Crevice Corrosion Penetration Rates of Alloy 22 in Chloride-Containing Waters

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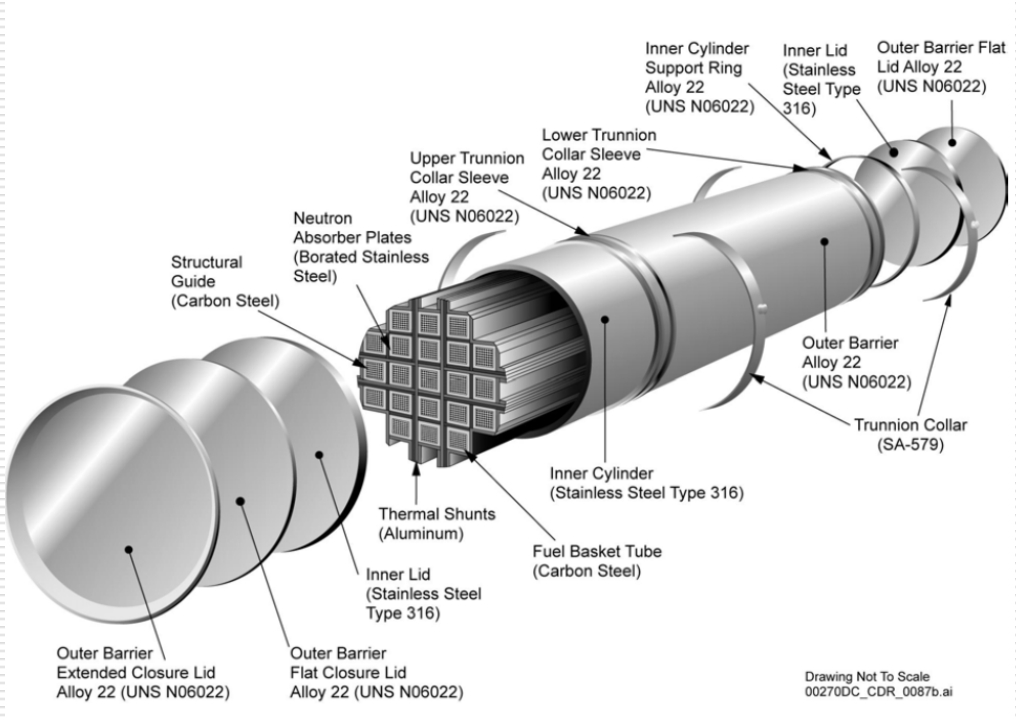
Outline

- Background
- Objectives
- Experimental Setup
- Test Results on Alloy 22 Crevice Corrosion
- Summary

High-Level Waste Disposal



- Engineered barrier system for the potential Yucca Mountain Repository
- Alloy 22 outer container
- Corrosion modes
  - Dry-air oxidation
  - Uniform corrosion
  - Loss of passivity
  - Localized (Crevice, Pitting, MIC) corrosion
  - Stress corrosion cracking

DOE. "Yucca Mountain Science and Engineering Report—Technical Information Supporting Site Recommendation Consideration." DOE/RW-0539-1. Rev. 1. Las Vegas, Nevada: DOE, Office of Civilian Radioactive Waste Management. 2002.

Model for Localized (Pitting and Crevice) Corrosion Initiation

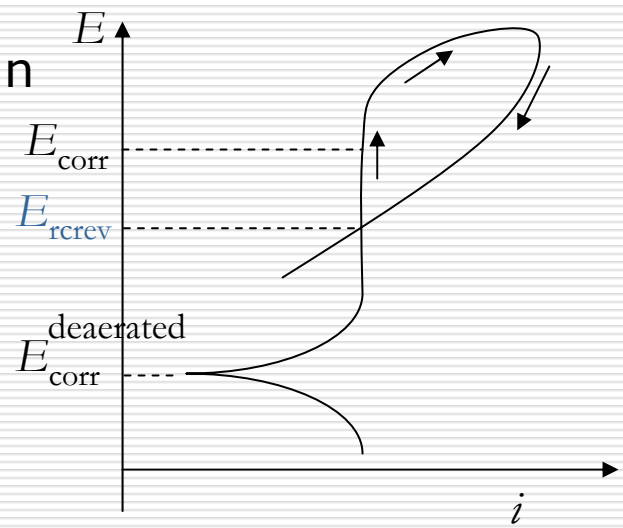
- It is assumed localized corrosion initiates if $E_{corr} > E_{rcrev}$
  - Where E_{corr} is the corrosion potential in an aerated environment

