

Progress in the Understanding of the Long-term Corrosion Behaviour of Copper Canisters

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Introduction

1978

- KBS TR-90 Swedish Corrosion Institute
- First review of corrosion of proposed copper canister

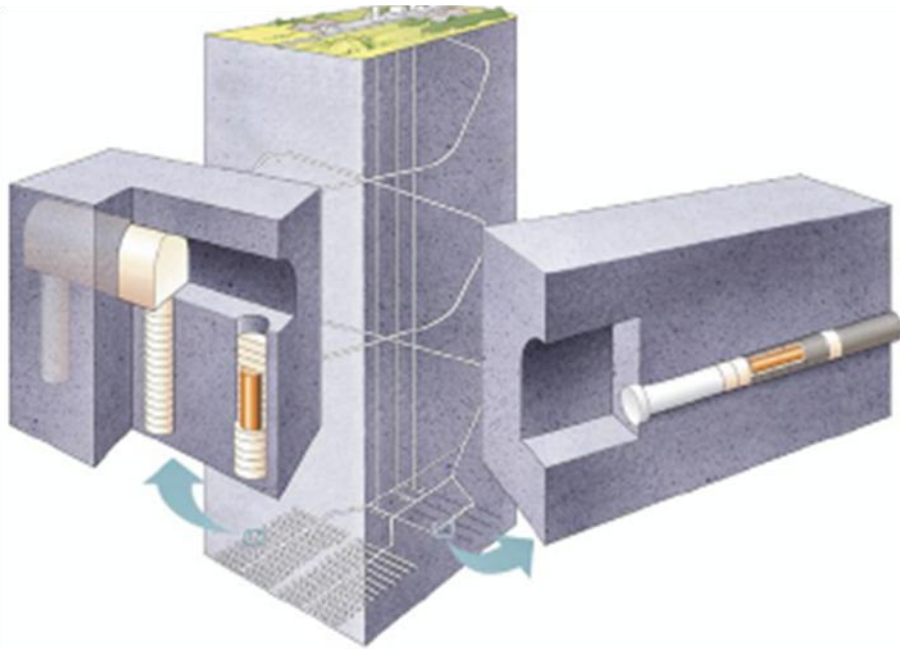
2001-2002

- SKB TR 2001-23, Posiva 2002-01
- State-of-the art report on the corrosion behaviour of copper canisters

2011-2012

- SKB SR-Site, part of the Forsmark License Application
- Posiva construction license PSAR

The amount of oxidant is limited

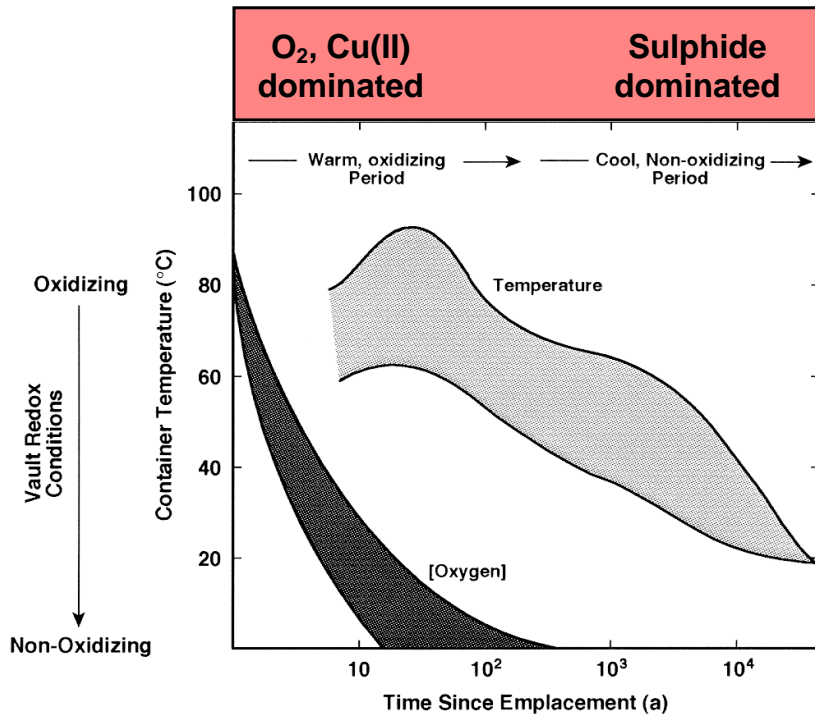


- Only other oxidant is HS^- (or rather H_2O in the presence of sulphide)
- Limited supply
- Discussed later

Oxygen

- KBS3-V SR-Site
 - Total 27 mol/m^2 ($= 768 \mu\text{m Cu as Cu(I)}$)
 - Backfill 96%, bentonite in borehole 4%
 - 99% gaseous, 1% dissolved
- KBS3-H Olkiluoto
 - Total 1.17 mol/m^2 ($= 33 \mu\text{m Cu as Cu(I)}$)
 - Bentonite buffer 100%
 - 92% gaseous, 8% dissolved
- Most of the initially trapped O_2 is in sealing materials with low initial moisture content

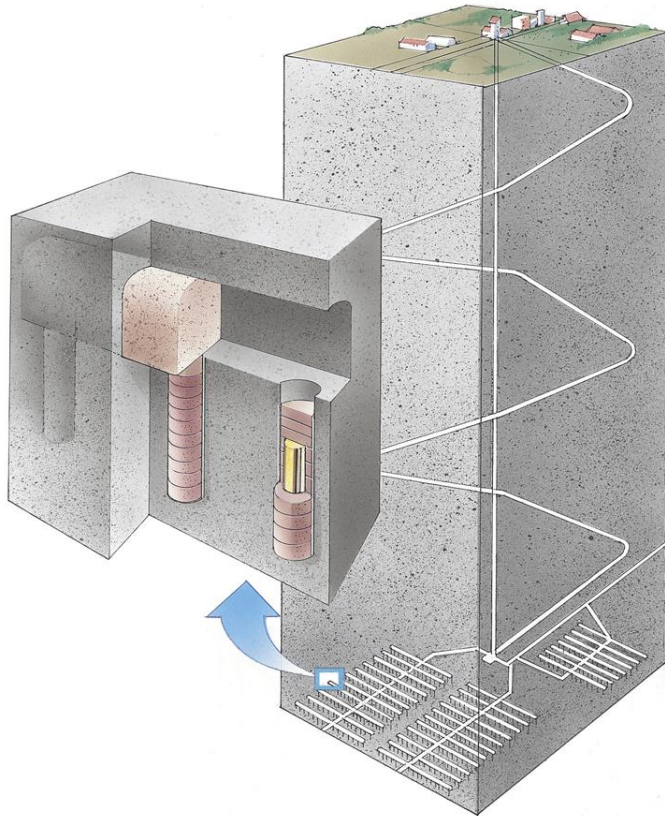
The environment changes over time



- Evolution of environment
 - Temperature/heat transfer
 - Redox conditions
 - Pore-water salinity
- >99% of the service life of the canister corresponds to the long-term, cool anoxic, sulphide-dominated phase

- This evolution is important because it means that certain corrosion processes are only important during certain periods of time

Environment at the canister surface



Steady-state mass-transfer coeffs

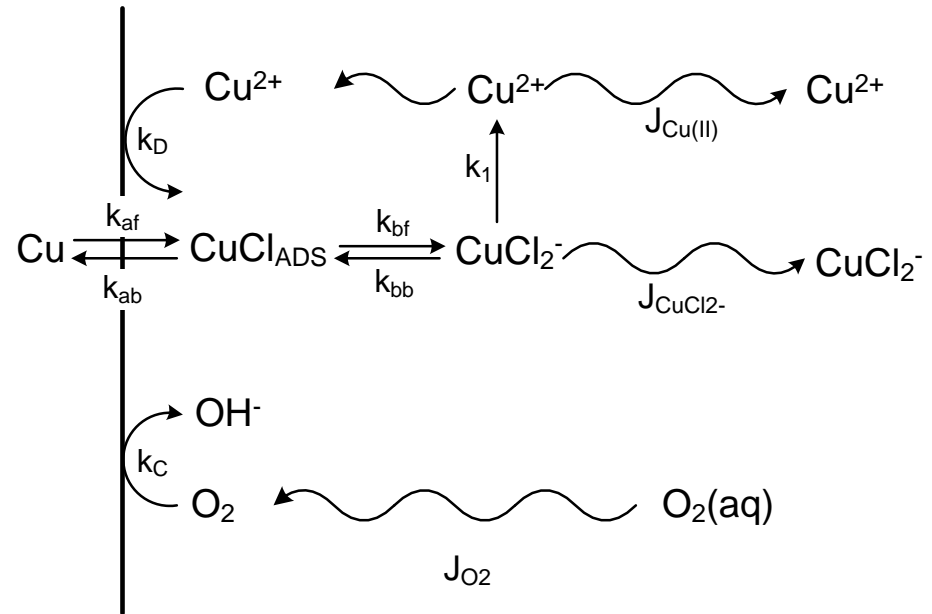
	$k_m = D/\delta$ (cm s ⁻¹)
RDE	10 ⁻² – 10 ⁻³
Stagnant solution	10 ⁻³ – 10 ⁻⁴
10 cm compacted bentonite	10 ⁻⁸

