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Corrosion Model to Support Total System Performance Assessments

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Yucca Mountain Environments

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Outline

- Summary of proposed model to support total system performance assessments
- Approach to assess probability of environments potentially supporting localized corrosion
- Results

Key Points

- Localized corrosion should be considered in performance assessment
  - Localized corrosion depends on the feasibility for seepage water to contact waste packages at temperatures near 100°C
  - Uncertainties exist in localized corrosion persistence (stifling and repassivation) and extent of attack

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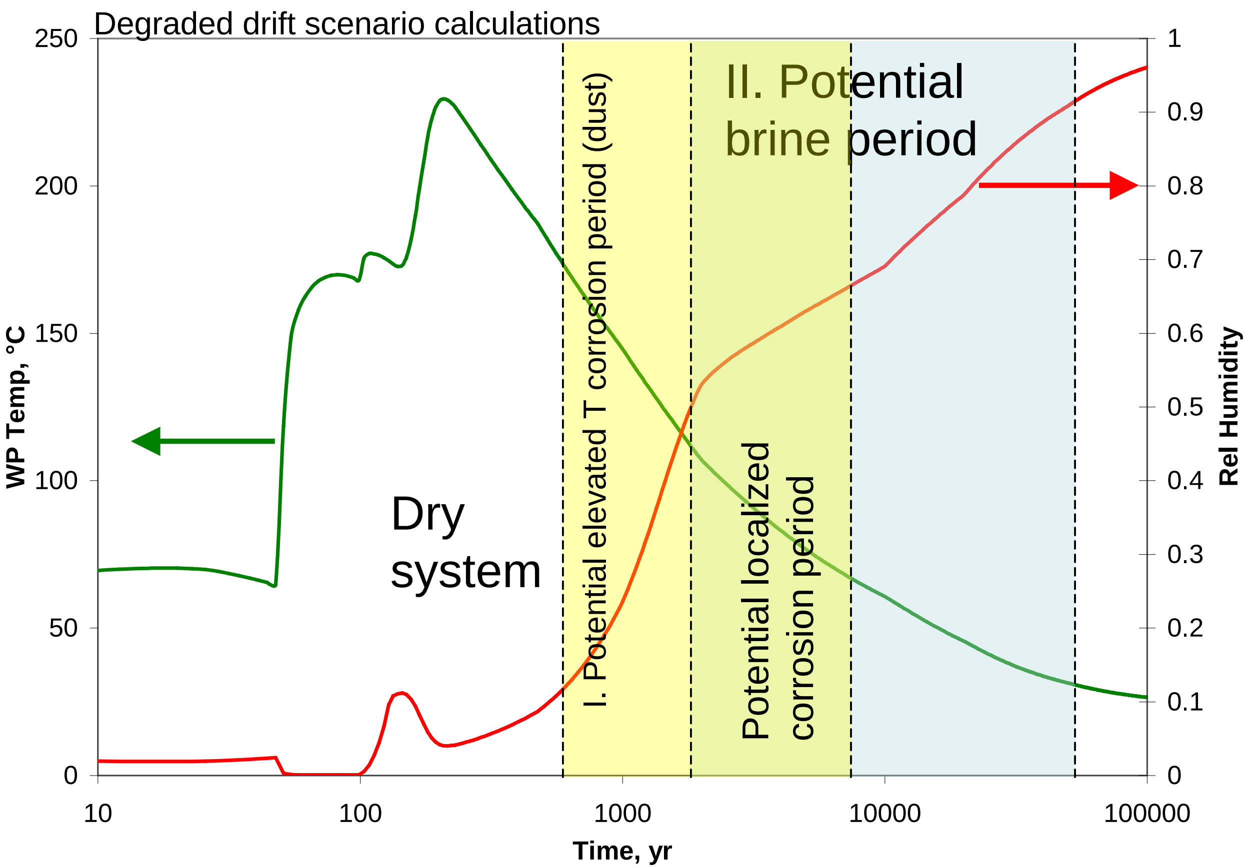
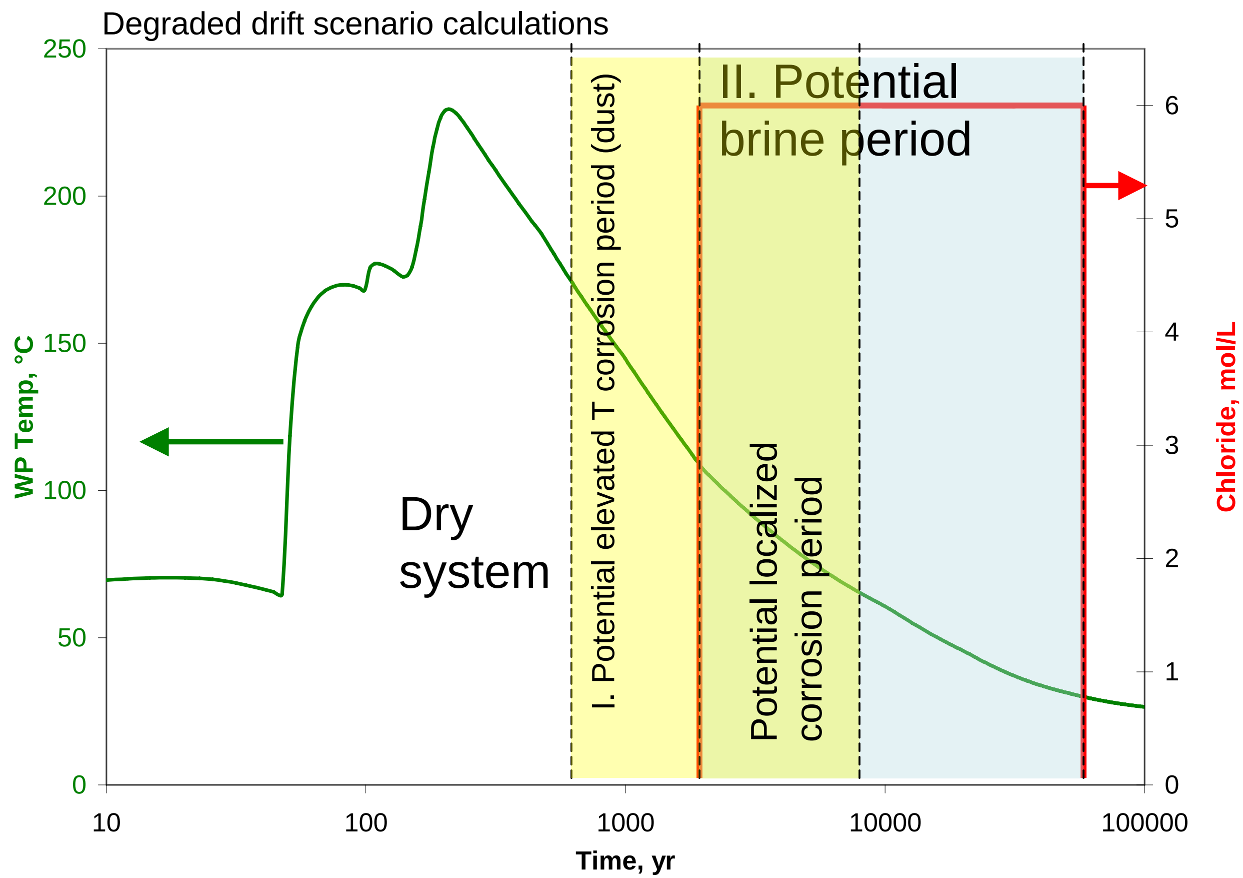
Thermal Periods



