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Understanding Conditions for Localized Corrosion and Stress Corrosion Cracking of Alloy 22 in Repository Settings

Osvaldo Pensado and Roberto Pabalan

Center for Nuclear Waste Regulatory Analyses (CNWRA)
Southwest Research Institute®, San Antonio, Texas

3rd International Workshop on Long-Term Prediction of Corrosion Damage in Nuclear Waste Systems, May 14–18, 2007, State College, Pennsylvania

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Outline

- Introduction
- Objectives
- Probabilistic Approach
- Brine Composition Estimates
- Numerical Examples
- Proposed Approach for Performance Assessments (PA)
- Conclusions

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Introduction

- Alloy 22 (Ni-22Cr-13Mo-3W-3Fe in weight percent) is currently considered by the U.S. Department of Energy as material for construction of packages to isolate radioactive waste from the environment
- Alloy 22 is susceptible to localized corrosion (LC), in the form of crevice corrosion (CC), and stress corrosion cracking (SCC)
- CC and SCC can only occur under a defined set of environmental, material, and electrochemical conditions

Objectives

- Propose a methodology to evaluate consequences of corrosion processes such as CC and SCC
- Develop approach to estimate probabilities of processes to support performance assessments

Thermal Periods

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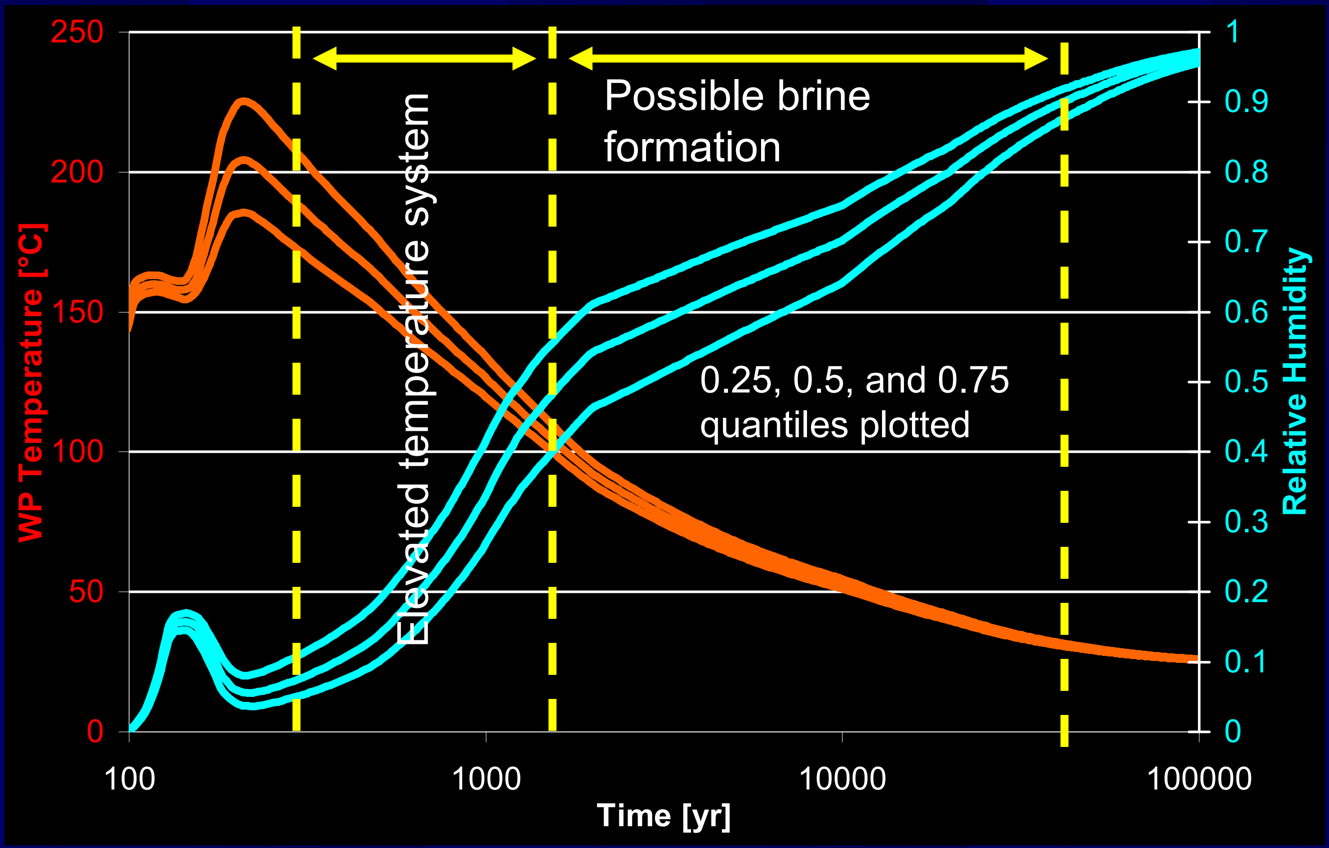

Crevice corrosion (CC) and stress corrosion cracking (SCC) could occur during the "brine formation period"

Brine formation is a necessary but not sufficient condition for CC and SCC to occur