The rate of mass transport through compacted bentonite is so low that interfacial electrochemical reactions will be transport controlled

- Interfacial concentration of reactants will approach zero
- Interfacial concentration of corrosion products will be high

Chloride ions are “beneficial” for copper

- Chloride ions:
 - Stabilize Cu(I) over Cu(II)
 - Cu(II) is the primary oxidant in the localised corrosion and SCC of copper
 - Promote general dissolution over passivation
 - Suppresses SCC and localised corrosion

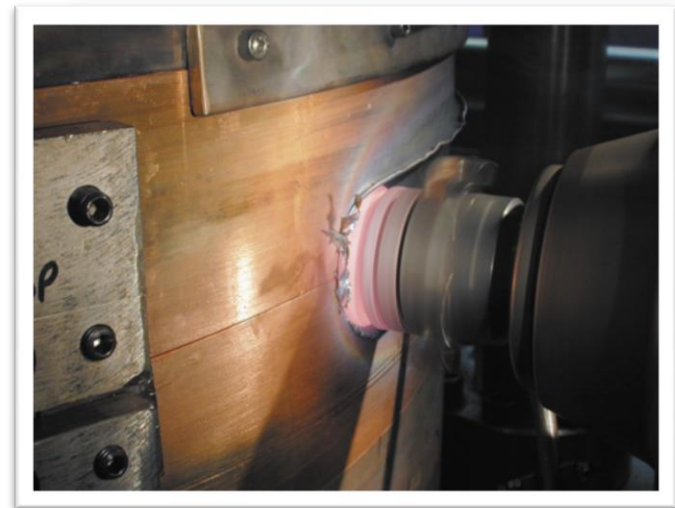


- The [Cl⁻] of Swedish-Finnish ground waters are not sufficiently high that the reaction

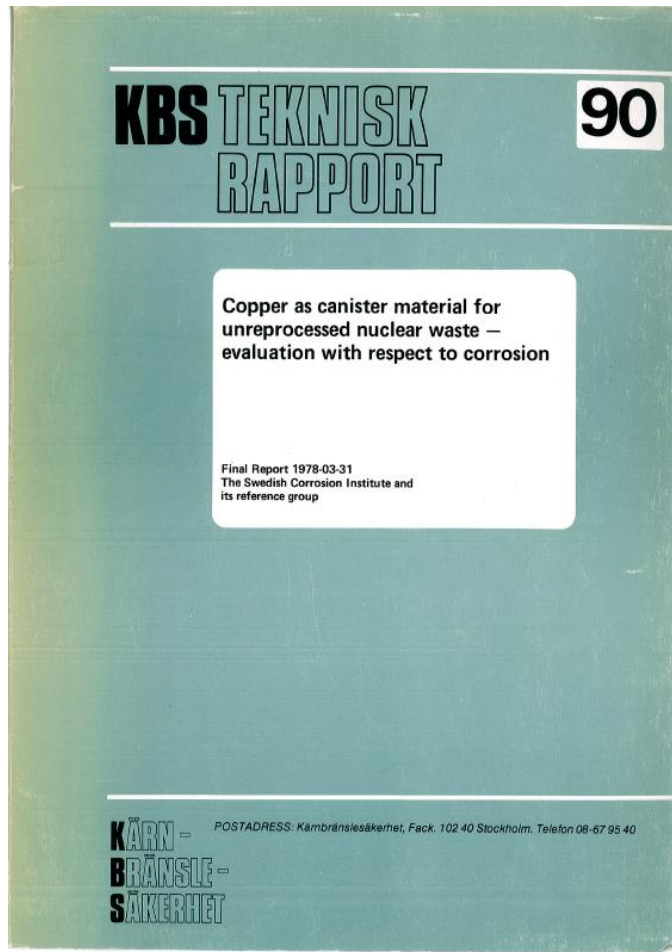
$$Cu + 2Cl^- + H_2O = CuCl_2^- + \frac{1}{2}H_2 + OH^-$$
 is significant

Corrosion control through good engineering practice and design

- Control over temperature
 - Age of fuel
 - Container spacing/waste loading
- Limited mass transport
 - Highly compacted bentonite
- Suppression of microbial activity
 - Highly compacted bentonite
- Residual stress
 - Weld and canister design
- Radiation
 - Age of fuel
 - Design/thickness of canister wall
- Creep behaviour
 - Proper alloy selection



KBS TR-90 (1978)



- Nuclear Stipulation Act (1977)
- Swedish Corrosion Institute reference group
 - Einar Mattsson (Chair)
 - L. Ekbom
 - R. Carlsson
 - G. Eklund
 - I. Grenthe
 - R. Hallberg
 - S. Henrikson
 - N-G. Vannerberg
 - G. Wranglén
 - T. Eckerred (Observer)

KBS TR-90

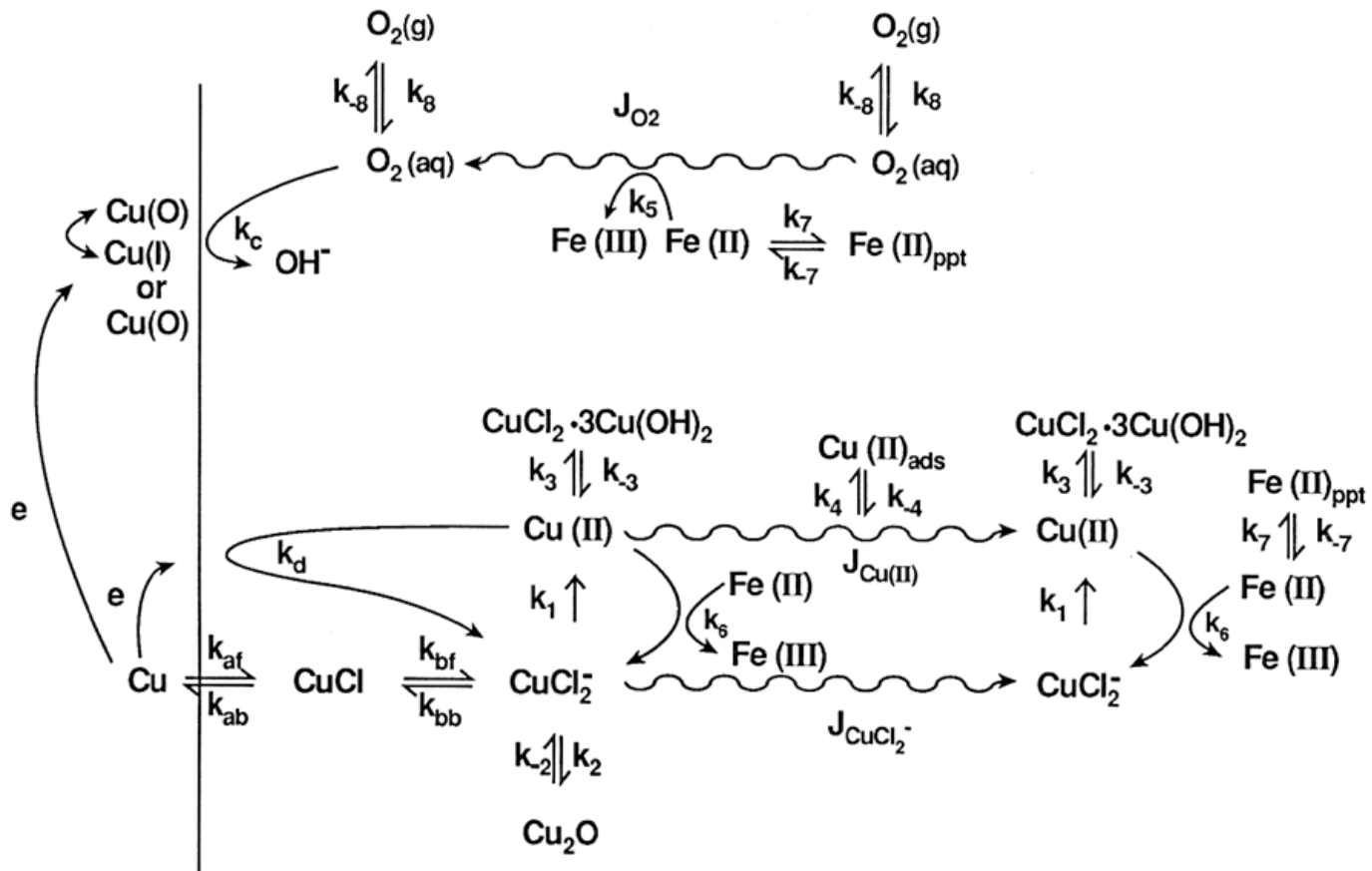
- Thermodynamic analysis of a wide range of possible reactions to determine those that could lead to canister corrosion
 - Only oxidants were O_2 and H^+/H_2O in presence of HS^-
 - Abiotic reduction of SO_4^{2-} or reduction of NO_3^- kinetically hindered
- Rate of corrosion transport limited
- Pyrite impurities in clay not a source of HS^- because of low solubility
- Sulphide in ground water and that produced by microbial activity only sources of HS^-
 - Microbial activity limited by availability of organic C
- Degree of localised corrosion assessed based on pitting factor from Denison-Romanoff NBS study
 - Although limitations on pit growth were recognized
- SCC not considered possible for OFHC copper

