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

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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

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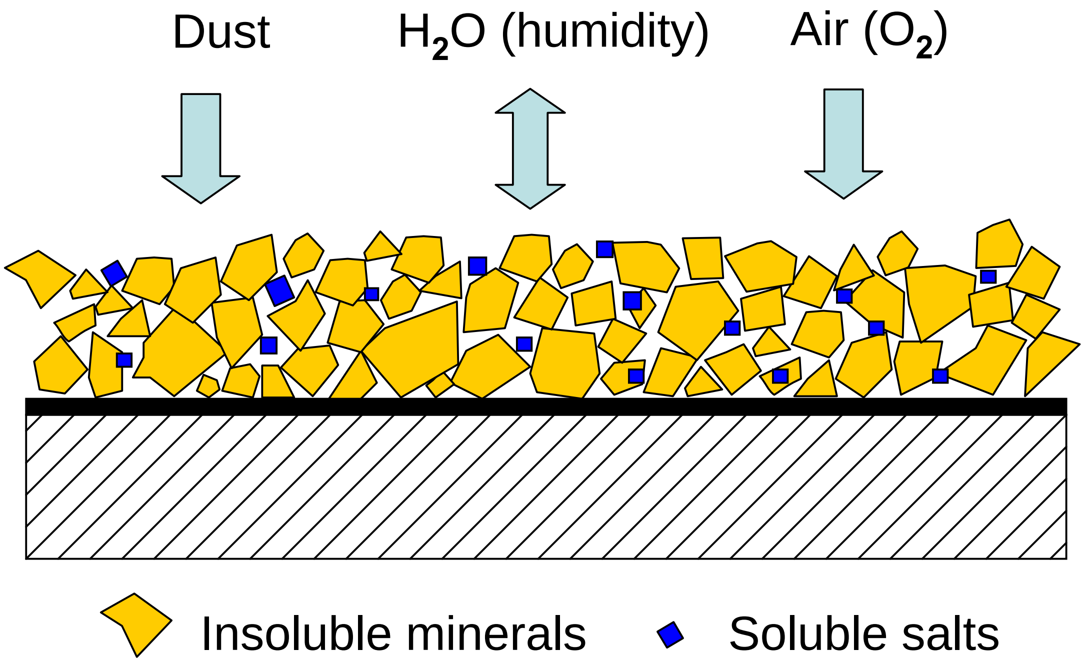
- The views, opinions, findings, and conclusions or recommendations of authors expressed herein do not necessarily state or reflect those of the DOE/OCRWM

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



Dust

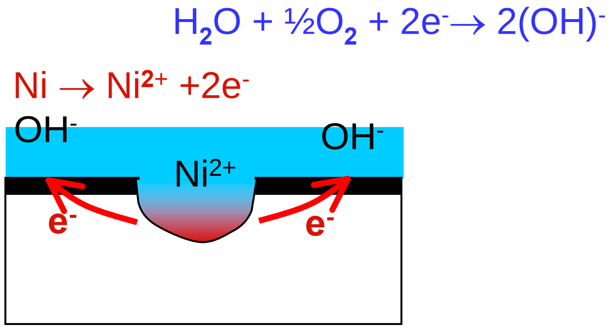
H_2O (humidity)

Air (O_2)

Insoluble minerals

Soluble salts

Electrochemical Corrosion Cell under Particulate Layer



$H_2O + \frac{1}{2}O_2 + 2e^- \rightarrow 2(OH)^-$

$Ni \rightarrow Ni^{2+} + 2e^-$

OH^-

Ni^{2+}

OH^-

e^-

e^-

- **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: $H_2O + \frac{1}{2}O_2 + 2e^- \rightarrow 2(OH)^-$**

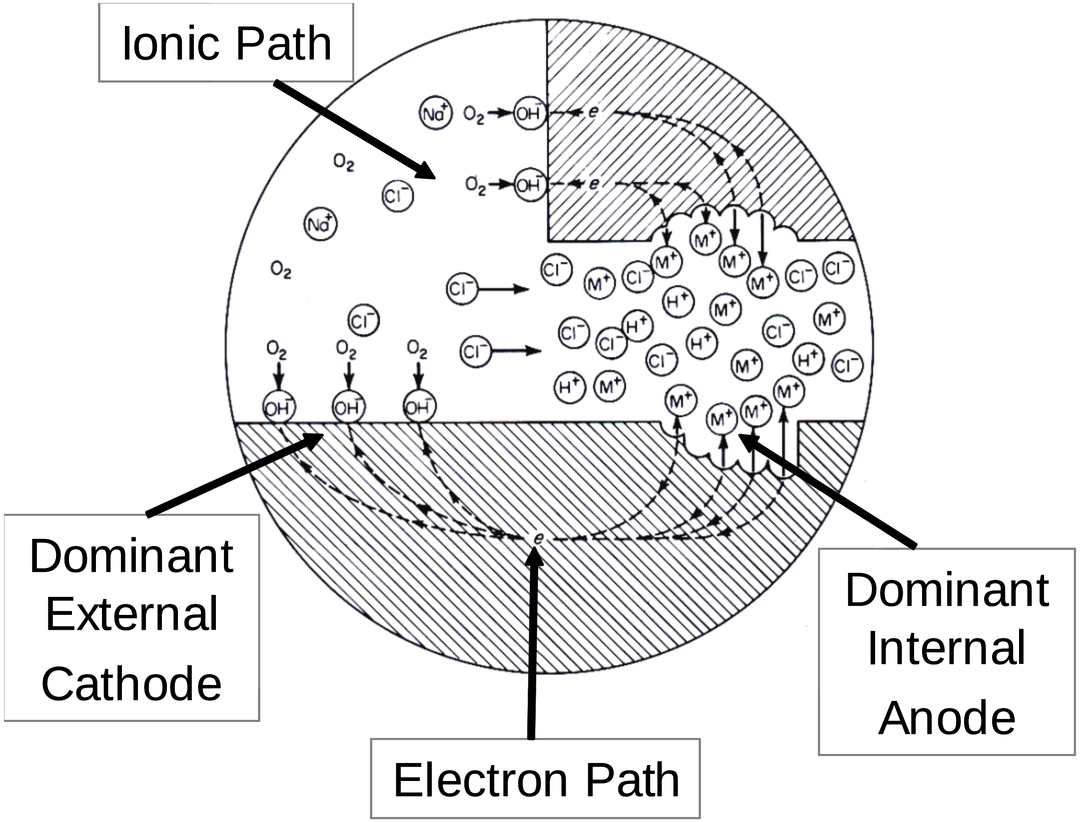
Materials Performance Thrust

- 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

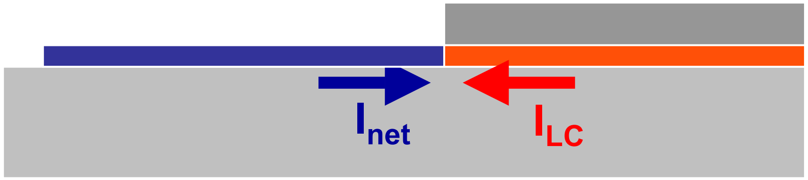
- **Aggressive environment**
- **Tight, impermeable crevice**
- **$E_{corr} > E_{repass}$**
- **Separated and coupled anode and cathode**
- **Develop critical crevice chemistry**

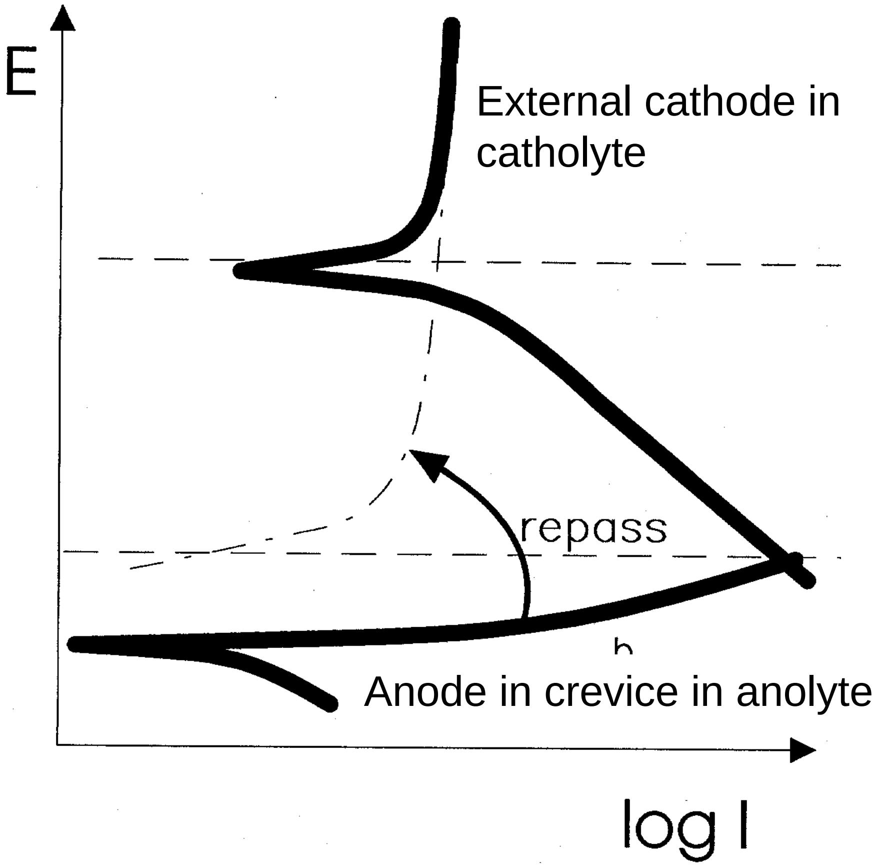
Propagation

- **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**

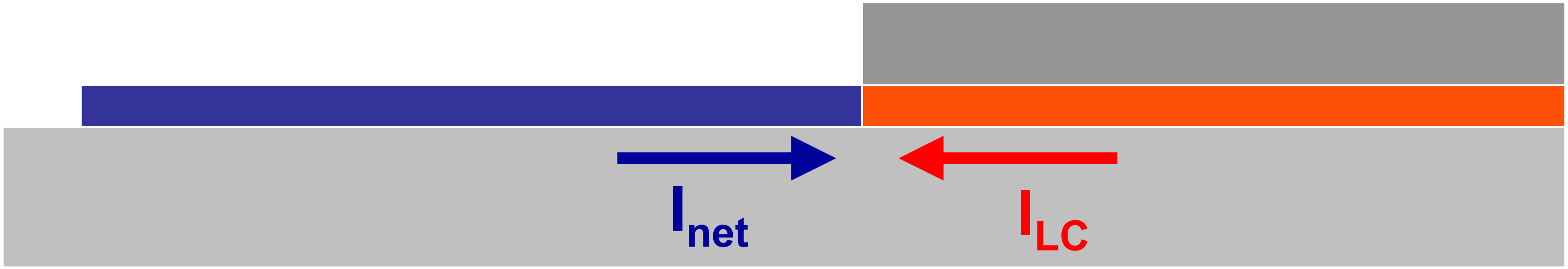




Stability of Localized Corrosion

Crevice with Thin Layer External Cathode

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



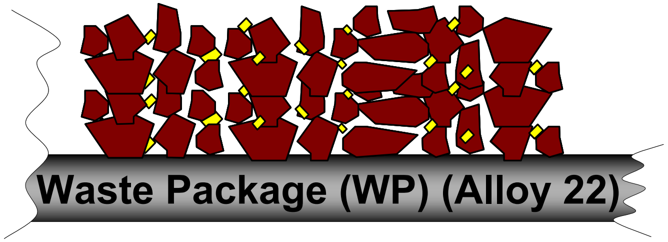
I_{net} = total cathodic current from freely exposed surface surrounding crevice
I_{LC} = total anodic from crevice

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



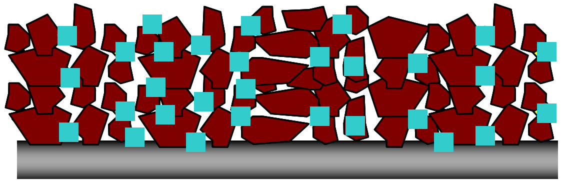
Dry particulate-No moisture

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

Particulate layer: thickness, porosity, density

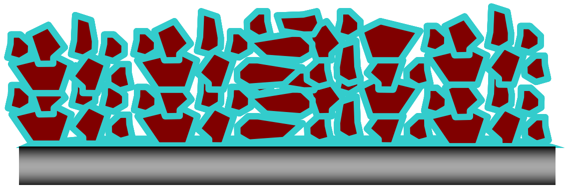
Temperature and Relative Humidity (activity of water)