$$E_{corr} = f(T, pH, p_{O_2})$$

  - E_{rcrev} is the repassivation potential for crevice corrosion

$$E_{rcrev} = f(T, [Cl^-], [Inhibitors])$$

Typical Potentiodynamic Polarization Curve in Deaerated Solution



Inhibitors: NO_3^-, CO_3^{2-}, HCO_3^-, SO_4^{2-}

Model for Localized (Pitting and Crevice) Corrosion Propagation

- Localized corrosion propagation typically conforms to

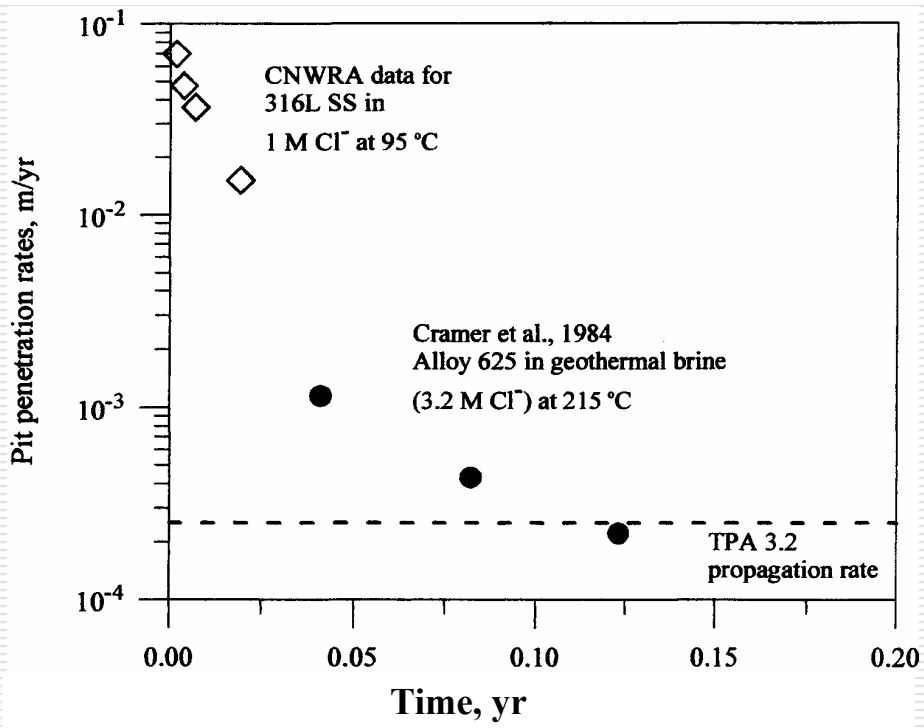
$$d = kt^n$$

d— penetration depth
t — time
n — time exponent
k — coefficient

- Total-system Performance Assessment (TPA) code

$$d = kt$$

Literature Data Supporting Penetration Rate



n = 1 and K = 0.25 mm/yr

Objectives

- Conduct laboratory tests to obtain *k* and *n* in

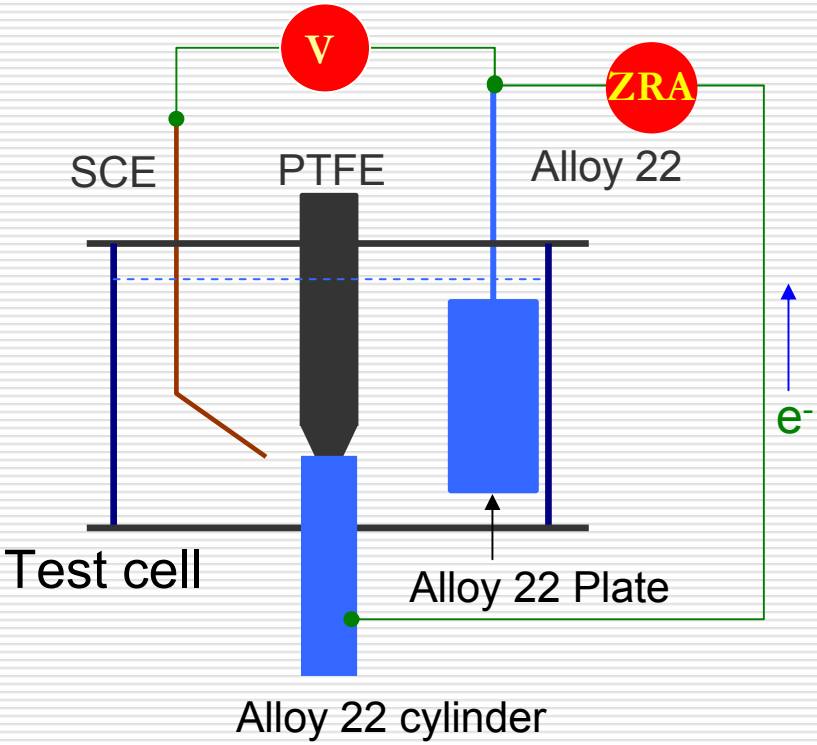
  $$d = kt^n$$

  that can be incorporated into the TPA code

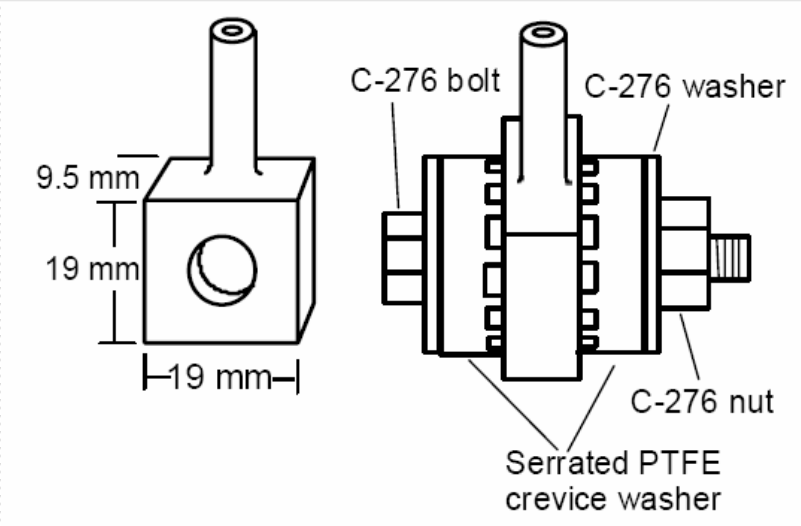
- Understand Alloy 22 localized corrosion propagation behavior as a function of environmental conditions

Experimental Setup

Single Crevice Assembly and Test Cell



Multiple Crevice Assembly (ASTM G78)



- Potentiostat functions as a zero resistance ammeter (ZRA)

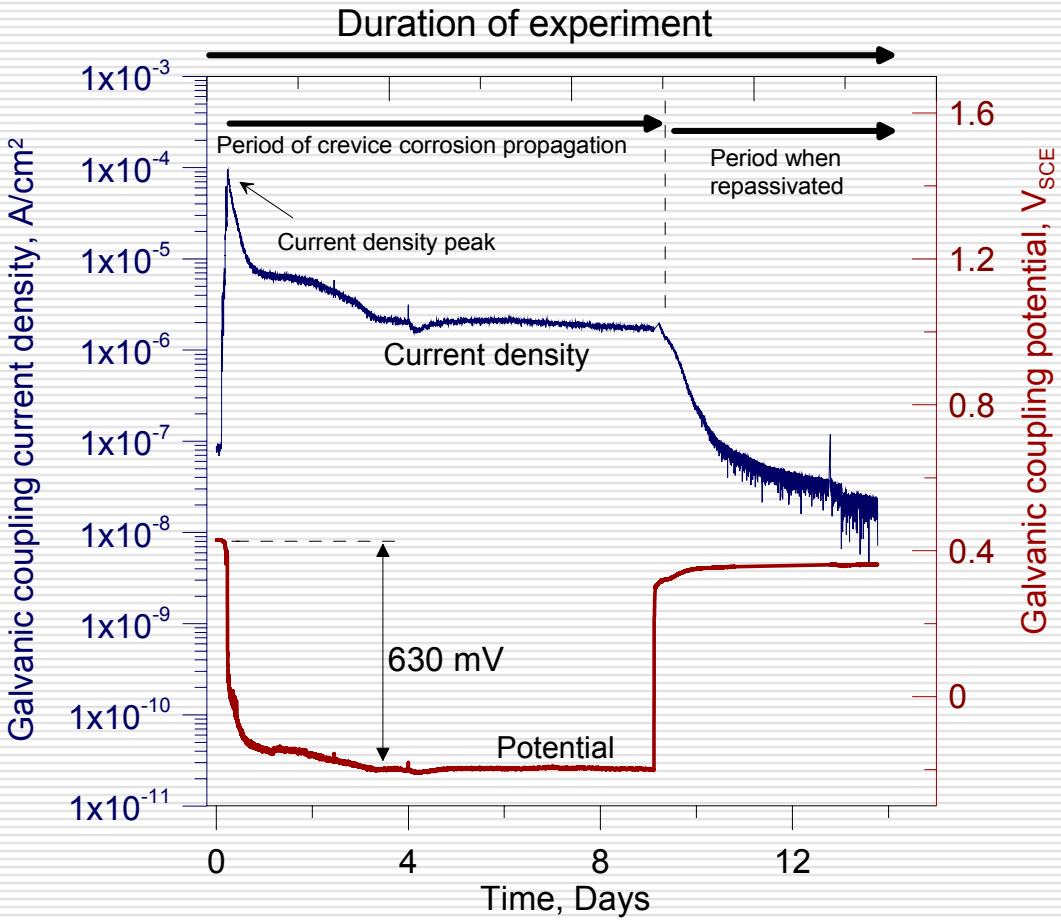
Test Conditions and Chemical Composition of Alloy 22

