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Long-Term Electrochemical Criteria for Crevice Corrosion in Potential Repository Environments at Yucca Mountain, Nevada

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ASTM Seminar, Accelerated Testing of Materials in Spent Nuclear Fuel and High Level Waste Storage System

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Purpose

- **Review relevant literature data on the electrochemical criteria for the initiation of crevice corrosion of Alloy 22 in the potential Yucca Mountain repository environment.**

- **Review the applicability of repassivation potential and breakdown potential for assessing crevice corrosion of Alloy 22 in the potential Yucca Mountain repository environment.**

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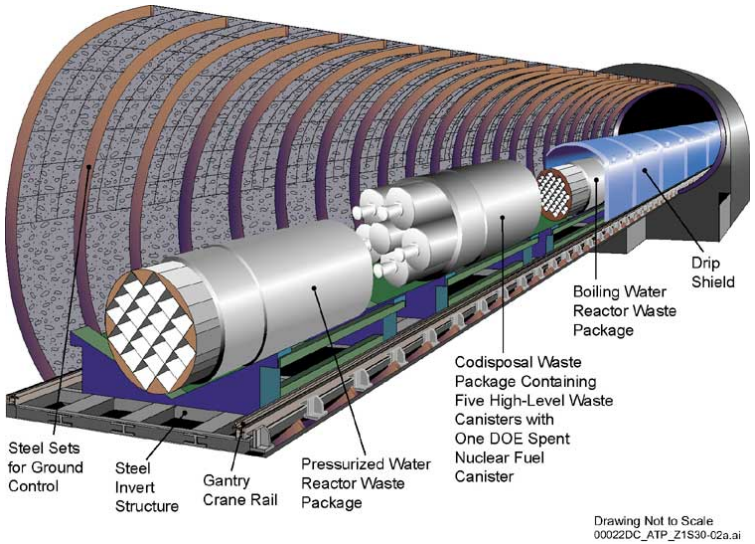
Outline

- Engineered Barrier System
- Waste Package (WP) Environment and Corrosion Modes
- Crevice Corrosion Data
- Capacity and Modification of Cathode
- Induction Time
- Summary
- References

