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

www.ocrwm.doe.gov

Localized Corrosion Data and Analyses from the Materials Performance Thrust of the OCRWM Science and Technology Program

Presented to:
Nuclear Waste Technical Review Board
Workshop on Localized Corrosion

Presented by:
Joe H. Payer, Case Western Reserve University
Robert G. Kelly, University of Virginia

September 25-26, 2005
Las Vegas, Nevada

Acknowledgement and Disclaimer

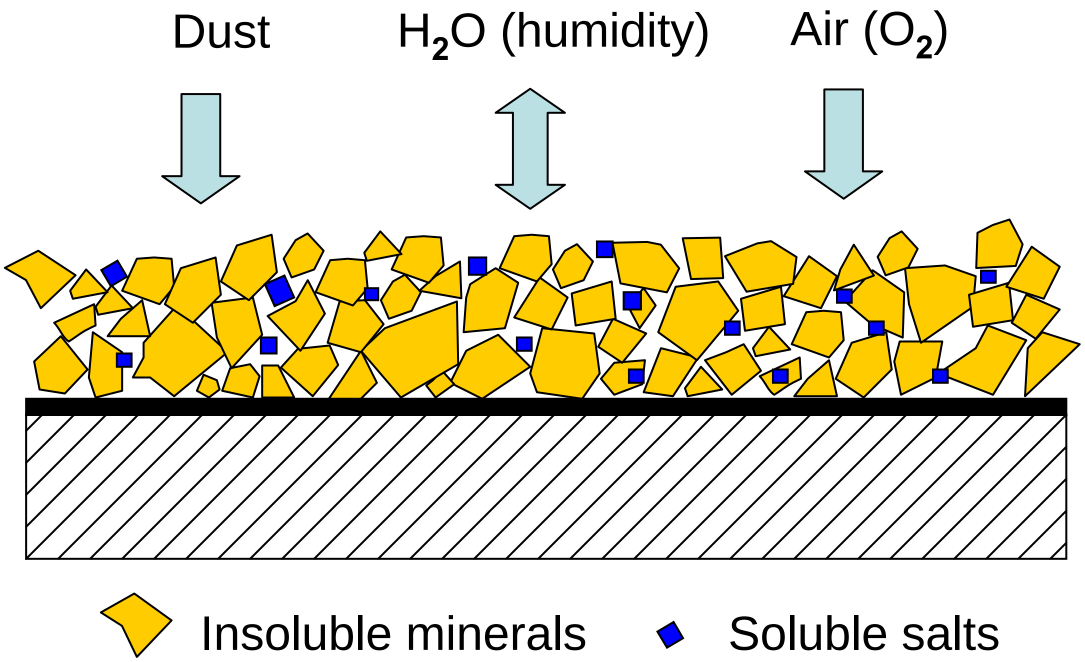
- Support of the Science and Technology Program of the U.S. Department of Energy (DOE), Office of Civilian Radioactive Waste Management (OCRWM) is gratefully acknowledged. The work was performed under the Corrosion and Materials Performance Cooperative, DOE Cooperative Agreement Number: DE-FC28-04RW12252

- The views, opinions, findings, and conclusions or recommendations of authors expressed herein do not necessarily state or reflect those of the DOE/OCRWM

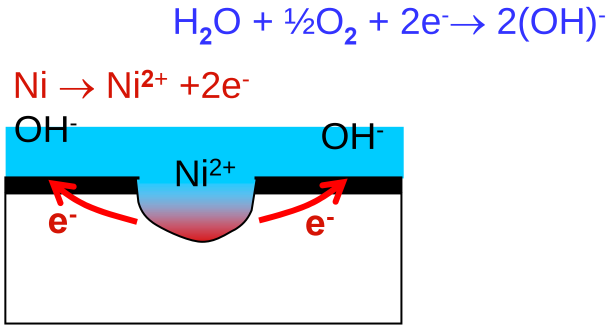
Outline of Presentation

- Decision tree approach to analysis
- Localized corrosion requirements
- Particulate layer properties and processes
- Factors influencing localized corrosion
  - Cathode processes
  - Anode processes
  - Coupled anode and cathode processes
- Summary

Corrosion in Thin Layers of Particulate



Electrochemical Corrosion Cell under Particulate Layer



- **Dust deposited**
- **Degree of wetness**
- **Soluble salts**
- **Gas composition and property, T, RH**
- **Particulate layer properties, such as conductivity, temperature, pH, degree of wetness etc.**
- **Localized environment on the surface**
- **Anode: Ni $Ni^2 + 2e^-$**
- **Cathode: $H_2O + ½O_2 + 2e^- \rightarrow 2(OH)^-$**

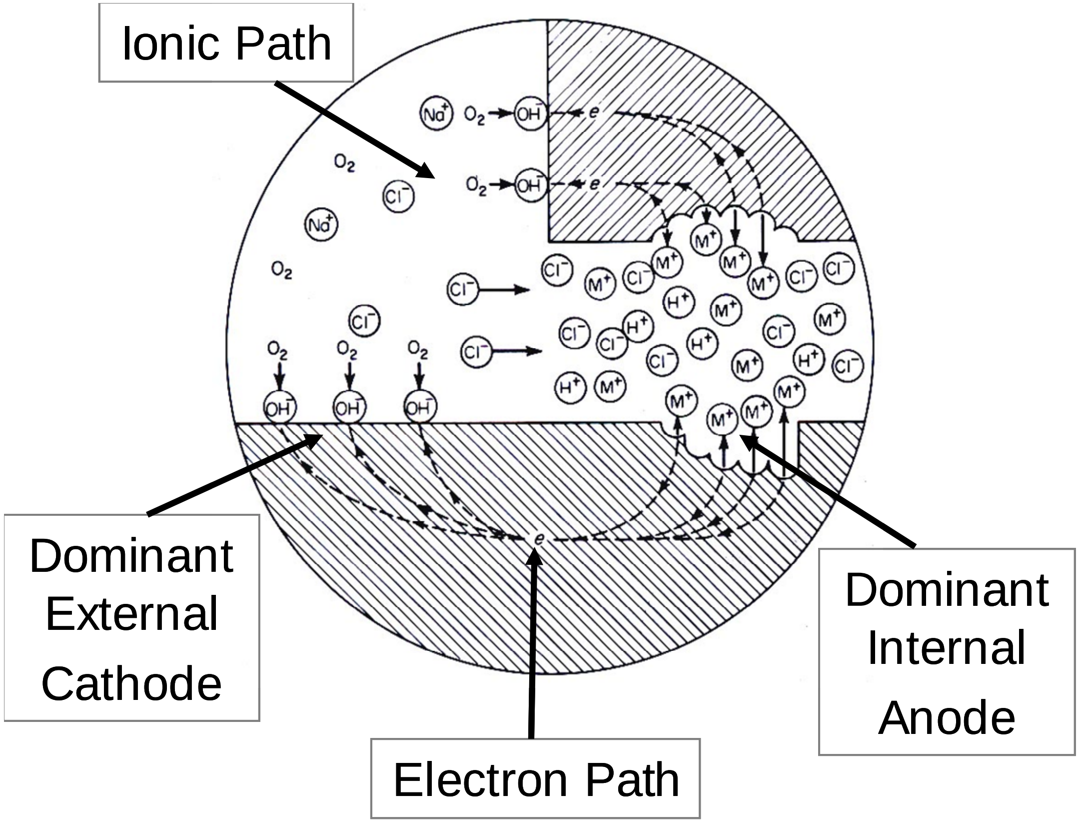
Materials Performance Thrust

- A decision-tree approach for localized corrosion
  - Are environments and crevices present to induce localized corrosion?
    - Consider conditions in moist layers of particulate and deposits
  - If localized corrosion initiates, will it persist?
    - Consider stifling and arrest processes as the corrosion proceeds
  - What amount of metal penetration occurs?
  - What is the size and distribution of corrosion sites?

Materials Performance Thrust (cont'd)

- Application of decision-tree approach
  - Relevant conditions over time and within relevant time periods
  - Deliquescent salt conditions
  - Seepage and drips conditions

Requirements for Localized Corrosion



Ionic Path

Dominant External Cathode

Electron Path

Dominant Internal Anode

Initiation

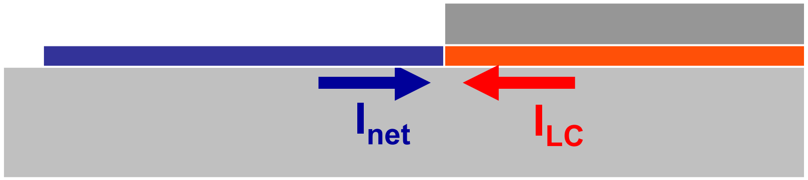
- **Aggressive environment**
- **Tight, impermeable crevice**
- **$E_{corr} > E_{repass}$**
- **Separated and coupled anode and cathode**
- **Develop critical crevice chemistry**

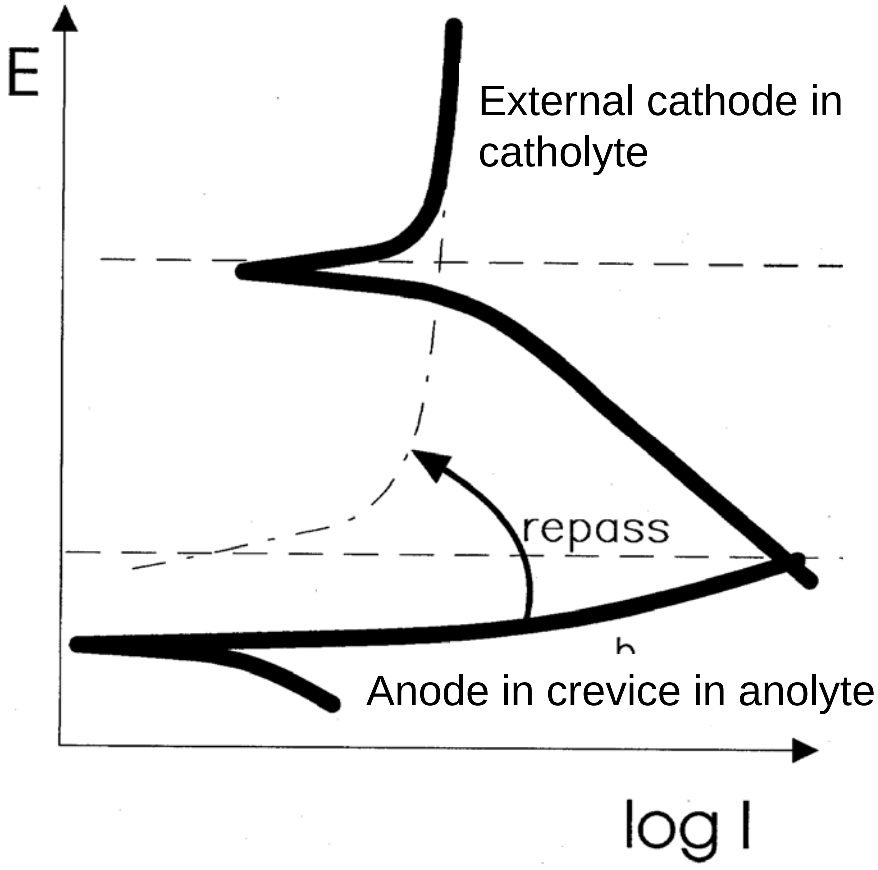
Propagation

- **Maintain critical crevice chemistry**
- **Maintain sufficient cathodic current capacity**
- **Maintain separate and coupled anode and cathode**
- **Maintain tight, impermeable crevice**

Crevice Corrosion Propagation as a Galvanic Couple

- **Metal inside crevice undergoes transition behavior**
- **Remainder of sample is cathode and must supply current to support dissolution at anode**

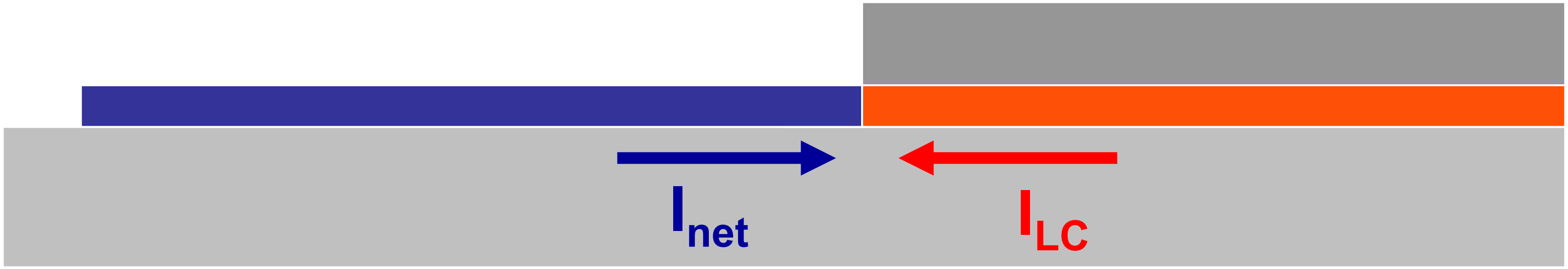




Stability of Localized Corrosion

Crevice with Thin Layer External Cathode

Current demand from crevice must be met by cathodic current from external surface for stable growth



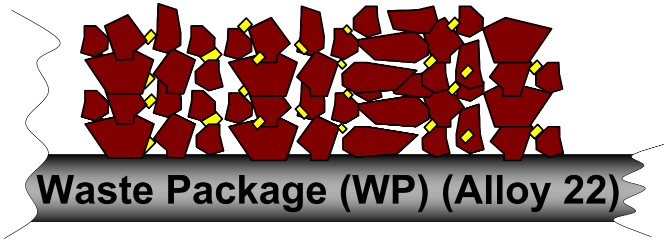
I_{net} = total cathodic current from freely exposed surface surrounding crevice
I_{LC} = total anodic from crevice

Analysis of Crevice Corrosion Stability vs. Stifling

- Analysis of post-initiation stage
- Categories of processes to control corrosion
  - Electrolyte layer: resistance limits current between anode and cathode
  - Cathode current capacity cannot meet anode demand
  - Anode current requirement for stability not met
  - Anode/cathode coupling incompatible
- Demonstrate a number of processes that affect crevice corrosion initiation, propagation and arrest

