



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



# Perspectives on Localized Corrosion in Thin Layers of Particulate

**Presented to:**

**Scientific Basis for Nuclear Waste Management XXX  
Materials Research Society Symposium**

**Presented by:**

**Joe H. Payer, Case Western Reserve University  
Robert G. Kelly, University of Virginia**

**November 29, 2006**

**Boston, Massachusetts**

# Acknowledgement and Disclaimer

- **Support of the Science and Technology Program of the Office of the Chief Scientist (OCS), Office of Civilian Radioactive Waste Management (OCRWM), U.S. Department of Energy (DOE) 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/OCS.**

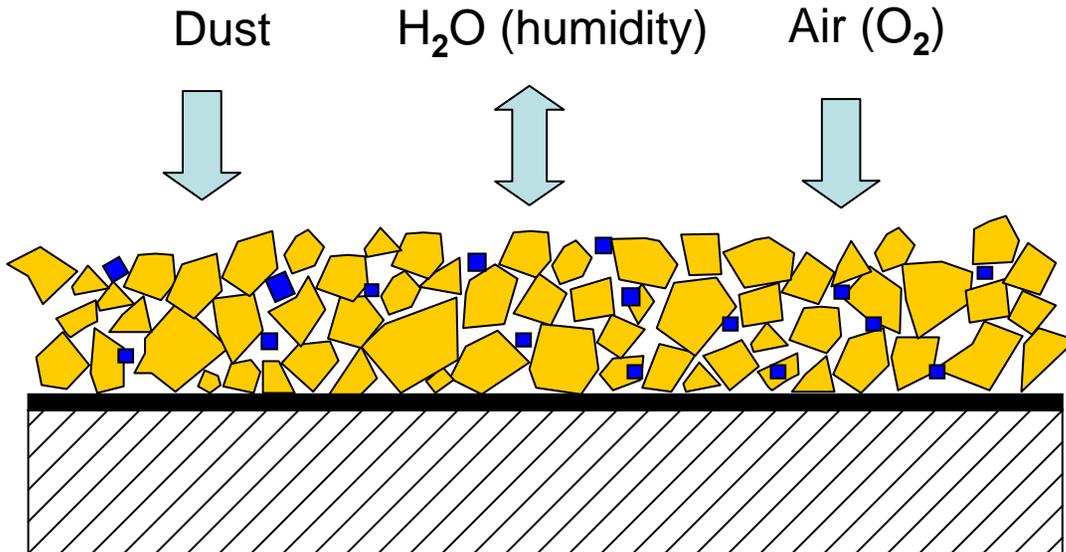


# Outline of Presentation

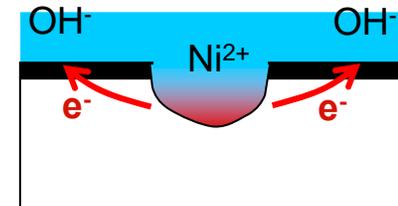
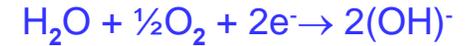
- **Localized corrosion requirements**
- **Particulate layer properties to support localized corrosion**
  - Particulate layer as an electrolyte
  - Particulate layer as a crevice former
- **Conditions for stability of localized corrosion**
  - Cathode processes
  - Anode processes
  - Coupled anode and cathode processes



# Corrosion in Thin Layers of Particulate



Electrochemical  
Corrosion Cell under  
Particulate Layer



 Insoluble minerals       Soluble salts

- 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:  $\text{Ni} \rightarrow \text{Ni}^{2+} + 2\text{e}^-$
- Cathode:  $\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + 2\text{e}^- \rightarrow 2(\text{OH})^-$

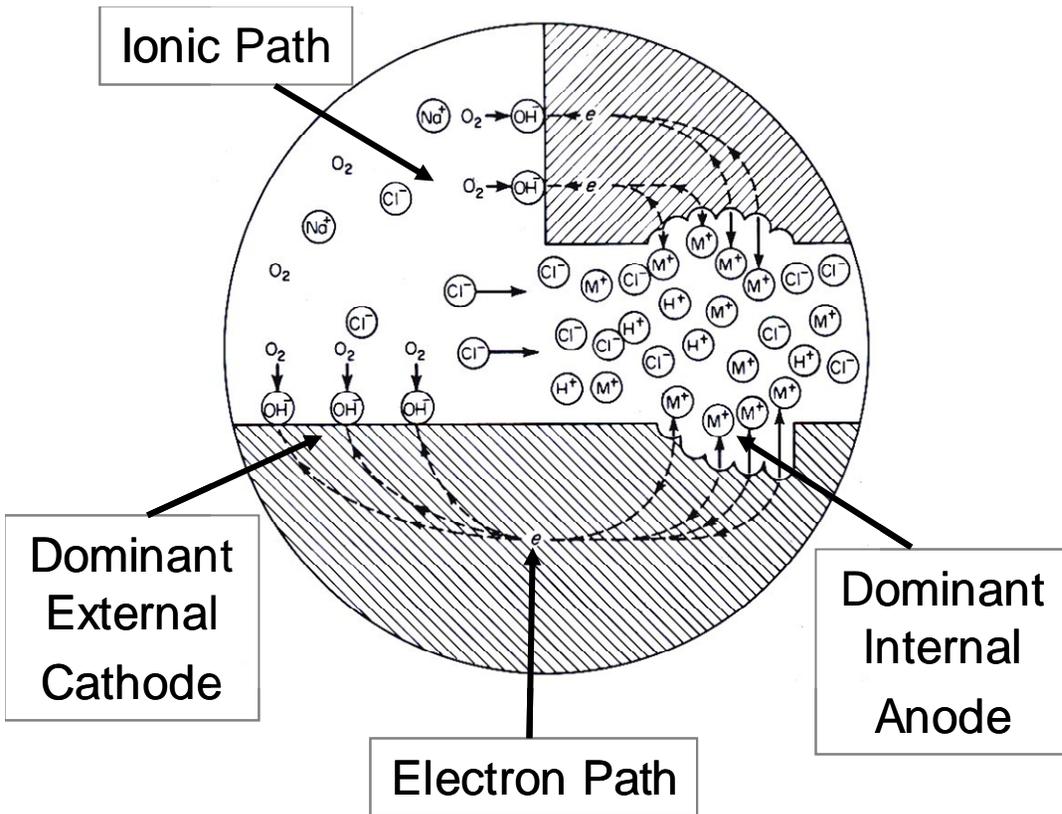


# A Framework for Analysis of Localized Corrosion

- **A decision-tree analysis 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?**
- **Application of decision-tree analysis**
  - **Relevant conditions over time and within relevant time periods**
  - **Deliquescent salt conditions**
  - **Seepage and drips conditions**



# Requirements for Localized Corrosion



## Initiation

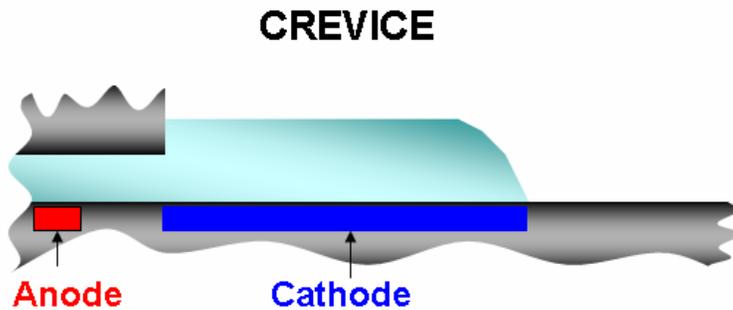
- Aggressive environment
- Tight, impermeable crevice
- $E_{corr} > E_{repas}$
- Separated and coupled anode and cathode
- Develop critical crevice chemistry

## Propagation

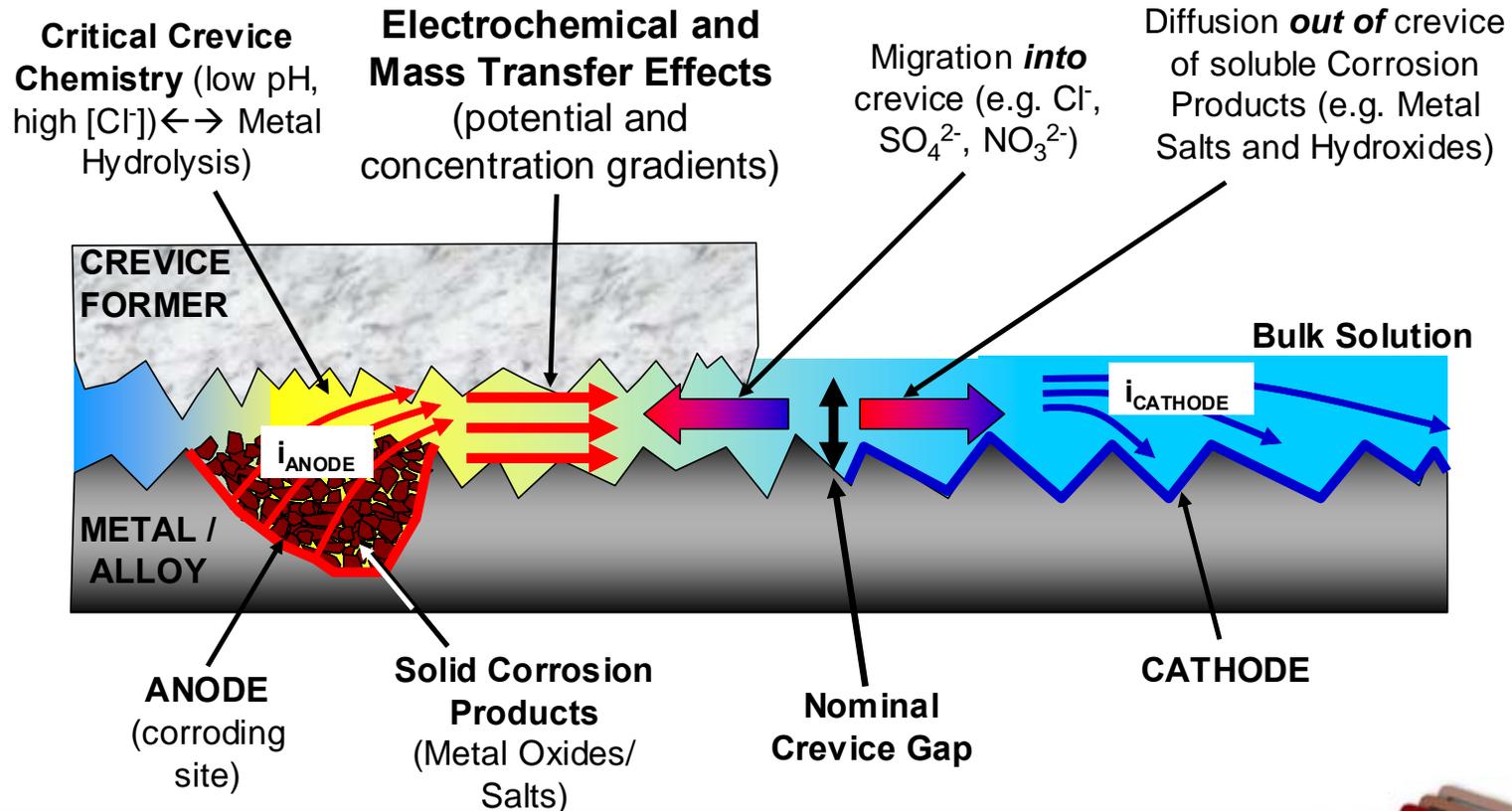
- Maintain critical crevice chemistry
- Maintain sufficient cathodic current capacity
- Maintain separate and coupled anode and cathode
- Maintain tight, impermeable crevice