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Probabilistic Approach

- Initiation criterion for CC and SCC
  - Corrosion potential, E_{corr}, exceeds a critical potential, E_{crit} (specific for each corrosion process)
- $P_T = P_S \times P_R \times P(E_{corr} > E_{crit}) \times P_{WF}$
  - P_T – probability for a waste package (WP) to be a radionuclide source
  - P_S – probability for water to contact a WP
  - P_R – probability of existence of initiation sites (e.g., crevices or stressed regions) on the WP, including availability of concentrated solutions to support corrosion processes
  - $P(E_{corr} > E_{crit})$ – probability that E_{corr} exceeds E_{crit}
  - P_{WF} – probability that the waste form is contacted and mobilized by water
- Proposed approach disregards propagation rates, stifling, and arrest of crevice corrosion of cracks
- Only $P(E_{corr} > E_{crit})$ is estimated in detail in this study

E_{corr} and E_{crit}

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- Corrosion potential computed based on semi-empirical expression derived from electrochemical kinetics laws and experimental data
  - $E_{corr} = f(T, pH, pO_2)$
- Critical potential for LC, E_{crit_CC}, selected as the repassivation potential for CC, E_{rcrev}
  - $E_{rcrev} = f(T, [Cl^-], [NO_3^-], [HCO_3^-]$, metallurgical condition)
- Critical potential for SCC, E_{crit_SCC}, determined from slow strain rate tests conducted as function of potential and temperature
  - $E_{crit\_SCC} = f(T)$
  - Bicarbonate and chloride ions must be simultaneously present in solution for SCC to occur

Brine Compositions

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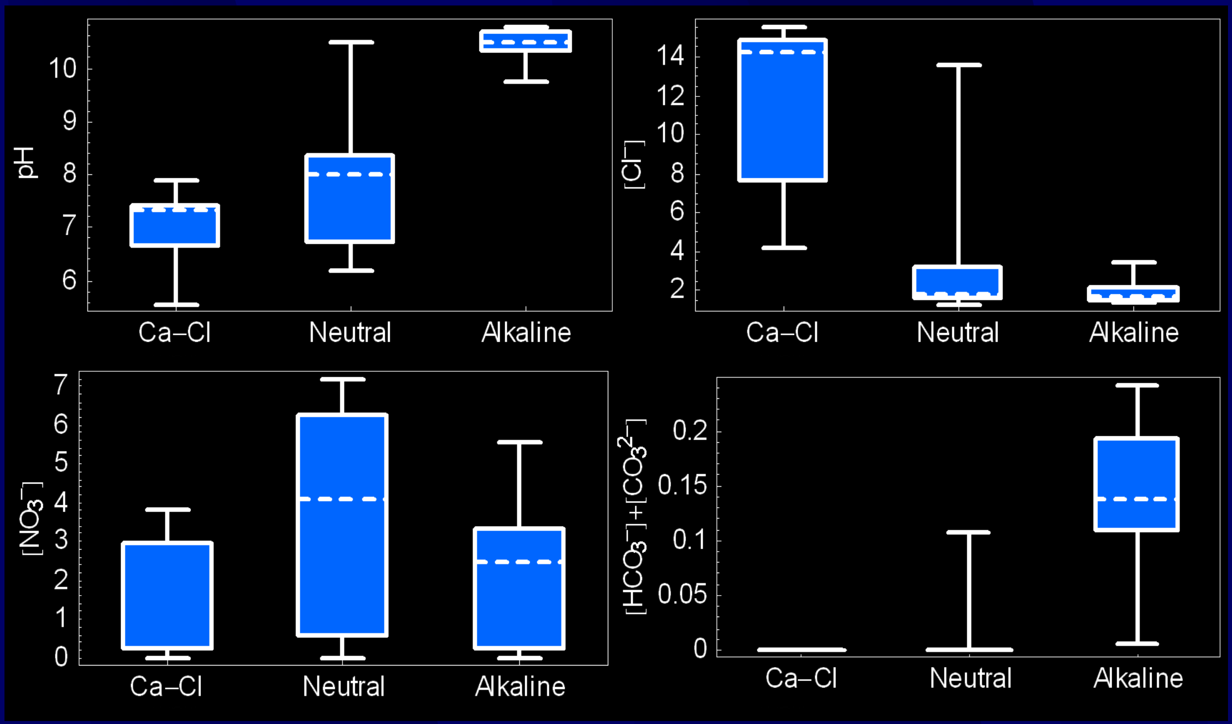
110 °C [230°F] and 0.44 atm [6.5 psi]



Concentration units in mol/L

Calculations repeated for temperatures 50, 70, 90, and 110 °C [122, 158, 194, and 230 °F]

- Thermodynamic simulations of water evaporation using Yucca Mountain porewater compositions as input
- A chemical divide approach was used to classify 156 Yucca Mountain porewaters into 8, 24, and 68 percent calcium chloride-, neutral- and alkaline-type brines, respectively.
- Numerical probability distribution functions derived as well as correlation matrices

