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Use of Alloy 22 as Long-Term Radioactive Waste Containment Material

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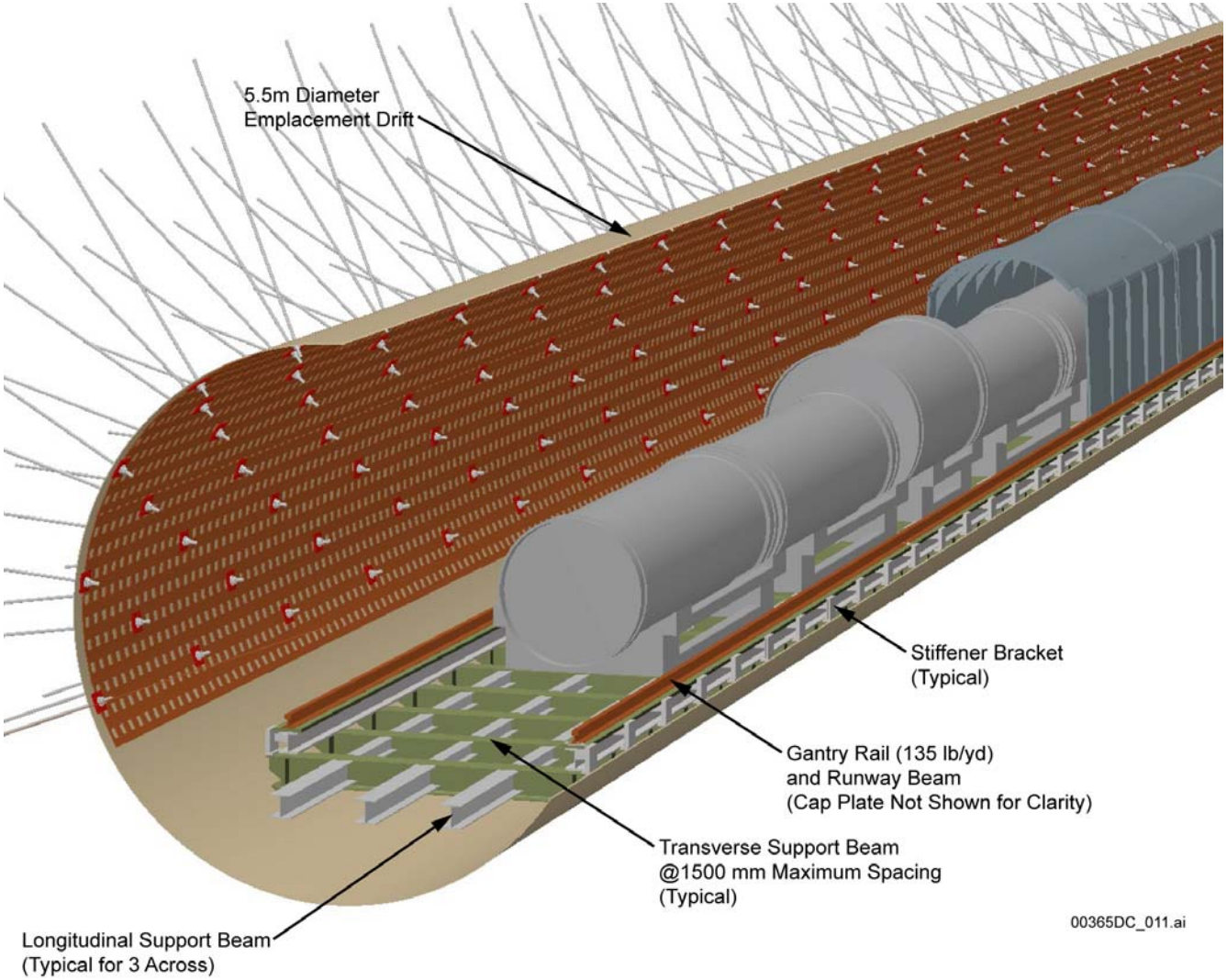
Outline

- Background
- Approach to Assess Localized Corrosion Probability
- Results
- Conclusions

Background

- Alloy 22 (Ni-22Cr-13Mo-4Fe-3W) is proposed as the outer container material for high-level radioactive waste at a potential repository in Yucca Mountain, USA
- Evaluation of alloy stability is difficult because of the long time scales of interest
- Particular environmental conditions, occurring only in a limited period, appear capable of causing passivity breakdown
- The objective is to estimate the likelihood of the establishment of these environmental conditions