PARTICULATE LAYER PROPERTIES AND PROCESSES

Scenarios for Distribution of Moisture in Particulate Layer



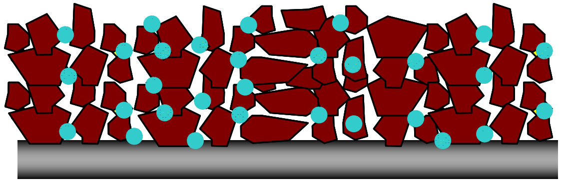
Dry particulate-No moisture

Particulate: size, shape, soluble salts, insoluble constituents, distribution

Particulate layer: thickness, porosity, density

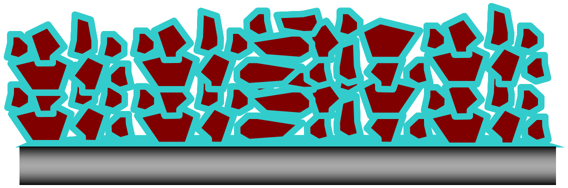
Temperature and Relative Humidity (activity of water)

Solution properties



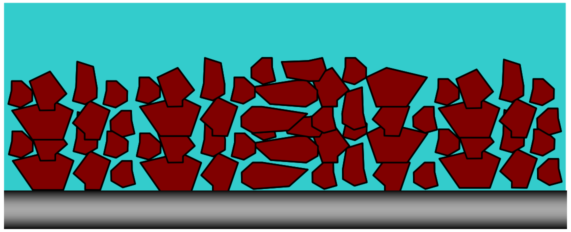
Droplets of moisture

- Higher temperatures
- Highly concentrated brines
- Limited solution contact with metal



Unsaturated particulate layer

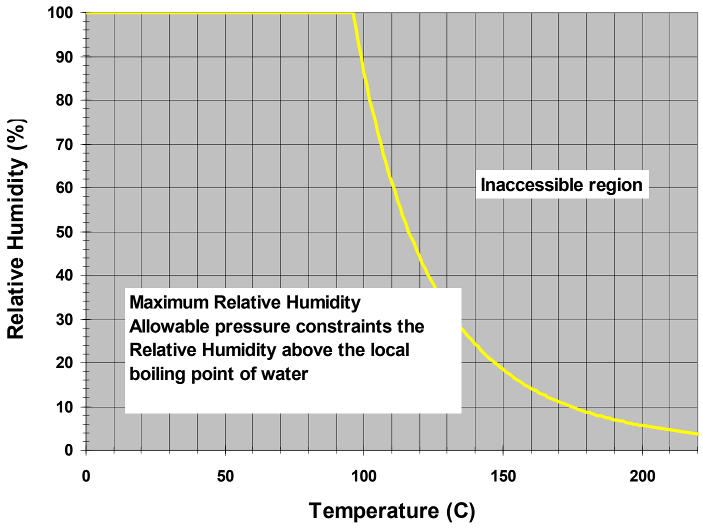
- Lower temperatures
- Less concentrated brines

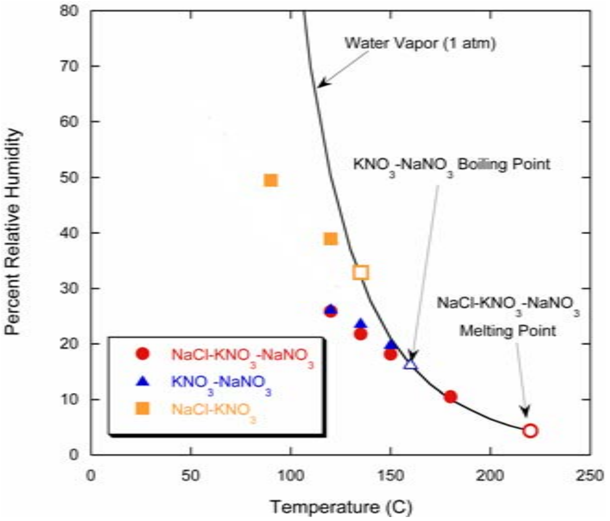


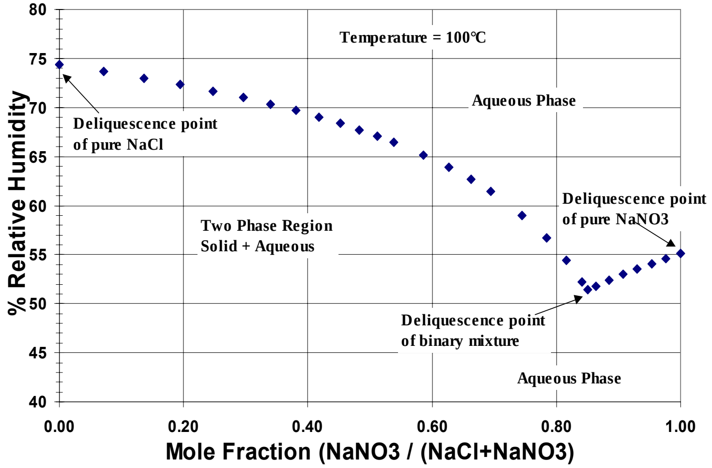
Solution layer on metal

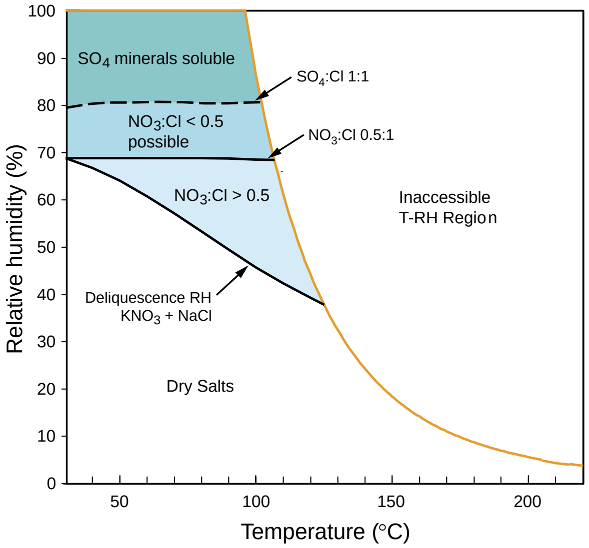
- Lower temperatures
- Less concentrated brines

Sampling of Technical Basis for Solution Chemistry



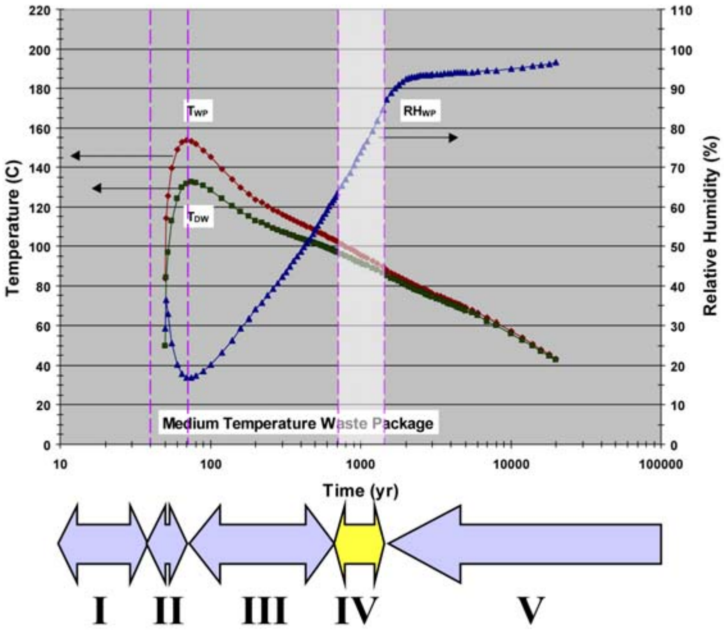






Example of WP Temperature & Relative Humidity Control of Solution Composition

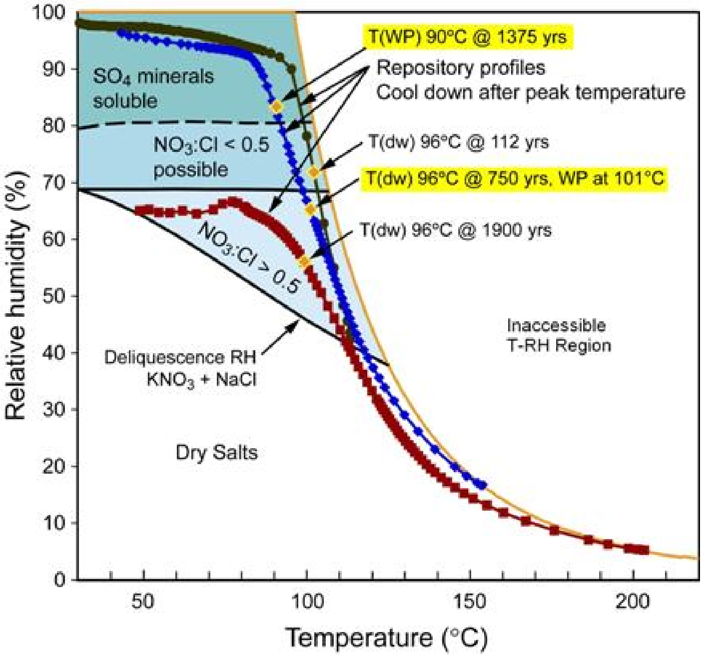
From Period IV analysis scenario presented at NWTRB Meeting; J. Payer, May 2004



Drift wall 96°C at 750 years;

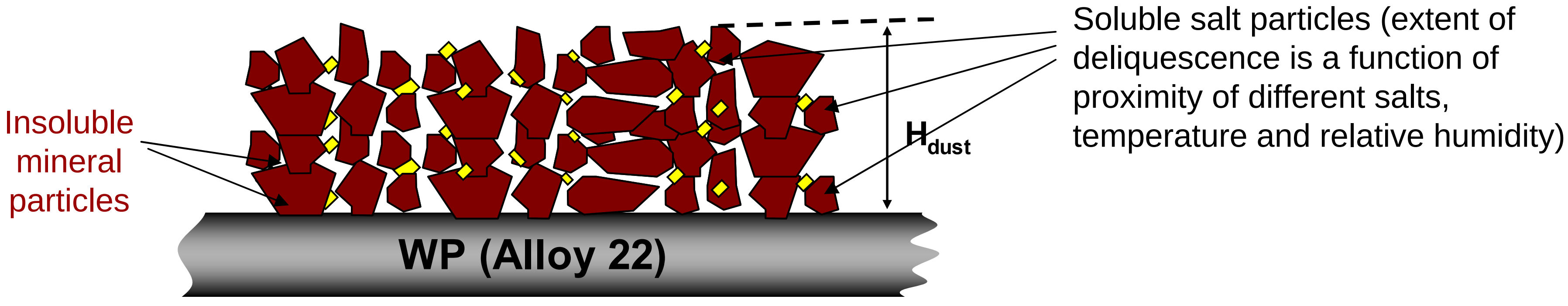
WP at 101°C
Relative Humidity 65%

Critical Corrosion Temp 90°C at year 1375;
Relative Humidity 85%



- **The Temp-RH at any time determines the possible waters**
- **Time trajectory can be related to solution chemistry**
- **Solution composition can be related to corrosivity, e.g. nitrate to chloride ratio**

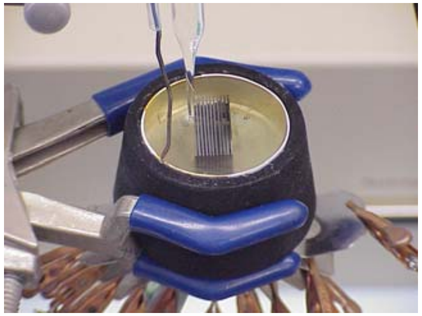
Characteristic Dust Layer on WPs

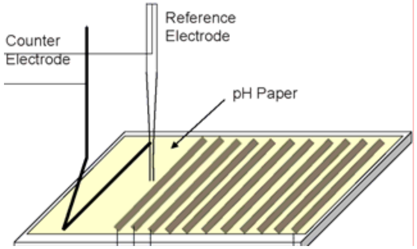


Soluble salt particles (extent of deliquescence is a function of proximity of different salts, temperature and relative humidity)

Property	Symbol	Range Given	Selected Value	Units
Density of deposited dust	$rho_{deposit}$	1 - 2	1.0	g/cm^3
Density of deposited minerals	rho_{dust}	2.0 – 2.6	2.6	g/cm^3
Porosity of deposited dust	(%phi)	50 - 60	60	%
Soluble salt content in dust	(%SS)	5	5	% wt.
Thickness of dust layer	δ_{dust}	180 - 10	150	μm
Size of particle	$\delta_{particle}$	30 - 10	30	μm
Mass of dust deposit	m_{dust}	18 - 26	18	mg/cm^2
Effective conductivity of layer	κ_{eff}	$(\%phi/100)^{3/2} \times \kappa_{bulk}$	$0.465 \times \kappa_{bulk}$	S/cm
Effective electrode area			0.85	fraction
Number of particle Layers		2 - 20		number
Surface area of particles to metal surface area (for 30 μm particles)			~10:1	

Changes in Solution Properties due to Electrochemical Cells

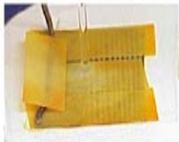
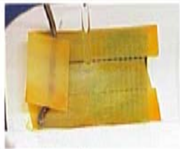
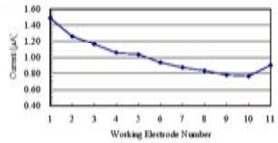
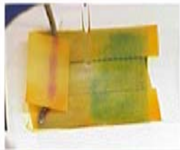
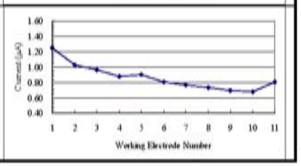




Experiment:

- Control potential on plate #1
- Monitor current distribution along segmented cathode
- Monitor pH changes

- **Anode:**
  - OH^- and Cl^- migrate to anode
  - Oxidation Reaction,
$4OH^- \rightarrow O_2 + 2H_2O + 4e$
  - OH^- consumed, solution more acidic
  - Oxygen produced
  - Water produced
- **Cathode:**
  - H^+ and Na^+ migrate to cathode
  - Reduction Reaction,
$O_2 + 2H_2O + 4e \rightarrow 4OH-$
  - OH^- produced, solution turns alkaline
  - O_2 and H_2O consumed