Brine Compositions

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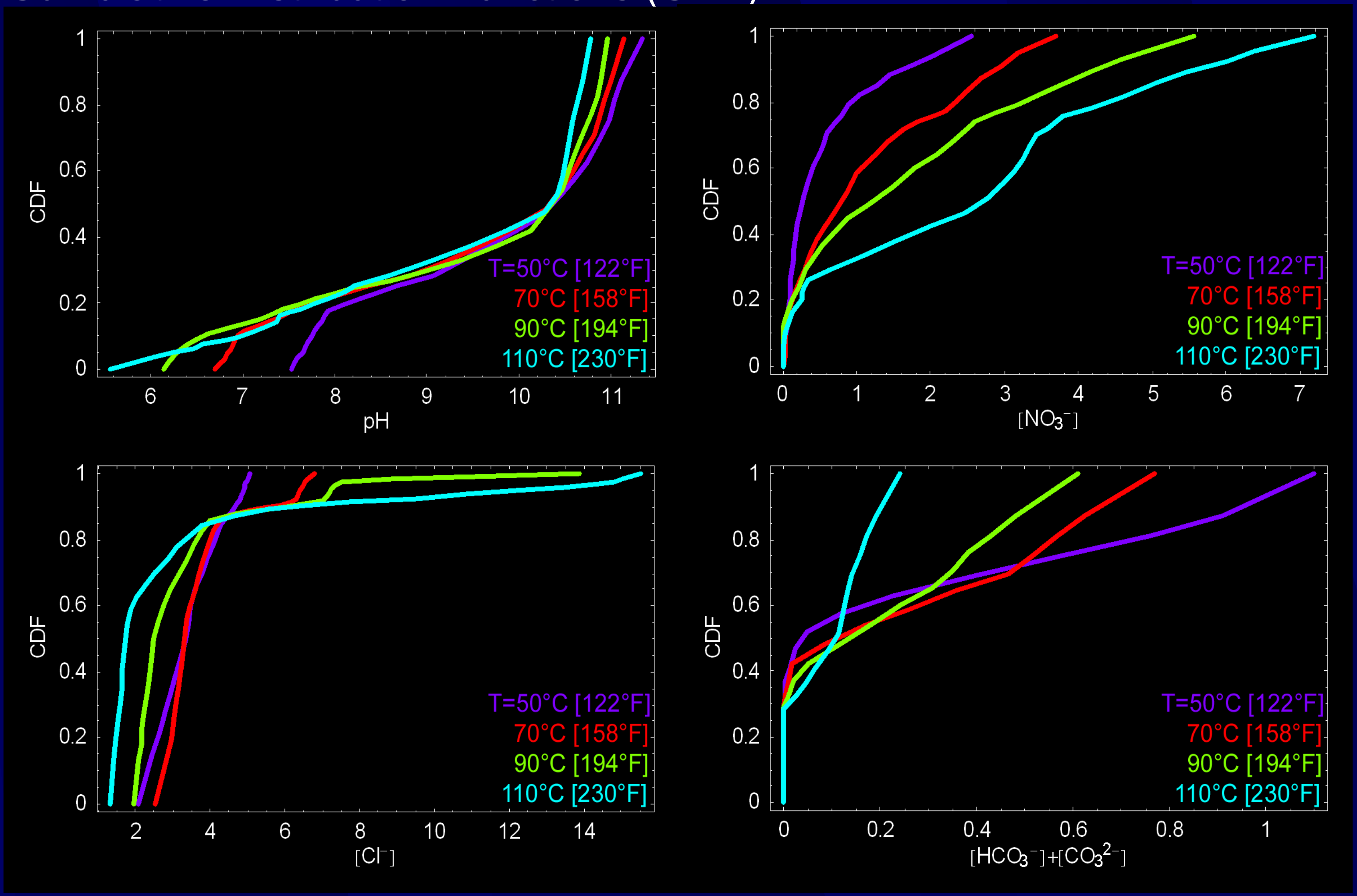
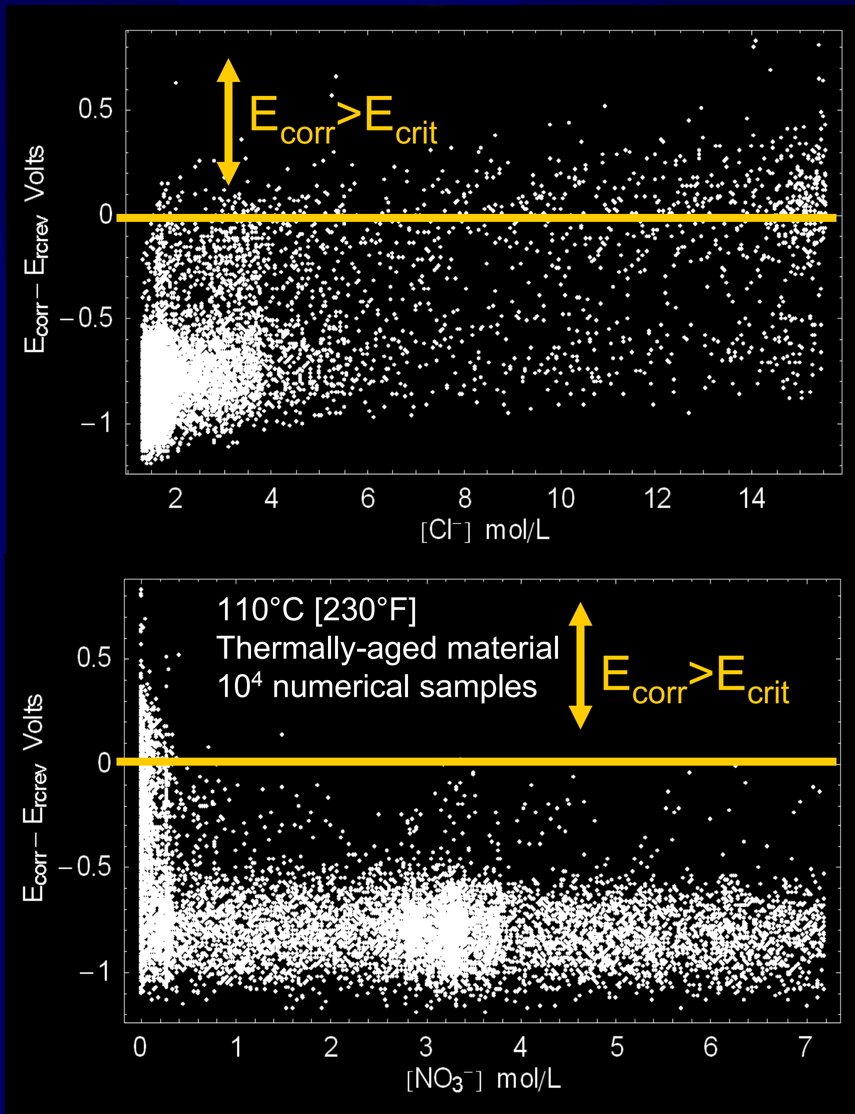
Cumulative Distribution Functions (CDF)