- Solution: 5 M NaCl + 2×10^{-4} M $CuCl_2$ (oxidant added to raise E_{corr})
- Temperature: 95 °C
- Chemical composition of Alloy 22 (in wt%)

Material	Ni*	Cr*	Mo*	W*	Fe*	Co*	Si*	Mn*	V*	P*	S*	C*
Alloy 22 Heat 2277-3-3266	Bal	21.40	13.30	2.81	3.75	1.19	0.03	0.23	0.14	0.008	0.004	0.005
Alloy 22 Heat 2277-1-3133	Bal	21.44	13.27	2.85	4.76	0.65	0.22	0.15	0.030	0.012	0.002	0.005

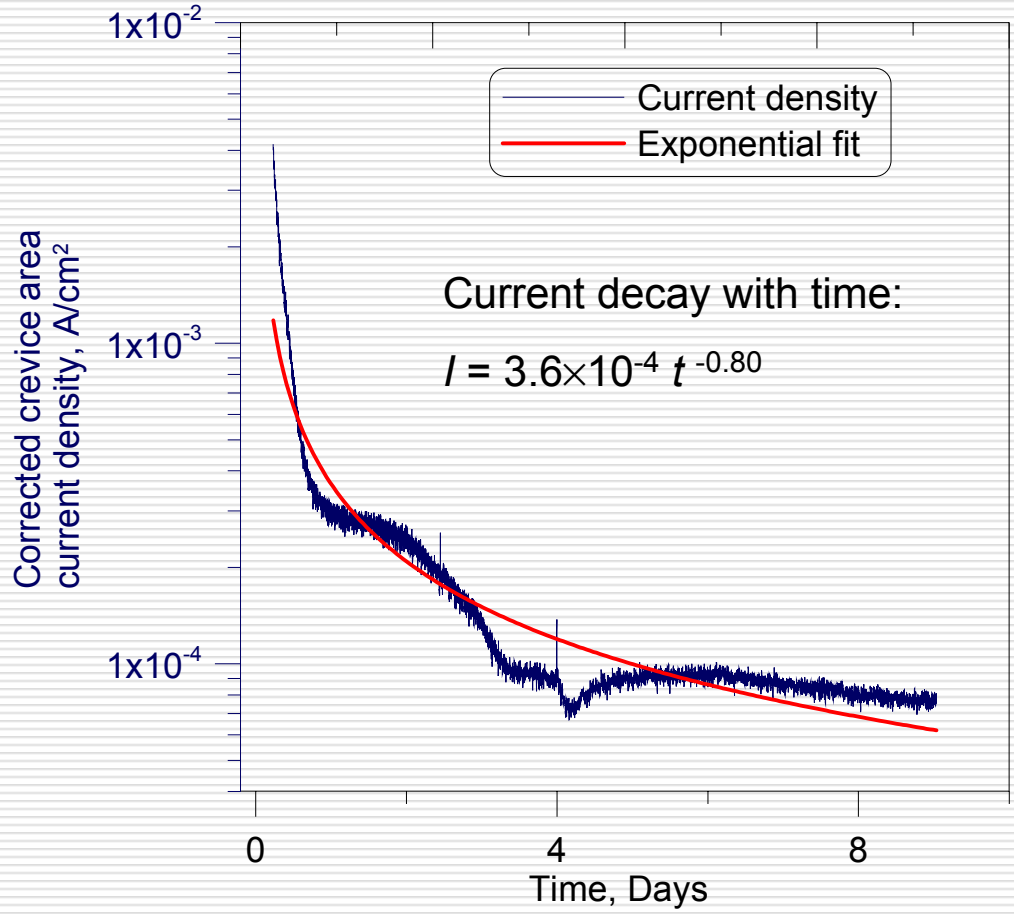
*Ni—nickel, Cr—chromium, Mo—molybdenum, W—tungsten, Fe—iron, Co—cobalt, Si—silicon, Mn—manganese, V—vanadium, P—phosphorus, S—sulfur, C—carbon

Galvanic Coupling Current and Potential from Single Crevice Assembly



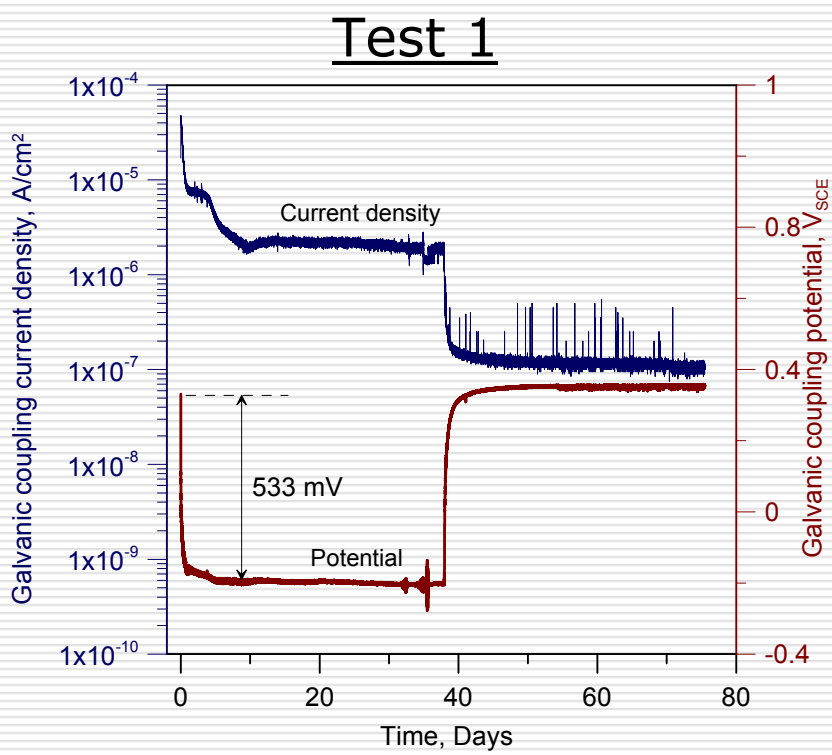
- Crevice corrosion propagation led to ~630 mV potential drop
- Current density decayed quickly with time
- Crevice corrosion repassivated (arrested) after 9 days

