YUCCA MOUNTAIN PROJECT

U.S. Department of Energy
Office of Civilian Radioactive Waste Management

Materials Performance

Presented to:
Nuclear Waste Technical Review Board

Presented by:
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Washington, DC

The Three Temperature Regions

- Dry-out … Orange Area on Poster
  - Ventilation and Initial Heat-Up
    - Drift walls and waste package dry; no significant corrosion
  - Heat-Up Above Deliquescence and Boiling Points
    - Radioactive decay heat continues to dry the drift wall
    - No seepage; no significant corrosion
  - Cool-Down Below Deliquescence Point
    - Formation of deliquescence brines below 150°C
    - Possible corrosion underneath deliquescence film
- Transition ... Tan Area on Poster
  - Cool-Down Below Boiling Point
    - Seepage water enters drift
    - Possibility of aqueous-phase corrosion, depending on chemistry

The Three Temperature Regions

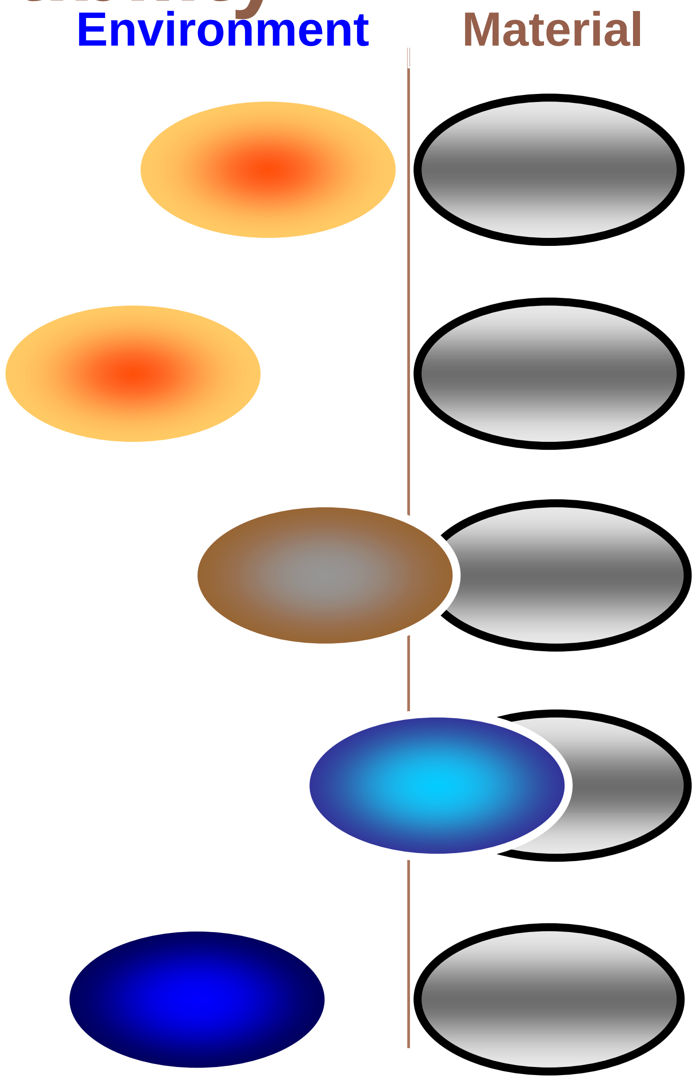
(Continued)

- Low Temperature … Blue Area on Poster
  - Cool-Down Below Threshold Temperature for Crevice Corrosion
    - Protection by Alloy 22 in worst-than-expected environments
    - Insensitive waste package surface chemistry

- The Waste Package is protected by different mechanisms in each of the Three Temperature Regions illustrated on the poster
- The Dry-out Region provides an additional barrier, and additional protection for the waste package
- The Project’s overall strategy is consistent with conceptual models of other experts in the field
- This consistency is apparent when casting the Project’s strategy in the form of Professor Payer’s Zones of Susceptibility

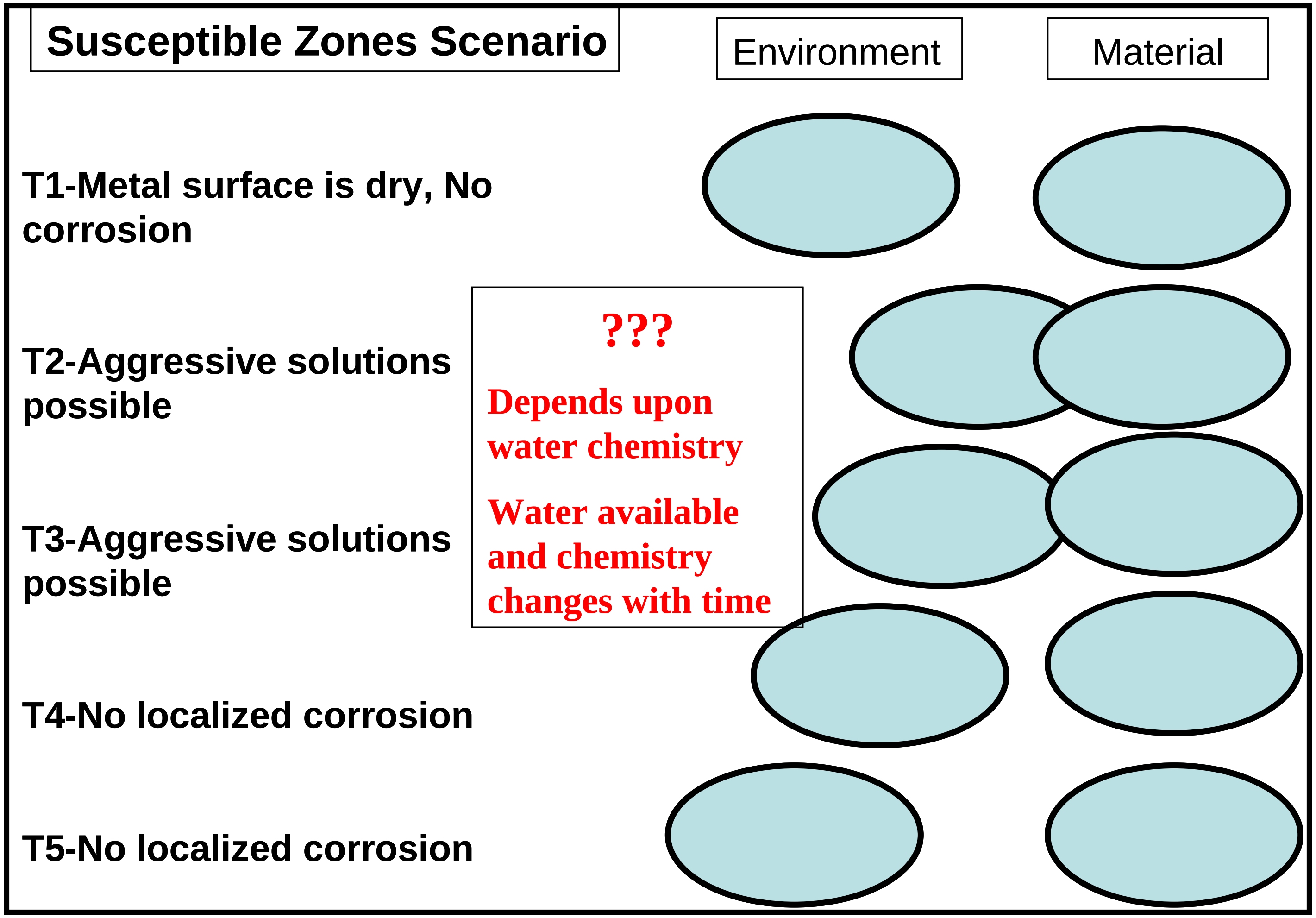
Zones of Susceptibility

- Ventilation and Initial Heat-Up
  - Ventilation keeps waste package dry; no corrosion
- Dry-out: Above Deliquescence and Boiling Point
  - Radioactive decay heat dries the drift wall; no seepage; no corrosion
- Cool-Down: Below Deliquescence
  - Formation of deliquescence brines below 150°C; possible corrosion
- Cool-Down: Below Boiling Point
  - Seepage water enters drift; possibility of aqueous-phase corrosion
- Cool-Down: Below Crevice Corrosion Threshold
  - Protection by Alloy 22 in worst-than-expected environments; insensitive waste package surface chemistry



Graphical convention developed by Payer – ACNW Meeting

Zones of Susceptibility



Susceptible Zones Scenario

Environment

Material

T1-Metal surface is dry, No corrosion

T2-Aggressive solutions possible

T3-Aggressive solutions possible

T4-No localized corrosion

T5-No localized corrosion

???

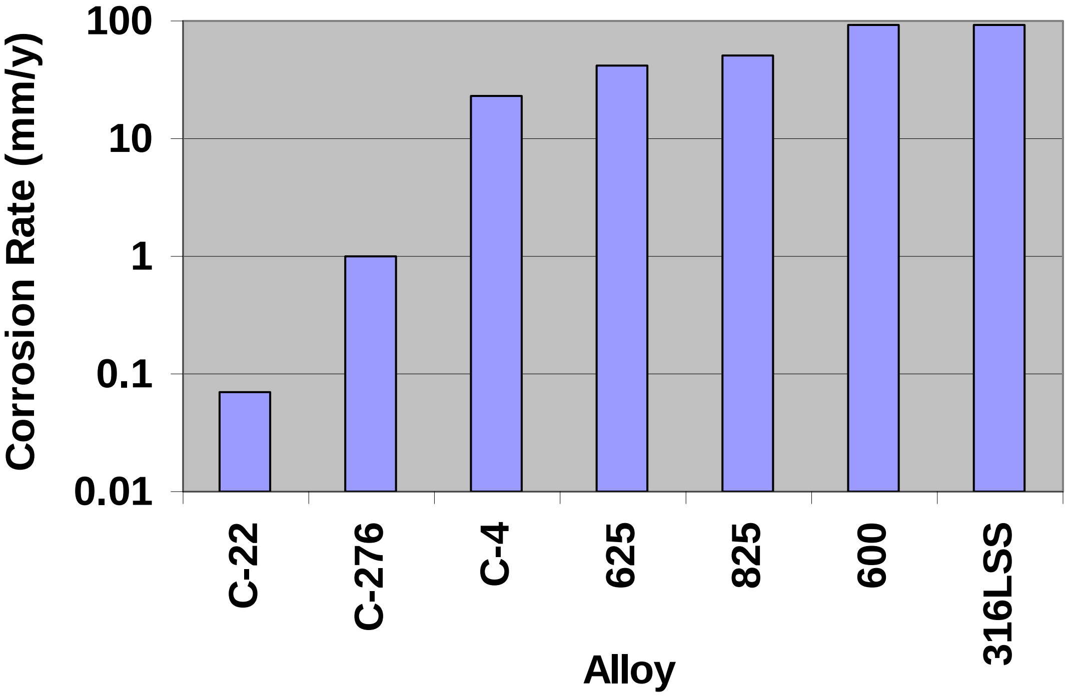
Depends upon water chemistry

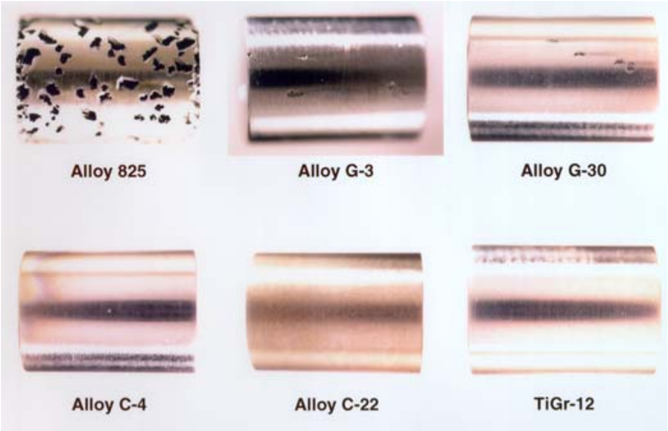
Water available and chemistry changes with time

Materials Selection

Boiling Green Death Solution

11.5% H_2SO_4 + 1.2% HCl + 1% $FeCl_3$ + 1% $CuCl_2$

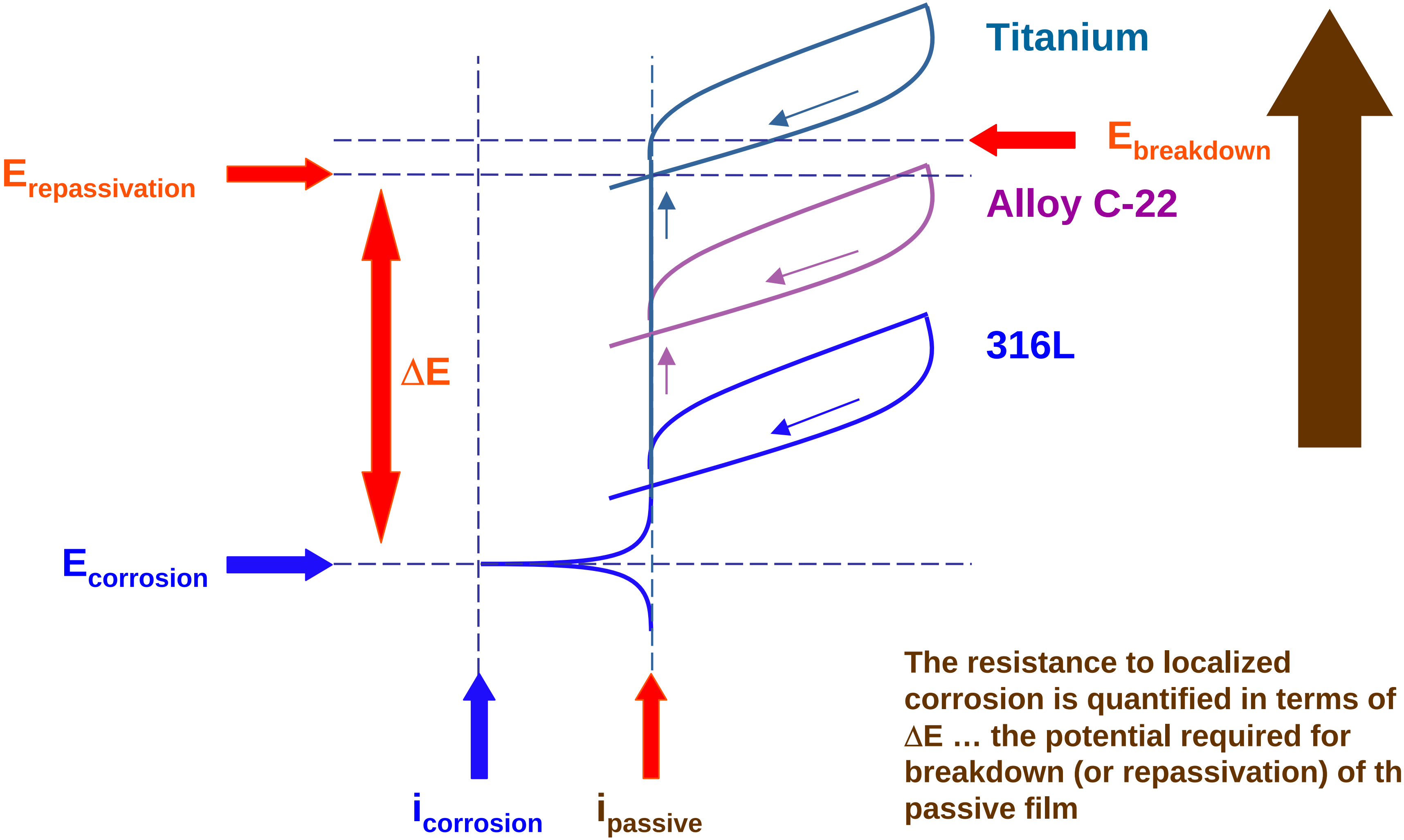




Testing in Acidic NaCl Solution

Alloy 22 is one of the best commercially-available corrosion-resistant materials for construction of the waste package. In regard to its corrosion resistance, it has been referred to as the “end of the diving board.”