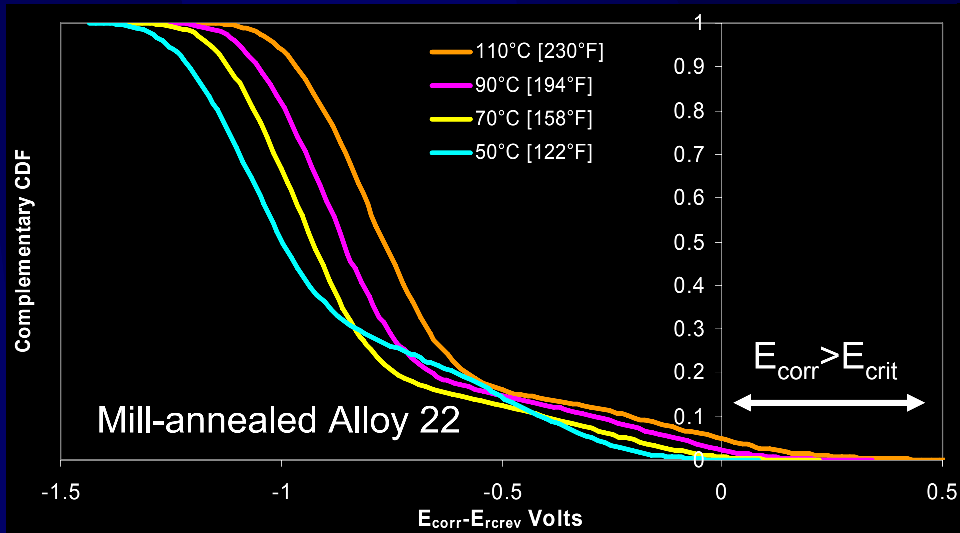
Concentration units in mol/L

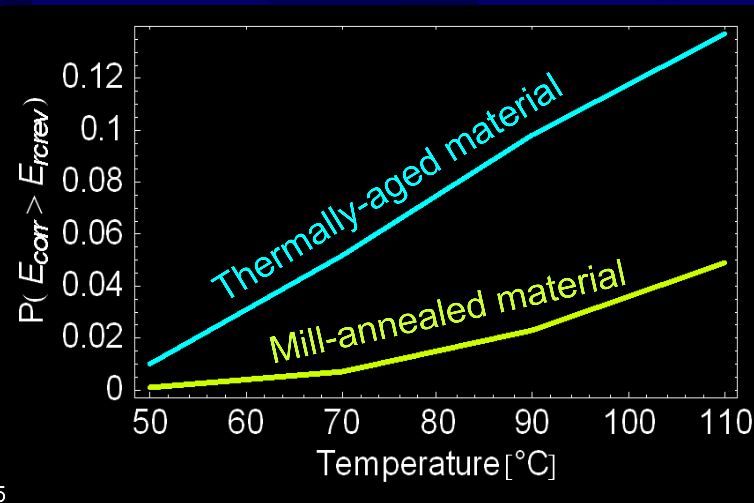
Numerical Approach

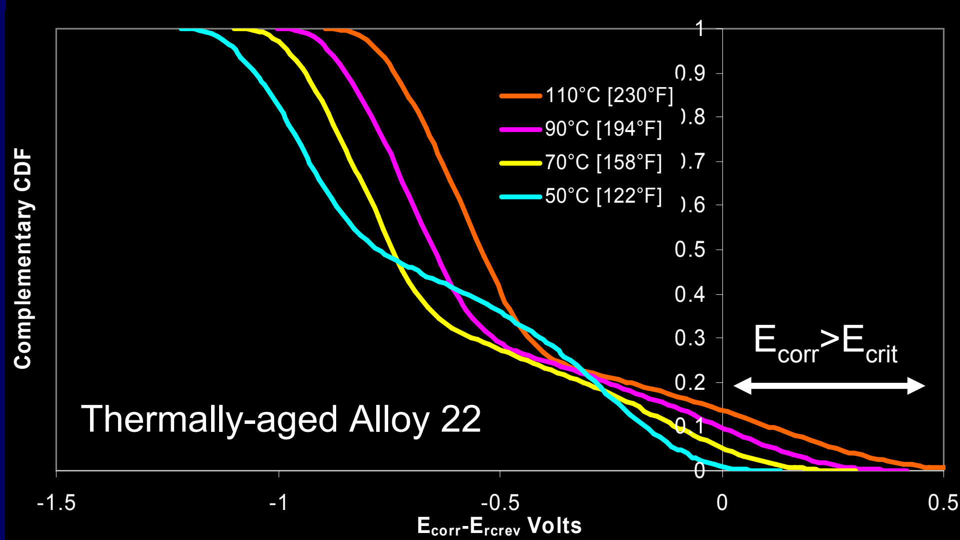


- Construct "feasible" compositions: Sample distribution functions preserving correlations
  - {[pH], $[Cl^-]$,$[NO_3^-]$,$[HCO_3^-]$+$[CO_3^{2-}]$, $[SO_4^{2-}]$}
- Count the number of samples with $E_{corr} > E_{crit}$
- The fraction of samples defines $P(E_{corr}>E_{crit})$
- Use similar process to evaluate crevice corrosion and stress corrosion cracking