Time	Photograph	Current Distribution
0 s		
60 s		
180 s		

Increased pH (green) on cathode and decreased pH (red) on anode

Particulate Effects on Bulk Solution Conductivity

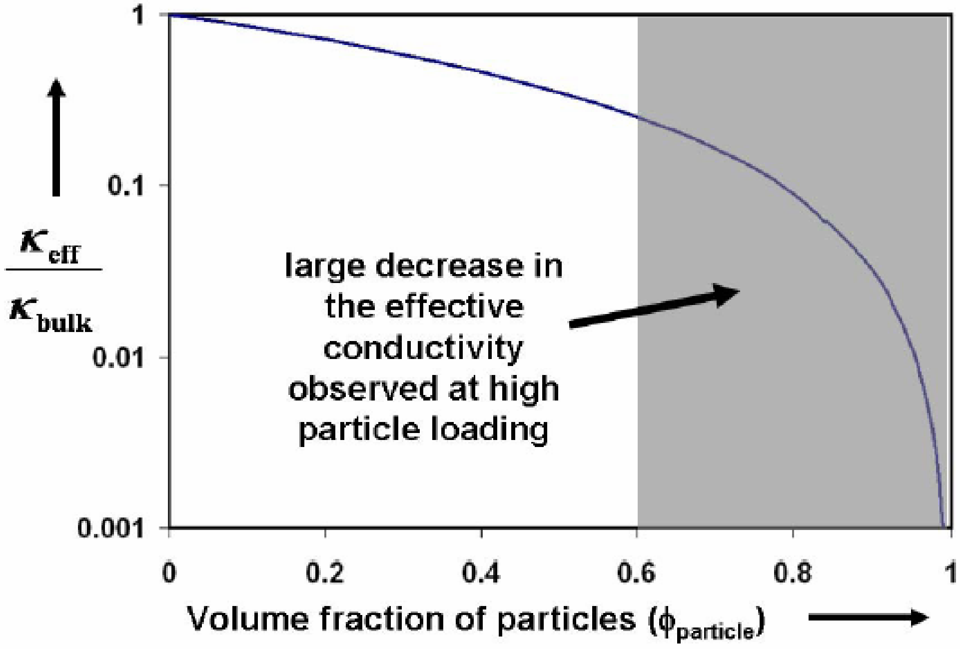
- Decreased conductivity in the particulate layer
  - Higher particle volume fraction
  - Lower solution volume fraction in pores (unsaturated)

Bruggeman's Equation

$$\kappa_{\text{eff}} = \kappa(1 - \phi_{\text{sand}})^{\frac{3}{2}}$$

where

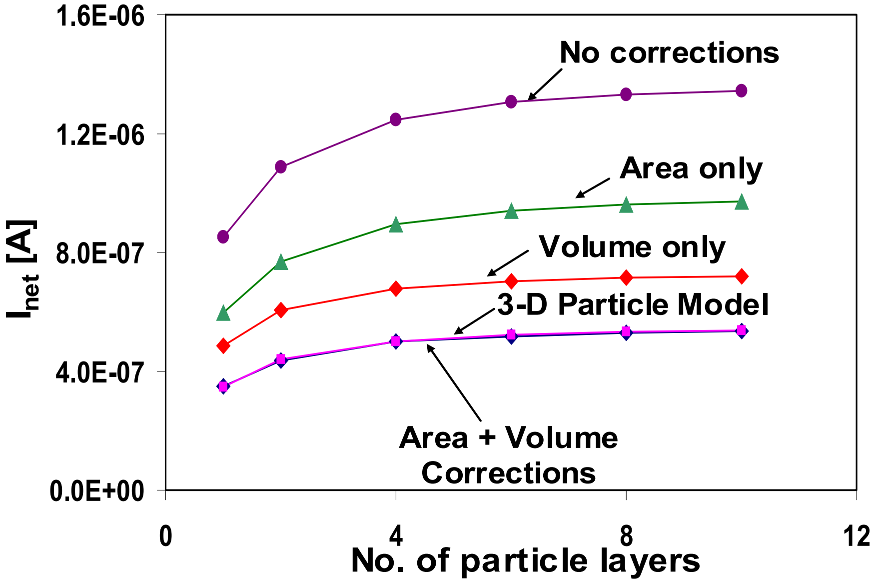
$$\phi_{\text{sand}} = \frac{\text{Vol(sand)}}{\text{Vol(sand + solution)}}$$

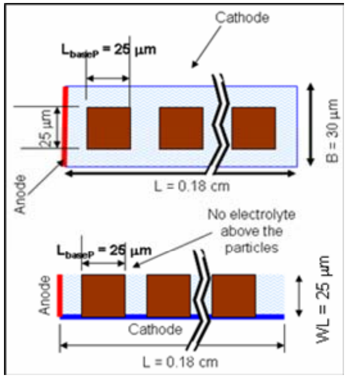


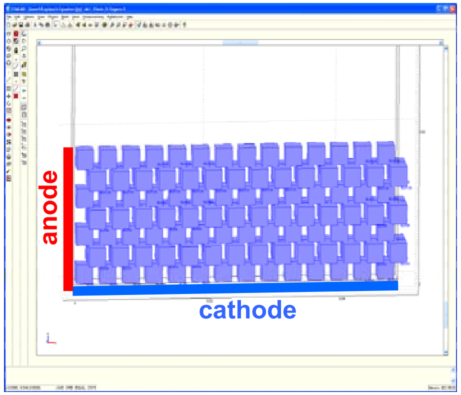
large decrease in the effective conductivity observed at high particle loading

Analysis of the Effects of Particulate

Analysis of multiple layers of particles







Combination of volume factor and area factor account for particle effects in good agreement with 3-D modeling result for single layer and multiple layer of particles

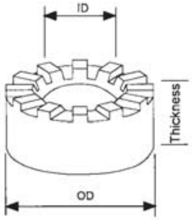
Effect of Crevice Formers on the Localized Corrosion Damage and Propagation

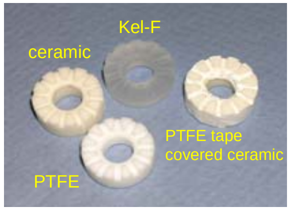
Specimen assembly

Multiple Crevice Assembly (MCA)

- **Two segmented washers**
- **Grade 2 Ti bolts and nuts**
- **Applied Torque**
  70 in-lb for ceramic, Kel-F
  2.5 to 25 in-lb for PTFE

Crevice formers: after ASTM G48-03

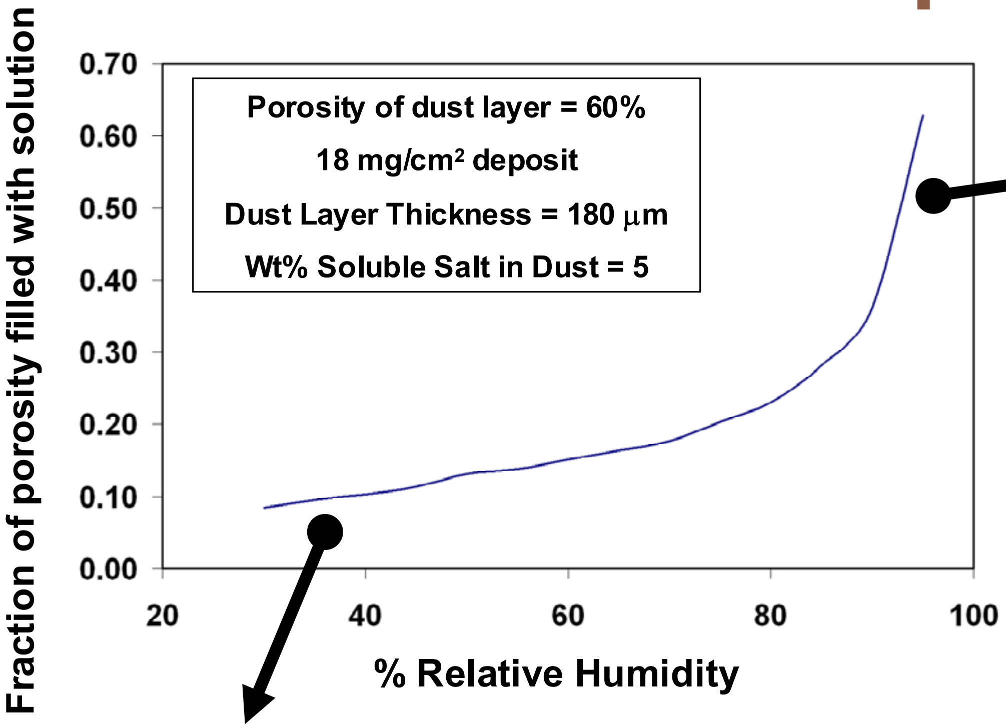




- **12 contact plateaus (feet)**
- **ID: 9.9 mm   OD: 15.9 mm   Thickness: 6.3 mm**
- **Contact area: 6 mm^2/foot**

- **Determine effect of the crevice former under aggressive laboratory conditions**
  - **4M NaCl at 100C**
  - **Applied potential (no cathodic limitations)**
- **Ceramic/PTFE tape was most severe crevice former**
  - **Crevice corrosion initiation and arrest events observed**
- **Solid polymer crevice formers (PTFE or Kel-F) were less severe**
- **Ceramic crevice former caused no crevice corrosion**

Variation of the Solution Volume with % RH in the Deposited Dust Layer

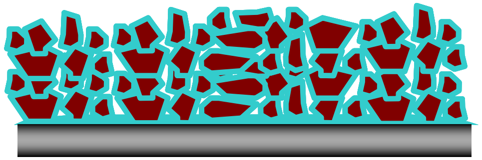


Porosity of dust layer = 60%

18 mg/cm² deposit

Dust Layer Thickness = 180 μm

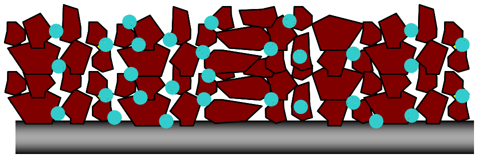
Wt% Soluble Salt in Dust = 5



Available porous volume for solution in a 180 μm thick dust layer with 60% porosity = 10.8 μl

Fraction occupied by solution = (Solution Vol.) / (Total Porous Vol.)

Rel Humidity	Solution Fraction	Molality
40 %	0.1	26.9
60%	0.16	15.2
95%	0.63	2.5

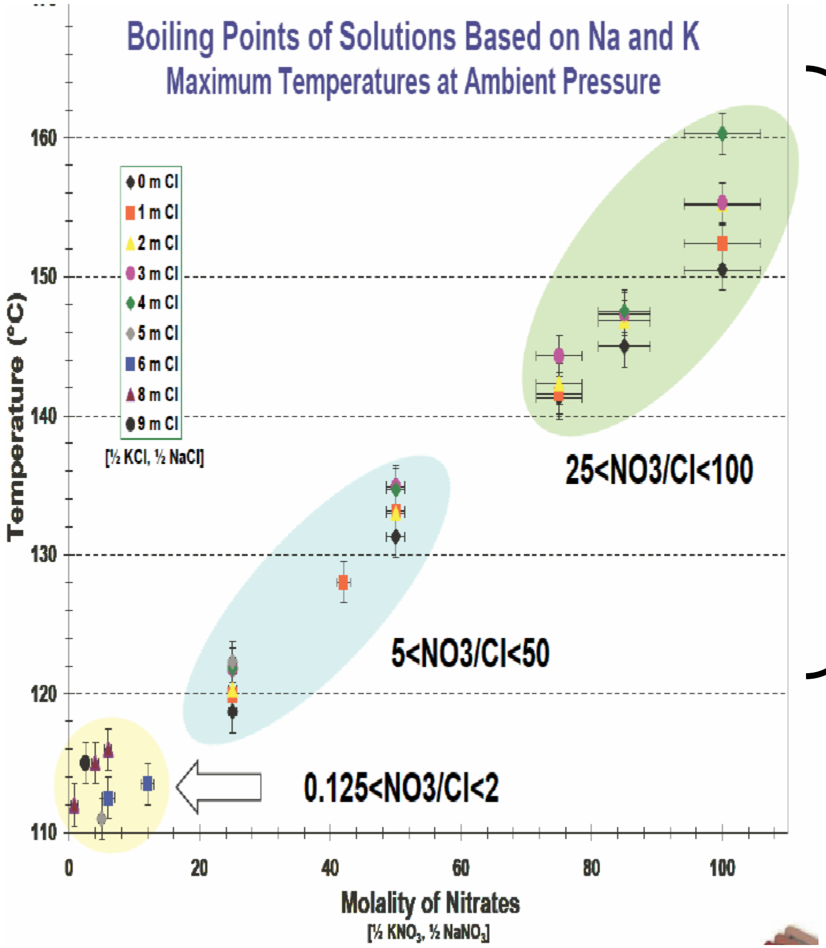


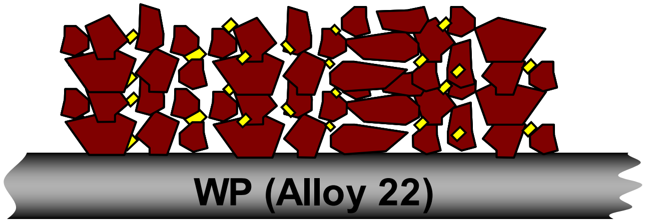
Droplets of Moisture

Droplets of moisture and limited contact with metal pertain until higher relative humidity's and less concentrated solutions

Based on dust layer data from Table 6.4-3 and Table 6.4-4 in *Analysis of Dust Deliquescence for FEP Screening, ANL-EBS-MD-000074 Rev 01, August 2005*

Analysis of High Temperature Salt Deliquescence





Droplets of Moisture

- Formation based on soluble salts, T, RH
- Highly concentrated, nitrate rich solutions
- Small fraction of porosity filled with solution
- Limited direct contact with metal surface
- Highly permeable layer
- Low conductivity layer
- Large surface area for reaction with minerals

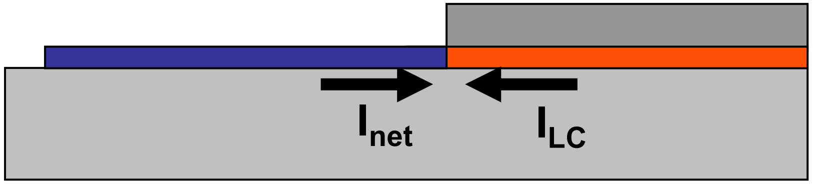
Particulate Layer as an Electrolyte and Crevice Former for Localized Corrosion

