Cathodic Capacity of Alloy 22 in the Potential Yucca Mountain Repository Environment

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Presentation Outline

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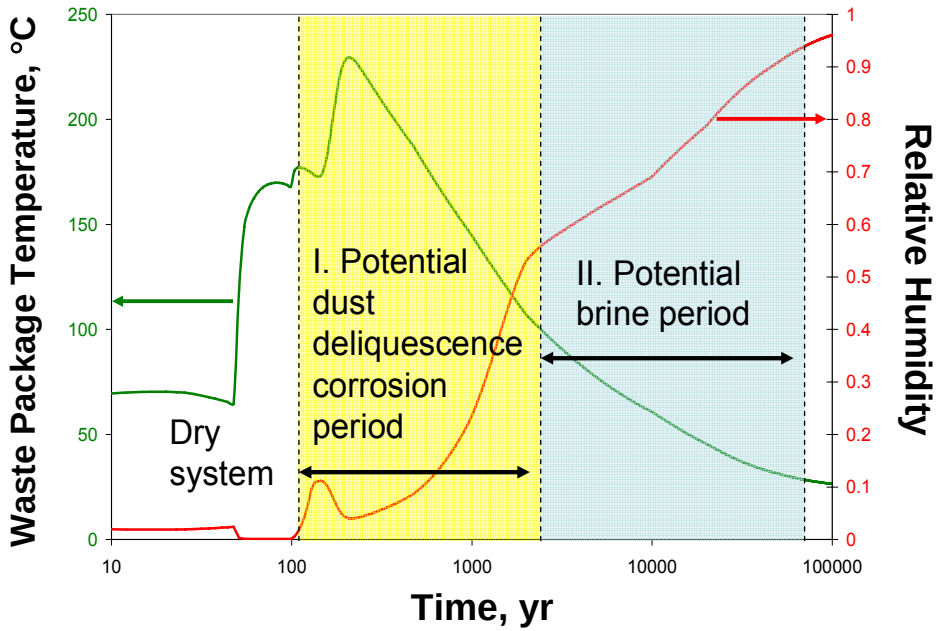
- Objectives
- Cathodic Capacity Model
- Model Parameters
  - Dust Deliquescence Brines
  - Seepage Water Brines
- Results
- Summary

Background

- Alloy 22 is being considered by DOE as the waste package outer container material

- Brines could contact the waste package surface
  - Dust deliquescence
  - Seepage water



Calculated Waste Package Temperature and Relative Humidity‡

- Cathodic capacity of Alloy 22 in the limited brine quantity could affect the localized corrosion process

‡Pensado, O. 2006. "Corrosion Model to Support Total System Performance Assessments." Nuclear Waste Technical Review Board Meeting. September 25−26, 2006. http://www.nwtrb.gov/meetings/2006/sept/pensado.pdf

Background: What Is Cathodic Capacity?

- Anodic dissolution (oxidation) and reduction reaction must occur simultaneously