Background

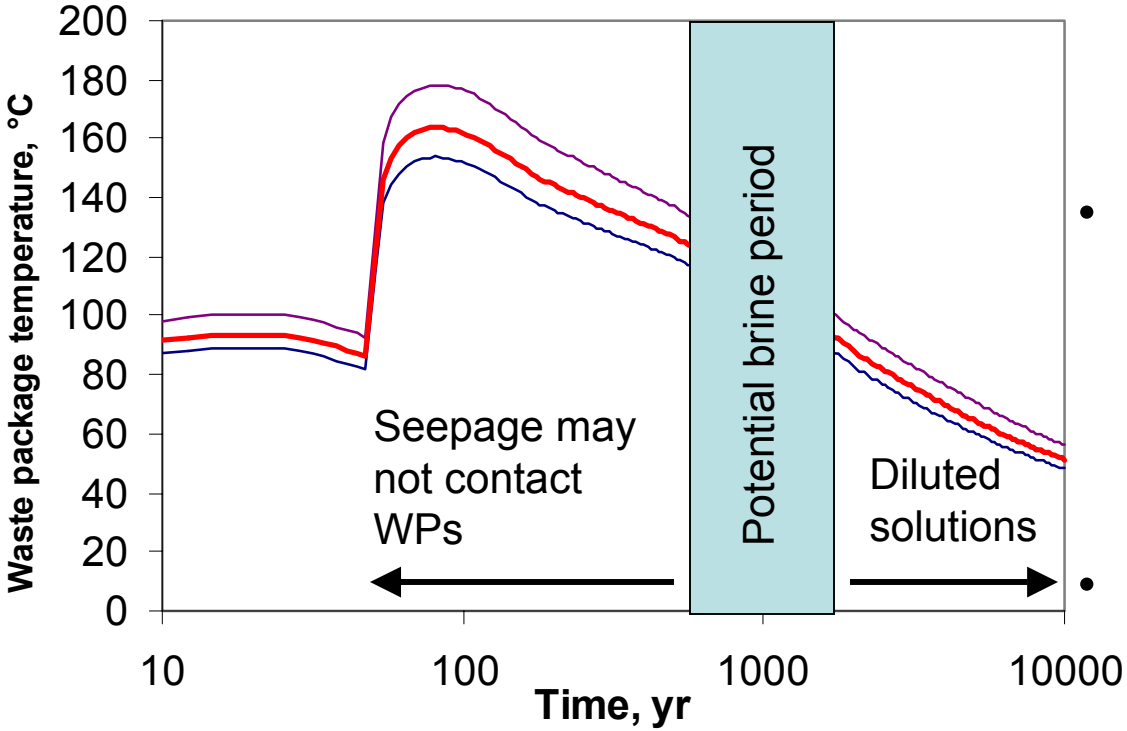


Passivity breakdown (crevice corrosion) could occur if

- Seeping water directly contacts waste packages (shields made of titanium alloy are intended to protect waste packages from seeping water)
- Seepage evaporation causes brines to develop on the waste package