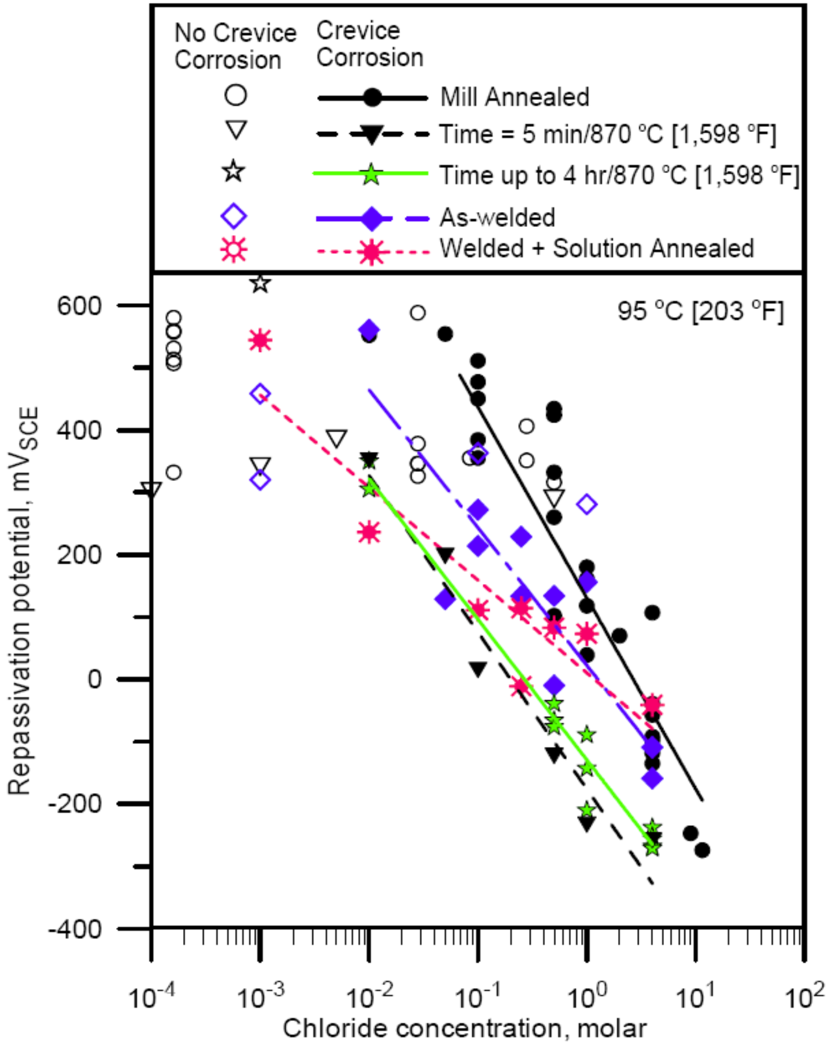
- I. No seepage (elevated temperature)
- II. Evaporation rate > seepage rate. Brine formation if seepage were to contact waste packages
- Localized corrosion susceptibility decreases with decreasing temperature

