

# Modeling of Crevice Corrosion Stability and Stifling

Presented to:  
**Research in Progress Symposium  
Corrosion '06**

Presented by:  
**F. J. Presuel-Moreno, R. G. Kelly**

**Center for Electrochemical Science and  
Engineering  
University of Virginia**

March 14, 2006  
San Diego, CA

# Acknowledgements

- **Support by the Office of Science and Technology and International (OST&I) 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/OST&I.**

# Outline

- **Introduction and background**
- **Model Description**
- **Results**
- **Conclusion**

# Background

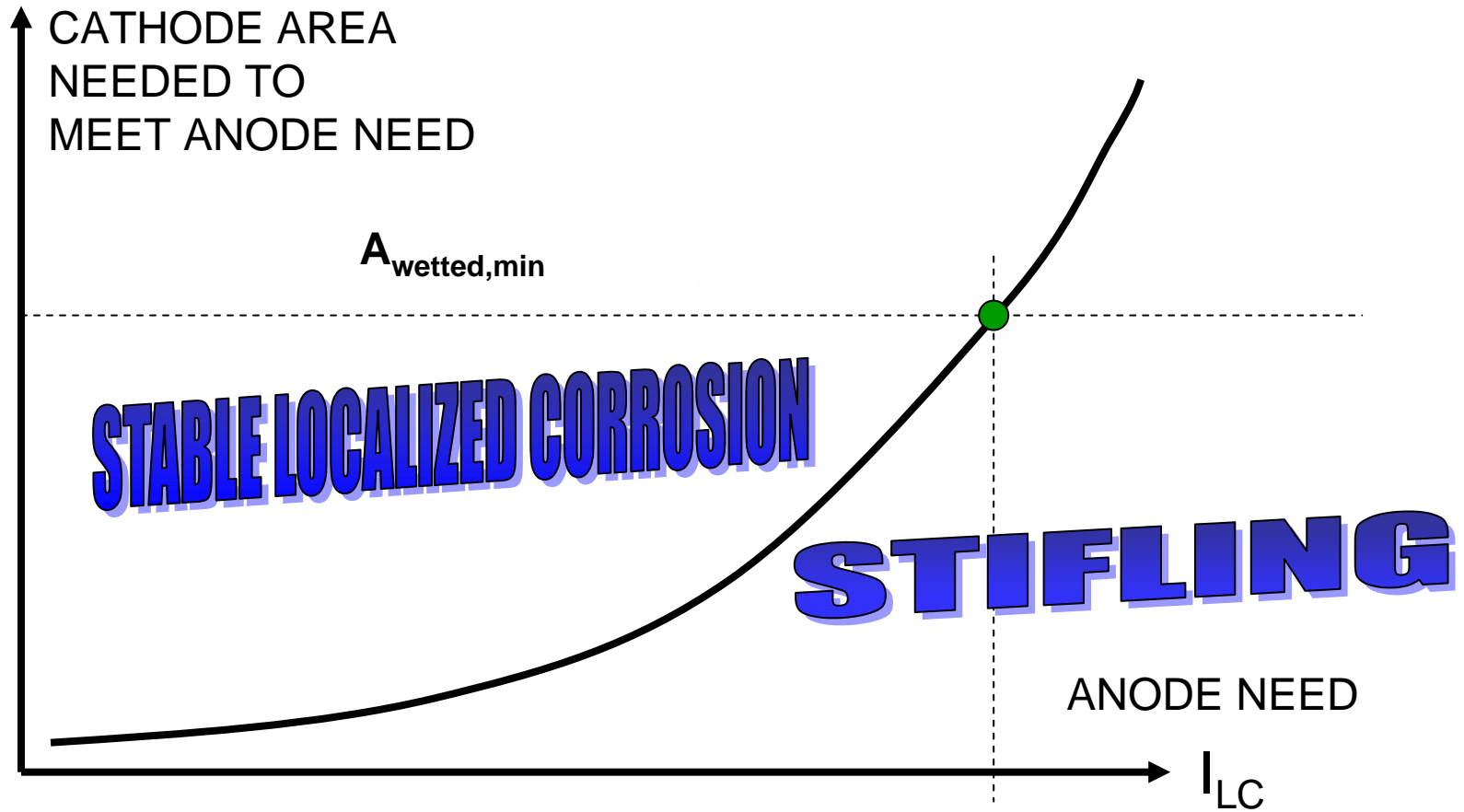
- **Crevice corrosion modeling has often focused on estimation of initiation time and critical chemistry**
  - e.g., Oldfield and Sutton, Postlethwaite et. al., Watson, Sharland, Gartland, Alkire et al.
- **Propagation models have been developed for pitting**
  - e.g. Laycock and White
- **Propagation models for crevice corrosion are less common**
  - Walton, et. al., Garland, Sridhar

# Research Objectives

- Investigate conditions under which an initiated crevice can remain stable
- Quantify the total anodic current that a crevice requires under a given set of conditions
  - Total current provides insights into the stability of localized corrosion when coupled to an external cathode
  - Current distribution allows calculation of spatial distribution of damage

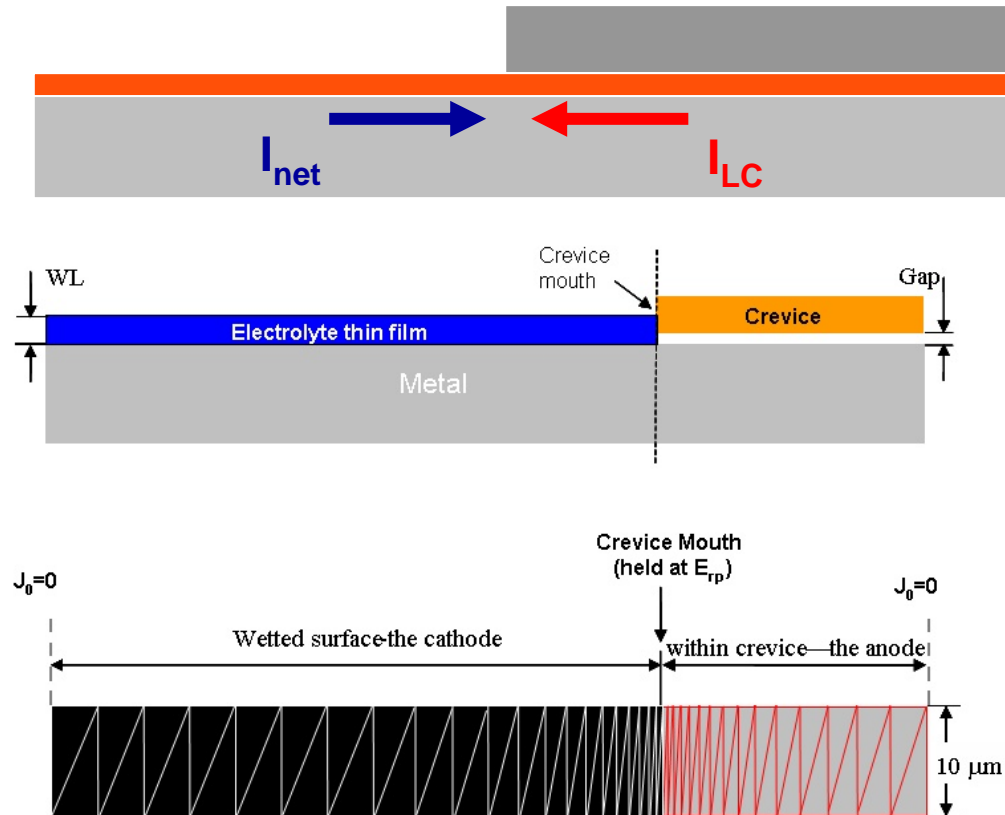
# For Stability:

Cathode Current Capacity  $\geq$  Anode Current Demand

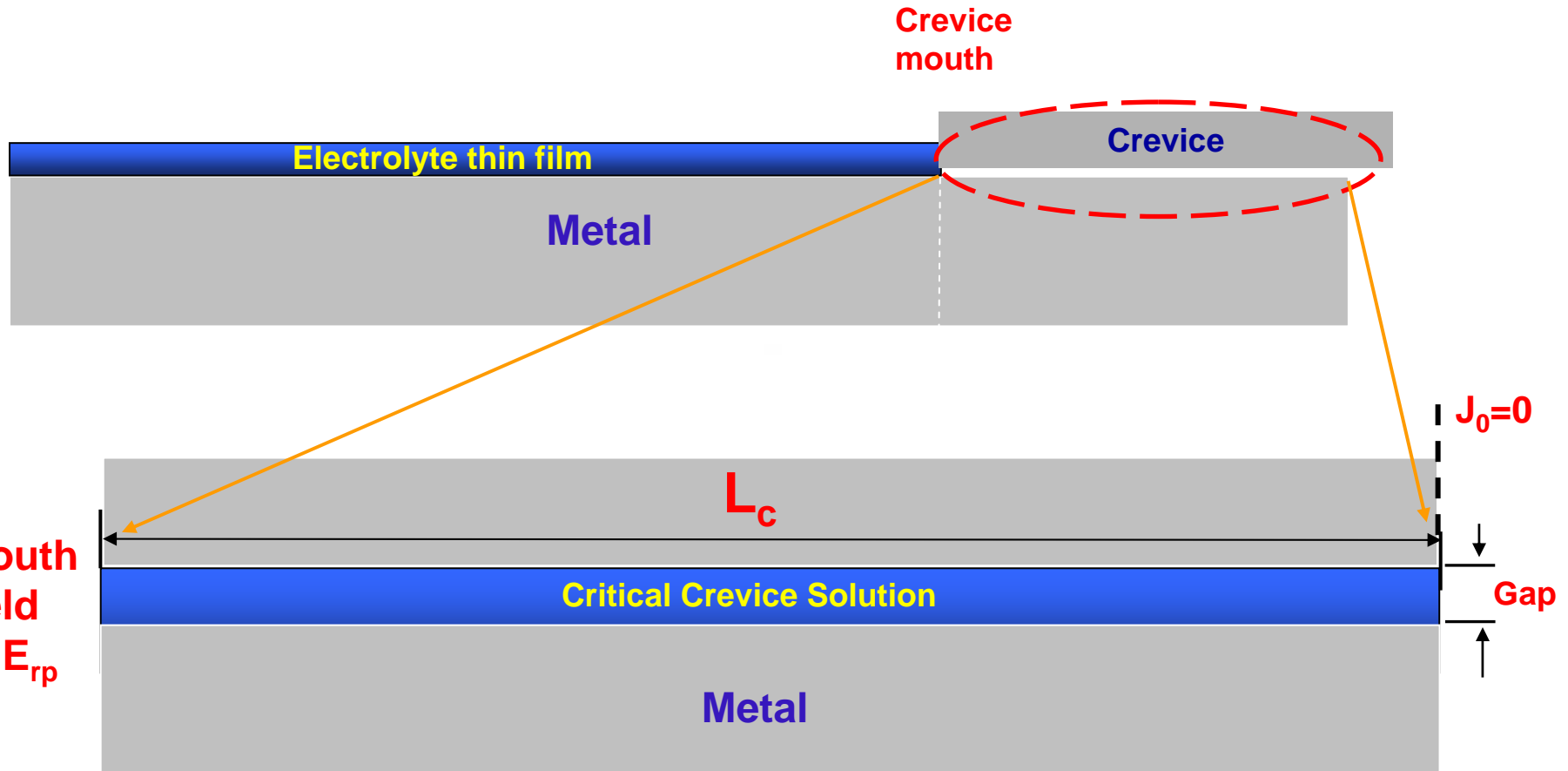


# Approach

- Potential and current distributions were computationally modeled
- Effects of
  - > relevant kinetic parameters
  - > physiochemical parameters
    - >> Gap
    - >>  $E_{\text{mouth}}$
    - >> Ionic strength effects on pH and conductivity
    - >> Internal Cathodic Reaction
- Material: 316L Stainless Steel(SS)
- Post initiation, focuses on maintaining aggressive conditions



# Anode Modeling

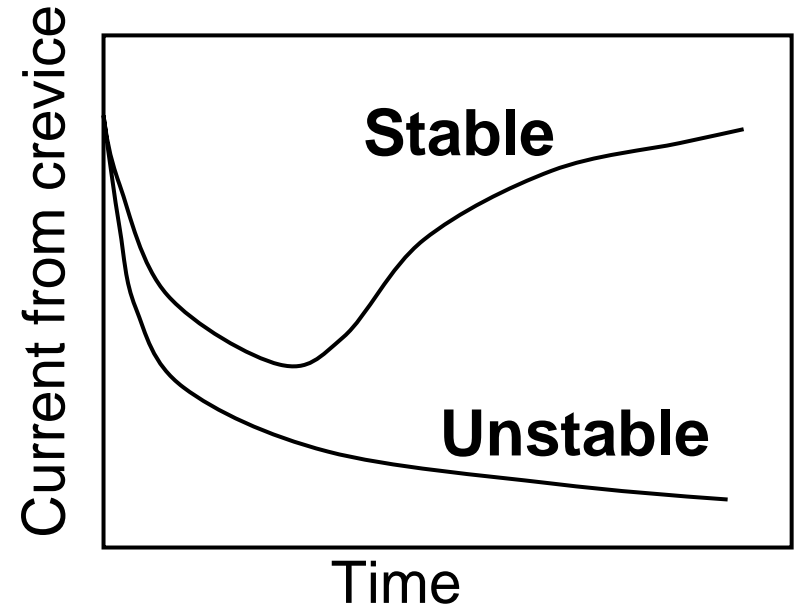


Crevice  
mouth



# Explore Impact on Crevice Corrosion Stability of:

- **Crevice Geometry**
  - > Gap, Length
- **Potential at mouth**
  - >  $E_{\text{mouth}} = E_{\text{rp}}$  or  $E_{\text{mouth}} > E_{\text{rp}}$
- **Dependence of anodic kinetics on pH and ionic strength**
- **Presence of cathodic reactions inside crevice**



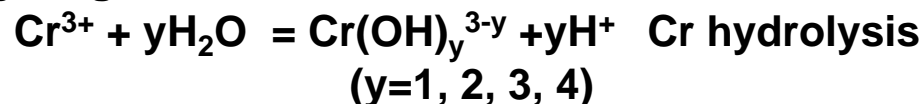
# Boundary Conditions

- Consideration of important species
- First-order evaluation of physiochemical properties
  - > Effect of ionic strength on conductivity ( $\kappa$ ) and pH from literature
- Hydrolysis of  $\text{Cr}^{3+}$  assumed to control  $[\text{H}^+]$
- Analyze SS316L based on published data
  - > Anode kinetic parameters as  $f(\text{pH})$
- Transport modes: diffusion and migration

Complex reaction system:



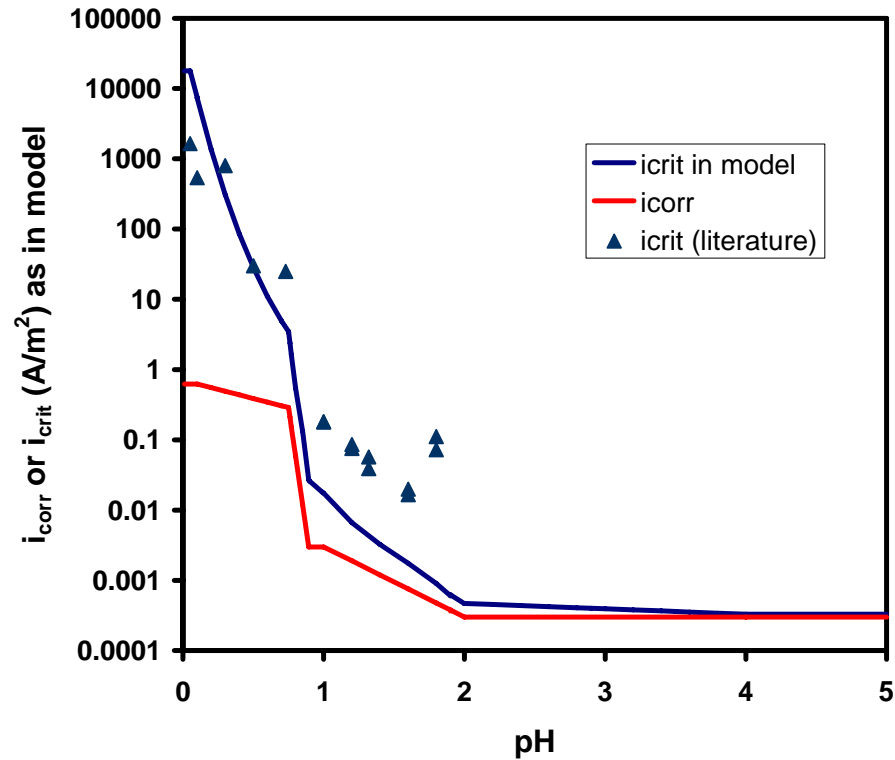
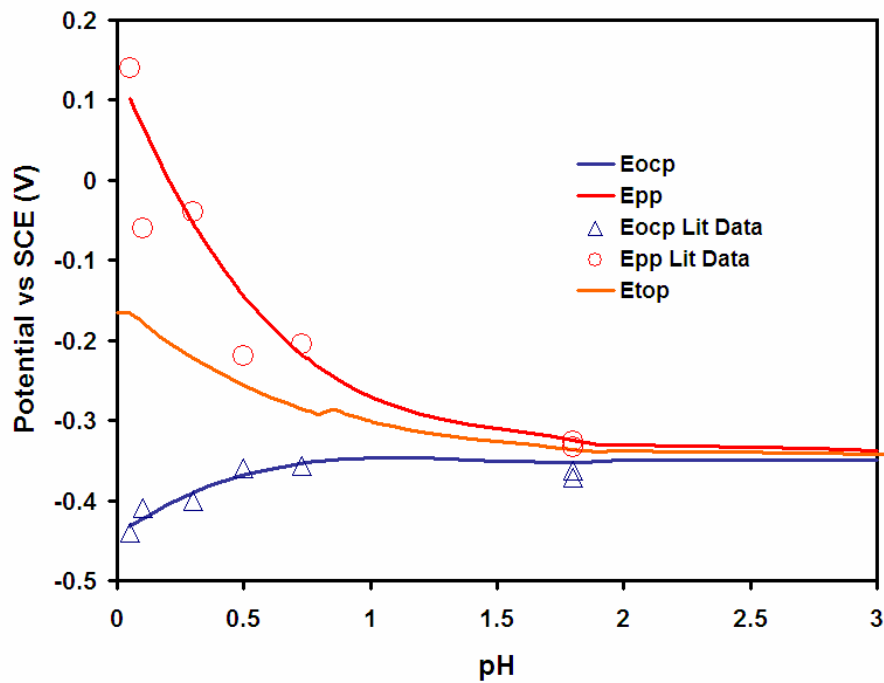
Hydrogen Evolution Reaction cathodic reaction



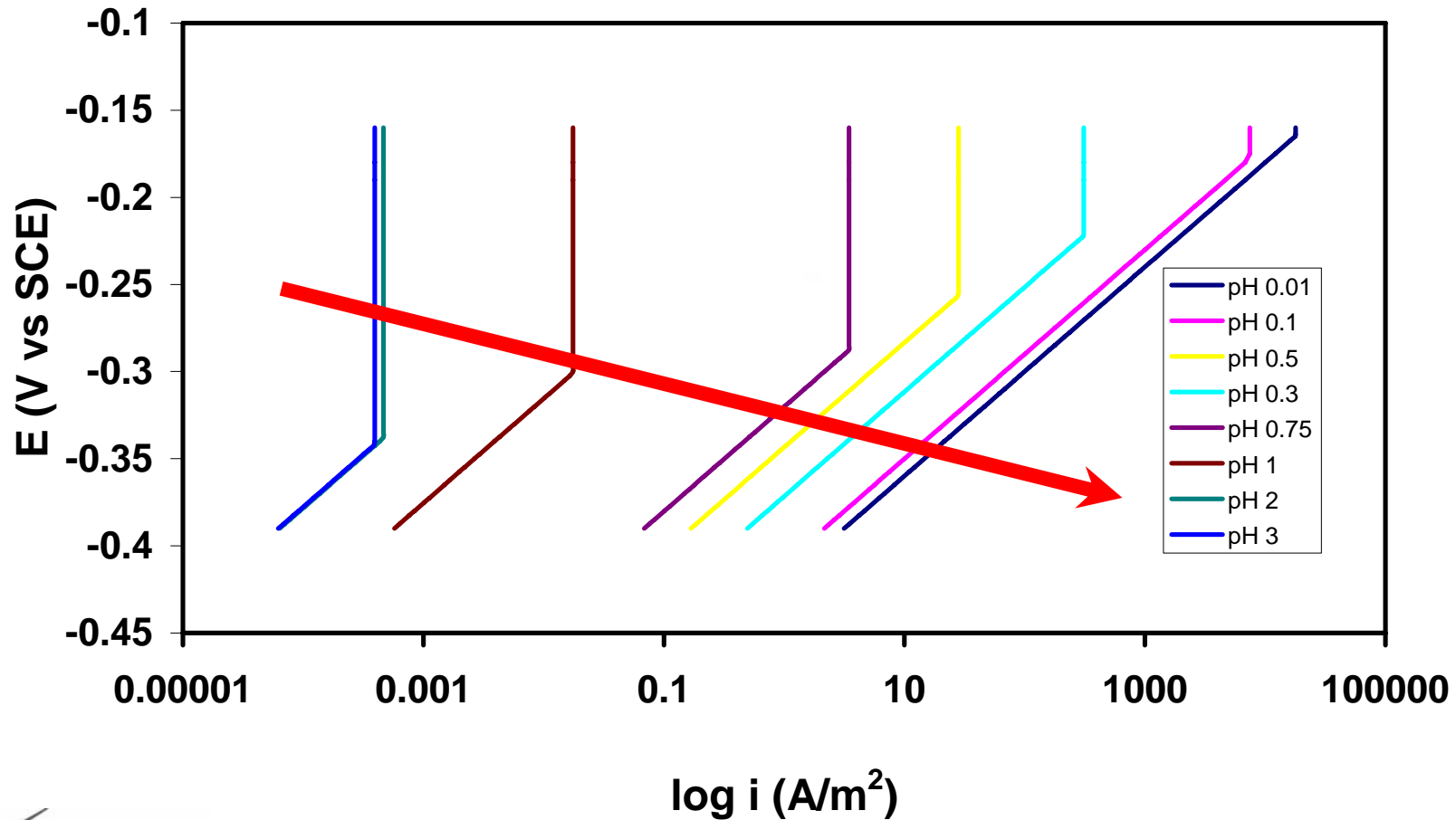
# Base Case

- Neutral pH bulk solution maintained at the mouth
- SS 316L, 25 C, initially filled with Critical Crevice Solution (CCS)
  - CCS: pH 0.75,  $[Cl^-] = 5 \text{ M}$ ,  $[Cr^{3+}] = 1 \text{ M}$
- Anode kinetics controlled by pH
- pH evolution controlled by  $Cr^{3+}$  hydrolysis
- Ionic strength affects hydrogen activity ( $\gamma_{H^+}$ ) and therefore pH
  - Effects on anode kinetics and conductivity
- Cathodic reaction with  $\beta_c = 100 \text{ mV/dec}$ , if present

