-2}
Mg	7.48×10^{-3}	7.64×10^{-3}	8.91×10^{-3}	6.15×10^{-3}
K	5.65×10^{-3}	1.55×10^{-3}	1.67×10^{-3}	1.38×10^{-3}
SO_4	2.40×10^{-2}	6.16×10^{-2}	6.39×10^{-2}	5.59×10^{-2}
Cl	1.60×10^{-1}	1.66×10^{-1}	2.06×10^{-1}	8.61×10^{-2}
Fe	4.33×10^{-5}	4.33×10^{-5}	7.74×10^{-5}	8.00×10^{-6}
Al	2.17×10^{-8}	1.92×10^{-8}	1.53×10^{-8}	7.55×10^{-8}
Si	1.78×10^{-4}	1.80×10^{-4}	1.80×10^{-4}	1.84×10^{-4}

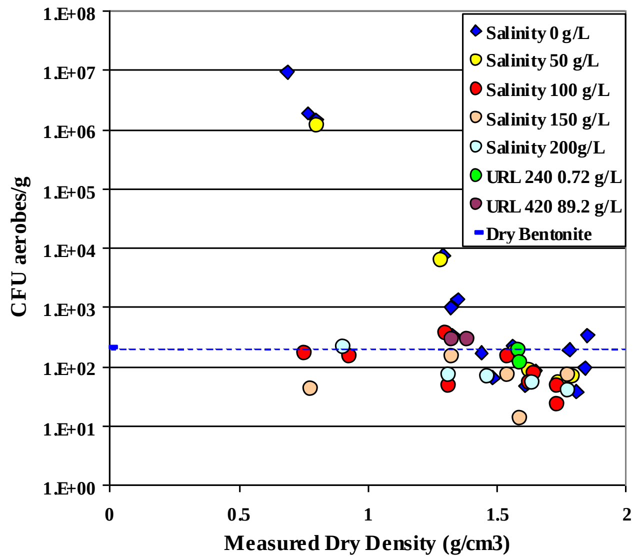
Mechanical loading

- Combination of external loading and residual stress from canister manufacture



Microbial activity

- Opalinus Clay contains microbes that are likely to be viable but, probably as a result of space (average pore size 10-20 nm) and water restriction, only a very small, metabolically inactive population (ongoing studies at Mont Terri, with similar results at Andra's Bure URL)
- Microbial activity in compacted bentonite is suppressed by a combination of low water activity and/or high swelling pressure
- Culturability is significant only in low density bentonite – at a dry density above 1.4 to 1.5 Mg m^{-3} (swelling pressure of >2MPa) microbes do not appear to be viable