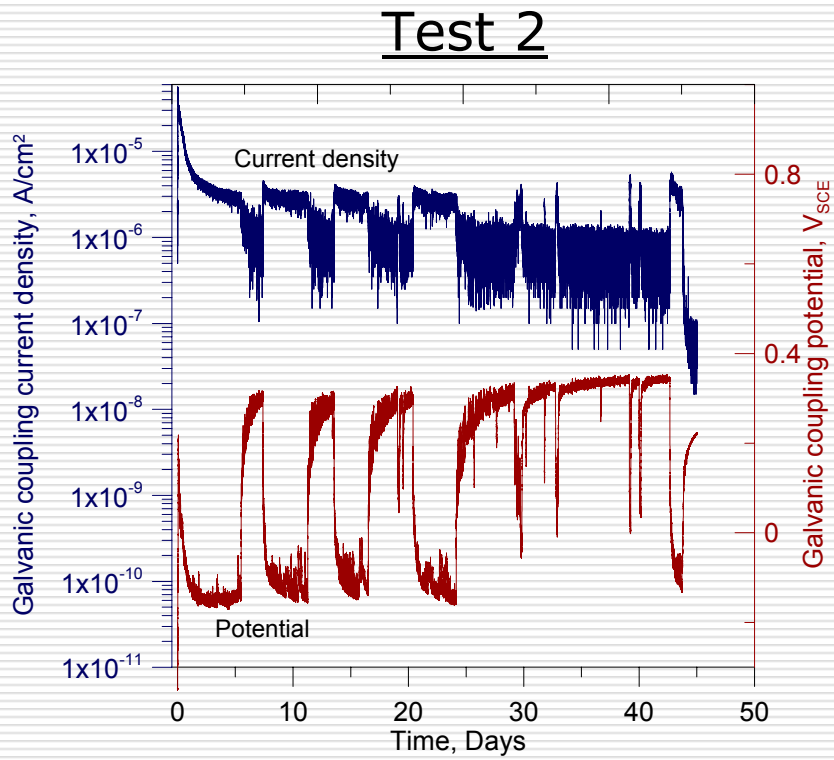
Galvanic Coupling Current Decay Behavior



- Current decayed in stages: fast decay followed by a slower decay
- The time exponent, n = -0.80, suggests a rapid decrease in propagation rate
- Crevice corrosion of Alloy 22 has a strong stifling tendency at 95°C

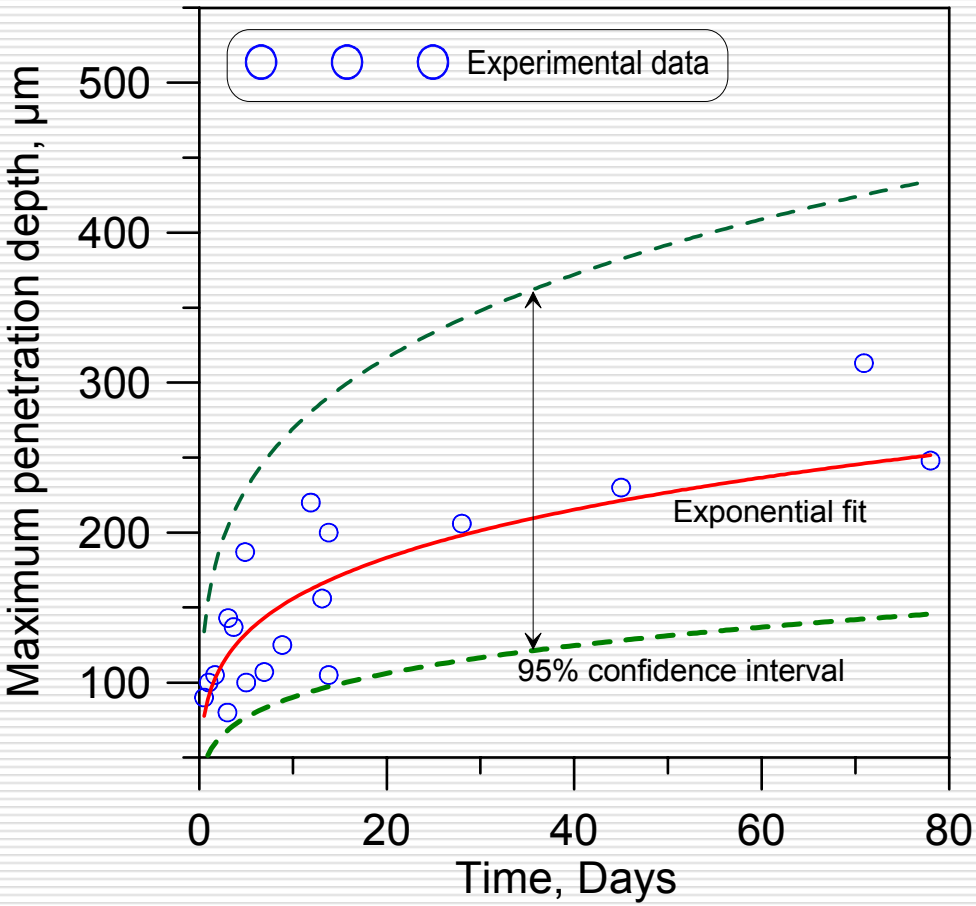
Galvanic Coupling Current and Potential from Multiple Crevice Assembly





- Strong stifling after initiation, repassivation at 38 days and no reinitiation
- Stifling after initiation, reinitiation in several cycles

Localized Corrosion Penetration Behavior



- Tests were conducted for specific time intervals
- Penetration depths were measured with an optical microscope
- Fitted equation

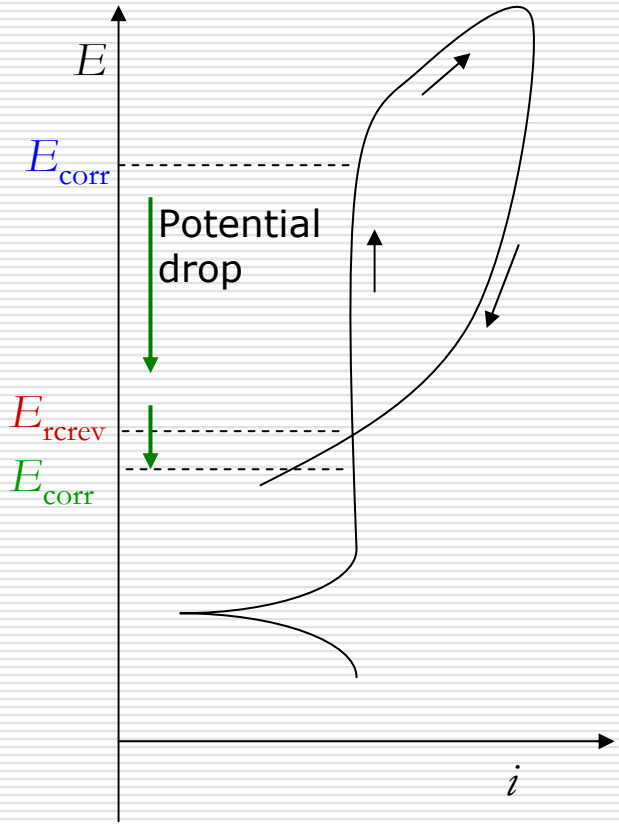
$$d_{max} = 0.0912\, t^{0.233}$$

d_{max} — Maximum penetration depth in mm

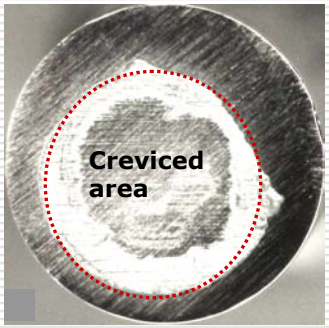
t — time in days

Discussion of Localized Corrosion Stifling and Arrest (Repassivation)