KBS TR-90 Conclusions

- “Copper is a relatively noble metal and is therefore thermodynamically stable in oxygen-free pure water”
- “In the case in question, however, some corrosion can occur due to the presence of oxygen or sulphide in the water which comes into contact with the canister”
- “Even when these reactants are taken into consideration, however, it is considered realistic to anticipate a service life of hundreds of thousands of years for a copper canister with a wall thickness of 200 mm”

Level of understanding as of 2001-02

Mechanism of uniform corrosion in compacted bentonite saturated with O₂-containing saline ground water



Localised corrosion

- Relaxation of original conservatism of pitting factor approach
 - Instead of a value of 25, values of 2-5 thought more realistic
- Alternative approaches
 - Mechanistic pit modelling based on stifling of mass transport of reactants and products by precipitated corrosion products
 - Predicts effects of solution composition on pit potentials
 - Extreme-value statistics of literature pit-depth data
 - Probability of pit >6 mm deep on canister 10^{-11} after 10^6 years
- Lifetime assessments still based on concept of growth of discrete pits

Taxén, SKB TR-02-22, 02-23

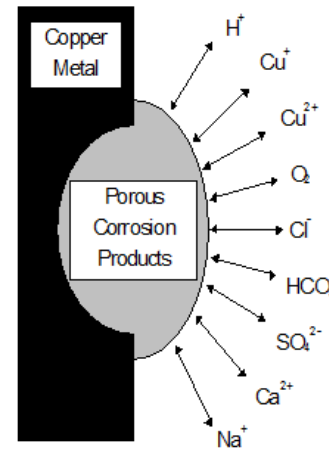


Figure 6-20: Schematic Illustration of the Site of a Corrosion Pit in Copper with Aqueous Species Diffusing and Migrating.

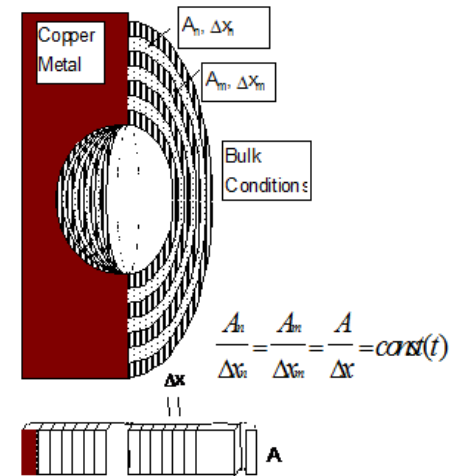
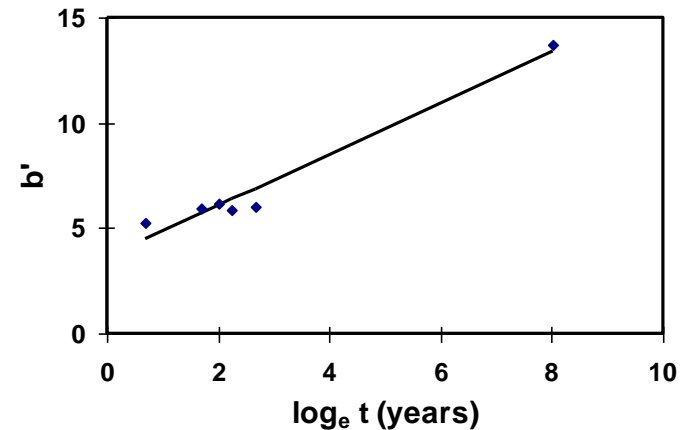
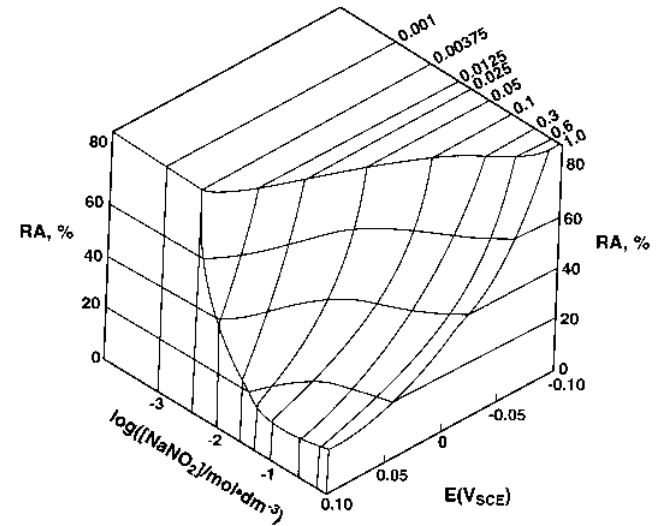


Figure 6-21: Description of the Site of a Corrosion Pit as Consisting of Thin Shells.

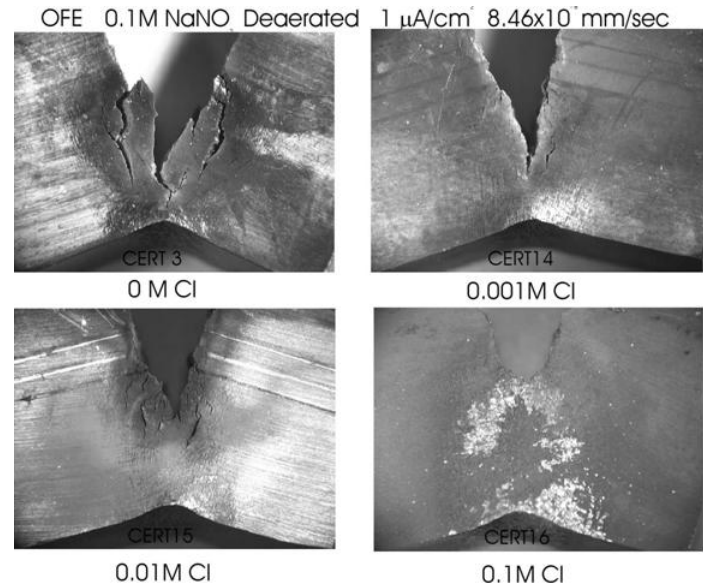


SCC

- Unlike TR-90, acceptance that SCC of “pure” metals is possible
 - Nitrite, ammonia, acetate
- Reasoned argument that SCC of copper canisters is unlikely because of a combination of:
 - Potential below threshold
 - [SCC agent] below threshold



