Stress Corrosion Cracking Model for Alloy 22 in the Potential Yucca Mountain Repository Environment

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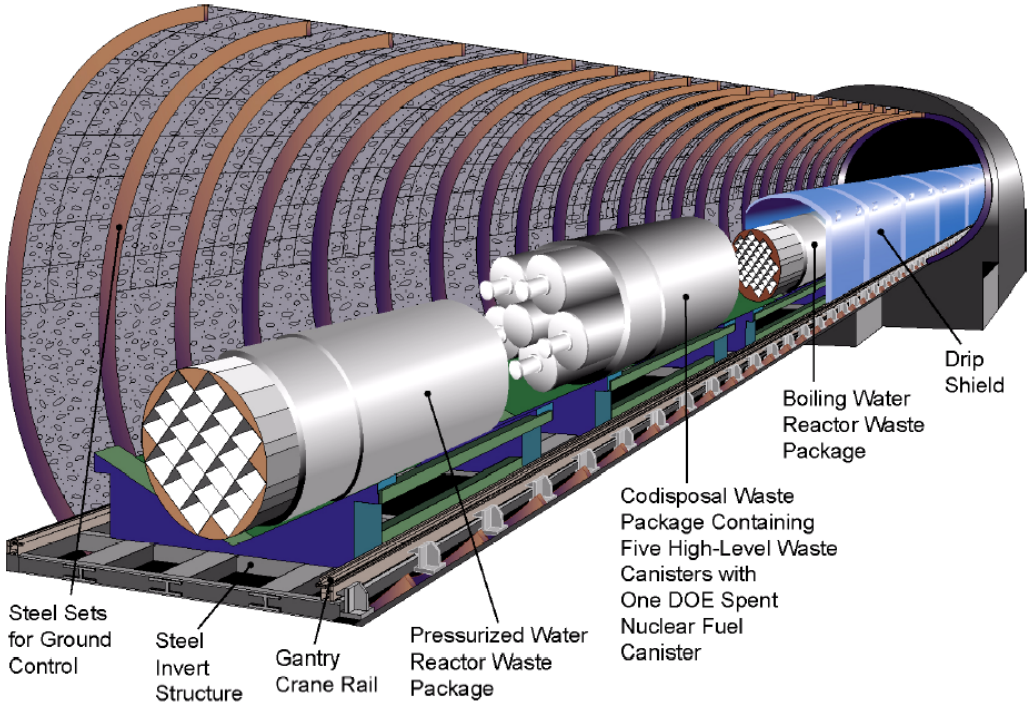
Outline

- Background
- Objective and Scope
- Stress Corrosion Cracking (SCC) Model Abstraction
  - Corrosion potential model
  - Speciation calculations
  - Analysis of slow strain rate test data
- Detection of Environmental Conditions for SCC
- Summary

Background

- Alloy 22 has been Identified as the Potential Waste Package Outer Barrier Material
- SCC is a Possible Mode of Failure for Waste Packages
- Radionuclides could be Released into the Aqueous Environment Through Stress Corrosion Cracks



Background (Continued)

- SCC Susceptibility of Alloy 22 has been Experimentally Evaluated in Basic Saturated Water, Simulated Acidified Water, and Simulated Concentrated Water Using
  - Slow strain rate tests and constant deformations tests at applied potentials
  - Cyclic and constant load tests to measure crack growth rate as a function of stress intensity factor

- Tensile Stresses of Sufficient Magnitude may Exist on the Waste Packages to Induce SCC

Composition of Water Chemistries Used in SCC Tests

Ion	Simulated Concentrated Water (mg/L)	Simulated Acidified Water (mg/L)	Basic Saturated Water (mg/L)
K^+	3.4×10^3	3.4×10^3	6.762×10^4
Na^+	4.09×10^4	3.769×10^4	1.0584×10^5
Mg^{2+}	< 1	1.0×10^3	0
Ca^{2+}	< 1	1.0×10^3	0
F^-	1.4×10^3	0	1.47×10^3
Cl^-	6.7×10^3	2.425×10^4	1.3083×10^5
NO_3^-	6.4×10^3	2.3×10^4	1.3965×10^6
SO_4^{2-}	1.67×10^4	3.86×10^4	1.47×10^4
HCO_3^-	7.0×10^4	0	0
Si	27 [60 °C], 49 [90 °C]	0	0
pH	9.8 to 12	2.7	12

K.G. Moon, F. Hua, "Materials Degradation Issues in the U.S. High-Level Nuclear Waste Repository." 12th International Conference on Environmental Degradation of Materials in Nuclear Systems–Water Reactors. Salt Lake City, Utah. The Minerals, Metals and Materials Society. 2005.