- Electrical and ionic charge neutrality is maintained when
  - $I_A + I_C = 0$

    I_A: net anodic current due to oxidation reactions

    I_C: net cathodic current due to reduction reactions

- Reduction of oxygen is the dominant cathodic reaction

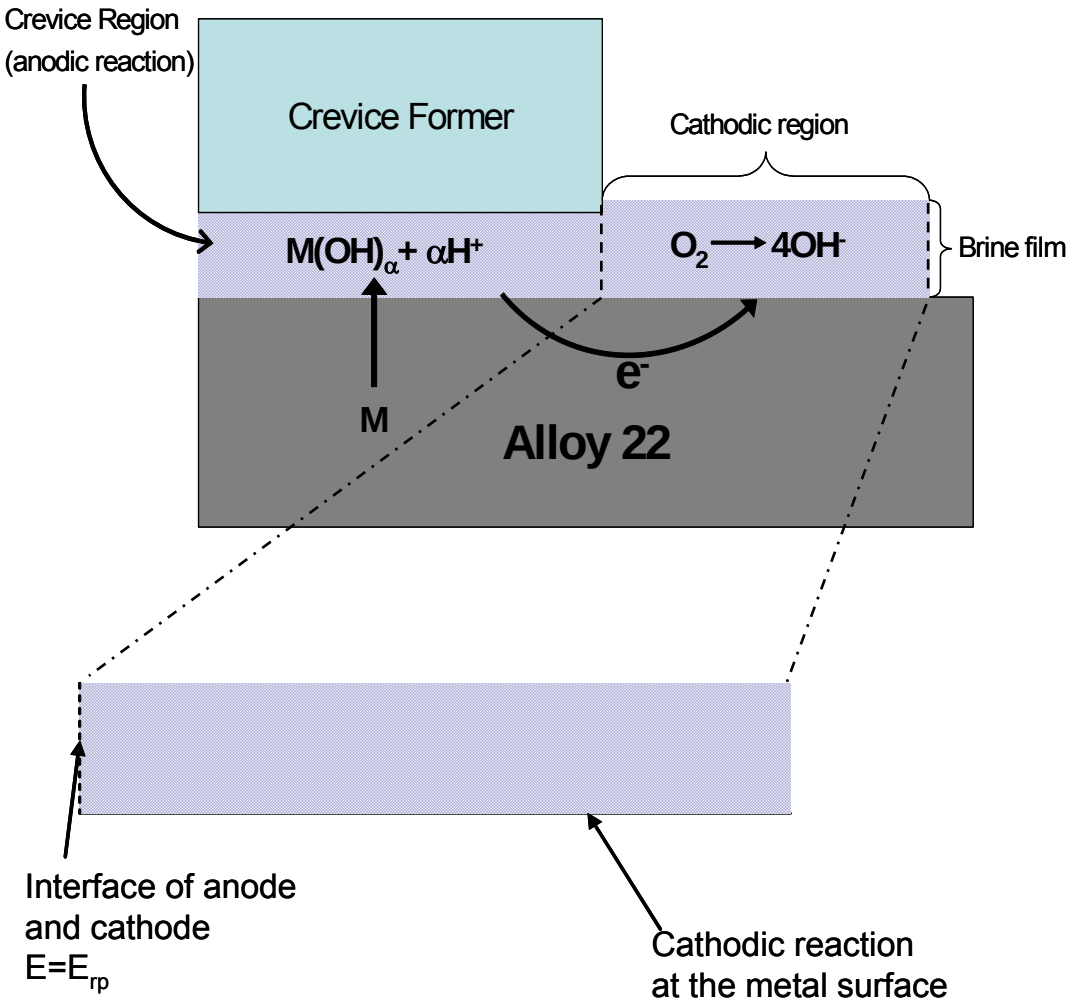
- Cathodic capacity: total current generated by the oxygen reduction reaction