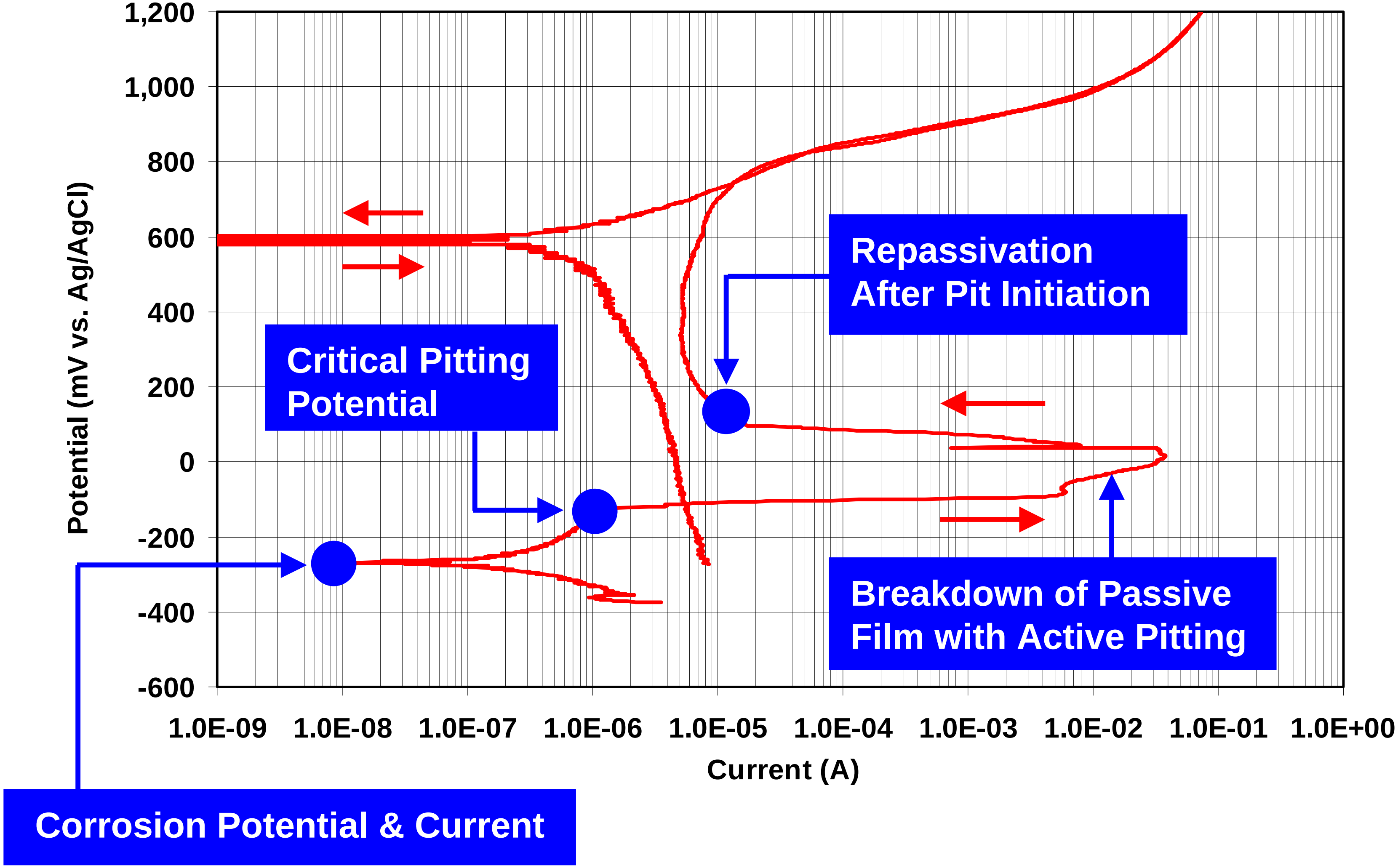
Materials Selection



The resistance to localized corrosion is quantified in terms of ΔE … the potential required for breakdown (or repassivation) of the passive film

Materials Selection

316L in SSW at 100°C (PEA016)



Repassivation After Pit Initiation

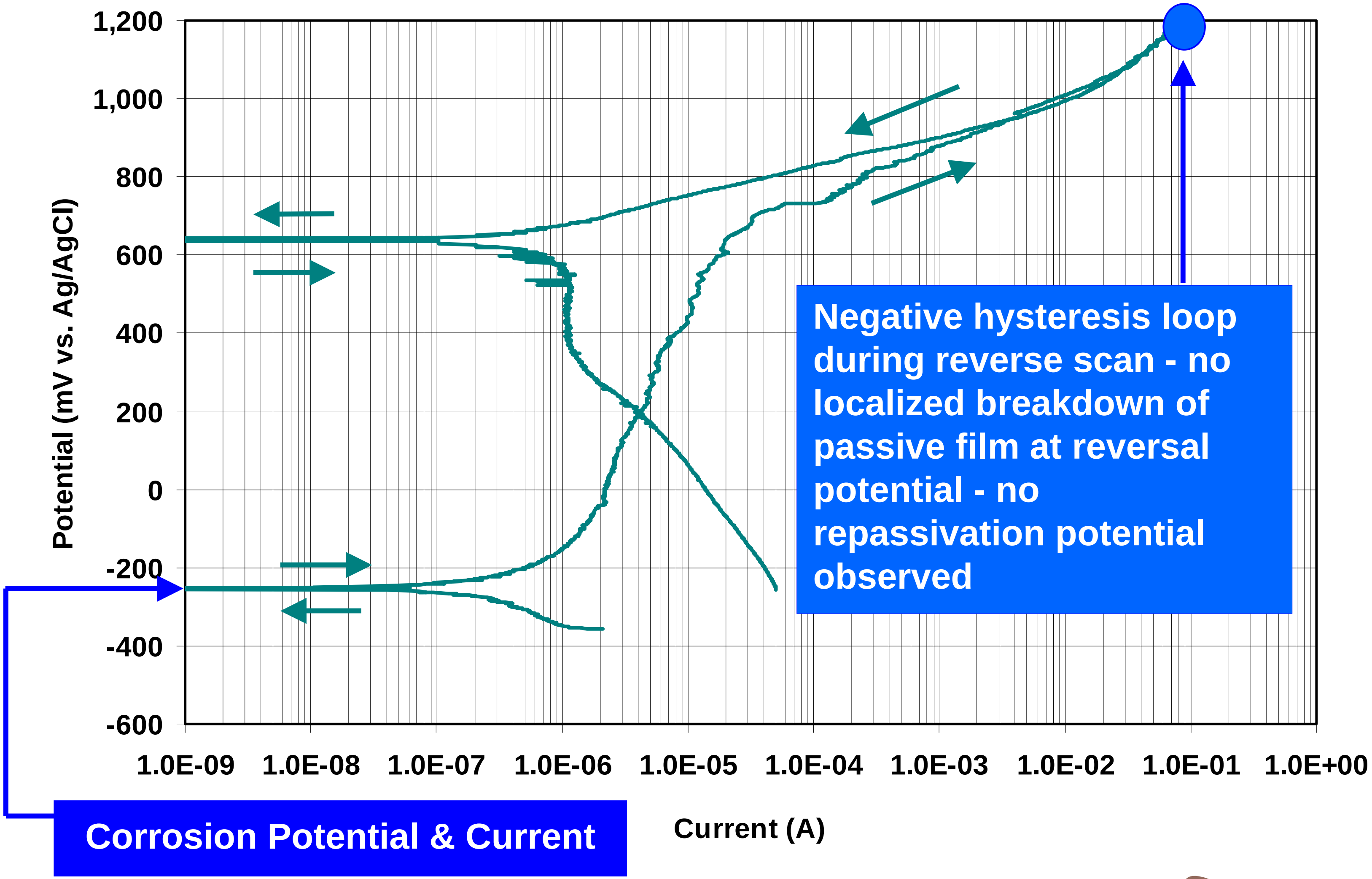
Critical Pitting Potential

Breakdown of Passive Film with Active Pitting

Corrosion Potential & Current

Materials Selection

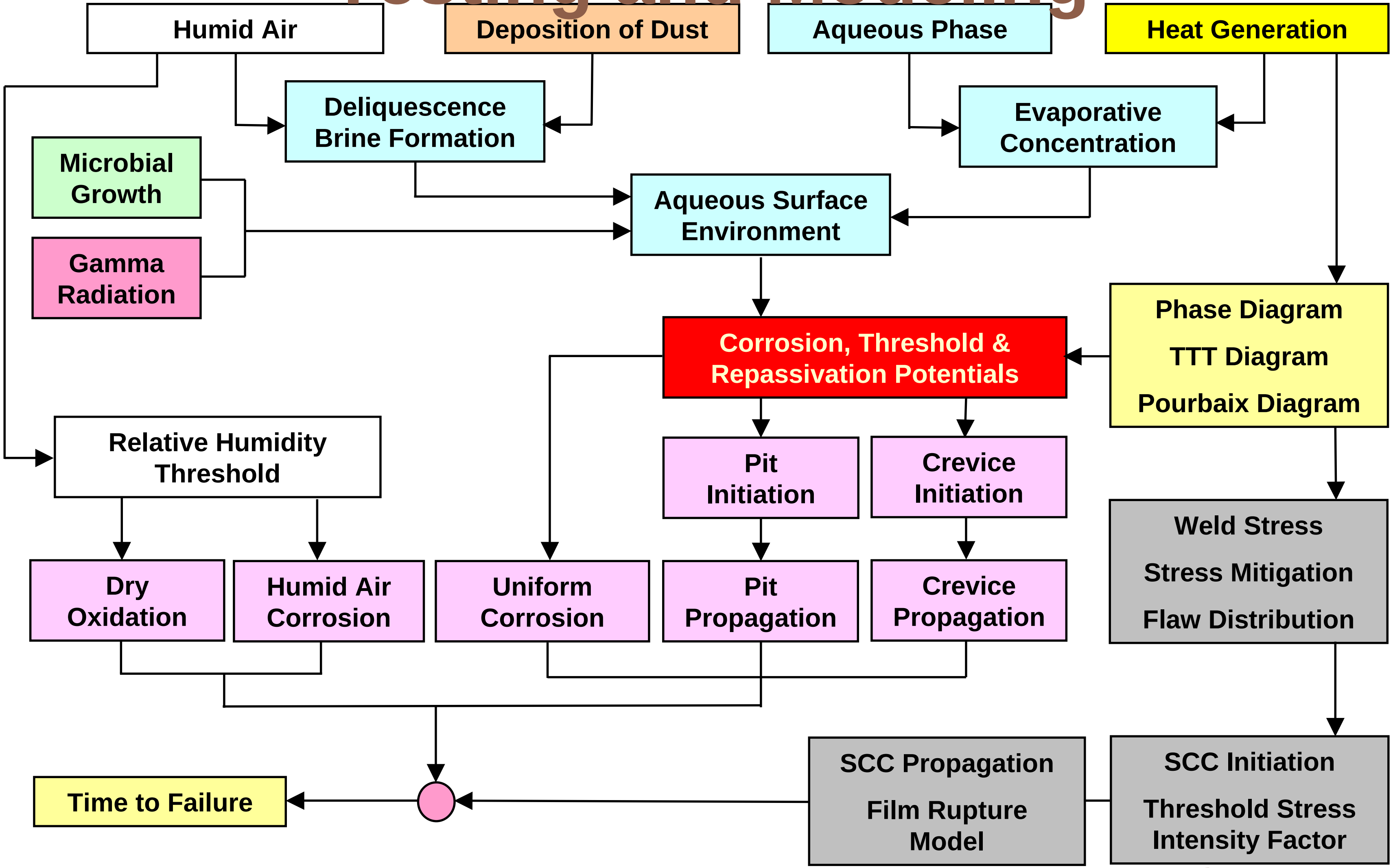
Alloy 22 in SSW at 120°C (DEA033)



Negative hysteresis loop during reverse scan - no localized breakdown of passive film at reversal potential - no repassivation potential observed

Corrosion Potential & Current

Integrated Approach to Corrosion Testing and Modeling



Humid Air

Deposition of Dust

Aqueous Phase

Heat Generation

Deliquescence Brine Formation

Evaporative Concentration

Microbial Growth

Gamma Radiation

Aqueous Surface Environment

Phase Diagram

TTT Diagram

Pourbaix Diagram

Corrosion, Threshold & Repassivation Potentials

Relative Humidity Threshold

Pit Initiation

Crevice Initiation

Weld Stress

Stress Mitigation

Flaw Distribution

Dry Oxidation

Humid Air Corrosion

Uniform Corrosion

Pit Propagation

Crevice Propagation

Time to Failure

SCC Propagation

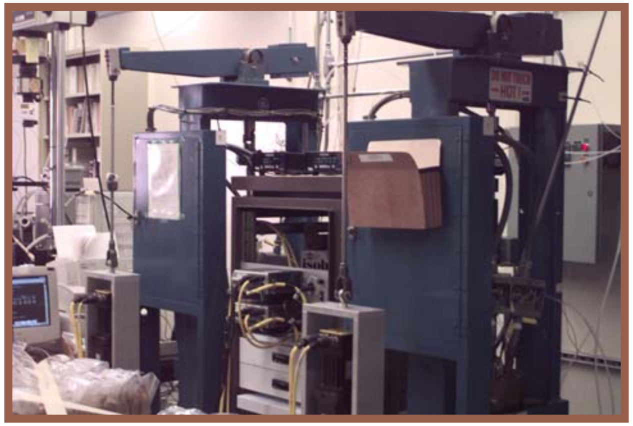
Film Rupture Model

SCC Initiation

Threshold Stress Intensity Factor

Yucca Mountain Project’s Corrosion Laboratory Accelerated and Long Term Testing

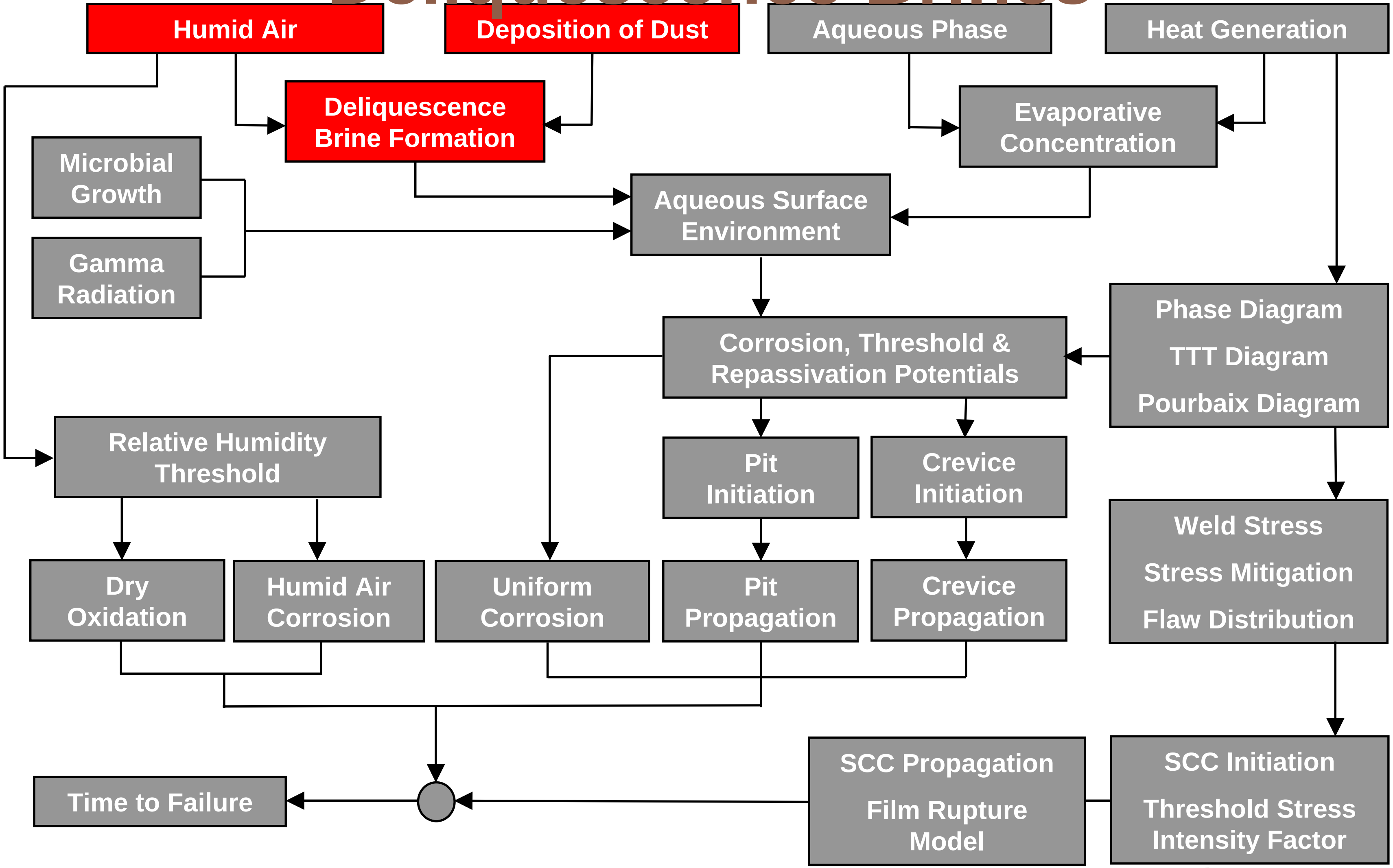
Thousands of waste package samples are exposed to repository-relevant conditions in the Long Term Corrosion Test Facility