Objective and Scope

- Develop an Abstracted Model for SCC that Accounts for Environmental Conditions Such as
  - Temperature
  - Groundwater chemistry
  - pH
  - Electrochemical potential of Alloy 22

- Stress Corrosion Cracking Abstraction Can be Used as a Tool to Calculate Probabilities for Waste Package Failure in Repository Settings

Criterion and Conditions for SCC

- SCC Will Occur if Corrosion Potential E_{corr} of the Alloy in an Environment Is Greater Than the Critical Potential for SCC E_{scc}:

$$E_{corr} - E_{scc} \geq 0$$

- Environmental Conditions:
  - Sixty-three slow strain rate test data points were analyzed to evaluate environmental conditions that promote SCC
  - The dependence of SCC susceptibility of Alloy 22 on temperature, solution composition, pH, and electrochemical potential was identified

Corrosion Potential Model

$$E_{corr} = \frac{E_a^a - E_a^{ef}}{Z_r \beta_r^{ef} F} - \frac{E_a^a T}{Z_r \beta_r^{ef} F T_{ref}^a} + \frac{RT}{Z_r \beta_r^{ef} F} \ln\left[\left(\frac{[H^+]}{c_0}\right)^{n_H} \left(\frac{p_{O_2}}{p_o}\right)^{n_o} \frac{i_r^{ef}}{i_a^o} \frac{C_{O_2}^{bulk}(T)}{C_{O_2}^{bulk}(T_{ref})}\right]$$

E_a^a – activation energy (anodic current)

E_a^{ef} – effective activation energy

Z_r – electrons in the cathodic reduction

T_{ref}^a – reference temperature

i_a^o – anodic current density at T_{ref}^a

F – Faraday's constant $= 96488$

i_r^{ref} – reference current density

$C_{O_2}^{bulk}(T)$ – oxygen concentration

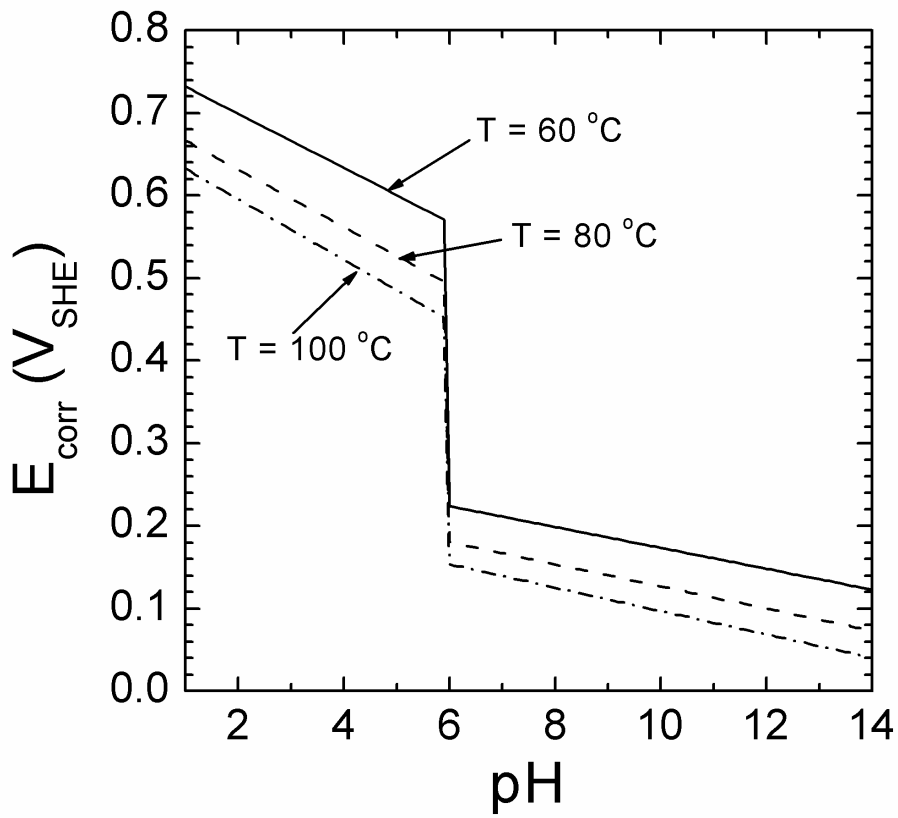
β_r^{ef} – effective charge transfer coefficient