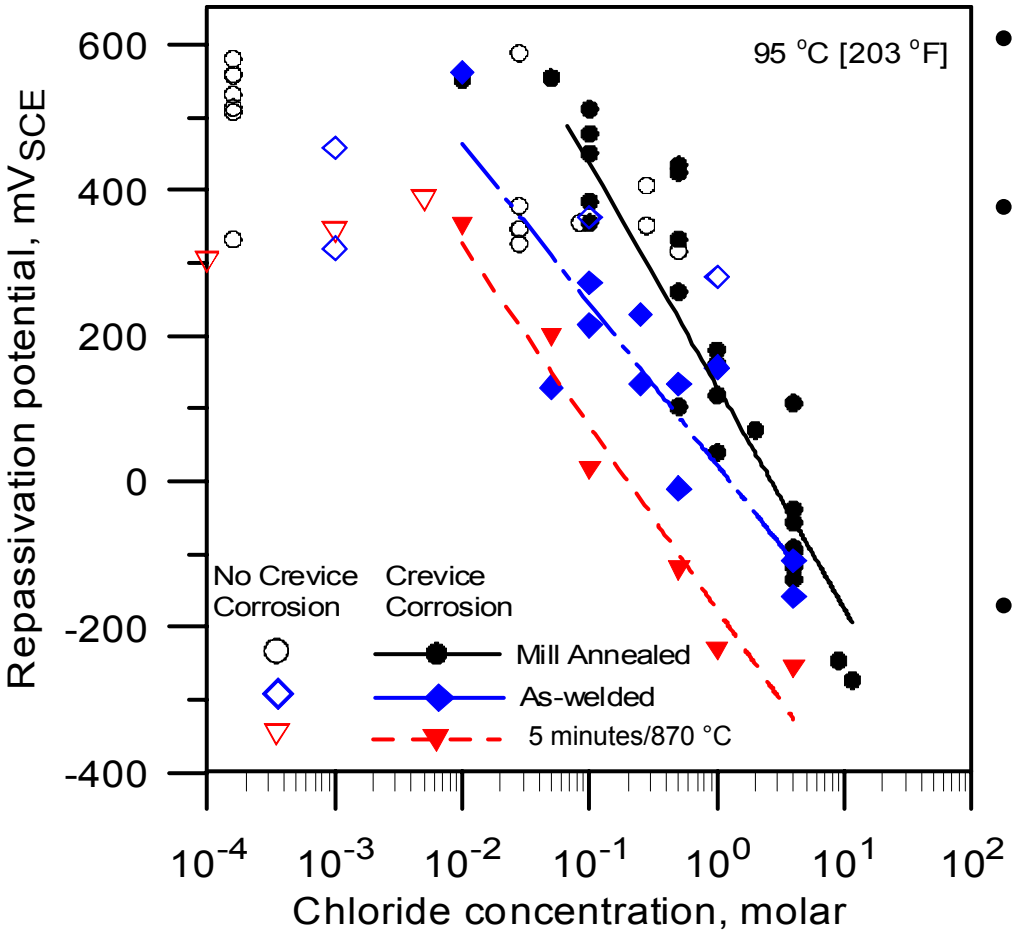
Figure source:
http://www.nwtrb.gov/meetings/sept2004/craun.pdf

Thermal Periods



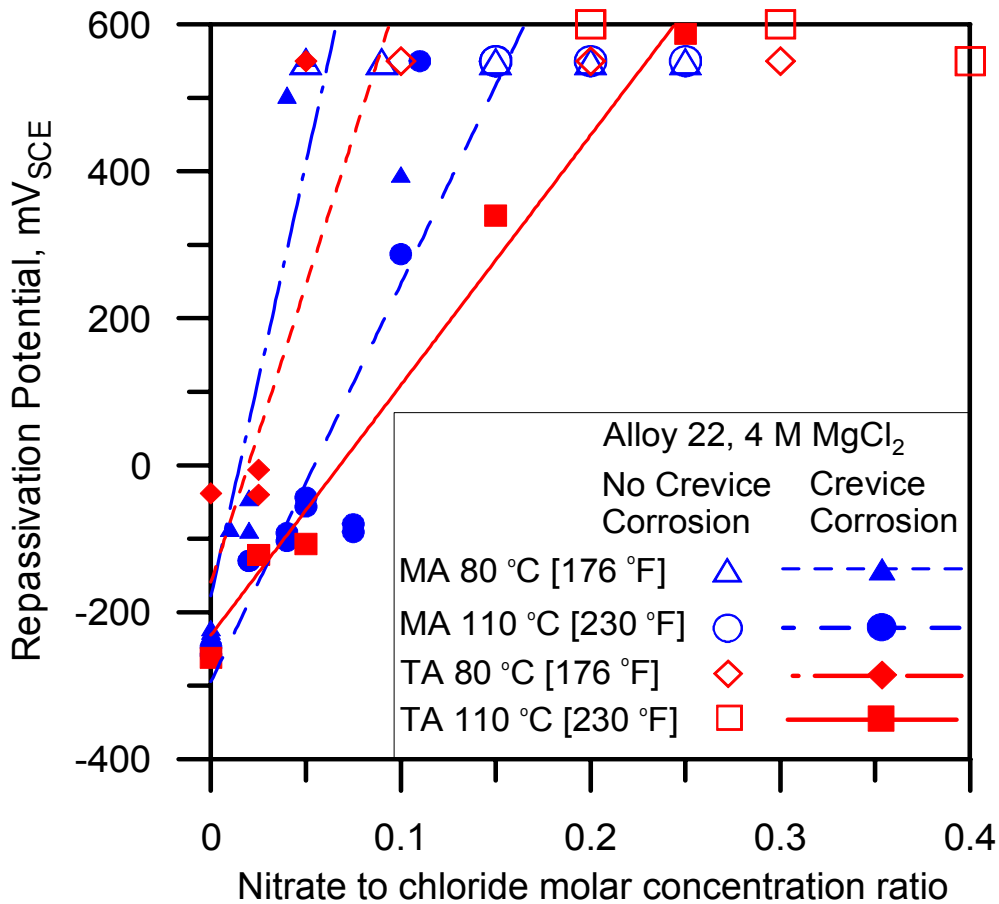
- Brines can form when seepage evaporation rate exceeds the seepage rate (blue region)
- Solutions tend to unsaturated water compositions when the seepage rate exceeds the evaporation rate (right of blue region)
- Initially, water is mobilized away from the repository drifts due to heat released by radioactive decay (left of blue region)