# pH Controls Kinetics of Anode

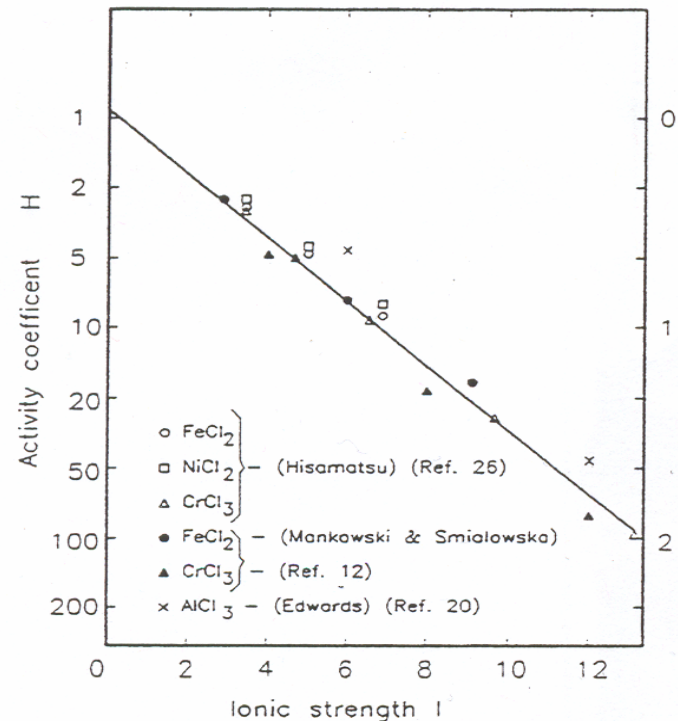
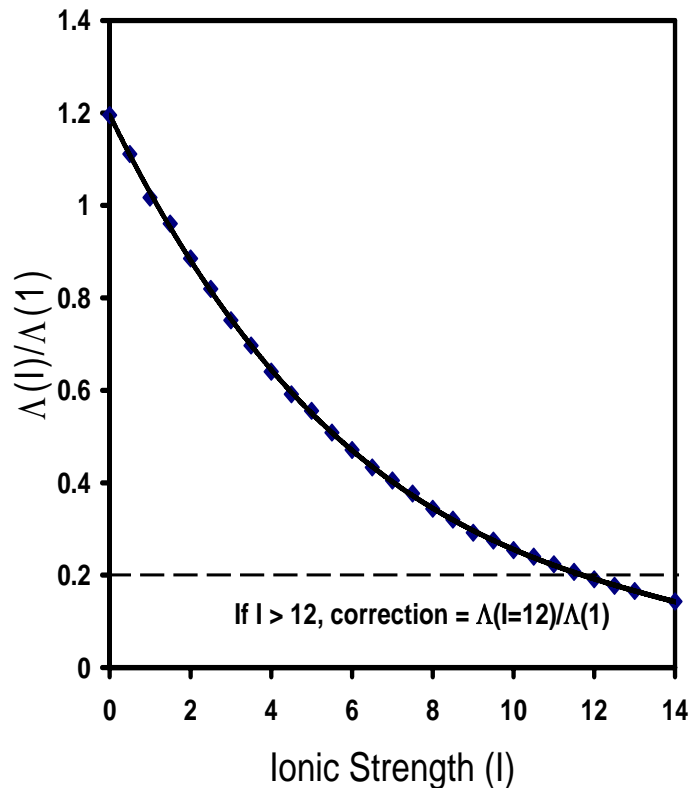


# Anode Kinetics as f(pH)



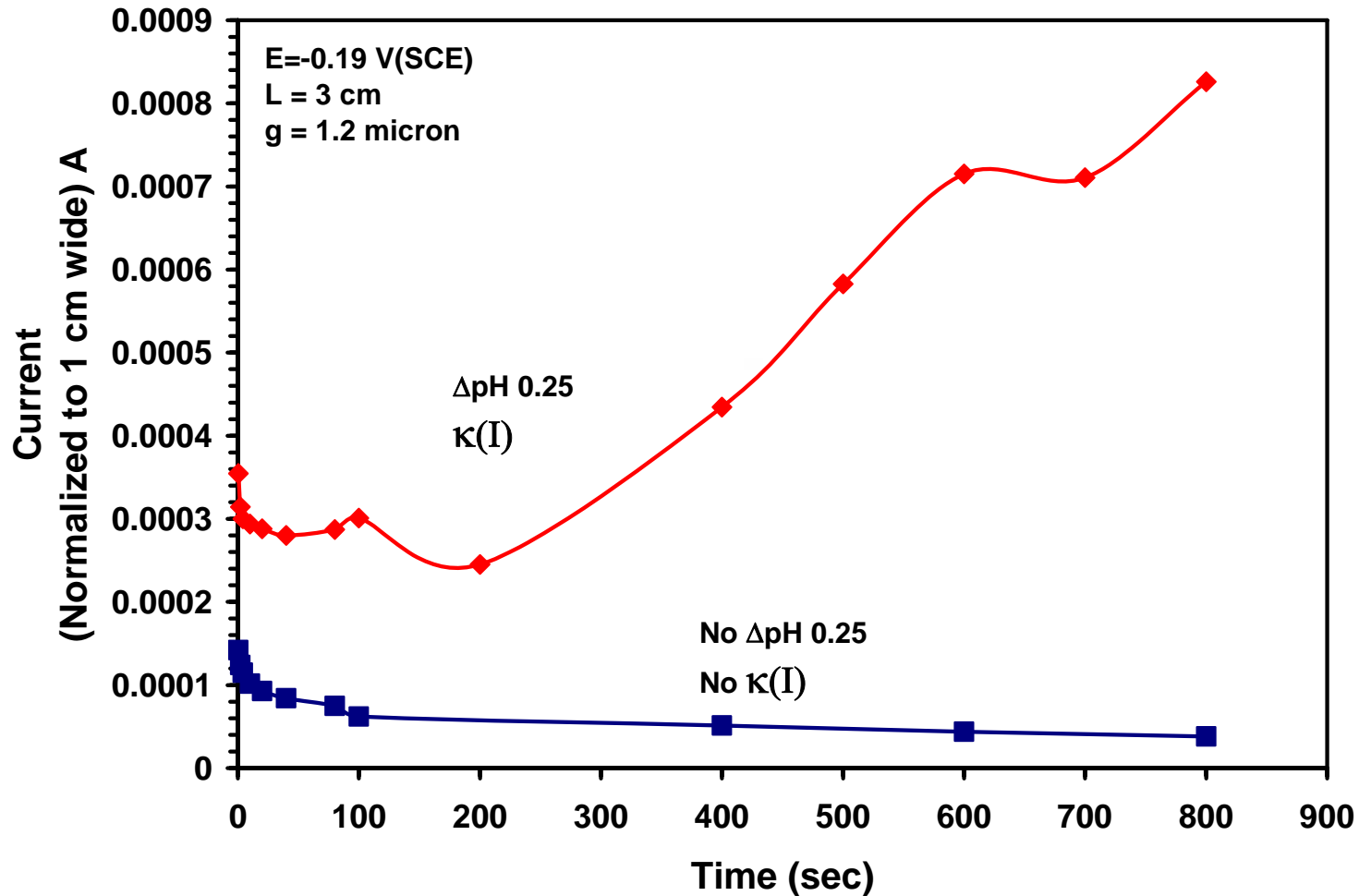
# Ionic Strength Affects pH and Conductivity