Propagation of stress corrosion cracks (SCC) is monitored *in situ* with the Reverse DC Technique

Arrays of potentiostats are used to measure threshold potentials for localized corrosion and the time-evolution of the corrosion potential

Dry-out: Temperature ≥ 110°C
Deliquescence Brines



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SCC Propagation

Film Rupture Model

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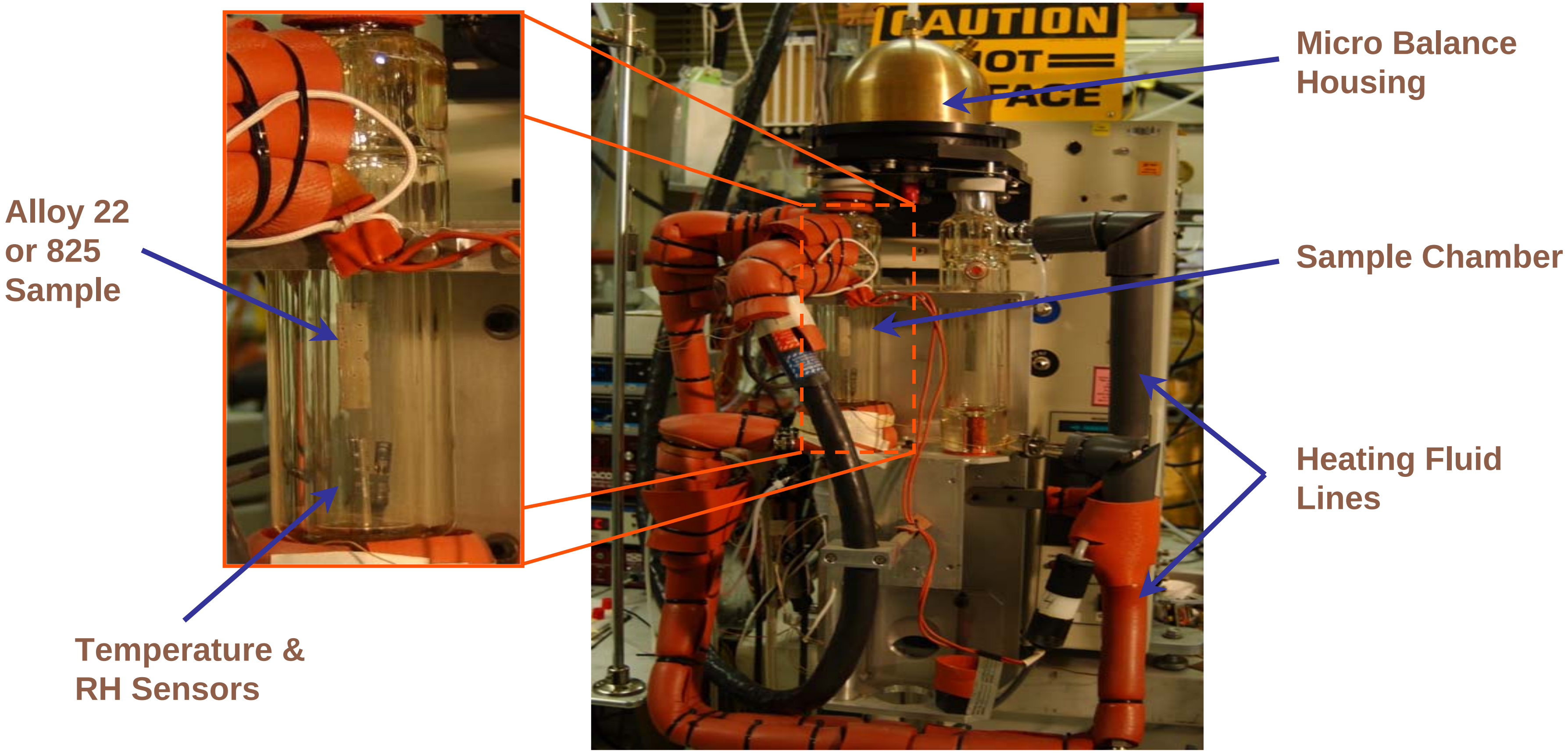
Threshold Stress Intensity Factor

Time to Failure

Dry-out: Temperature ≥ 110°C Deliquescence Brines Studied with Thermogravimetric Analysis



Alloy 22 or 825 Sample

Temperature & RH Sensors

Micro Balance Housing

Sample Chamber

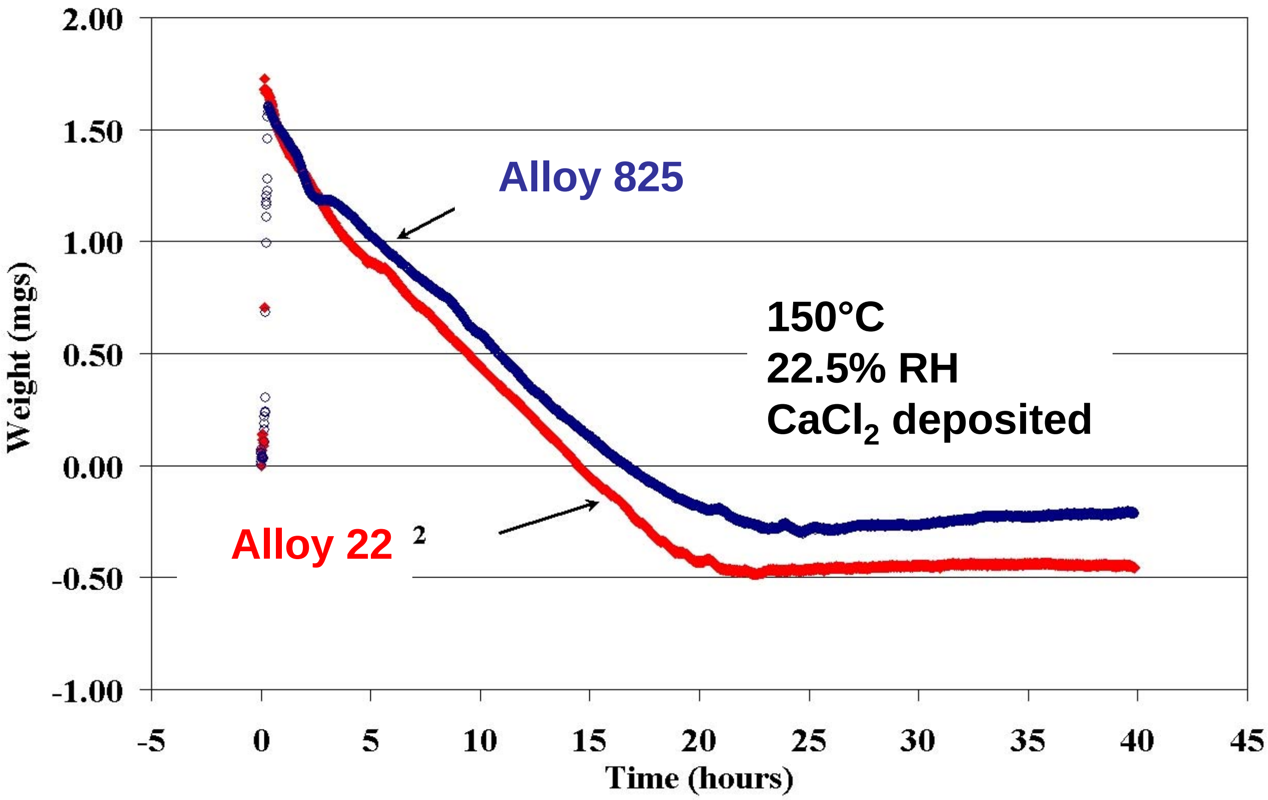
Heating Fluid Lines

- **Sensitive to weight changes as small as "tens of micrograms"**
- **Operation at temperatures up to 150°C**

Dry-out: Temperature ≥ 110°C Deliquescence Brines Studied with Thermogravimetric Analysis

(Continued)

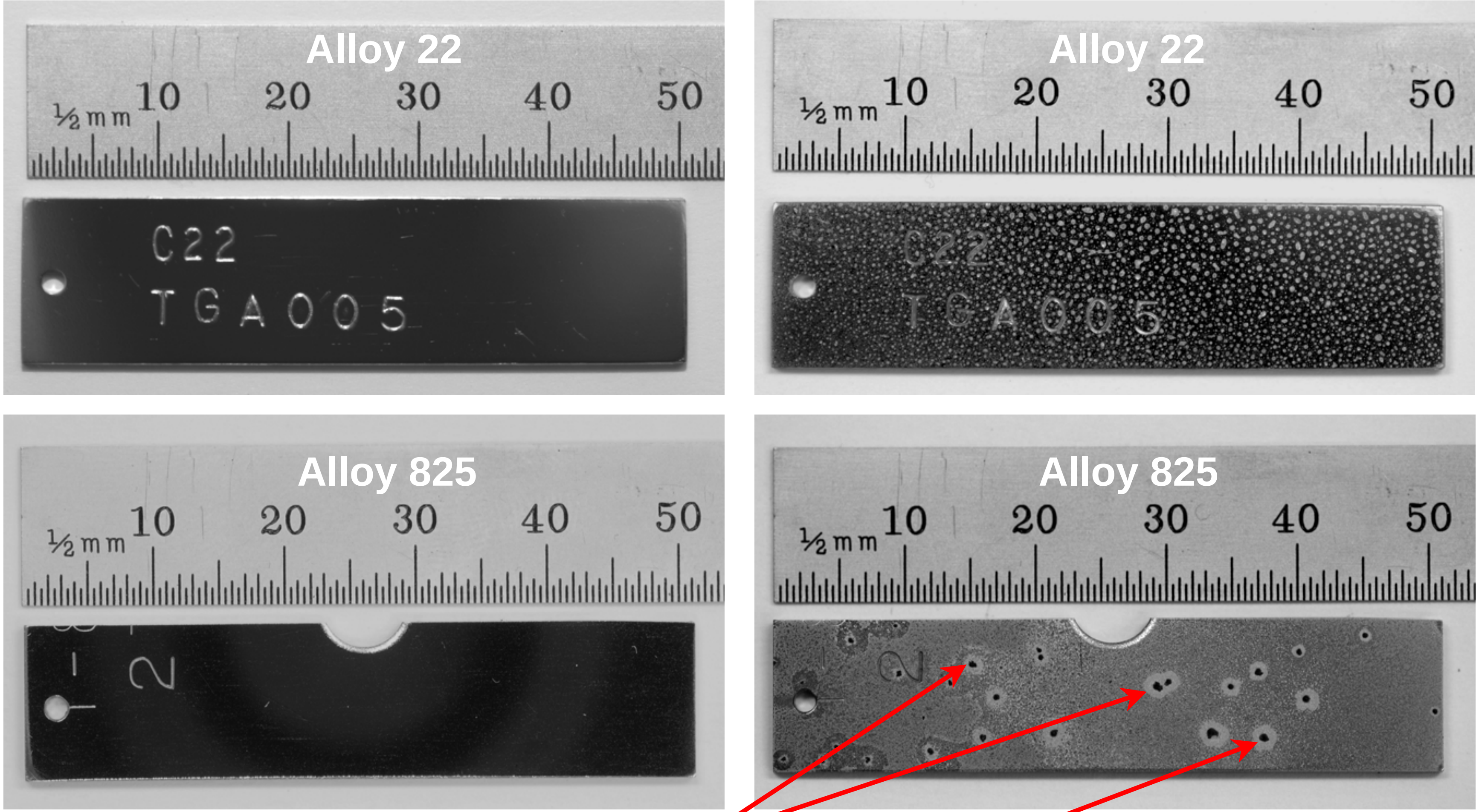
- **Initial weight gains are due to the formation of films of deliquescence brine from dust and humidity**
- **The subsequent weight loss is due to the thermal-driven decomposition of the deliquescence brine, with the volatilization of hydrogen chloride**
- **No further change in weight after loss of chlorine from surface**



- **There is no evidence of localized corrosion of Alloy 22 due to deliquescence**
- **However, substantial attack of Alloy 825 (a less corrosion resistant material) is evident**

Dry-out: Temperature ≥ 110°C Deliquescence Brines - Alloy 22 vs 825

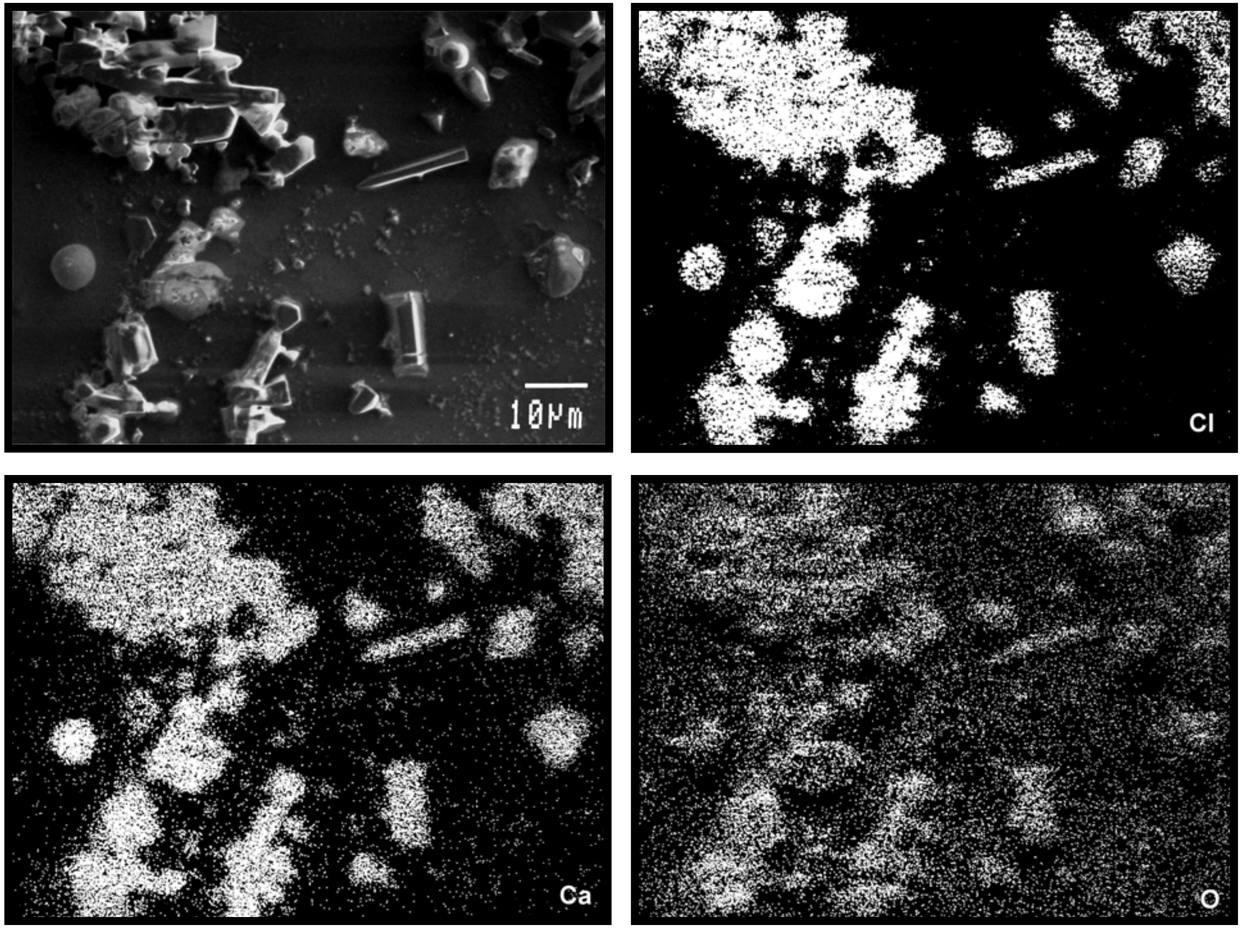
Pre-Test Specimen **Post-Test Specimen**