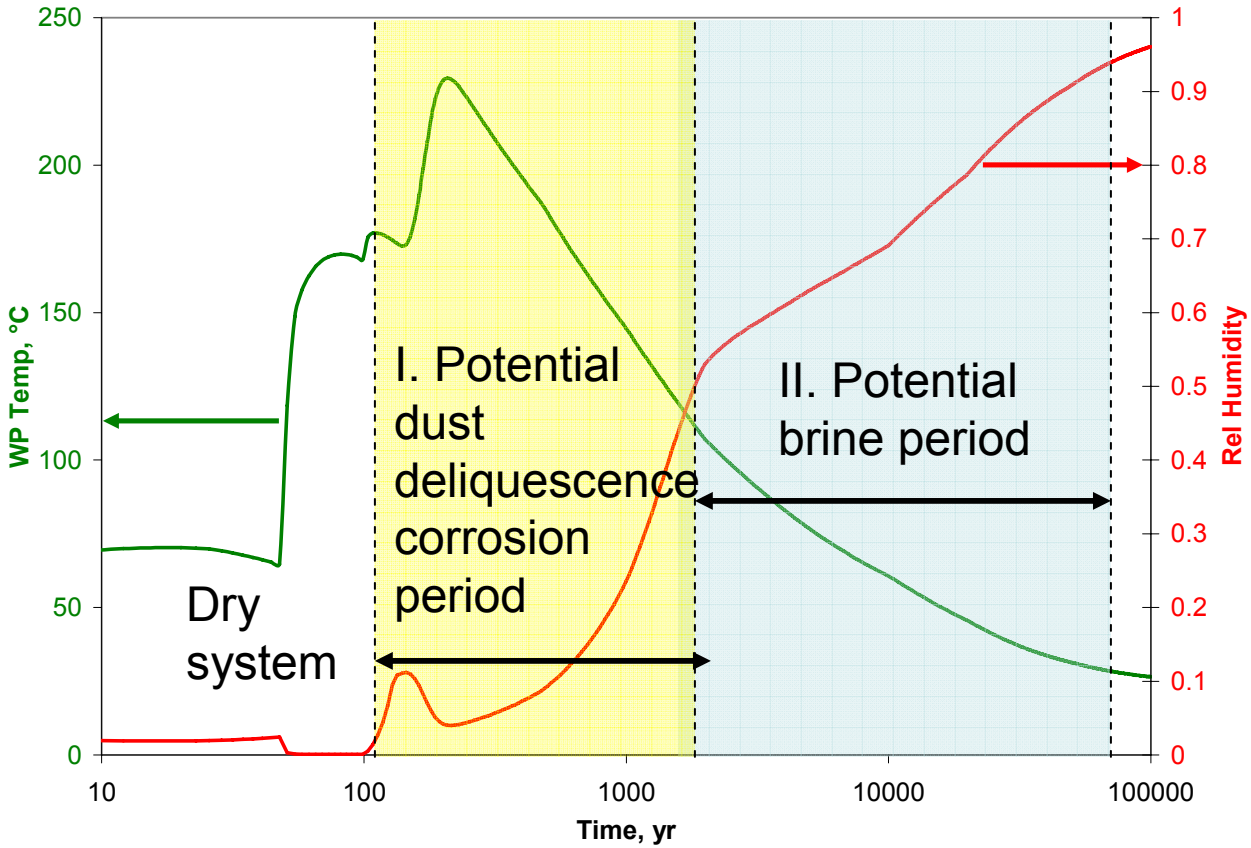
Engineered Barrier System

(DOE, 2002)



- **Drip Shield (DS) – Titanium Alloys (Grades 7 and 29)**
  - **(i) intend to prevent contact of seepage water with WP**
  - **(ii) intend to prevent rockfall impact on WP**
- **Waste Package – Alloy 22 (Ni-22Cr-13Mo-3W-4Fe)**
  - **(i) intend to prevent water contact with waste form**
  - **(ii) intend to control radionuclide release**
- **Good understanding of potential corrosion mechanisms, with residual uncertainties**

WP Environment and Corrosion Modes



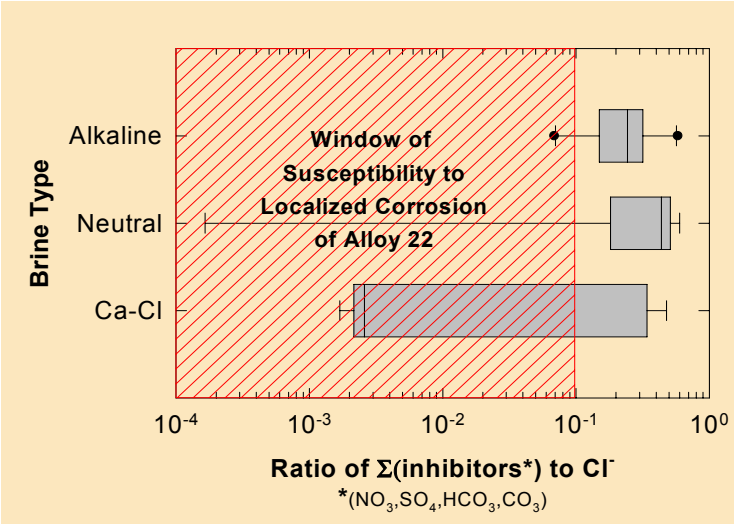
(After Pensado, 2006)

- Persistence of long-term passive film in general corrosion (I, II, and longer period)
- Dust deliquescence corrosion (I)
- Seepage water brines - crevice corrosion (II)
- Microbially influenced corrosion (II, and longer period)
- Hydrogen effects on Titanium (II, and longer period)

Seepage Water Brines:
Crevice Corrosion

- Brines that form by evaporation of seepage waters are mostly benign to Alloy 22, but some compositions (less than approximately 10 percent) could initiate crevice corrosion for approximately 2,000 to tens-of-thousands of years post closure.

  - Contact of seepage water may be prevented by DS.
  - The susceptibility of crevice corrosion decreases with decreasing temperature below approximately 110 ºC.