Abstractions Used Were Fits to Experimental Data



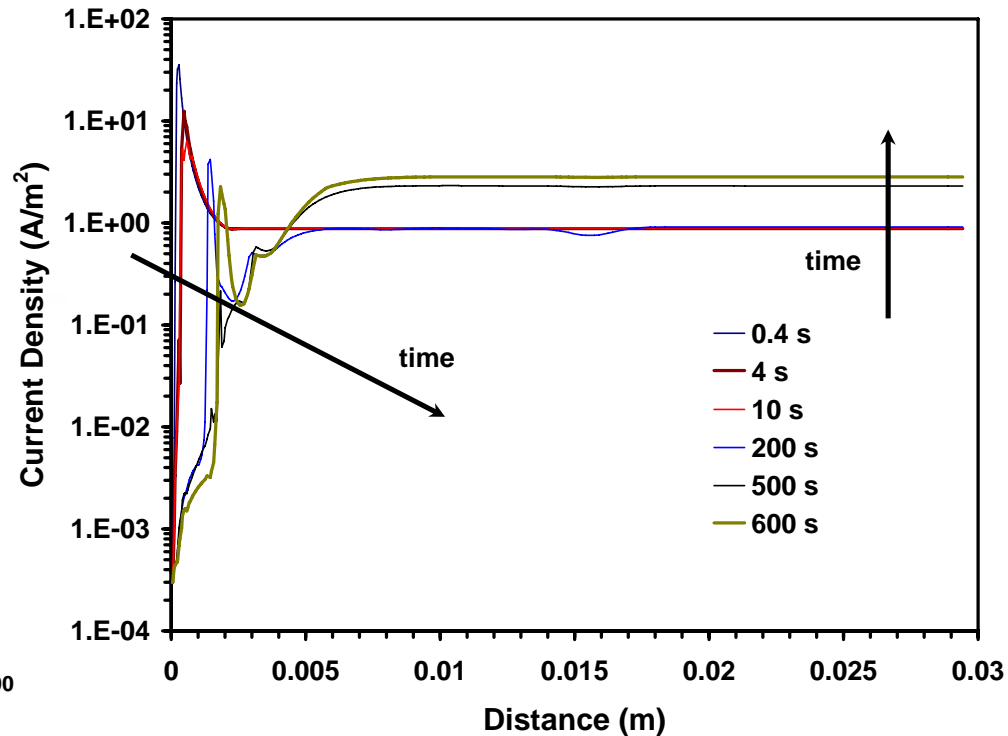
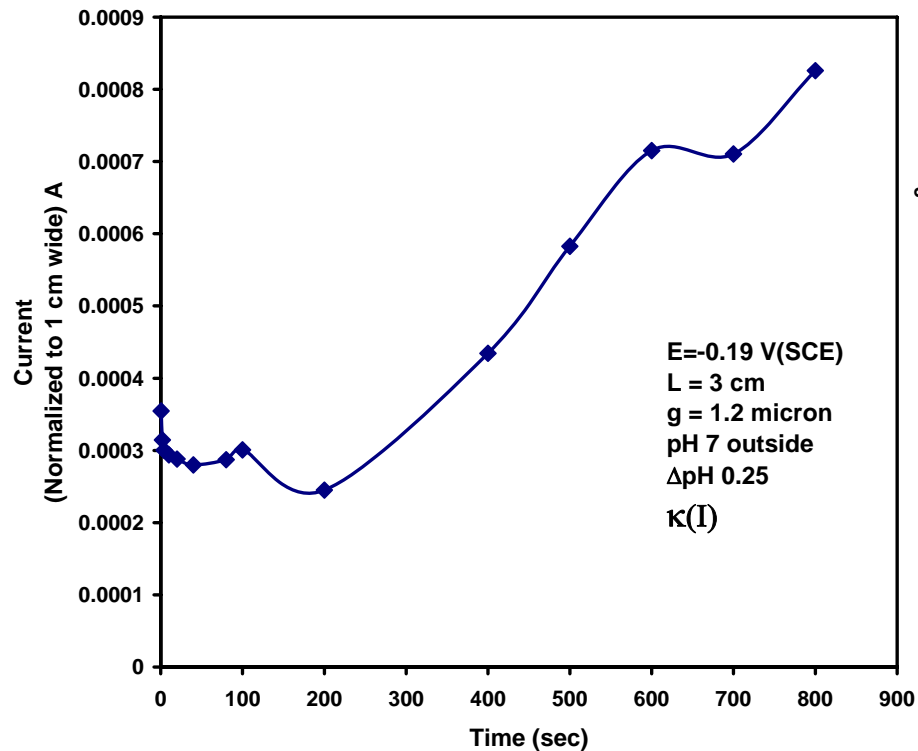
*Fit line to subset of data used by Gartland*

# Ionic Strength Effects are Important in Stabilizing Crevices



# Results: $I_{LC}(t)$ and $i(x,t)$

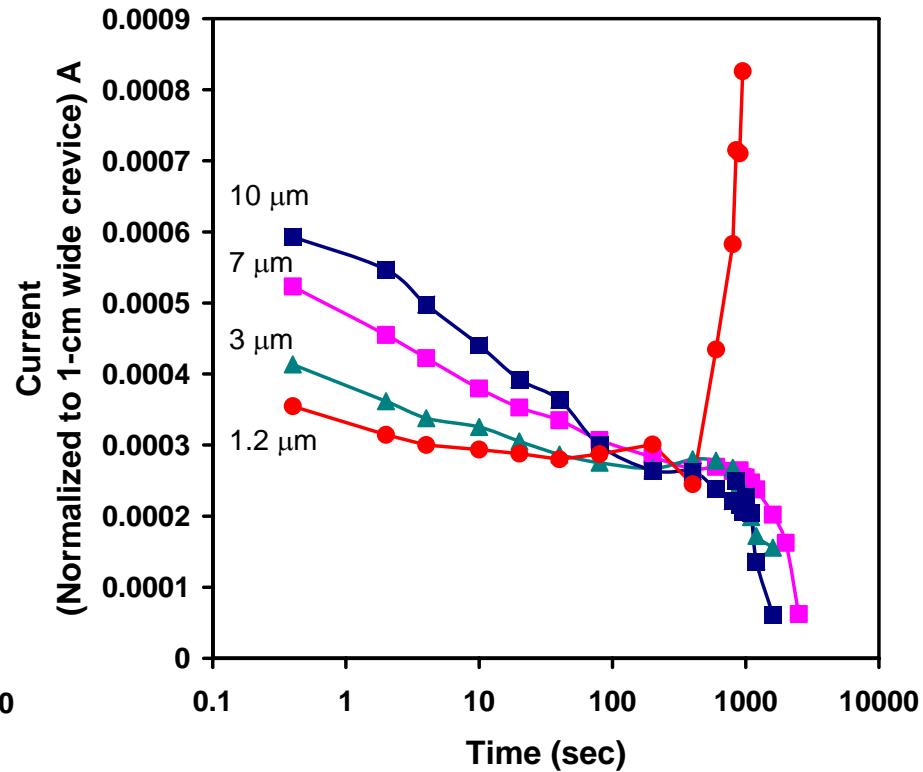
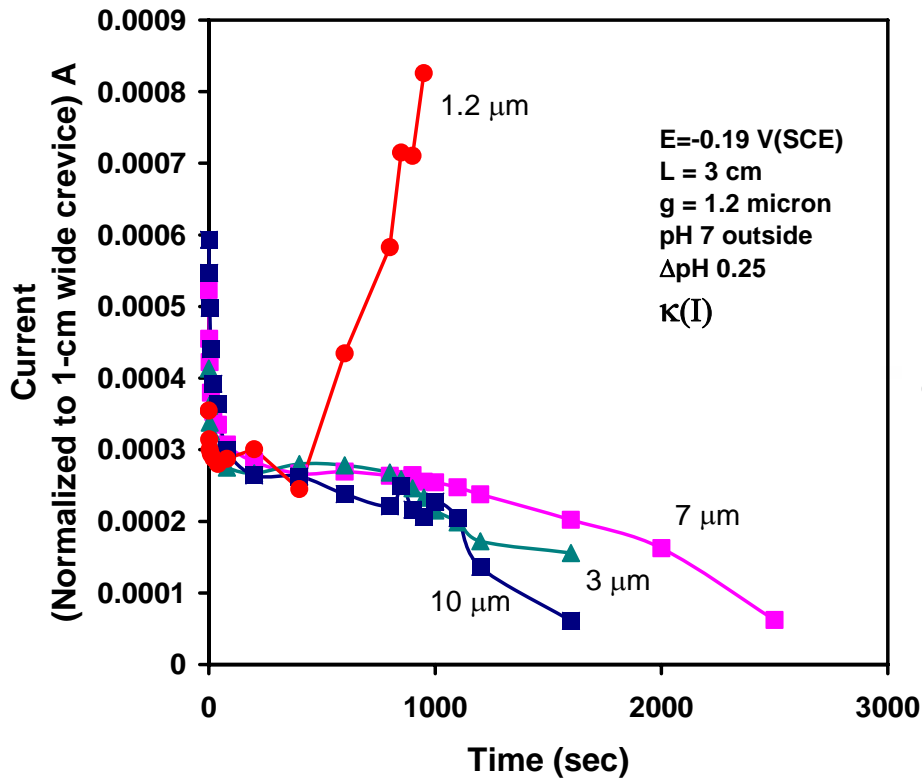
$E_{mouth} > E_{rp}$