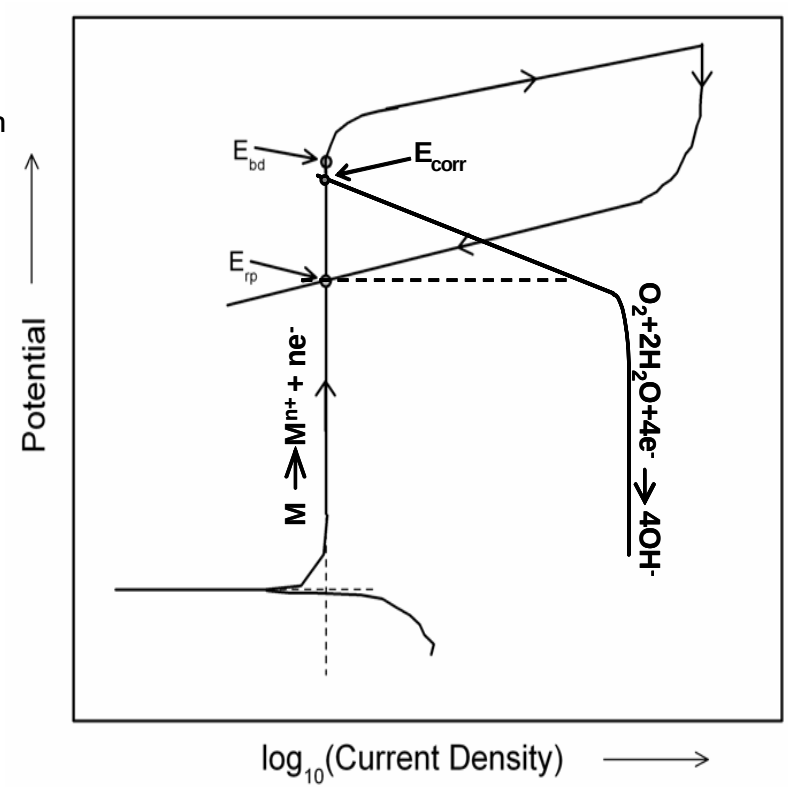
Objectives

- Evaluate the effect of brine quantity on localized corrosion process of Alloy 22 by evaluating cathodic capacity in
  - Dust deliquescence
  - Seepage water

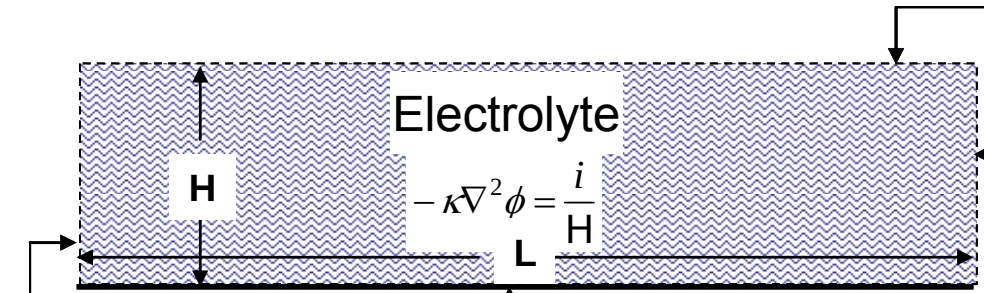
- Evaluate factors affecting the cathodic capacity
  - Brine chemistry, dissolved oxygen concentration, ionic conductivity
  - Kinetics of the cathodic reaction
  - Electrochemical and environmental conditions

Localized Corrosion Process in Form of Crevice Corrosion





Cathodic Capacity Model



$$i = -\kappa\left(\vec{n}\cdot\nabla\phi\right) = 0$$

$$E = E_{rp}$$

$$i = -\kappa\left(\vec{n}\cdot\nabla\phi\right) = i_p + i_c = i_p - \frac{i_{o,c}\, exp\left(-\frac{\alpha nF\left(E - E_{o,c}\right)}{RT}\right)}{1 + \frac{i_{o,c}}{i_{lim}} exp\left(-\frac{\alpha nF\left(E - E_{o,c}\right)}{RT}\right)}$$

ϕ – electrolyte potential = $-E_{rp}$ (at the cathode and anode interface)

i – net current density

κ – ionic conductivity of electrolyte

E – potential drop across metal-solution interface = $V_m - \phi$

V_m – metal potential = 0 (free corroding condition)

$i_{o,c}$ – reference current density at reference potential $E_{o,c}$

i_p – passive current density

i_{lim} – mass-transfer-limited current

i_c – cathodic current density

α – charge transfer coefficient

n – number of electrons / mole of O_2

R – universal gas constant

F – Faraday's constant

T – temperature

Model Parameters: Dust Deliquescence Brines (Assumptions and Calculations)

- Dust layer
  - 26 mg/cm^2 of dust on waste package surface
  - Dust particles of 10 or 30 μm diameters
  - Soluble salts (Na/K/Cl/NO_3 system): 10 percent of dust mass
- Brine properties (T = 150 °C)
  - Deliquescence of NaCl + $NaNO_3$ + $NaNO_3$·KNO_3 salts
  - Ionic conductivity: 0.01834 ohm^{-1}cm^{-1}
  - Average film thickness: 45.4 μm
  - Passive current density (i_p) = 6.77 × 10^{-8} A/cm^2
  - Dissolved oxygen concentration: 0.385 ppm
- Corrosion potential of Alloy 22 (E_{corr}) = 0.6 V_{SHE}