# Crevice Corrosion

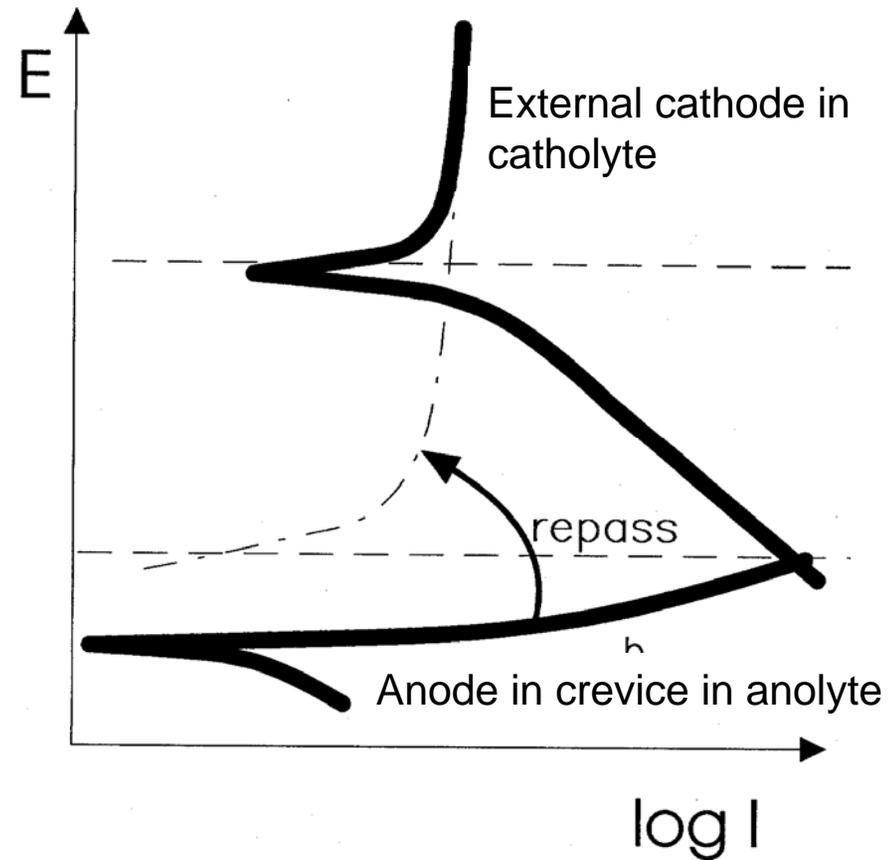
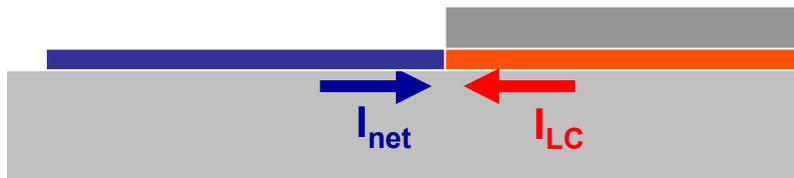


- Crevice corrosion may occur in restricted regions due to **transport limitations**, followed by a build-up of a **highly corrosive chemistry**, capable of dissolving the metal
- The dissolution rate is potential-dependent



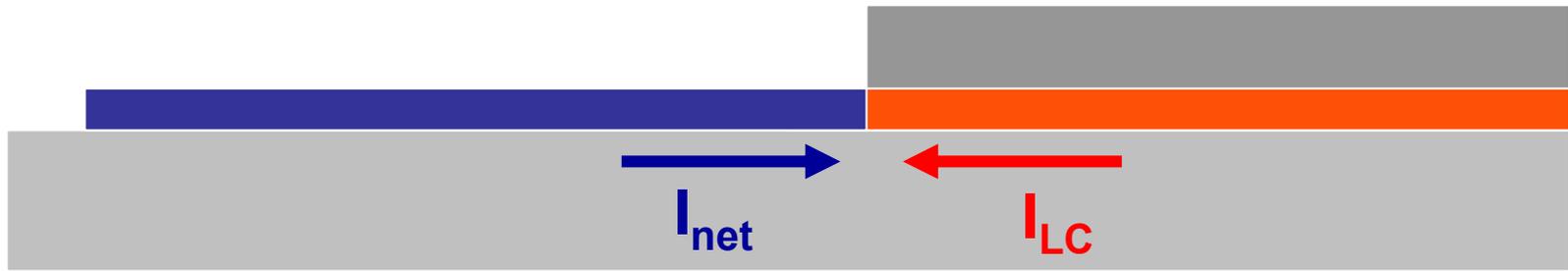
# Crevice Corrosion Propagation as a Galvanic Couple

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



# Stability of Localized Corrosion

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

Crevice coupled to external cathode in thin layer of electrolyte more likely limited by cathode current capacity



# Analysis of Crevice Corrosion Stability vs. Stifling

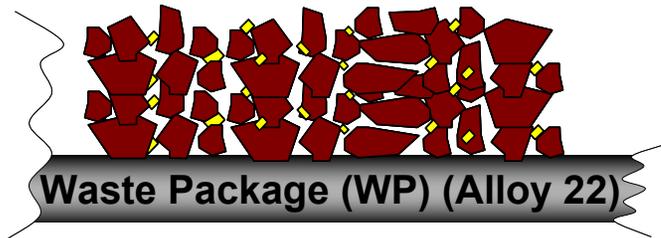
- Analysis of post-initiation stage
- Categories of processes to control corrosion
  - Electrolyte layer: resistance limits current between anode and cathode
  - Cathode current capacity cannot meet anode demand
  - Anode current requirement for stability not met
  - Anode/cathode coupling incompatible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



# Particulate layer as an electrolyte and crevice former to support Localized Corrosion



# Scenarios for Distribution of Moisture in Particulate Layer



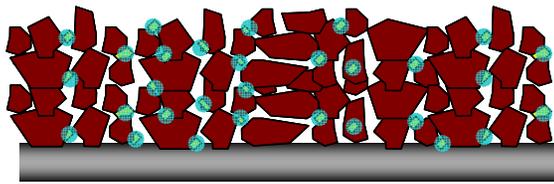
Dry particulate-No moisture

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

Particulate layer: thickness, porosity, density

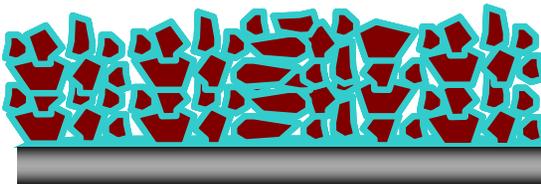
Temperature and Relative Humidity (activity of water)

Solution properties



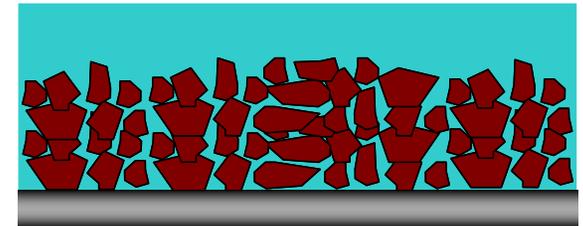
## Droplets of moisture

- 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



# Particulate Effects on Bulk Solution Conductivity

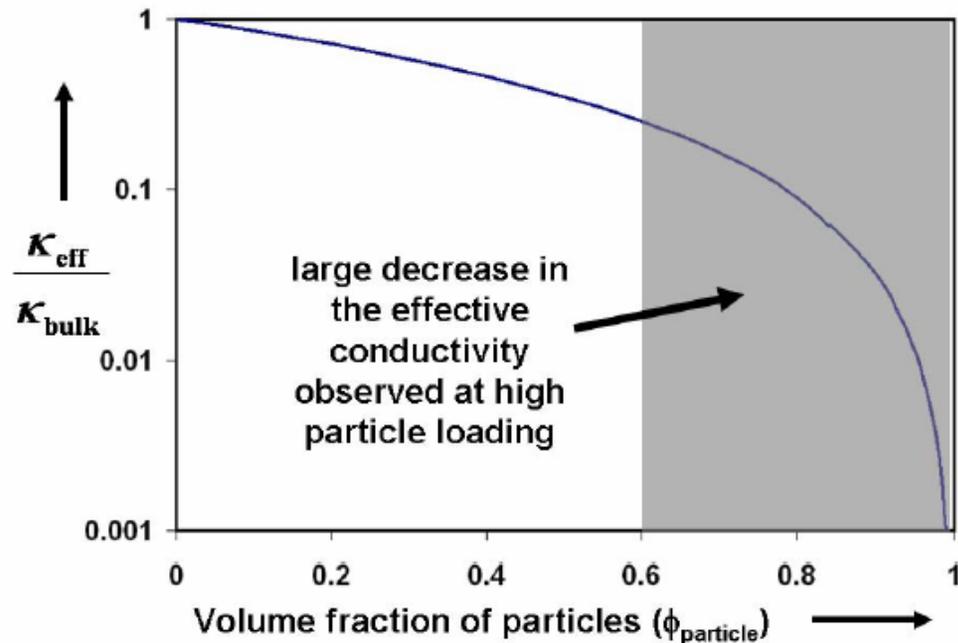
- **Decreased conductivity in the particulate layer**
  - Higher particle volume fraction
  - Lower solution volume fraction in pores (unsaturated)