Model Assumptions



- Elevated T corrosion is disregarded until more information is available
- Localized corrosion could occur during (II), if seepage were to contact waste packages
- Brine compositions during (II) are assumed constant (from 110 °C simulations)
- Absent contact of seepage water with waste packages, localized corrosion is assumed not to initiate

Repassivation Potential



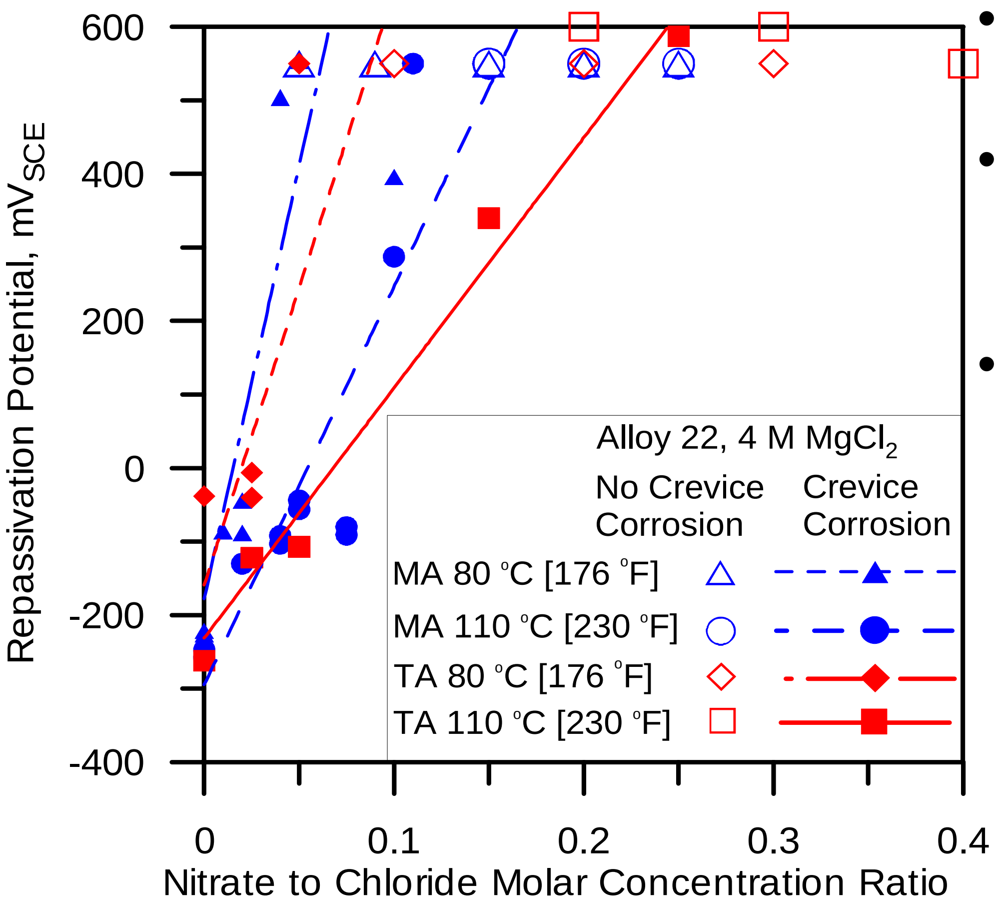
- Criterion for localized corrosion: $E_{corr} > E_{rcrev}$
- E_{rcrev} (repassivation potential) function of [Cl^-] and T
- Thermally aged and welded materials are more susceptible to localized corrosion