Localized Corrosion Analysis

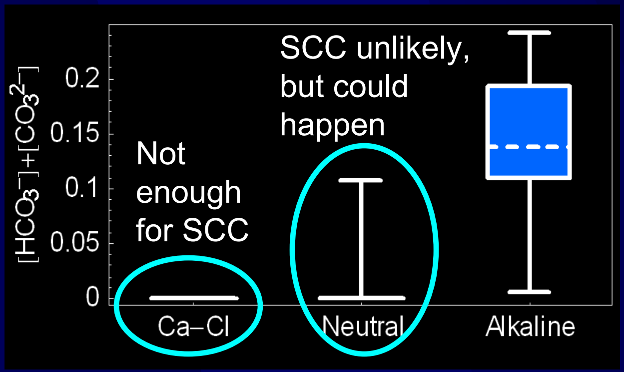






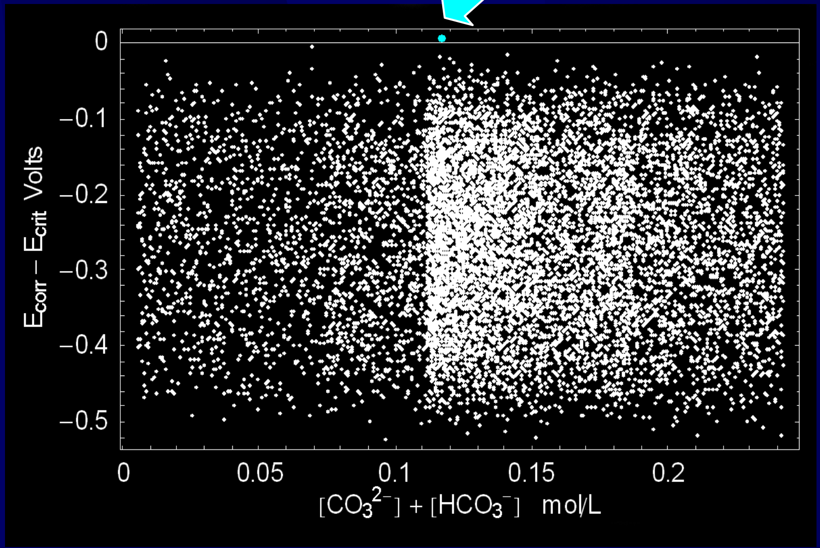
- P(E_{corr}>E_{crit}) is of the order of a few to 10 percent for localized corrosion
- Localized corrosion, in the form of CC, appears feasible in a range of temperatures

SCC Analysis



SCC is not feasible in Ca-Cl brines due to the low bicarbonate concentrations

Only point with $E_{corr} > E_{crit}$



- Neutral brines: $P(E_{corr} > E_{crit}) = 4\times10^{-5}$
- Alkaline brines: $P(E_{corr} > E_{crit}) = 4\times10^{-5}$
- Combined average: $P(E_{corr} > E_{crit}) = 4\times10^{-5}$

Alkaline brines, 110 °C [230 °F], 10^4 numerical samples

SCC Analysis

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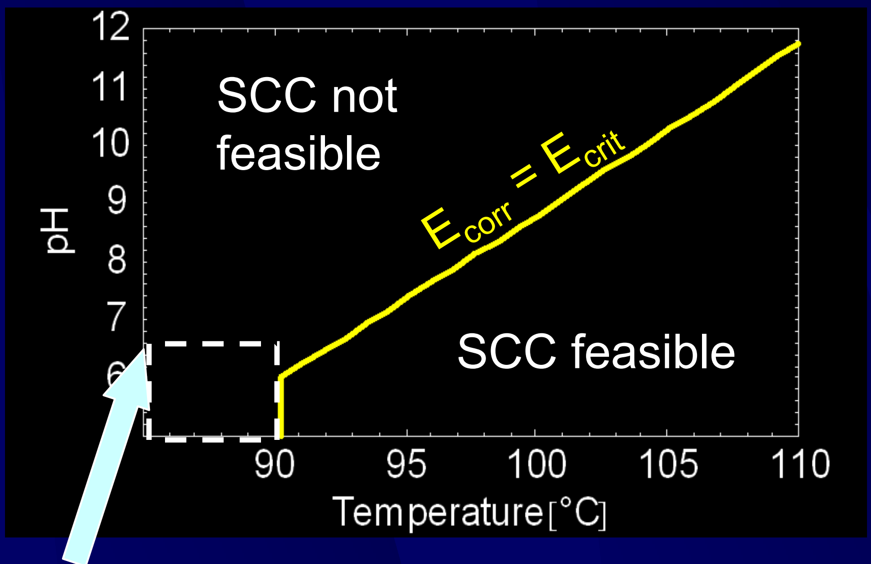

Not enough bicarbonate concentration due to pH limitations

- SCC appears not feasible at temperatures below 90°C [194°F]
- Additional experiments and data evaluation are needed to address uncertainty in E_{crit}
- Experiments needed to determine the lowest bicarbonate and chloride concentrations capable of promoting SCC

P_R and P_{WF}

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- Currently probabilities can only be assessed via expert opinion
- Opinions on P_R should account for
  - Probability of formation of crevice sites on the waste package (considering welded areas)
  - Probability of development of brines next to crevices
  - Probability of development of tensile stresses of sufficient magnitude to support propagation of SCC
  - Probability of development of brines next to stressed regions
  - Timeframes of interest
- Opinions on P_{WF} should account for
  - Size of regions compromised by CC and SCC (characteristic lengths are usually micron size)
  - Timeframes of interest