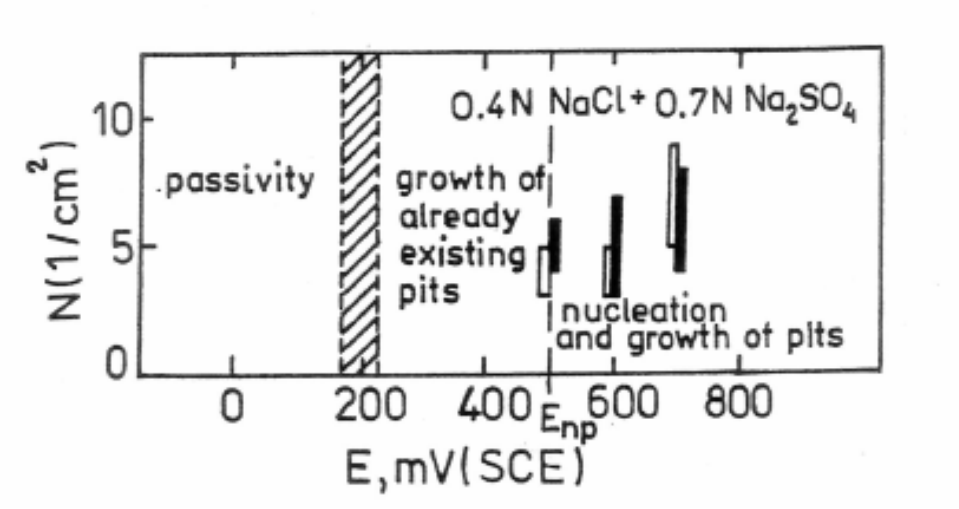


Pabalan (2006); localize corrosion is crevice corrosion

- Uncertainties associated with likelihood of seepage-water brines to initiate crevice corrosion

Potentiostatic Electrochemical Criteria of Localized Corrosion

Example of Different Stages of Localized Corrosion



Number of pits (stationary value) vs. potential for (110) and (111) planes of Fe-1Cr single crystals. E_{np} is potential of pit nucleation and marked by rectangles (Szklarska-Smialowsak, NACE, 1986).

Localized Corrosion (LC): crevice corrosion or pitting corrosion

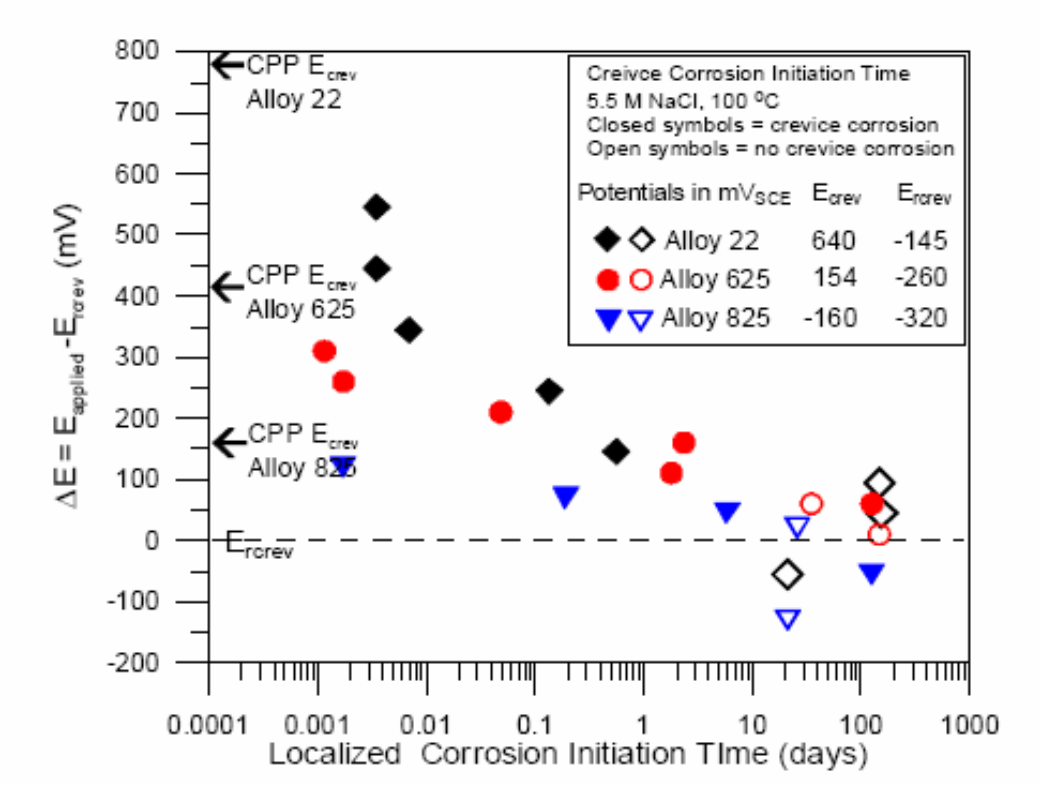
$E_{break} < E_{corr}$: LC initiation

$E_{repass} < E_{corr} < E_{break}$: propagation of existing LC

$E_{corr} < E_{repass}$: no LC initiation

E_{corr}: corrosion potential
E_{break}: passive film breakdown potential
E_{repass}: repassivation potential