Repassivation Potential



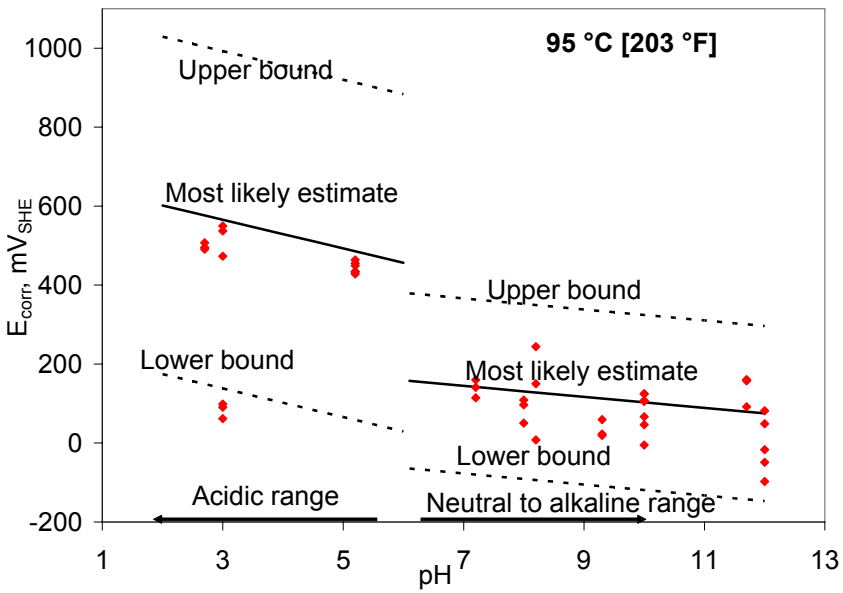
- Criterion for localized corrosion: $E_{corr} > E_{crit}$
- E_{crit} (repassivation potential) defined as an empirical function of chloride concentration and temperature
- Thermally aged material is more susceptible to localized corrosion

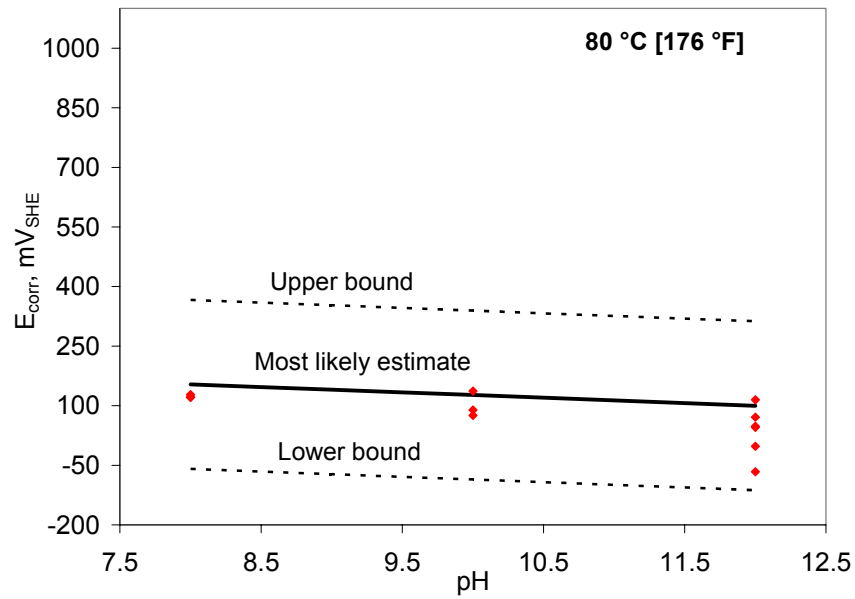
Effect of Inhibitors



- Nitrate is an effective localized corrosion inhibitor
- Inhibitor effect modeled as an increase in E_{crit} as function of the inhibitor to chloride ratio