Proposed Approach for PA

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- $P_T = P_S \times P_R \times P(E_{corr} > E_{crit}) \times P_{WF}$
- Localized corrosion
  - P_S – an output of the PA model (probability for water to contact a WP)
  - P_R – agreement that $P_R<1$, but disagreement in value
    - Propose considering only order of magnitude estimates; e.g., 0.1
  - $P(E_{corr}>E_{crit})$ – an output of the PA model
  - P_{WF} – difficult to assign small values due to long timeframes
- Stress corrosion cracking
  - Disregard P_S, P_R, and P_{WF}
  - Consider value of $P(E_{corr} > E_{crit})$ as a recurrence rate for a Poisson distribution
    - $P_n = (\lambda W)^n \exp(-\lambda W)/n!$
    - n = number of waste packages with SCC
    - $\lambda = P(E_{corr} > E_{crit}) = 4\times10^{-5}$; W=total number of waste packages in the system

Conclusions

- Approach proposed to support total system performance assessments and estimate radionuclide release consequences associated with CC and SSC
- Crevice corrosion
  - $P(E_{corr} > E_{crit})$ estimated of the order of a few to 10 percent
  - It is recommended to include representation of LC accounting for uncertainty in water compositions in a PA model
- Stress corrosion cracking
  - $P(E_{corr} > E_{crit})$ estimated of the order of 4×10^{-5}
  - It is reasonable to estimate the number of WPs affected by SCC using a Poisson distribution

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Acknowledgment

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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.

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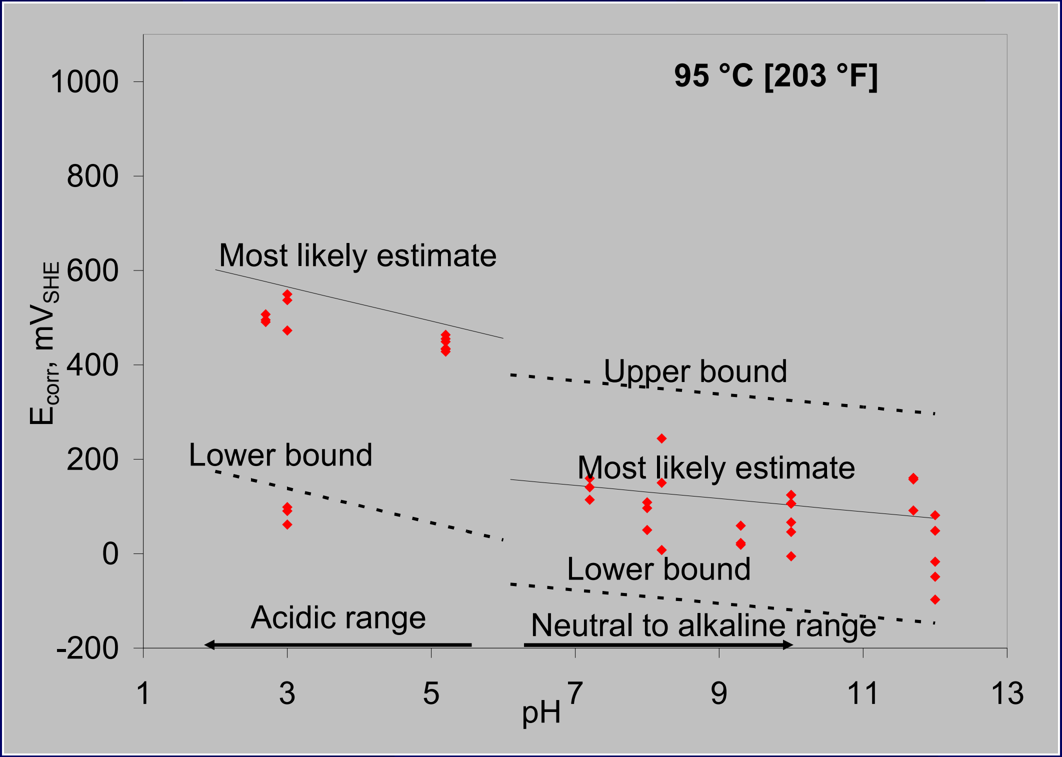
Corrosion Potential, E_{corr}



- $E_{corr} = f(T, pH, pO_2)$
- E_{corr} is a decreasing function of the temperature
- E_{corr} decreases with increasing pH, with a substantial drop around pH 6
- E_{corr} uncertainty is assumed to be due to uncertainty in anodic current density

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

$$i_a^o \in (5\times10^{-9}, 2\times10^{-8})\ \mathrm{A/cm^2}\ \text{at}\ T_{ref}^a = 95^\circ \mathrm{C}$$

D.S. Dunn, O. Pensado, Y.-M. Pan, R.T. Pabalan, L. Yang, X. He, and K.T. Chiang. “Passive and Localized Corrosion of Alloy 22—Modeling and Experiments.” CNWRA 2005-02, San Antonio, Texas (2005).