Benjamin et al. BCJ 23, 1988, 89



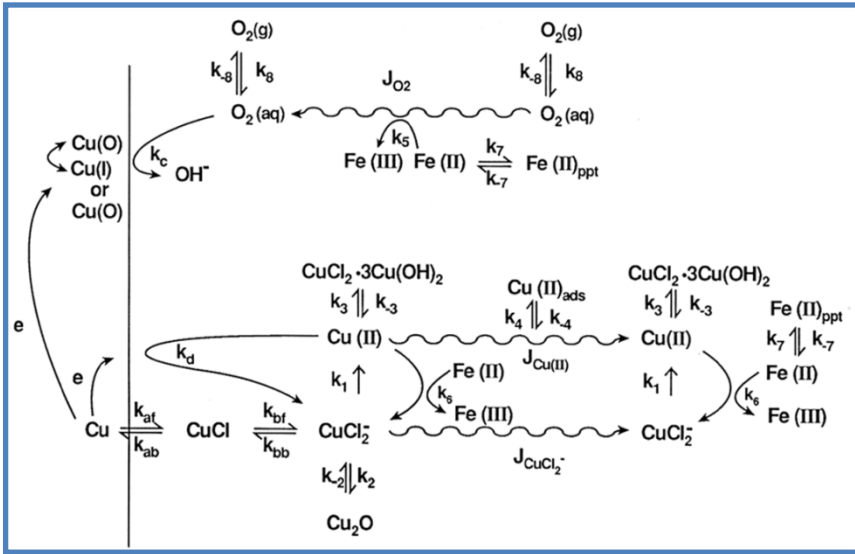
King et al., OPG report, 1999

“Recent” developments

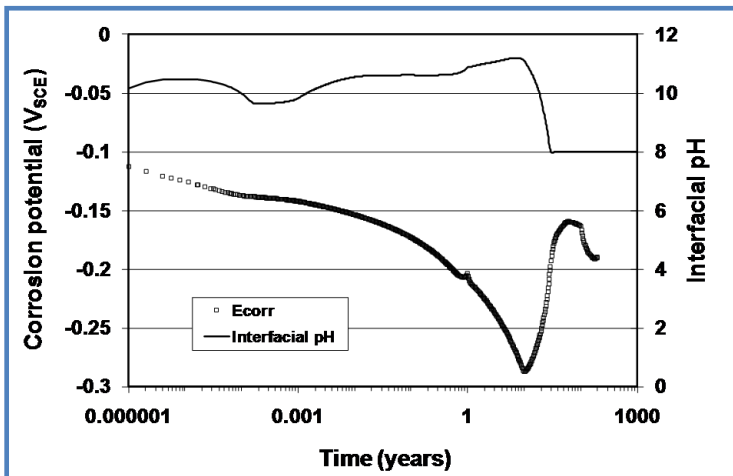
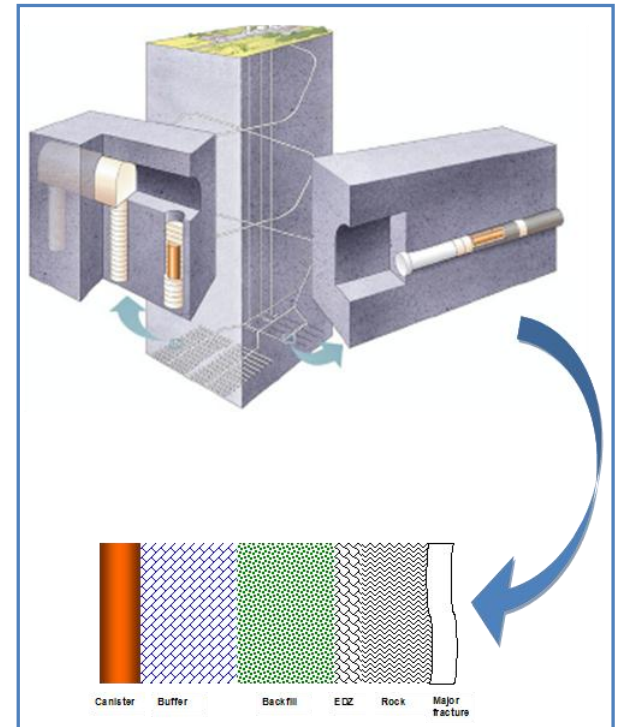
(2001-02 – present)

- Mechanistic modelling
- Localised corrosion
- Effect of sulphur species
- SCC
- MIC
- Corrosion of copper in pure water
- Eroded bentonite

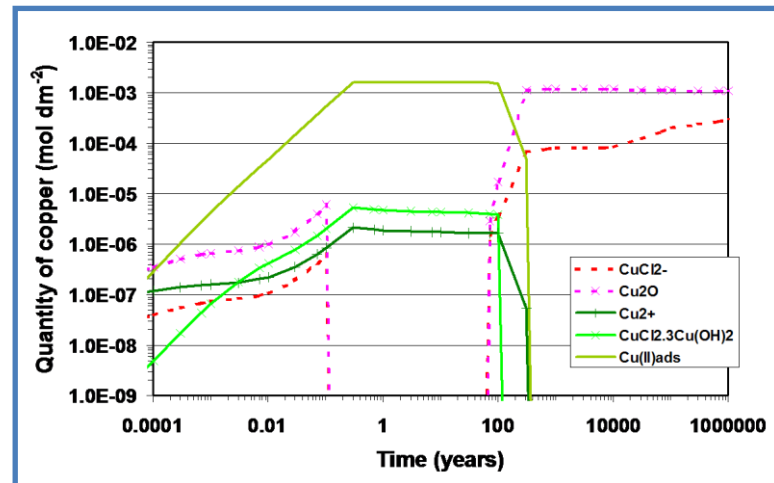
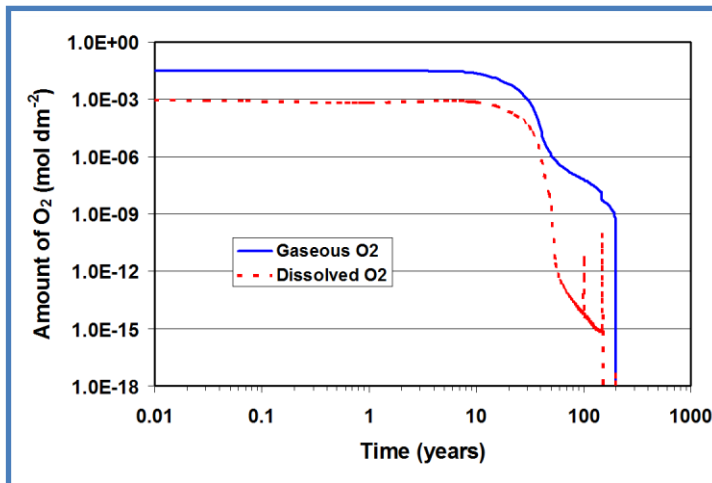
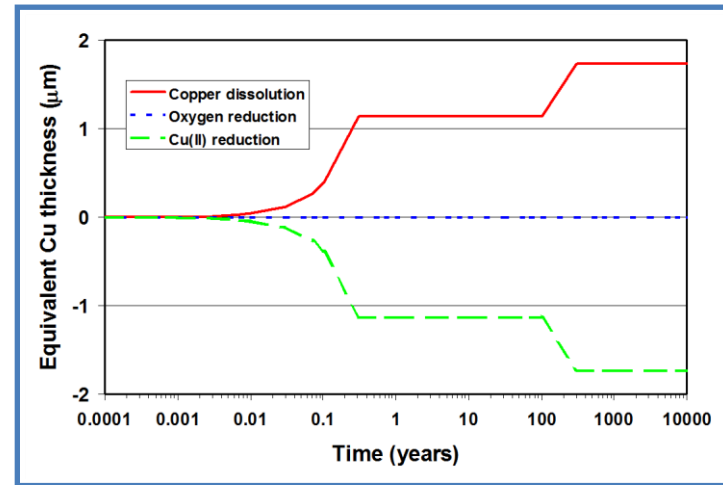
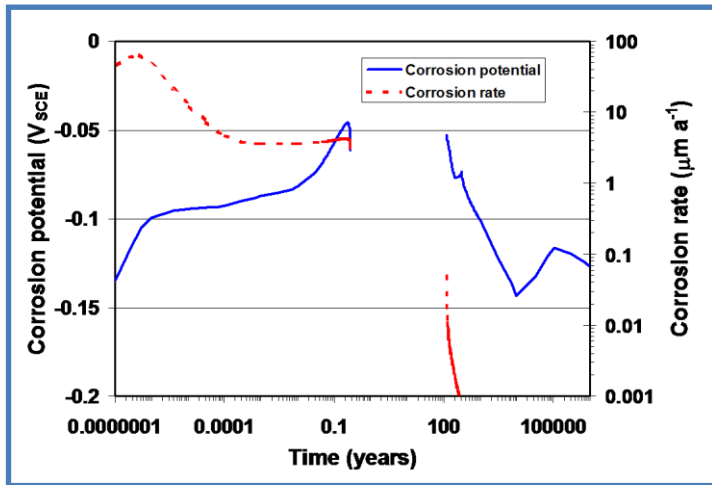
Mechanistic modelling



$$\epsilon_a \frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(\epsilon_e \tau D \frac{\partial c}{\partial x} \right) + \epsilon_a R$$

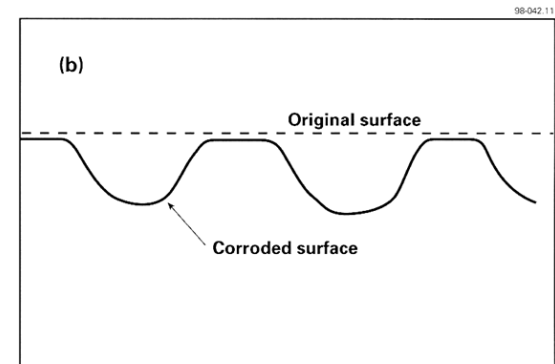
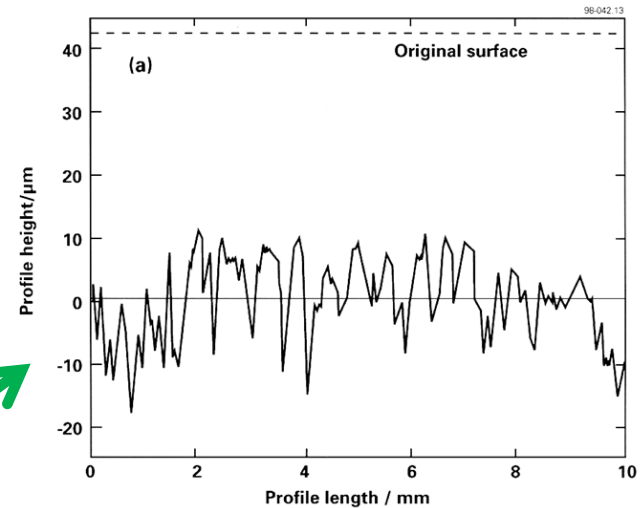
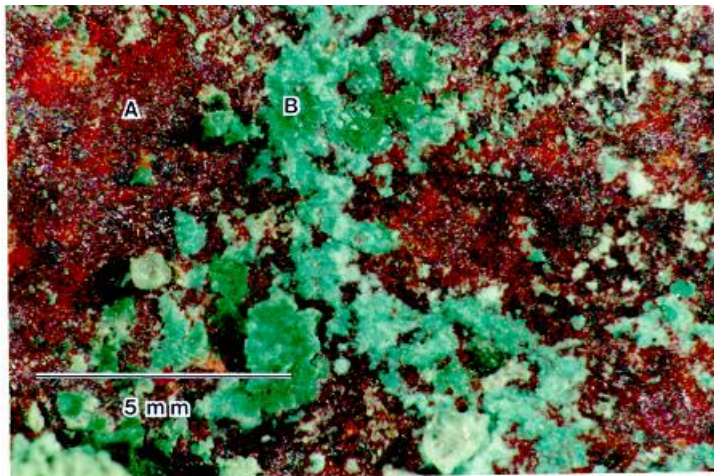