n_H, n_o – dimensionless constants

p_{O_2} / p_0 – 0.21

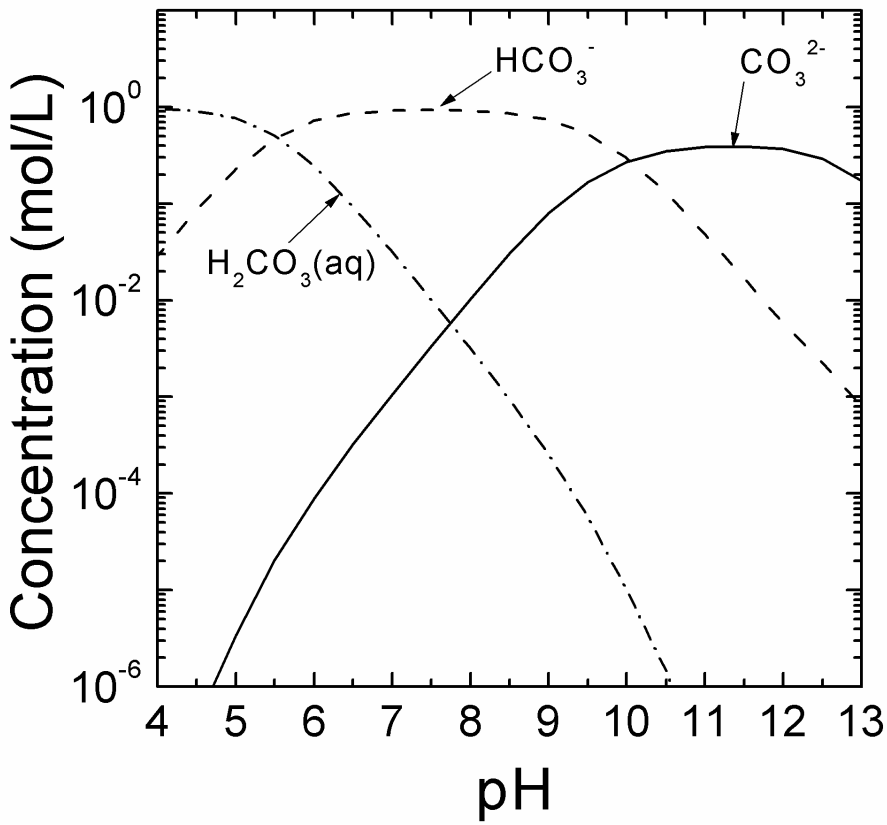
D.S. Dunn, O. Pensado, Y.-M. Pan, R.T. Pabalan, L. Yang, X. He, and K.T. Chiang. "Passive and Localized Corrosion of Alloy 22—Modeling and Experiments." CNWRA 2005-02. San Antonio, Texas: CNWRA. 2005.