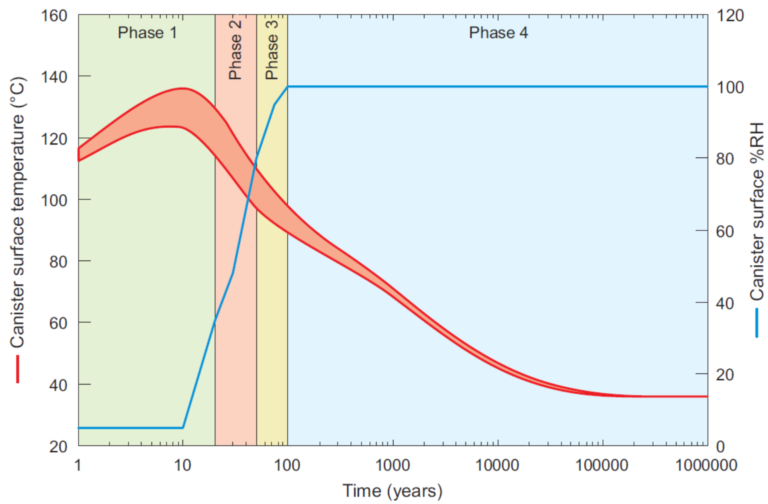


Nagra minimum bentonite density

1.45 g/cm^3

Evolution of repository environment

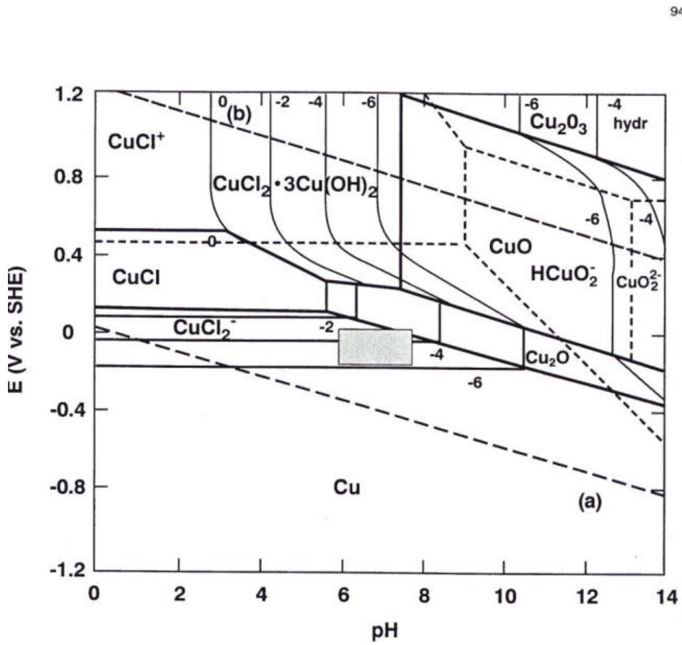
- Repository environment evolves over time
- Evolution is from “bad” to “good” in terms of the effect on corrosion
  - Initial warm/oxidizing to eventual cool/anoxic
  - Long-term conditions can be expected to remain relatively benign indefinitely
  - Depending upon canister lifetime, >99% of service life corresponds to relatively benign cool/anoxic period



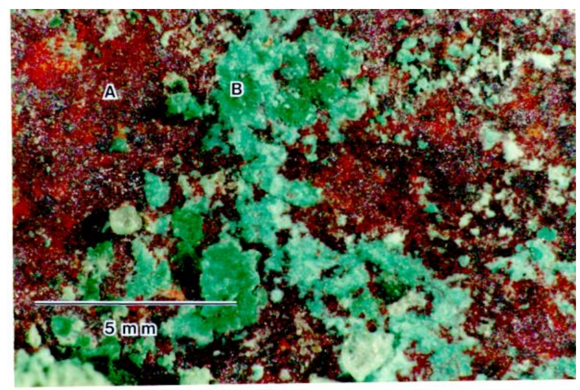
- Implications for predicting long-term corrosion behaviour
  - Most aggressive, and perhaps the most difficult to predict, forms of corrosion occur during the first few years
    - **Localized corrosion, SCC**
  - General corrosion processes only under cool/anoxic conditions
  - Therefore, the problem of predicting corrosion behaviour over periods of 1000’s-10,000’s years is greatly simplified

CORROSION BEHAVIOUR OF CANDIDATE CANISTER MATERIALS

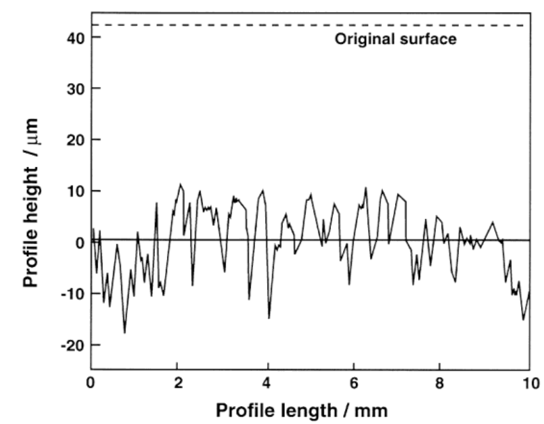
Copper



- Effectively thermodynamically stable in water and Cl^- solutions at neutral-alkaline pH
- Will corrode with the evolution of H_2 in the presence of sulphide