Predicted evolution of corrosion behaviour (no sulphide)



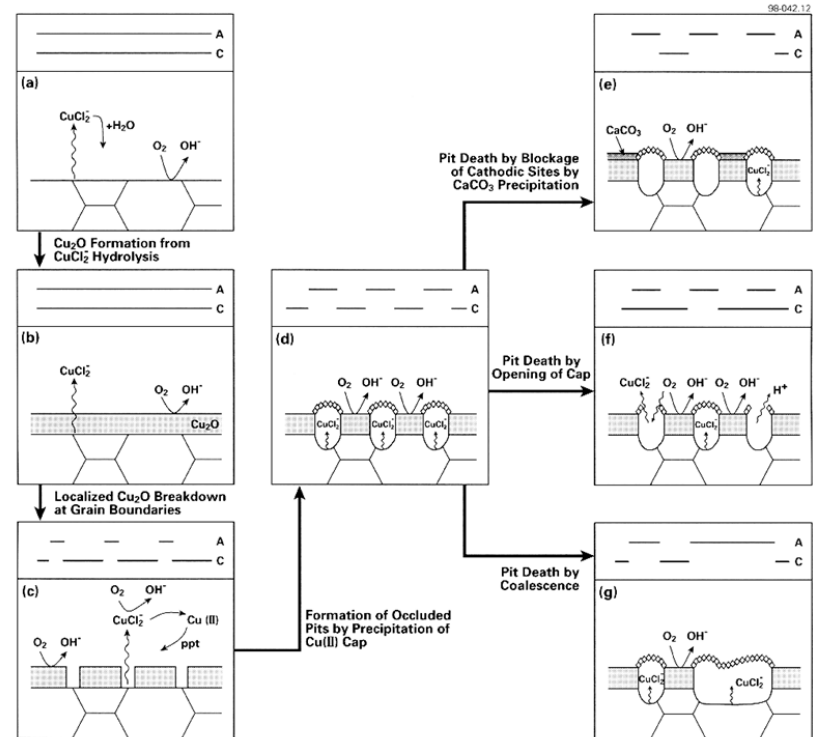
Localised corrosion

- In contact with compacted clay, copper undergoes surface roughening rather than “pitting”



Surface roughening

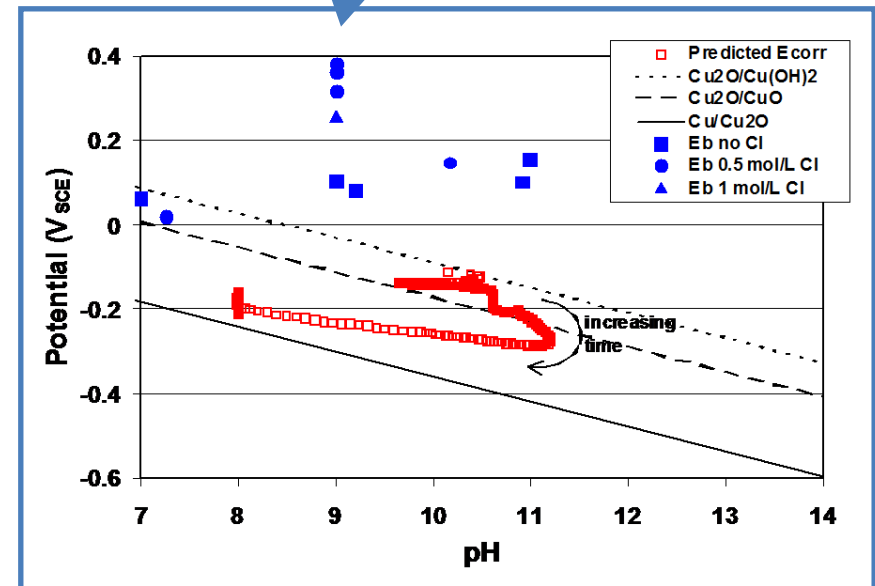
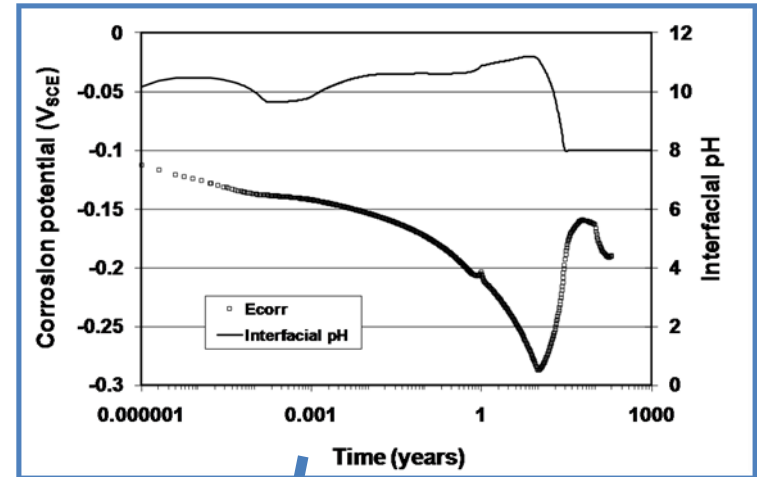
- Observed surface profile is consistent with a non-permanent separation of anodic and cathodic sites
- Mechanism involves repeated “pit” birth, growth, and death events
- More appropriate to use a surface-roughening allowance of 30-50 μm rather than a pitting factor



Alternative treatments of localised corrosion

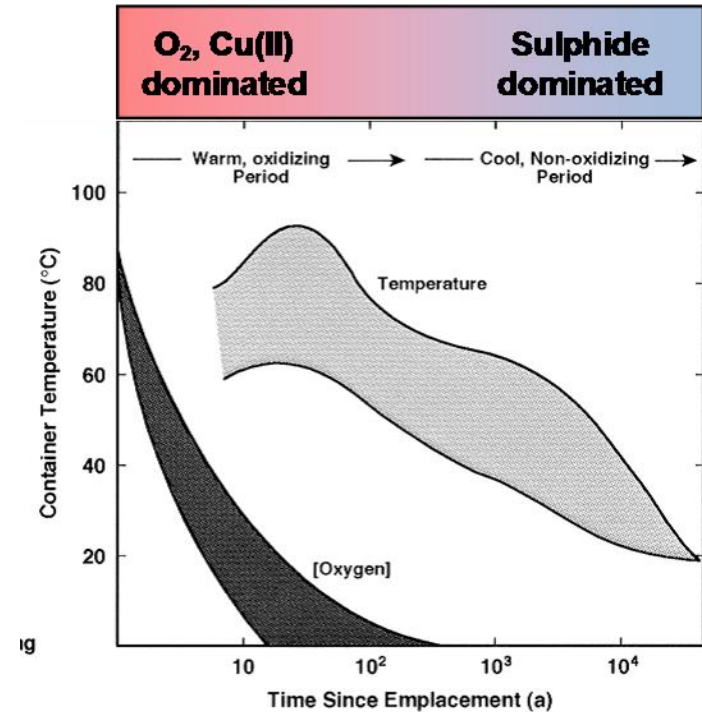
- The probability of localised corrosion is often predicted by comparing E_{CORR} and E_B or E_{RP}
- Condition for pitting/crevice corrosion

$$E_{CORR} > E_B / E_{RP}$$



Sulphur species

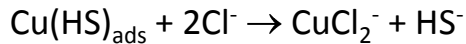
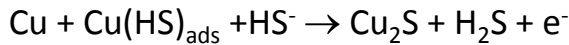
- Sulphate
 - Present in bentonite (as gypsum impurity) and in ground water
 - Reduction of S(VI) kinetically hindered (over geological timescales)
- Sulphide
 - $\text{H}^+/\text{H}_2\text{O}/(\text{H})\text{S}^-$ acts as oxidant in presence of HS^-
 - Limited sources
 - Ground water
 - Microbial activity outside (and inside) bentonite
 - Dissolution of pyrite?
 - SCC agent?
- Other S species
 - Availability?