Precipitates (dark) contain Fe

Ca-rich precipitates (light)

Dry-out: Temperature ≥ 110°C Deliquescence Brines - Deposit Formation



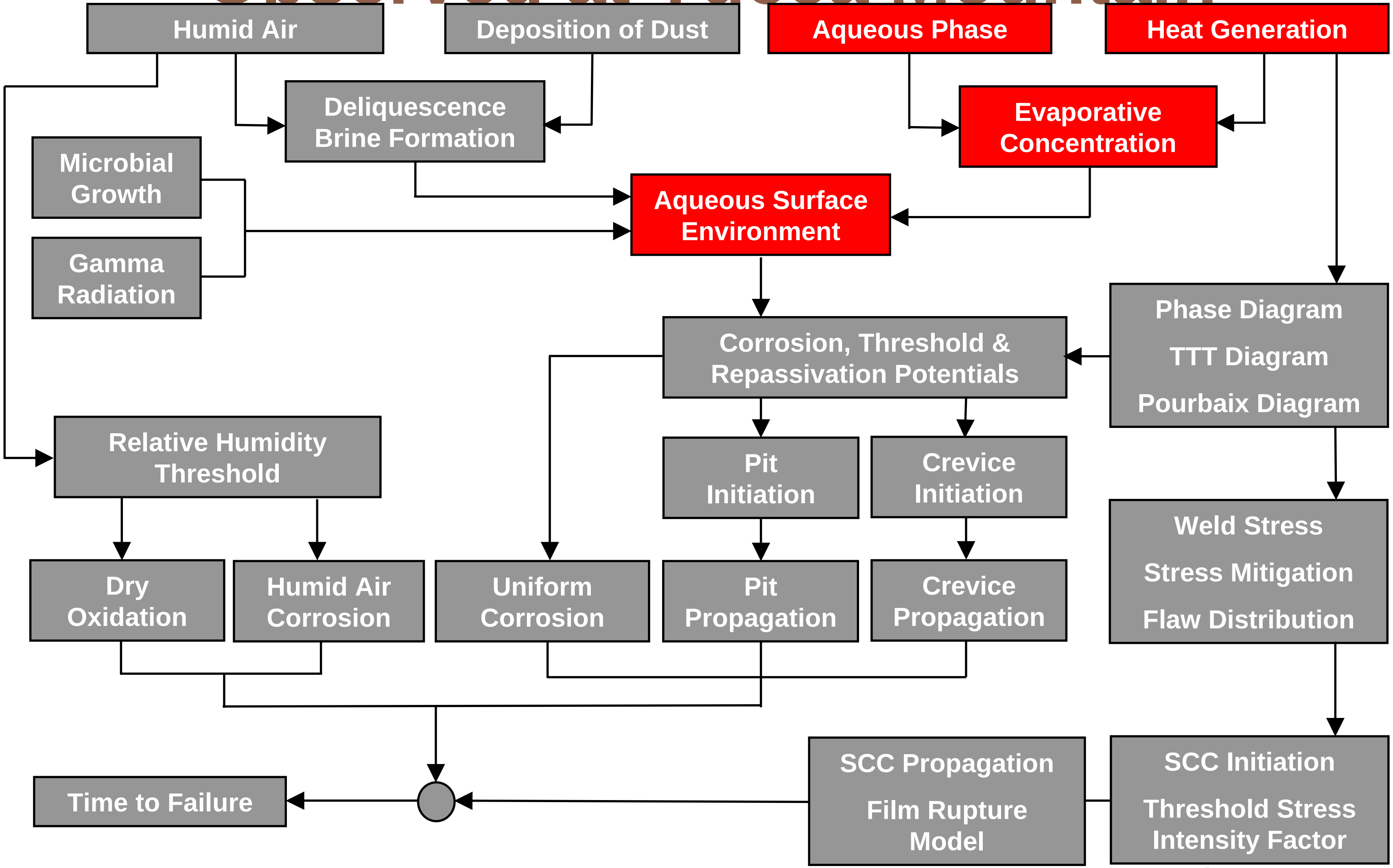
- Electron dispersive spectroscopy (EDS) analysis indicates precipitates contain Ca, Cl, and O
- Raman spectroscopy indicates that precipitates are not $Ca(OH)_2$ or $CaCO_3$
- Precipitates are possibly a CaOHCl
- EDS and wet-chemical analyses indicate a loss of Cl relative to Ca, believed to be HCl volatilization

Dry-out: Temperature ≥ 110°C Deliquescence Brines - Alloy 22 vs 825

(Continued)

- **Alloy 22 was shown to be resistant to localized attack under representative deliquescence brines (aqueous films)**
  - **Alloy 22 is identified as UNS # N06022**
  - **55.5 Ni – 22 Cr – 13 Mo – 3 W – 4 Fe – 2.5 Co**
- **Alloy 825 is a less corrosion-resistant material and was tested in parallel to provide insight into localized modes of attack**
  - **Alloy 825 is identified as UNS # N08825**
  - **42 Ni – 22 Cr – 3 Mo – 0.9 Ti – 2.2 Cu – 1 Mn – 28.9 Fe**

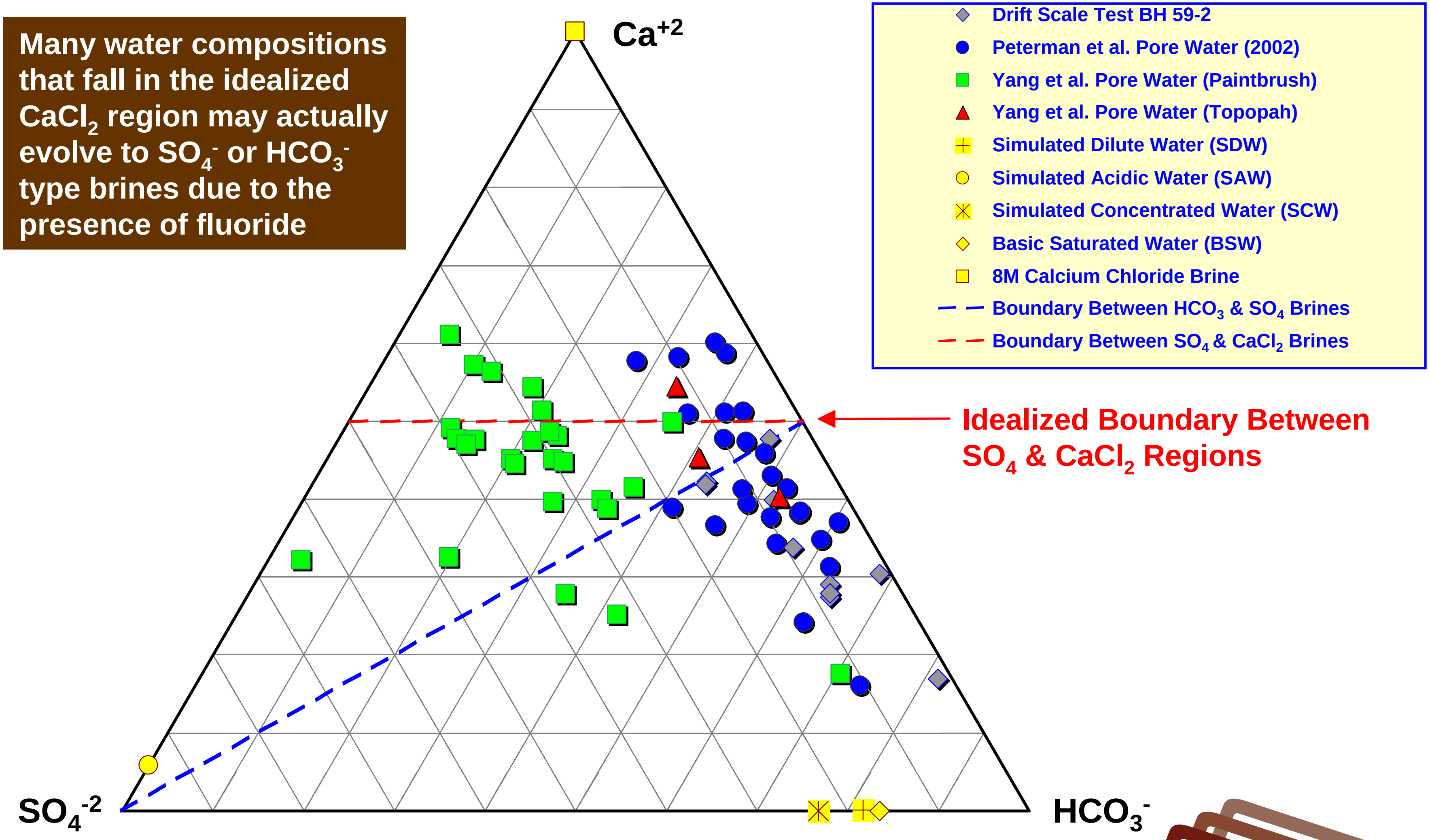
Distribution of Water Chemistries Observed at Yucca Mountain



Distribution of Water Chemistries Observed at Yucca Mountain

(Continued)

Many water compositions that fall in the idealized $CaCl_2$ region may actually evolve to SO_4^- or HCO_3^- type brines due to the presence of fluoride



Idealized Boundary Between SO_4 & $CaCl_2$ Regions

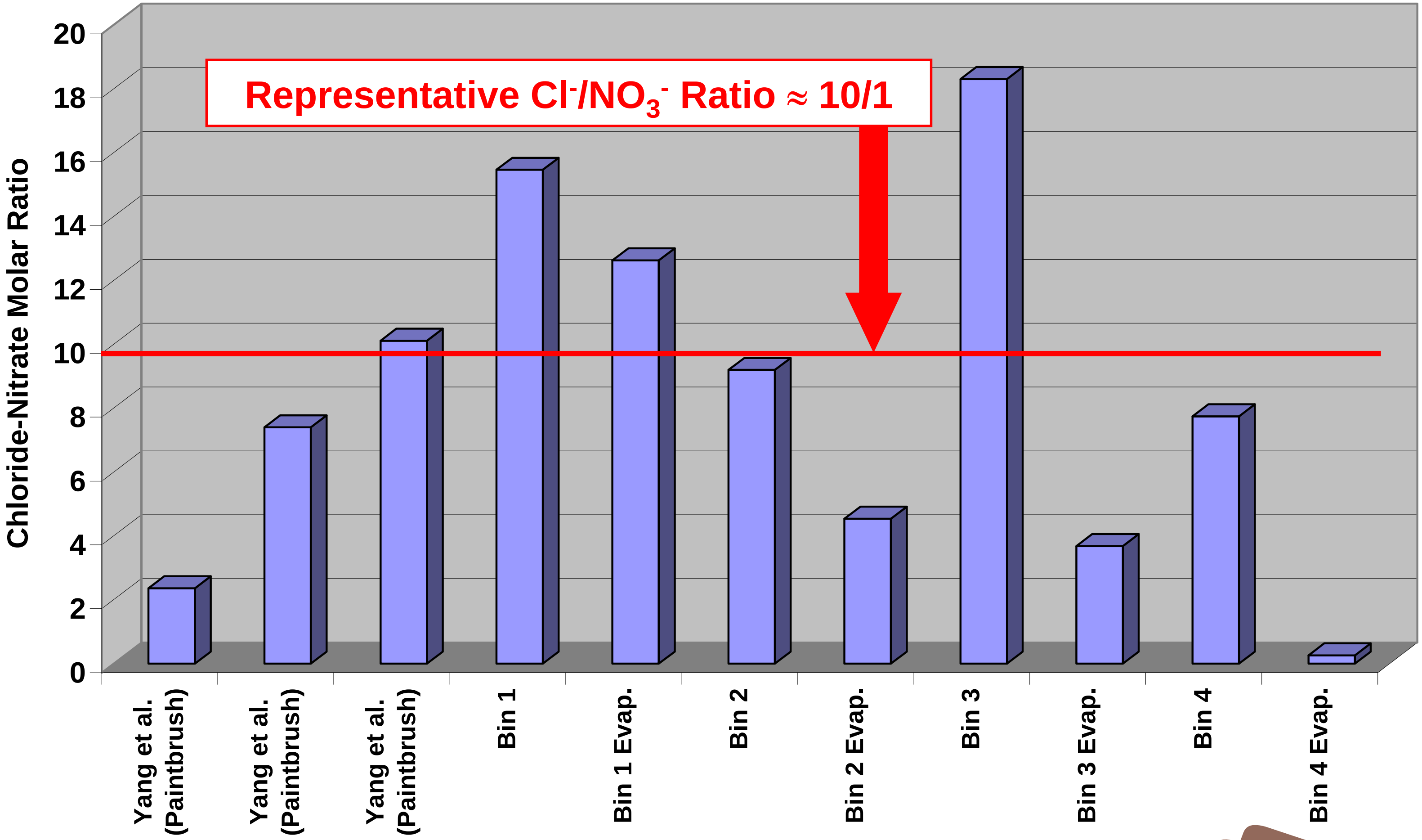
Evolution of Crown Seepage Brine Probability of Occurrence

Bin	Time Integrated Relative Frequency for Crown Waters	Average End-Point RH	98% RH Bin	End Point Brine	Representative Corrosion Test Solution
1	~ 0%	20%	Ca-Cl	Ca-Cl	5-8 M $CaCl_2$ + Nitrate
2	~ 0%	24%	Na-Cl	Ca-Cl	5-8 M $CaCl_2$ + Nitrate
3	~ 1%	40%	Na-Cl	K-Ca-Cl-NO_3	5-8 M $CaCl_2$ + Nitrate
4	~ 15%	50%	Na-Cl	Na-K-Cl-NO_3	SSW, SAW
5	~ 10%	60%	Na-Cl	Na-K-Cl	SSW, SAW
6	~ 1%	60%	Na-Cl	Na-K-Cl-NO_3	SSW, SAW
7	~ 1%	60%	Na-Cl	Na-K-Cl-NO_3	SSW, SAW
8	~ 1%	60%	Na-CO_3	Na-K-Cl	SDW, SCW, BSW
9	~ 20%	60%	Na-CO_3	Na-K-NO_3-Cl	SDW, SCW, BSW
10	~ 1%	60%	Na-CO_3	Na-K-CO_3-Cl	SDW, SCW, BSW
11	~ 50%	60%	Na-CO_3-Cl	Na-K-CO_3-Cl	SDW, SCW, BSW