*Bruggeman's Equation*

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

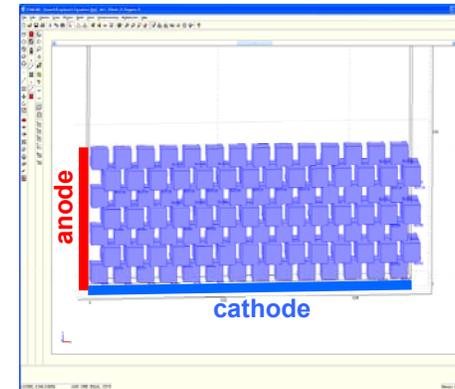
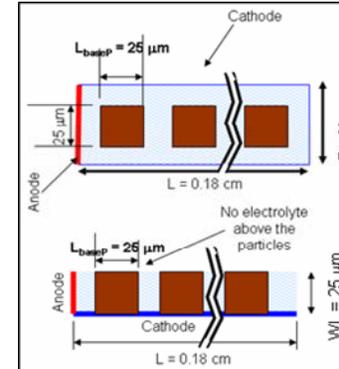
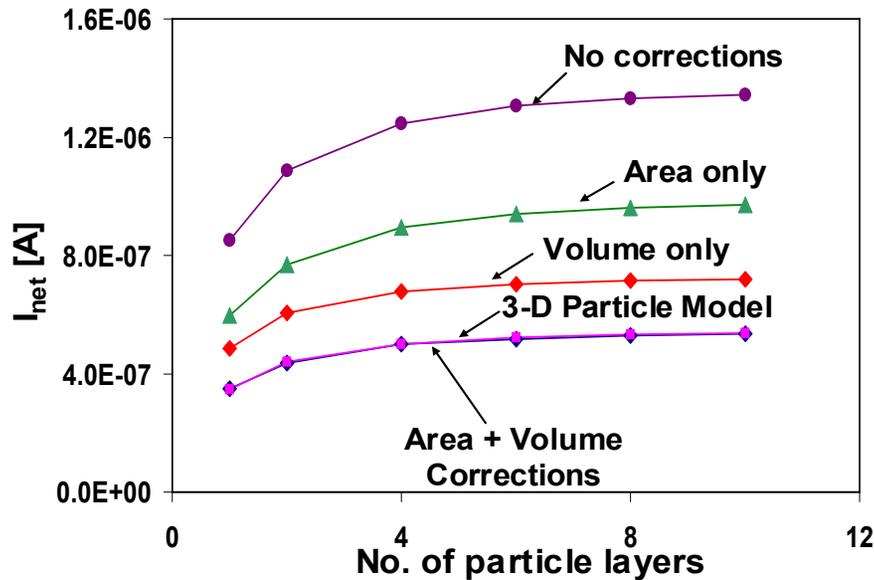
where

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



# Analysis of the Effects of Particulate in Bulk Electrolyte on Metal Surface

## 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

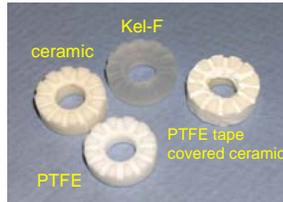
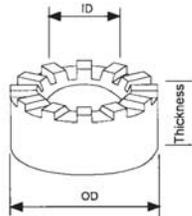
## Specimen assembly

### 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<sup>2</sup>/foot

- Determine effect of the crevice former under aggressive laboratory conditions
  - 4M NaCl at 100C
  - Applied potential (no cathodic limitations)
- Ceramic/Polytetrafluoroethylene (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



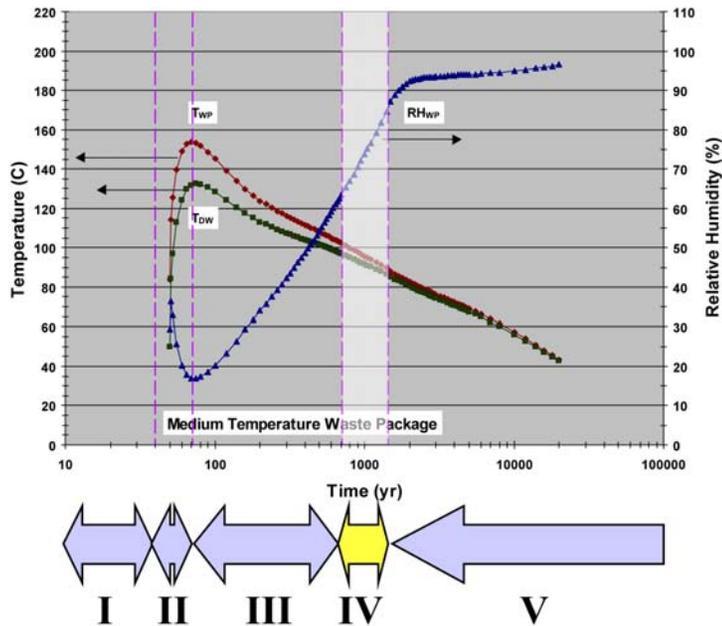
# Particulate Layer as an Electrolyte and Crevice Former for Localized Corrosion

- **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
- **Conclusions: For high-temperature deliquescent salts in deposited dust layer**
  - Too little moisture
  - Unlikely to fulfill the requirements for localized corrosion



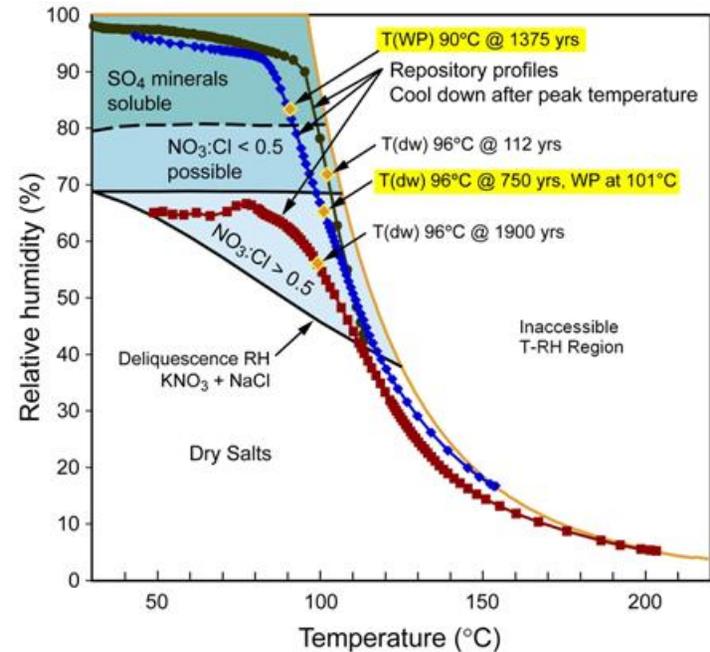
# Example of Waste Package Temperature & Relative Humidity Control of Solution Composition

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



Drift wall 96°C at 750 years;  
Waste Package at 101°C  
Relative Humidity 65%

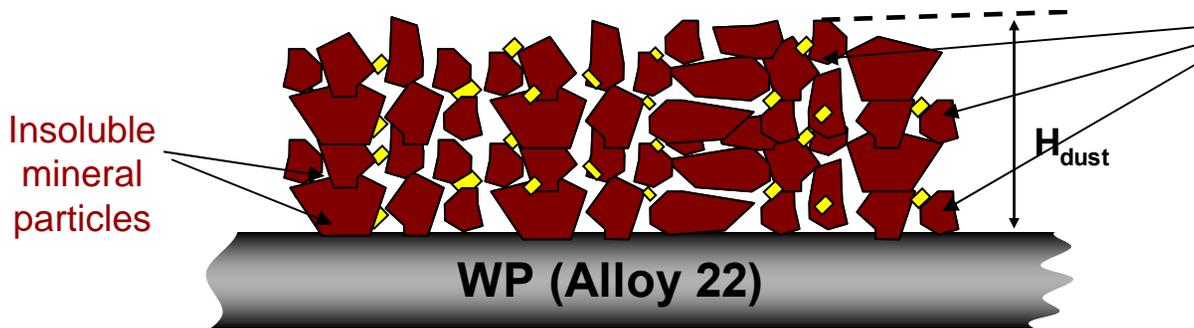
Critical Corrosion Temp 90°C at year 1375;  
Relative Humidity 85%