Solution properties



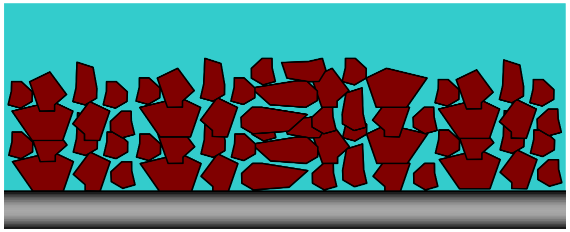
<u>Droplets of moisture</u>

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



<u>Unsaturated particulate layer</u>

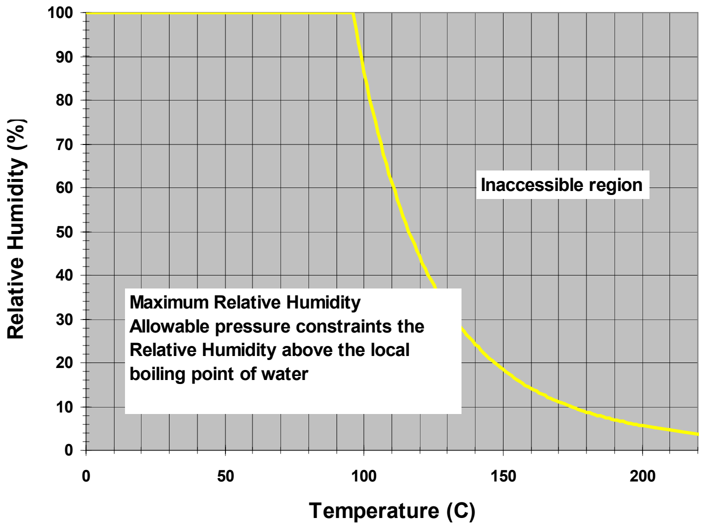
- **Lower temperatures**
- **Less concentrated brines**



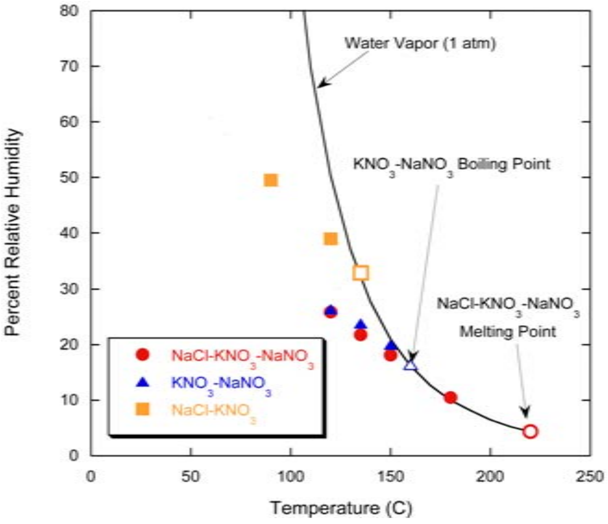
<u>Solution layer on metal</u>

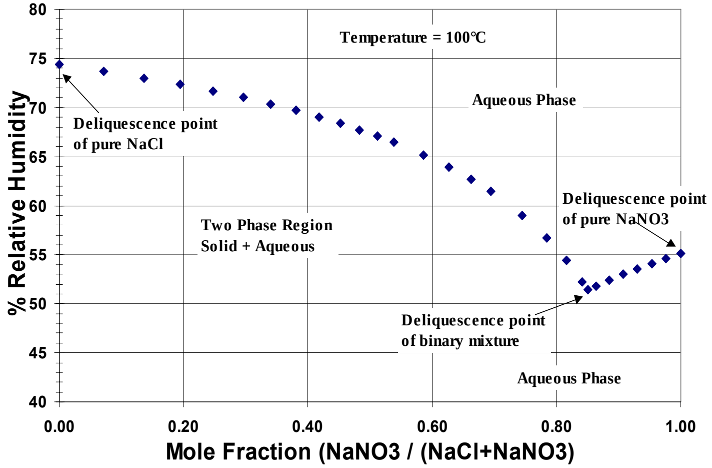
- **Lower temperatures**
- **Less concentrated brines**

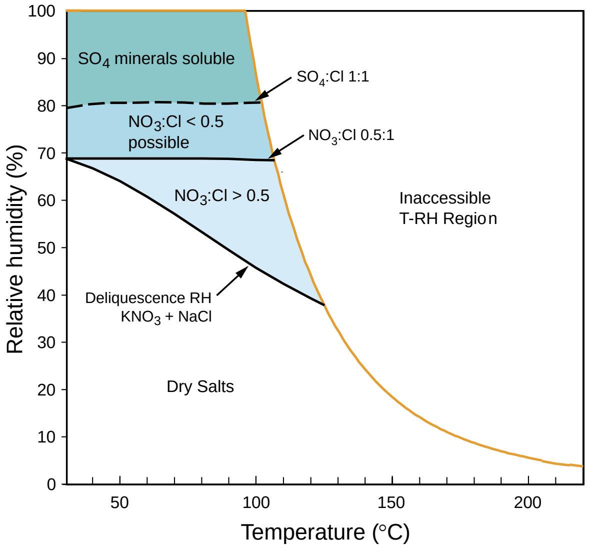
Sampling of Technical Basis for Solution Chemistry



Maximum Relative Humidity Allowable pressure constraints the Relative Humidity above the local boiling point of water

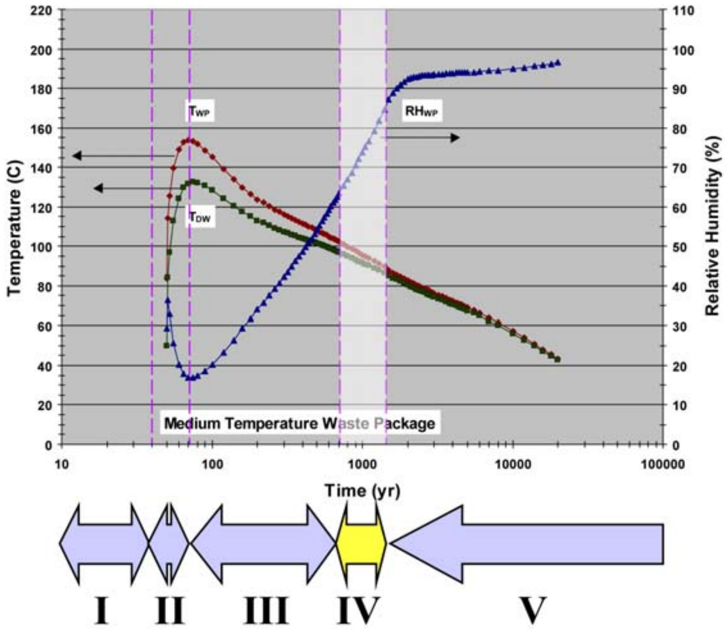


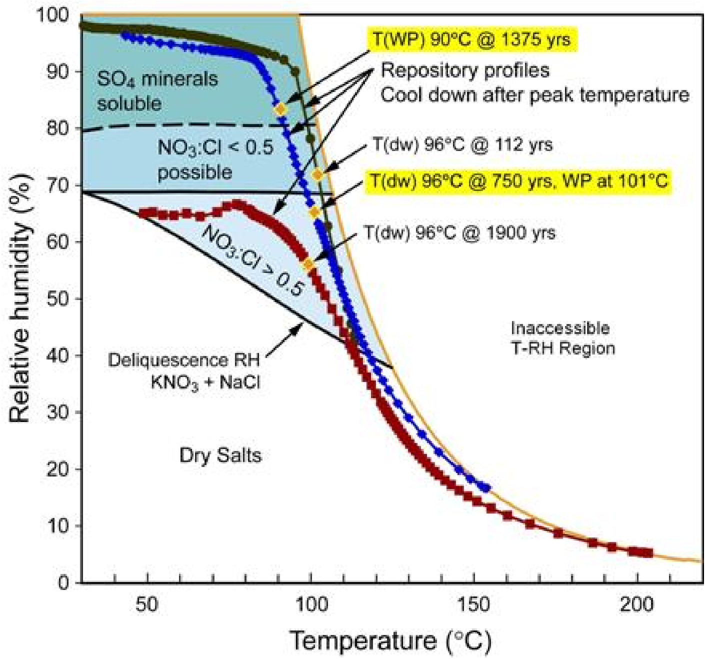




Example of WP Temperature & Relative Humidity Control of Solution Composition

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





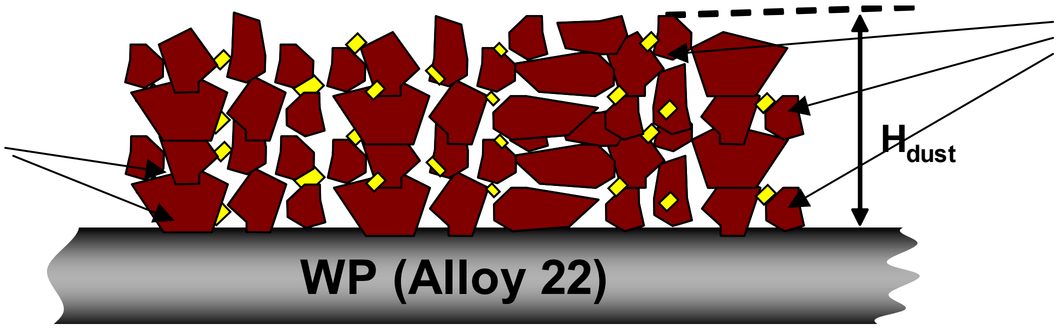
Drift wall 96°C at 750 years;

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

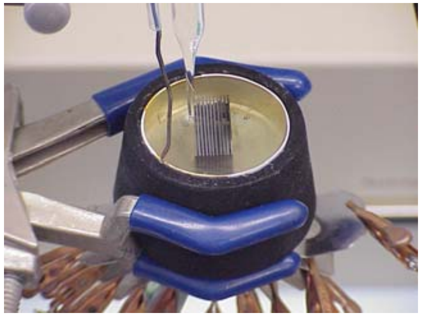


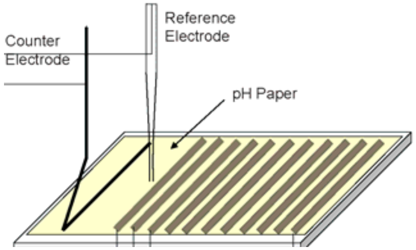
Insoluble
mineral
particles

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)$^{3/2}$ x κ_{bulk}	0.465 x κ_{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

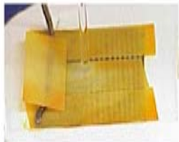
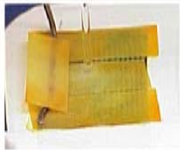
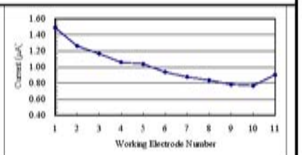
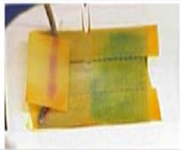
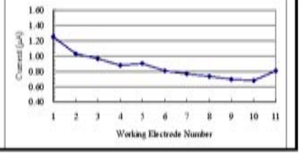




Experiment:

- 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

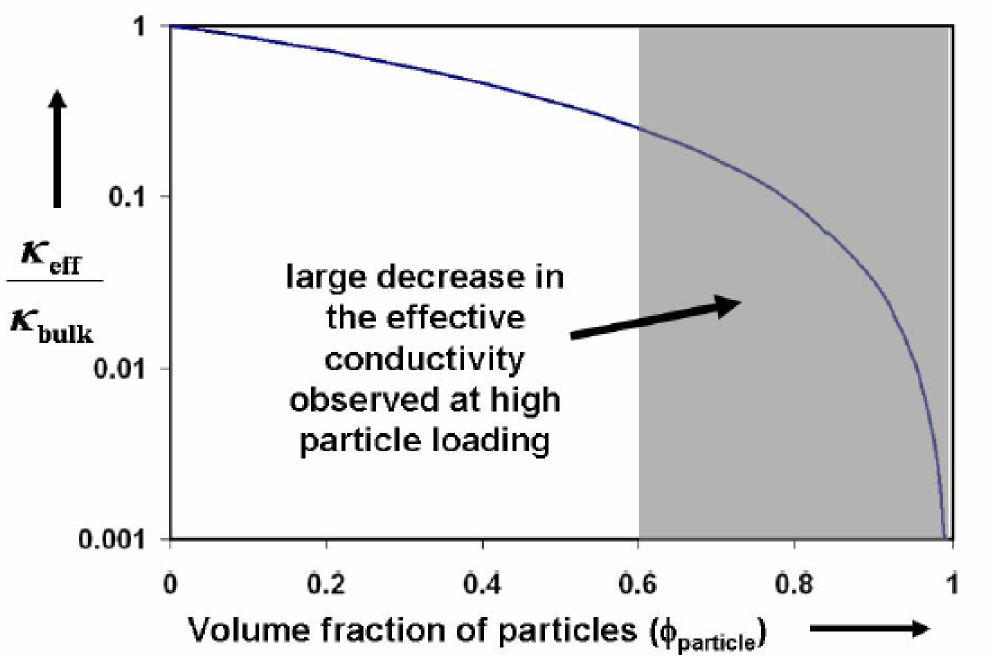
- **Decreased conductivity in the particulate layer**
  - **Higher particle volume fraction**
  - **Lower solution volume fraction in pores (unsaturated)**

Bruggeman's Equation

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

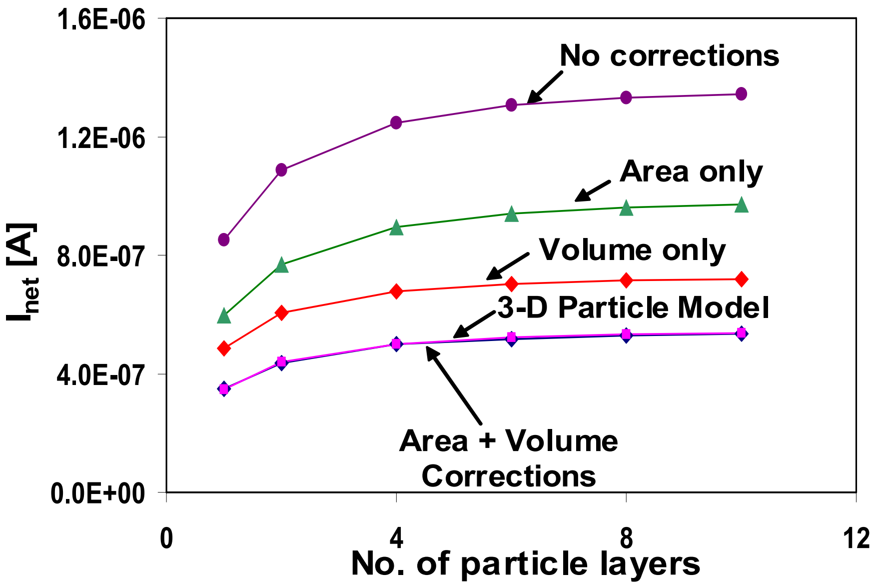
where

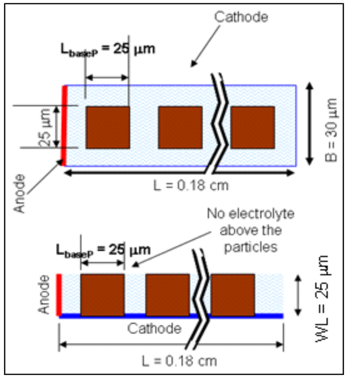
$$\phi_{\text{sand}} = \frac{\text{Vol(sand)}}{\text{Vol(sand + solution)}}$$

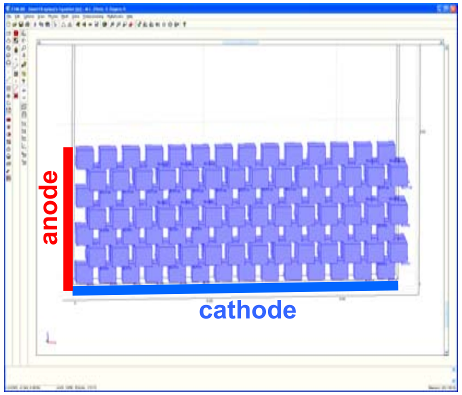


Analysis of the Effects of Particulate

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

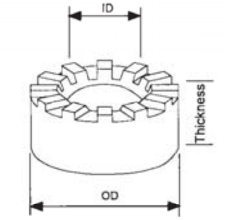
Effect of Crevice Formers on the Localized Corrosion Damage and Propagation

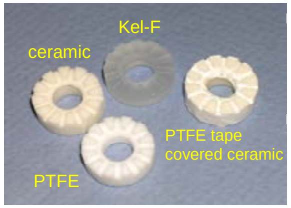
Specimen assembly

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

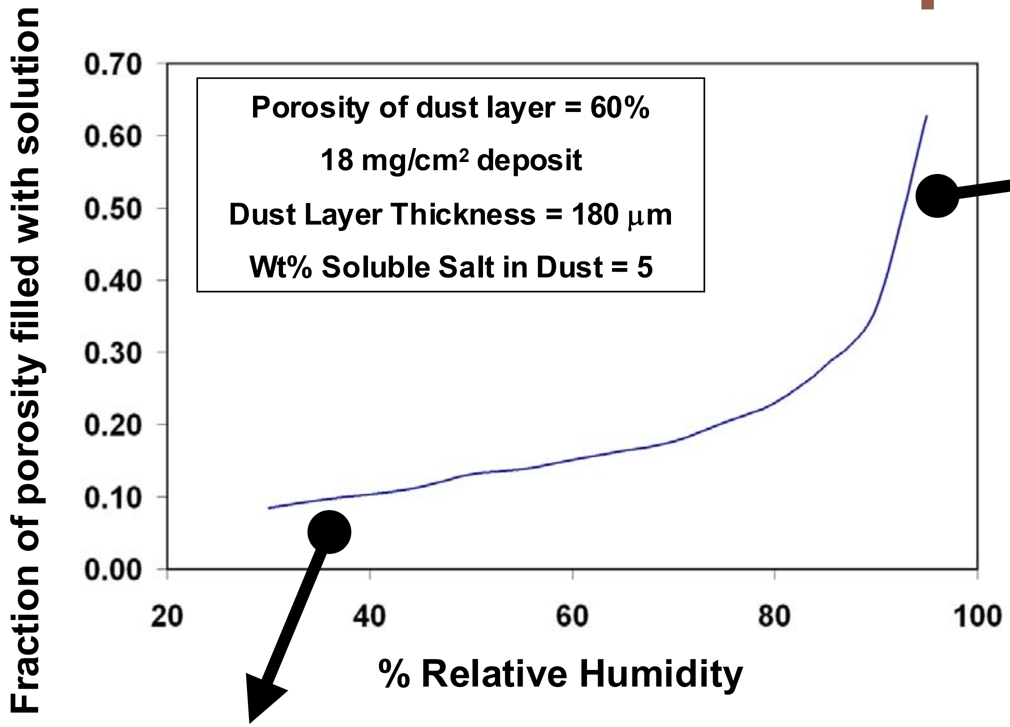




- **12 contact plateaus (feet)**
- **ID: 9.9 mm   OD: 15.9 mm   Thickness: 6.3 mm**
- **Contact area: 6 mm^2/foot**

- **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

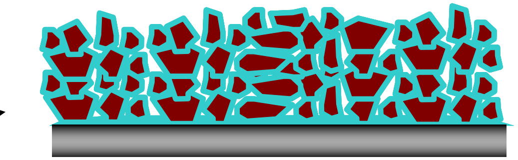


Porosity of dust layer = 60%

18 mg/cm^2 deposit

Dust Layer Thickness = 180 µm

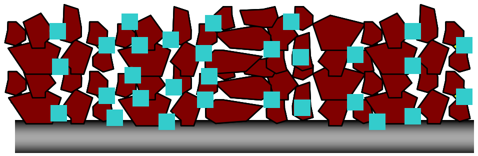
Wt% Soluble Salt in Dust = 5



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

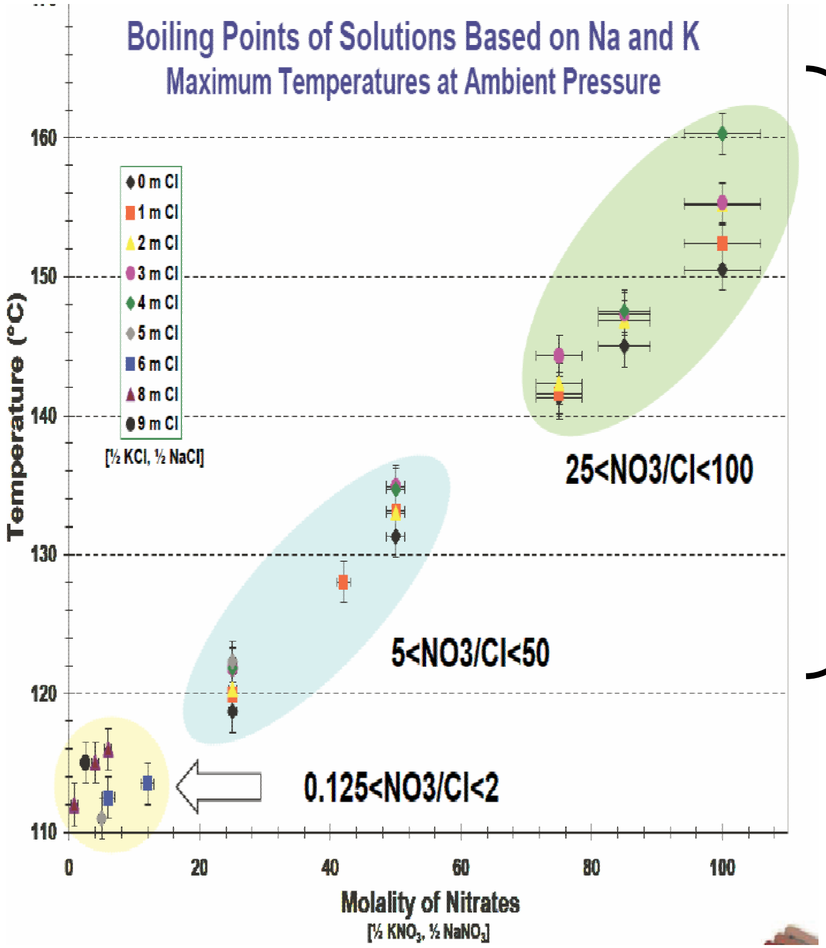


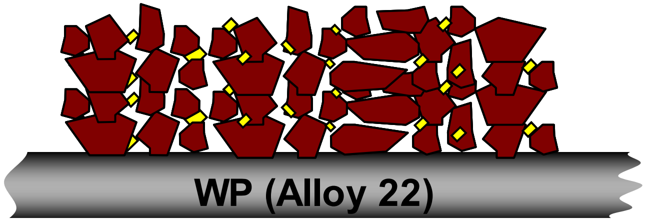
Droplets of Moisture

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

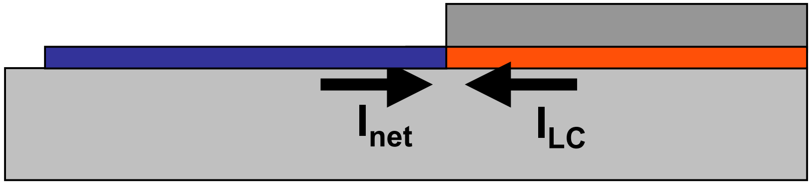
Particulate Layer as an Electrolyte and Crevice Former for Localized Corrosion