Repassivation Potential, E_{rcrev}

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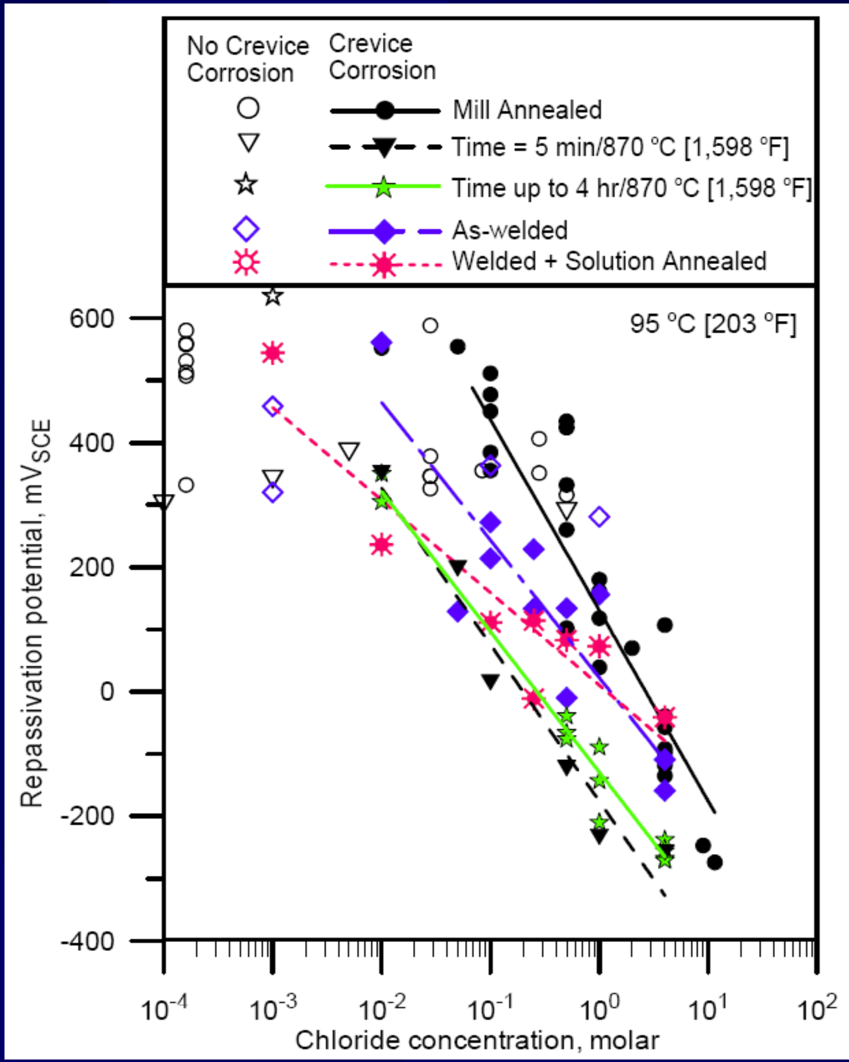

- Thermally aged and welded materials are more susceptible to localized corrosion than mill-annealed material

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

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

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

D.S. Dunn, O. Pensado, Y.-M. Pan, R.T. Pabalan, L. Yang, X. He, and K.T. Chiang. “Passive and Localized Corrosion of Alloy 22—Modeling and Experiments.” CNWRA 2005-02, San Antonio, Texas (2005).

Effect of Inhibitors

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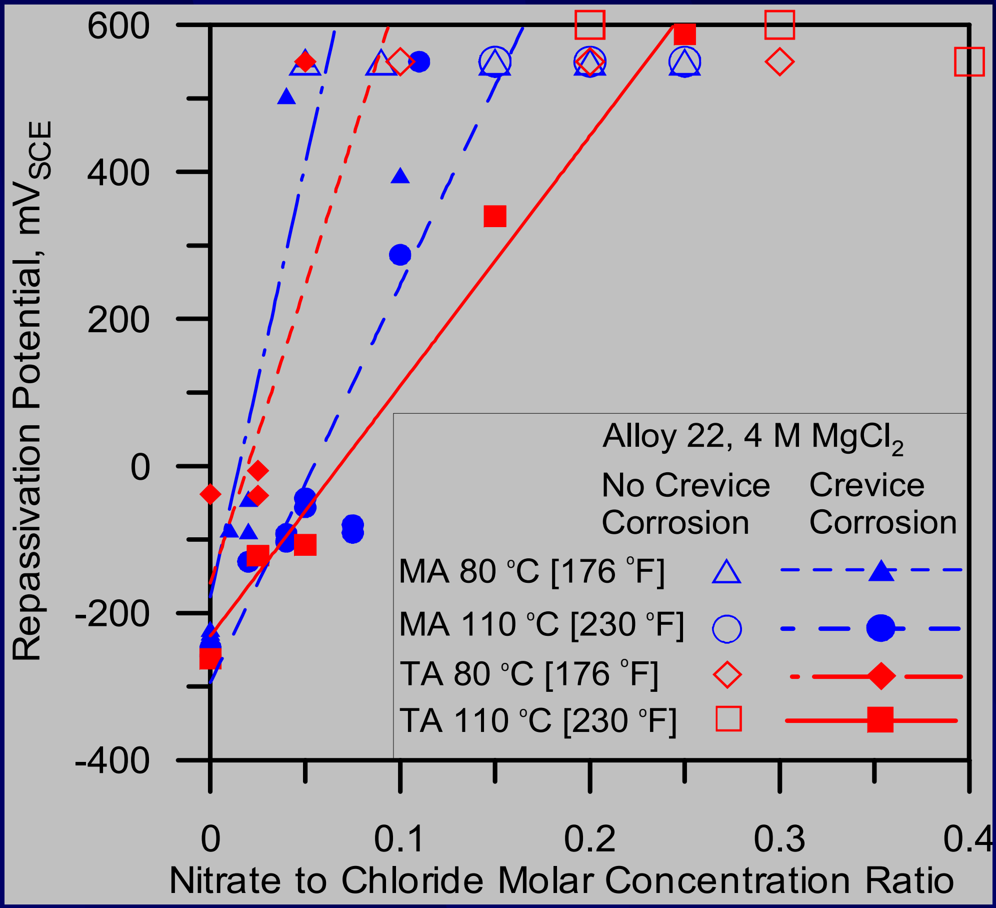

