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Center for Electrochemical Science and Engineering

University of Virginia

Computational Modeling of Crevice Corrosion Stability of Wetted SS316L

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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/OST&I

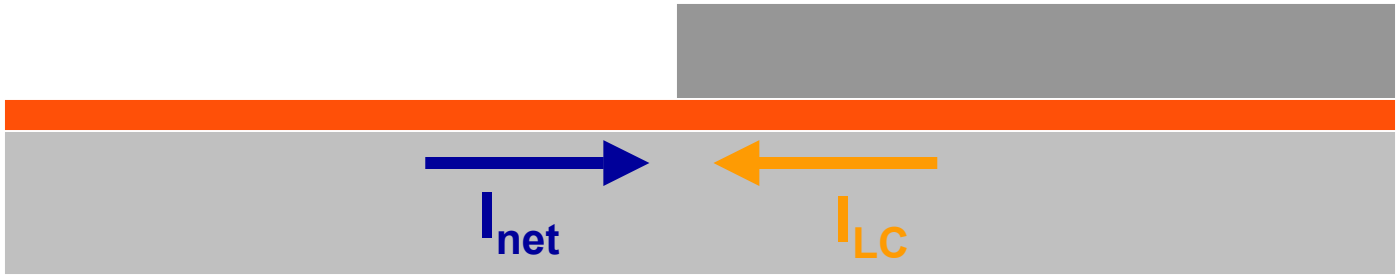
Introduction

- Corrosion resistant material are subject to localized corrosion under atmospheric conditions
- Corrosion rate and stability are controlled by both external cathodic and internal anodic reaction rates
  - Must match anode needs with cathode capacity
- There are many physiochemical and kinetic parameters
- Experimental work is challenging due to difficulties in measurements of interest