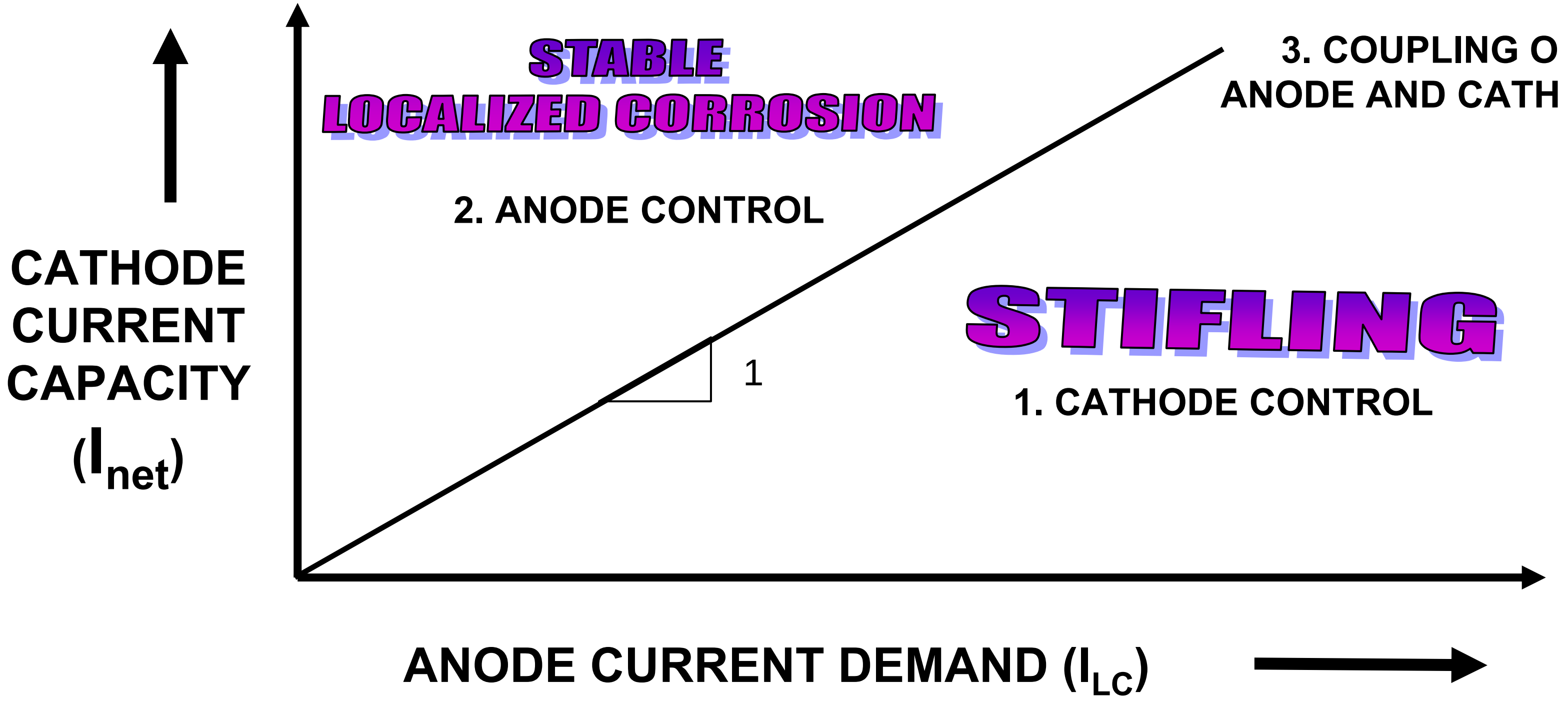
- **Can particulate layer act as an effective electrolyte and crevice former?**
  - **Composition, amount and distribution of moisture**
  - **Conductivity and permeability of the electrolyte layer**
  - **Separation of anode/cathode required for localized corrosion**
- **Will particulate layer fulfill requirements for crevice corrosion initiation and sustained propagation?**
  - **Corrosivity of moisture**
  - **Evolution of environment**
    - **Deliquescent moisture reaction with solid minerals**
    - **Evolution of volatile species**
    - **Composition changes due to electrochemical reactions**
    - **Interactions with corrosion products**
- **For high-temperature deliquescent salts in deposited dust layer**
  - **Too little moisture**
  - **Unlikely to fulfill the requirements for localized corrosion**

FACTORS INFLUENCING LOCALIZED CORROSION STABILITY

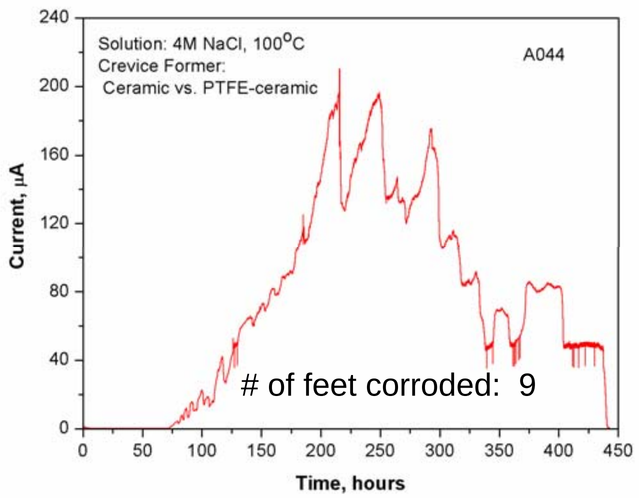
Factors Influencing Localized Corrosion Stability

Cathode Current Capacity ≥ Anode Current Demand

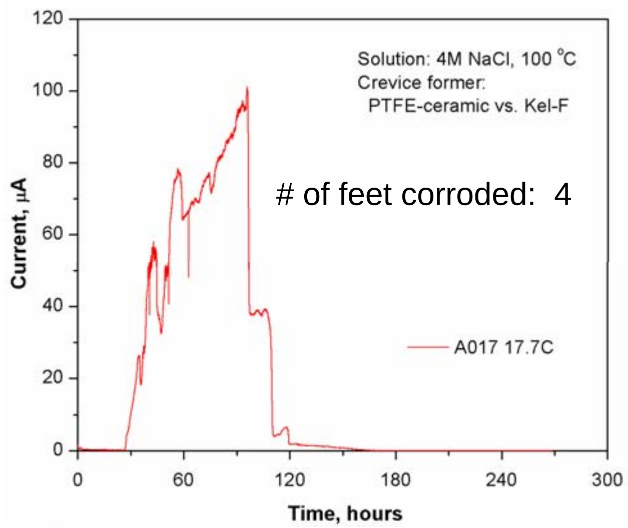




Arrest of Crevice Corrosion (Repassivation)



# of feet corroded: 9



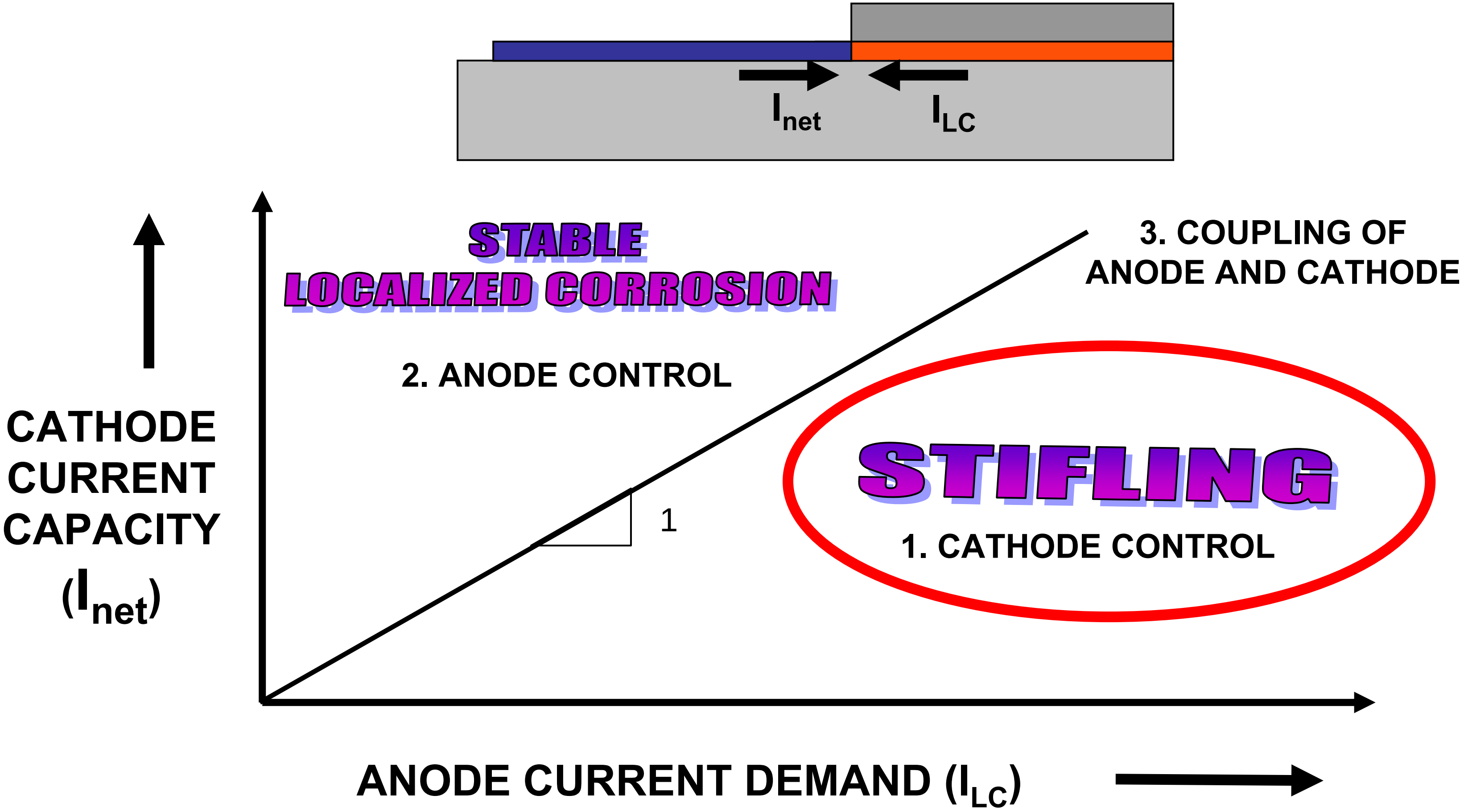
# of feet corroded: 4

- **Current indicates initiation and arrest of crevice corrosion throughout the test**
- **Tests were at constant applied potential *(no limiting cathode)***

Observations

- **Incubation time before initiation of crevice corrosion**
- **Serrated current response indicates multiple initiation/arrest events**
- **Arrest (repassivation) of crevice corrosion observed**
  - **Also seen by Rebak et al. (LLNL), Dunn et al. (CNWRA)**

Cathode Control

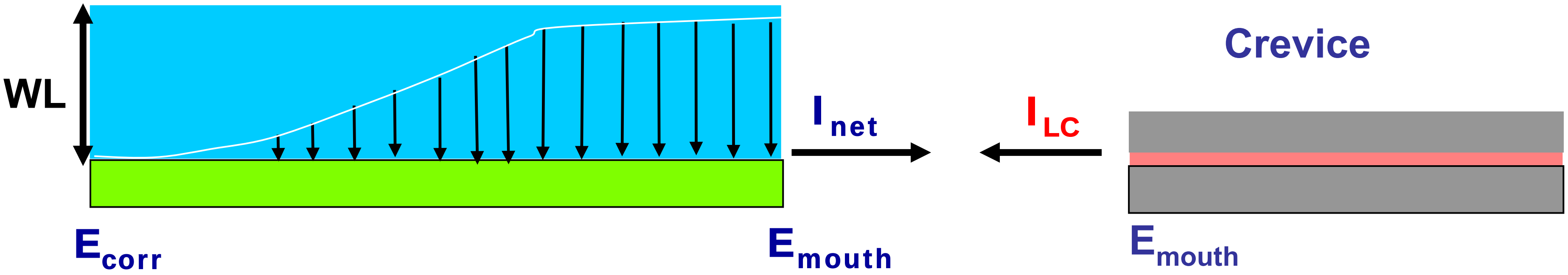


Cathode Limitations Can Stifle Crevice Corrosion

- **Corrosion behavior in moist particulate can differ from full immersion due to cathode limitations:**
  - **Limited cathodic <u>current</u> affects intensity and location of anodic reaction**
  - **Limited <u>size</u> of cathode affects minimum internal pH sustainable**

http://www.pbase.com/robertwhite/image/44870727

Maximum Total Current from Wetted Surface Can be Estimated

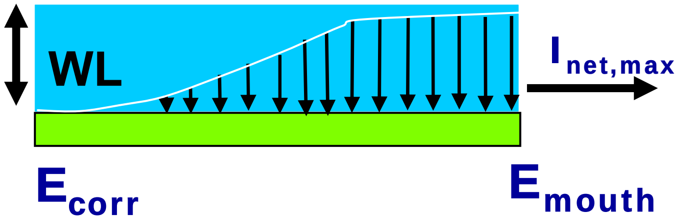


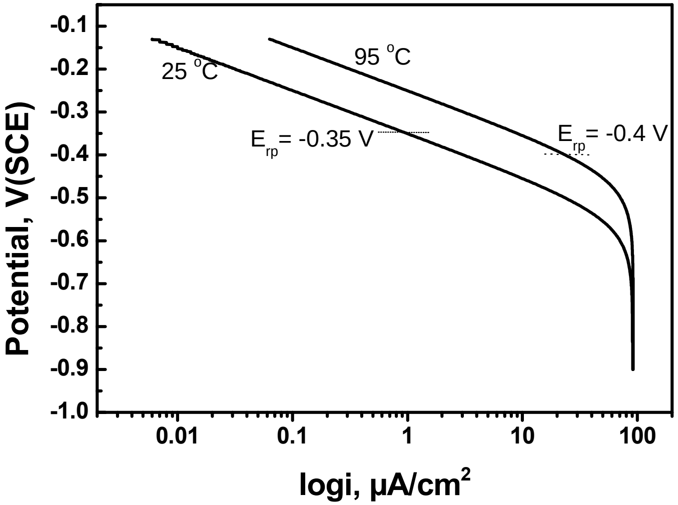
- Fixed potential at E_{mouth}, other end at E_{corr}
- Current along length per polarization curve