- 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 Waste Packages

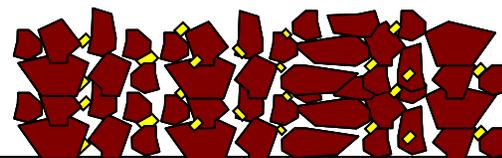
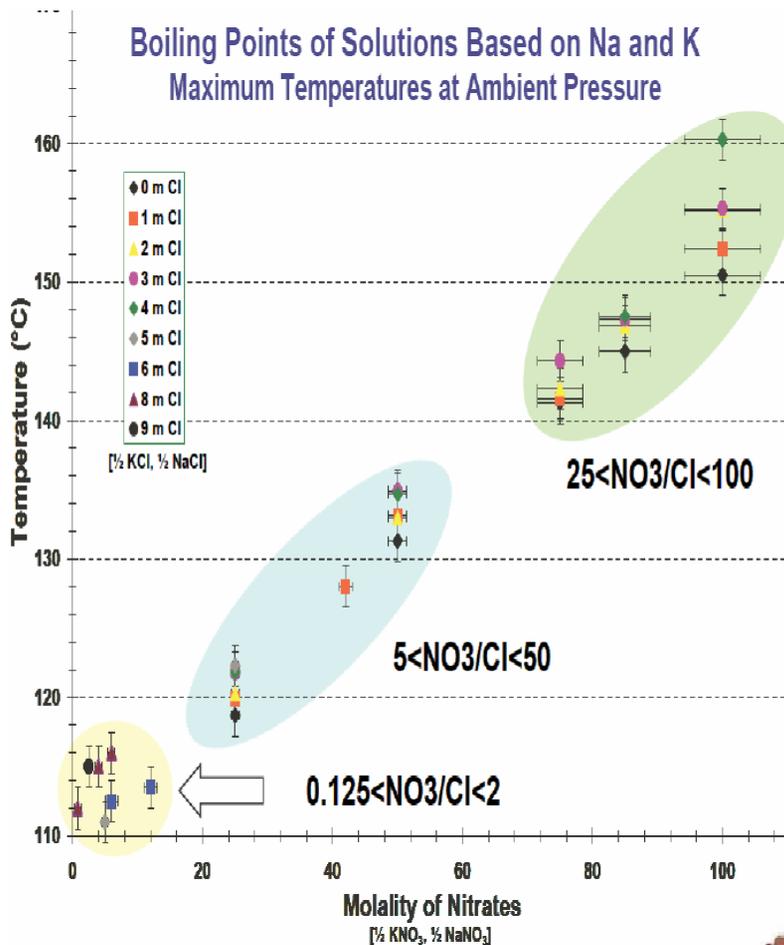


Soluble salt particles (extent of deliquescence is a function of proximity of different salts, temperature and relative humidity)

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	$\delta_{dust}$	180 - 10	150	$\mu m$
Size of particle	$\delta_{particle}$	30 - 10	30	$\mu m$
Mass of dust deposit	$m_{dust}$	18 - 26	18	$mg/cm^2$
Effective conductivity of layer	$\kappa_{eff}$	$(\%phi/100)^{3/2} \times \kappa_{bulk}$	$0.465 \times \kappa_{bulk}$	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 $\mu m$ particles)			~10:1	



# Analysis of High Temperature Salt Deliquescence



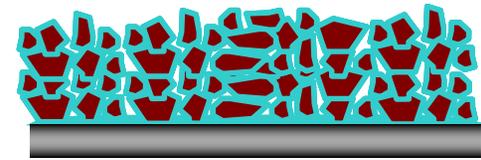
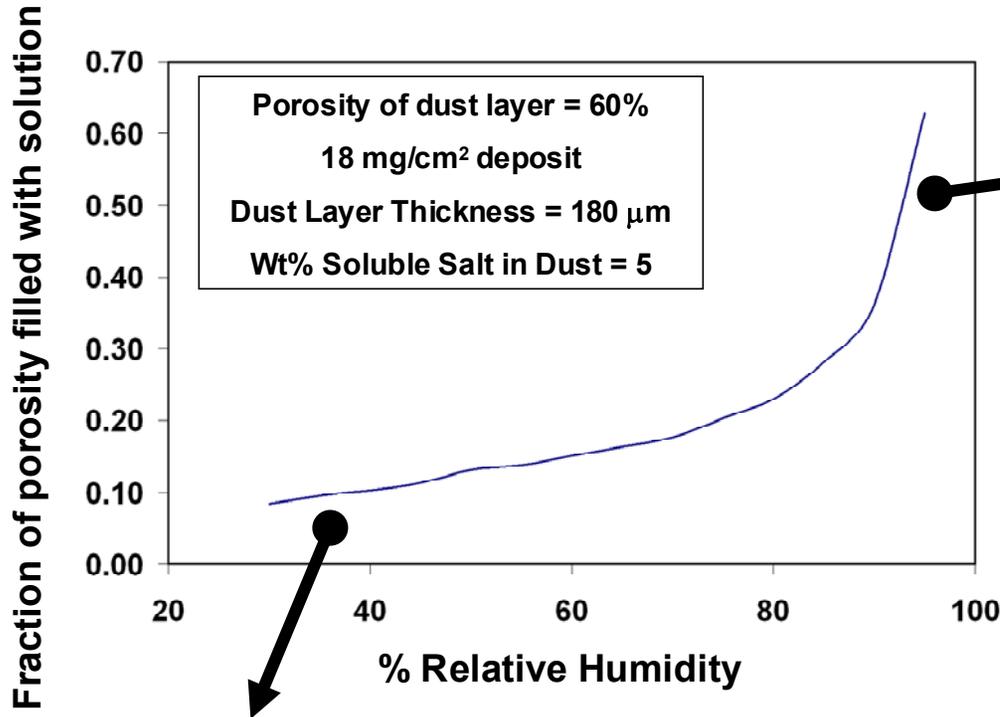
WP (Alloy 22)

## Droplets of Moisture

- 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



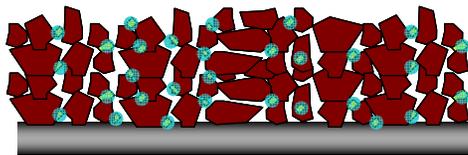
# Variation of the Solution Volume with % RH in the Deposited Dust Layer



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 humidities 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*



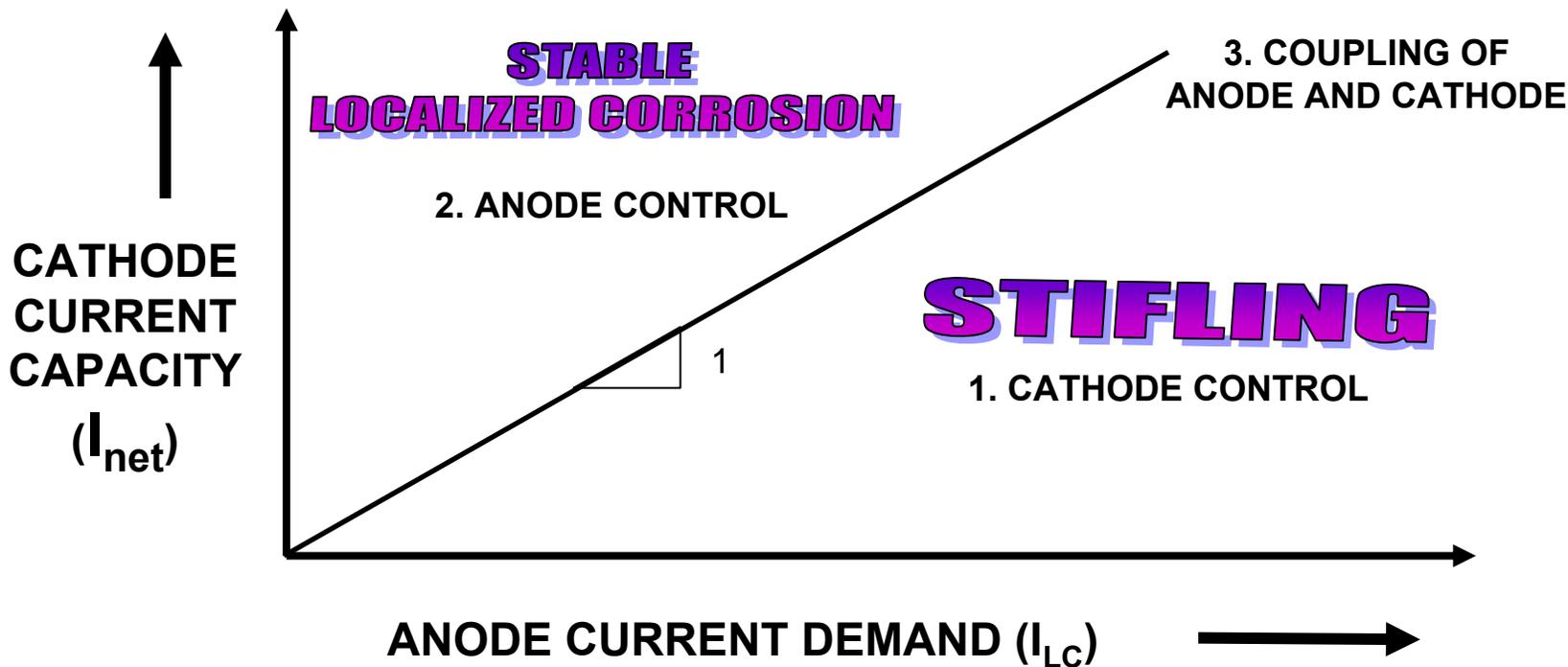
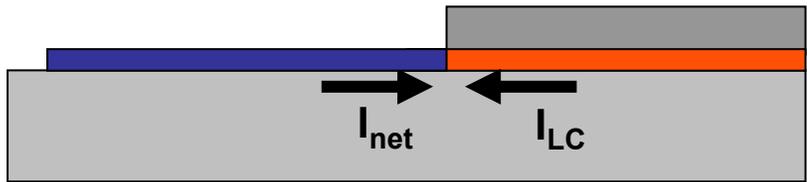
# Stability of Localized Corrosion