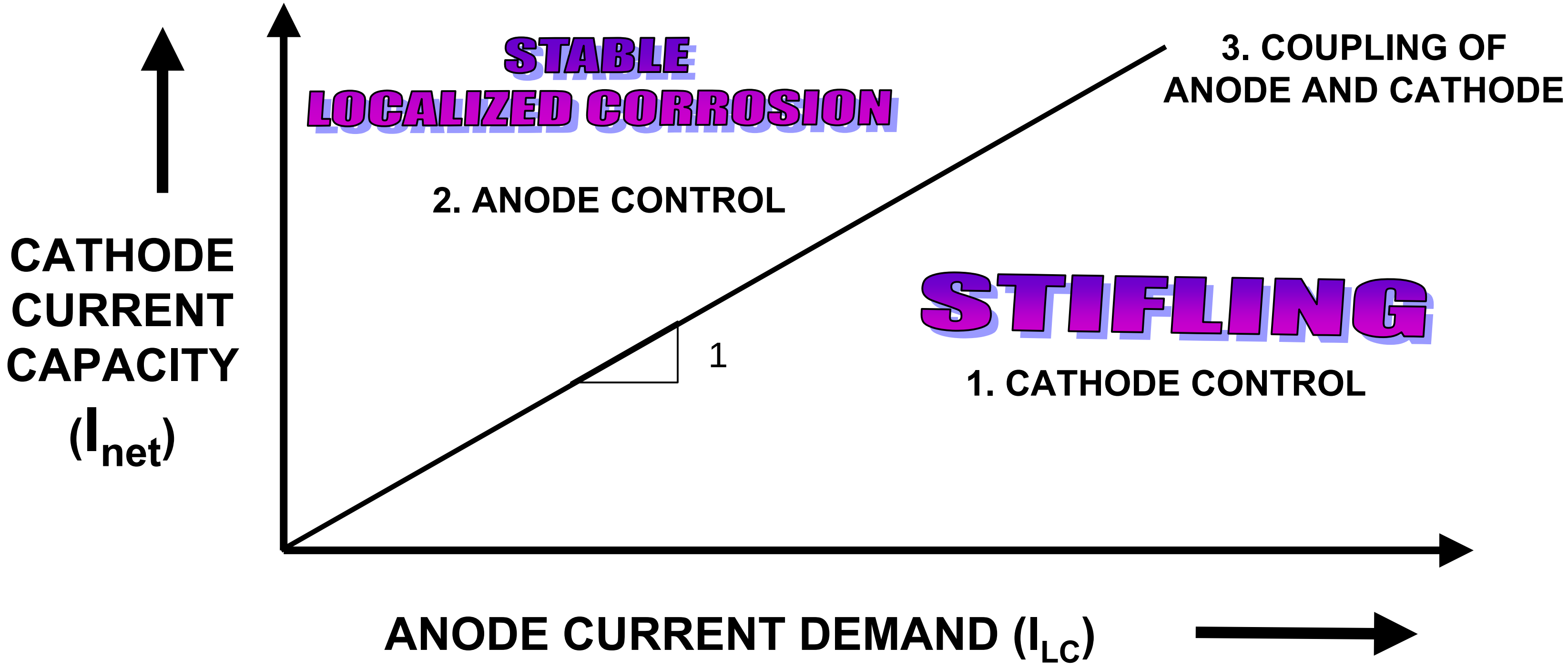
- Can particulate layer act as an effective electrolyte and crevice former?
  - Composition, amount and distribution of moisture
  - Conductivity and permeability of the electrolyte layer
  - Separation of anode/cathode required for localized corrosion
- Will particulate layer fulfill requirements for 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

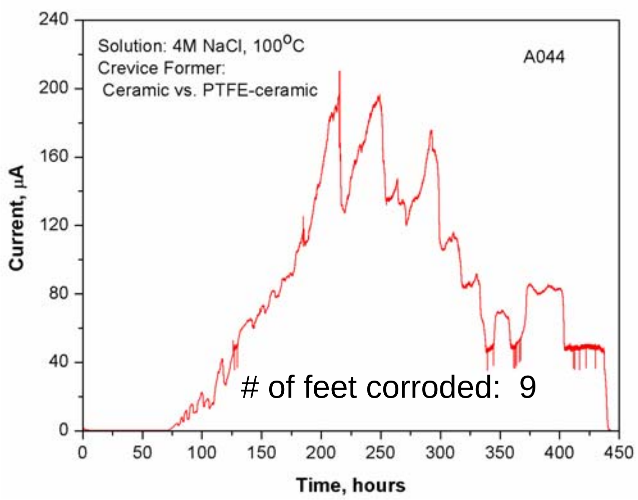
Factors Influencing Localized Corrosion Stability

Cathode Current Capacity **≥ Anode Current Demand**

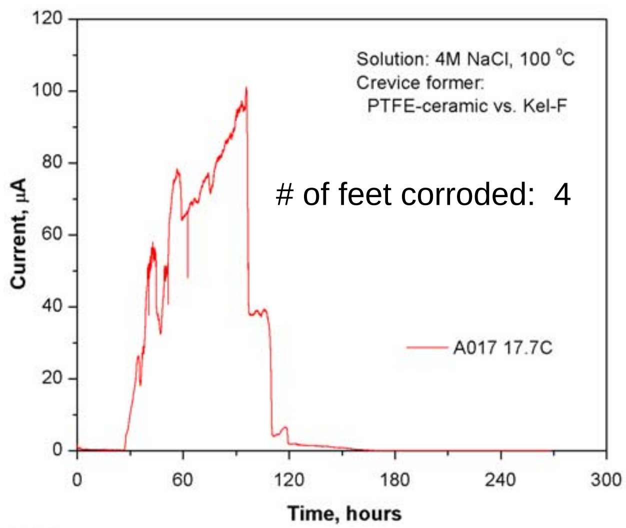




Arrest of Crevice Corrosion (Repassivation)



\# of feet corroded: 9



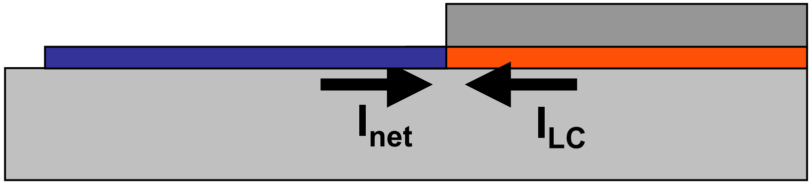
\# of feet corroded: 4

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

Observations

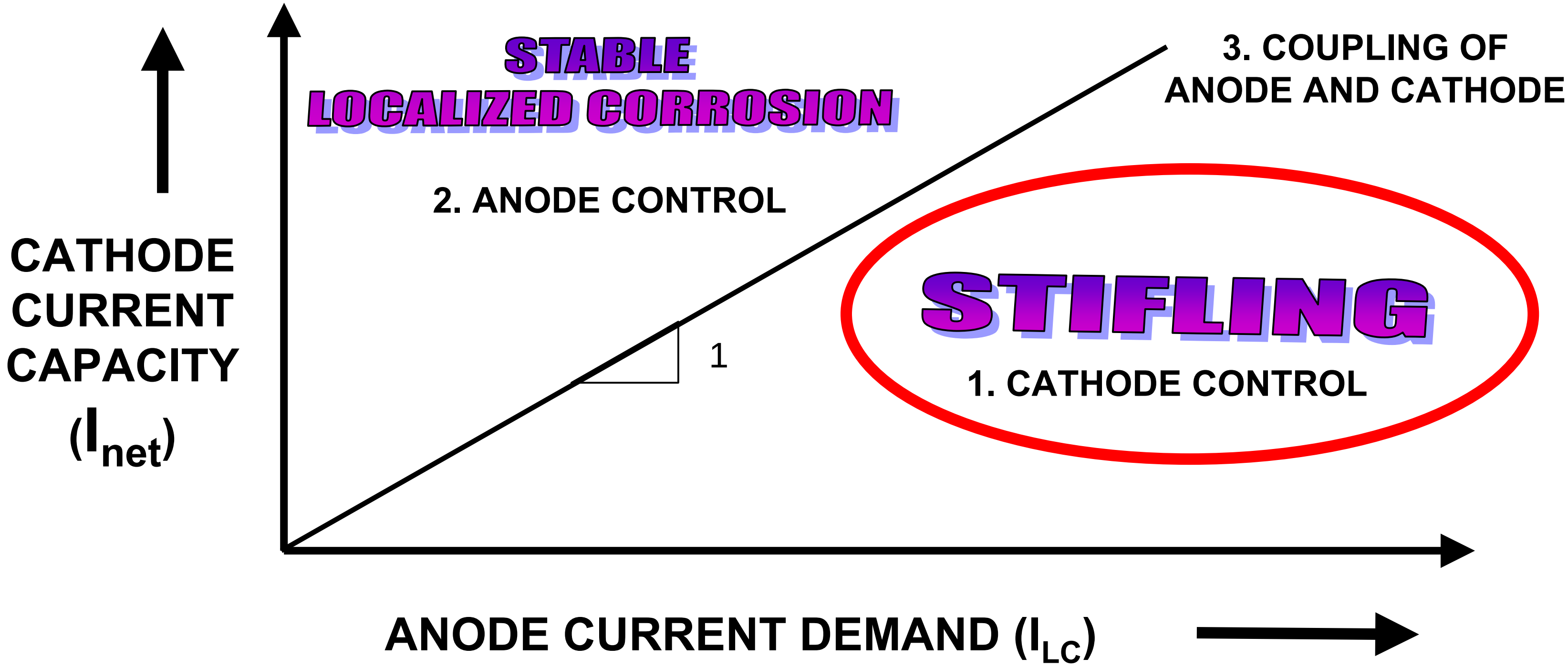
- **Incubation time before initiation of crevice corrosion**
- **Serrated current response indicates multiple initiation/arrest events**
- **Arrest (repassivation) of crevice corrosion observed**
  - **Also seen by Rebak et al. (LLNL), Dunn et al. (CNWRA)**

Cathode Control



I_{net}

I_{LC}



STABLE LOCALIZED CORROSION

3. COUPLING OF ANODE AND CATHODE

2. ANODE CONTROL

CATHODE CURRENT CAPACITY (I_{net})

1

STIFLING

1. CATHODE CONTROL

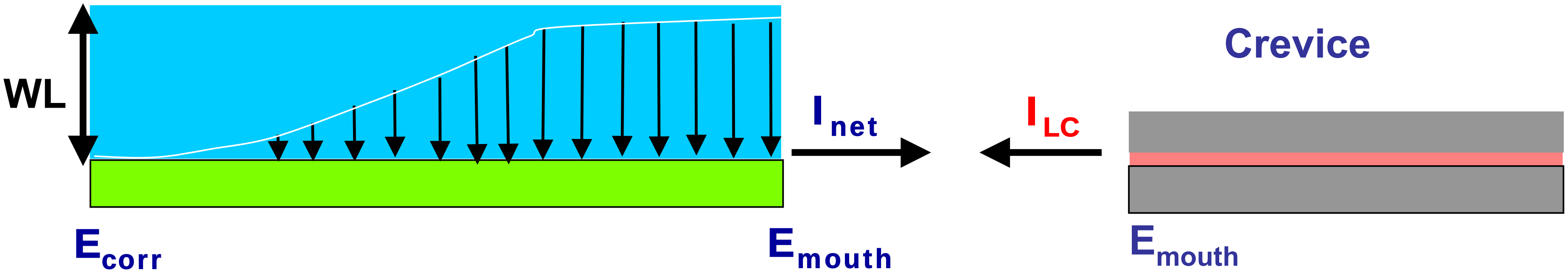
ANODE CURRENT DEMAND (I_{LC})

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

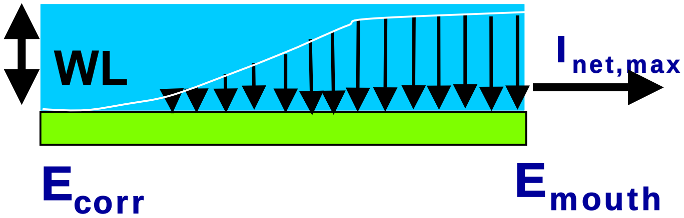


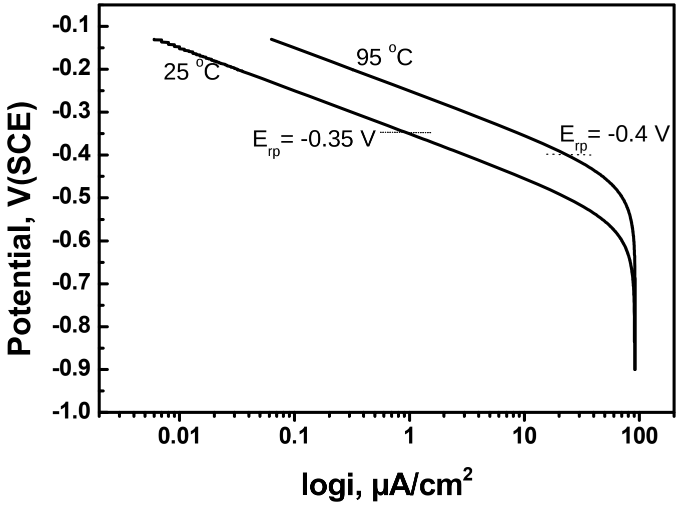
- **Fixed potential at E_{mouth}, other end at E_{corr}**
- **Current along length per polarization curve**