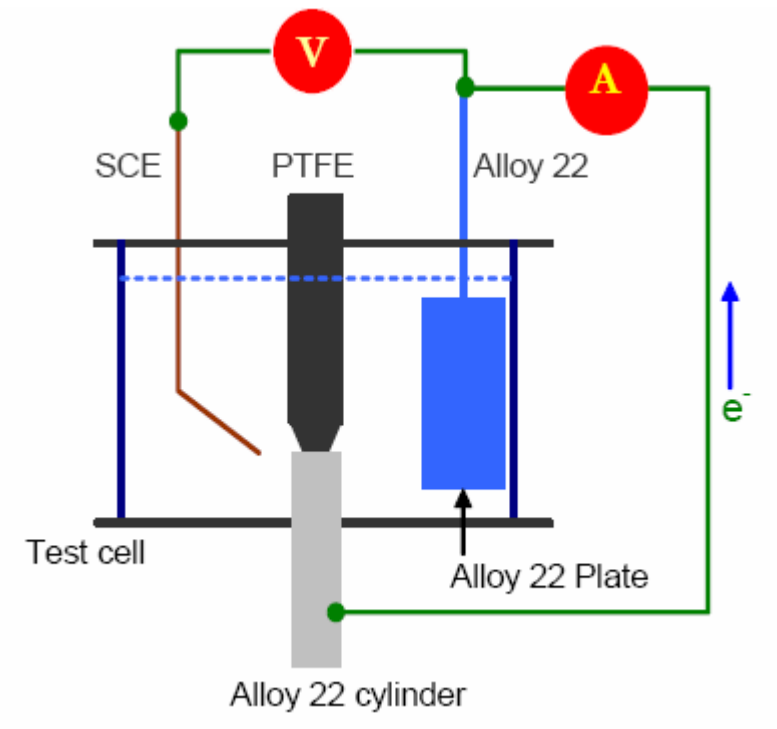
Initiation Time for Crevice Corrosion vs. Applied Potential



- **Initiation Time for Crevice Corrosion As a Function of Applied Potential for Alloys 825, 625, and 22 in 5.5 M NaCl at 100 ºC [212 ºF]. Initiation Times Measured Under Potentiostatic Conditions. Note: CPP–Cyclic potentiodynamic polarization (Dunn, et al., 2005)**

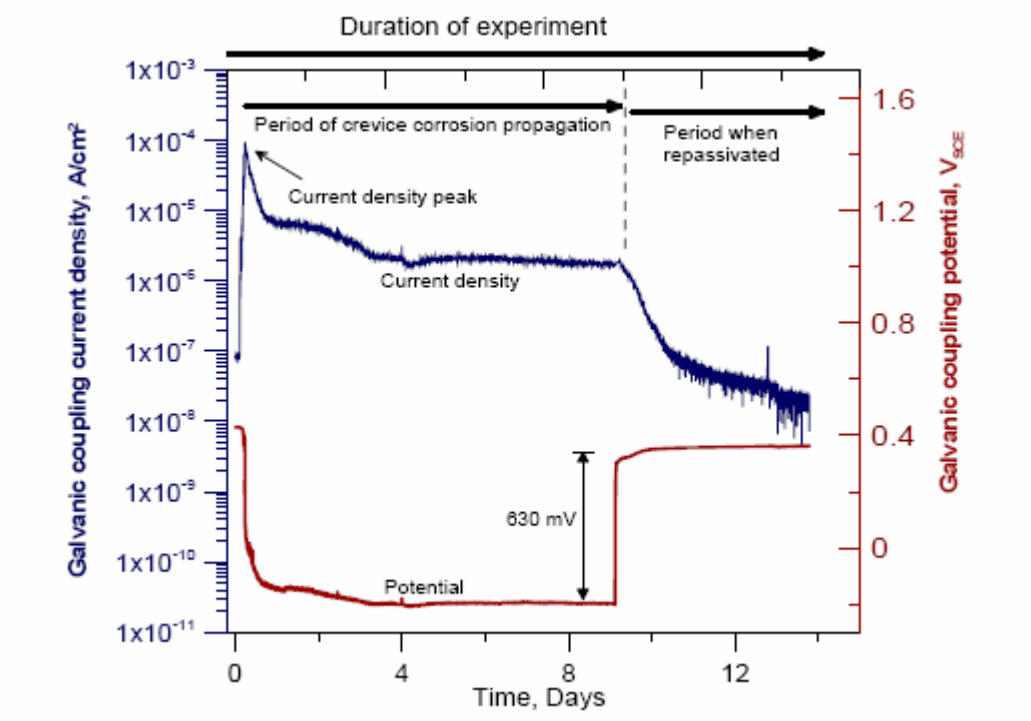
- **Initiation time was increased as applied potential was lowered toward repassivation potential**