- Cathode control
- Anode control
- Coupled Anode/Cathode Effects

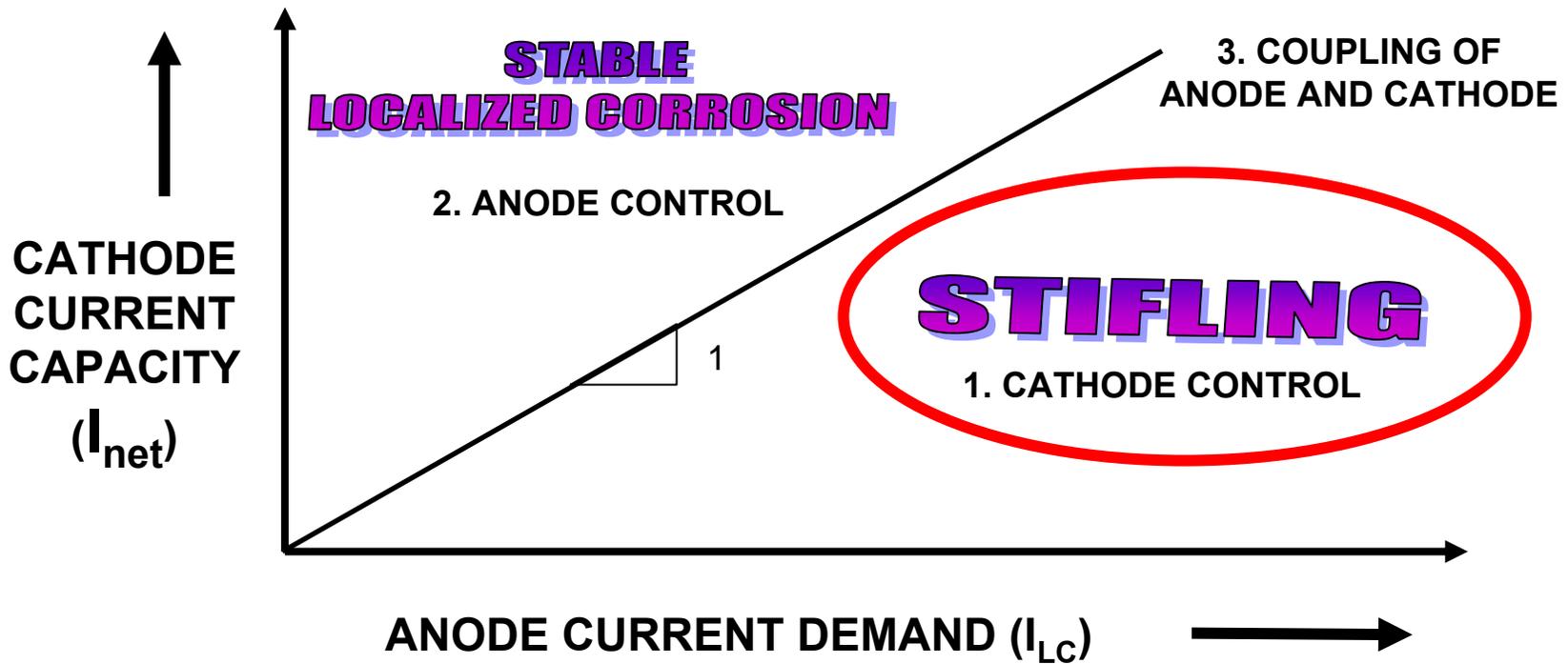
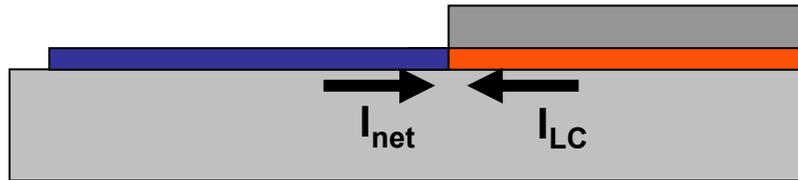


# Factors Influencing Localized Corrosion Stability

Cathode Current Capacity  $\geq$  Anode Current Demand



# Cathode Control



# Cathode Limitations Can Stifle Crevice Corrosion

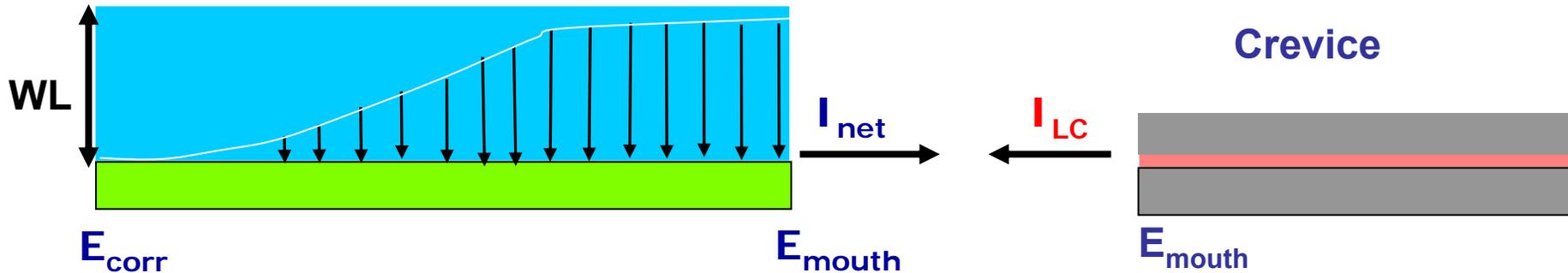
- Corrosion behavior in moist particulate can differ from full immersion due to cathode limitations:
  - Limited cathodic current affects intensity and location of anodic reaction
  - Limited size of cathode affects minimum internal pH sustainable



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



# Maximum Total Current from Wetted Surface Can be Estimated



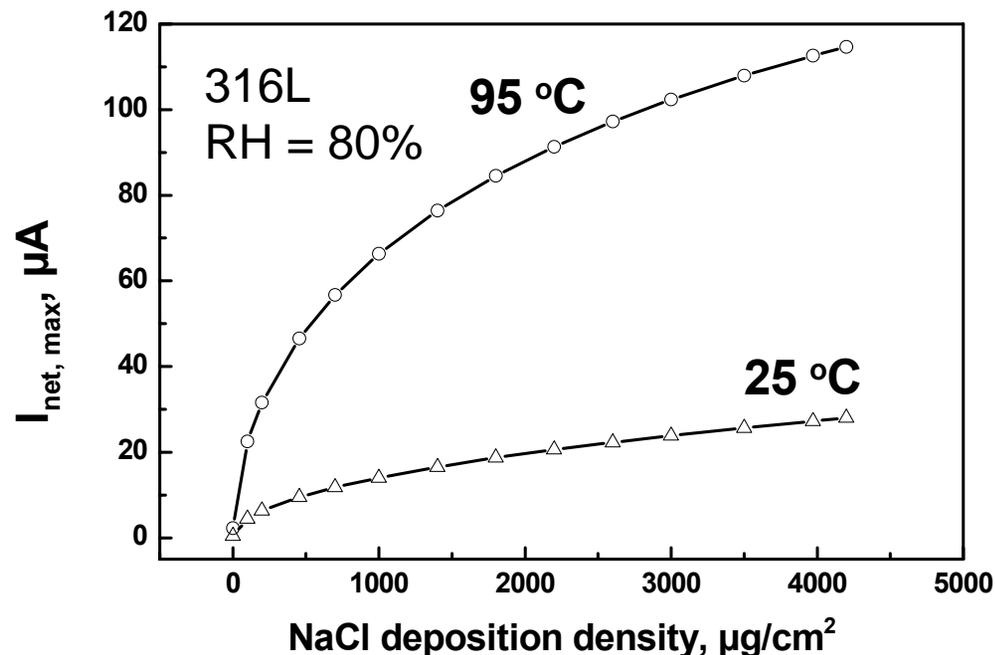
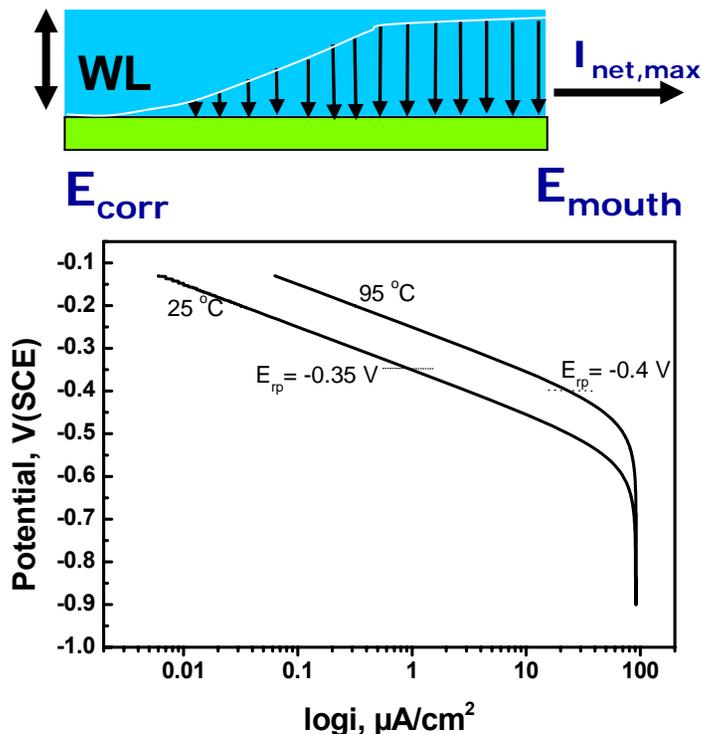
- Fixed potential at  $E_{\text{mouth}}$ , other end at  $E_{\text{corr}}$
- Current along length per polarization curve