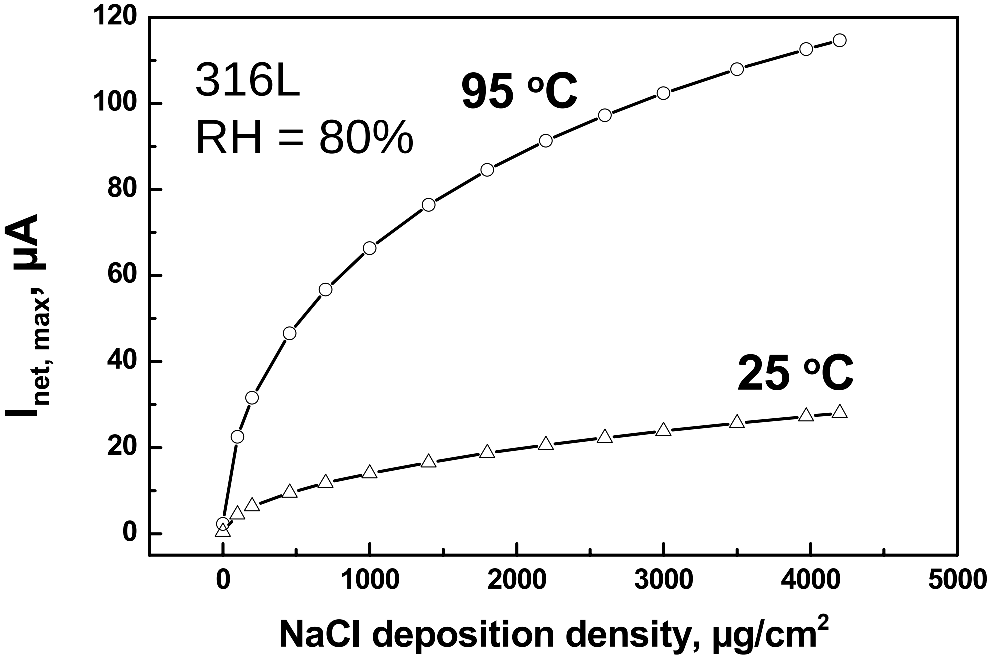
$$I_{net,max} = W \cdot \sqrt{2 \cdot \kappa \cdot WL \cdot \int_{E_{corr}}^{E_{mouth}} (i_c - i_p) \cdot dE}$$

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

Increasing Temperature Increases Cathode Capacity

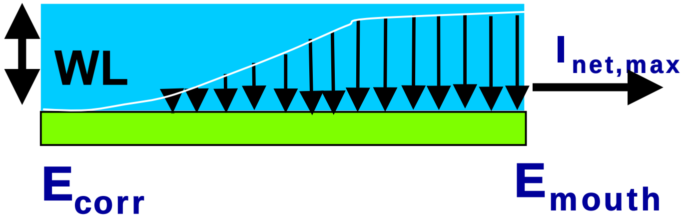


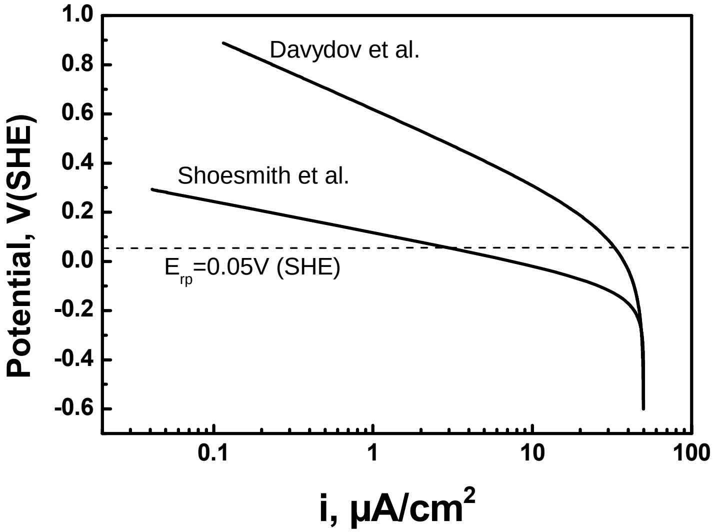


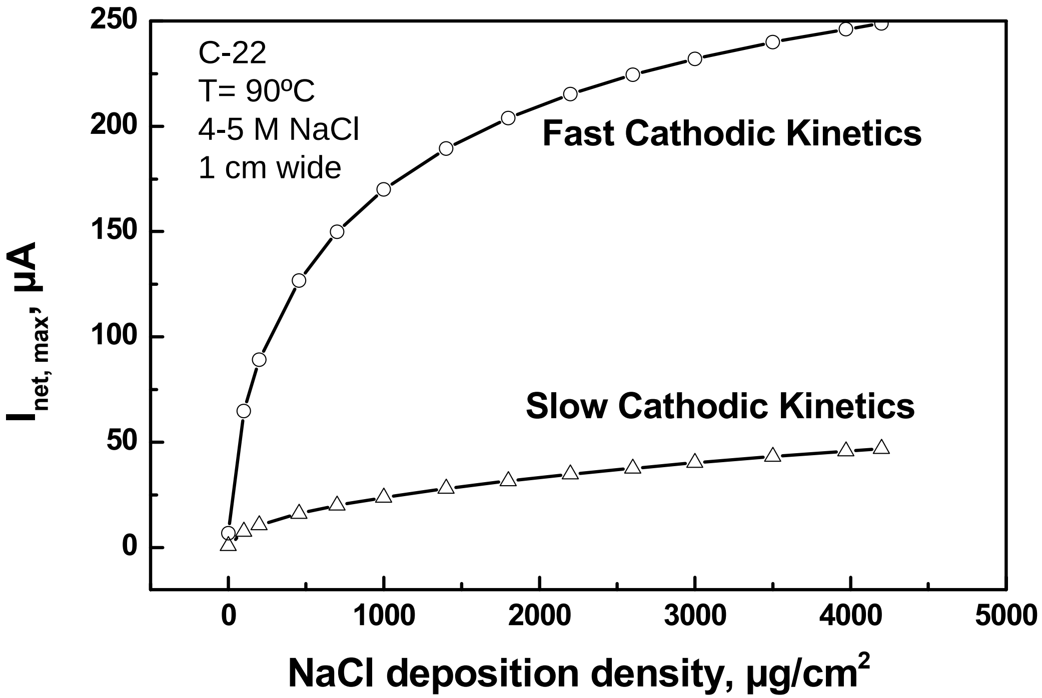


- **Factors controlling increased cathode capacity at higher T:**
  - **Increased conductivity**
  - **Faster electrode kinetics**
  - **Lowered E_{rp}**

Slower Cathodic Kinetics Decrease Cathode Capacity

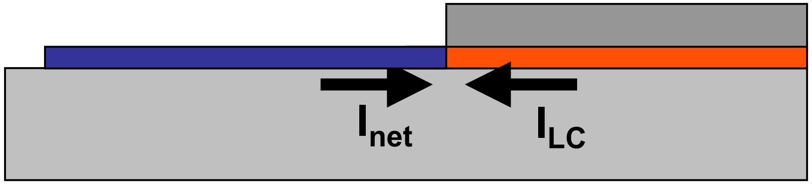


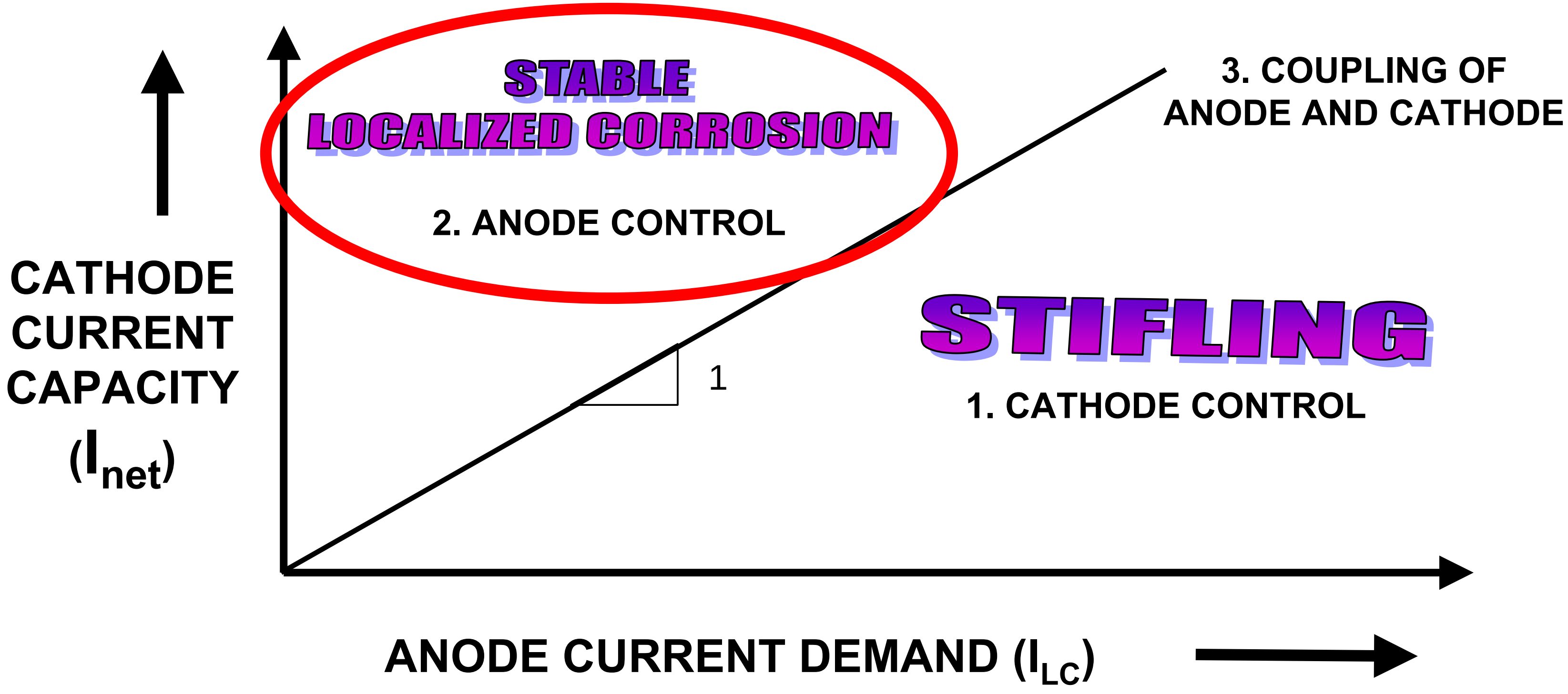




- **Factors that decrease cathode kinetics:**
  - **More protective oxide film inhibits electron transfer**
  - **Increased thin-layer pH**
  - **Diffusion limited current density**

Anode Control





STABLE

LOCALIZED CORROSION

2. ANODE CONTROL

3. COUPLING OF
ANODE AND CATHODE

STIFLING

1. CATHODE CONTROL

CATHODE
CURRENT
CAPACITY
(I_{net})

ANODE CURRENT DEMAND (I_{LC})

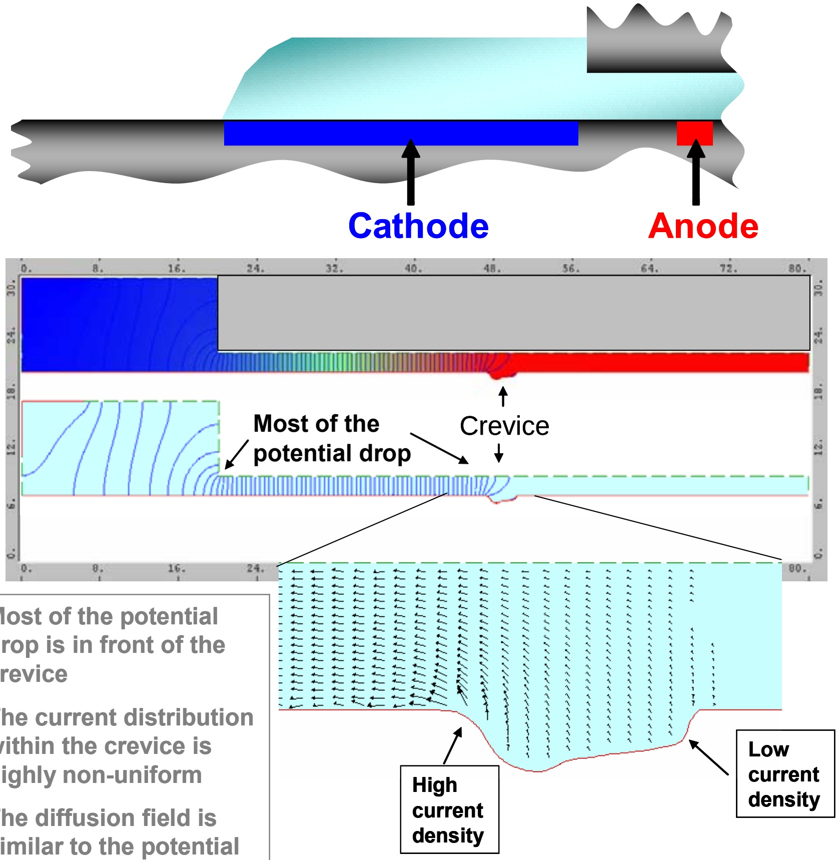
Anode Limitations Can Stifle Crevice Corrosion