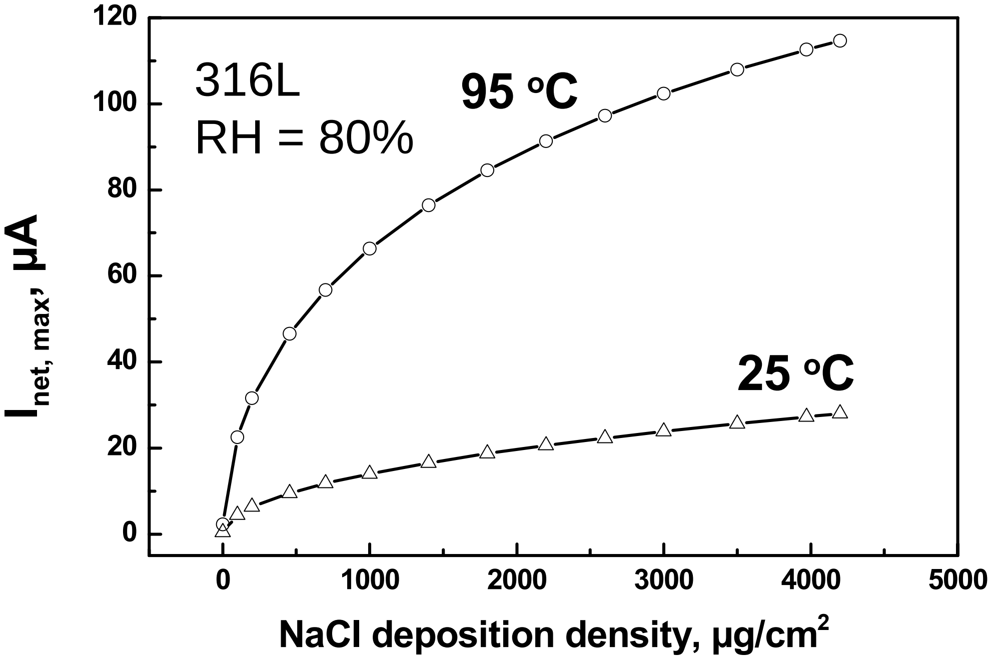
$$I_{net,max} = W \cdot \sqrt{2 \cdot \kappa \cdot WL \cdot \int_{E_{corr}}^{E_{mouth}} (i_c - i_p) \cdot dE}$$

Can relate κ and WL to RH and Deposition Density (mass/area) of salt

Increasing Temperature Increases Cathode Capacity

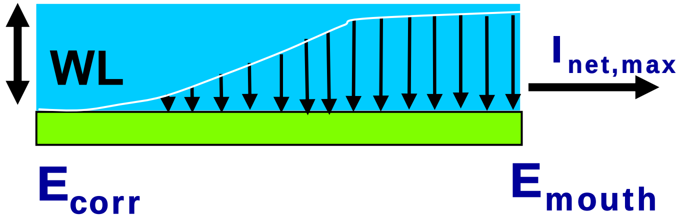


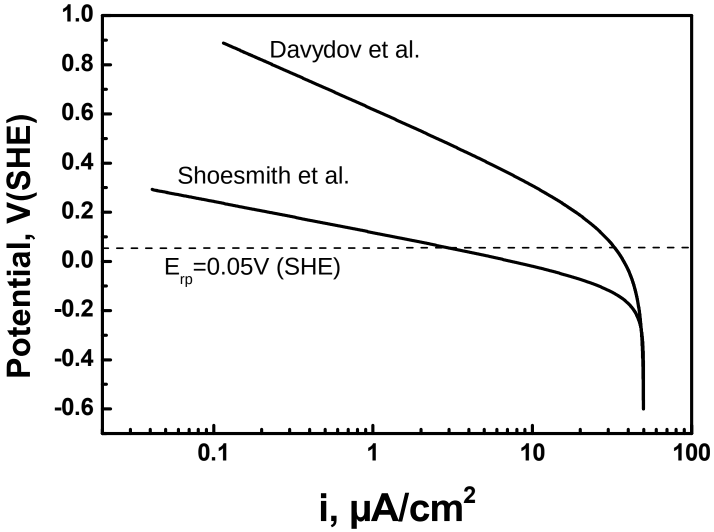


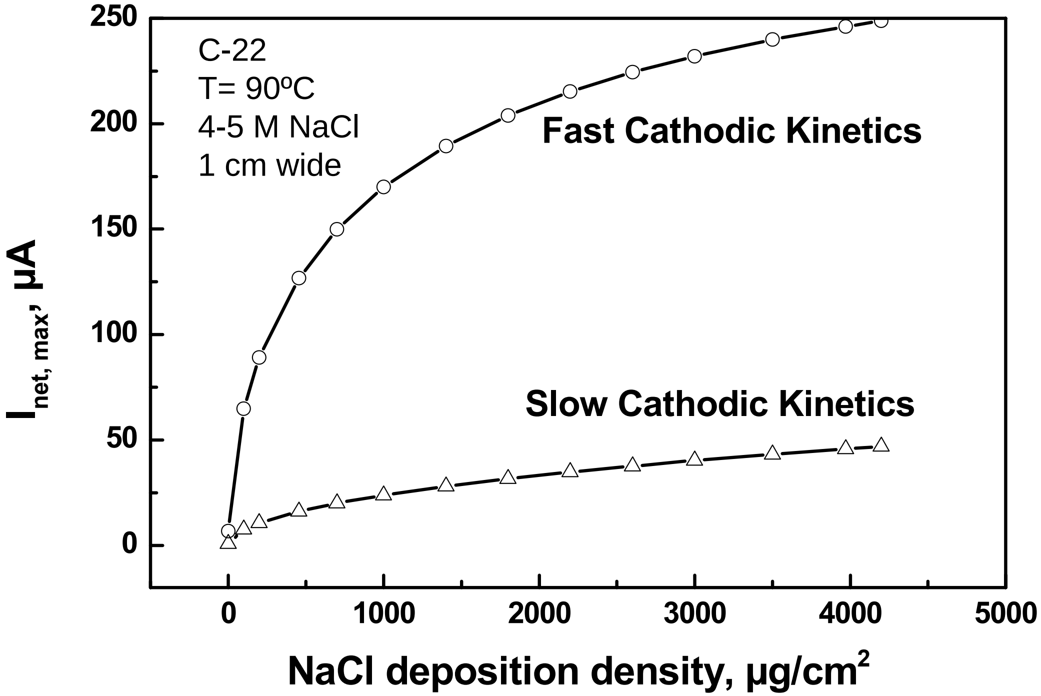


- Factors controlling increased cathode capacity at higher T:
  - Increased conductivity
  - Faster electrode kinetics
  - Lowered E_{rp}

Slower Cathodic Kinetics Decrease Cathode Capacity

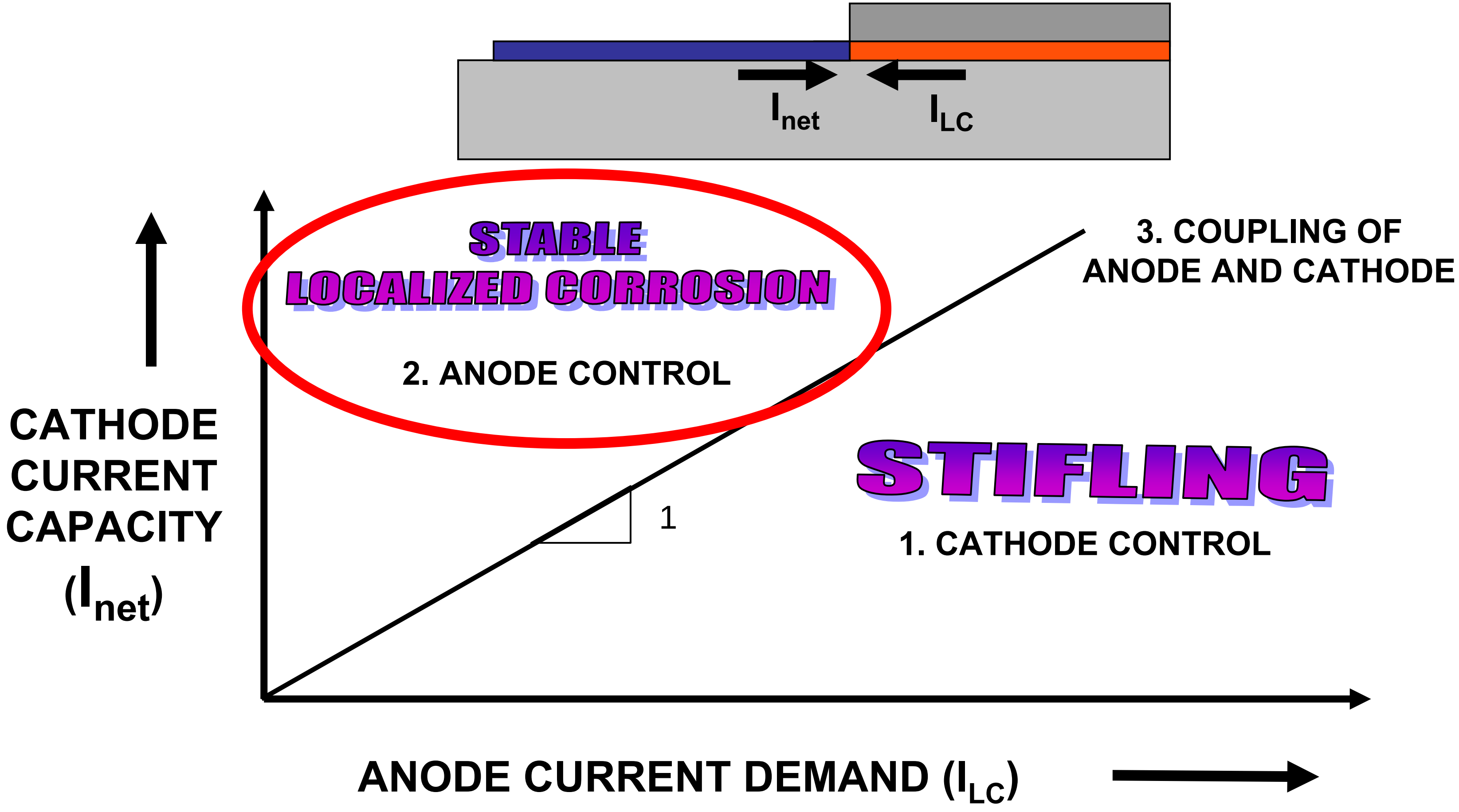






- **Factors that decrease cathode kinetics:**
  - **More protective oxide film inhibits electron transfer**
  - **Increased thin-layer pH**
  - **Diffusion limited current density**

Anode Control



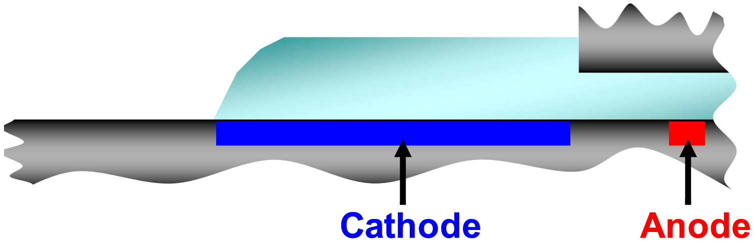
Anode Limitations Can Stifle Crevice Corrosion

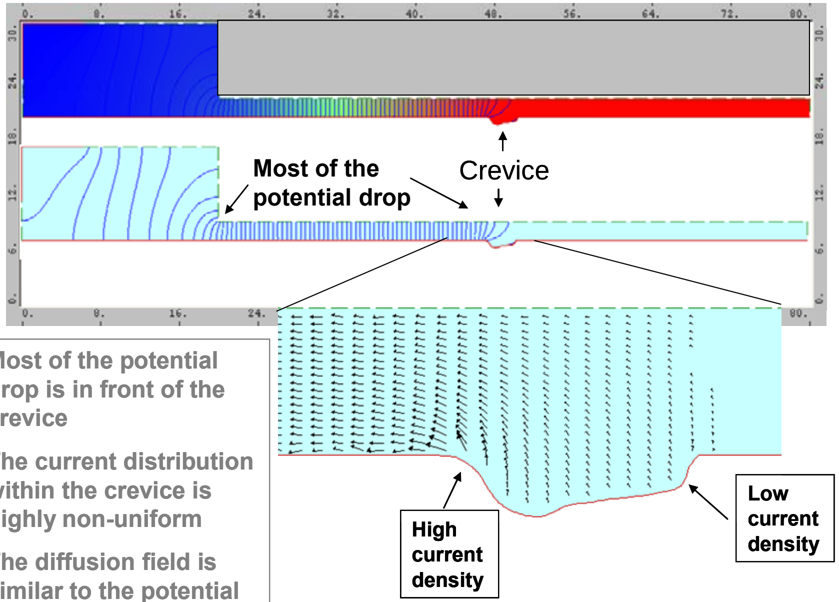
- **Must develop and maintain sufficiently aggressive local solution in terms of low pH and high [Cl$^-$]**
  - **Critical crevice solution (CCS) requires critical dissolution current density, i_{LC}, for given depth into the crevice, x**
- **More corrosion resistant alloys require solutions that are more aggressive to avoid stifling**
  - **Lower pH**
  - **Higher [Cl$^-$]**
  - **Higher dissolution current density for a given depth into crevice ($i \cdot x$)**
- **Examples of stifling:**
  - **Gap increases due to corrosion movement towards mouth**
  - **Protective precipitate forms within crevice**
  - **E_{mouth} of crevice falls, leads to insufficient dissolution rate in crevice**

Dissolution rate within crevice is overwhelmed by diffusion out of crevice

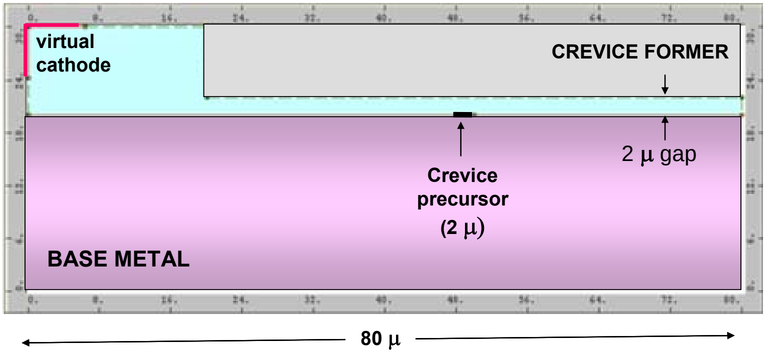
Repassivation by Dilution of Critical Crevice Chemistry

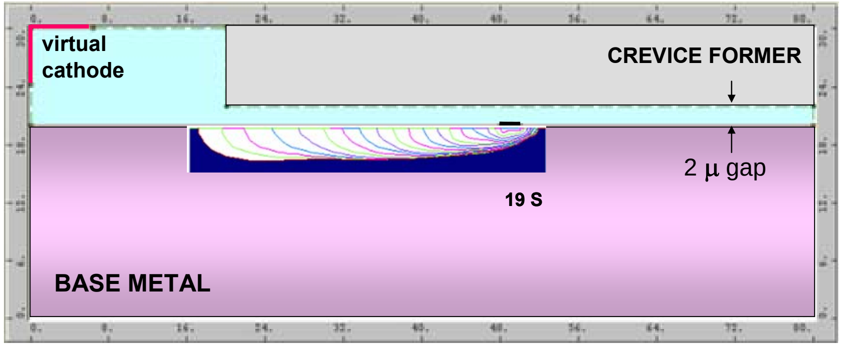
For <u>this</u> case: crevice gap opens, critical crevice chemistry is not maintained and corrosion arrests