Unit conversions: 1 mg/cm^2 = 0.014 mlb/in^2; 1 μm = 0.039 mil;
150 °C = 302 °F; 1 ohm^{-1}cm^{-1} = 2.54 ohm^{-1}in^{-1}; 1 A/cm^2 = 6.45 A/in^2

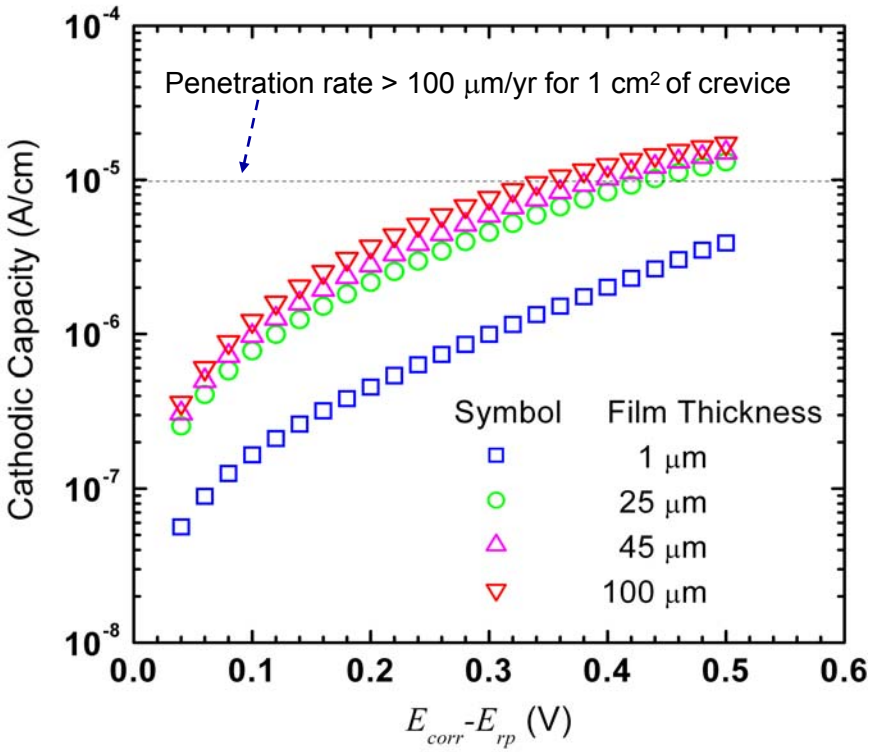
Model Parameters: Seepage Water Brines (Assumptions and Calculations)

- No dust layer
- Brine properties (T = 110 °C)
  - Chemical composition of pore waters
  - pH of the seepage solution = 10.9
  - Ionic conductivity: 0.778 $ohm^{-1}cm^{-1}$
  - Brine film thickness is determined by the balance of surface tension and gravitation force
  - Passive current density (i_p) = 1.77 × 10^{-8} A/cm^2
  - Dissolved oxygen concentration : 5.24 ppm
- Calculated corrosion potential (E_{corr}) = 0.08 V_{SHE}