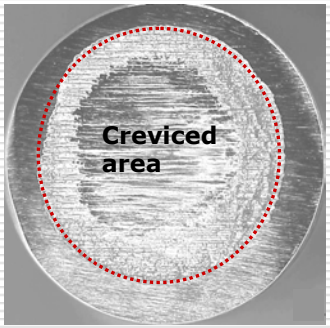
- For a diffusion controlled process, time exponent = 0.5
- Strong stifling mainly results from corrosion potential drop (experimentally determined: 550 ± 170 mV)
- $\Delta E = E_{corr} - E_{rcrev}$
  — If $\Delta E > 0$, localized corrosion initiates
  — If ΔE decreases, localized corrosion stifles
  — If $\Delta E < 0$, localized corrosion arrests (repassivates)



Single Crevice Corroded Specimens



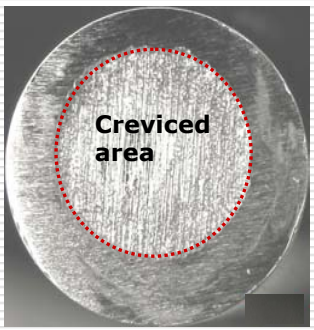
t = 0.5 day



t = 3.7 days

t = 8.8 days

6.2 mm



t = 28.0 days

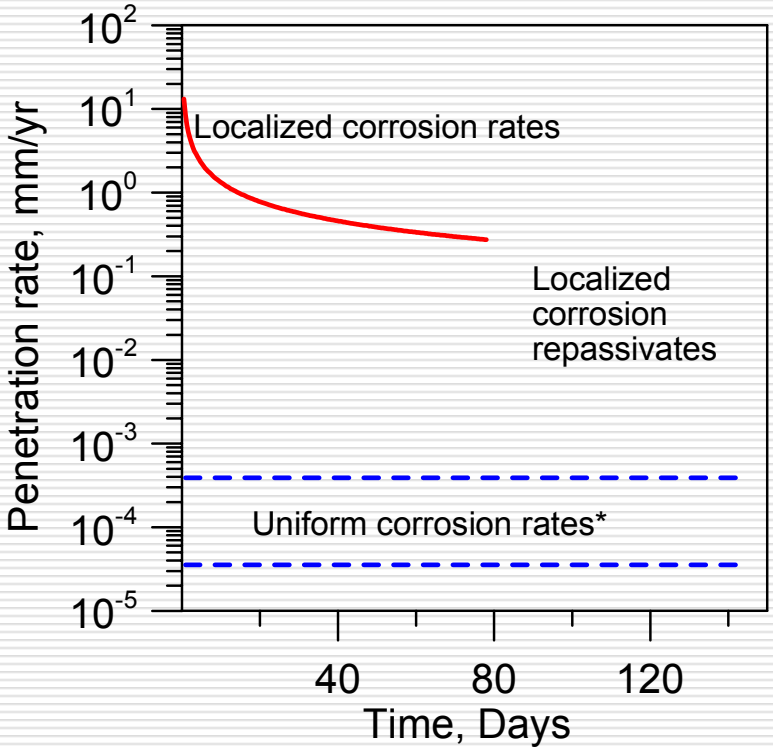
t = 70.9 days

- Corroding sites preferentially initiated around the edge and spread immediately following initiation
- Fewer changes were observed with increasing test time

Alloy 22 Localized Corrosion Penetration Rates

- *Penetration Rate* (mm/yr) = $7.8\ t^{-0.767}$

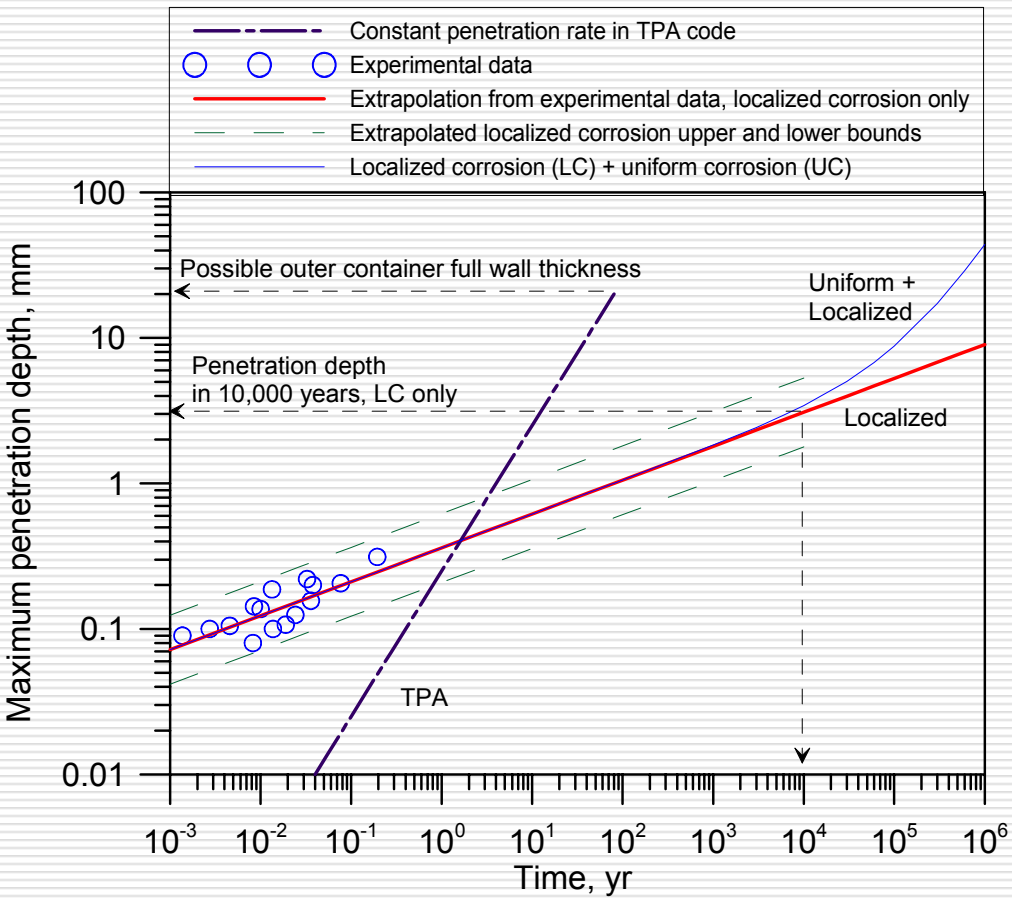
  (Derived from $d_{max} = 0.0912\ t^{0.233}$)