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

*Can relate  $\kappa$  and WL to RH and Deposition Density (mass/area) of salt*



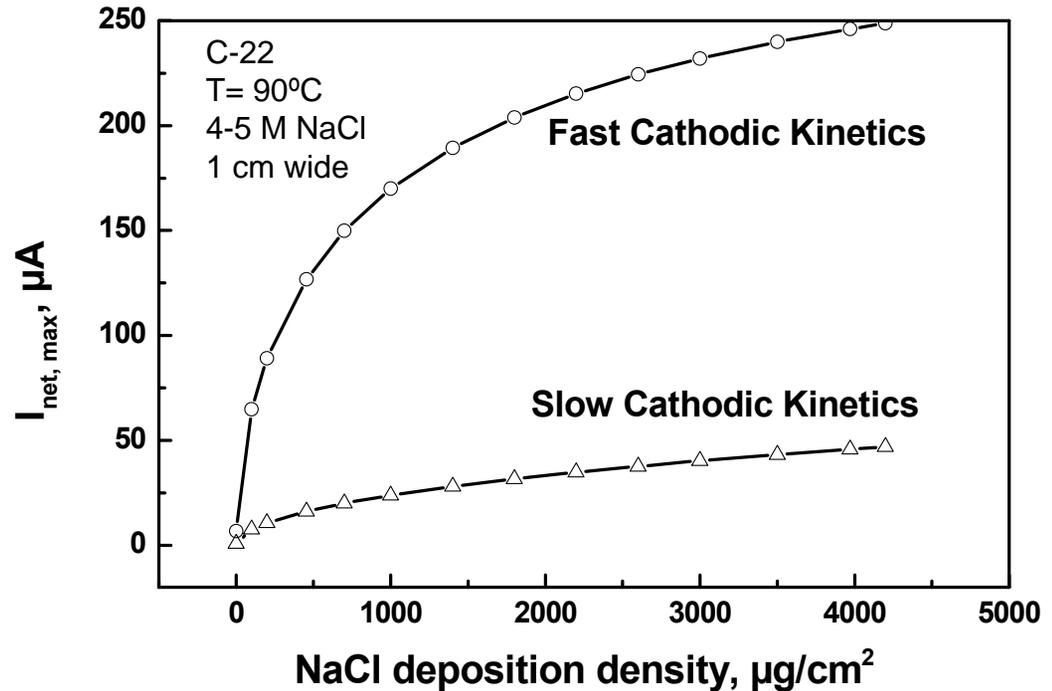
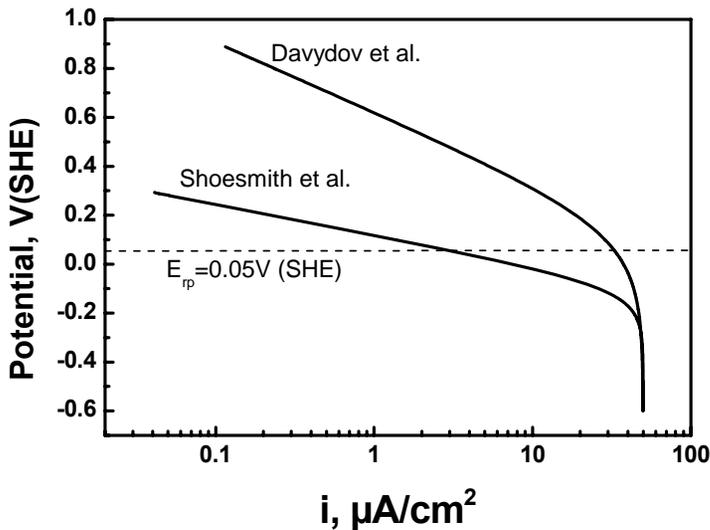
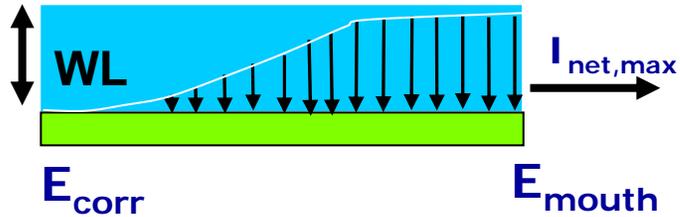
# Increasing Temperature Increases Cathode Capacity



- **Factors Controlling Increased Cathode Capacity at Higher T:**
  - Increased conductivity
  - Faster electrode kinetics
  - Lowered  $E_{rp}$



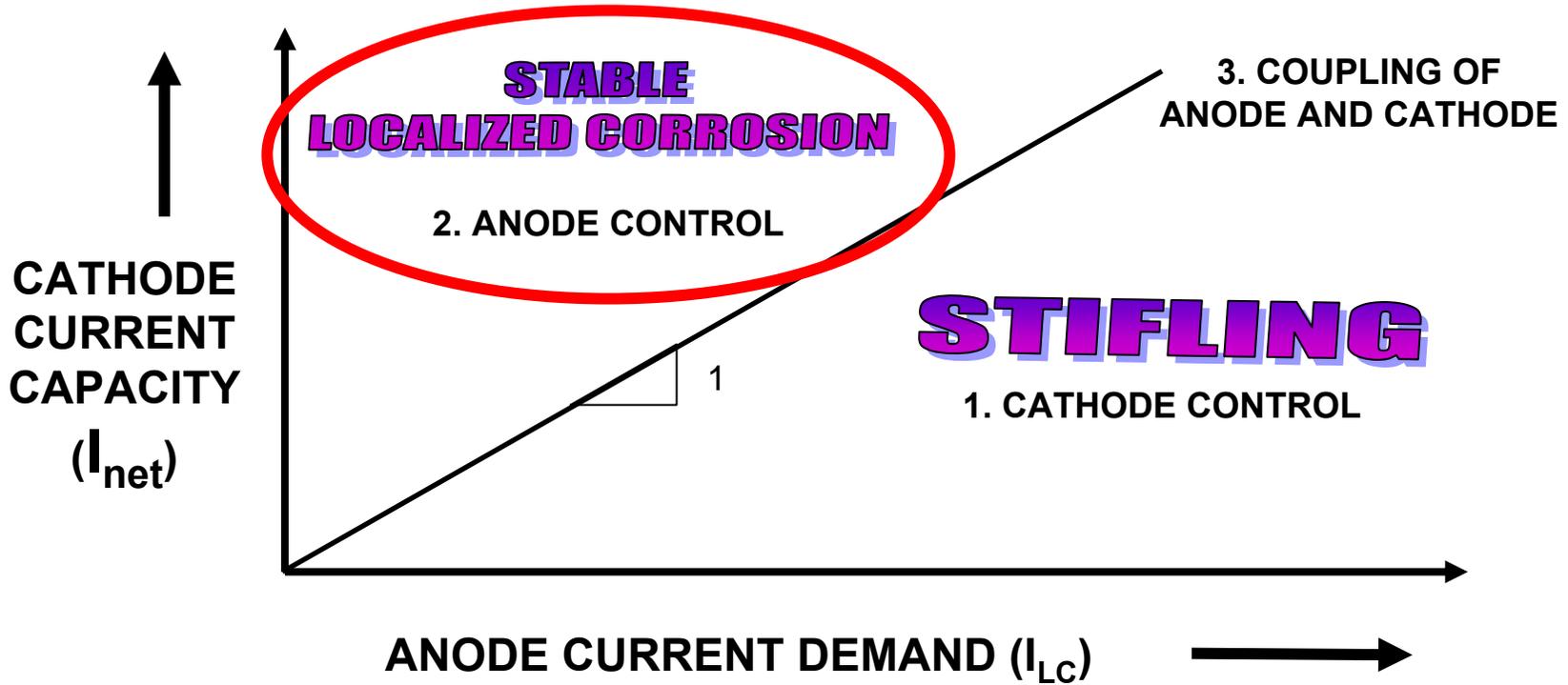
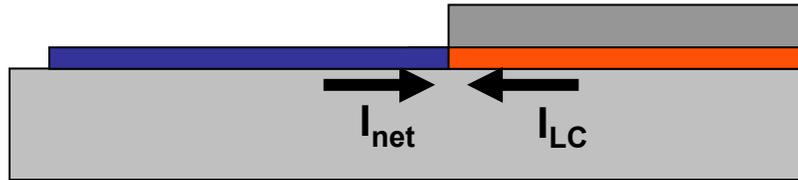
# Slower Cathodic Kinetics Decrease Cathode Capacity



- **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<sup>-</sup>]**
  - Critical Crevice Solution 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<sup>-</sup>]
  - 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
  - $E_{\text{mouth}}$  of crevice falls, leads to insufficient dissolution rate in crevice

***Dissolution rate within crevice is overwhelmed by diffusion out of crevice***

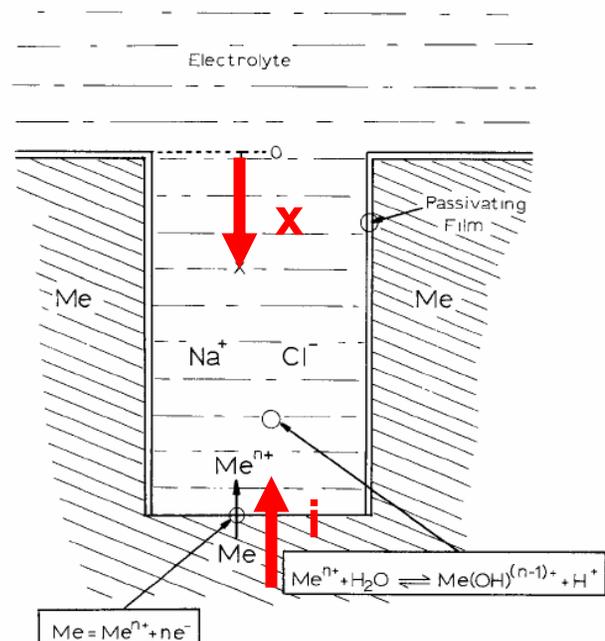


# Anode Stability Considerations: Maintenance of Critical Chemistry

- Pit stability product ( $ix$ ) must be exceeded for stable localized corrosion
  - $ix$  is required to maintain critical chemistry ( $C^*$ ) 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

