Corrosion Model to Support Total System Performance Assessments

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NWTRB Workshop on Localized Corrosion of Alloy 22 in Yucca Mountain Environments
Las Vegas, NV, September 25-26, 2006
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
Thermal Periods

Degraded drift scenario calculations

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

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

$$E_{\text{rcrev}}^o(T) = A_1 + A_2(T)$$

$$B(T) = B_1 + B_2(T)$$
Effect of Inhibitors

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

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

$$r = \frac{[\text{NO}_3^-]}{[\text{Cl}^-]} + r_n \frac{[\text{SO}_4^{2-}]}{[\text{Cl}^-]} + r_n \frac{[\text{CO}_3^{2-}]}{[\text{Cl}^-]} + \frac{[\text{HCO}_3^-]}{[\text{Cl}^-]}$$
Corrosion Potential

![Graphs showing E_{corr} vs pH at 95 °C and 80 °C](image)

\[ E_{corr} = \frac{E_{a}^{a} - E_{a}^{ef}}{Z_{r} \beta_{r} F} - \frac{E_{a}^{a}}{Z_{r} \beta_{r} F T_{ref}} + \frac{RT}{Z_{r} \beta_{r} F} \ln \left( \frac{[H^+]^{n_{H}}}{M} \right) \left( \frac{pO_{2}}{\text{atm}} \right)^{n_{O}} i_{r}^{ef} \frac{i_{a}^{o}}{C_{O_{2}^{bulk}}(T_{ref})} \]

- Equation derived from mechanistic arguments
- Parameters derived by adjusting to experimental data
- Uncertainty in \( E_{corr} \) is assumed due to anodic dissolution rate uncertainty
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 \{\text{pH, Cl}^-, \text{NO}_3^-, \text{CO}_3^{2-}+\text{HCO}_3^-, \text{SO}_4^{2-}\}
- Computed $E_{\text{corr}}$ and $E_{\text{rcrev}}$ for each feasible environment
  - Accounted for uncertainty in the anodic current density and empirical parameters that define $E_{\text{rcrev}}$
Results

- Mill-annealed material: $E_{\text{corr}} > E_{\text{crev}}$ in 3% of the samples
- Thermally aged material: $E_{\text{corr}} > E_{\text{crev}}$ 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
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
Acknowledgment

• 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.
BACKUP SLIDES
References


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)