Crevice Corrosion with Oxidant:
Electrochemical Test Cell



- **Schematics of the Electrochemical Test Cell with Single Crevice Assembly to Study the Crevice Corrosion Propagation in Alloy 22 (Note: PTFE–Polytetrafluoroethlene; SCE–Saturated Calomel Electrode) (He and Dunn, 2005)**
- **The Alloy 22 cylindrical specimen was galvanically coupled to Alloy 22 through a zero resistance ammeter and the voltmeter was used to measure the potential of the galvanic couple against the reference electrode**
- **Specimen for multiple crevice assembly was also used.**

Crevice Corrosion with Oxidant:
Measured Current Density and Potential for Alloy 22



- **Measured Current Density and Potential Using the Single Crevice Assembly for an Alloy 22 Cylindrical Specimen Galvanically Coupled to a Large Alloy 22 Plate in 5 M NaCl Solution with the Addition of 2 x 10^{-4} M $CuCl_2$ at 95 ºC [203 ºF] mV_{SCE} (He and Dunn, 2005)**

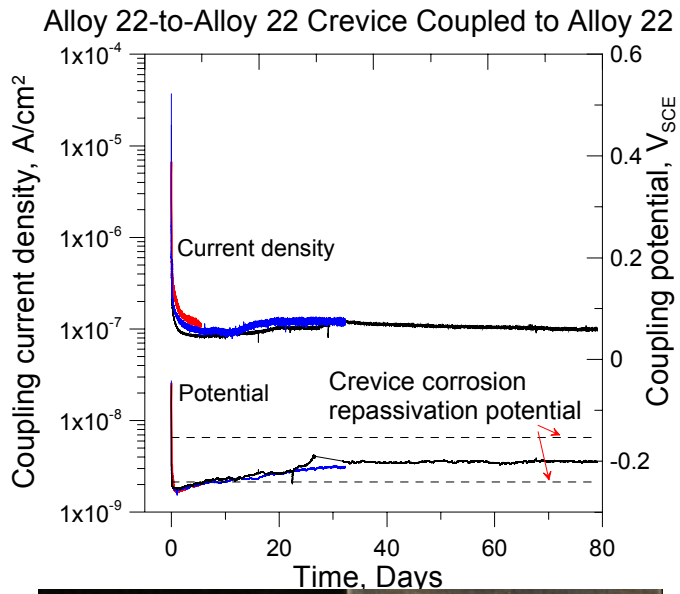
- **The current density is the measured current divided by the entire specimen area exposed in the solution. Initial potential of the couple after the addition of $CuCl_2$ is 429 mV_{SCE}. The potential at stable propagation is -201 mV_{SCE}.**

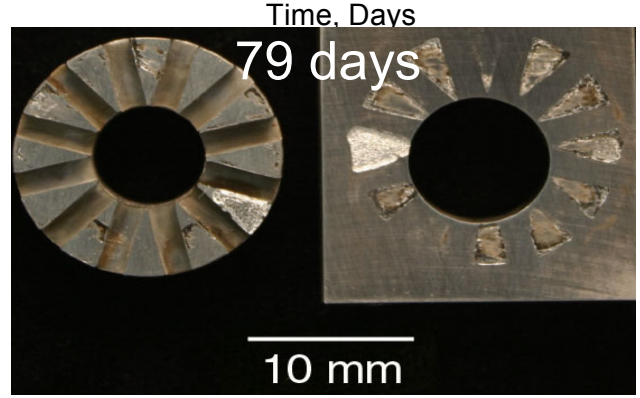
Crevice Corrosion with Oxidant:
Damage Characteristics of Alloy 22

- **Initially, the total crevice area was corroded.**
- **Gradually, corrosion propagation was localized to pits inside the crevice area.**
- **Gradually, the pit density was decreased.**
- **In the end, only a few pits of the size (10 – 100) micrometer [4 – 39 microinch] were active, and in some cases the total crevice area was completely repassivated.**