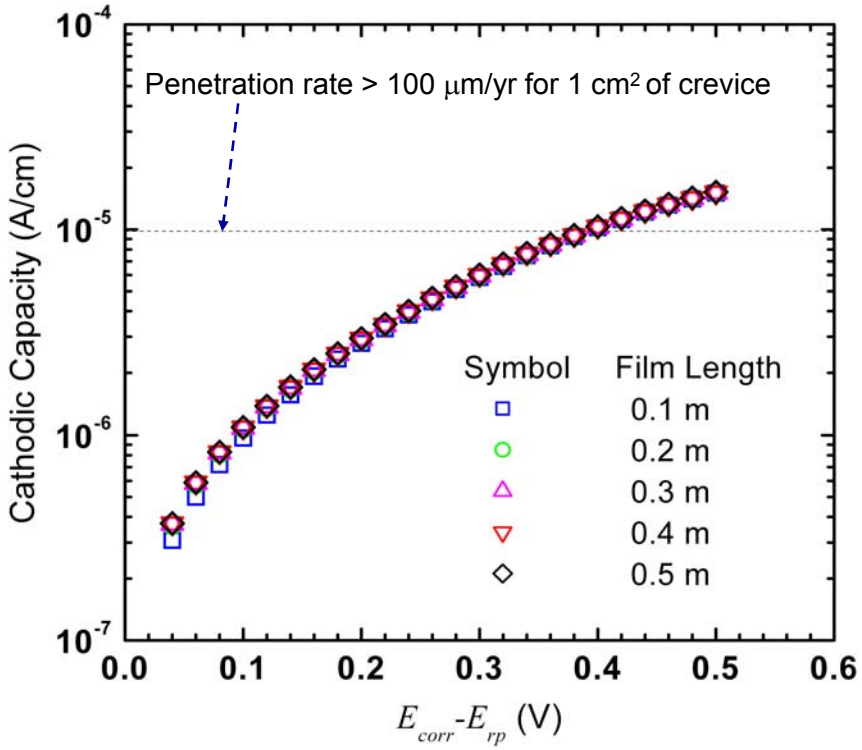
Unit conversions: 110 °C = 230 °F; 1 $ohm^{-1}cm^{-1}$ = 2.54 $ohm^{-1}in^{-1}$; 1 A/cm^2 = 6.45 A/in^2

Alloy 22 Cathodic Capacity in Dust Deliquescence Brines

Film Length = 0.1 m [3.94 in]



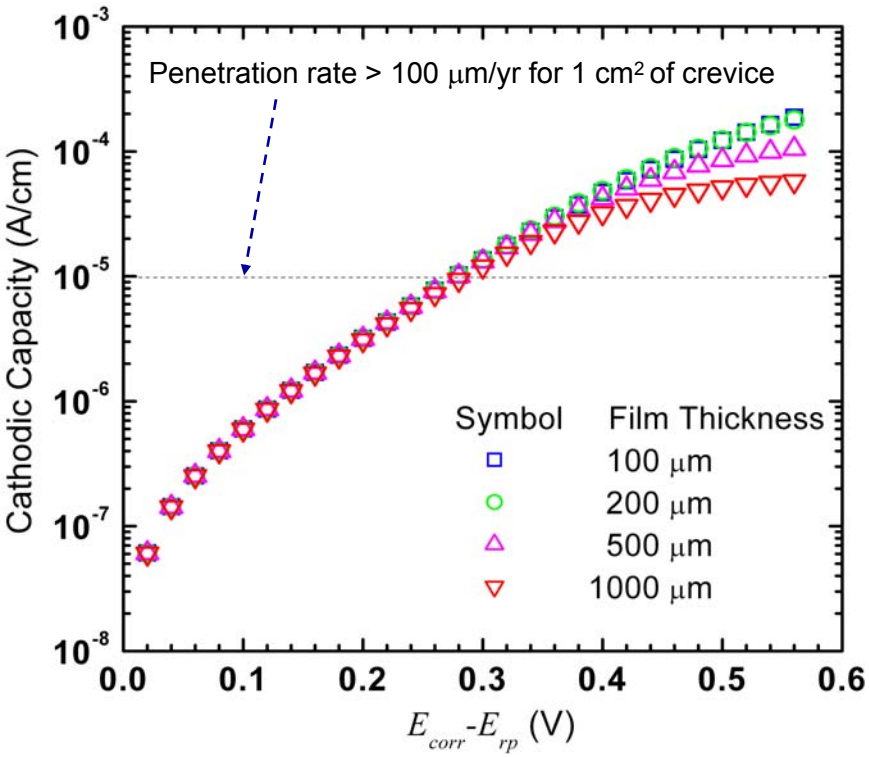
Film Thickness = 45 μm [1.77 mils]