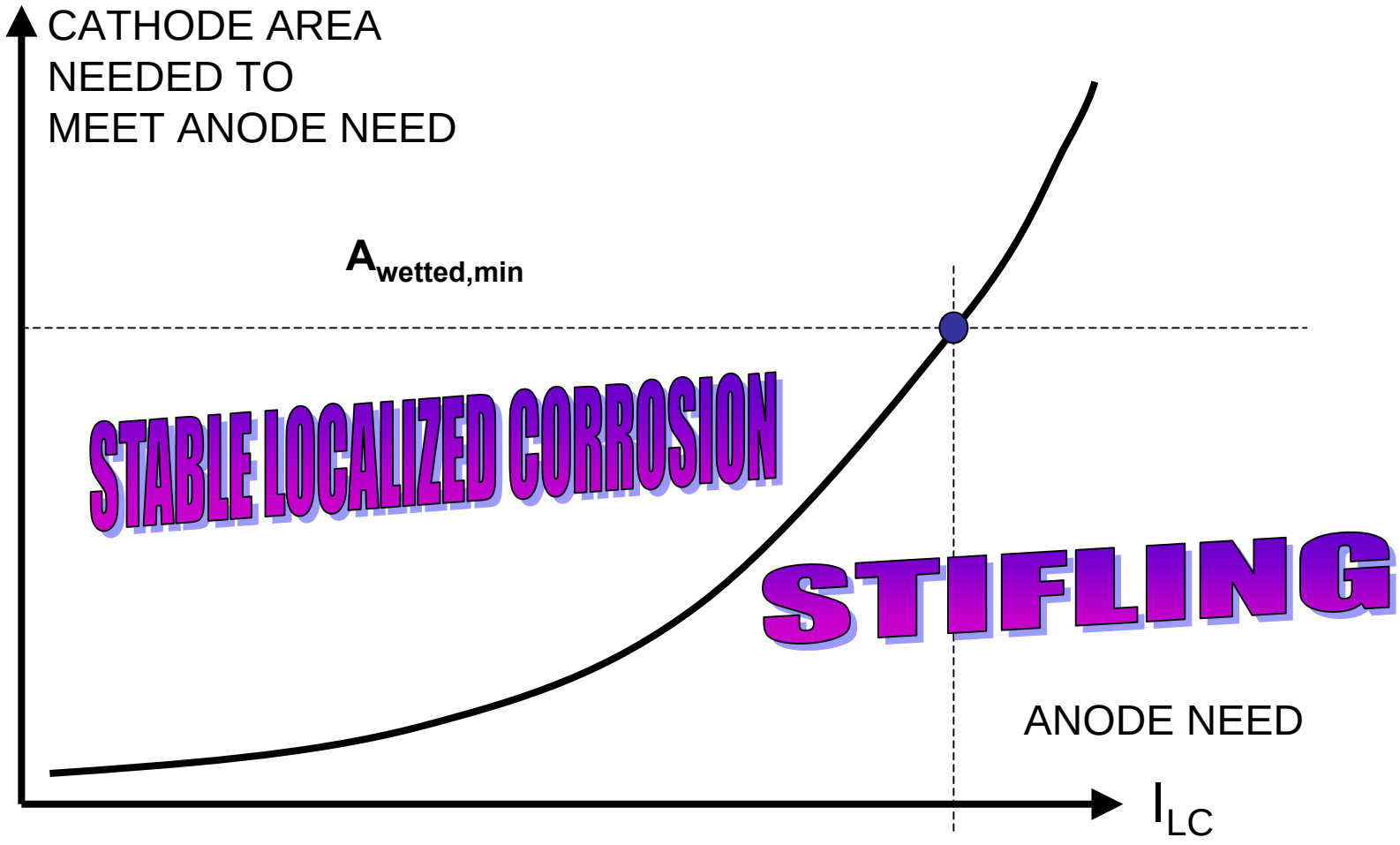
Stability of Localized Corrosion

Crevice with Thin Layer External Cathode

- Current demand from crevice met (or not) by current from external surface