Crevice Corrosion at Open Circuit Potential:
Alloy 22 in $MgCl_2$

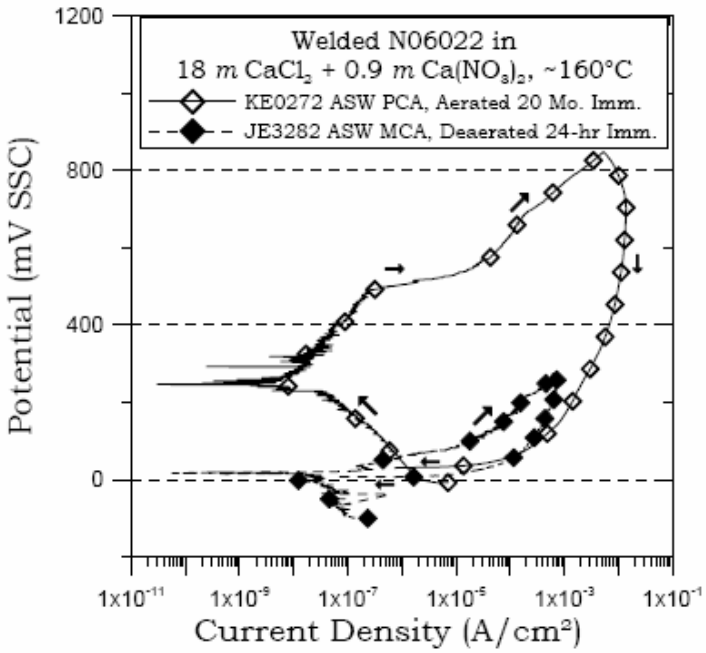
- Alloy 22 crevice specimen was galvanically coupled to Alloy 22 plate in 4 M $MgCl_2$ solution at 95 ºC [203 ºF].
- Crevice corrosion was initiated under open circuit condition.
- Open circuit potential decreased after crevice corrosion initiation to values close to the crevice corrosion repassivation potentital.
- Breakdown potential potentials were close to repassivation potentials.
- Most sites were corroded; however, the penetration depth was limited, and the deepest penetration was confined to a small area.