$$E_{rcrev} = E^{o}_{rcrev}(T) + B(T)\log_{10}\left[Cl^{-}\right]$$

$$E^{o}_{rcrev}(T) = A_1 + A_2(T)$$

$$B(T) = B_1 + B_2(T)$$

Effect of Inhibitors

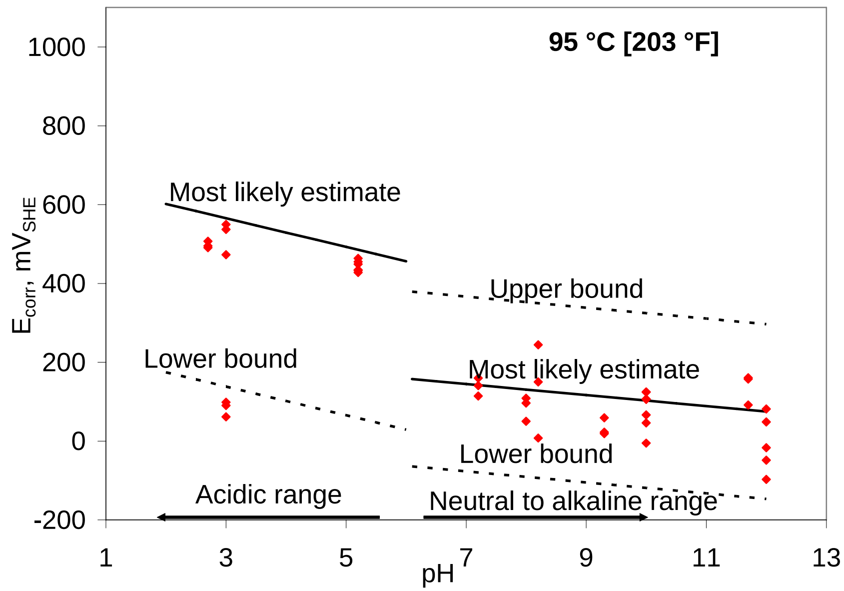


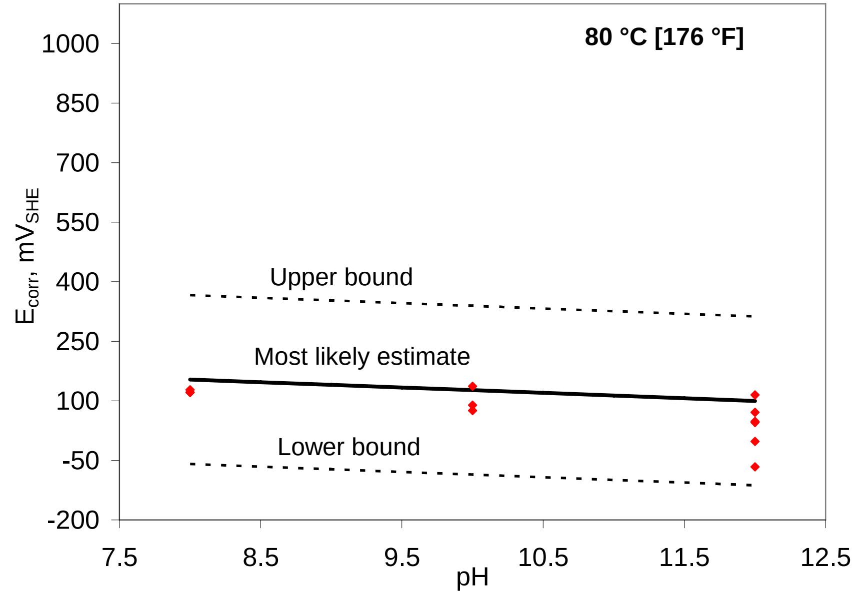
- Nitrate is an effective localized corrosion inhibitor
- Nitrate effect modeled as an increase in E_{rcrev} as a function of [inhibitor]/[Cl$^-$]
- Inhibitors (carbonate-bicarbonate, nitrate, and sulfate) considered assuming independent additive effects on E_{rcrev}

$$\Delta E_{rcrev} = 800\ \text{mV}\ \frac{\min(r, r_n)}{r_n}$$

$$r = \frac{[\mathrm{NO}_3^-]}{[\mathrm{Cl}^-]} + \frac{r_n}{r_s}\frac{[\mathrm{SO}_4^{2-}]}{[\mathrm{Cl}^-]} + \frac{r_n}{r_c}\frac{[\mathrm{CO}_3^{2-}] + [\mathrm{HCO}_3^-]}{[\mathrm{Cl}^-]}$$

Corrosion Potential





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

- Equation derived from mechanistic arguments
- Parameters derived by adjusting to experimental data
- Uncertainty in E_{corr} is assumed due to anodic dissolution rate uncertainty

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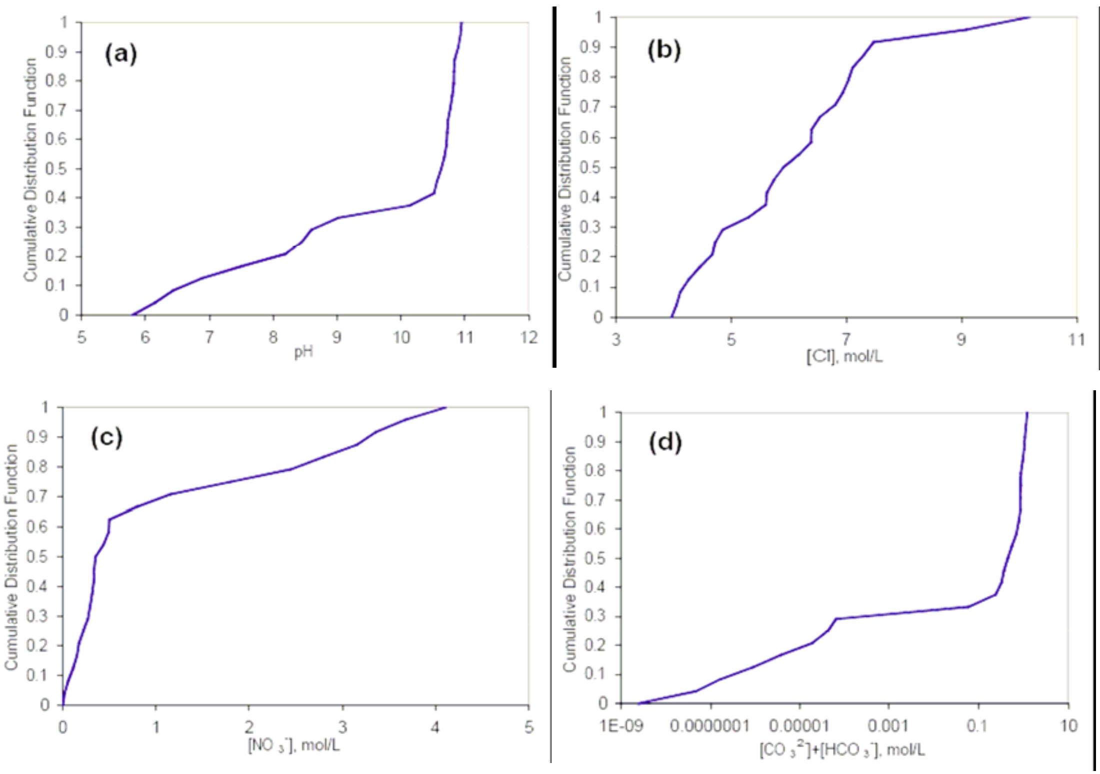
Localized Corrosion Probability