*Near crevice mouth passivates, deeper parts corrode faster with time*

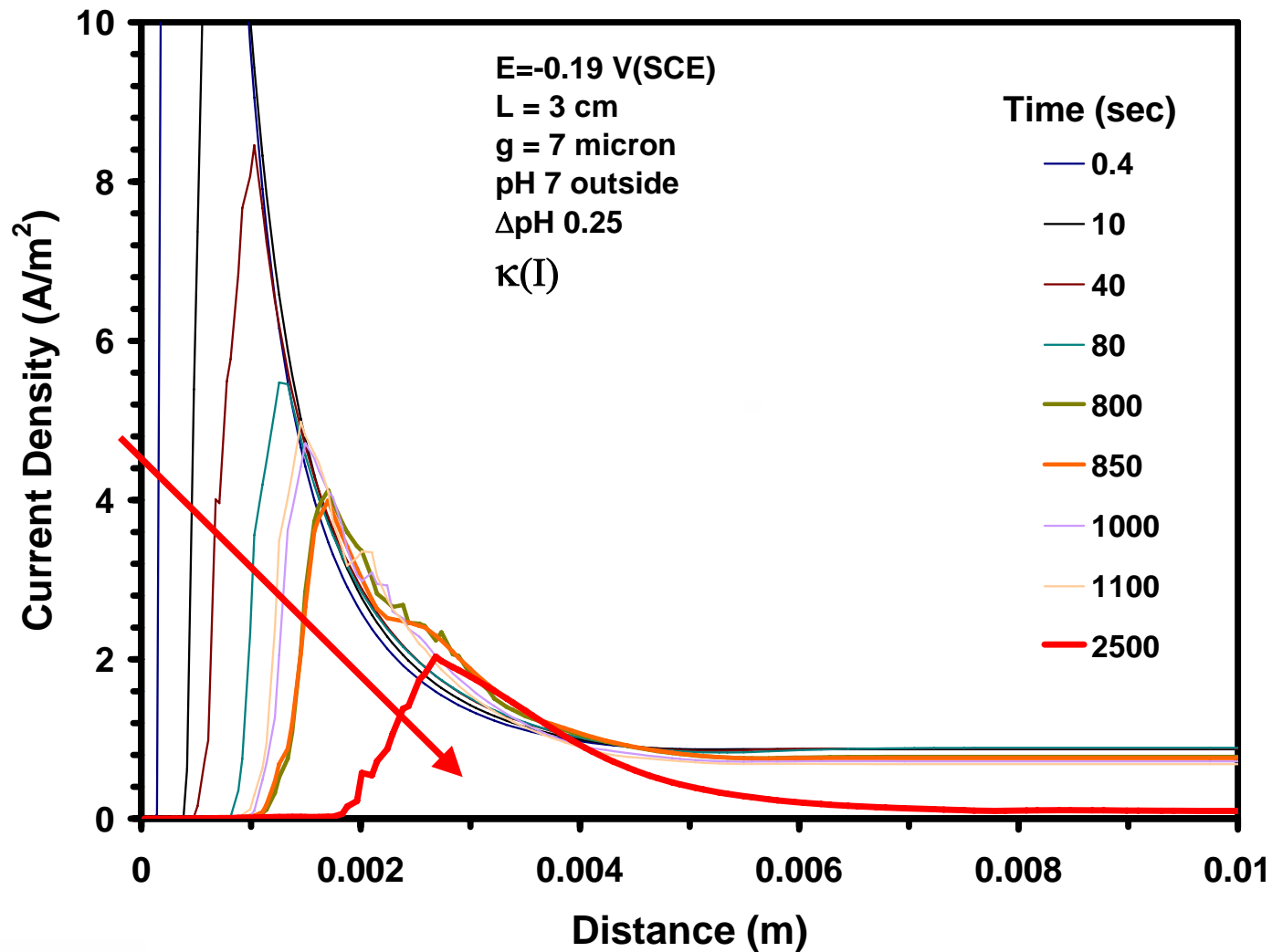


# Effect of Gap

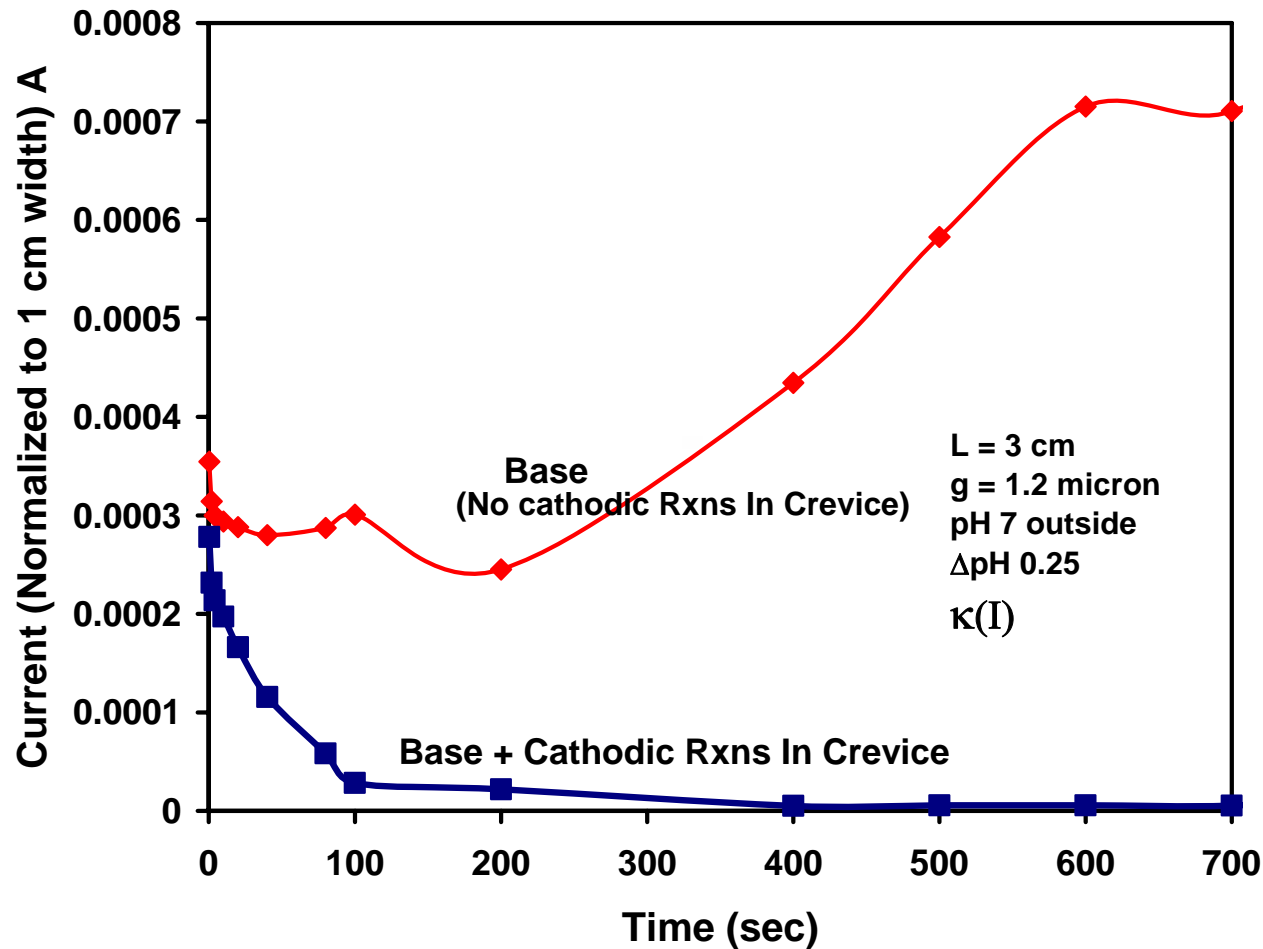


- *Crevice passivates with larger gaps*
- *Minimum crevice gap required for stable crevice growth*