Corrosion Potential





$$E_{corr} = \frac{E_a^a - E_a^{ef}}{Z_r \beta_r^{ef} F} - \frac{E_a^a}{Z_r \beta_r^{ef} F} \frac{T}{T_{ref}^a} + \frac{RT}{Z_r \beta_r^{ef} F} \ln\left[\left(\frac{[H^+]}{c_o}\right)^{n_H} \left(\frac{pO_2}{p_o}\right)^{n_O} \frac{i_r^{ef}}{i_a^o} \frac{C_{O_2}^{bulk}(T)}{C_{O_2}^{bulk}(T_{ref})}\right]$$

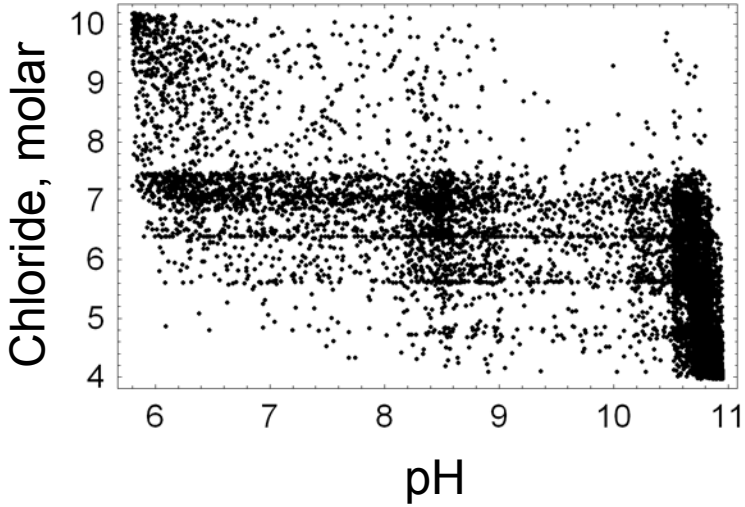
Localized Corrosion Probability

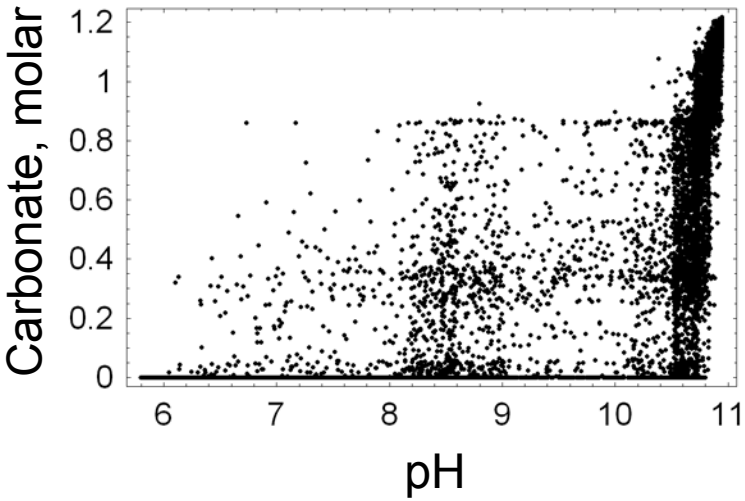
- $P = P_w \times P_c$
  - P_w is the probability of brines contacting the waste packages
  - P_w depends on
    - Probability of drip shield failure previous to or during the “potential brine period”
    - Probability of seepage water entering the emplacement drifts during the "potential brine period"
  - P_c is the probability of $E_{corr} > E_{crit}$ (quantified in this paper)

Brine Compositions

- Multiple thermodynamic simulations of water evaporation were performed using Yucca Mountain saturated waters as initial condition
- Thermodynamic simulations were supplemented by the chemical divide concept
- From 156 initial Yucca Mountain waters, 8, 24, and 68 percent resulted in calcium chloride-, neutral-, and alkaline-type brines
- Numerical probability distribution functions (PDF) were derived for each brine type, and combined according to the 8, 24, and 68 percent proportions to derive global PDFs as well as correlation matrices