Corrosion Potential Measurement and Model



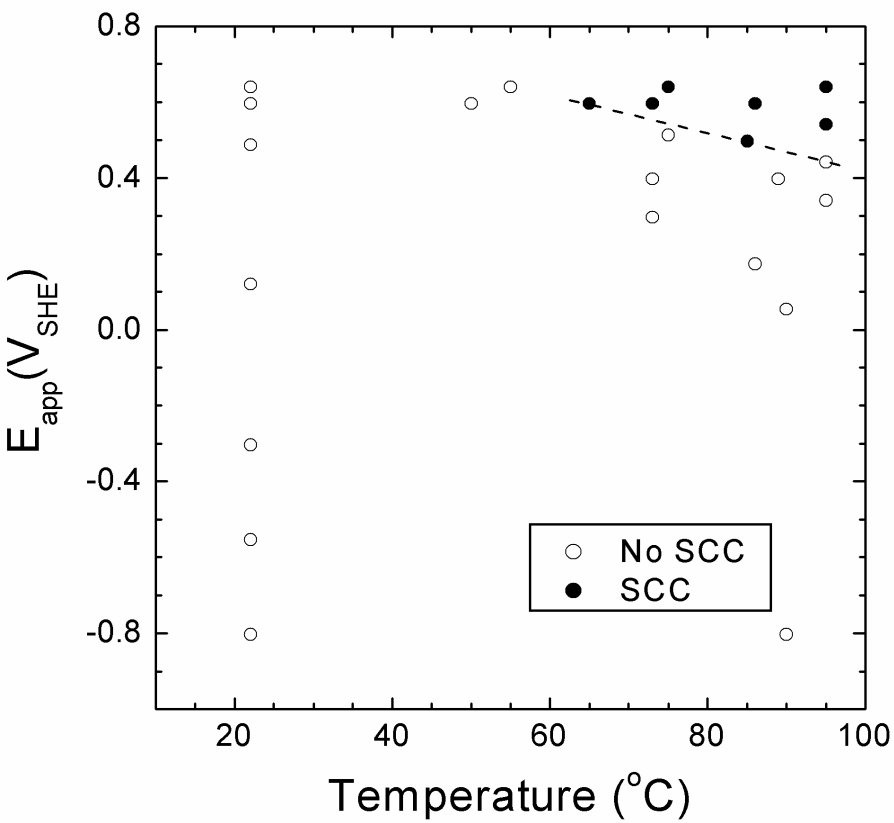
- Corrosion Potential in Aerated Solutions Containing Groundwater Anions (HCO_3^-, CO_3^{2-}, Cl^-, SO_4^{2-}, NO_3^-, F^-) Decreases With Temperature
- Sharp Transition at pH Equal to 6
  - H^+ ion reduction reaction predominates at low pH
  - O_2 reduction reaction at high pH
- $E_{corr} < 0.3\ V_{SHE}$ at pH > 6

Speciation Effects in Carbonated Waters



- Simulations for a Closed System
  - Total carbonate equal to 1.0 mol/L
  - 1.0 mol/L sodium chloride at 95 °C [203 °F]
- For the Closed System, at Low pH, HCO_3^- Concentration Is Higher Due to the Presence of H_2CO_3
- HCO_3^- Ions Dominate in pH Ranging From 6 to 10
- CO_3^{2-} is the Predominant Species at pH > 10
- At the Potential Yucca Mountain Repository, $H_2CO_3(aq)$ Concentrations Will Be Low, and a Near Neutral Environment Is Expected