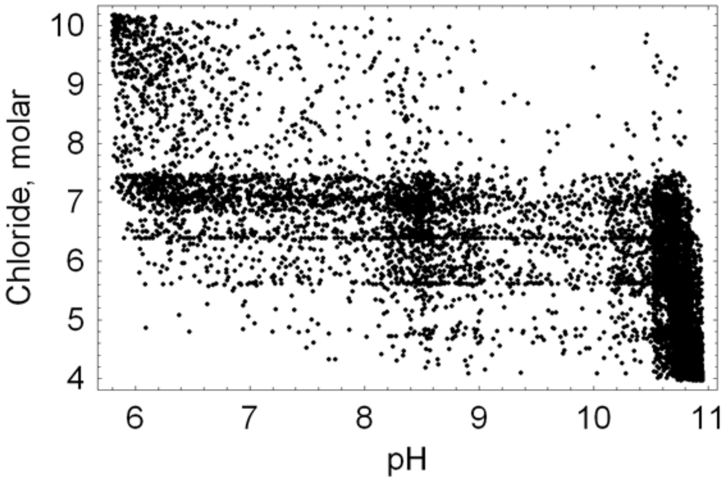
- $P = P_w \times P_c$
  - P_w : probability of seepage contacting waste packages
    - Drip shield failure prior to the “potential localized corrosion period”
    - Seepage water entering the emplacement drifts during the “potential localized corrosion period”
  - P_c : probability that $E_{corr} > E_{rcrev}$ (quantified in this work)
- The objective of the analysis is determining whether P_c alone is negligible or not

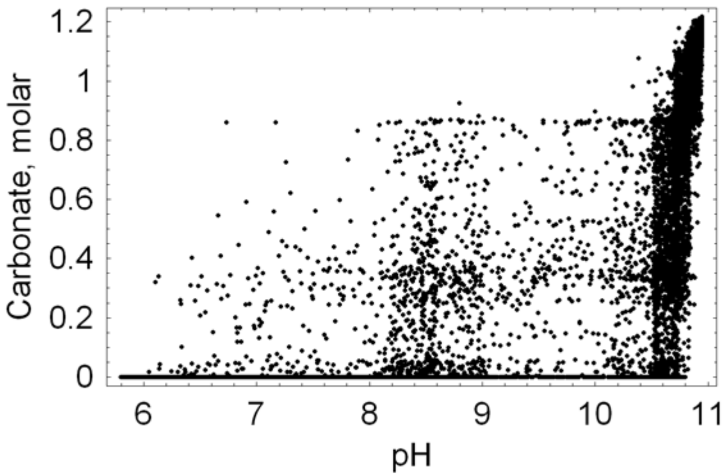
Brine Compositions



- Thermodynamic simulations of water evaporation (at 110 °C) performed using Yucca Mountain pore waters as initial condition
- From 156 initial Yucca Mountain waters, 8, 24, and 68 percent resulted in calcium chloride-, neutral-, and alkaline-type brines (Environment II)
- Numerical probability distribution functions derived as well as correlation matrices