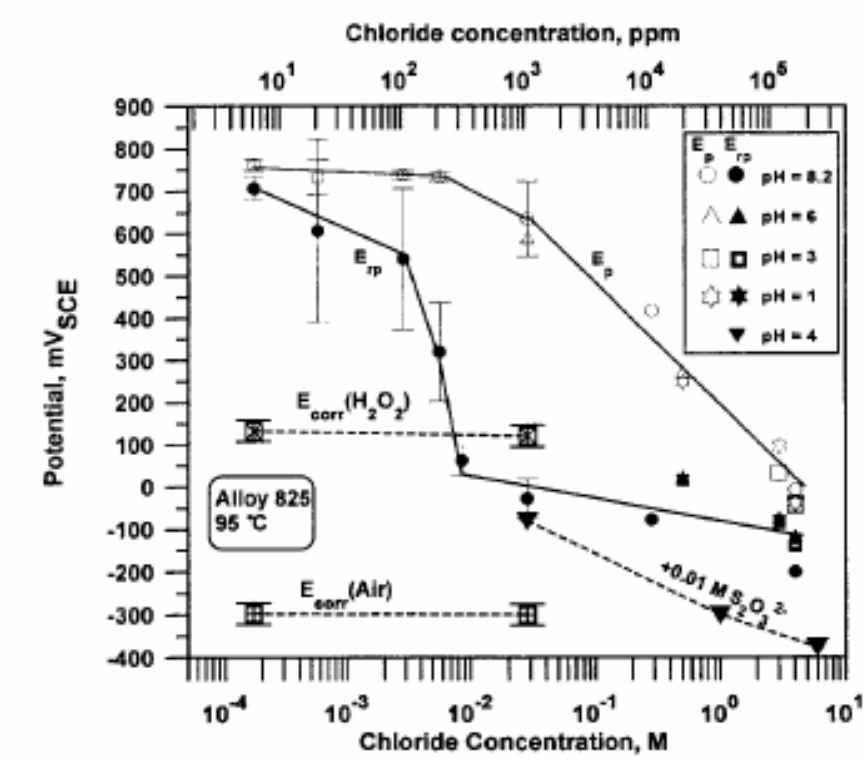
Penetration Depth, d_{max} = 245 µm

Crevice Corrosion at Open Circuit Potential:
Alloy 22 in $CaCl_2$



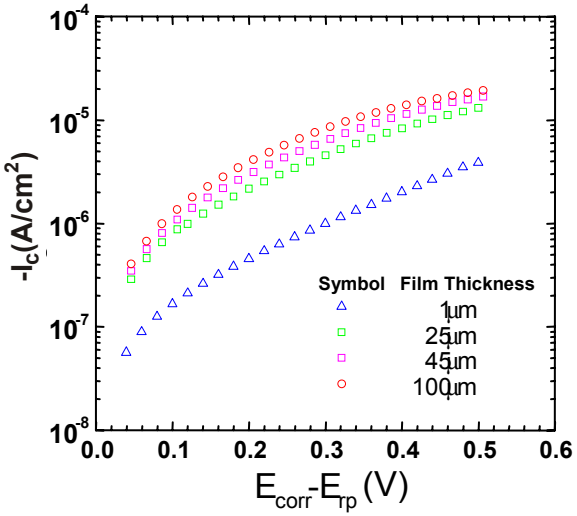
- **Cyclic Potentiodynamic Polarization for Alloy 22 in 18 m $CaCl_2$ + 0.9 m$Ca(NO_3)_2$, $[NO_3^-]/[Cl^-]$ = 0.05 at ~ 160 ºC [320 ºF] comparing short and long term immersion. Short term data is at 160 ºC [320 ºF] , long term at 155 ºC [311 ºF] (Rodriguez, et al., NACE, 2007).**
- **E_{corr} fluctuated up to near E_{break} and above near E_{repass}.**
- **Pitting was observed before polarization.**

Breakdown Potential and Repassivation Potential: Literature Data

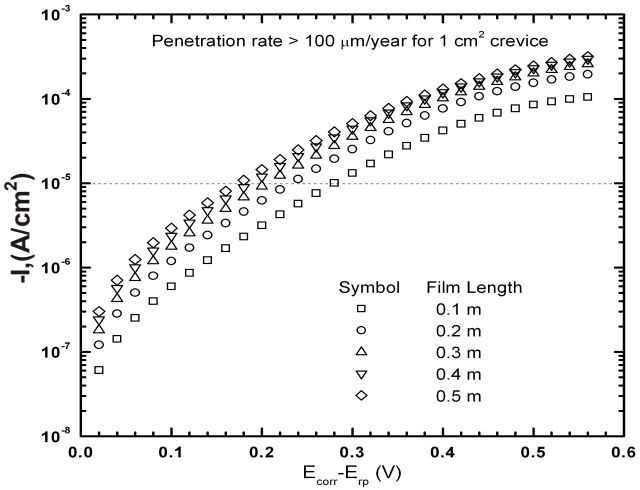


- Effect of chloride, thiosulfate, and pH on E_p and E_{rp} for Alloy 825 at 95 °C [203 °F (Sridhar, et al., 1995).
- Pitting potential (E_p) is equivalent to E_{break} and E_{rp} is E_{repass}.
- At high concentrations of chloride above 1 M, two potentials merge.

Capacity and Modification of Cathode in Crevice Corrosion at Open Circuit



Seepage Brine



Dust Deliquescence Brine

- Cathode Capacity: amount of excess cathodic current that will balance metal dissolution current
- Limited quantity of brine will control the rate of oxygen reduction. Cathodic capacity decreases with decrease of Ecorr – Erp.
- Thickening or more perfection of passive film in the outer area of crevice will decrease electrochemical reaction kinetics (e.g., exchange current density).

Induction Times for Pitting Corrosion:
Literature Models

- $t_{ind} = \acute{\varepsilon}\ [\ \exp\{\ (\chi\ F\ \alpha\ \Delta V)/(2\ R\ T)\} - 1]^{-1} + \zeta$

ΔV: applied potential minus the critical potential (i.e., pitting potential or breakdown potential)