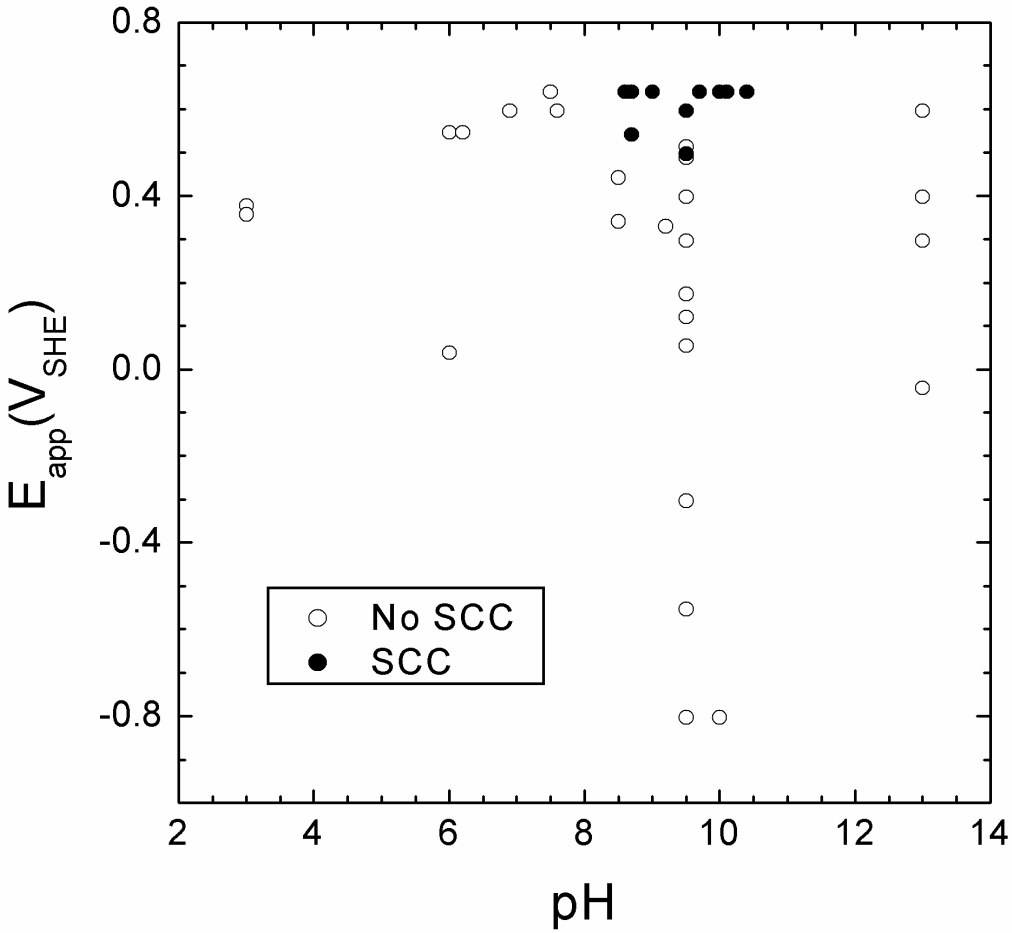
E_{app} Versus Temperature: Slow Strain Rate Tests



- 80 Percent Normalized Time to Failure Criterion (t_f/t_{fair}) Was Used for SCC Susceptibility
  - t_f: sample failure time
  - t_{fair}: sample failure time in air
- Relationship Between E_{app} Versus Temperature was Obtained by Fitting a Straight Line

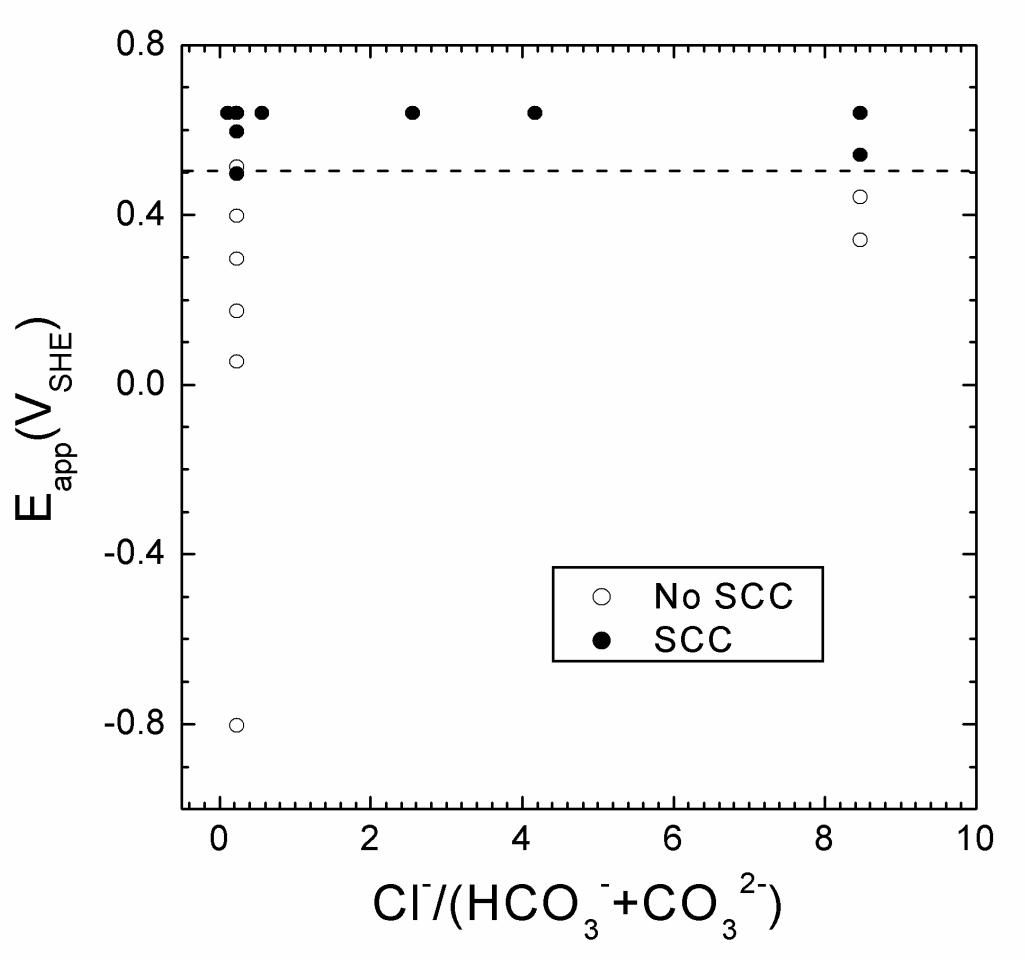
$$E_{app}(V_{SHE}) = [1 - 0.0084(T - 65)] \times 0.597$$