Note: "Crown Waters" are those waters in fractures above drift > 10% liquid saturation

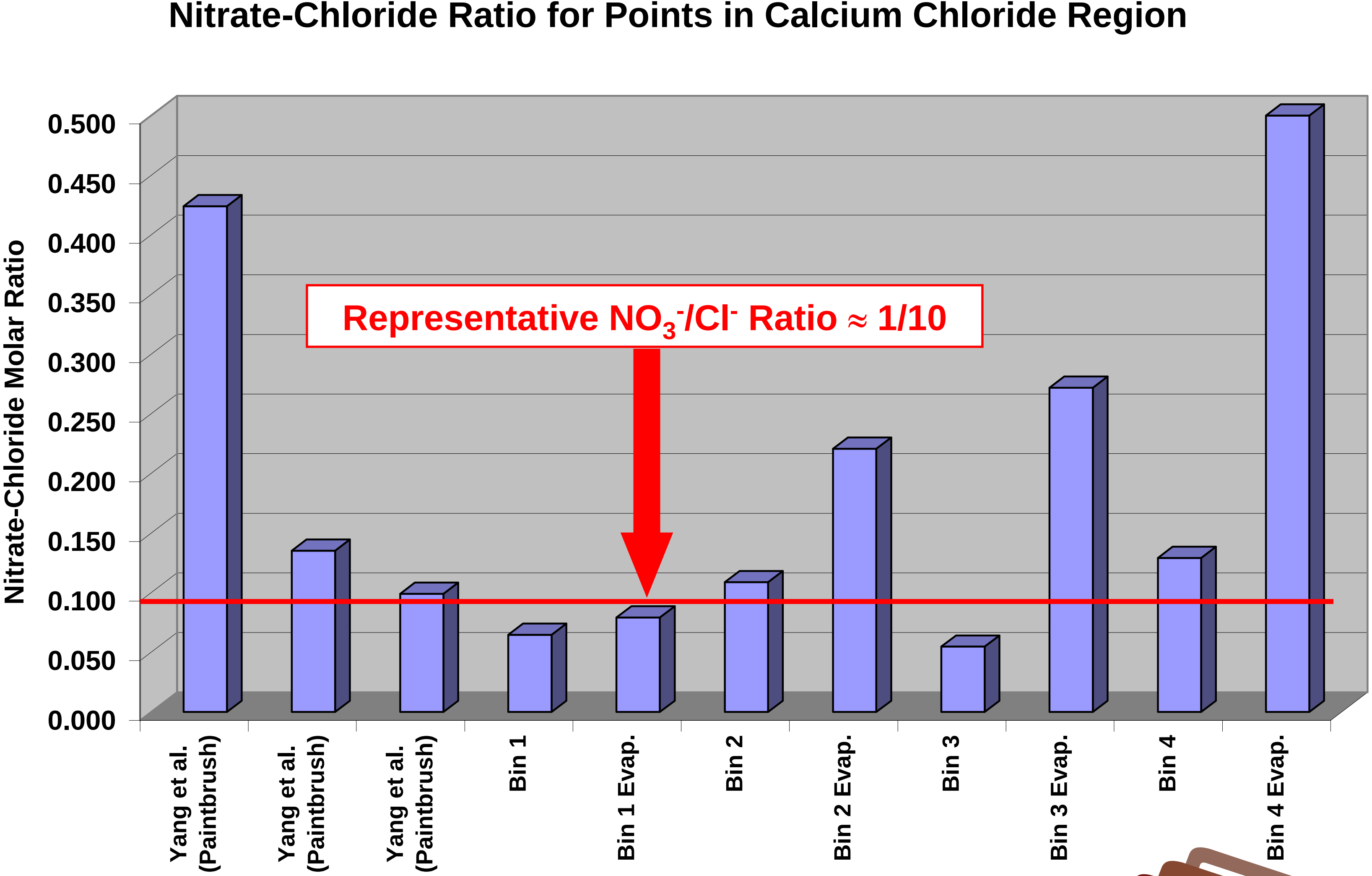
No localized corrosion or stress corrosion cracking after ~ 5 years in SDW, SCW & SAW

Significant Inhibitor Concentration Expected in Calcium Chloride Brines

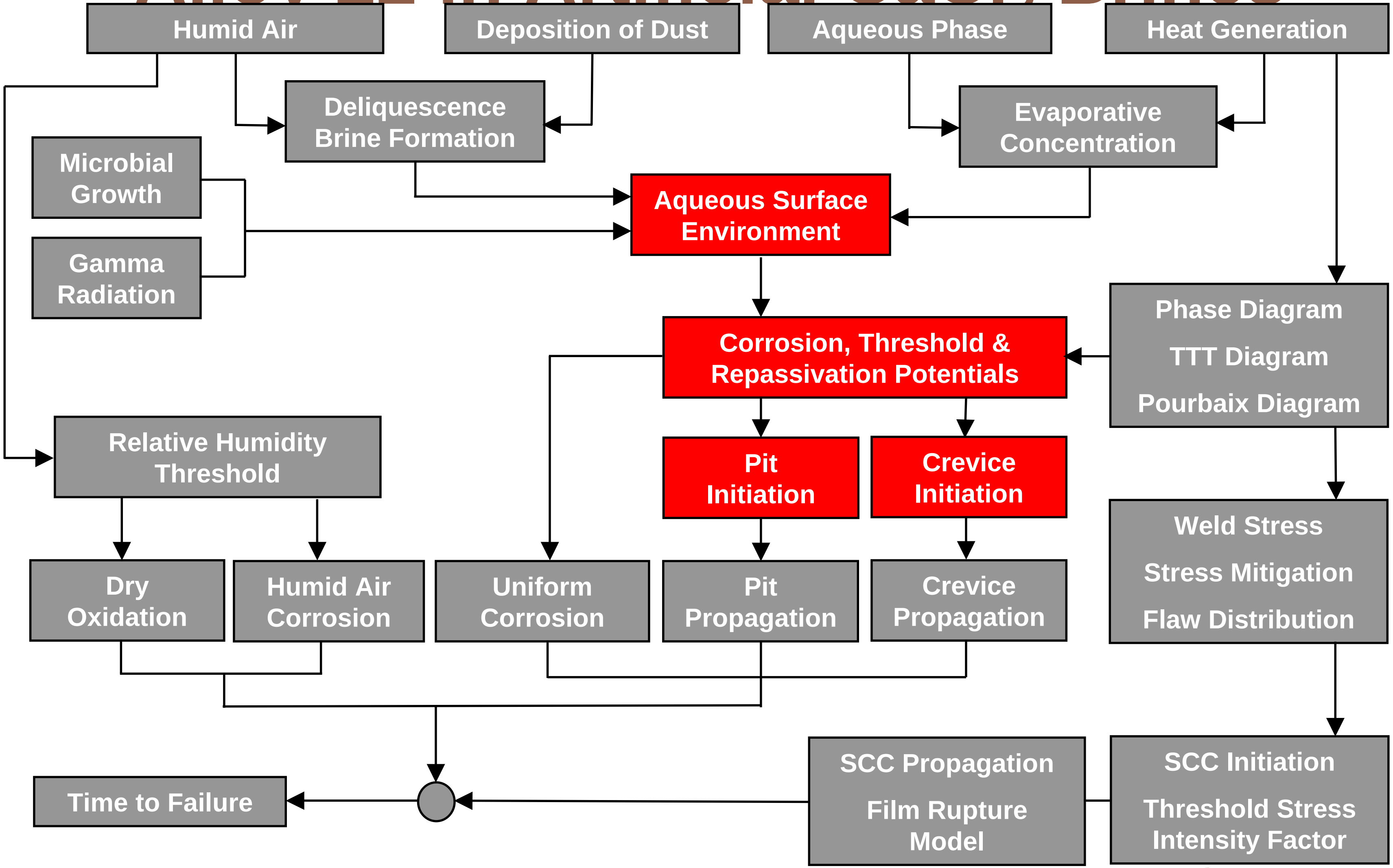


Significant Inhibitor Concentration Expected in Calcium Chloride Brines

(Continued)



Cyclic Polarization of Alloy 22 in Artificial $CaCl_2$ Brines



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Aqueous Phase

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Film Rupture Model

SCC Initiation

Threshold Stress Intensity Factor

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Cyclic Polarization of Alloy 22 in Artificial $CaCl_2$ Brines

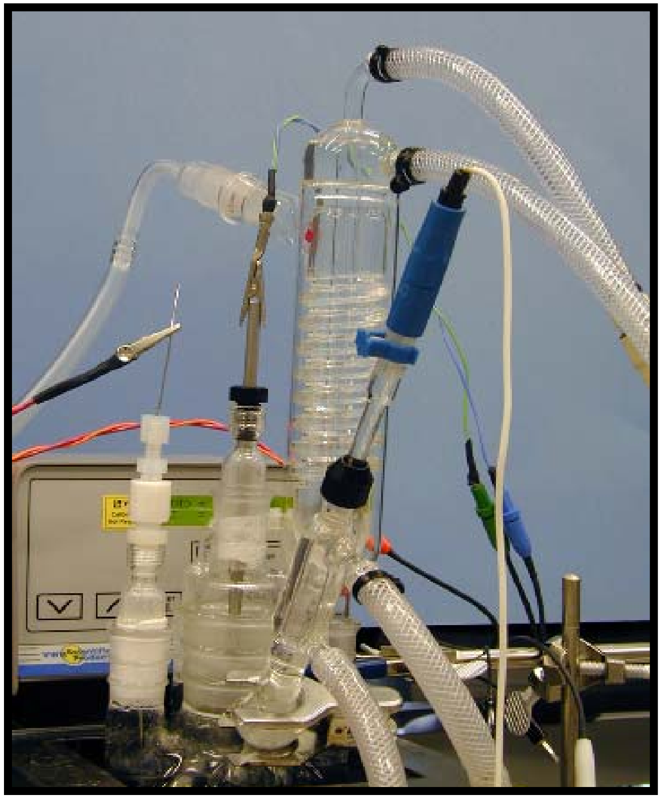
(Continued)

- **Objective of Study**
  - **Quantify the threshold for localized corrosion in aqueous solutions, believed to be comparable to deliquescence brines**
- **Test Conditions**
  - **Chloride Concentrations: 10 to 18 M**
  - **Inhibitor Level: $NO_3^-/Cl^- = 0.0$ and 0.1**
  - **Temperature Range: 45 to 160°C**
- **Measurements**
  - **Cyclic polarization in temperature controlled electrochemical cell**
  - **Alloy 22 samples: disks and multiple crevice assemblies**
  - **Surface analysis of specimens after exposure**

Cyclic Polarization of Alloy 22 in Artificial $CaCl_2$ Brines

(Continued)

Arrays of potentiostats are used to measure threshold potentials for localized corrosion and the time-evolution of the corrosion potential.



Special three-electrode electrochemical cells are equipped with coolers and condensers to maintain reference electrodes at ambient temperature, and to prevent the loss of volatile species.

Cyclic Polarization of Alloy 22 in Artificial $CaCl_2$ Brines

(Continued)

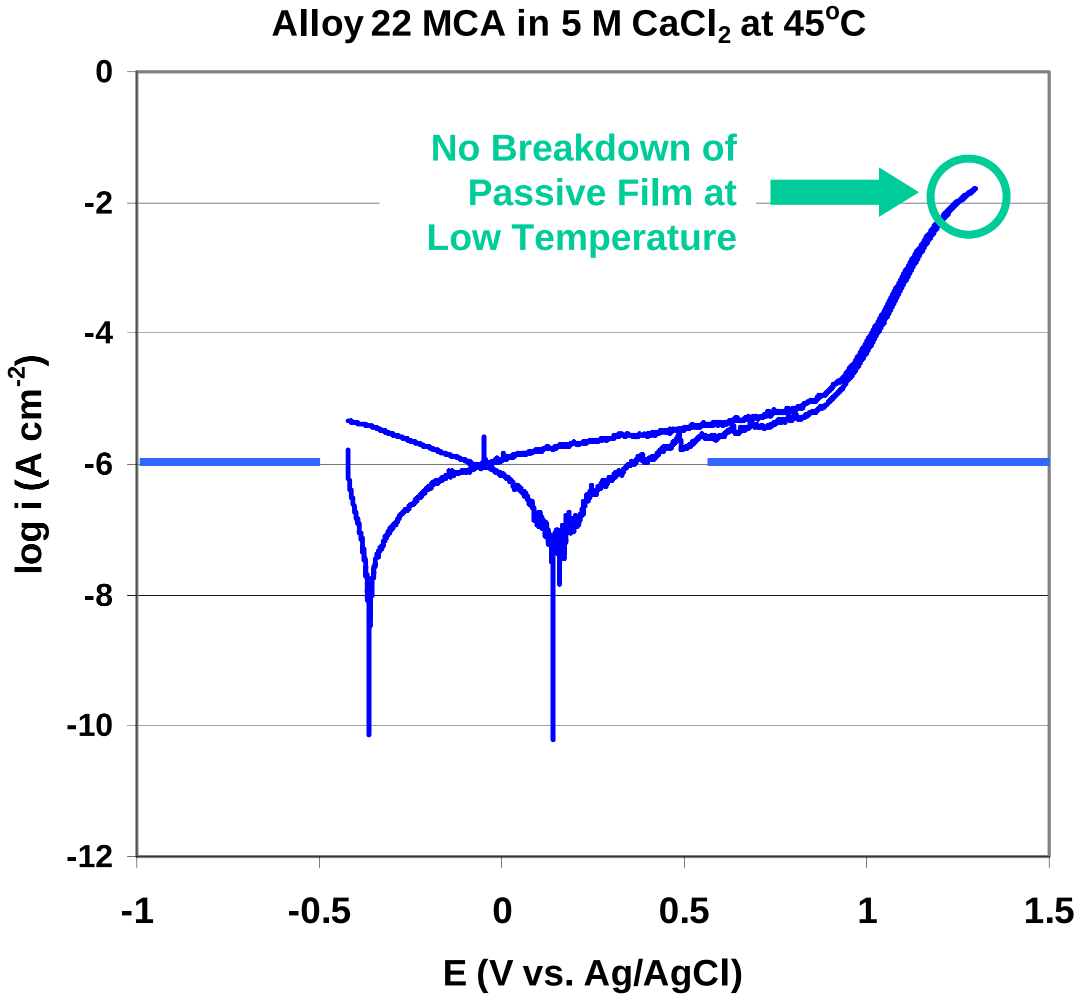
- Multiple crevice assembly (MCA)
- Surface finish: MCA-as received; some samples with edges ground with 600 grit SiC
- Exposed area: 7.43 cm^2
- Torque: 70 in-lb
- Teflon inserts in MCA fill micro voids
- Bolts of MCA Teflon wrapped for electrical insulation
- Welded Sample Weld Type: Narrow Groove Gas Tungsten Arch Weld (NG-GTAW)

Cyclic Polarization of Alloy 22 in Artificial $CaCl_2$ Brines

(Continued)

- **Method A - Initial Breakdown of Passive Film**
  - **Critical Potential (E_{crit}) = Breakdown Potential (E20)**
  - **Based on Threshold Current Density of 20 $\mu A/cm^2$**
- **Method B - Repassivation of Surface**
  - **Critical Potential (E_{crit}) = Repassivation Potential (ER1)**
  - **Based on Threshold Current Density of 1 $\mu A/cm^2$**
- **Method C - Repassivation of Surface**
  - **Critical Potential (E_{crit}) = Repassivation Potential (ERP)**
  - **Intersection of Forward Scan with Hysteresis Loop**
  - **Corresponds to Cross-Over Point**

Critical Temperature for Localized Corrosion in Artificial $CaCl_2$ Brine (No NO_3^- Inhibitor)