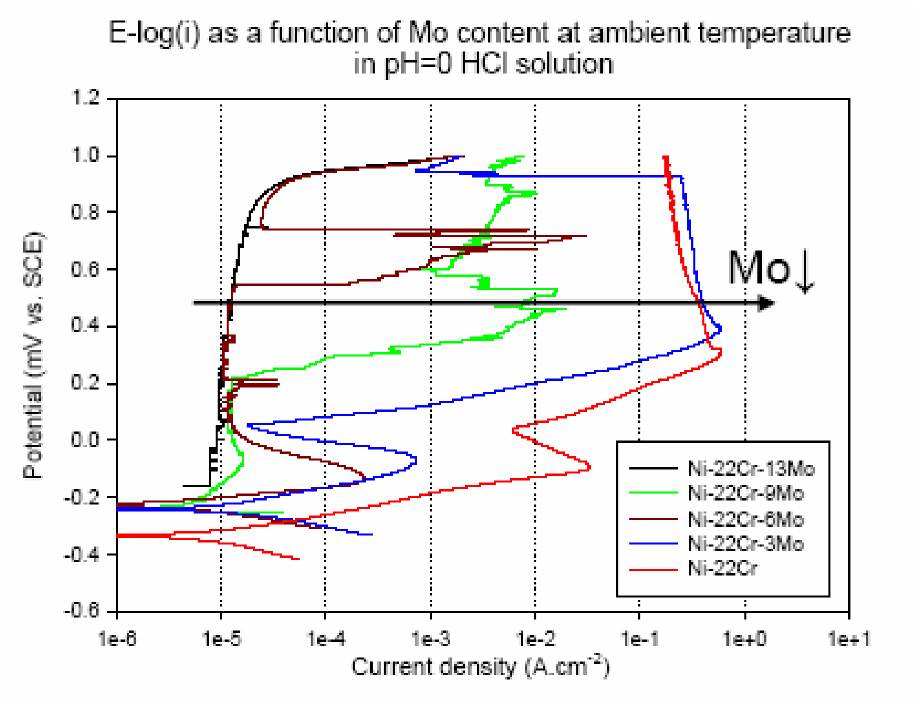


- Most of the potential drop is in front of the crevice
- The current distribution within the crevice is highly non-uniform
- The diffusion field is similar to the potential field





Slower Anodic Kinetics in CCS Makes Stability More Difficult to Maintain

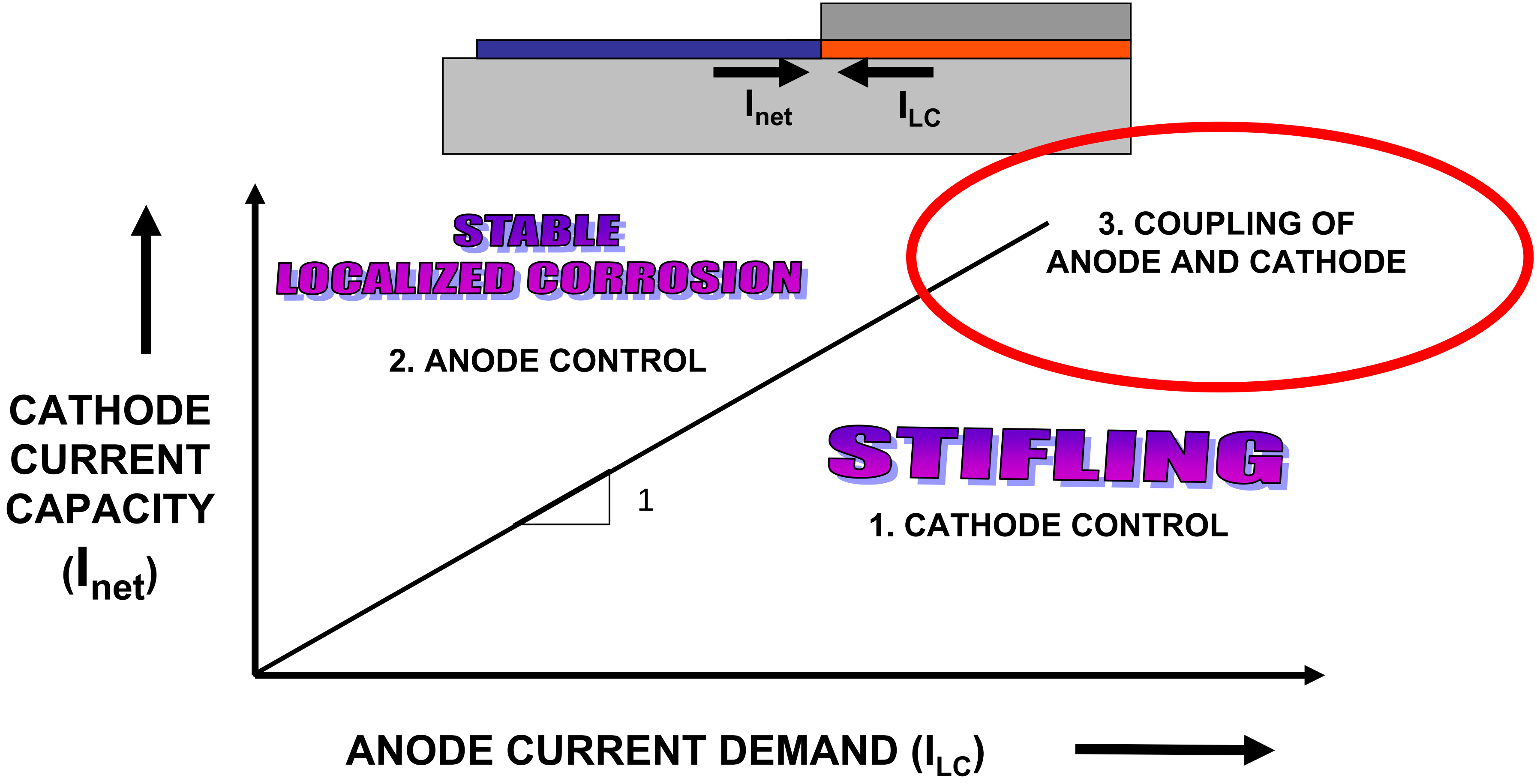


Increasing Mo Slows Anodic Kinetics in Pit Solutions

Experimental Values of CCS for Different Alloys

	pH_{crit}	$[Cl^-]_{crit}$
304L	**0.7**	**3.5**
316L	**0.1**	**6.5**
625	**-0.4**	**6**

Coupled Anode and Cathode Processes



I_{net} I_{LC}

STABLE LOCALIZED CORROSION

2. ANODE CONTROL

3. COUPLING OF
ANODE AND CATHODE

1

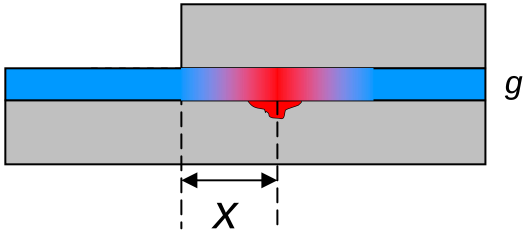
STIFLING

1. CATHODE CONTROL

CATHODE CURRENT CAPACITY (I_{net})

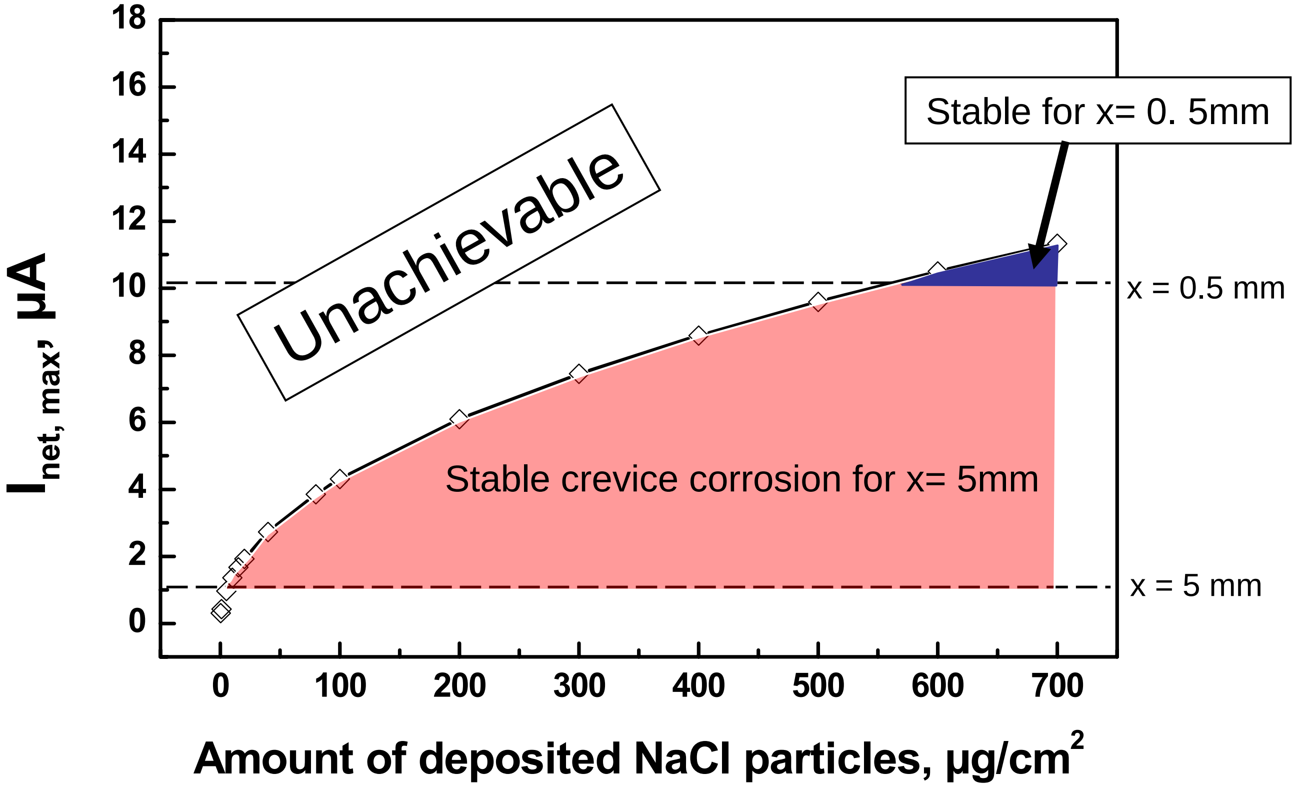
ANODE CURRENT DEMAND (I_{LC})

For Stable Crevice Corrosion, Cathode Must Supply Current Needed to Maintain Sufficiently High I_{LC}



$$I_{LC} \geq i \cdot g \cdot w = \frac{0.5}{x} g \cdot w$$

- Gap = 1 μm
- Width = 1 cm
- 316L
- ix = 0.5 A/m
- Room T, RH = 80%
- $E_{mouth} = -0.4\ V_{SCE}$



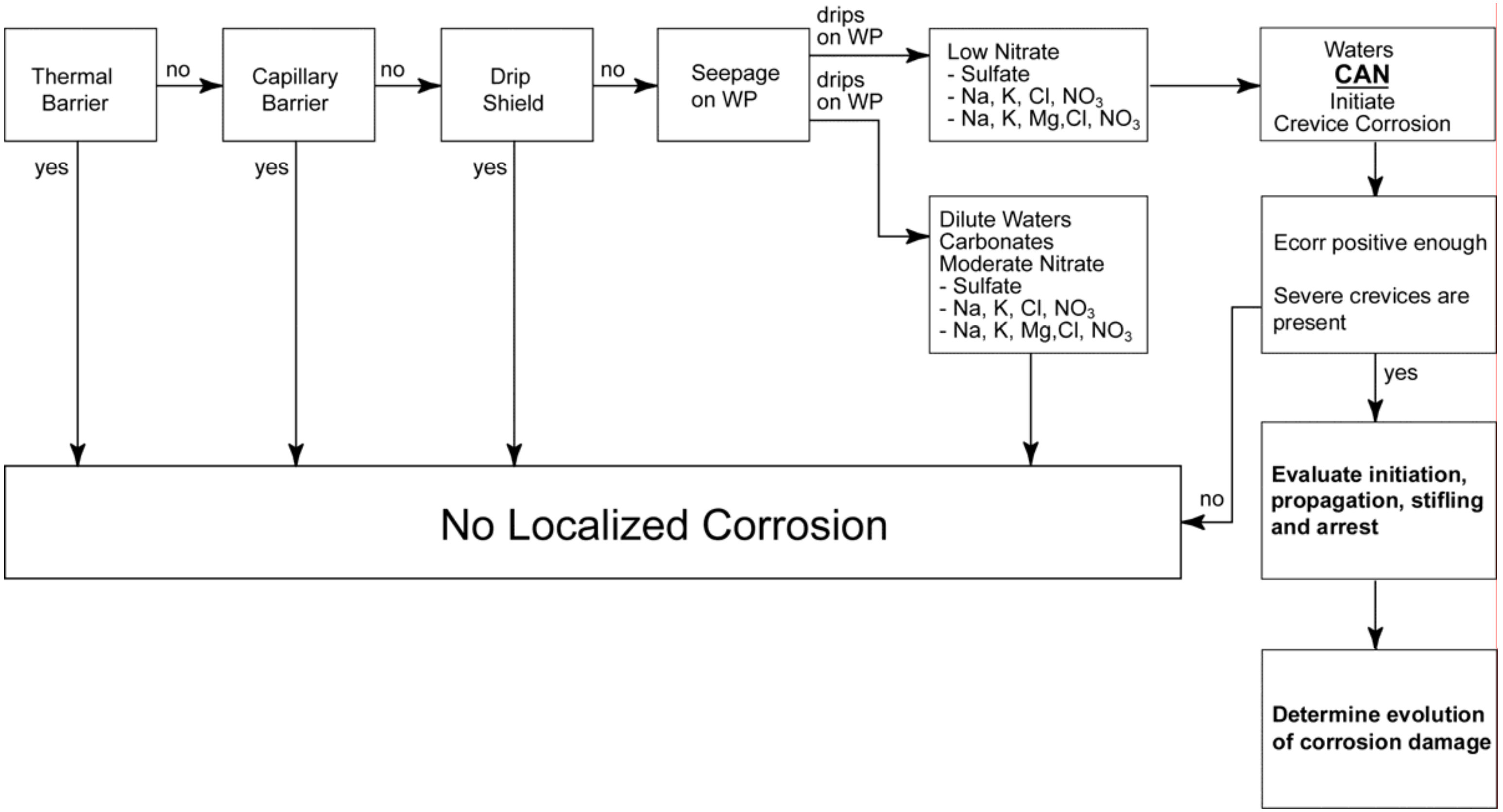
Summary

- A number of processes have been demonstrated to affect crevice corrosion propagation and arrest
  - Particulate layer, anode, cathode and coupled processes
- Findings add to the technical basis for the analysis of localized corrosion by a decision-tree approach
- Analysis is scenario specific — one must relate to expected conditions at Yucca Mountain
  - Evolution of the environment
  - Evolution of corrosion damage