- Important to remember that environment is dominated by sulphide for >99% of the canister service lifetime

Mechanism of copper dissolution in sulphide environments

- Interfacial dissolution reaction



- “High” sulphide concentration

- Protective film
- Parabolic kinetics
- Growth at film/solution interface
- Cu^+ film (HS^- solution) diffusion control

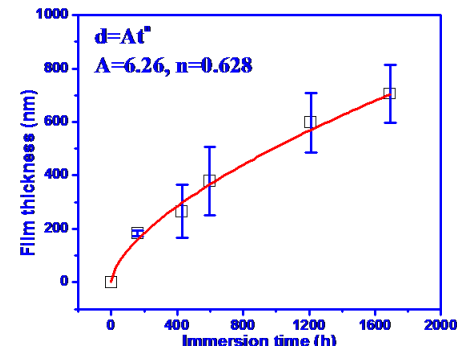
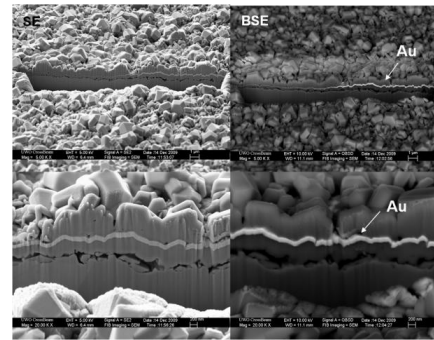
- “Lower” sulphide concentration

- Non-protective film
- Linear growth kinetics
- HS^- solution transport control

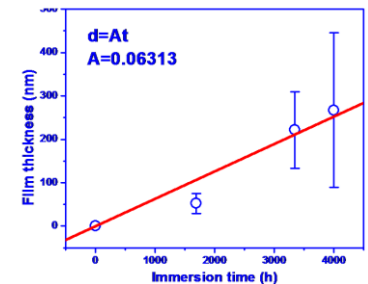
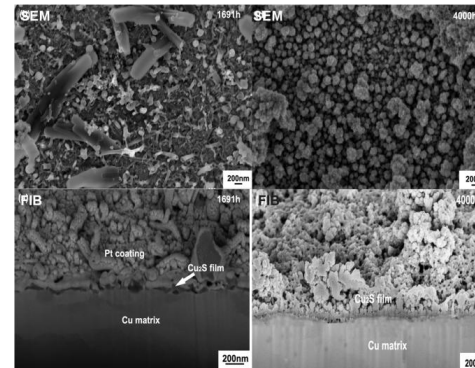
- Repository conditions

- Ground water $[\text{HS}^-]$ generally $<10^{-5}$ mol/L
- 4-5 orders magnitude lower k_M

5×10^{-4} mol/L HS^- + 0.1 mol/L NaCl

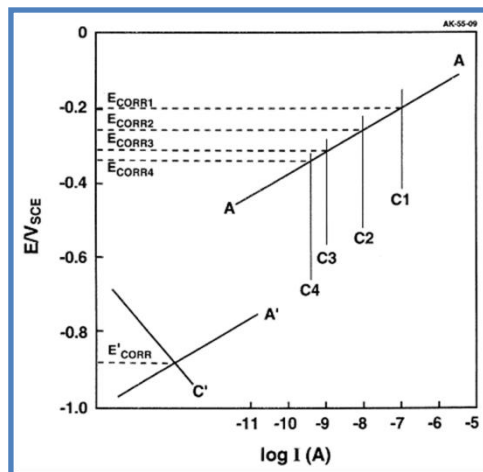
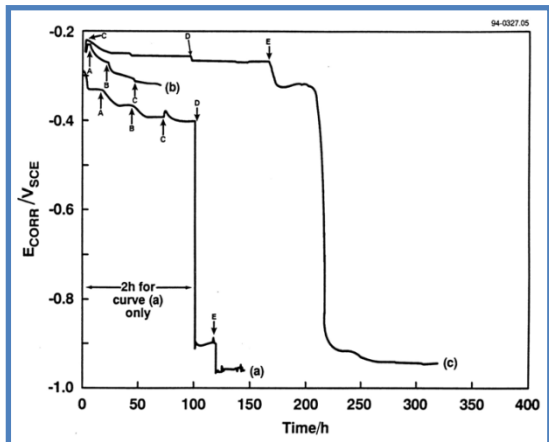


5×10^{-5} mol/L HS^- + 0.1 mol/L NaCl

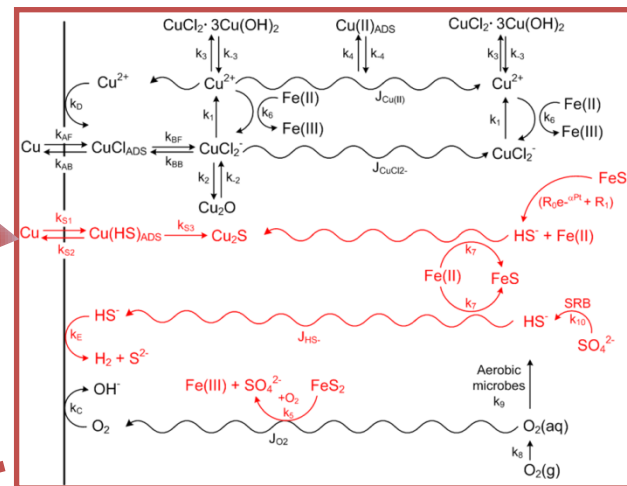


Mixed-potential modelling

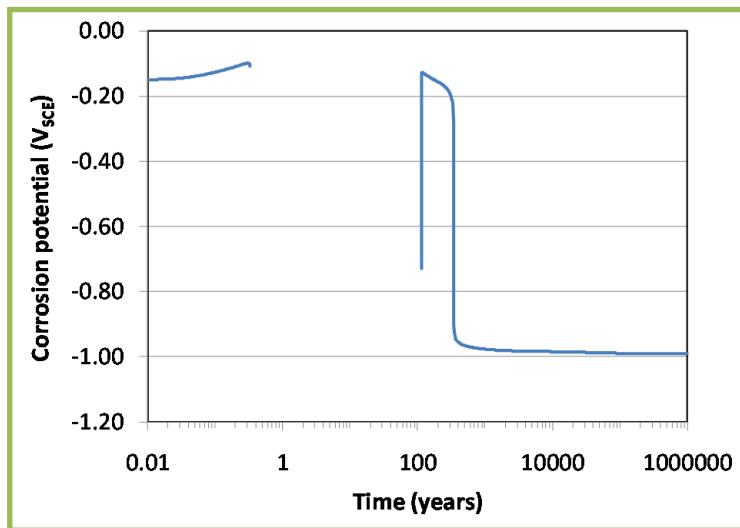
Experiment



Mechanism



Prediction

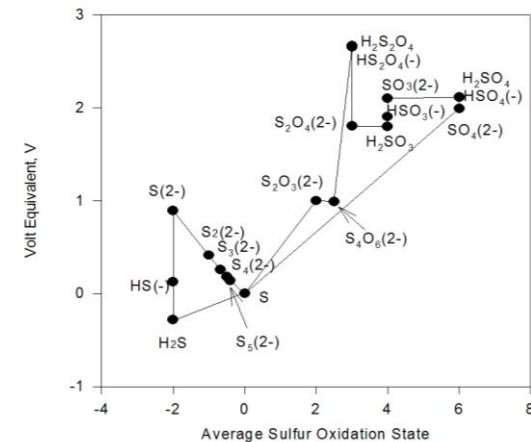
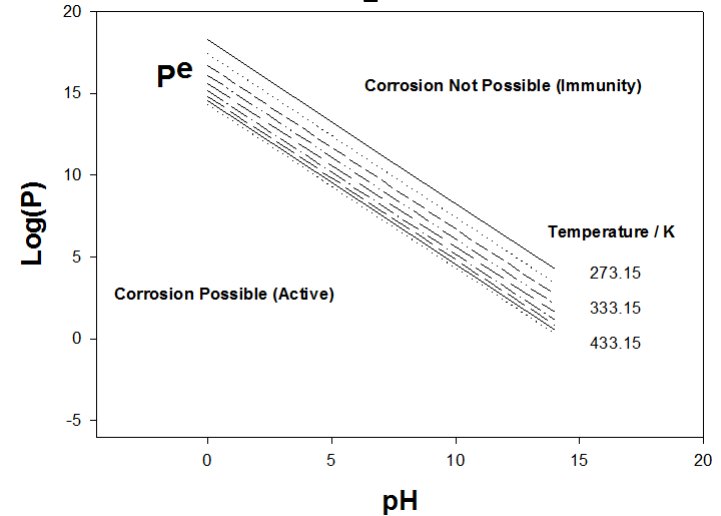