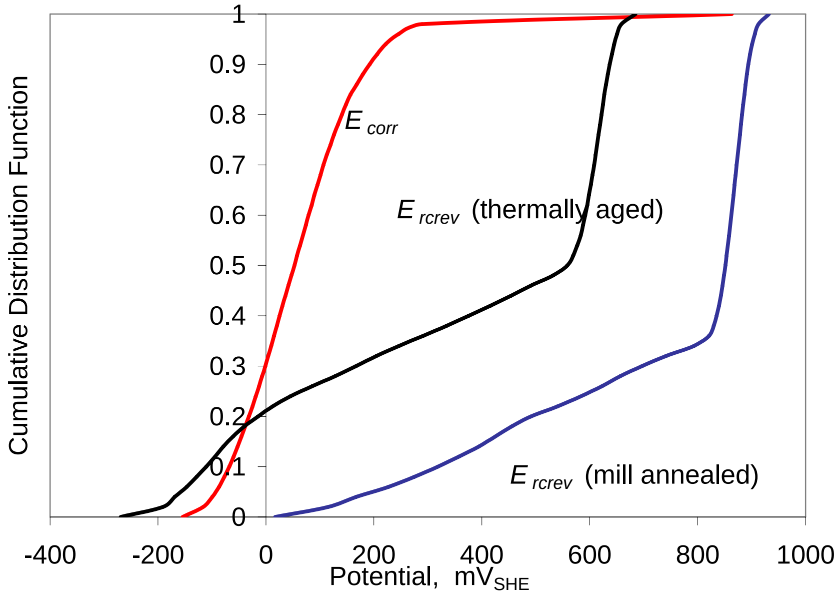
Brine Compositions (Cont'd)

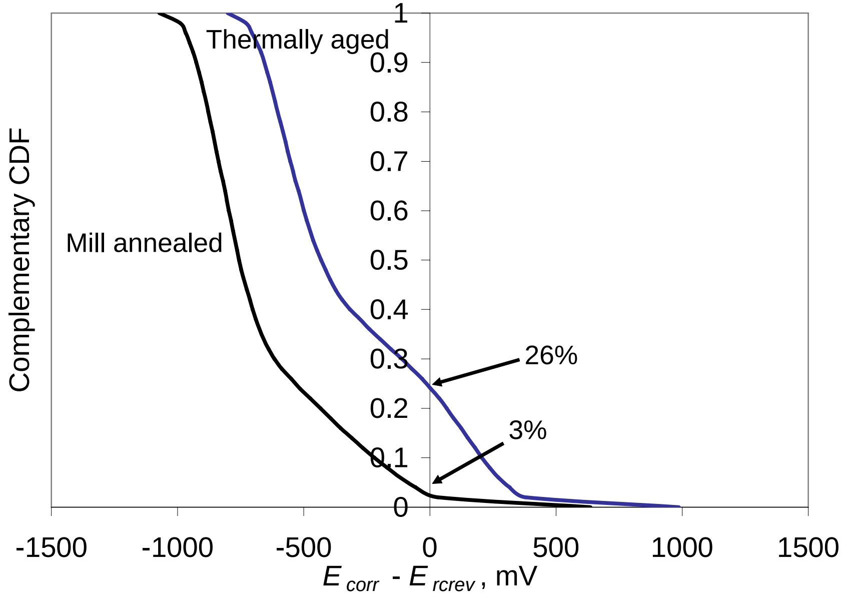




- Rank correlation(chloride, pH) = -0.8
- Rank correlation(carbonate, pH) = 0.9
- Sampled 10,000 vectors {pH, Cl^-, NO_3^-, CO_3^{2-}+HCO_3^-, SO_4^{2-}}
- Computed E_{corr} and E_{rcrev} for each feasible environment
  - Accounted for uncertainty in the anodic current density and empirical parameters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

Results





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

Conclusions

- An approach to estimate the probability for the onset of localized corrosion was discussed
  - feasible brine chemistries
  - components that promote (chloride) or inhibit (nitrate, carbonate-bicarbonate, sulfate) localized corrosion in Alloy 22
  - fabrication effects
- Localized corrosion should be considered in performance assessments if seepage water were to contact waste packages during the thermal pulse

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Uncertainties in Performance Assessment

- Elevated temperature corrosion
- Drip shield lifetime
- Composition of solutions in contact with waste packages
- Localized corrosion persistence during extended periods in limited-volume systems (stifling, repassivation)
- Surface extent of localized corrosion attack

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- This work is an independent product of CNWRA and does not necessarily reflect the view or the regulatory position of the NRC.