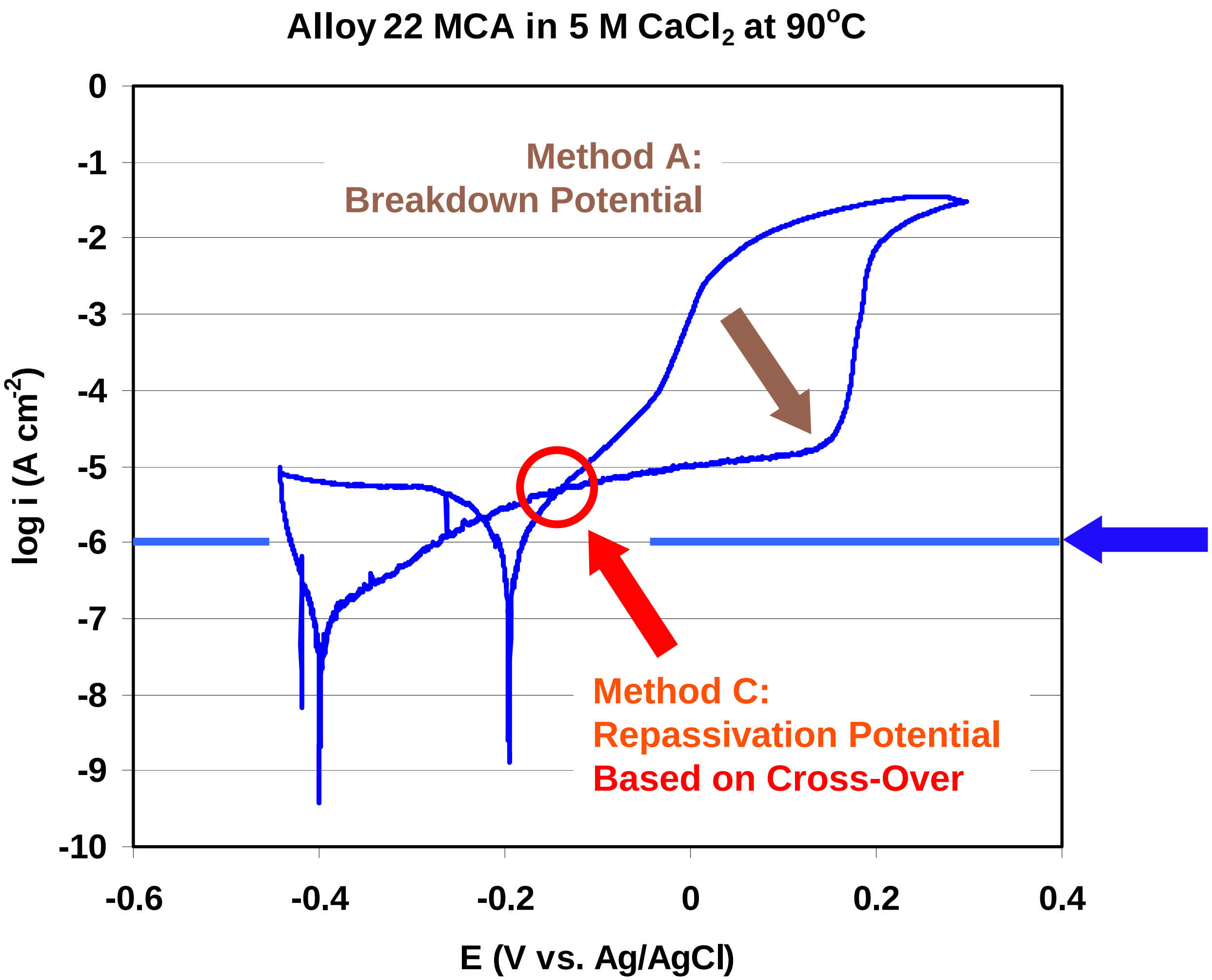
Method A:
Breakdown Potential
Undefined

Method B:
Repassivation Potential
Based on Fixed Current
Density (1 μA/cm^2)
Undefined

Method C:
Repassivation Potential
Based on Cross-Over
Undefined

Critical Temperature for Localized Corrosion in Artificial $CaCl_2$ Brine (No NO_3^- Inhibitor)

(Continued)



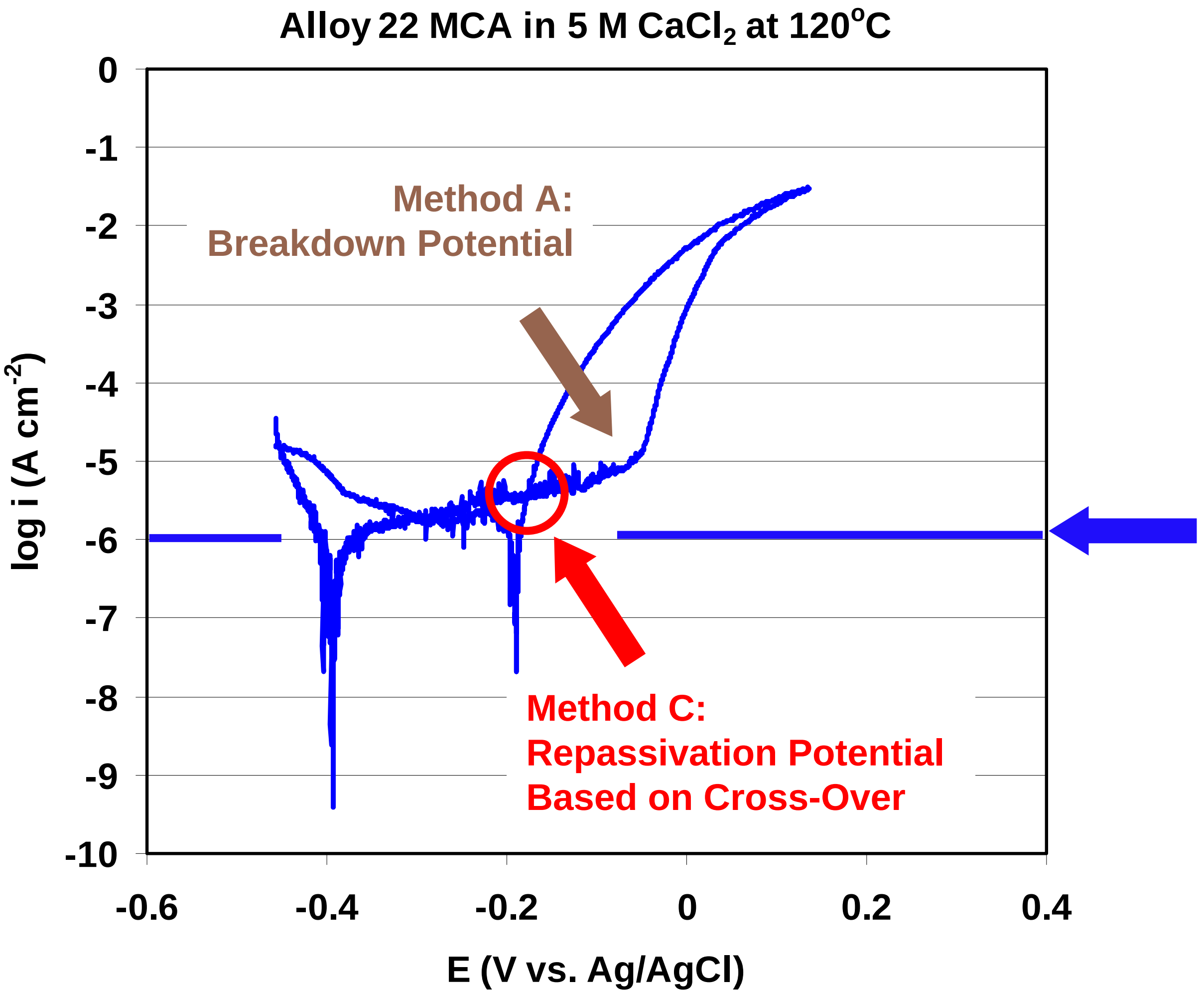
Method A:
Breakdown Potential

Method B:
Repassivation Potential Based on Fixed Current Density (1 μA/cm²)

Method C:
Repassivation Potential Based on Cross-Over

Critical Temperature for Localized Corrosion in Artificial $CaCl_2$ Brine (No NO_3^- Inhibitor)

(Continued)



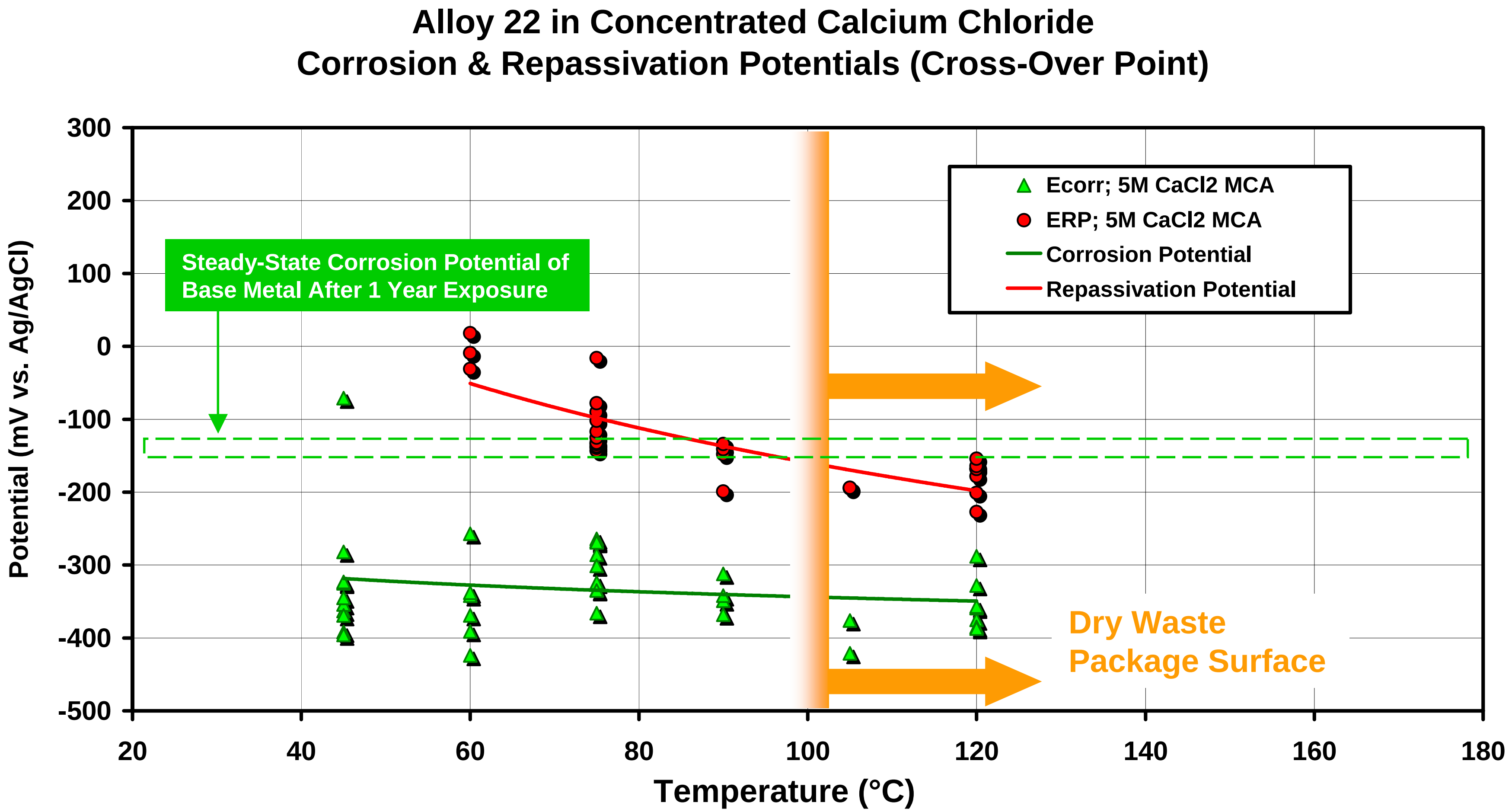
Alloy 22 MCA in 5 M $CaCl_2$ at 120°C

Method A:
Breakdown Potential

Method B:
Repassivation Potential
Based Fixed Current
Density (1 μA/cm²)

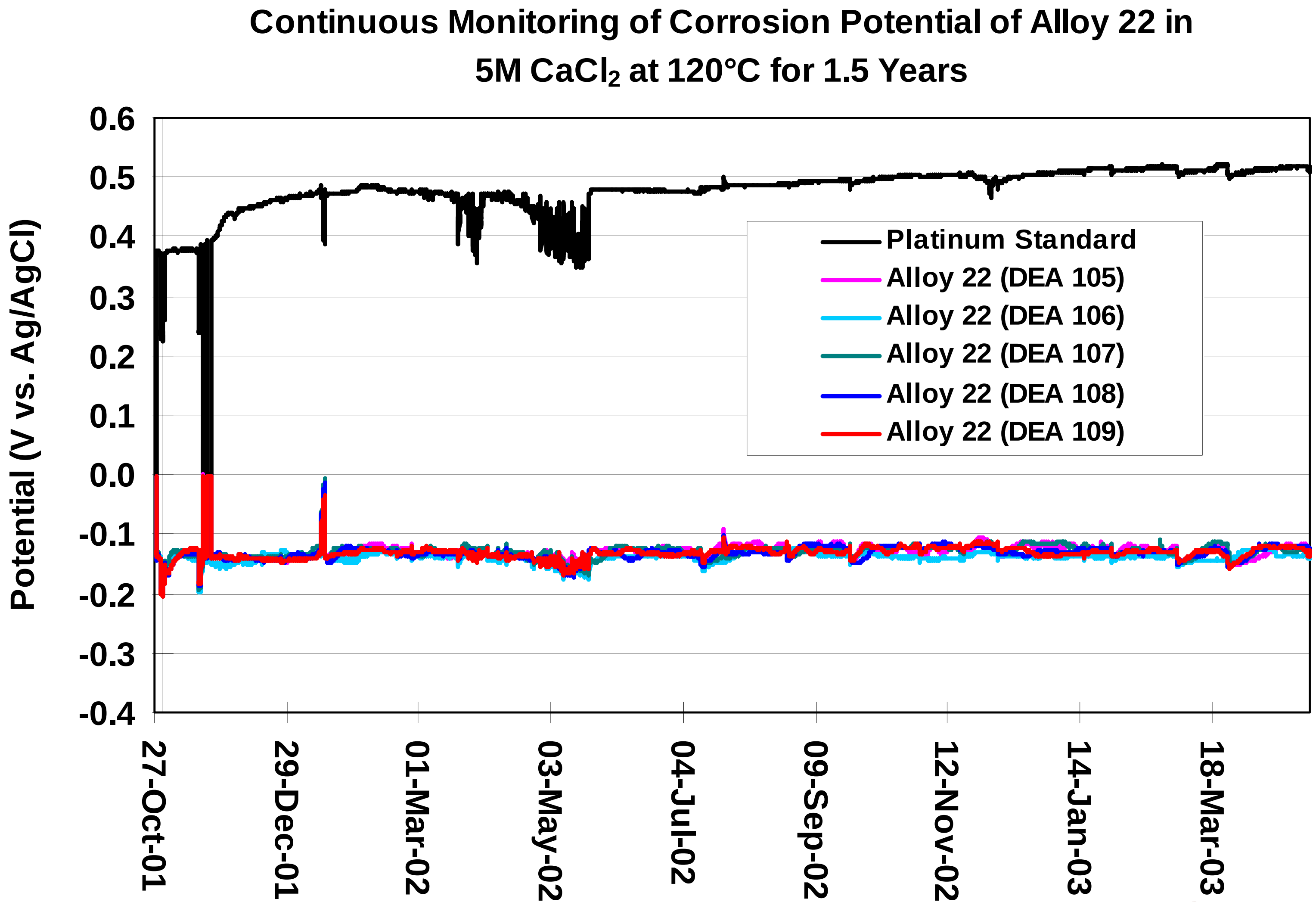
Method C:
Repassivation Potential
Based on Cross-Over