# Repassivation is Sometimes not Complete Through the Crevice



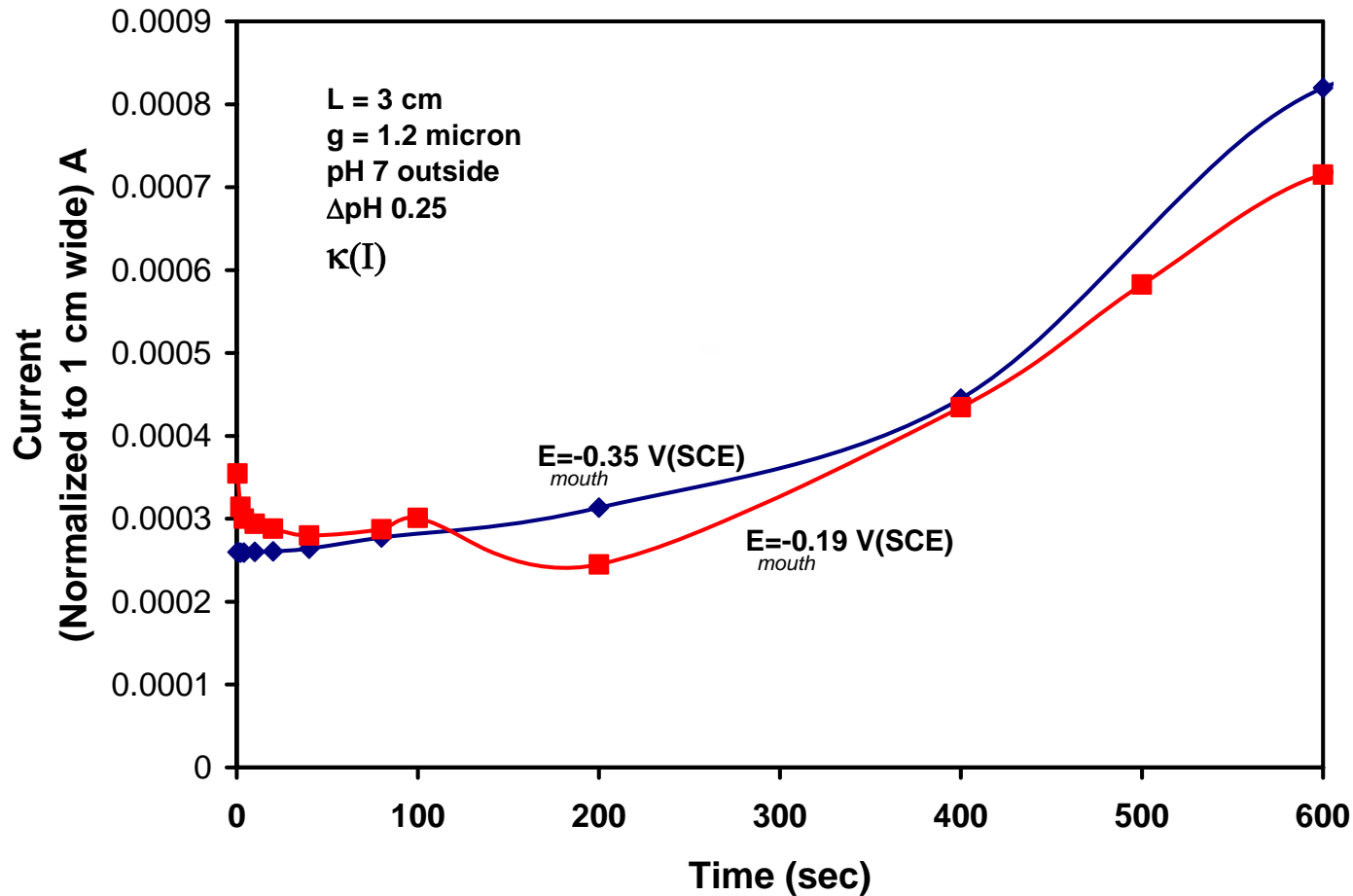
# Effect of Internal Cathodic Reaction



*Production of  $\text{OH}^-$  inside crevice prevents stabilization*

# Effect of Lower $E_{mouth}$

**Lower Initial  $I$ , but Still Stabilizes at  $E_{mouth} = E_{rp}$**



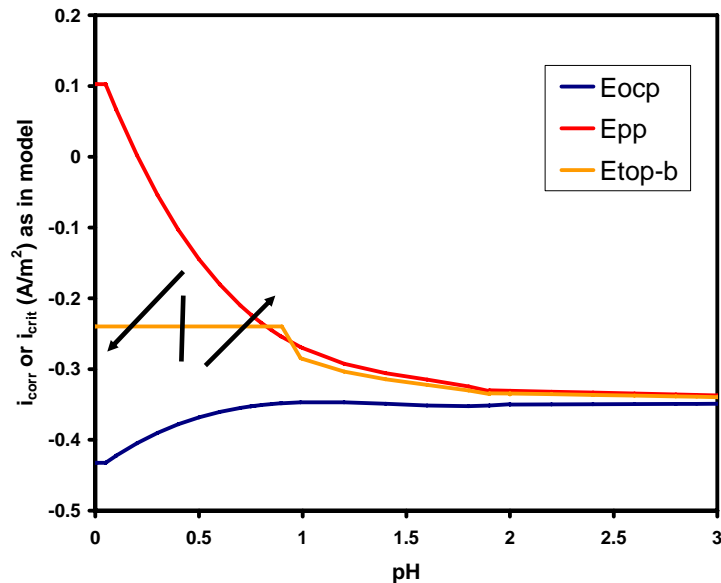
$E_{rp} = -0.35 \text{ V(SCE)}$  For this case

# Crazy Aunts in the Basement

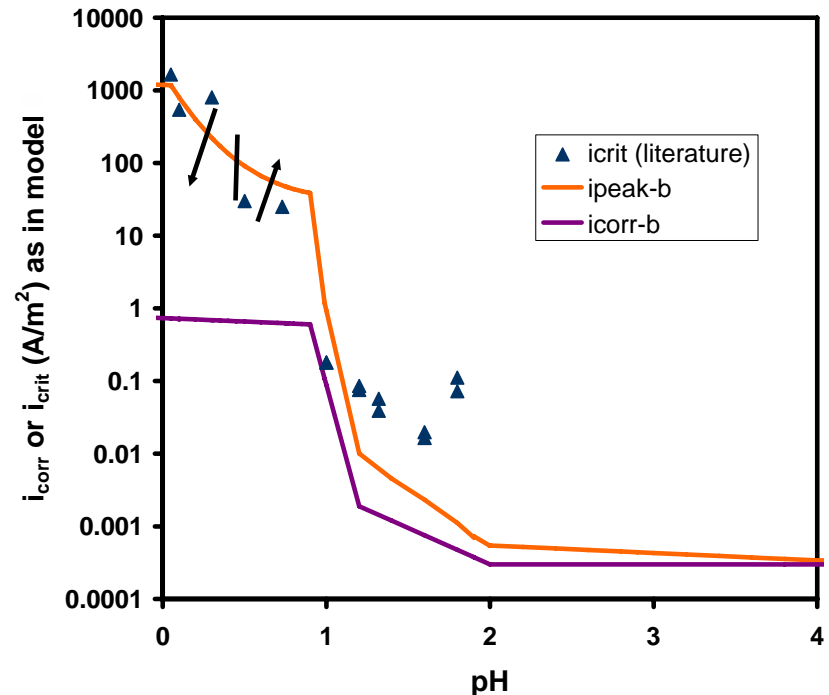
- **Not dealing with precipitation**
- **Engineering abstraction for effects of ionic strength**
  - **Simple effects on kinetics**
- **Simplified anodic kinetics – active/limiting  $i$**
- **No evolution of geometry**
- **Numerical stability issues arise occasionally**