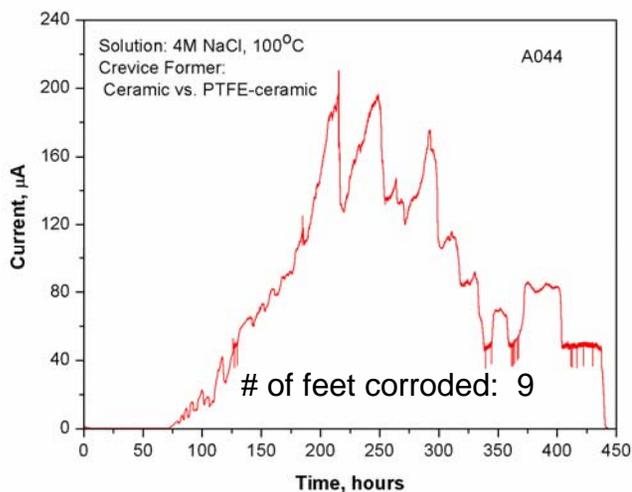
- alloying
- lower  $T$ ,  $[Cl^-]$



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

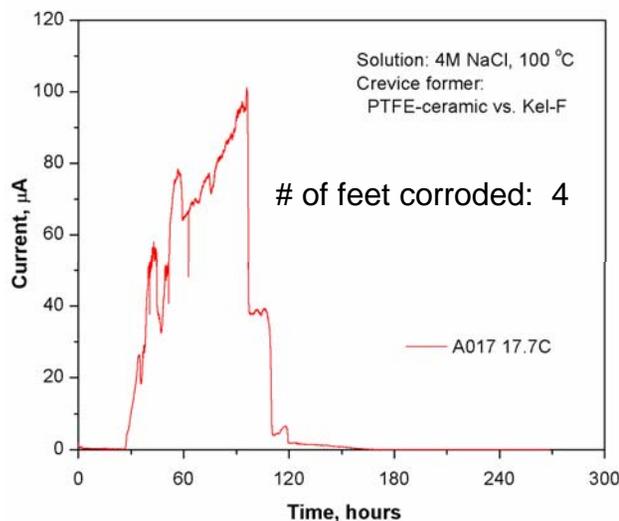


# Arrest of Crevice Corrosion (Repassivation)



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

## Observations



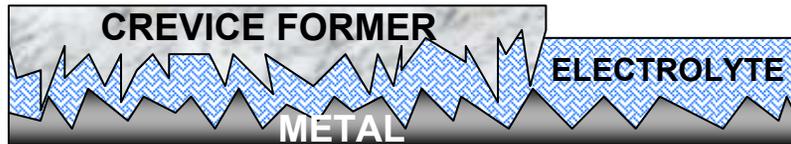
- Incubation time before initiation of crevice corrosion
- Serrated current response indicates multiple initiation/arrest events
- Arrest (repassivation) of crevice corrosion observed
  - Also seen by Rebak et al. (LLNL), Dunn et al. (CNWRA)



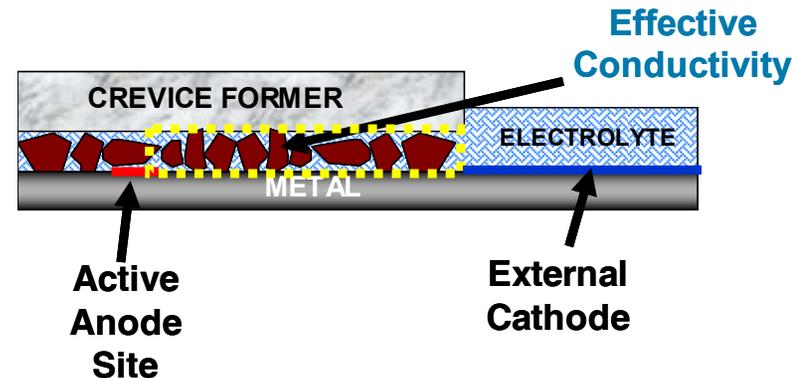
# Ohmic Effects within the Crevice

Model the **OHMIC (IR)** effects on current & potential distributions

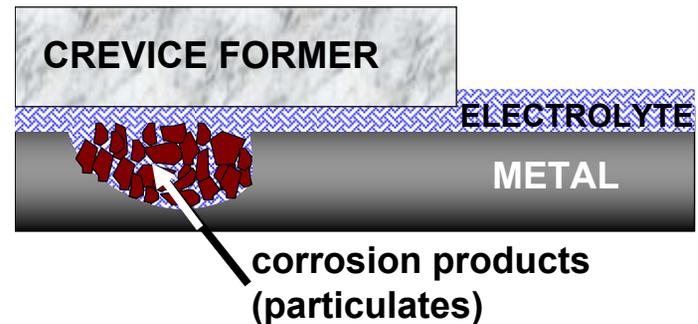
- **Crevice former irregularities (protrusions) and metal roughness**



- **Effect of particles under crevice former**



- **Particulates accumulation (corrosion products)**



Changes in solution chemistry  
not considered in this work

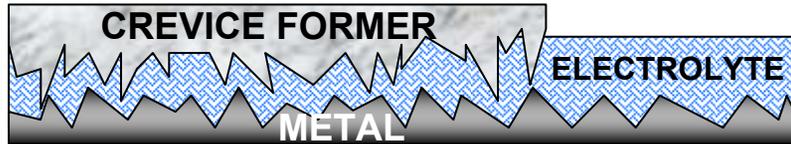


# Summary of Ohmic Effects within the Crevice

OHMIC (IR) effects on current & potential distributions were modeled

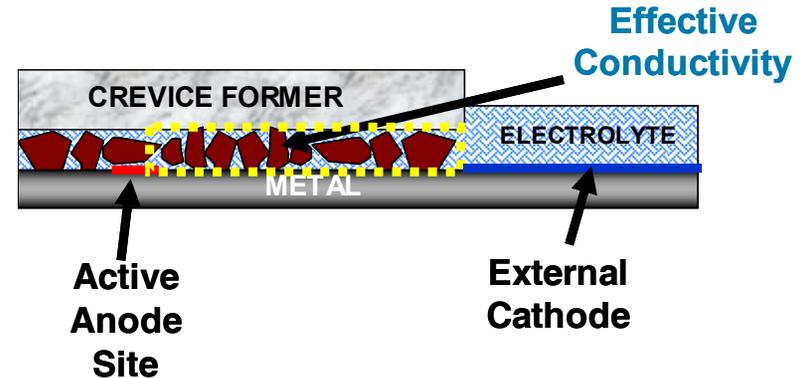
- Roughness elements accounted for in equivalent system →

## *Constriction Factor ( $\tau$ ) Analysis*



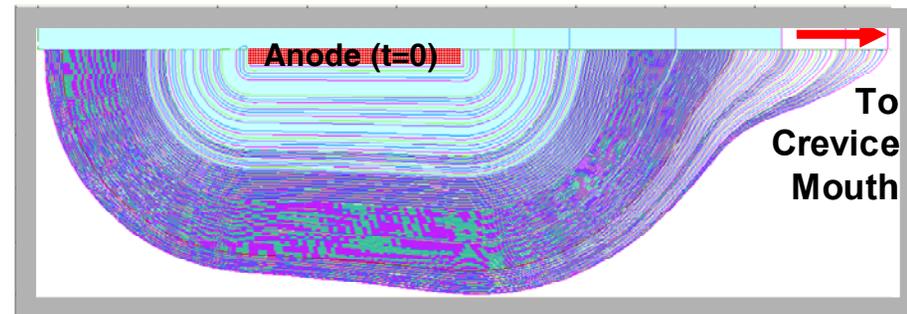
- Particles under crevice former could be accounted for based on volume fraction of particles →

## *Conductivity correction using Bruggeman's equation*



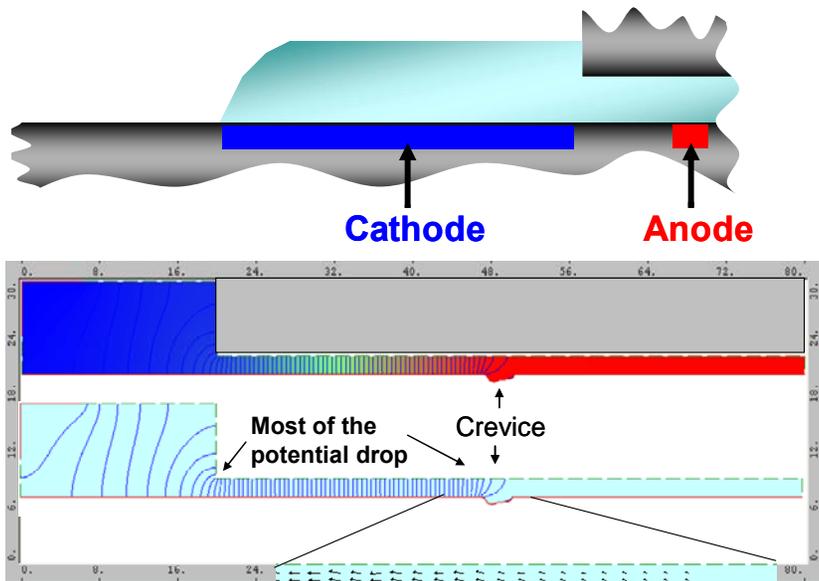
- Solid corrosion products at corroding site decreases effective conductivity →

## *Conductivity effects shown to propagate corroding site towards crevice mouth*



# Repassivation by Dilution of Critical Crevice Chemistry

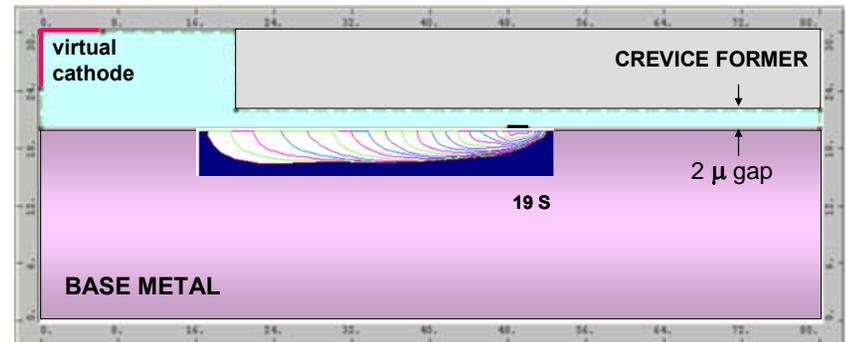
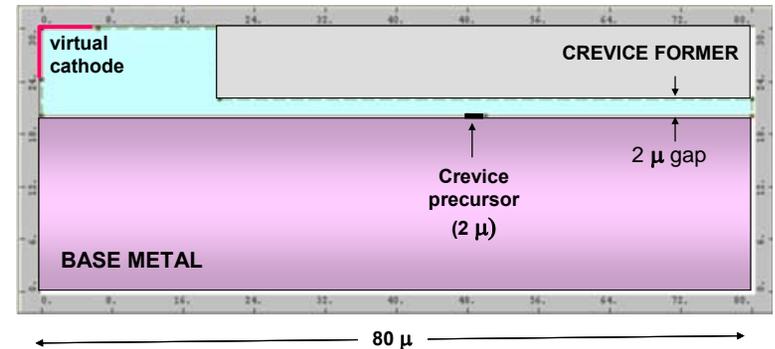
For this case: crevice gap opens, critical crevice chemistry is not maintained and corrosion arrests