- Localized corrosion penetration rates >> uniform corrosion rates
- Penetration rates decreased significantly with time, approaching very low values after localized corrosion repassivation
- Uniform corrosion rates*: 3.5×10^{-5} to 3×10^{-4} mm/yr

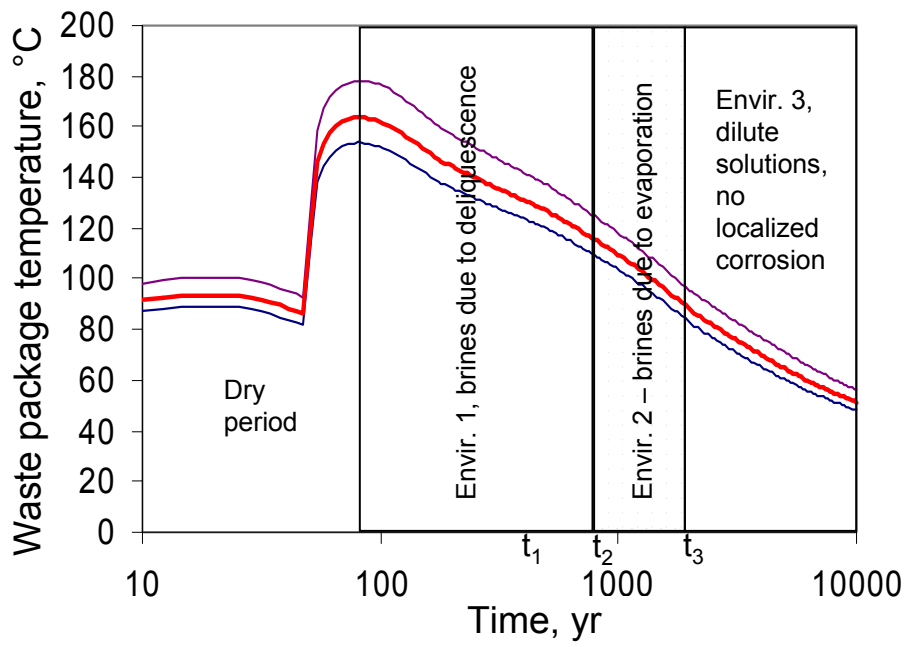
* D.S. Dunn, O. Pensado, Y.-M. Pan, R.T. Pabalan, L. Yang, X. He, and K.T. Chiang, "Passive and Localized Corrosion of Alloy 22 – Modeling and Experiments." CNWRA 2005-02. San Antonio, Texas: CNWRA. 2005.

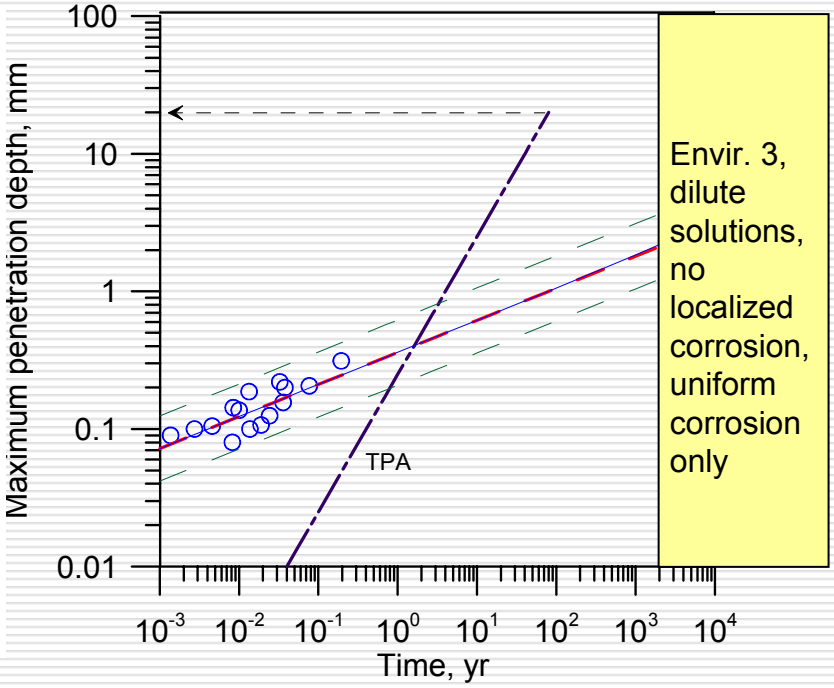
Evaluation of Localized Corrosion of the Waste Package Outer Container



- d_{max} by extrapolating $d_{max} = 0.0912t^{0.233}$ to 10^4 yrs is ~ 4 mm
- At t > 10 yr, the use of constant rate, 0.25 mm/yr, without considering stifling and arrest overestimates penetration depths
- Uniform corrosion rate used in the Figure is 3.5×10^{-5} mm/yr
- After ~10^4 yrs, uniform corrosion could be the dominant process

Implication from Evolution of Near-Field Environment





- Localized corrosion is only possible in environment 2 (brines due to evaporation)
- Using a constant propagation rate in the waste package localized corrosion model conservatively bounds the rates derived from experiments

Summary

- Crevice corrosion propagation tests on Alloy 22 were conducted for periods of 0.5 to 78 days in 5 M NaCl solution at 95 °C with the addition of $CuCl_2$ as an oxidant.
- Active propagation of crevice corrosion resulted in significant decreases in corrosion potential. Crevice corrosion shows a strong tendency of stifling and repassivation.
- Although the propagation rates for crevice corrosion are greater than the uniform corrosion rates, the maximum penetration depth of localized attack may be limited to depths significantly less than the container wall thickness.

Acknowledgments and Disclaimer

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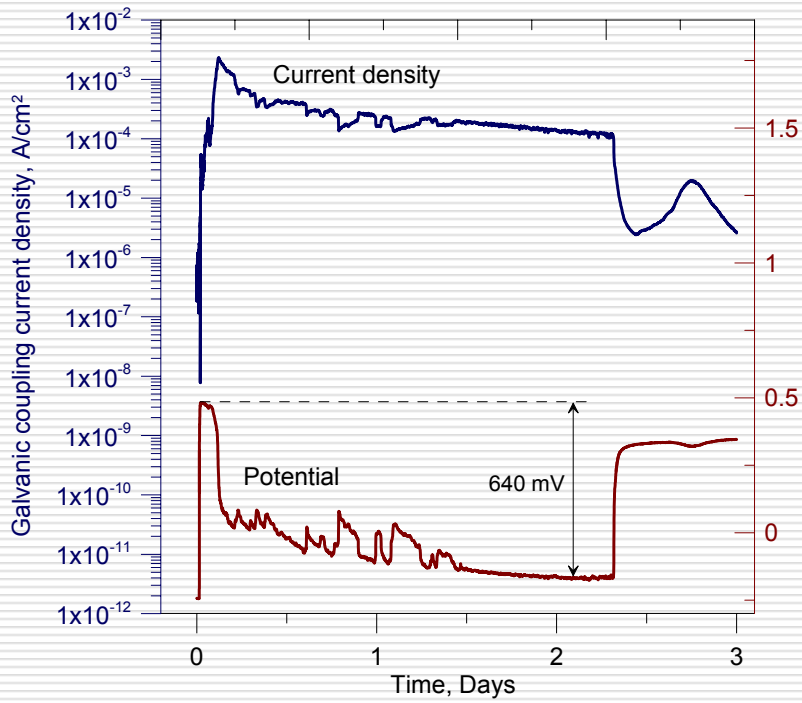
  This work is an independent product of the CNWRA and does not necessarily reflect the view or regulatory position of the NRC.