Critical Temperature for Localized Corrosion in Artificial $CaCl_2$ Brine (No NO_3- Inhibitor)



Time Integrated Relative Frequency ~ 0 to 1% for Bins 1 through 3

Effect of Long Term Exposure on Corrosion Potential in Worst-Case Scenario



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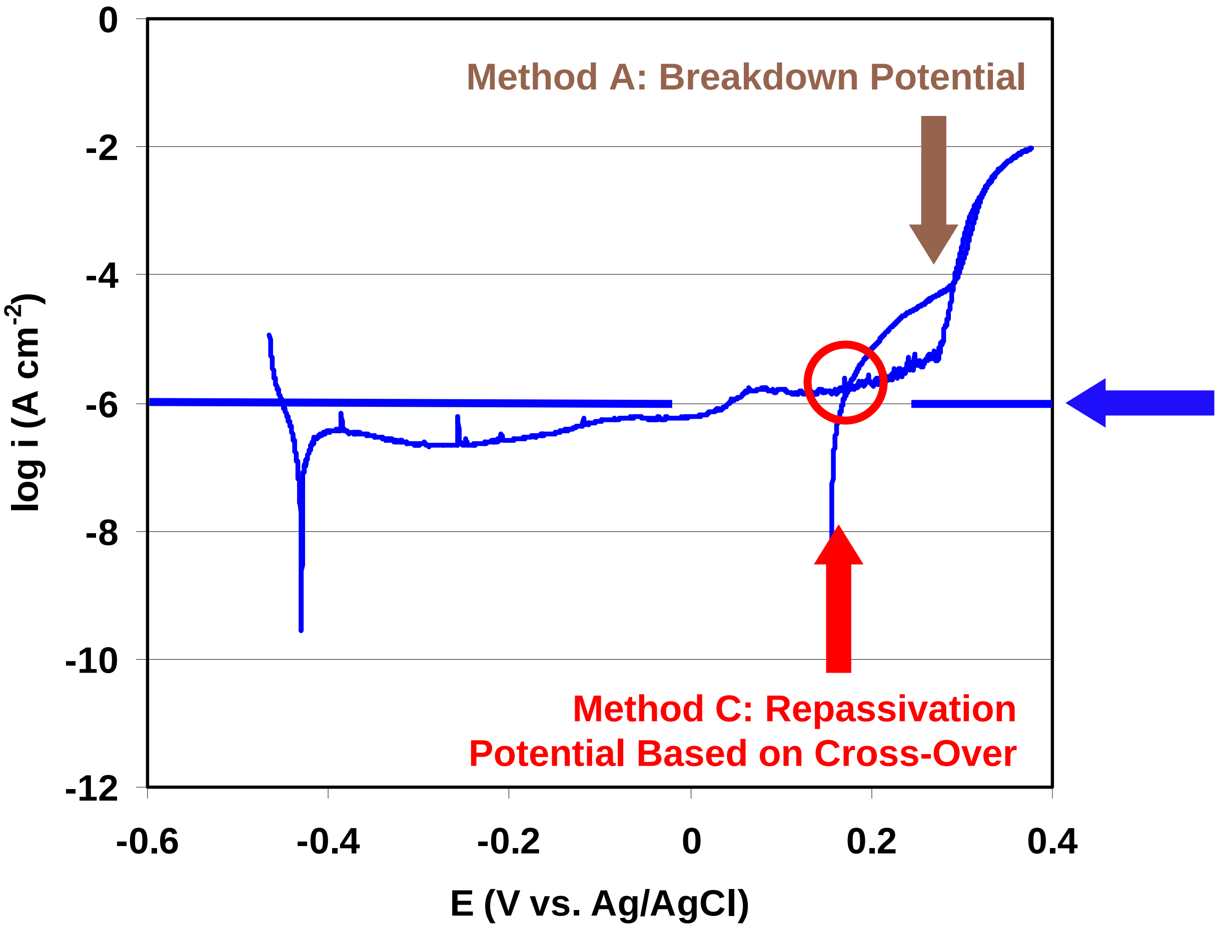
Critical Temperature for Localized Corrosion in Artificial $CaCl_2$ Brine with NO_3^- Inhibitor

Alloy 22 MCA 5 M $CaCl_2$ 0.5 M $Ca(NO_3)_2$ at 90°C

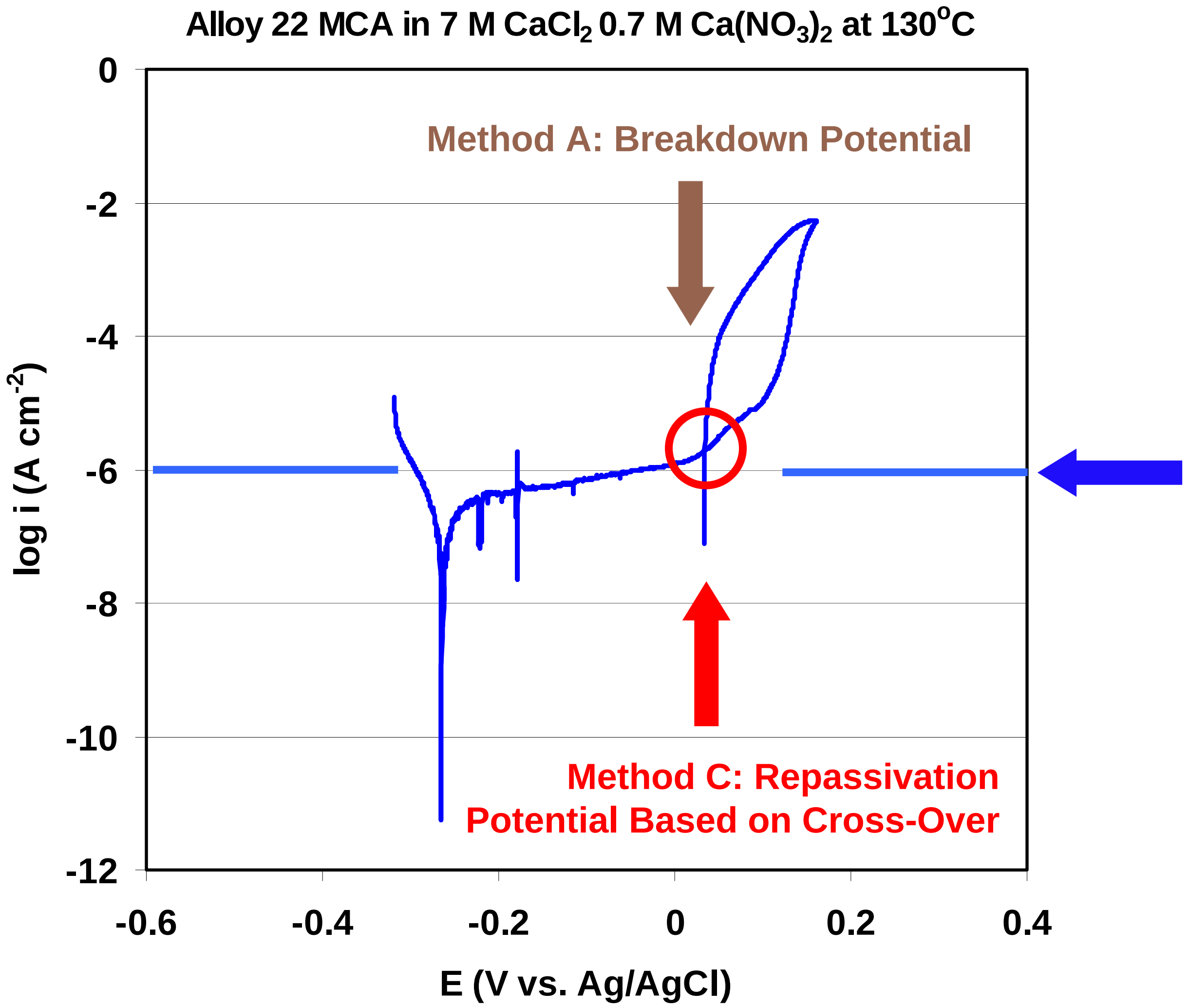


Method A: Breakdown Potential

Method B: Repassivation Potential Based Fixed Current Density (1 μA/cm²)

Method C: Repassivation Potential Based on Cross-Over

Critical Temperature for Localized Corrosion in Artificial $CaCl_2$ Brine with NO_3^- Inhibitor



Method A: Breakdown Potential

Method B: Repassivation Potential Based Fixed Current Density (1 μA/cm^2)

Method C: Repassivation Potential Based on Cross-Over

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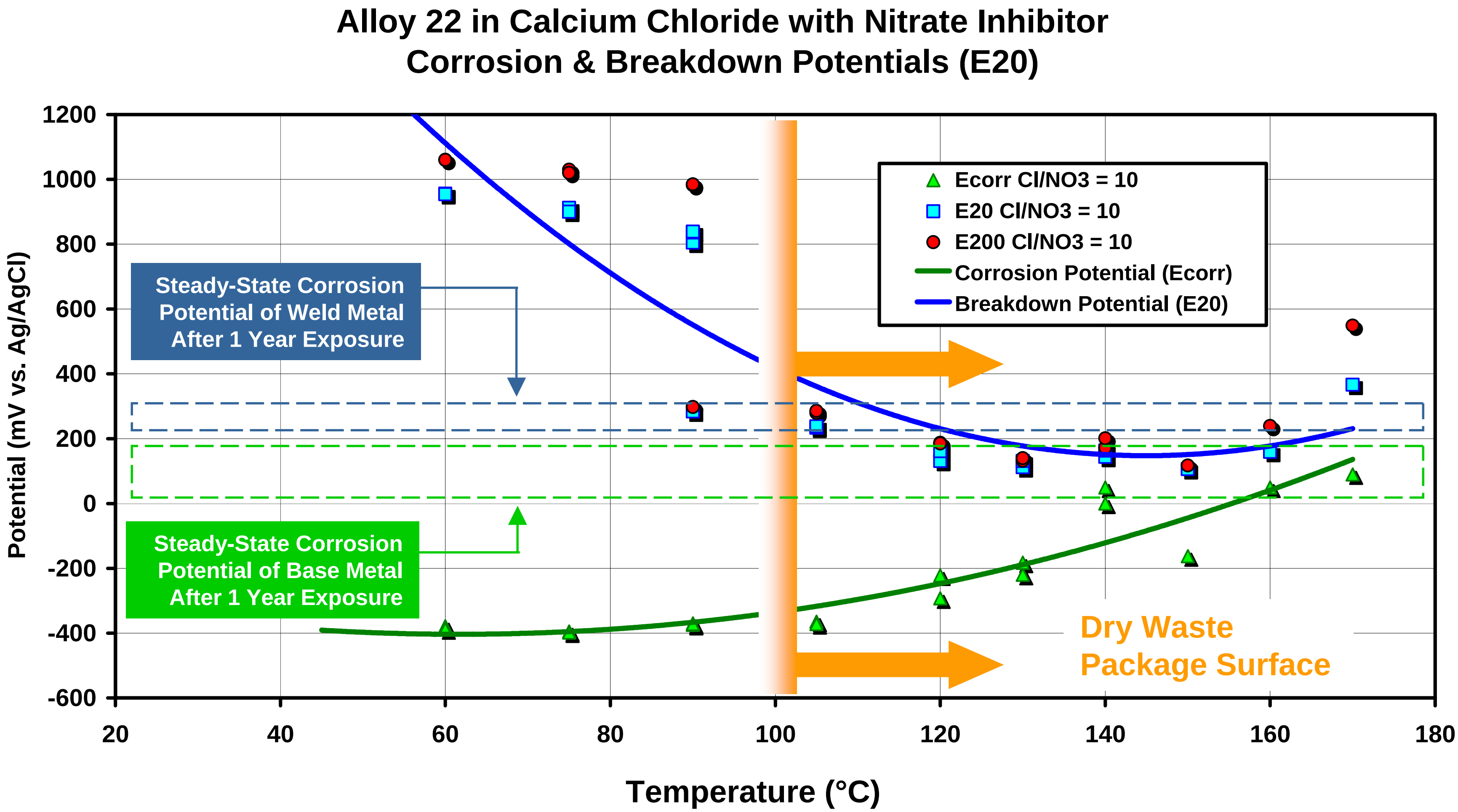
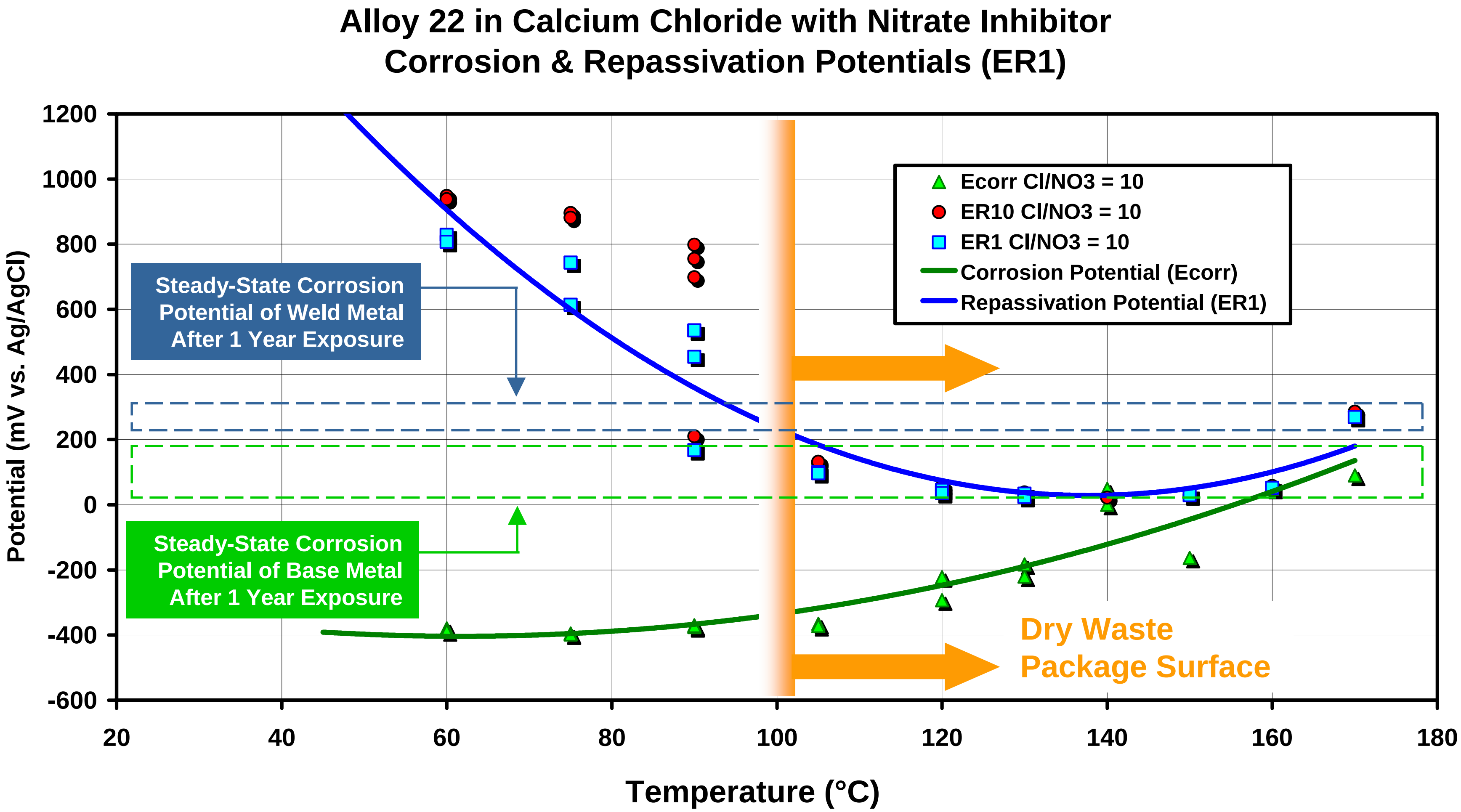