- Most important source of sulphide predicted to be microbial sulphate reduction in backfill some distance from canister
- Corrosion rate during long-term anaerobic period <1 nm/year

Thermodynamic considerations

- Wide range of thermodynamically possible S species in aqueous solution
 - Sulphide HS^-
 - Polysulphides S_x^{2-}
 - Polythionates $\text{S}_x\text{O}_y^{2-}$
 - Elemental S
- Macdonald and Sharifi-Asl (2011) carried out extensive thermodynamic analysis of those S species that would “activate” Cu
 - Use of Corrosion Domain Diagrams and Volt-equivalent Diagrams
 - Sulphide, polysulphides, certain polythionates “activate” Cu
- However, based on simple mass-balance arguments, even if all the SO_4^{2-} (S(VI)) in the buffer were reduced to HS^- (S(-II)), the maximum depth of corrosion would be 3 mm (King et al., unpublished data)

Copper/H₂O/sulphide



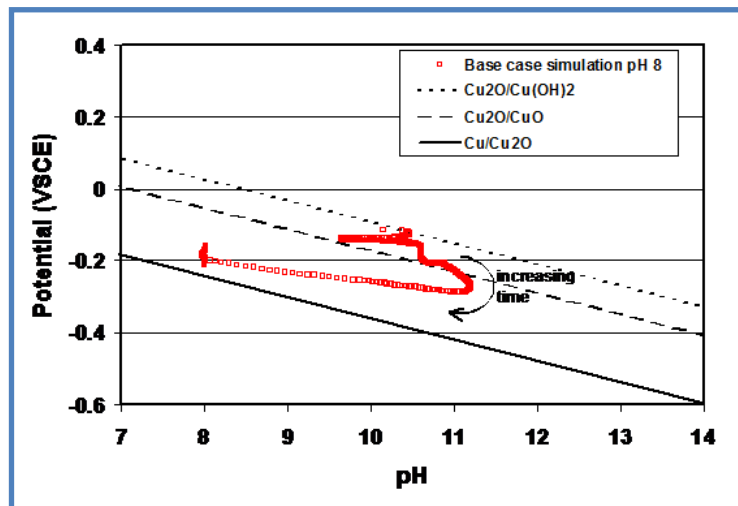
Volt Equivalent Diagram for S/H₂O System at pH=0 and at 25°C

SCC

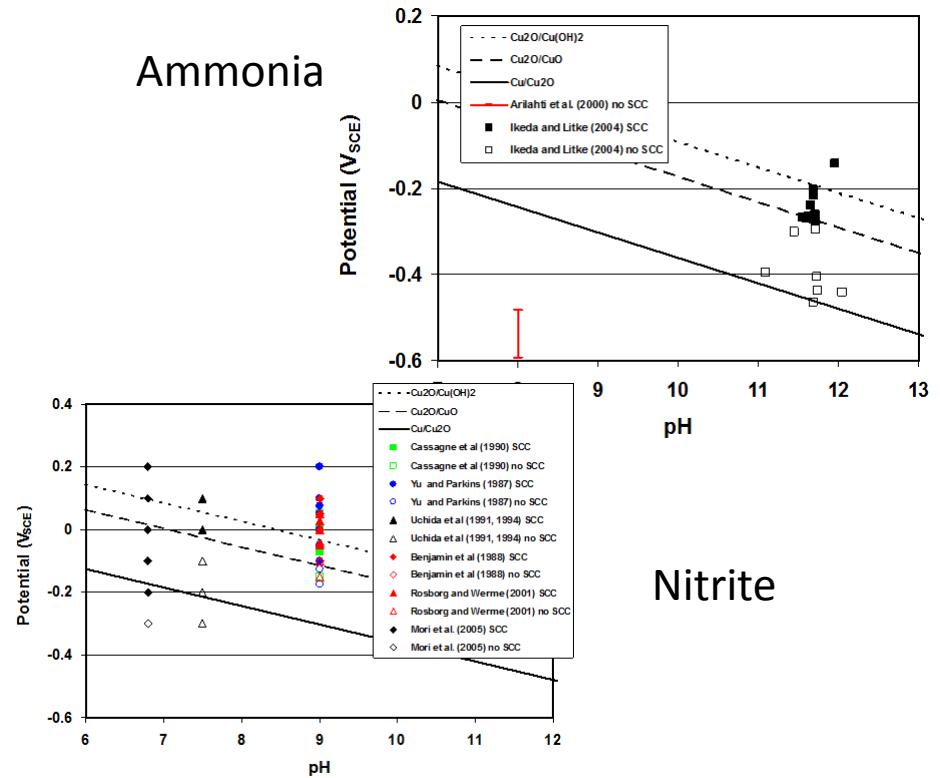
- Under aerobic conditions, SCC considered unlikely because all of the pre-requisite conditions are not present at the same time:

- Insufficient SCC agent
- Limited oxidant
- Elevated temperature
- E/pH not in permissive range
- Low levels of tensile stress
- Inhibitive effect of Cl-

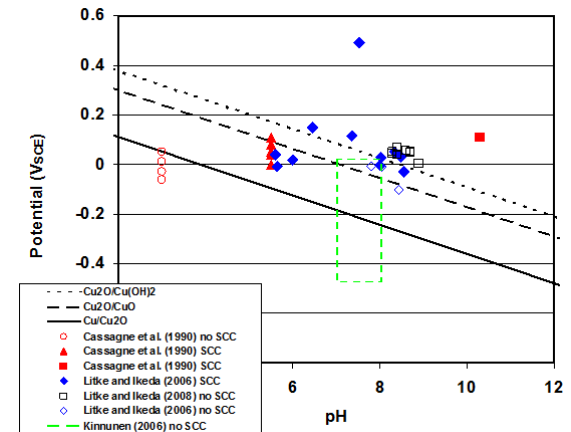
Predicted time dependence of E_{CORR}/pH of canister



Ammonia



Nitrite

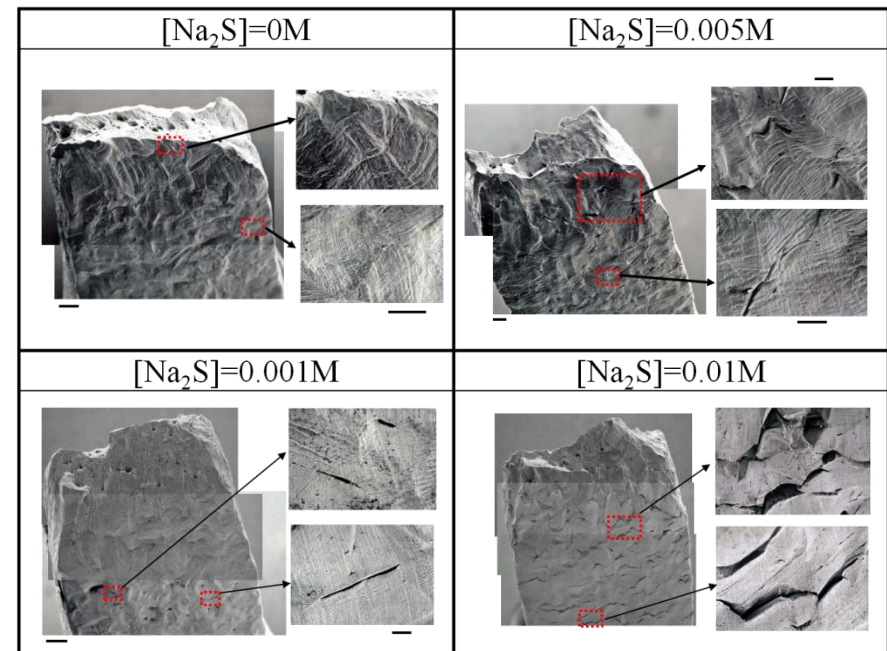
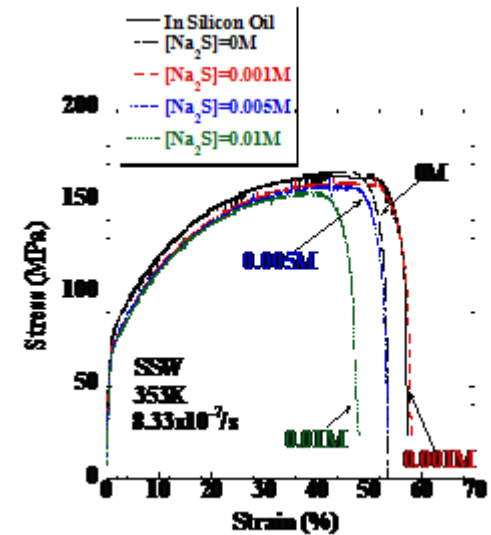