χ: charge on a cation

F: Faraday constant

R: gas constant

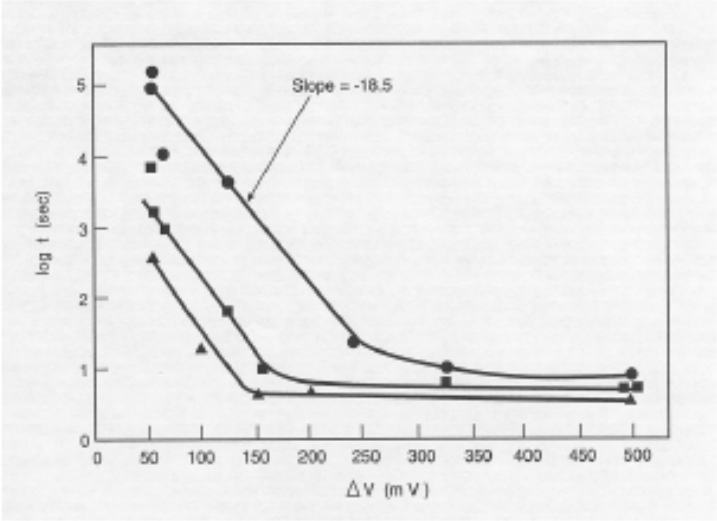
T: temperature

ζ: transient aqueous diffusion time

α: a constant relating the potential drop at the film/solution interface and applied potential, and

$\acute{\varepsilon}$: a function of chloride activity, critical potential, diffusivity of cation vacancy, and a critical amount of metal holes.

(Lin et al., 1981; Urquidi-Macdonald and Macdonald, 1987)



Induction Time vs. Δ V
Data for Pitting of Passive Iron in Borate Buffer Solution at 25 °C (77 °F)
Triangle: pH 7.3 0.1M NaCl, Rectangle: pH 7.3 0.01M NaCl, Circle: pH 8.3 0.01M NaCl
(Lin et al., 1981)

Reprinted from "The Electrochemical Society, Inc. [1981]. All rights reserved. Except as provided under U.S. copyright law, this work may not be reproduced, distributed, or modified without the express permission of the Electrochemical Society (ECS). The archival version of this work was published in A Point Defect Model for Anodic Passive Films, II. Chemical Breakdown and Pit Initiation, by L. F. Lin, C. Y. Chao and D. D. Macdonald, J. Electrochemical Society, Vol.128, p. 1194, 1981

Induction Times for Pitting Corrosion:
Literature Models (Continued)

- **Distribution:**

  with respect to Critical Potential and Averaged Induction Time from Inhomogeneities of Alloys (Lin, et al., 1981; Urquidi-Macdonald and Macdonald, 1987)

  - Increasing the distributed induction time from the averaged induction time of 100s seconds to ~ 1 year, the frequency decreased drastically.
  - Stifling could occur under free open-circuit conditions.

- **Repassivation Potential: behavior similarly in induction time (Dunn, et al., 1996). It involves nucleation process (e.g., oxide reformation, Okada, 1984) for the behavior.**

Induction Times for Pitting Corrosion:
Literature Models (Continued)

- **Point Defect Model in Alloy 22**
  - Excess amount of cation vacancies (void formation) at the metal-oxide interface in the p-type passive oxide film of stainless steel in NaCl-rich brines at 250 ºC [482 ºF] (Macdonald, 1992)
  - This approach partly adopted to explain the transpassive dissolution of p-type passive film on Alloy 22 in saturated NaCl solution at 80 ºC [176 ºF] (Macdonald, et al., 2004)

- **Times to Reach the Critical Chemistry**

  Constant potentials and pH arrive as a function of position from the crevice mouth and laboratory test times (Combrade, 2001; Shinohara, et al., 1997; Walton, et al., 1996)

- **Very slow temperature change; insulation from rock rubble considered to cause higher temperatures in first ~10,000 years (Manepally, et al., 2003)**

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Summary

- **The electrochemical criteria for the initiation of crevice corrosion was reviewed. An assessment was made about the potential applicability of the criteria to Alloy 22 corrosion in the potential Yucca Mountain repository.**

- **With forced applied current between anode and cathode of a crevice cell, crevice corrosion may be initiated at potential above repassivation potential.**

- **At open circuit potential, however, crevice corrosion may not be initiated until potential reaches breakdown potential without existing crevice corrosion (e.g., active pits inside crevice).**

Disclaimer

The NRC staff views expressed herein are preliminary and do not constitute a final judgment or determination of the matters addressed or of the acceptability of a license application for a geological repository at Yucca Mountain. This presentation describes work performed by the Center for Nuclear Waste Regulatory Analyses (CNWRA) for the NRC under contract number NRC-02-02-012. The activities reported here were performed on behalf of the NRC office of Nuclear Material Safety and Safeguards, Division of High Level Waste Repository Safety. This presentation is an independent product of the CNWRA and does not necessarily reflect the view or regulatory position of the NRC.

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