Backup Slides

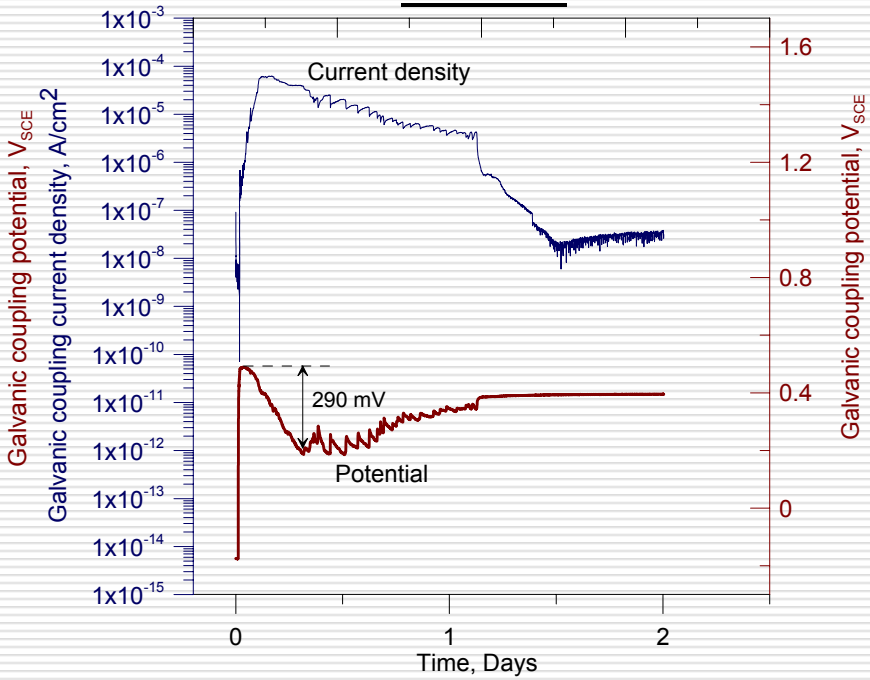
Reproducibility Tests from Single Crevice Assembly

Test 1



- Repassivated at 2.3 days
- Potential drop: 640 mV
- d_{max}: 150 μm

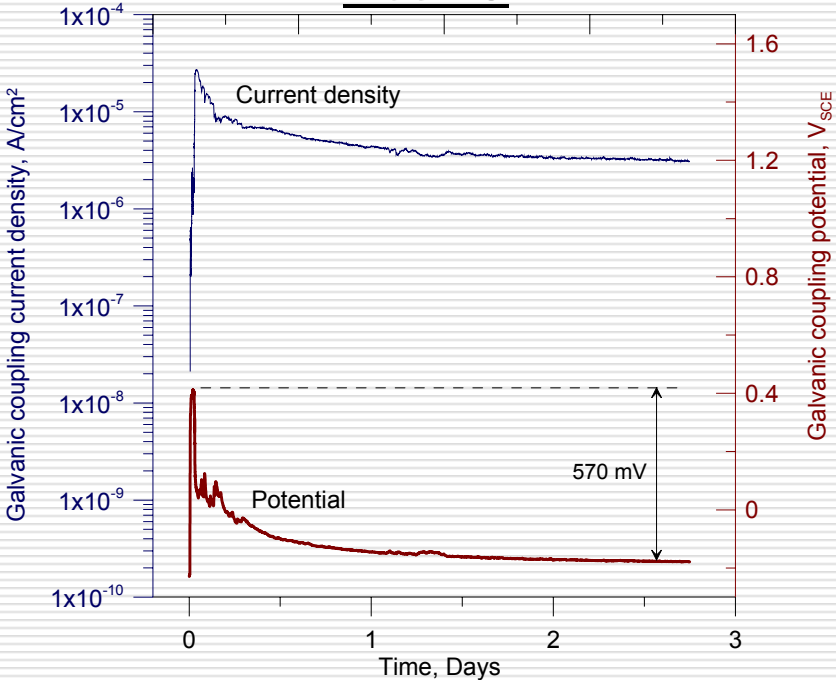
Test 2



- Repassivated at 1.3 days
- Potential drop: 290 mV
- d_{max}: Not available. Corrosion occurred at the side of the specimen