- 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

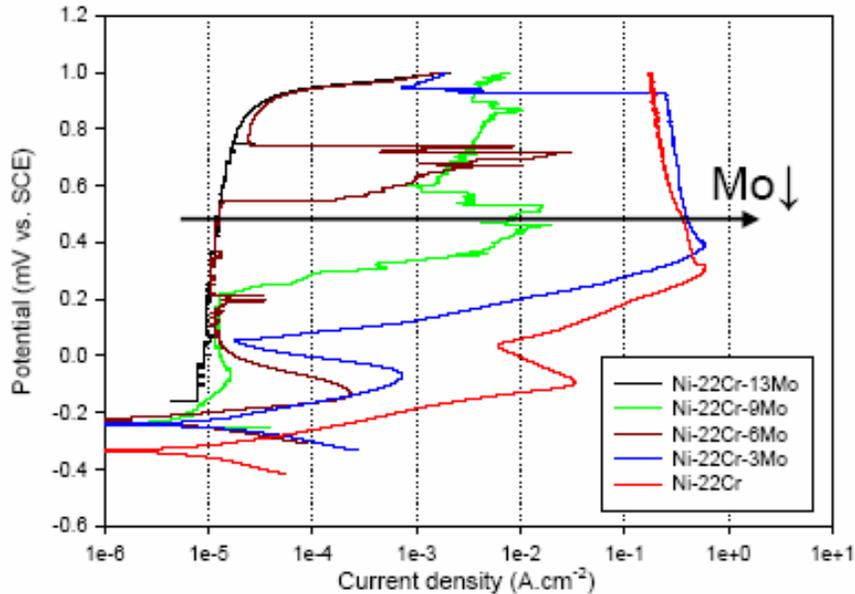
High current density

Low current density



# Slower Anodic Kinetics in Critical Crevice Solution Makes Stability More Difficult to Maintain

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



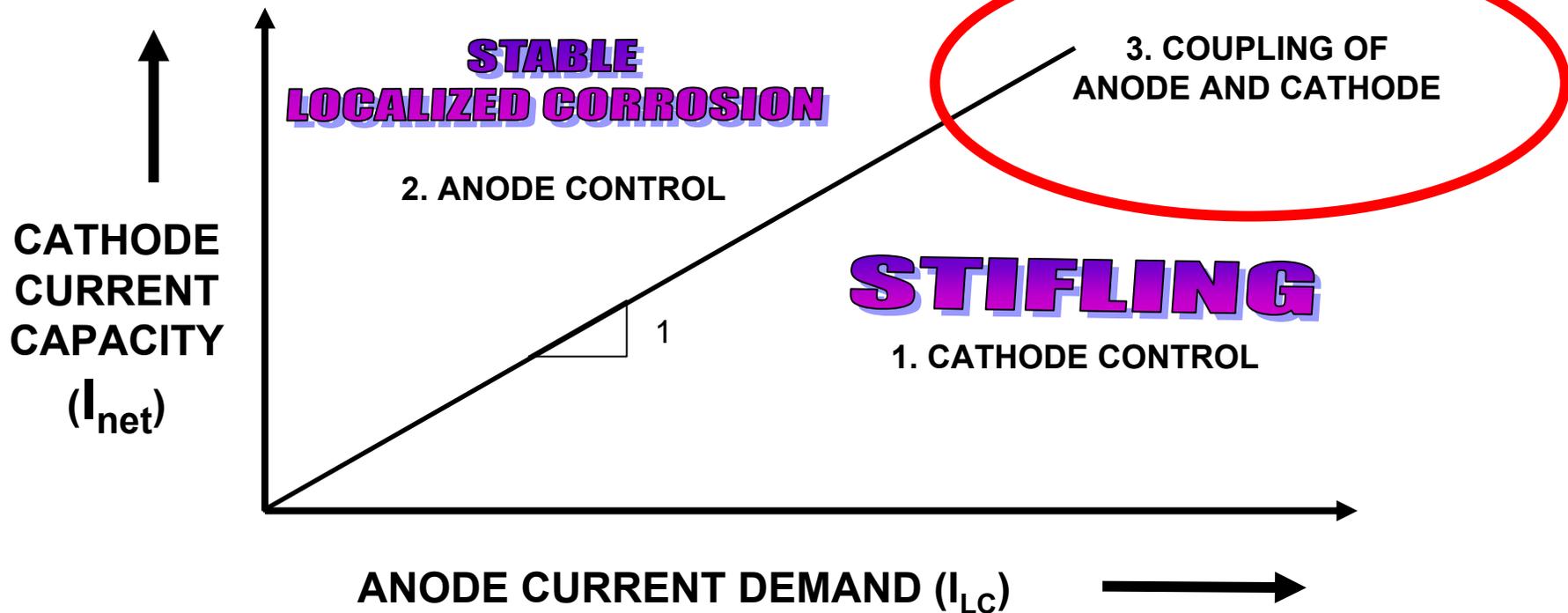
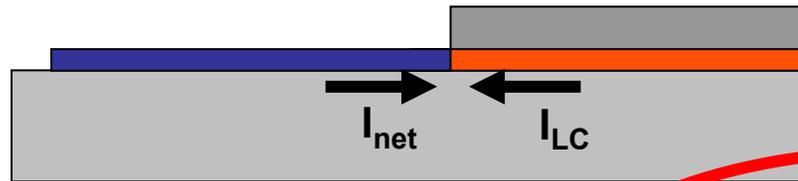
## Experimental Values of CCS for Different Alloys

	$\text{pH}_{\text{crit}}$	$[\text{Cl}^-]_{\text{crit}}$
<b>304L</b>	<b>0.7</b>	<b>3.5M</b>
<b>316L</b>	<b>0.1</b>	<b>6.5M</b>
<b>625</b>	<b>-0.4</b>	<b>6M</b>

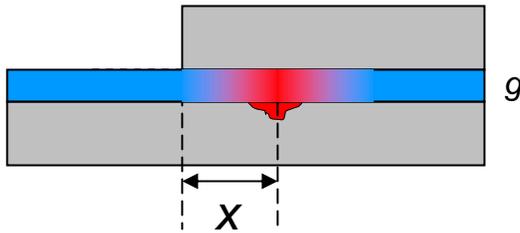
*Increasing Mo Slows Anodic Kinetics in Pit Solutions*



# Coupled Anode and Cathode Processes

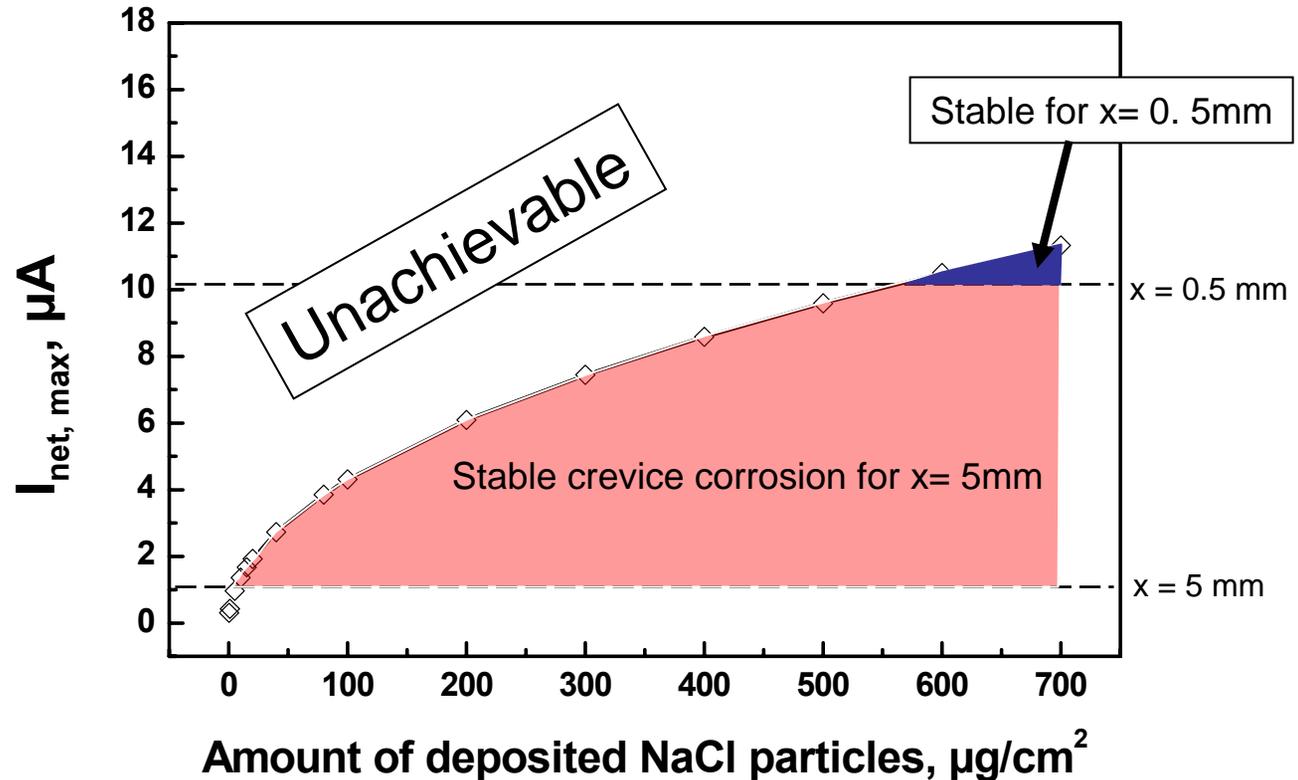


# For Stable Crevice Corrosion, Cathode Must Supply Current Needed to Maintain Sufficiently High $I_{LC}$



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

- Gap = 1  $\mu\text{m}$
- Width = 1 cm
- 316L
- $i_x = 0.5 \text{ A/m}$
- Room T, RH = 80%
- $E_{\text{mouth}} = -0.4 \text{ V}_{\text{SCE}}$



# 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**