- Tendency to corrode uniformly with surface roughening but no localized corrosion
- Susceptible to MIC if microbes are active
- Susceptible to SCC in a few specific environments, and then only under aerobic/oxidizing conditions



Advantages and disadvantages: Copper

- Advantages:
  - Possibility of indefinite containment (in the correct environment)
  - Excellent corrosion behaviour, especially in Cl^- dominated environments
  - Minimal impact on other barriers (except for steel/iron insert)
  - Over 30 years of international experience
  - Robust lifetime predictions
  - Natural and archaeological analogues
- Disadvantages:
  - More complex design and fabrication (Swedish-design Cu shell-cast iron design)
    - Requires internal support
    - Welding and inspection of thick sections
  - Copper coating technology under development would largely resolve these issues

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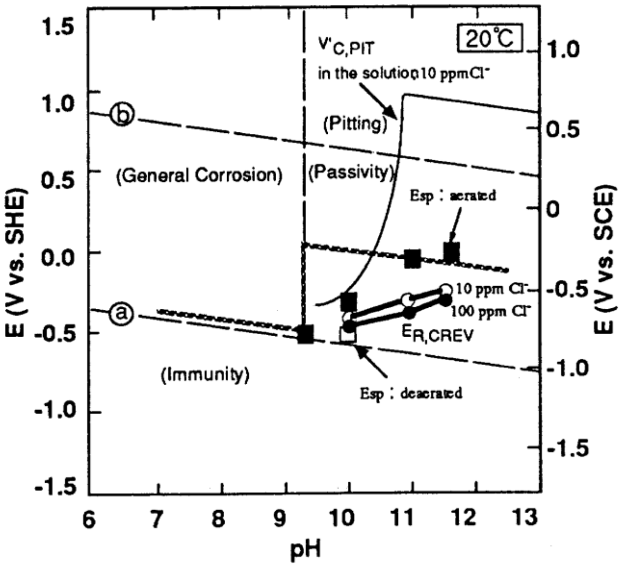
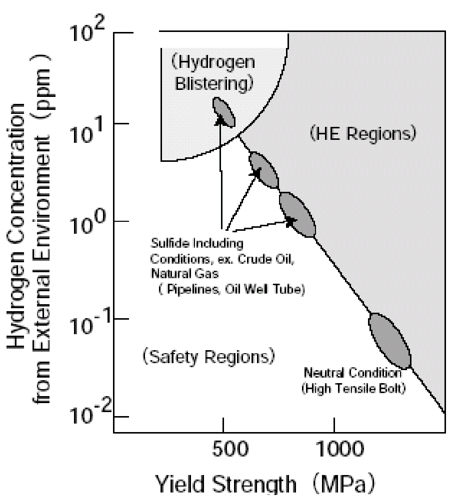
Carbon steel