Acetate

SCC under anaerobic conditions

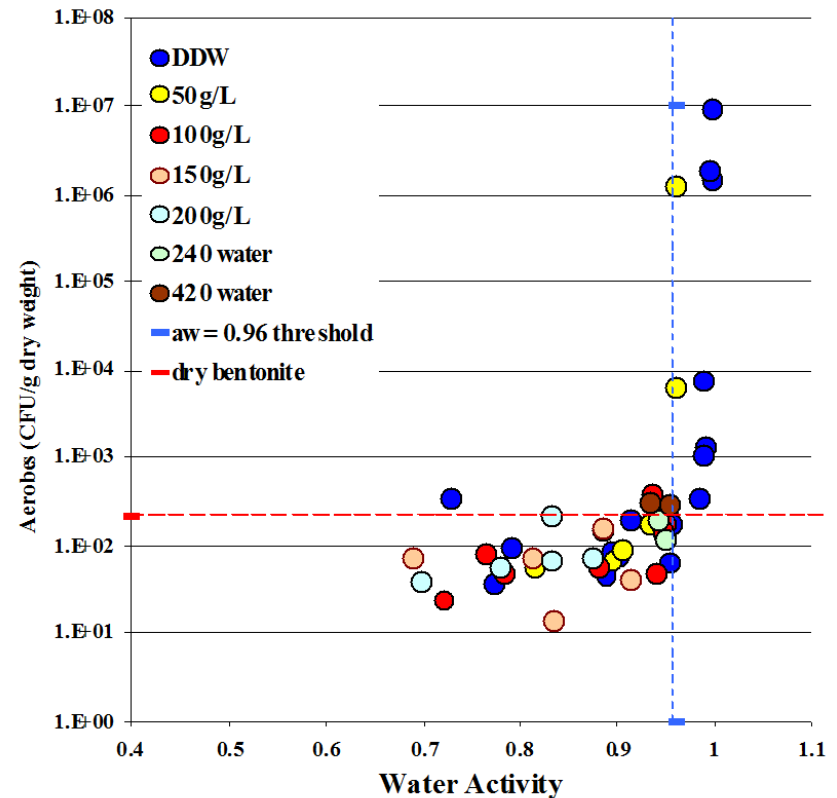
- Taniguchi and Kawasaki (2008) reported the SCC of copper in sulphide-containing seawater
 - Threshold $[HS^-] \sim 0.001$ mol/L
- Two attempts to replicate observations have not been successful
 - Arilahti et al. (2011) report enhanced gb diffusion of sulphide
- Under repository conditions, SCC due to HS^- is not possible because the interfacial concentration $\rightarrow 0$ and there will be no driving force for transport of sulphide to crack tip

Taniguchi and Kawasaki, J. Nucl. Mater. 379, 2008, 154



MIC

- The key to predicting MIC of the canister is to determine where and when microbial activity is possible
- Lots of evidence to indicate that microbial activity is suppressed by compacted bentonite
 - No agreement on mechanism
 - Low water activity
 - High swelling pressure
 - Regardless of mechanism, microbial activity is suppressed at saturated bentonite density of 2 Mg/m³ and higher
 - Very small rates of SRB activity measurable (equivalent to corrosion rates of 0.2 nm/yr)
- Therefore, microbial activity is only possible further away from the canister
 - No surface microbial activity
 - Transport limited supply of HS⁻

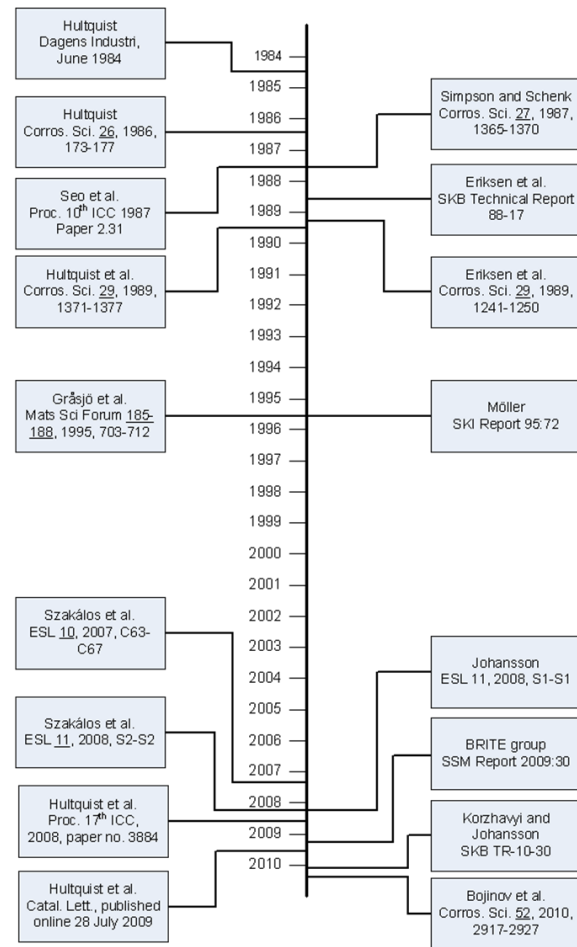


Stroes-Gascoyne et al. 2006

Corrosion of copper by water

- Lots of discussion recently about reports by Hultquist, Szakálos and co-workers
- Proposed mechanism

$$\text{Cu} + y\text{H}_2\text{O} \rightarrow \text{H}_x\text{CuO}_y + (2y - x)\text{H}_{\text{ads}}$$
- Reported observations
 - H₂ evolved from Cu in pure water
 - Equilibrium p_{H₂} ~1 mbar at 73°C
 - Portion of H absorbed and embrittles Cu
 - Reduction of H₂O supports oxidation of Cu to both Cu(I) and Cu(II)
 - In aerated solution, O₂ is not an oxidant but is instead consumed by reaction with H produced by the reduction of H₂O
 - Corrosion rate increases with time
 - Anaerobic corrosion rate of up to 5 μm/yr
- Despite repeated attempts, no-one has been able to reproduce the observations



Corrosion of copper by water

- Possible explanations
 - Corrosion of stainless steel components in cell
 - Extremely pure initial conditions ($a_{\text{Cu}^+}(f_{\text{H}_2})^{1/2} < 10^{-15.6}$ at 298.15 K)
 - Re-oxidation of highly reactive nanoscale Cu formed by reduction of pre-existing Cu_2O
 - Oxidation of pre-existing Cu_2O to Cu(II) coupled to reduction of H_2O
 - Out-gassing of H absorbed during manufacture
 - Catalysis by reactive $\text{Cu}(\text{OH})_{\text{ads}}$ sub-monolayer species
- Lost in this scientific debate is the implication for the canister
 - If we assume that the proposed mechanism is true, corrosion rate will be limited by rate of H_2 transport away from canister
 - Of the order of 1 nm/yr
 - Therefore, the consequence of the proposed mechanism on the canister lifetime (even if correct) is minimal
- However, because of the potential importance of this claim, if correct, work continues in this area

Eroded bentonite

- Corrosion behaviour of canister influenced by the presence of compacted bentonite
 - Transport-limited HS^- supply
 - Suppression of microbial activity
 - During future glaciation, dilute ground water could reach the repository and erode bentonite
 - Formation of clay gels and colloids
 - Resulting in partial loss of bentonite
 - Advective transport possible
- Analyses suggest a small number of canisters could be affected
 - Probabilistic analysis of enhanced HS^- transport
 - Distribution of fracture flow rates
 - Distribution of HS^- concentration
 - Analyses indicate only one canister will fail within 10^6 years

Future studies

- Although much is already understood, it is considered prudent to continue studies
 - Effect of HS^- on the SCC of copper
 - Is pyrite (FeS_2) a source of sulphide?
 - Thermodynamic assessment of the effect of $[\text{Cl}^-]$ on the corrosion of copper
 - Effect of early unsaturated conditions
 - Resolution of the question of whether copper corrodes in pure water

Summary

KBS TR-90 (1978)	SKB TR-01-23 Posiva 2002-01	SR-Site (2011) Posiva PSAR (2012)
<ul style="list-style-type: none"> • General corrosion supported by O₂ and HS⁻ • Pitting • Microbial activity limited by available organic C • No SCC for pure OFHC Cu 	<ul style="list-style-type: none"> • General corrosion supported by O₂ and HS⁻ • Pitting • SRB activity in tunnel and ground water only • No SCC based on threshold E and [SCC agents] 	<ul style="list-style-type: none"> • General corrosion supported by O₂ and HS⁻ • Surface roughening • SRB activity in tunnel and ground water only • No SCC based on threshold E/pH, [SCC agents], inhibitive effect of Cl⁻, low levels of tensile stress, elevated temperature
<p>“... it is considered realistic to anticipate a service life of hundreds of thousands of years for a copper canister ...”</p>	<p>Canister lifetimes >10⁶ years</p>	<p>Canister lifetimes >10⁶ years (In the event of eroded buffer, one canister failure within 10⁶ years for case of high flow rate and high [HS⁻])</p>