E_{app} Versus pH: Slow Strain Rate Tests



- SCC Is Observed
  - $8.5 < pH < 10.5$
  - $E_{app} > 0.5\ V_{SHE}$

E_{app} Versus $Cl^-/(HCO_3^- + CO_3^{2-})$: Slow Strain Rate Tests



$$[Cl^-] > 0.09\,M$$

$$\frac{[Cl^-]}{[HCO_3^-] + [CO_3^{2-}]} > 0.12$$

Proposed SCC Abstraction

- Model for SCC Was Obtained by Lowering E_{app} Versus Temperature by 0.05 V_{SHE} (To Account for Measurement Uncertainties and Strain Rate Effects)

$$E_{SCC}(V_{SHE}) = [1 - 0.0084(T - 65)] \times 0.55$$

- Temperature Would Have to Be Greater Than 65 °C [149 °F]

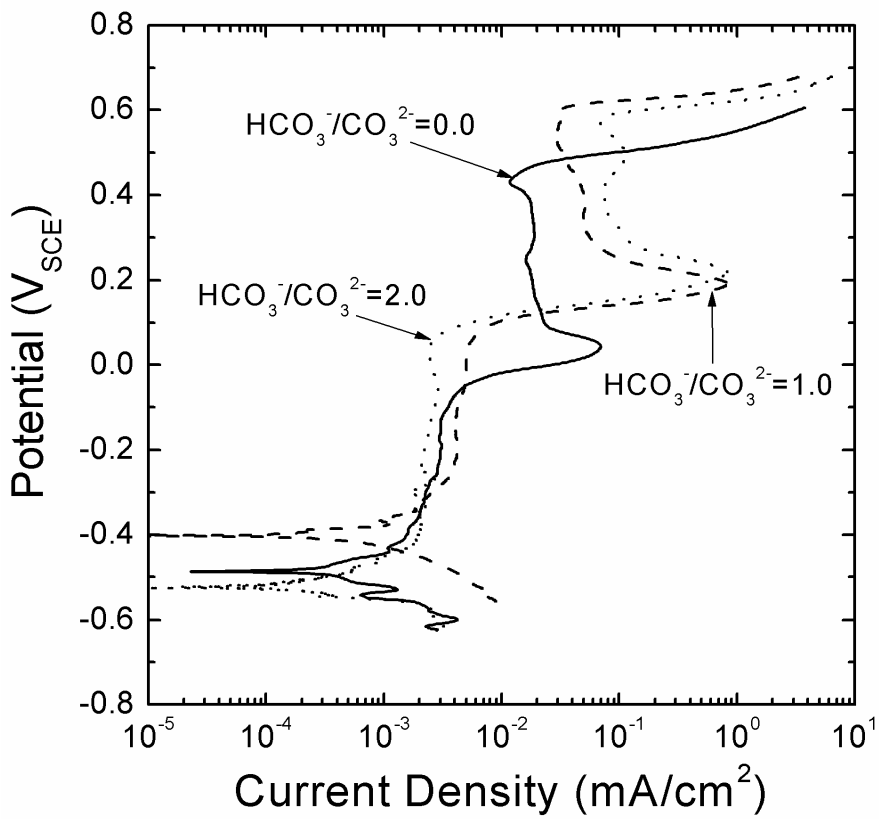
  E_{scc} at 95 °C [203 °F] = 0.41 V_{SHE}