- **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·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**

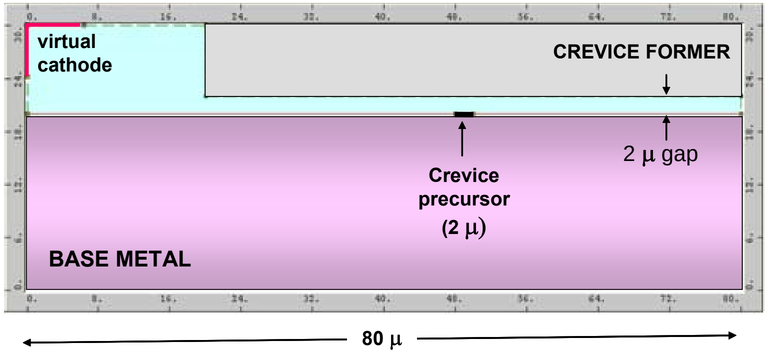
Dissolution rate within crevice is overwhelmed by diffusion out of crevice

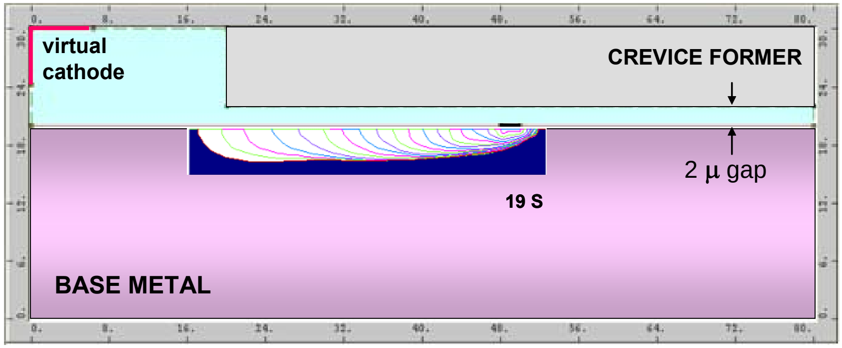
Repassivation by Dilution of Critical Crevice Chemistry

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

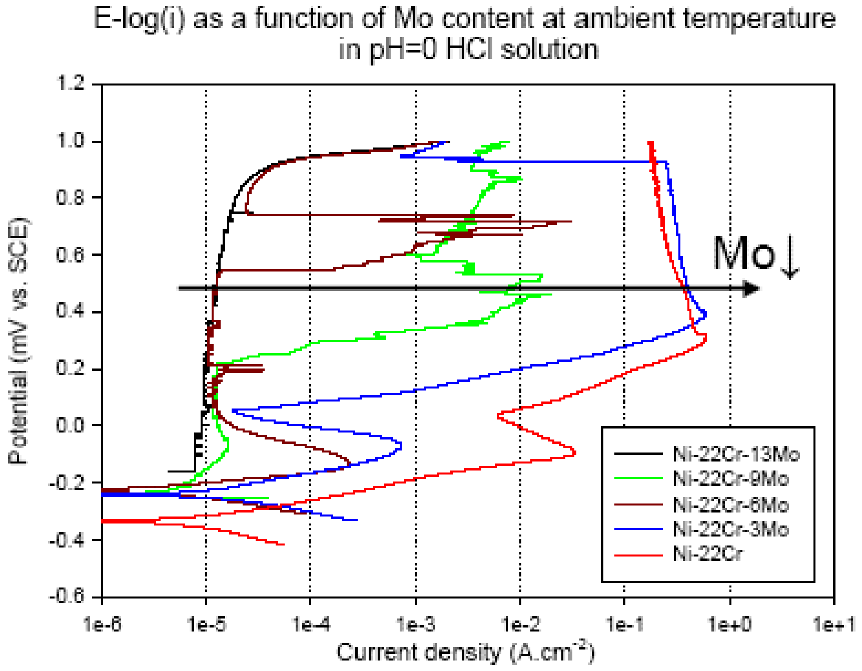


- Most of the potential drop is in front of the crevice
- The current distribution within the crevice is highly non-uniform
- The diffusion field is similar to the potential field





Slower Anodic Kinetics in CCS Makes Stability More Difficult to Maintain

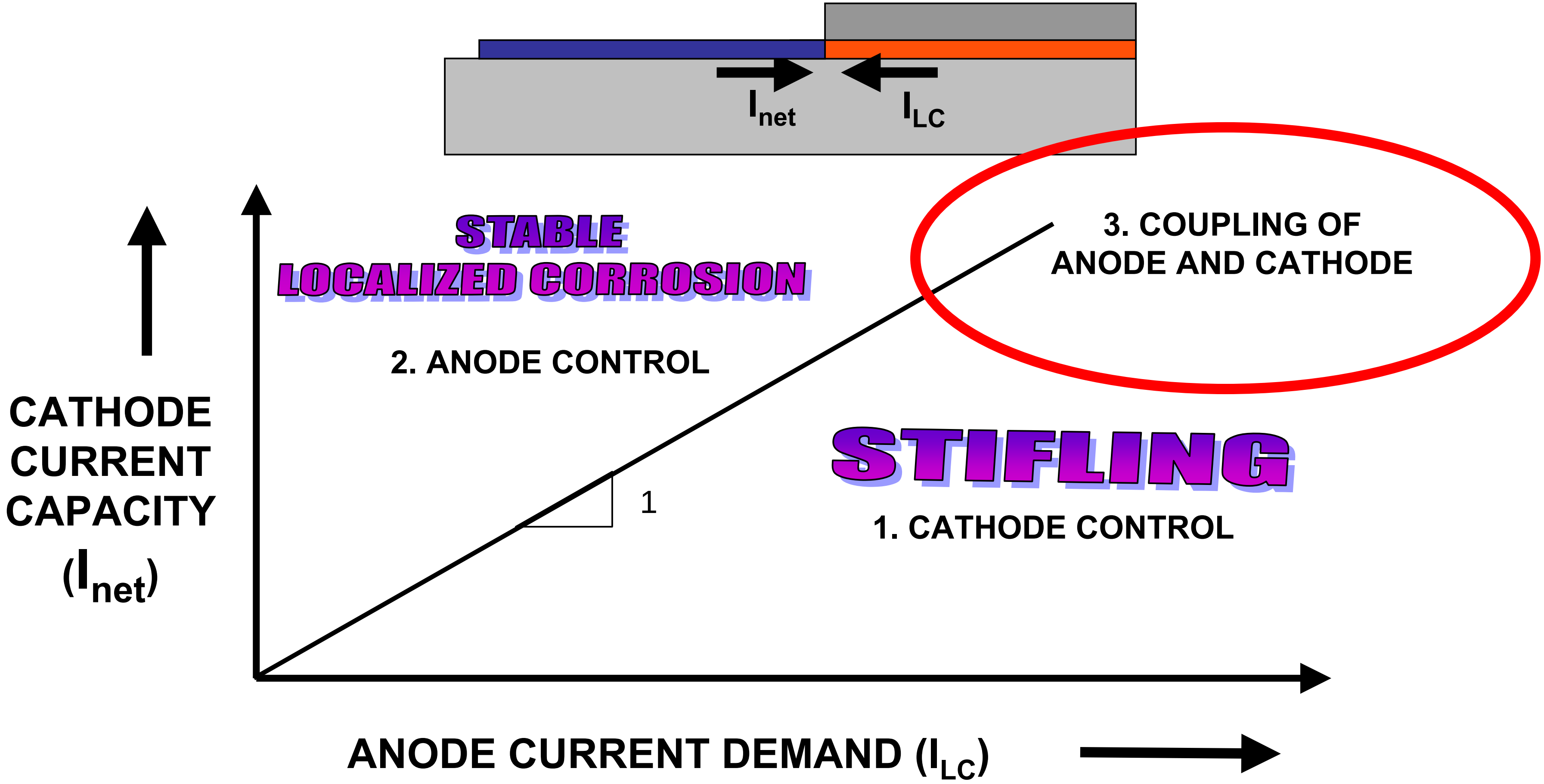

E-log(i) as a function of Mo content at ambient temperature in pH=0 HCl solution

Increasing Mo Slows Anodic Kinetics in Pit Solutions

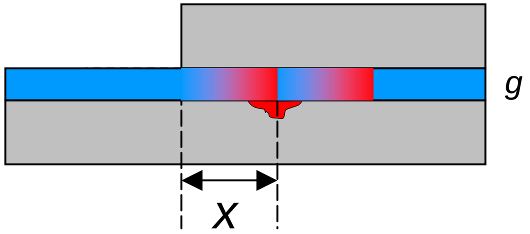
Experimental Values of CCS for Different Alloys

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

Coupled Anode and Cathode Processes

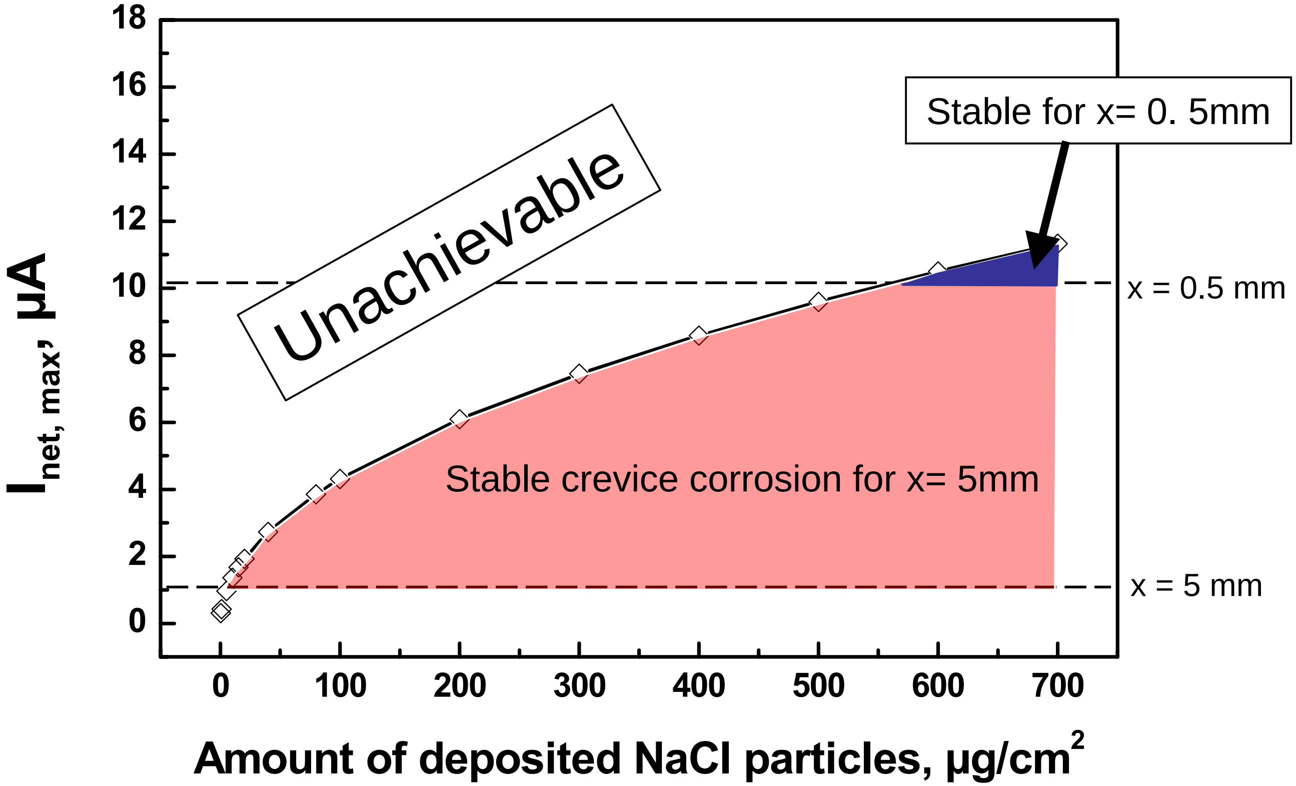


For Stable Crevice Corrosion, Cathode Must Supply Current Needed to Maintain Sufficiently High I_{LC}