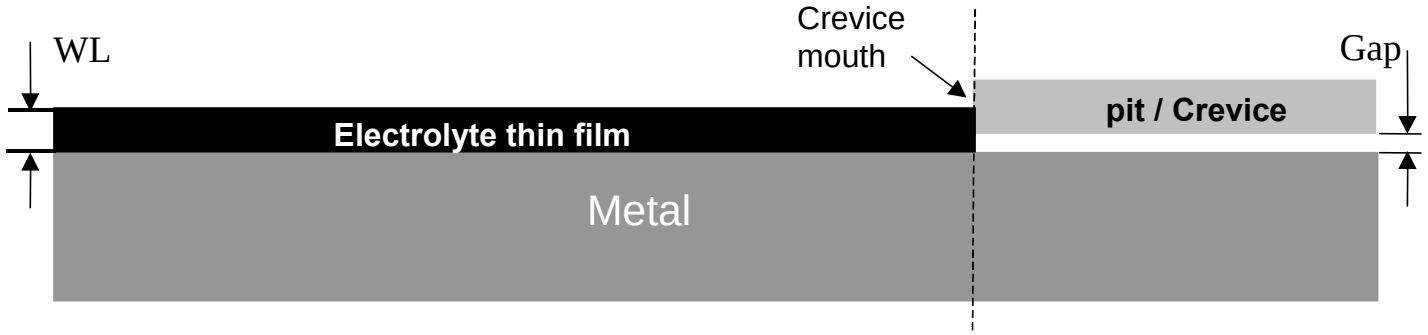


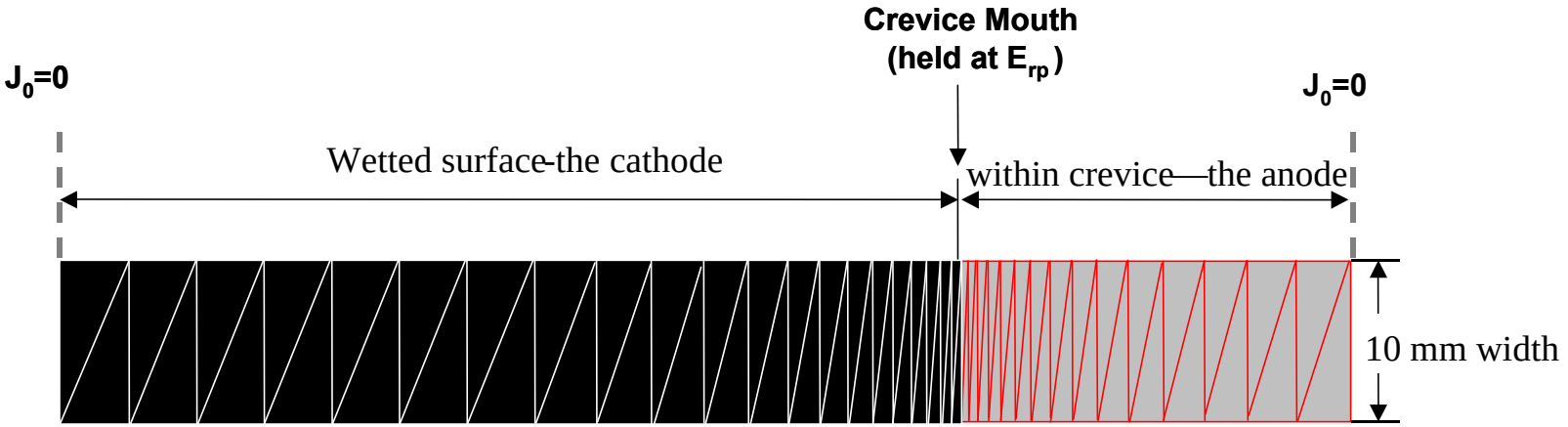
Stability Requires Cathode Current Capacity Meets Anode Current Demand