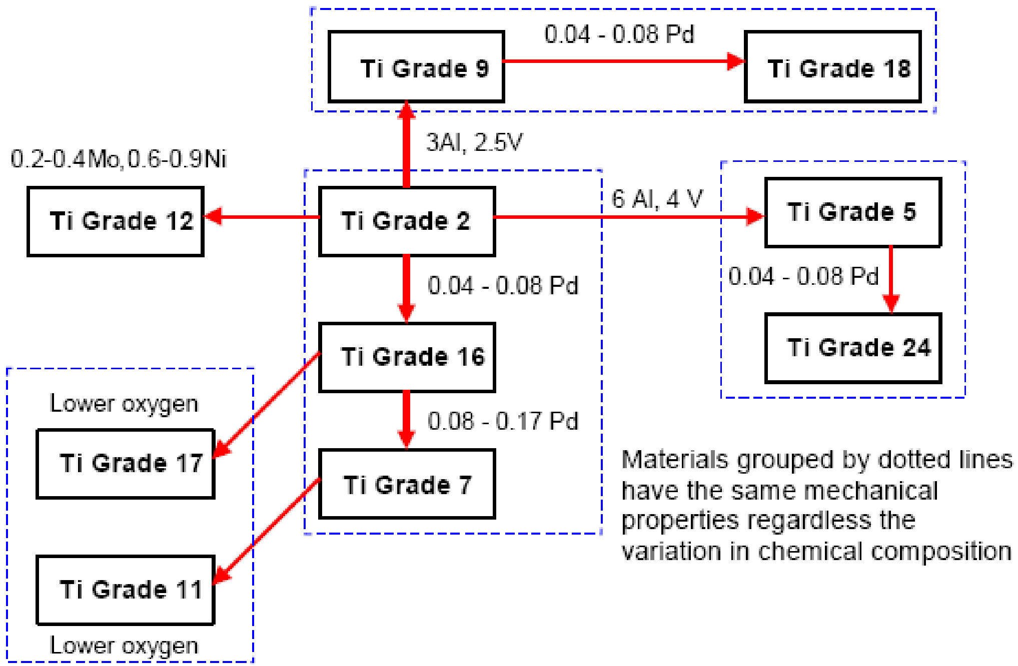
- Thermodynamically unstable in water
- Corrosion rate decreases with time
- Passivates at pH greater than ~pH 9
  - Active in bentonite buffer
- Lifetime predictions based on mass-balance (aerobic phase) arguments and empirical data, supported by (natural and) archaeological analogues
- Susceptible to MIC if microbes are active
- C-steels are susceptible to H effects
  - Careful material specification
  - Care in design and sealing
- C-steels are susceptible to SCC
  - Not a major issue under repository conditions

Advantages and disadvantages: Carbon Steel

- Advantages:
  - Long canister lifetimes possible
  - Simple, single-shell canister design
  - Good corrosion behaviour under active (bentonite) conditions
  - Robust lifetime predictions supported by archaeological analogues
  - Over 25 years international nuclear waste management experience
    - Much longer general industrial experience
- Disadvantages:
  - Potential impacts of H_2 and Fe(II) on bentonite and tight host rock

Titanium Alloys

- Ti alloys can be susceptible to:
  - General corrosion
  - Crevice corrosion
  - Hydrogen-induced cracking
- Extremely stable TiO_2 passive film
- Considered to be immune to MIC
- Immune to pitting under repository conditions
- Since rapid H pick up is associated with crevice conditions, advantage to using a crevice-corrosion resistant grade



Advantages and disadvantages: Titanium alloys

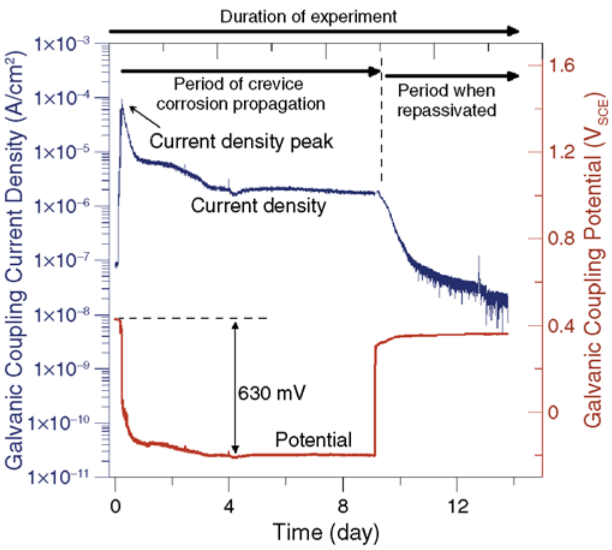
- Advantages:
  - Very long canister lifetimes with crevice-corrosion resistant grades
  - Minimal impact on other barriers

- Disadvantages:
  - Need to make long-term prediction for passive material
  - Requires internal support
    - Material too costly to produce single-shell canister