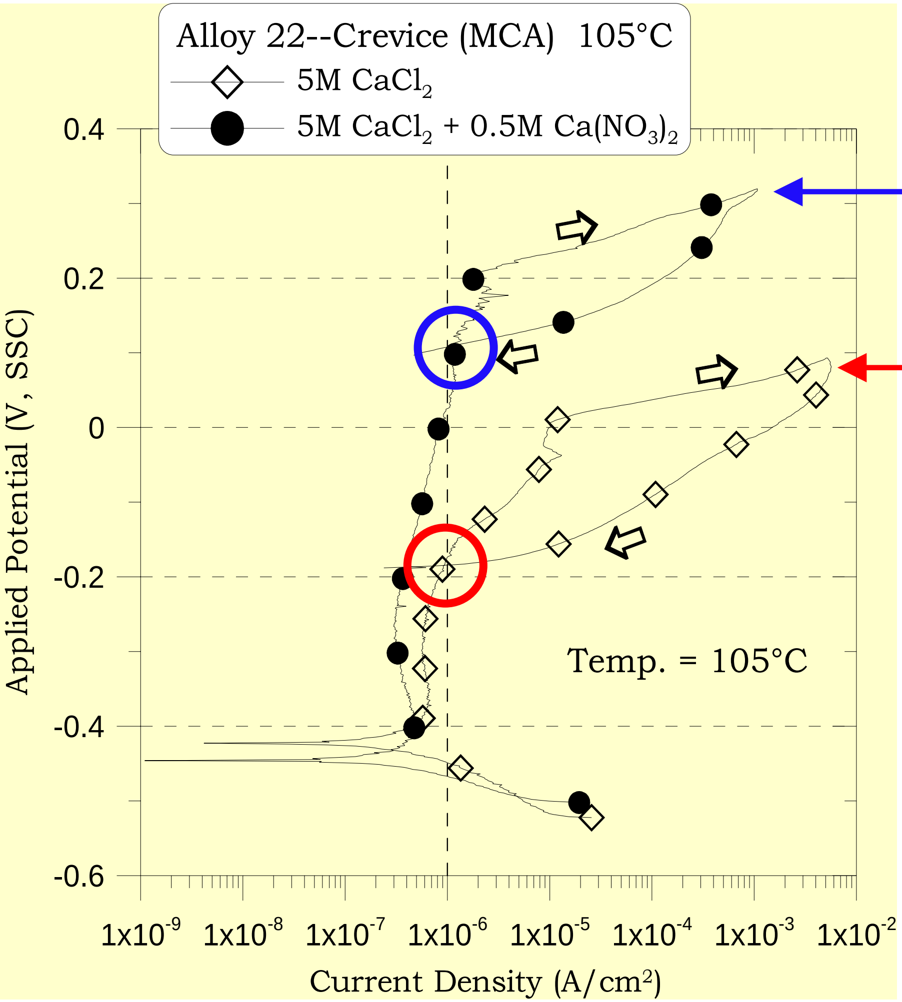
Time Integrated Relative Frequency ~ 0 to 1% for Bins 1 through 3

Critical Temperature for Localized Corrosion in Artificial $CaCl_2$ Brine with NO_3^- Inhibitor

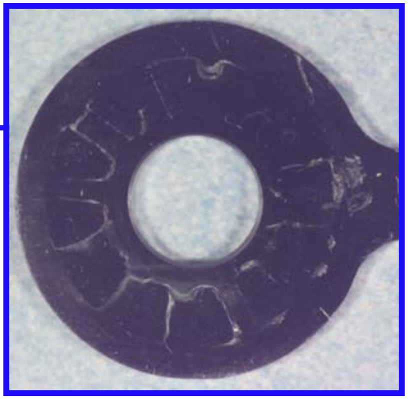


Time Integrated Relative Frequency ~ 0 to 1% for Bins 1 through 3

Localized Corrosion of Alloy 22 in $CaCl_2$ Brine at 105°C Inhibited by NO_3^-



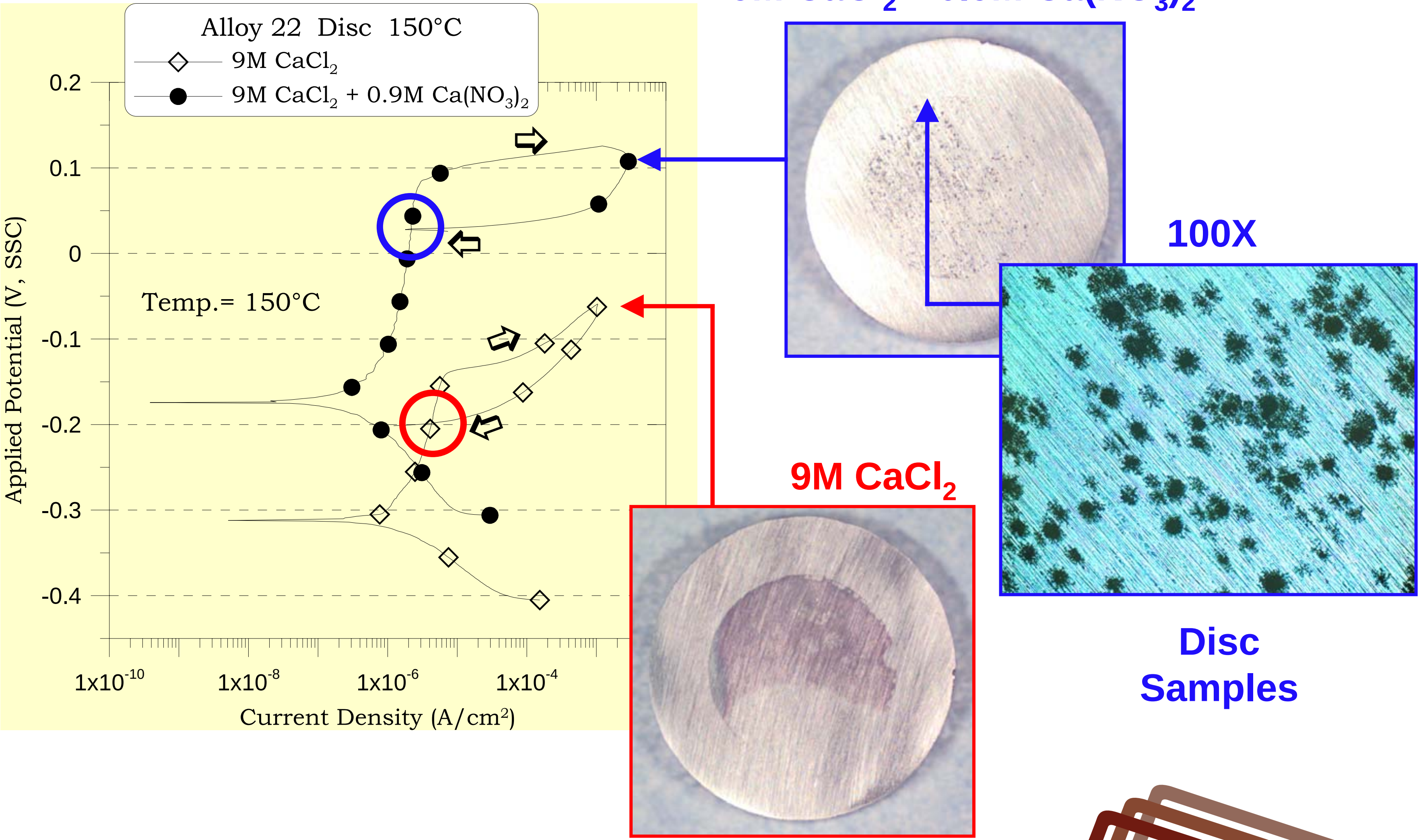
5M $CaCl_2$ + 0.5M $Ca(NO_3)_2$



5M $CaCl_2$

MCA Samples

Localized Corrosion of Alloy 22 in $CaCl_2$ Brine at 150°C Inhibited by NO_3^-



9M $CaCl_2$ + 0.9M $Ca(NO_3)_2$

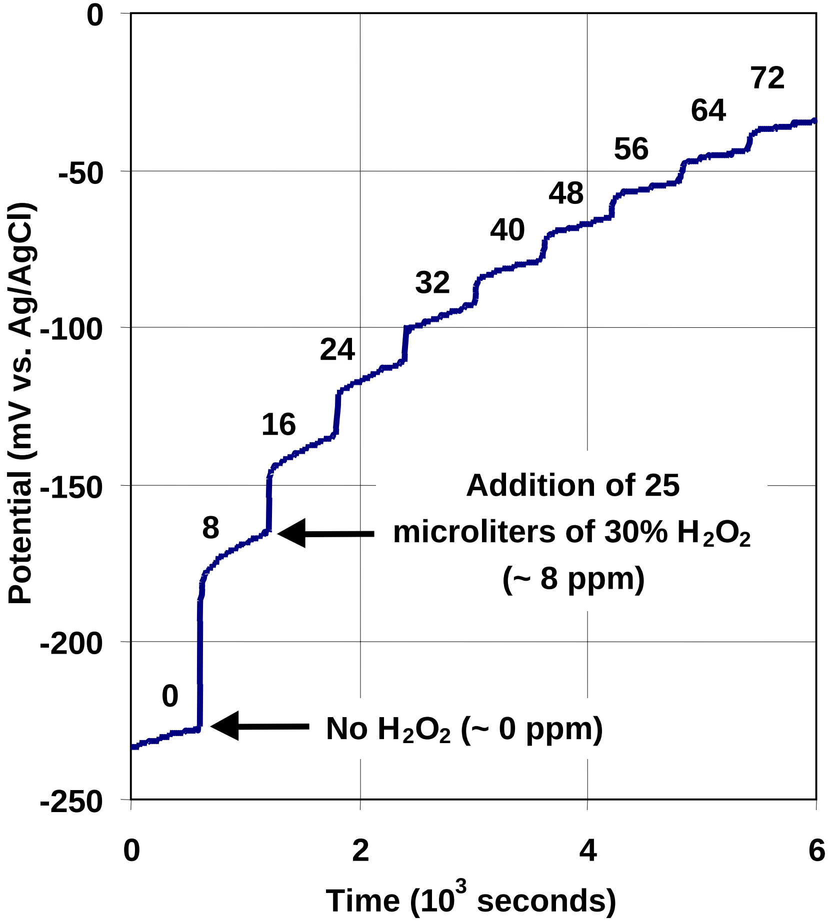
100X

9M $CaCl_2$

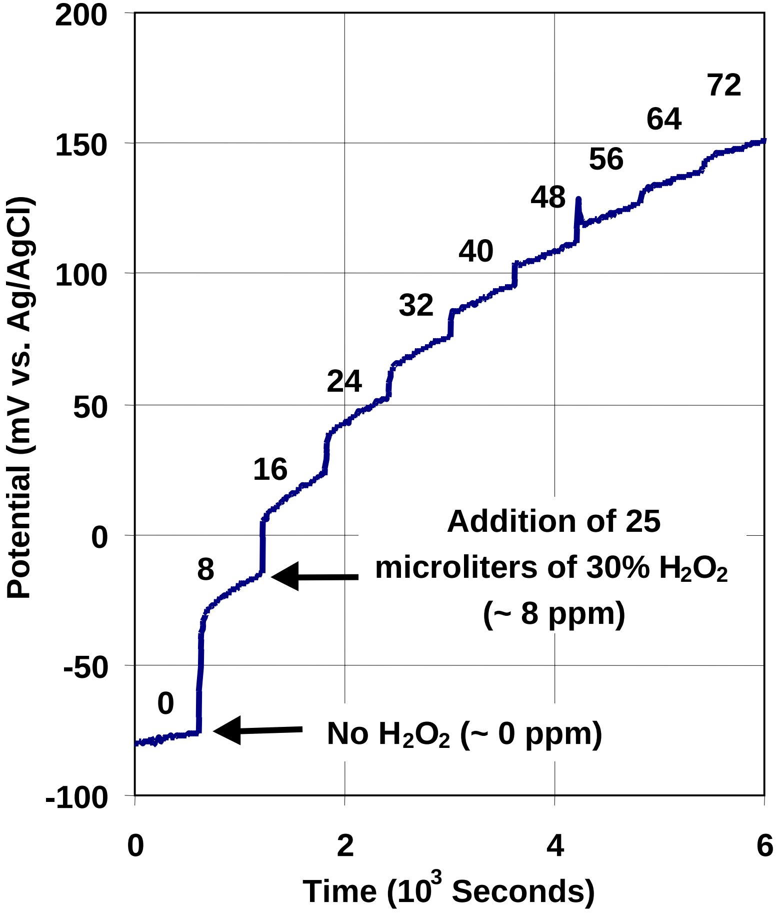
Disc Samples

Radiation Effects
Hydrogen Peroxide from Gamma Radiolysis

Effect of H_2O_2 on Corrosion Potential of Alloy 22 in SCW at 25° Centigrade



Effect of H_2O_2 on Corrosion Potential of Alloy 22 in SAW at 25° Centigrade



Radiation Effects
Hydrogen Peroxide from Gamma Radiolysis

(Continued)

- **Dry-out will help mitigate the impact of gamma radiolysis on the open-circuit corrosion potential**
- **Decay heat will prevent seepage water from contracting the waste package until the gamma dose is very low**
- **The time-dependent dose for a standard 21 pressurized water reactor waste package is predicted to be**
  - **~ 700 rad h-1 at emplacement**
  - **~ 20 rad h-1 at 90 years**
  - **< 0.1 rad h-1 at 375 years**
- **Though seepage may be possible at 1000 years, the corresponding gamma dose is expected to be too low to cause much effect on the corrosion potential**

Conclusions
Dry-out (Orange Area on Poster)

- Ventilation and Initial Heat-Up (T ≈ 25-150°C)
  - Drift walls and waste packages are dry; no significant corrosion
- Heat-Up Above Deliquescence and Boiling Points (T ≥ 150°C)
  - Data on moisture content in rock as a function of temperature indicate that dry-out will occur at T ≥ 100-110°C
  - Detailed thermal hydrology modeling by the Project shows that porous rock (matrix) and fractures in close proximity to drift walls will be dry at T ≥ 100°C (boiling point)
  - Decay heat will dry the drift walls
  - No seepage; no significant corrosion
- Cool-Down Below Deliquescence (T ≈ 150-100°C)
  - Possible formation of deliquescence $CaCl_2$ brines at T ≤ 150°C
  - Corrosion tests of Alloy 22 underneath $CaCl_2$ deliquescence brines have shown no localized corrosion at T ≤ 150°C

Conclusions
Transition (Tan Area on Poster)

- **Cool-Down Below Boiling Point (T ≈ 90 to 100°C)**
  - **Seepage can enter drifts; aqueous corrosion may be possible**
  - **Synthetic waters representative of samples taken from Yucca Mountain have been concentrated by evaporation to simulate the effect of hot waste package surfaces**
  - **A broader range of environments have been explored with a comprehensive geochemical model**
  - **Water concentrated on the waste package surface by evaporative concentration is expected to be relatively benign**
  - **While pure near-saturation $CaCl_2$ solutions are not expected, the project has performed numerous tests in this "worse-than-expected" environment**
  - **Seepage waters that may evolve to $CaCl_2$ brines are expected to have a sufficiently high NO_3^-/Cl^- ratio to inhibit localized attack of Alloy 22 at temperatures above boiling**

Conclusions
Low Temperature (Blue Area on Poster)

- Cool-Down Below Threshold for Crevice Corrosion (T ≤ 90°C)
  - Waste package performance is insensitive to water chemistry
  - Protection in worst-case $CaCl_2$ brine by Alloy 22
  - Ti Grade 7 drip shields provide defense in depth

➢ The Waste Package is protected by different mechanisms in each of the Three Temperature Regions illustrated on the poster

➢ The Dry-out Region provides an additional barrier, and additional protection for the waste package

➢ The Project’s overall strategy is consistent with conceptual models of other experts in the field

➢ This consistency is apparent when casting the Project’s strategy in the form of Professor Payer’s Zones of Susceptibility