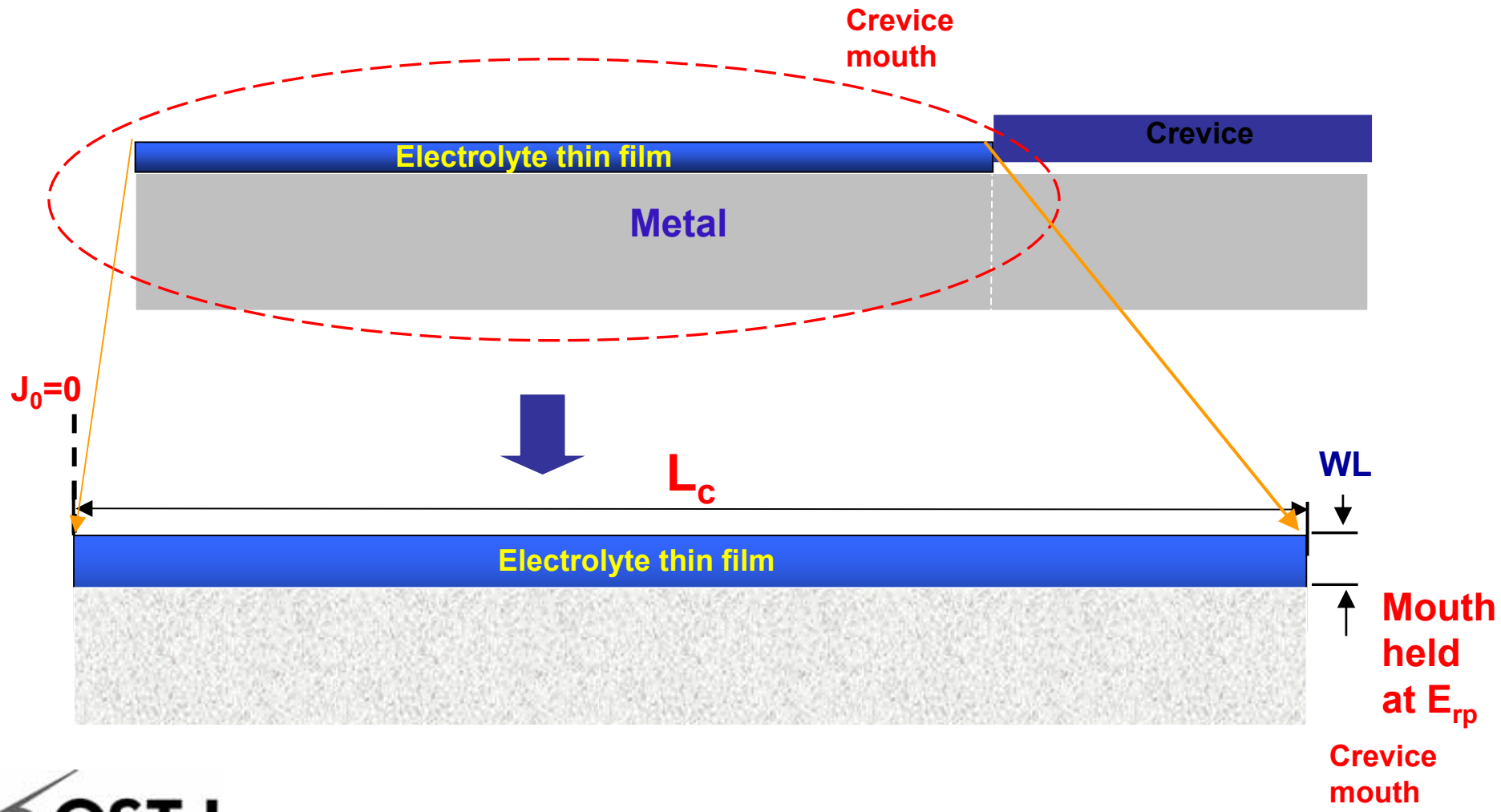
Approach

Model cathode and anode separately, link by E_{rp} of the anode at crevice mouth





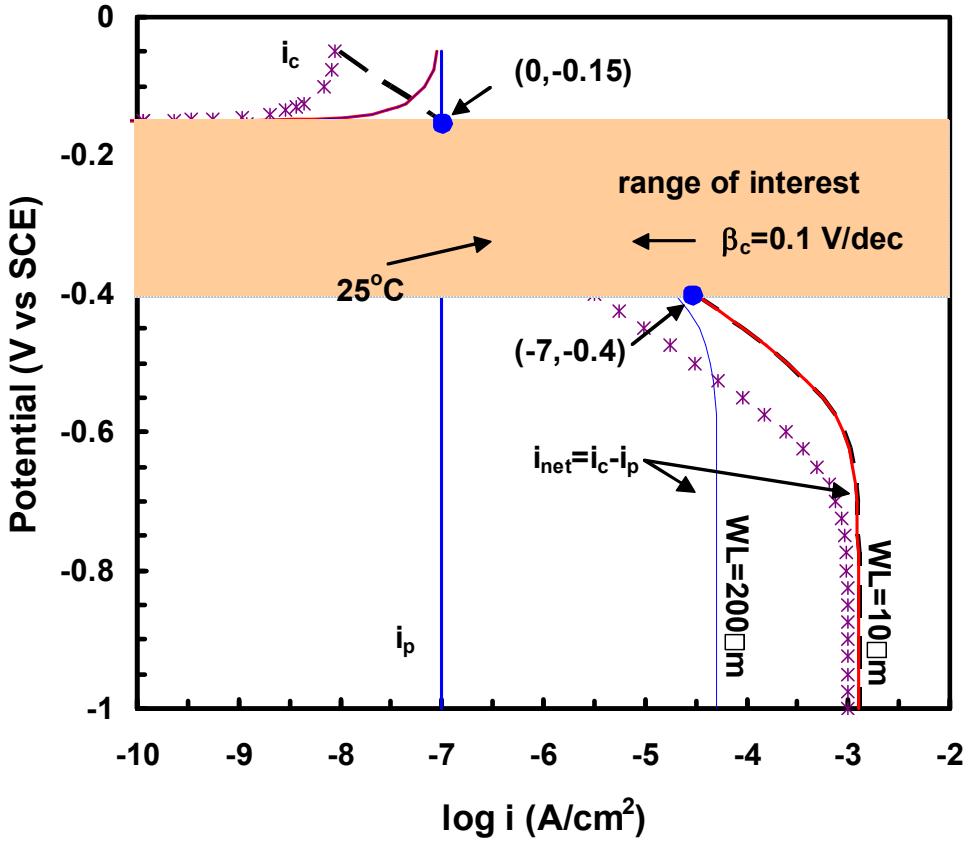
Cathode Modeling



Modeling on the External Wetted SS316L Surface (Cathode)

- Consider only the cathode in detail
  - Potential hold at E_{rp} at mouth
- Calculate total net cathodic current, I_{net}
  - Effects of WL, [Cl-] and Lc
    - Using a 3^3 factorial design
  - Effect of T
    - 95 vs 25°C
  - Effect of kinetic parameters
    - (io,c, bc, Erp and ip) (full factorial of [Cl-] and Lc)