- Test Solutions With Chloride, Bicarbonate, and Carbonate Ions Would Have to Satisfy the Following Criterion:

$$\frac{[Cl^-]}{[HCO_3^-] + [CO_3^{2-}]} > 0.12$$

$$[Cl^-] > 0.09\,M$$

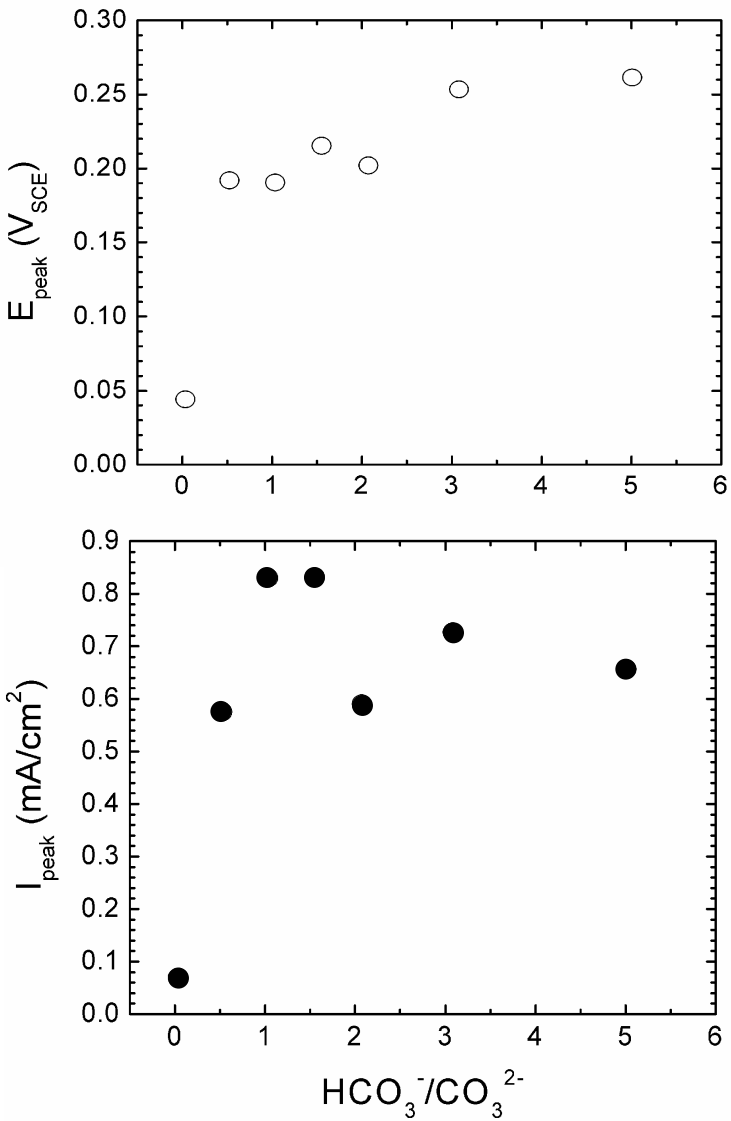
Electrochemical Detection of Environmental Conditions That Induce SCC



- Polarization Tests Were Conducted With Cylindrical Samples in Solutions Containing Cl^-, CO_3^{2-}, and HCO_3^- Ions
  - To evaluate water compositions that promote SCC
  - Approach is similar to one adopted by R.N. Parkins for determining SCC susceptibility of low strength ferritic steel
  - Peak current in the anodic potential range relates to SCC susceptibility