Nickel Alloys

- Wide range of alloys with properties to suit a wide range of conditions
  - All alloys considered as canister materials have come from Ni-Cr-Mo or Ni-Cr-Mo-Fe groups
  - Hastelloys, especially, offer excellent corrosion resistance
    - Considered for some of the harshest repository environments
      - E.g., highly aggressive brine inclusions in evaporites
- Corrosion processes of concern:
  - General corrosion
  - Localized corrosion (crevice corrosion, pitting)
  - Sensitivity to radiation at high dose rates
    - Typically not an issue at dose rates expected for canister

- Key is to select an alloy of sufficient resistance to localized corrosion and/or tendency to stifle that canister remains un-perforated during initial warm, aerobic phase



Advantages and disadvantages: Nickel alloys

- Advantages:
  - Potential for very long-lived containment with proper alloy selection
  - Corrosion resistance can be tailored to specific environmental conditions
  - Minimal impact on other barriers
- Disadvantages:
  - Need to make long-term prediction for passive material
  - Requires internal support

LIFETIME PREDICTION

Approach to modelling corrosion processes

- General corrosion
  - Various approaches
    - Detailed mechanistically based numerical modelling
    - Mass-balance (based on amount of O_2) and/or mass-transport (based on flux of HS^-) approaches
- Localised corrosion
  - Various approaches
    - Pitting factor (ratio of maximum to mean penetration) based on empirical data
    - Extreme-value statistical analysis of empirical data
    - Comparison of E_{CORR} to critical potential for pitting
    - Mechanistic arguments based on maximum depth of surface roughening
- SCC
  - Excluded from consideration based on mechanistic evidence
- MIC
  - Contribution to flux of HS- during anaerobic phase
  - Other effects of microbes excluded based on mechanistic evidence

Lifetime prediction for copper canisters

- General corrosion
  - Due to O_2/Cu(II)
    - Both detailed reactive-transport modelling and simpler mass-balance calculations indicate maximum depth of corrosion <100 μm
  - Due to HS^-
    - Limited by mass transport of HS^- from pyrite dissolution and/or pore water sulphide
    - SRB predicted to be minor contributor to total [HS^-]
    - Maximum attack 0.9 mm in 100,000 years (Johnson and King 2002)
- Localized corrosion
  - "Best estimate" <100 μm due to under-deposit corrosion
- Predicted lifetime for 5-mm thick Cu shell is >100,000 years

Lifetime prediction for carbon steel canisters

- General corrosion
  - Based on mass-balance arguments for aerobic period
    - Maximum penetration <0.1 mm
  - Long-term anaerobic corrosion
    - Assumed rate 2 μm/year
    - Equivalent to 20 mm penetration in 10,000 years
    - Additional 0.2 mm possible due to HS^- from pyrite in Opalinus clay (mass-transport limited)
- Localized corrosion during aerobic phase
  - 1 mm based on conservative „pitting factor“ of 10
    - Ratio of maxium pit depth to depth of general corrosion
- Total corrosion depth in 10,000 years is ~21 mm of the proposed 140 mm wall thickness