Electrochemical Kinetics Used for Cathode



Base Case

E_{corr}=-0.15 V

$E_{o,c}$=-0.05 V

E_{rp}=-0.4 V

$i_{o,c}=10^{-8}$ A/cm^2

$i_p=10^{-7}$ A/cm^2

B_c=100 mV/dec

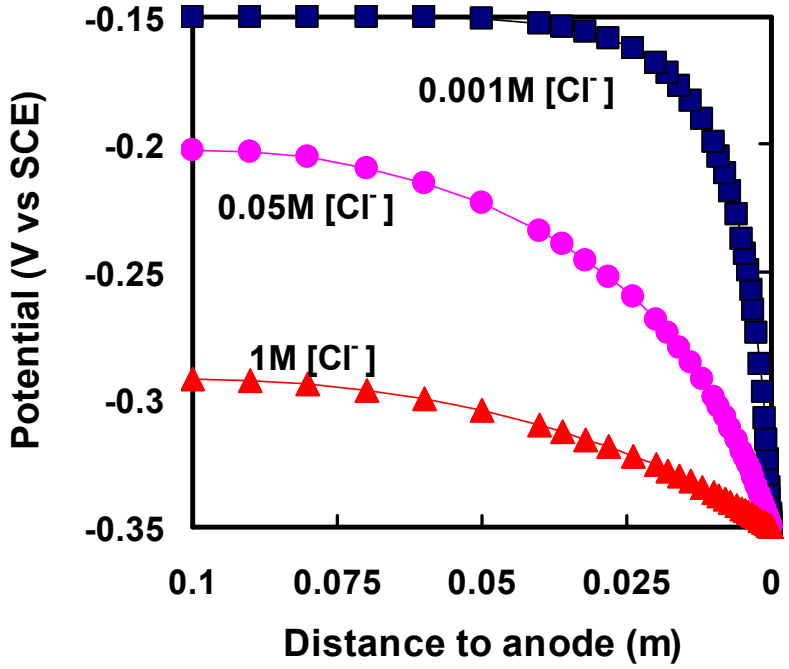
$i_{lim}=nFDC_{o2}/WL$

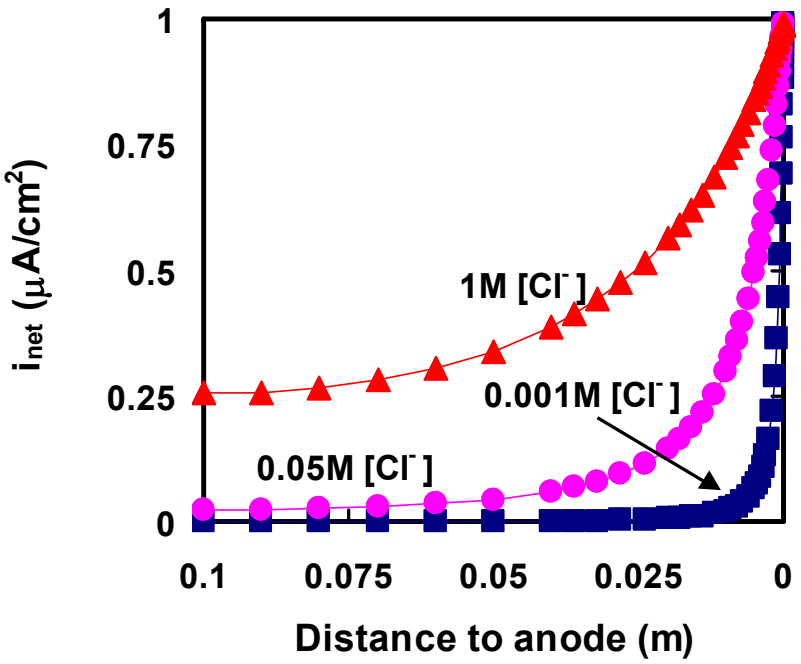
T=95°C

D.S. Dunn, G.A. Cragnolino, N. Sridhar, Corrosion 56, 1 (2000). p. 90
N. Scridhar and G.A. Cragnolino, Corrosion 49, 11 (1993), p885

Typical Model Outputs

(Base cases, WL=25 mm, L_c=10cm)





Potential increased and i_{net} decreased with distance to anode

Analysis of Variance

Quantified Effect of WL, L_c and [Cl^-] from 3^3 Factorial Design

Source of Variation	Ratio to WL
WL	1
L_c	1.97
Cl	4.74
WL x L_c	0.60
WLxCl	0.24
ClxL$_c$	1.28
WLxL$_c$xCl	0.36
Total	

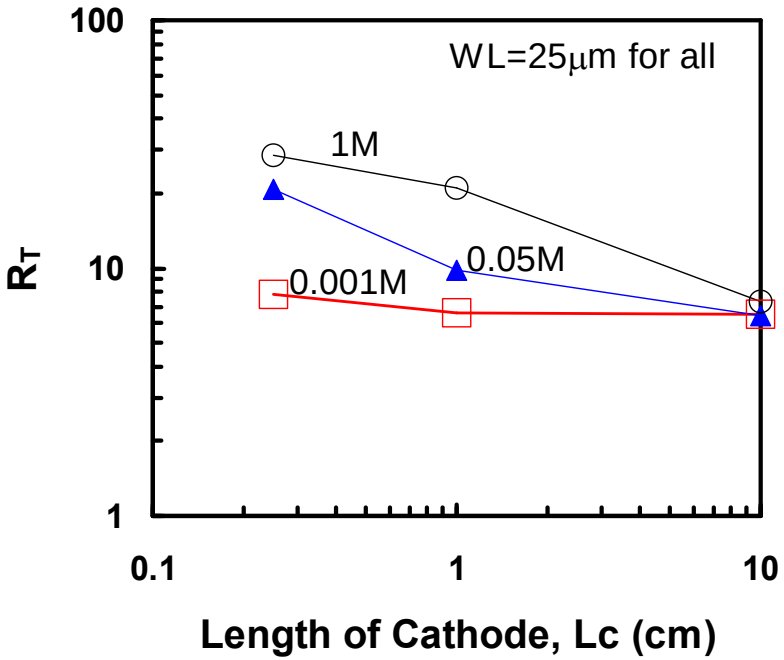
For Cathode Area =0.01cm^2 (10cmx10μm)