- Nitrate is an effective localized corrosion inhibitor
- Nitrate effect modeled as an increase in E_{rcrev} as a function of [inhibitor]/[Cl$^-$]
- Inhibitors (carbonate-bicarbonate, nitrate, and sulfate) considered assuming independent additive effects on E_{rcrev}

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

$$r = \frac{[\mathrm{NO_3^-}]}{[\mathrm{Cl^-}]} + \frac{r_n}{r_s}\frac{[\mathrm{SO_4^{2-}}]}{[\mathrm{Cl^-}]} + \frac{r_n}{r_c}\frac{[\mathrm{CO_3^{2-}}]+[\mathrm{HCO_3^-}]}{[\mathrm{Cl^-}]}$$

D.S. Dunn, O. Pensado, Y.-M. Pan, R.T. Pabalan, L. Yang, X. He, and K.T. Chiang. “Passive and Localized Corrosion of Alloy 22—Modeling and Experiments.” CNWRA 2005-02, San Antonio, Texas (2005).

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Repassivation Potential, E_{rcrev}

	Mill-annealed	Thermally-aged
A_1 [mV_{SHE}]	(1025, 1336.5) Assumed symmetric triangular distribution	(991.2, 1091.2) Assumed symmetric triangular distribution
A_2 [mV/°C]	-9.35	-10
B_1 [mV]	-752	-584.2
B_2 [mV/°C]	5.2	3.7
r_n	0.1	0.3
r_c	0.2	0.2
r_s	0.5	0.5

D.S. Dunn, O. Pensado, Y.-M. Pan, R.T. Pabalan, L. Yang, X. He, and K.T. Chiang. “Passive and Localized Corrosion of Alloy 22—Modeling and Experiments.” CNWRA 2005-02, San Antonio, Texas (2005)

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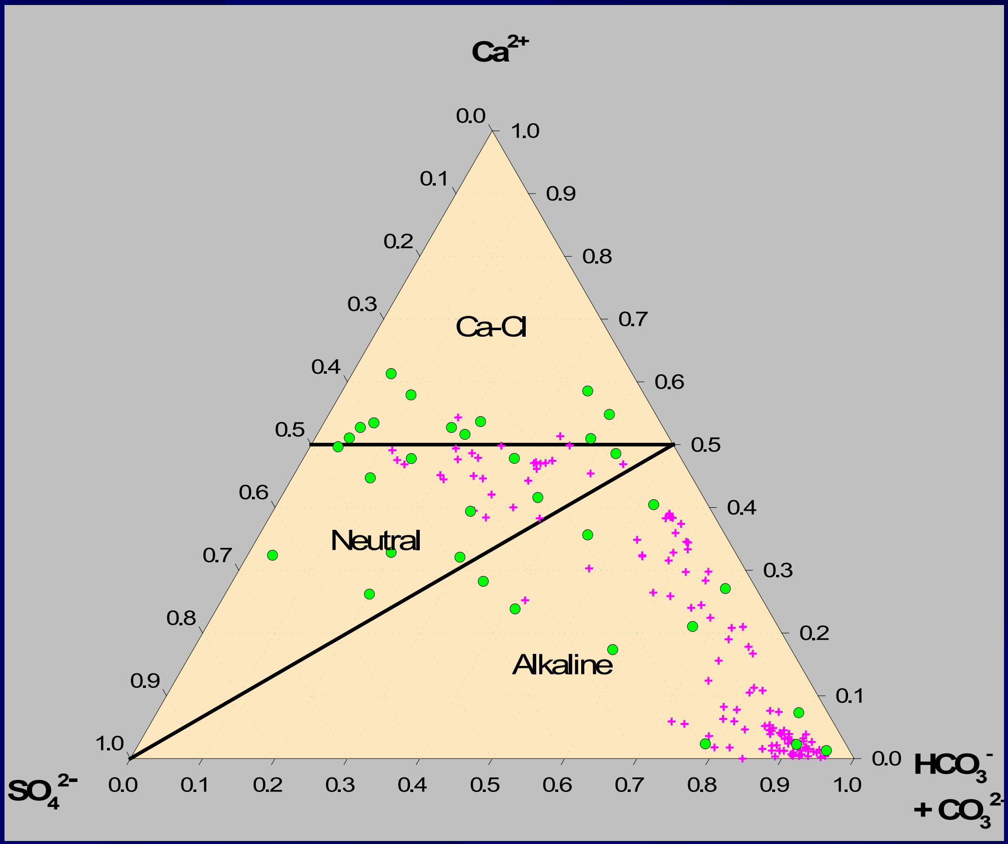
Thermodynamic Modeling



- Chemistry data (+) on Yucca Mountain (YM) unsaturated zone porewaters published by USGS (Yang et al., 1996, 1998, 2003)
- Data on selected samples (●) used as input
  - Seepage water assumed similar to ambient YM porewaters
  - Neglected interactions with natural and in-drift engineered materials
- Supplemented by chemical divide approach
  - Three brine types: calcium-chloride, neutral, and alkaline

D.S. Dunn, O. Pensado, Y.-M. Pan, R.T. Pabalan, L. Yang, X. He, and K.T. Chiang. “Passive and Localized Corrosion of Alloy 22—Modeling and Experiments.” CNWRA 2005-02, San Antonio, Texas (2005).