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

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



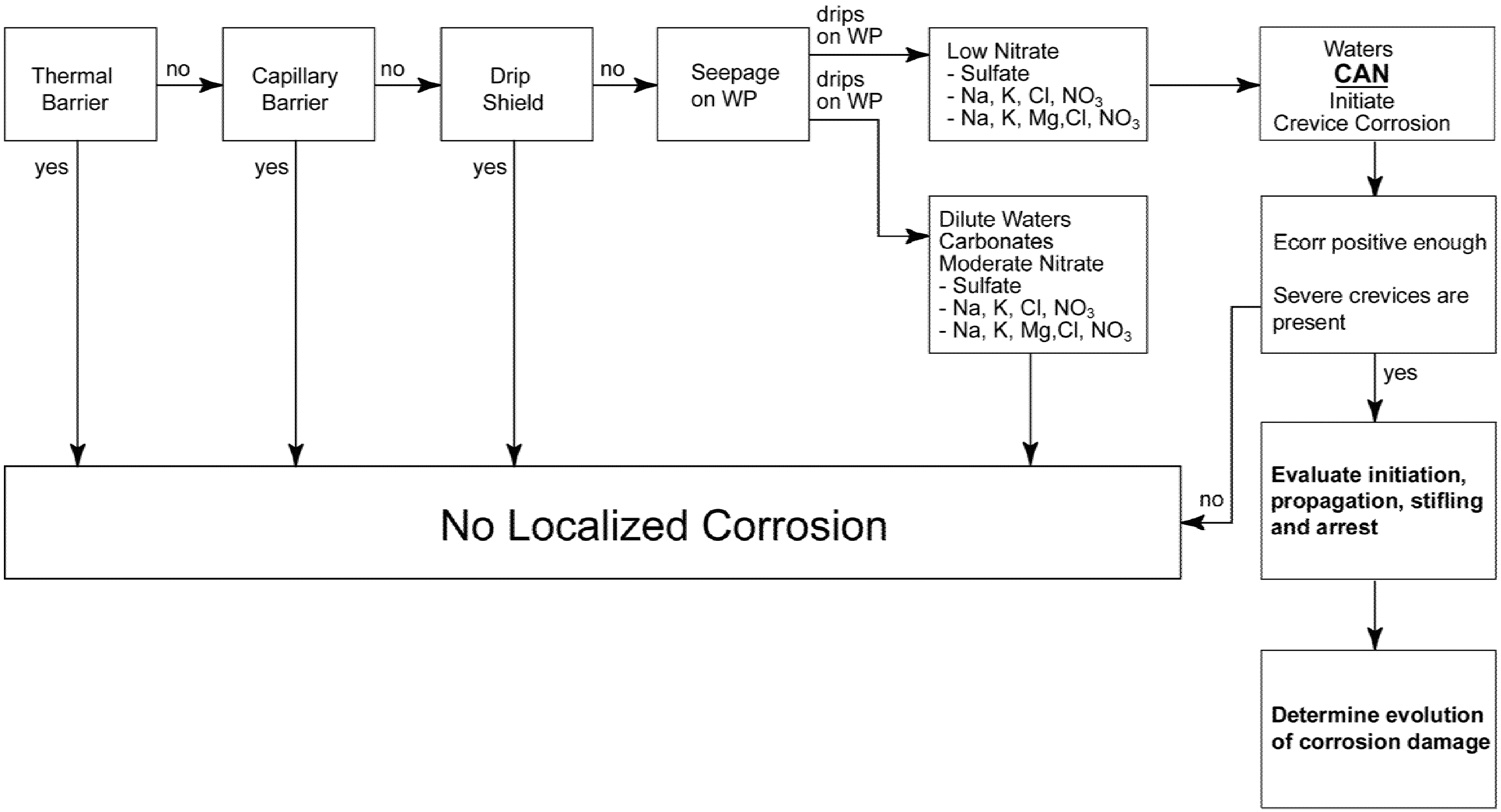
Summary

- 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

Capillary Barrier

no

Drip Shield

no

Seepage on WP

drips on WP

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

Waters **CAN** Initiate Crevice Corrosion

drips on WP

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

yes

yes

yes

Ecorr positive enough

Severe crevices are present

yes

no

No Localized Corrosion

Evaluate initiation, propagation, stifling and arrest

Determine evolution of corrosion damage

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

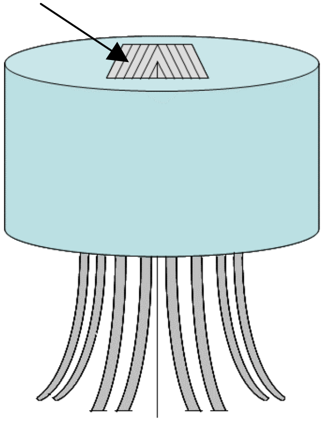
Columns (1) – (4) from Table 6.4-3, Column (5) Table 6.4-4, *Analysis of Dust Deliquescence for FEP Screening, ANL-EBS-MD-000074 Rev 01, August 2005,* Column (6) – (7) based on calculations using data from (1) – (5)

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.)

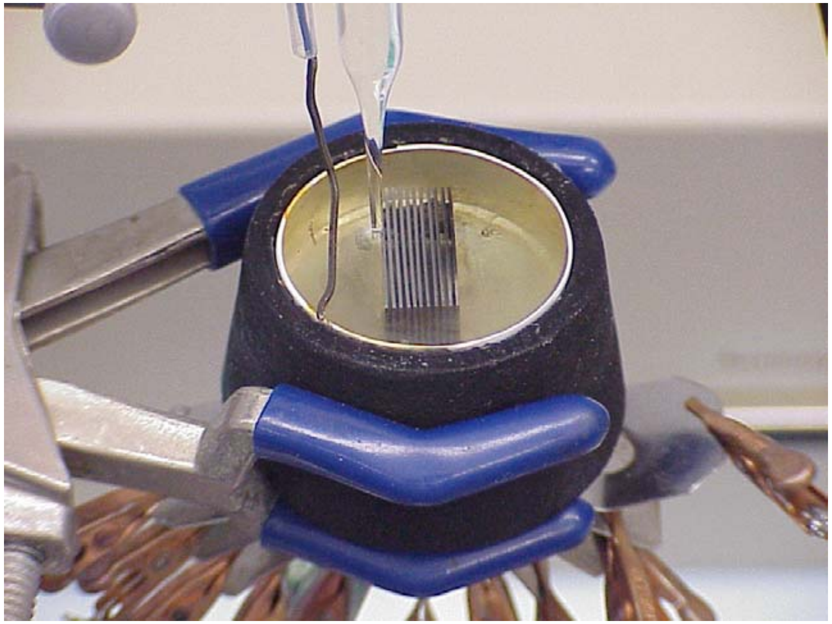
Multi-plate Assembly for Corrosion Cells in Particulate

- **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

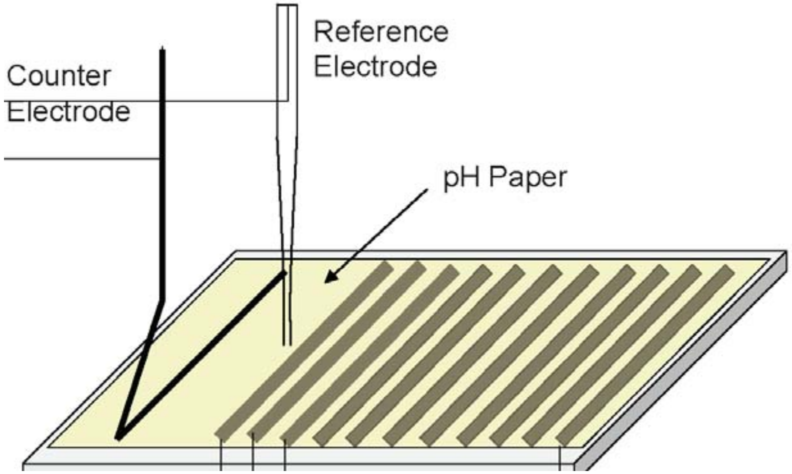


Anodic and Cathodic Processes

- **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

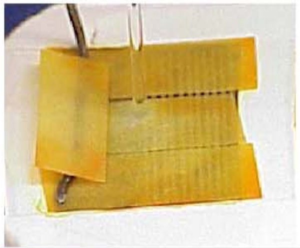
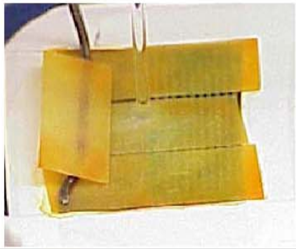
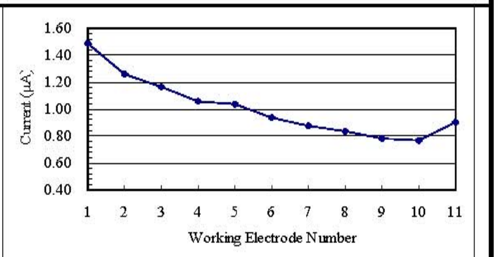
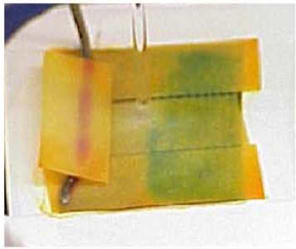
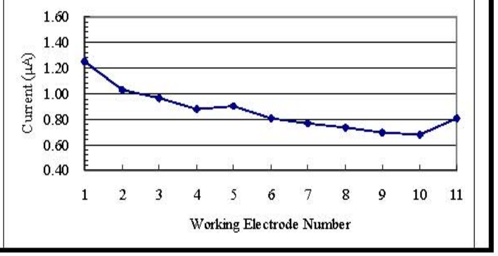
Experiment:

- 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**

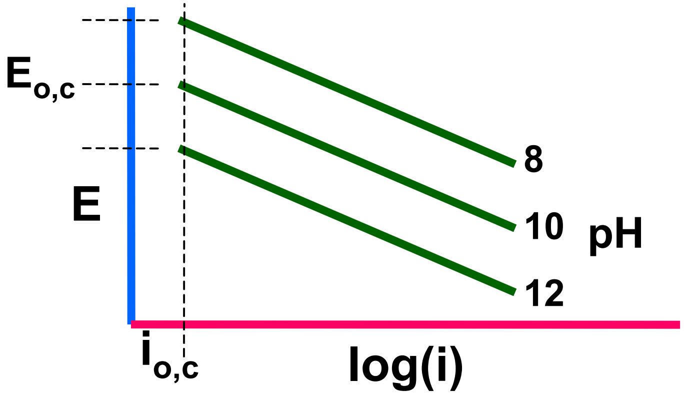
Time	Photograph	Current Distribution
0 s		
60 s		
180 s		

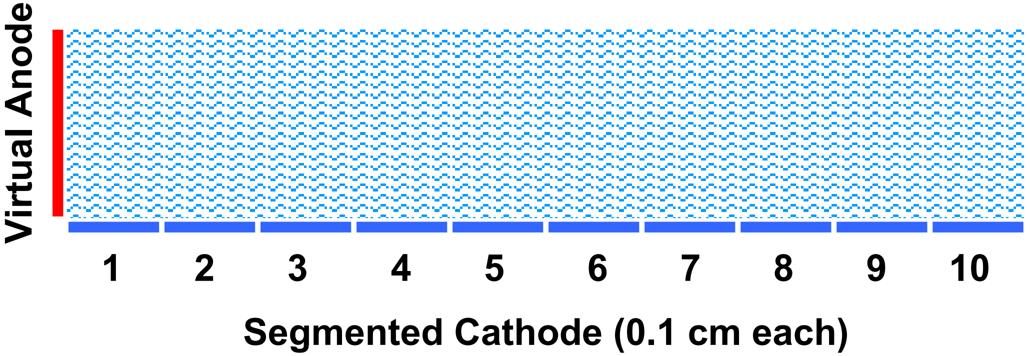
pH Effect due to Cathodic Reaction Chemistry