Additional Slides

Decision-Tree Analysis with Seepage and Drips

- **Localized corrosion analysis with seepage & drips**



Thermal Barrier

no

yes

Capillary Barrier

no

yes

Drip Shield

no

yes

Seepage on WP

drips on WP

Low Nitrate
- Sulfate
- Na, K, Cl, NO_3
- Na, K, Mg,Cl, NO_3

drips on WP

Dilute Waters
Carbonates
Moderate Nitrate
- Sulfate
- Na, K, Cl, NO_3
- Na, K, Mg,Cl, NO_3

Waters **CAN** Initiate Crevice Corrosion

Ecorr positive enough

Severe crevices are present

yes

no

Evaluate initiation, propagation, stifling and arrest

Determine evolution of corrosion damage

No Localized Corrosion

Decision-Tree Analysis with No Seepage and Drips

- Localized corrosion analysis-no seepage/drips
  - Are environments and crevices present to induce localized corrosion?
    - Make-up and amount of particulate on metal surface
    - Composition, amount and distribution of moisture
    - Properties of the electrolyte layer
  - Will localized corrosion initiate?
    - Sufficient cathodic capacity
    - Development of critical crevice chemistry
  - Will it persist?
    - Cathode, anode and coupled processes
  - What amount of metal penetration occurs?
  - What is the size and distribution of corrosion sites?

Fraction of Porous Volume Occupied and Molality of Salt Solution as a Function of Temp. and % RH:

(1) %RH	(2) Solvent/Solute Mass Ratio	(3) Approximate Density (g/ml)	(4) Maximum Temperature at which RH can be achieved	(5) μL of brine per cm^2 of WP	(6) Fraction of porosity filled with solution	(7) Molality gmol(solute) per kg(solvent)
95	6.76	1.05	—	6.8	0.63	2.5
90	3.67	1.1	—	3.9	0.36	4.5
85	2.64	1.1	—	3.0	0.28	6.3
80	2.11	1.15	—	2.5	0.23	7.9
75	1.74	1.15	105°C	2.2	0.20	9.6
70	1.46	1.2	—	1.9	0.18	11.4
65	1.26	1.2	110°C	1.8	0.16	13.2
60	1.1	1.2	—	1.6	0.15	15.2
55	0.98	1.25	—	1.5	0.14	17.0
50	0.88	1.25	—	1.4	0.13	18.9
45	0.73	1.25	120°C	1.2	0.11	22.8
40	0.62	1.25	—	1.1	0.10	26.9
35	0.53	1.25	130°C	1.0	0.10	31.4
30	0.41	1.25	—	0.9	0.09	40.7

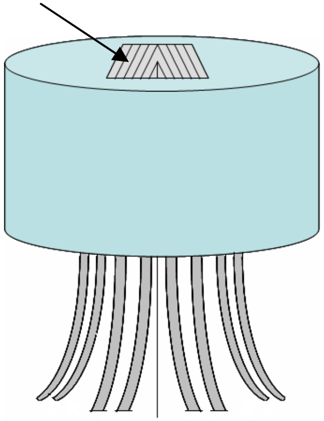
Columns (1) – (4) from Table 6.4-3, Column (5) Table 6.4-4, *Analysis of Dust Deliquescence for FEP Screening, ANL-EBS-MD-000074 Rev 01, August 2005,* Column (6) – (7) based on calculations using data from (1) – (5)

Available porous volume for solution in a 180 μm thick dust layer with 60% porosity = 10.8 μl

Fraction of porous volume occupied by solution = (Solution Vol.) / (Available Vol.)

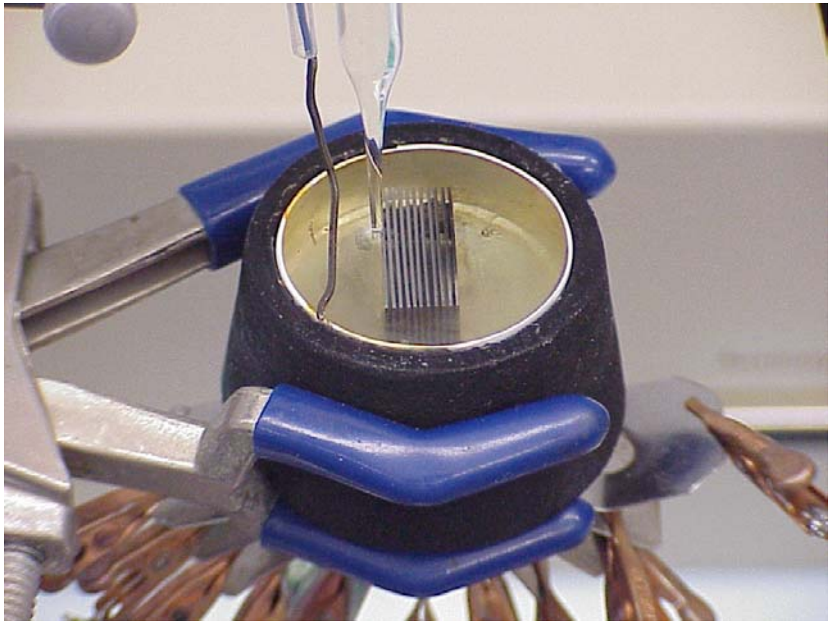
Multi-plate Assembly for Corrosion Cells in Particulate

- **Segmented electrode acts as single electrode, but permits measurement of current distribution along the surface**



Parallel plates are insulated from each other by epoxy

Electrodes are connected to each SS 316 plate

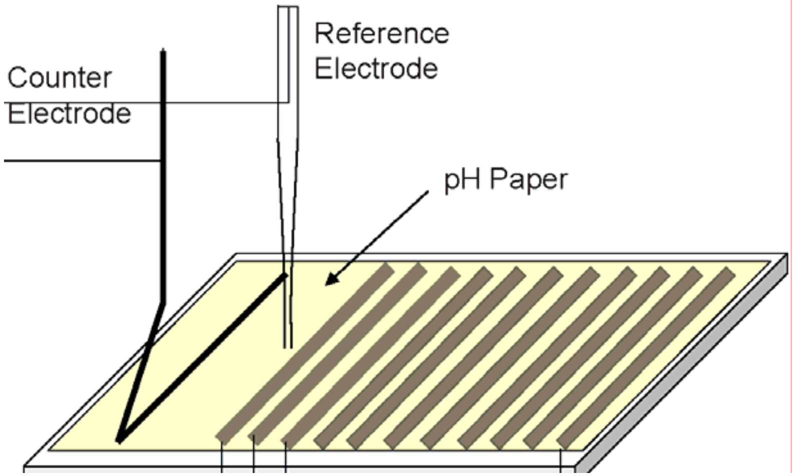


Anodic and Cathodic Processes

- **Anode:**
  - OH^- and Cl^- moving towards it
  - Oxidation Reaction, $4OH^- \rightarrow O_2 + 2H_2O + 4e$
  - OH^- consumed, solution turns acidic
  - Oxygen produced
  - Water produced
- **Cathode:**
  - H^+ and Na^+ moving towards it
  - Reduction Reaction, $O_2 + 2H_2O + 4e \rightarrow 4OH^-$
  - OH^- produced, solution turns alkaline
  - O_2 and H_2O consumed

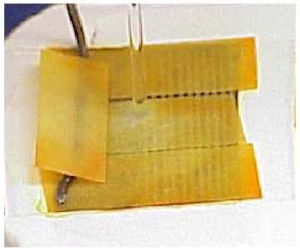
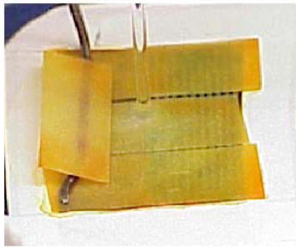
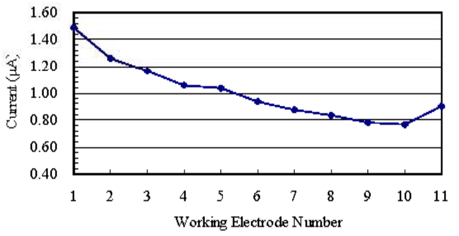
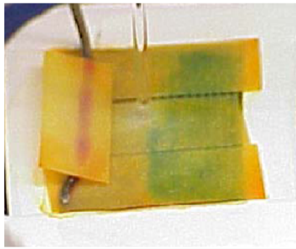
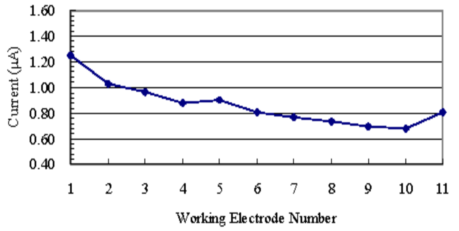
Experiment:

- Control potential on plate #1
- Monitor current distribution along segmented cathode
- Monitor pH changes



Chemical Changes in Electrolyte Layer

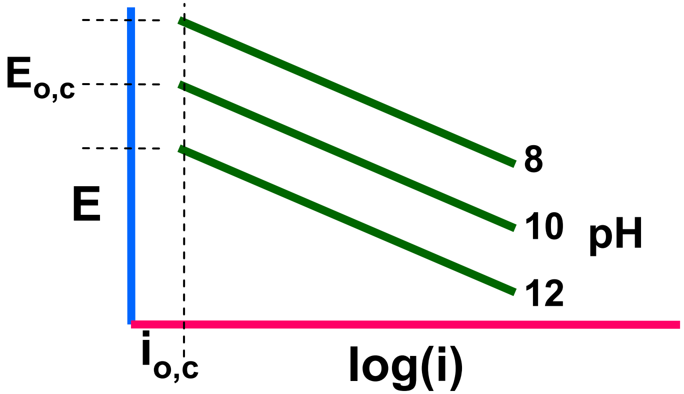
- **Increased pH (green) on cathode and decreased (red) on anode**

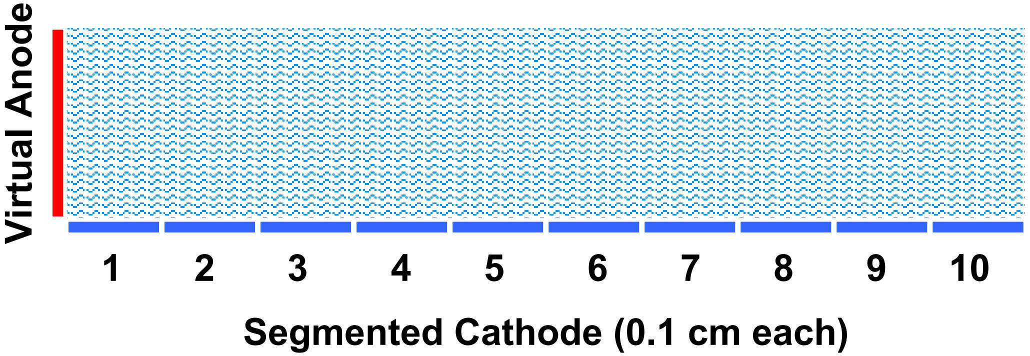
Time	Photograph	Current Distribution
0 s		
60 s		
180 s		

pH Effect due to Cathodic Reaction Chemistry

- Cathode Reaction (oxygen reduction): $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$
- Generation of OH^- will increase the local pH in the thin electrolyte film
- Modified kinetics due to pH increase: $E_{o,c}^{pH} = E_{o,c} - 0.059*pH$

Effect of pH on O_2 Reduction Kinetics:
$E_{o,c}$ ↓ as pH ↑





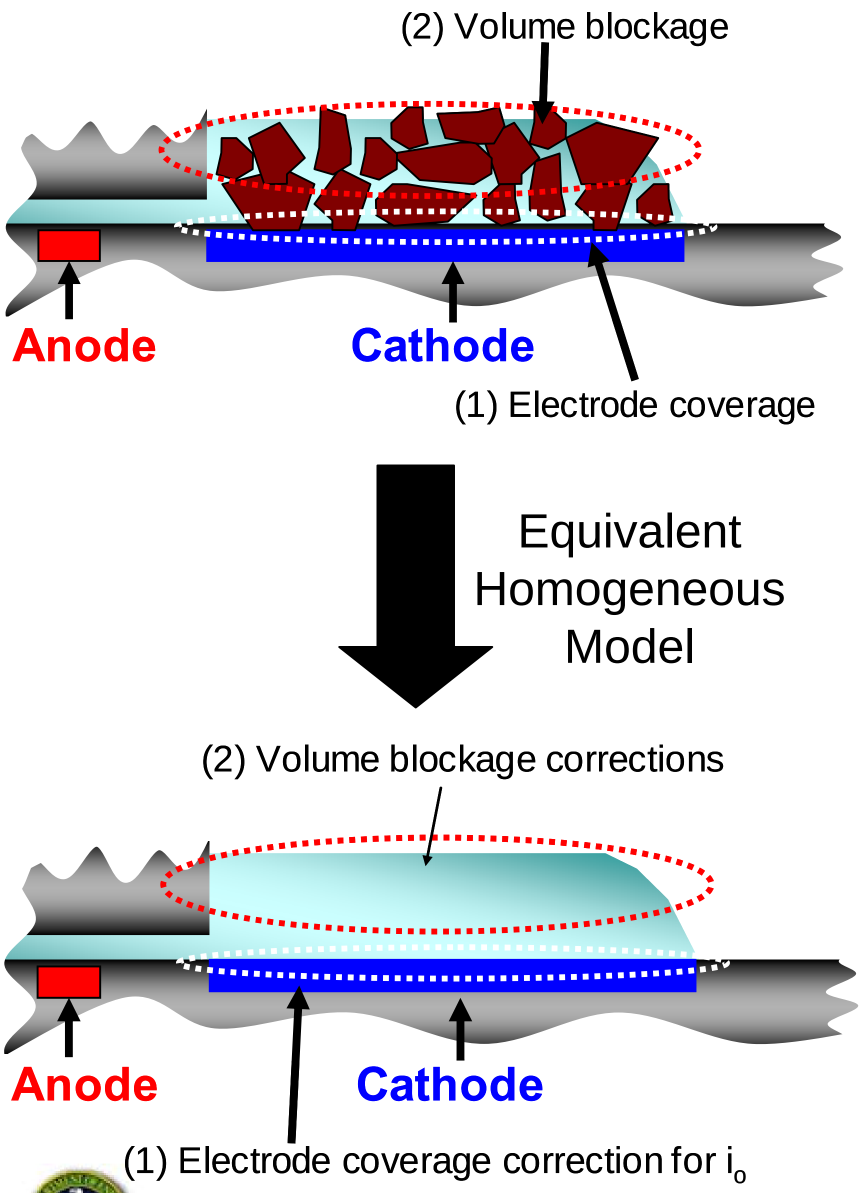
Segmented electrode geometry with varying reduction kinetics ($E_{o,c}$) based on pH is used