# Modified $i(\text{pH})$ and Lower Cathodic Rxn

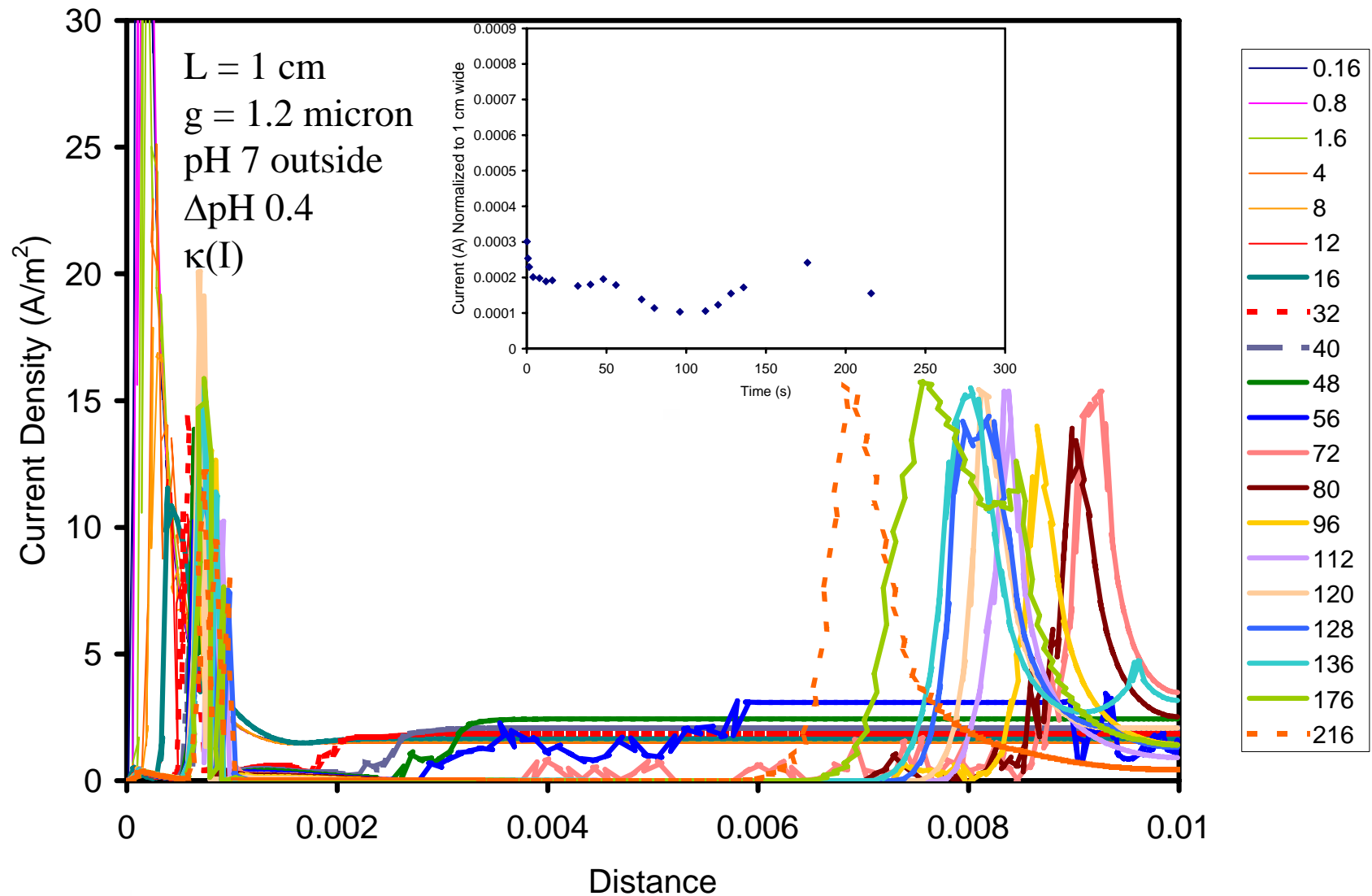
- SS 316L, room temperature, initially CCS
  - > CCS: pH 0.4,  $[\text{Cl}^-] = 5 \text{ M}$ ,  $[\text{Cr}^{+3}] = 1 \text{ M}$
- Anode kinetics controlled by pH (Model 2)
- $\beta_c = 40 \text{ mV/dec}$  instead of  $100 \text{ mV/dec}$



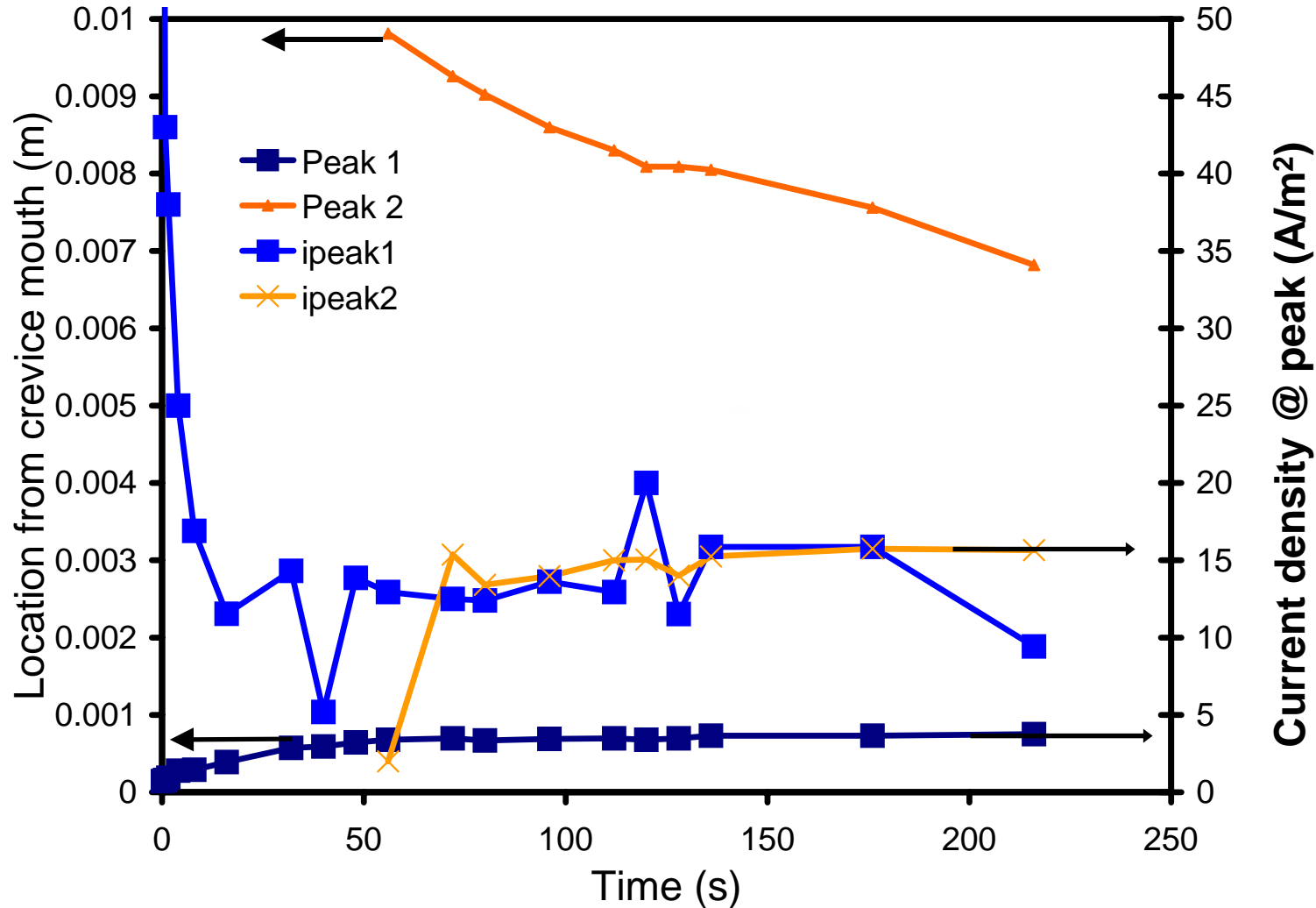
$E_{\text{pp}}$  modified as to better fit  $i_{\text{peak}}$



# Stabilization with Reduced Cathodic Reaction might be Possible



# Stabilization with Reduced Cathodic Reaction might be Possible





# Conclusions

- **Approach to stability calculation demonstrated to be useful.**
  - **Post initiation, focuses on maintaining aggressive conditons**
- **Using abstractions of key parameters from experimental data, reasonable predictions can be made regarding effects of:**
  - **Ionic strength (pH dependence of kinetics)**
  - **Crevice Gap**
  - **Cathodic reaction within crevice**
- **Effect of ionic strength on pH is critical to stabilization**
  - **Need lower pH due to high ionic strength to keep dissolution high**
- **Internal cathodic reaction inhibits stabilization under most conditions**
- **Crevice stabilization could occur with reduced cathodic reactions or when cathodic reaction is suppressed inside the crevice**