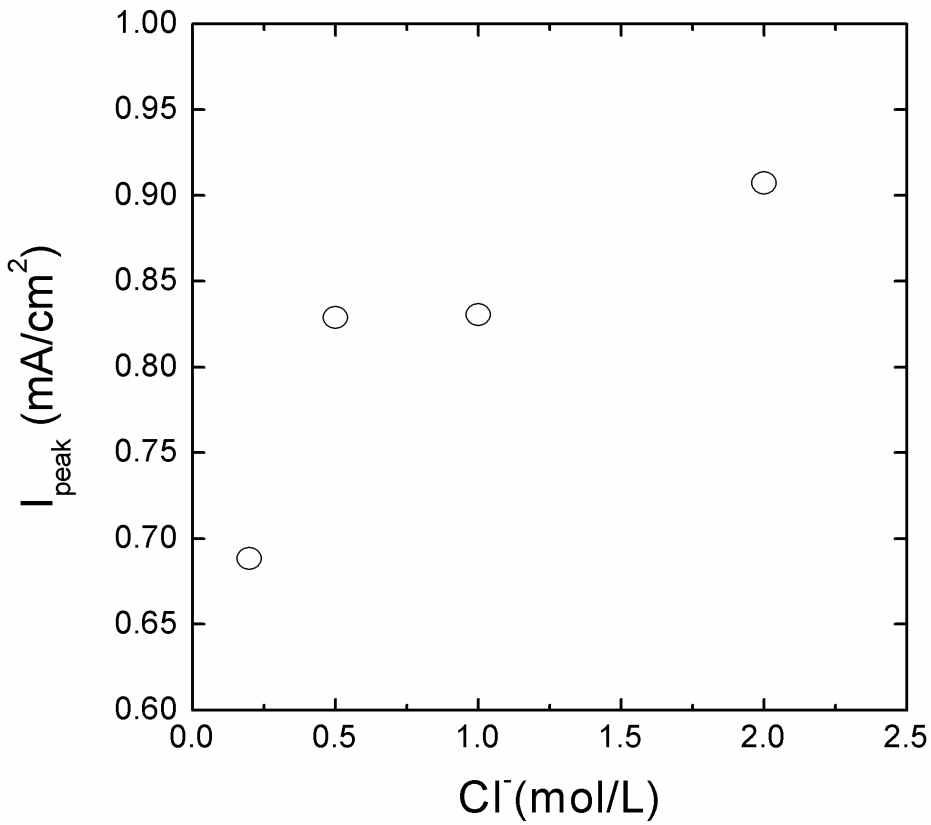
R.N. Parkins. "Environmental Aspects of Stress Corrosion Cracking in Low Strength Ferritic Steels." NACE–05, pp. 601–624, NACE International, Houston, Texas. 1977.

Cyclic Potentiodynamic Polarization: Peak Potential and Current Density



- At $[HCO_3^-]/CO_3^{2-}] > 0.5$, $I_{peak} > 0.5$ mA/cm^2, and $0.18\ V_{SCE} < E_{peak} < 0.27\ V_{SCE}$
- Experimental Details
  - 0.5 M $[Cl^-]$ concentration at 95 °C [203 °F]
  - Test solutions were purged with nitrogen to remove dissolved oxygen
  - Potential scan rate: 0.167 mV/sec
  - Total carbonate was fixed at 0.74 M
- Equilibrated Concentrations of CO_3^{2-} and HCO_3^- Ions were Determined by Speciation Calculations

Cyclic Potentiodynamic Polarization: Peak Current Density Versus Chloride Ion Concentration



- Peak Current Increases With Increasing Cl^- Ion Concentration
- Results Are Analogous to Slow Strain Rate Tests Where SCC Susceptibility Increases With Cl^- Ion Concentration
- Test Solution: 0.74 mol/L Total Carbonate
- $HCO_3^-/CO_3^{2-} = 2.0$

Summary

- The Corrosion Potential Model Predicts That the Corrosion Potential of Alloy 22 Is Less Than 0.3 V_{SHE} in the pH range of 6 to 14

- Speciation Calculations
  - Bicarbonate ions dominate in the pH range of 6 to 10
  - Carbonate is the predominant species at pH > 10

- The Proposed Suggests that SCC Susceptibility of Alloy 22 Is Increased
  - In bicarbonate and chloride ion solutions
  - In the pH range of 8 to 11—bicarbonate ions cannot exist in the solution at pH < 6
  - In simulated concentrated water
  - If corrosion potential is higher than SCC potential

- SCC Susceptibility of Mill-Annealed Alloy 22 Is Low Under Potential Repository Environments Because Conditions Where the Critical Potentials in Aerated Solutions Are Higher Than Critical Potential for SCC Are Not Easily Achieved

Acknowledgments and Disclaimer

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