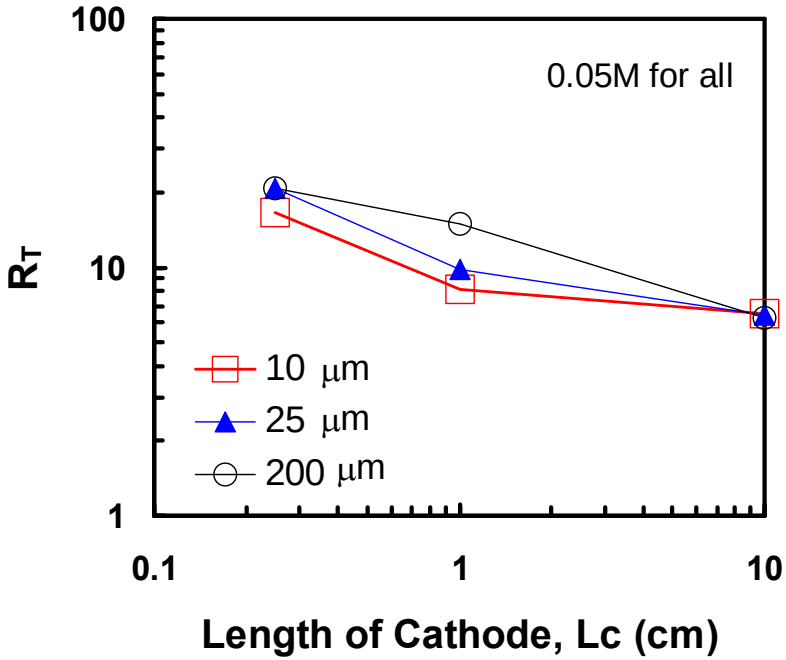
6.6 x10^{-10} < I total <7.2 x10^{-8} (A)

Significant interactions between L_c x Cl; None of the three effects include WL

Effect of Temperature (95 vs 25° C)