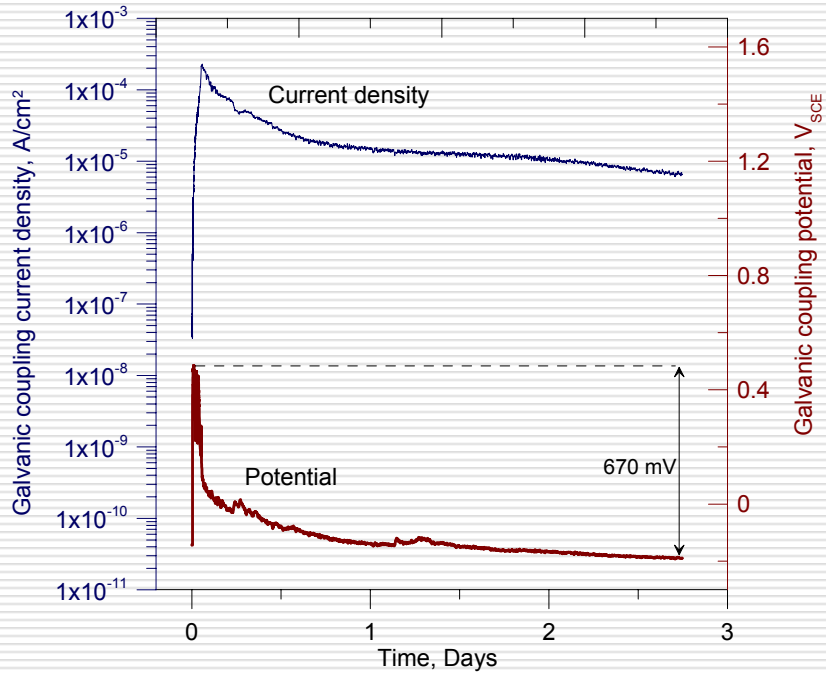
Reproducibility Tests - continued

Test 3



- Test time: 2.7 days
- Potential drop: 570 mV
- d_{max}: 63 μm

Test 4

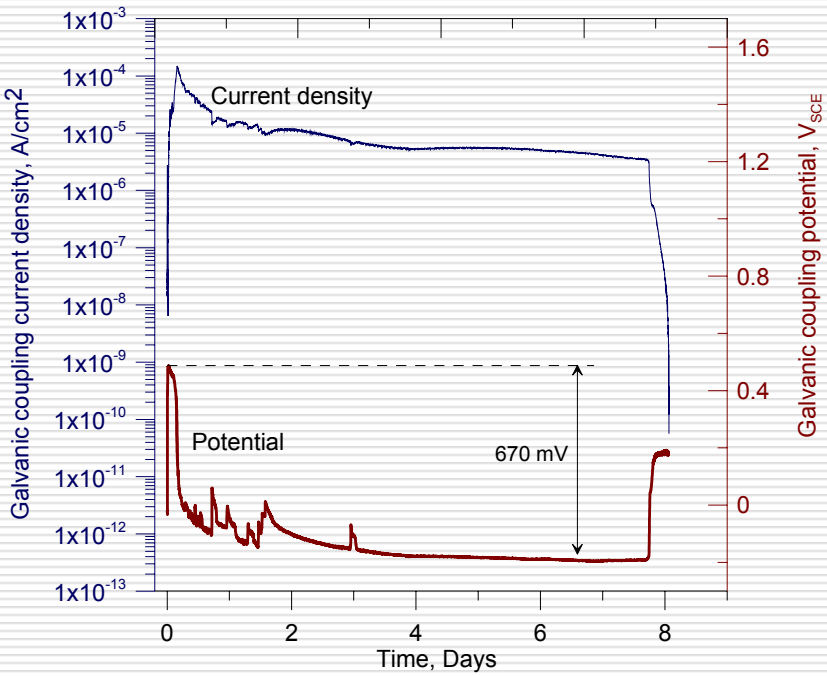


- Test time: 2.7 days
- Potential drop: 670 mV
- d_{max}: 61 μm

Variability: ~2%

Reproducibility Tests - continued

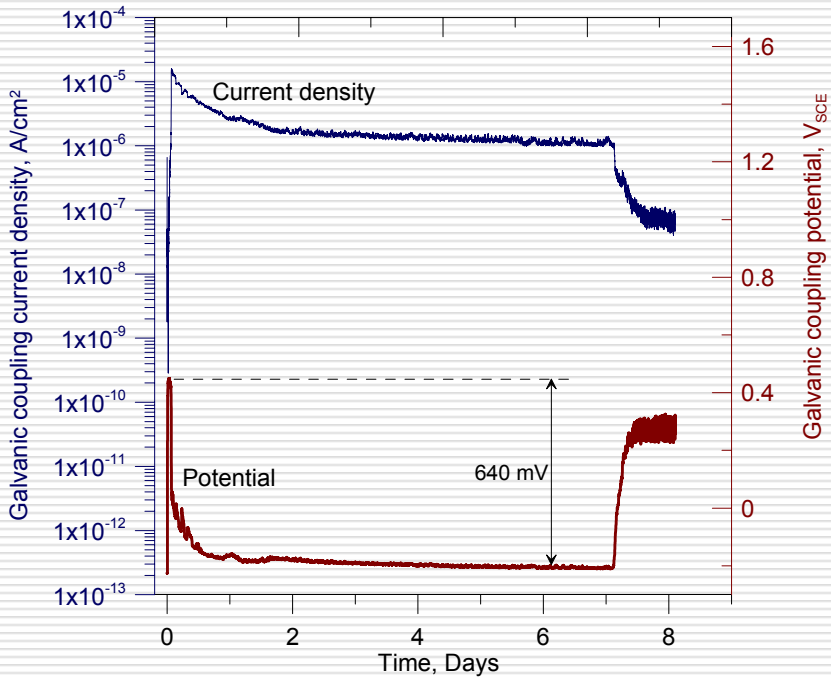
Test 5



- Repassivated at 7.7 days
- Potential drop: 670 mV
- d_{max}: 95 µm

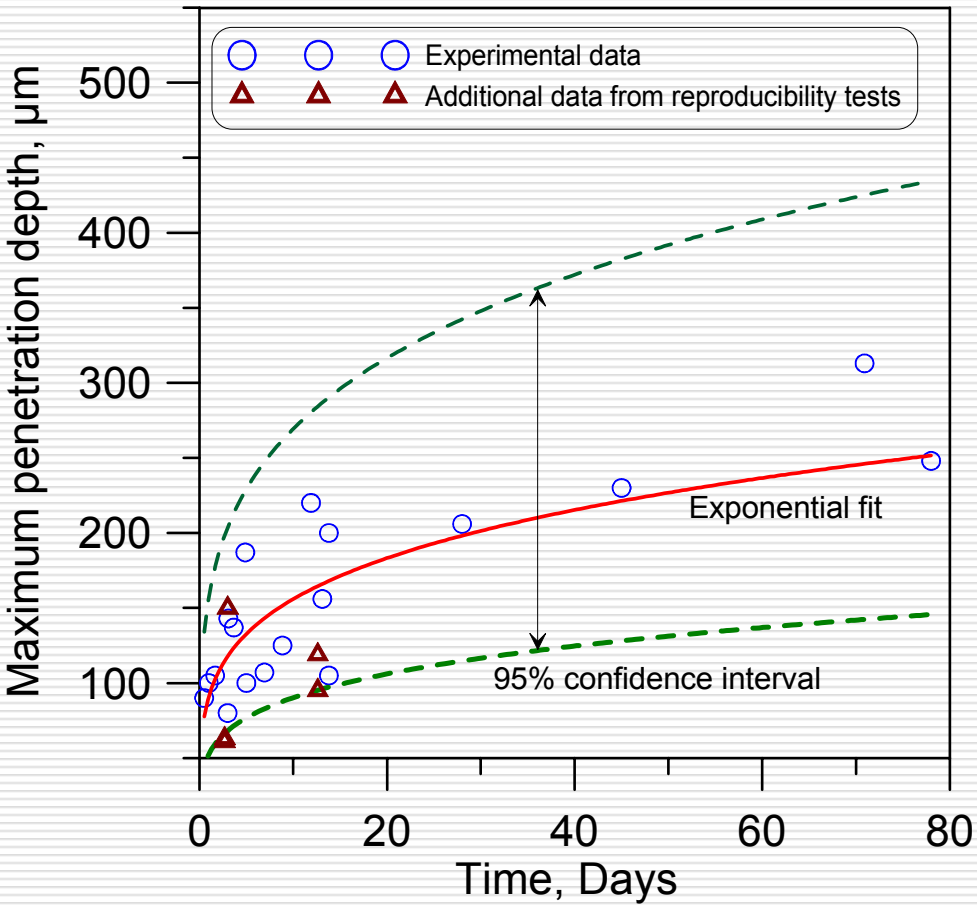
Variability: ~25%

Test 6



- Repassivated at 7.1 days
- Potential drop: 640 mV
- d_{max}: 119 µm

Summary on Reproducibility Tests



- Stifling and arrest of crevice corrosion were observed consistently
- Except for two data points slightly off the lower bound, all other measured penetration depths were bounded by the 95-percent confidence interval