BACKUP SLIDES

References

- D. S. Dunn et al. *Passive and Localized Corrosion of Alloy 22—Modeling and Experiments*. CNWRA 2005-02. San Antonio, Texas, December 2005.
- O. Pensado, R. Pabalan, D. Dunn, and K.-T. Chiang. *Use of Alloy-22 as a Long-Term Radioactive Waste Containment Material*. Passivation of Metals and Semiconductors, and Properties of Thin Oxide Layers —A Selection of Papers from the 9th International Symposium, Paris, France, 27 June – 1 July, 2005. Philippe Marcus and Vincent Maurice, Editors; The Netherlands: Elsevier, pp. 53-57, 2006.

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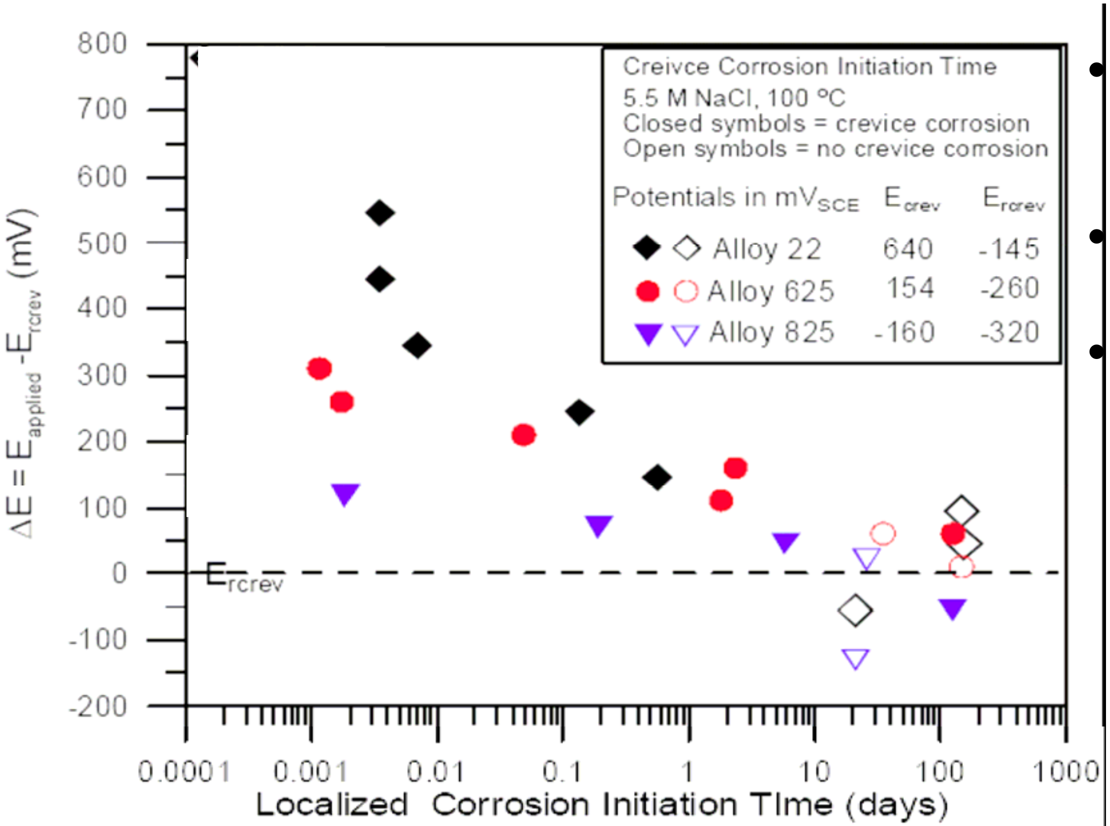
Verification of E_{rcrev} *Criterion*



- Localized corrosion occurs if the applied potential exceeds E_{rcrev}
- The initiation time is a function of $E_{applied} - E_{rcrev}$
- The initiation time is conservatively ignored in the proposed model (no delay is assumed for initiation of localized corrosion)