$$R_T = \frac{I_{net}(T = 95\,^{\circ}C)}{I_{net}(T = 25^{\circ}C)}$$

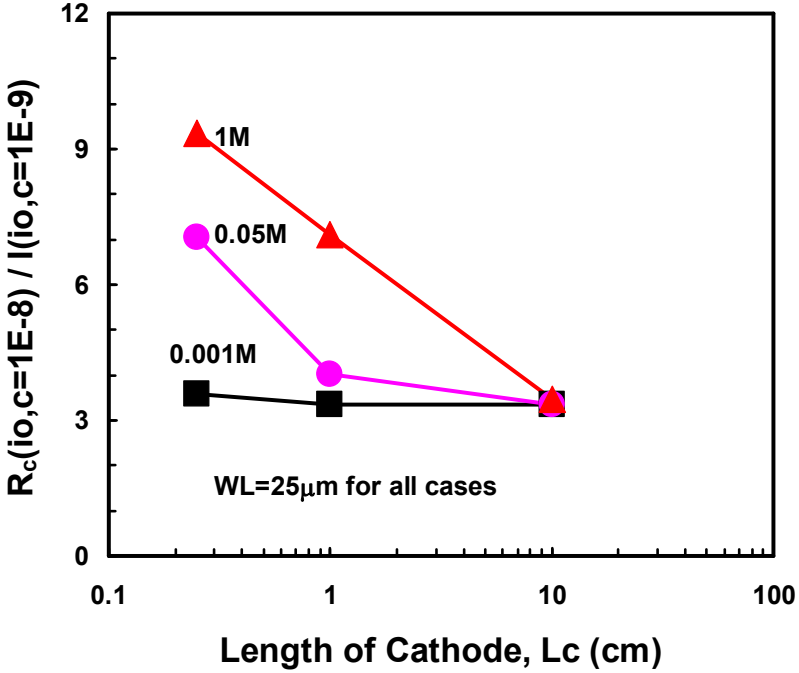




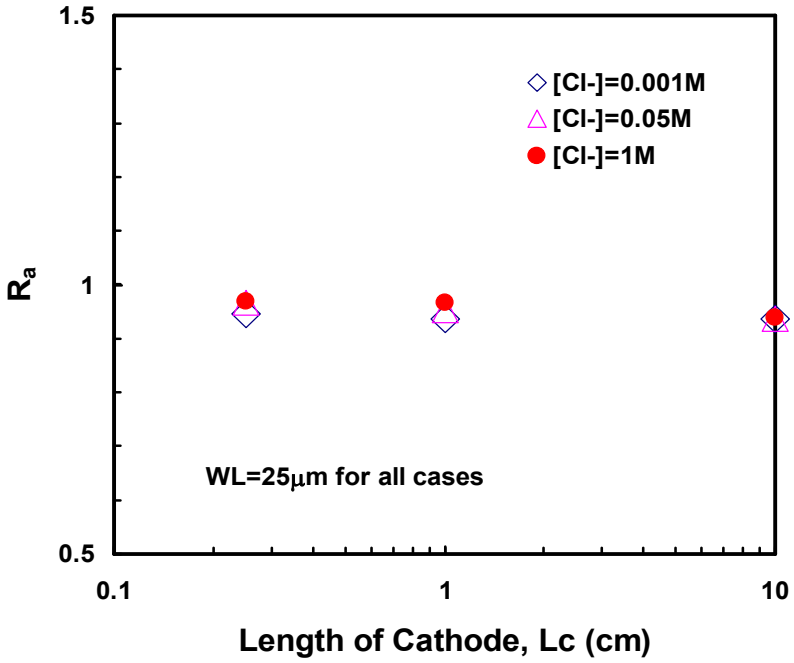
- **Total net cathodic current increased at least 5.5 times**
- **R_T decrease with L_c**