Calculate Maximum Current Capacity Given Measurable Parameters

- κ and WL are related to measurable quantities:
  - RH and Deposition Density (mass/area) of salt
- <u>Inputs</u>: T, RH, DD, i(E), pO_2 (for i_{lim})
  - RH and DD set m_{NaCl} via deliquescence behavior
  - m_{NaCl} determines κ, ρ
- <u>Output:</u>

$$I_{net,\max} = W \cdot \sqrt{2\frac{\kappa(RH)\cdot DD\cdot(1+m_{NaCl}\cdot MW_{NaCl})}{\rho(RH)\cdot m_{NaCl}(RH)\cdot MW_{NaCl}}\cdot\int_{E_{corr}}^{E_{mouth}}(i_c-i_p)\cdot dE}$$

Methodology for Effects of Particulate



(2) Volume blockage

Anode

Cathode

(1) Electrode coverage

Equivalent Homogeneous Model

(2) Volume blockage corrections

Anode

Cathode

(1) Electrode coverage correction for i_o

1. Cathode <u>surface blockage</u> by particles (first mono layer) → Equivalent Exchange Current Density (i_o') - ***area effect***

$$\frac{A_{\text{exposed}}}{A_{\text{total}}} = \frac{\text{Area(total)} - \text{Area(covered)}}{\text{Area(total)}}$$

$$i_0' = i_0 \times \frac{A_{\text{exposed}}}{A_{\text{total}}}$$

2. Particles block solution volume: Effective Conductivity (κ_{eff}) – ***ohmic effect***

Bruggeman's Equation

$$\kappa_{\text{eff}} = \kappa(1 - \phi_{\text{sand}})^{\frac{3}{2}}$$

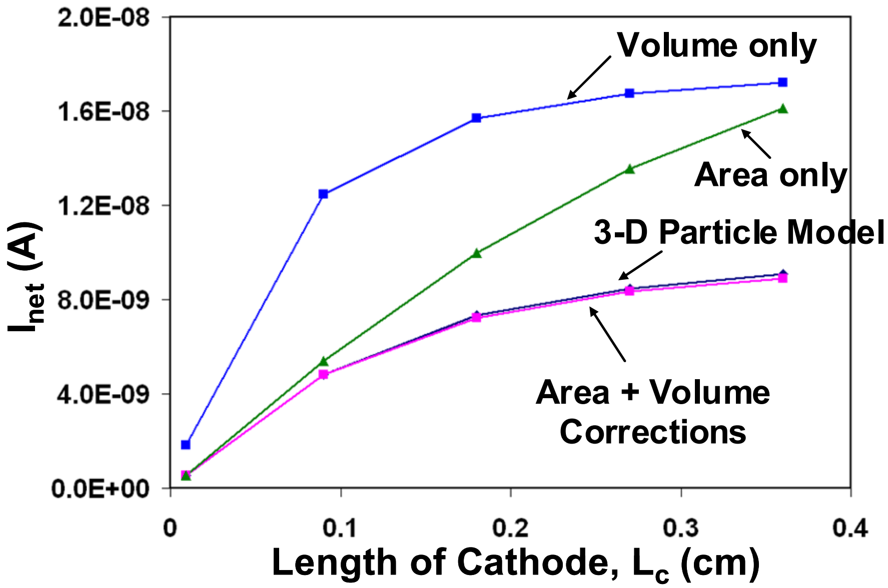
where

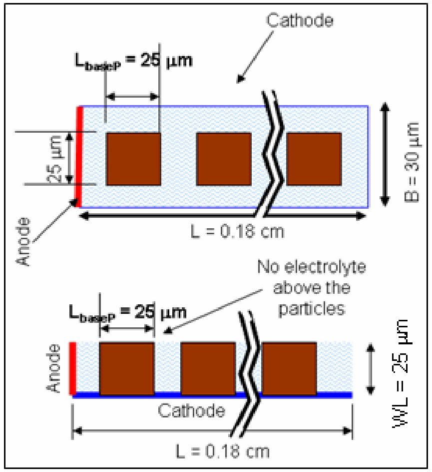
$$\phi_{\text{sand}} = \frac{\text{Vol(sand)}}{\text{Vol(sand + solution)}}$$

3. Effective diffusivity (D_{eff}) as a function of particulate tortuosity (τ) and porosity ($1-\Phi_{\text{sand}}$) – ***mass transfer effect.*** This effect is employed in the limiting current (i_L).

$$D_{\text{eff}} = D\frac{(1 - \varphi_{\text{sand}})}{\tau}$$

Comparison of Particle Layer Simulations to Volume and Area Corrections





$i_o = 10^{-9}$ A/cm^2

κ= 121 mS/cm

β_c = 0.1 V/dec

E_{rp} = -0.31 V_{NHE}

$E_{o,c}$ = 0.19 V_{NHE}

i_L = 2.2e-4 A/cm^2

G_a = 25 μm (constant)

G_f = 25 μm to 250 μm

Particles – 25 μm cubes

Porosity – 70%

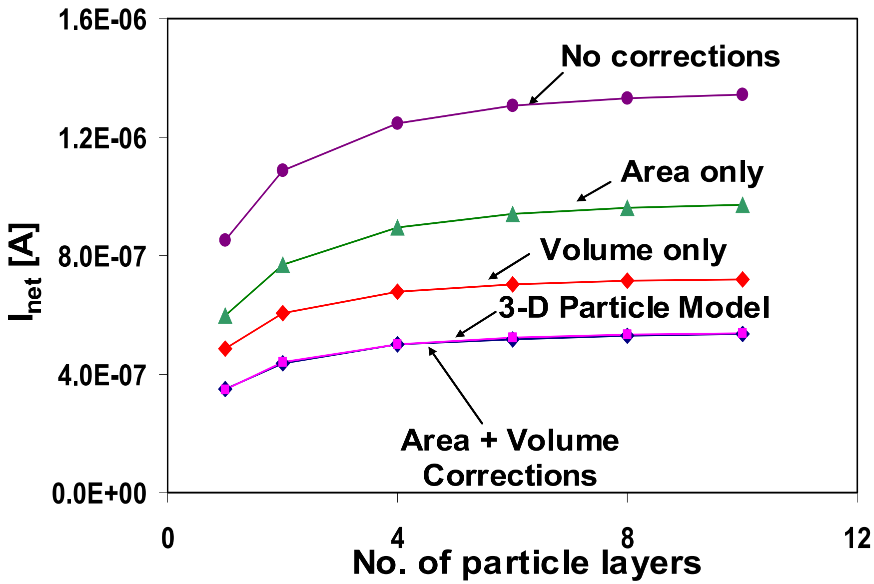
Area Coverage – 30%

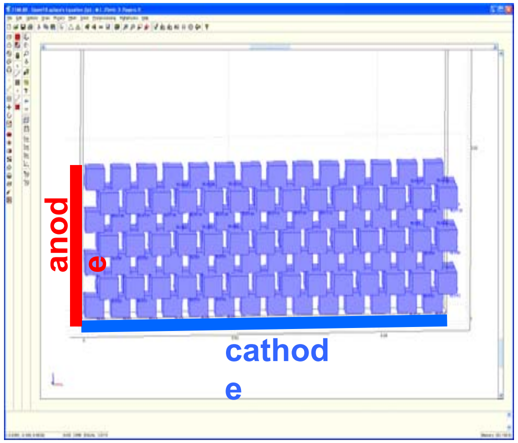
Area Correction: i_o' = 0.306 x 10^{-9} A/cm^2

Volume Correction: κ_{eff} = 70 mS/cm

- Volume (Bruggeman) and surface coverage (area) corrections in 2-D simulations produce accurate 3-D results
- Independently area or volume correction are insufficient
- Similar results obtained without mass transfer limitations

Multi-Layer Particle System





$i_o = 10^{-6}$ A/cm^2

β_c = 0.1 V/dec

E_{rp} = -0.31 V_{NHE}

$E_{o,c}$ = 0.19 V_{NHE}

κ = 12.1 mS/cm

L_c = 0.05 cm (constant)

G_a = 25 μm (constant)

G_f = 25 μm to 250 μm

(1 to 10 particle layers)

Particles – 25 μm cubes

49 % porosity

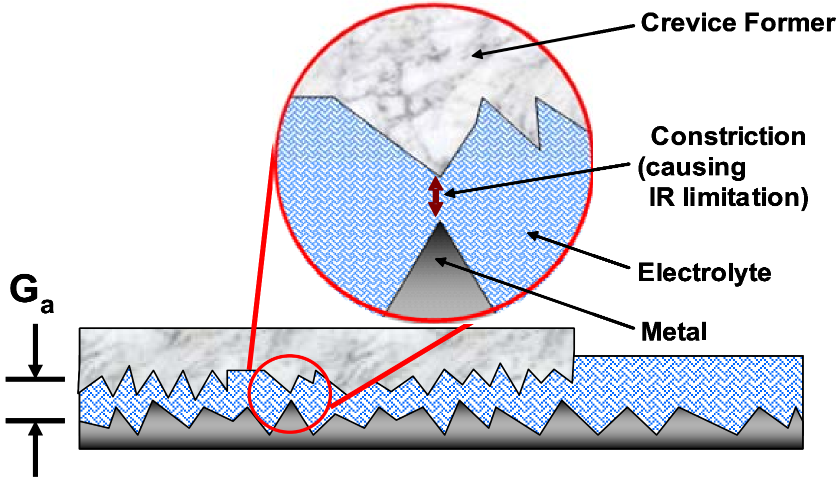
49 % area coverage

Area Correction: i_o' = 0.49 x 10^{-6} A/cm^2

Volume Correction: κ_{eff} = 4.148 mS/cm

- Volume (Bruggeman) and surface coverage (area) corrections in 2-D simulations produce accurate 3-D results
- Independently, area or volume correction are insufficient

Modeling the Effect of Crevice Former, Metal Roughness and Particulate Corrosion Products

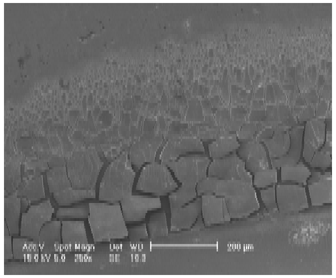


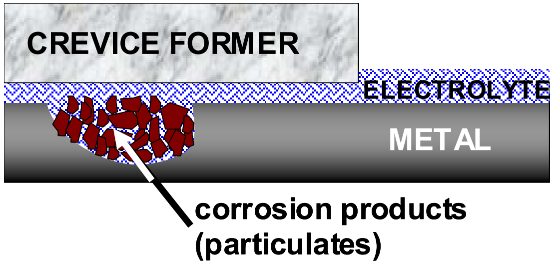
Metal - crevice former roughness can be of the order of nominal crevice gap (G_a).

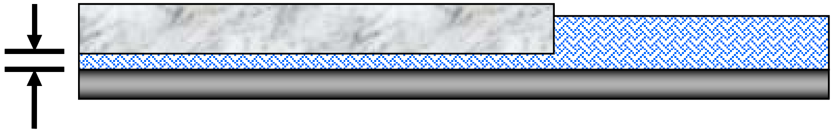
Constrictions along the rough surface create narrow passages to the current flow, causing high localized IR drop.

Solid corrosion products:

- Increase IR resistance to further corrosion of underlying metal
- Affect on the evolution of corrosion profile







Modified G_a’ (based on constriction effects)

GOAL: develop an equivalent ‘idealized’ smooth crevice in terms of a modified crevice gap (G_a’).

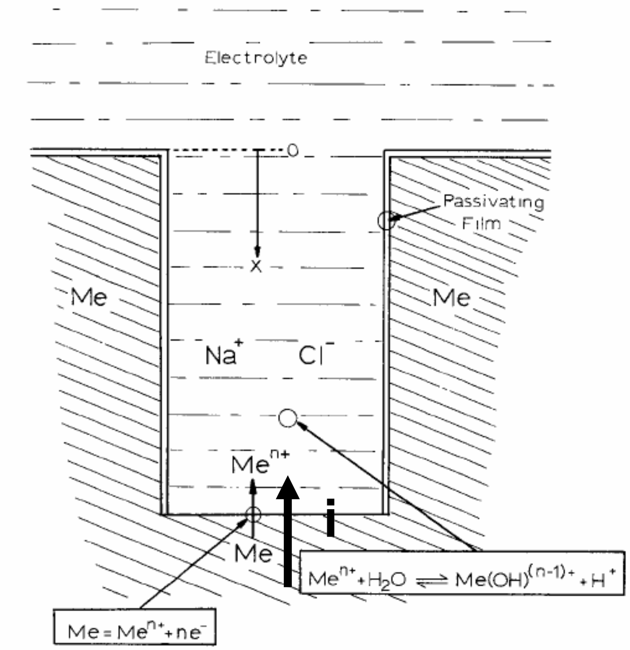
Anode Stability Considerations: Maintenance of Critical Chemistry

- **Pit stability product (ix) must be exceeded for stable localized corrosion:**
  - **ix is required to maintain C^* at base of pit**
    - **i =dissolution current density**
    - **x = depth of pit**
- **If $ix < ix_{crit}$, pit repassivates**

ix_{crit} increases with increased resistance to localized corrosion

- alloying

- lower T, $[Cl^-]$



J.R. Galvele, JECS, 123(4), 1976

As Cathode Shrinks, Anode/Cathode Separation Becomes Less Complete, Low pH Cannot be Maintained Inside Crevice