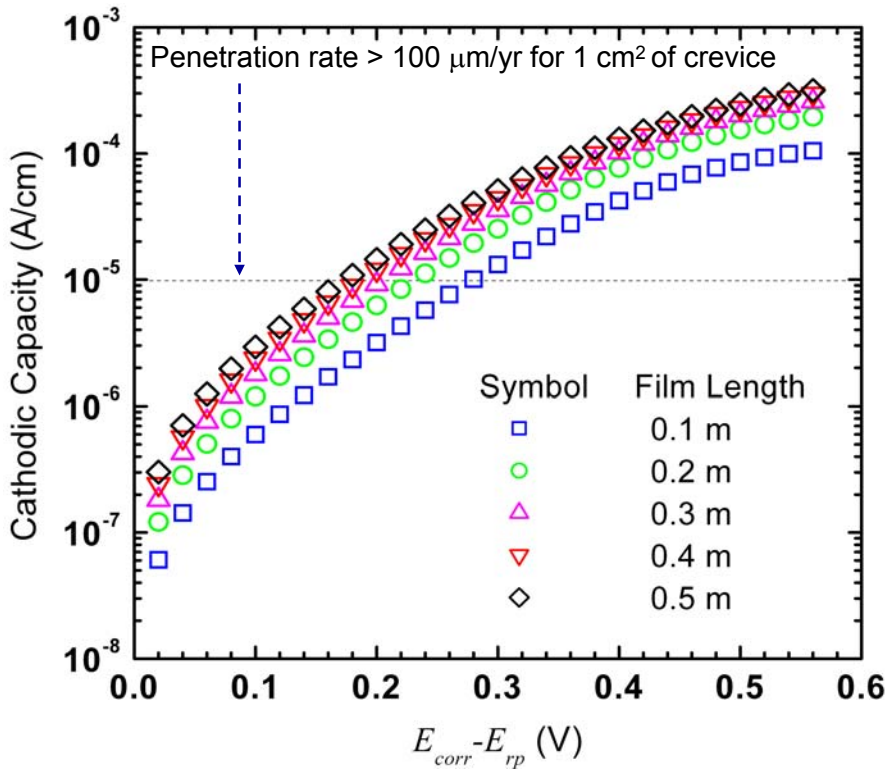
- Cathodic capacity increases with film thickness when $0 < E_{corr} - E_{rp} < 0.55$ V
- Cathodic capacity is only marginally affected by the film length

Alloy 22 Cathodic Capacity in Seepage Water Brines

Film Length = 0.1 m [3.94 in]



Film Thickness = 500 μm [19.7 mils]



- Cathodic capacity decreases with film thickness greater than 200 μm when E_{corr} - E_{rp} > 0.4 V
- Cathodic capacity increases with film length when 0 < E_{corr} - E_{rp} < 0.55 V

Summary

- Dust Deliquescence Brines: If volume of the available brine is spread as uniform film with thickness ≥ 25 μm [0.99 mils], localized corrosion with penetration rate of 100 μm/yr [3.96 mils/yr] for 1-cm² [0.16-in²] crevice region could occur when $E_{corr} - E_{rp} > 0.3\ V_{SHE}$
- Dust Deliquescence Brines: Cathodic capacity increases with film thickness but it's only marginally affected by the film length
- Seepage Water Brines: Localized corrosion with penetration rate of 100 μm/yr [3.96 mils/yr] for 1-cm² [0.16-in²] crevice region could occur when $E_{corr} - E_{rp} > 0.28\ V_{SHE}$ for a 0.1-m [3.94-in]-long brine film
- Seepage Water Brines: The critical value of $E_{corr} - E_{rp}$ for achieving the penetration rate of 100 μm/yr [3.96 mils/yr] for 1-cm² [0.16-in²] crevice region decreases with increasing film length

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