- 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 O_2 Reduction Kinetics: —

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





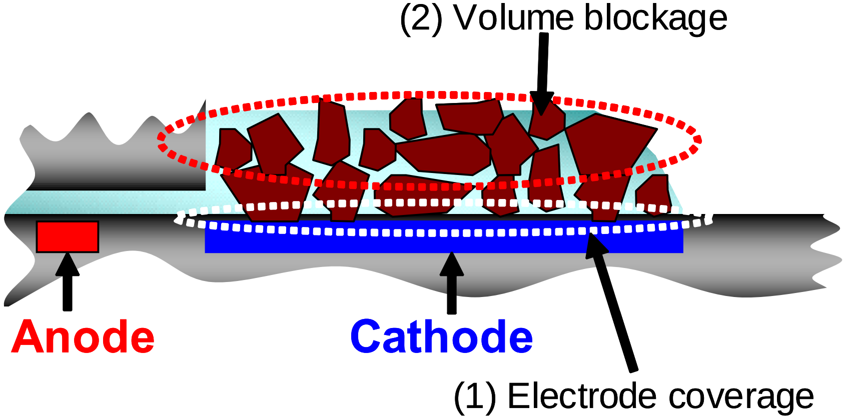
Segmented electrode geometry with varying reduction kinetics ($E_{o,c}$) based on pH is used

Calculate Maximum Current Capacity Given Measurable Parameters

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

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

Methodology for Effects of Particulate



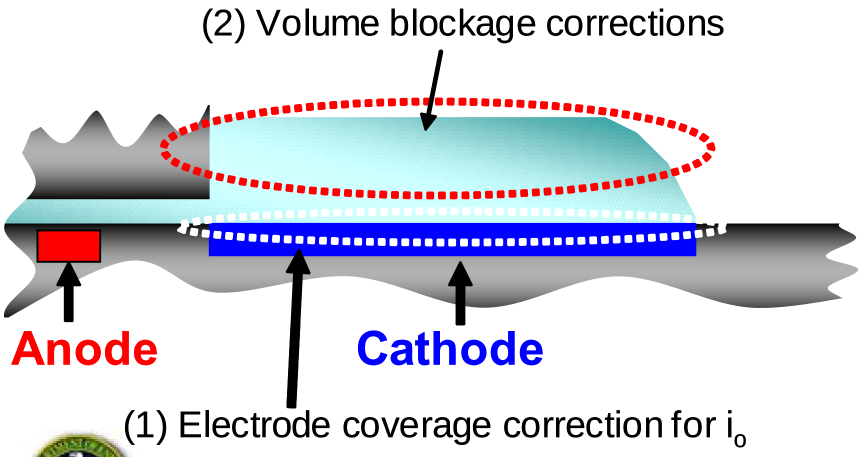
(2) Volume blockage

Anode

Cathode

(1) Electrode coverage

Equivalent Homogeneous Model



(2) Volume blockage corrections

Anode

Cathode

(1) Electrode coverage correction for i_o

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

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

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

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

Bruggeman's Equation

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

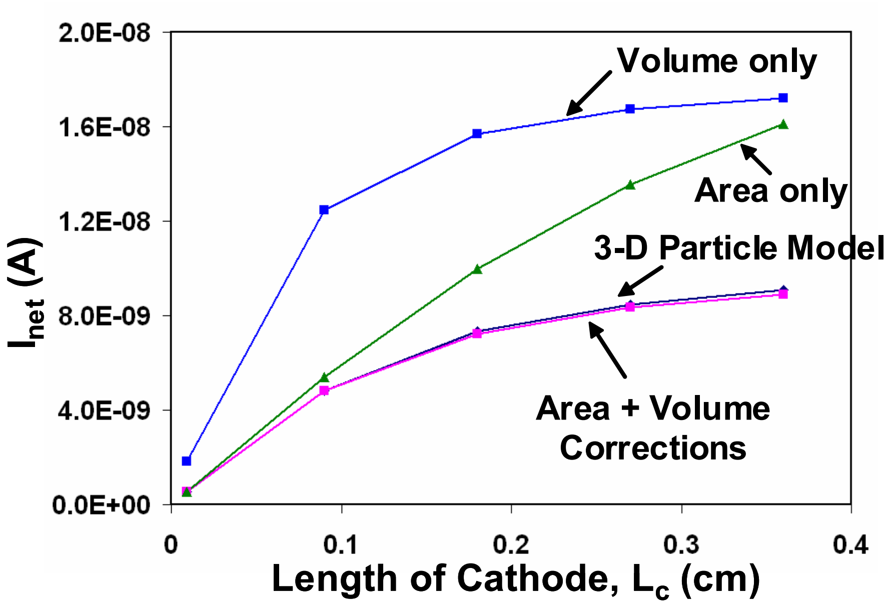
where

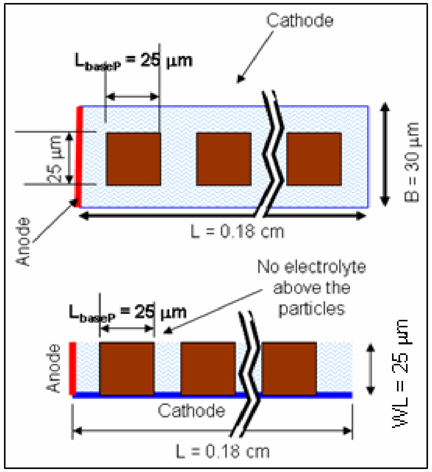
$$\phi_{sand} = \frac{\text{Vol(sand)}}{\text{Vol(sand + solution)}}$$

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

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

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%

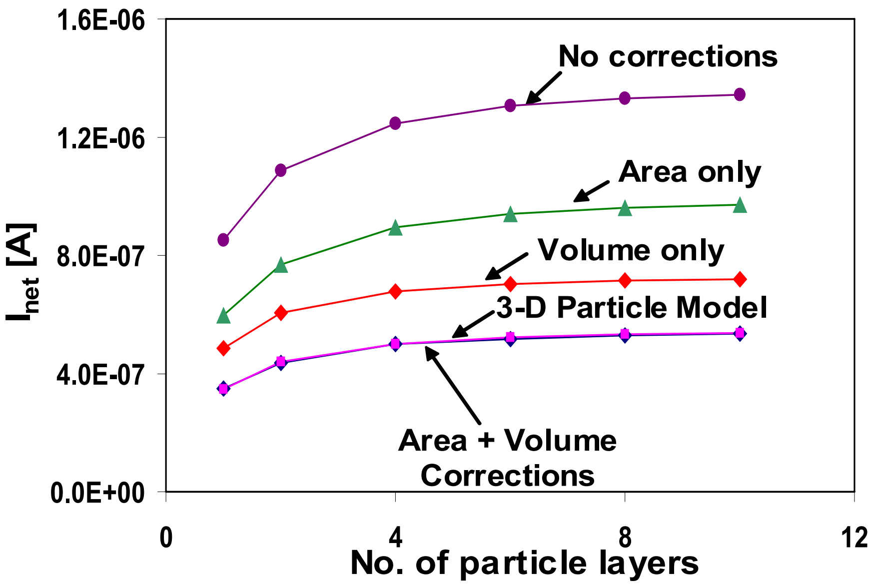
Area Coverage – 30%

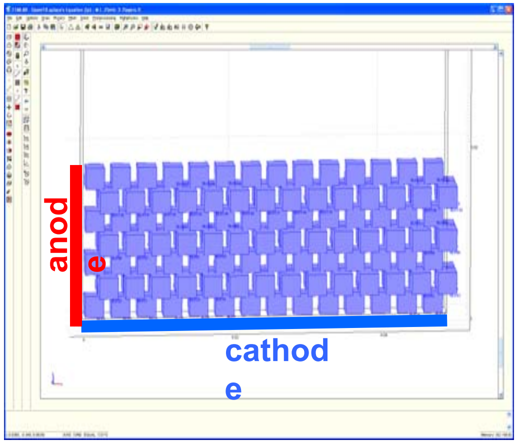
Area Correction: $i_o' = 0.306 \times 10^{-9}$ A/cm^2

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

$\beta_c = 0.1$ V/dec

$E_{rp} = -0.31$ V$_{NHE}$

$E_{o,c} = 0.19$ V$_{NHE}$

$\kappa = 12.1$ 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

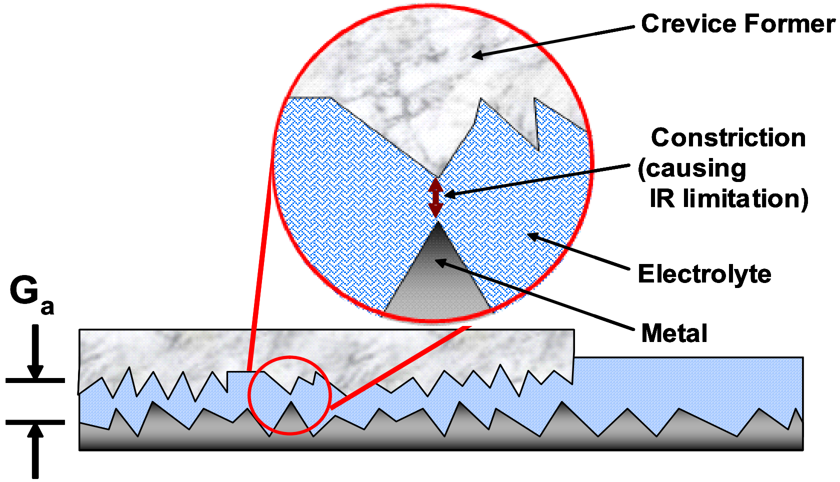
49 % area coverage

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

Volume Correction: $\kappa_{eff} = 4.148$ 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

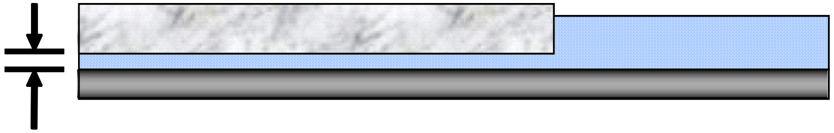


Metal - crevice former roughness can be of the order of nominal crevice gap (G_a).

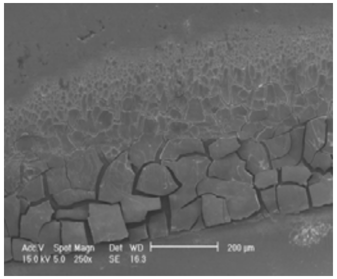
Constrictions along the rough surface create narrow passages to the current flow, causing high localized IR drop.

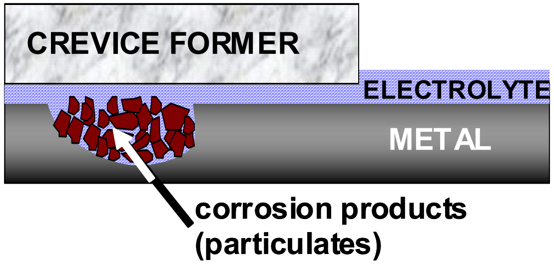
Solid corrosion products:

- **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’).

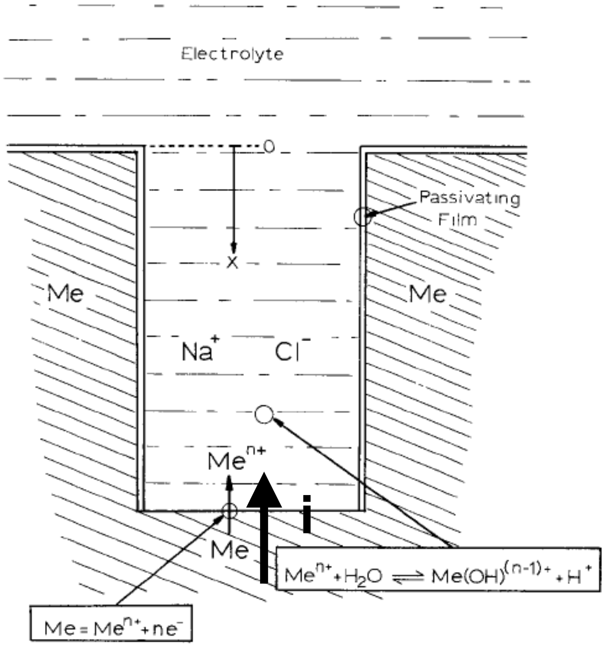
Anode Stability Considerations: Maintenance of Critical Chemistry

- **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