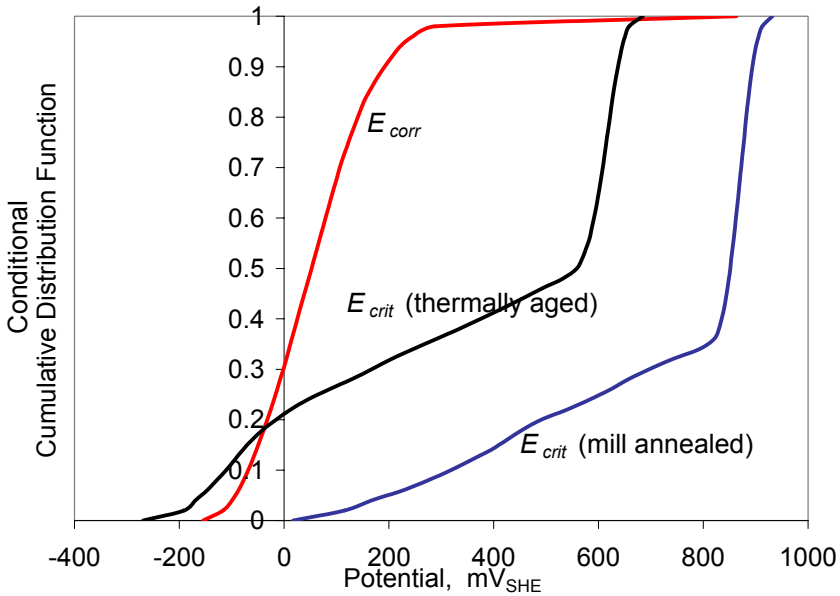
Brine Compositions

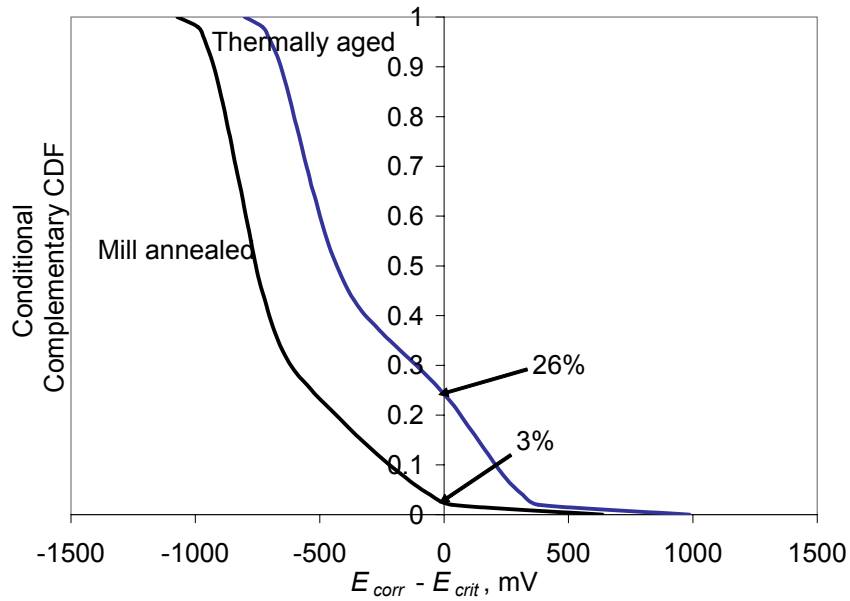




- Rank correlation(chloride, pH) = -0.8
- Rank correlation(carbonate, pH) = 0.9
- Sampled 10,000 vectors {pH, Cl^-, NO_3^-, CO_3^{2-}+HCO_3^-, SO_4^{2-}}
  - Accounted for rank correlations between chloride, pH, and carbonate
- Computed E_{corr} and E_{crit} for each Monte Carlo realization
  - Accounted for uncertainty in the anodic current density and empirical parameters that define E_{crit}

Results





- Mill-annealed material: $E_{corr} > E_{crit}$ in 3% of the realizations
- Thermally aged material: $E_{corr} > E_{crit}$ in 26% of the realizations

Conclusions

- The persistence of Alloy 22 passivity in the repository setting is mainly dependent on the quantity and chemistry of water that could contact waste packages.
- An approach to estimate the probability for the initiation of localized corrosion on the waste packages was discussed. The approach accounted for
  - possible range of brine chemistries
  - components that promote (chloride) or inhibit (nitrate, carbonate, and sulfate) localized corrosion in Alloy 22, and
  - fabrication processes.
- Estimates of P_w (probability of brines contacting the waste packages) are needed to assess the probability of localized corrosion.

Disclaimer

- This work was performed by the CNWRA for the U.S. Nuclear Regulatory Commission (NRC) under Contract No. NRC–02–02–012 on behalf of the NRC Office of Nuclear Material Safety and Safeguards, Division of High Level Waste Repository Safety.
- This work is an independent product of CNWRA and does not necessarily reflect the view or the regulatory position of the NRC.