Lifetime prediction for nickel alloy canisters

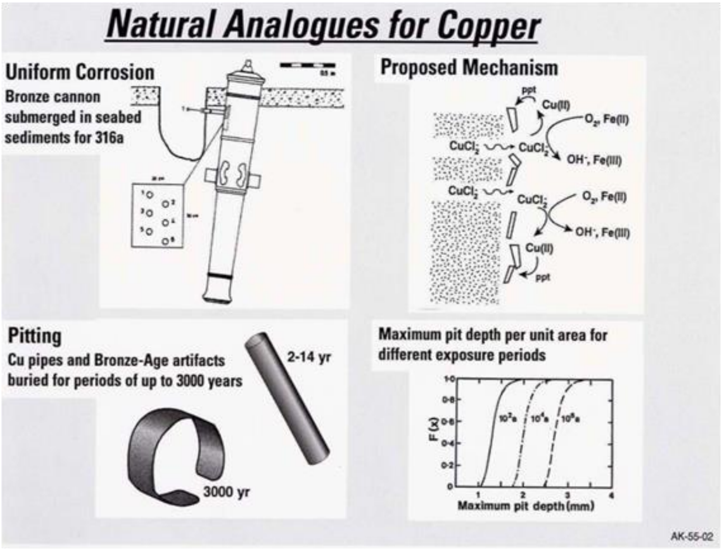
- General corrosion
  - For Ni-Cr-Mo and Ni-Cr-Mo-Fe alloys, rate of general corrosion under repository conditions is of the order of 1-10 nm/yr
- Localised corrosion
  - Increasing resistance to pitting and crevice corrosion with increasing Cr, Mo, W, Co content
  - Possible to specify a grade of material that would be immune to localised corrosion under repository conditions
  - Alternatively, specify a grade that is susceptible but for which propagation is limited
- Environmentally assisted cracking/MIC
  - Ni alloys are broadly immune to EAC under repository conditions and highly alloyed materials exhibit great resistance to MIC
- Lifetime prediction
  - >10,000 yrs for wall thicknesses of 5-10 mm

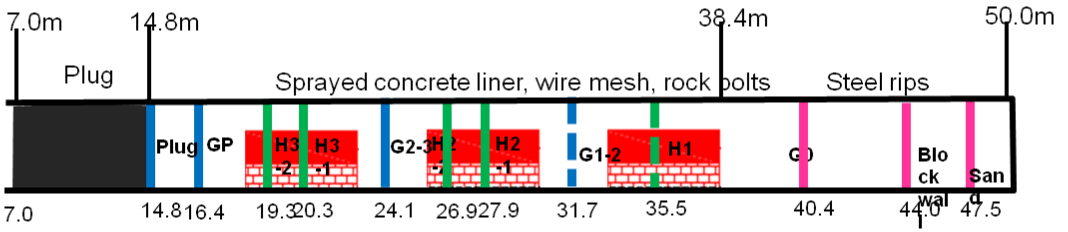
Lifetime prediction for titanium canisters

- General corrosion
  - Rate of general corrosion under repository conditions is of the order of 1-10 nm/yr due to highly protective TiO_2 passive film
- Localised corrosion
  - Pitting potential for Ti alloys >2 V under repository conditions and are therefore immune
  - Pd-containing alloys (such as Grades 7 and 16) are essentially immune to crevice corrosion under repository conditions
  - Less-resistant alloys (such as CP Grade 2 and Ni-Mo alloy Grade 12) may be susceptible to crevice corrosion, but propagation limited by availability of O_2
- Environmentally assisted cracking/MIC
  - Ti alloys are broadly immune to EAC under repository conditions and immune to MIC
- Lifetime prediction
  - >10,000 yrs for wall thicknesses of 5-10 mm

Confidence building in lifetime prediction

- The requirement to be able to predict canister integrity over periods of 100’s to 1000’s of years, and to be able to <u>justify</u> those predictions, is a significant technological challenge
- Confidence building
  - Natural and man-made analogues
  - Large-scale in situ experiments
  - Alternative models
  - Mechanistic basis and understanding





Summary

- Various alloys have been considered as candidate HLW/SF canisters
  - Active alloys (copper, carbon steel)
    - General corrosion
    - Minor (localised) surface roughening
    - SCC/H effects unlikely under repository conditions
    - MIC can be minimised through use of compacted bentonite
  - Passive materials (nickel, titanium alloys)
    - Very low rates of general corrosion
    - Certain alloys immune to localised corrosion, others may be susceptible but propagation likely to be limited
    - Ni alloys immune to SCC/H, Ti alloys susceptible to H effects
    - Ti immune to MIC, Ni alloys highly resistant
- 10,000 canister lifetime achievable with a range of different alloy options