Effect of Kinetic Parameters

$$R_C = \frac{I_{net}(i_{oc} = 10^{-8})}{I_{net}(i_{oc} = 10^{-9})}$$



$$R_a = \frac{I_{net}(i_p = 10^{-6})}{I_{net}(i_p = 10^{-7})}$$

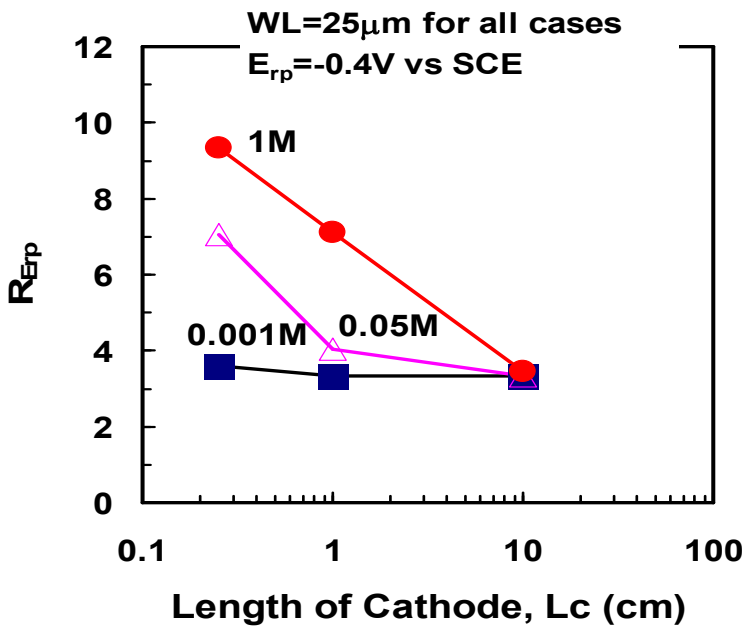


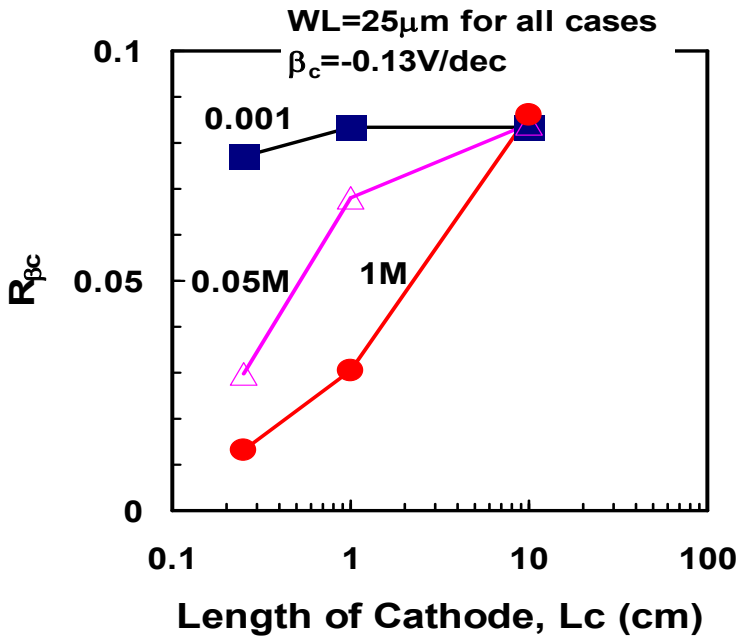
- i_{oc} has significant effect while i_p has very small effect;
- R_c approach a constant at large L_c

Effect of Kinetic Parameters (continued)

$$R_{E_{rp}} = \frac{I_{net}(E_{rp} = -0.4V)}{I_{net}(E_{rp} = -0.3V)}$$

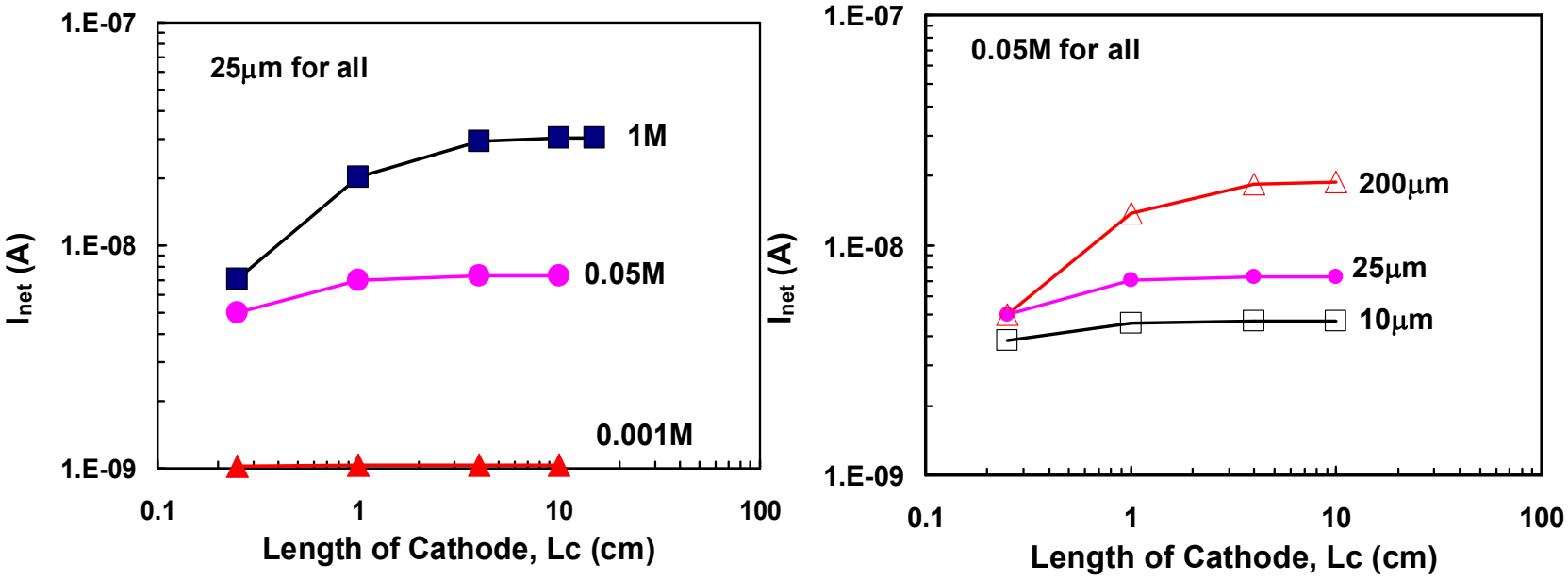
$$R_{\beta_c} = \frac{I_{net}(\beta_c = 0.1\text{V/dec})}{I_{net}(\beta_c = 0.06\text{V/dec})}$$





- E_{rp} and βc both have significant effects on I_{net}
- R values approach to a constant value at large L_c

Total Current from Cathode Saturates



(WL=25mm)

For anode= 1 x 10 μm

[Cl-] increases I_{net} less than linearly

WL increases I_{net} more significantly at larger cathodes

Model Projections for Cathode Size at Saturation

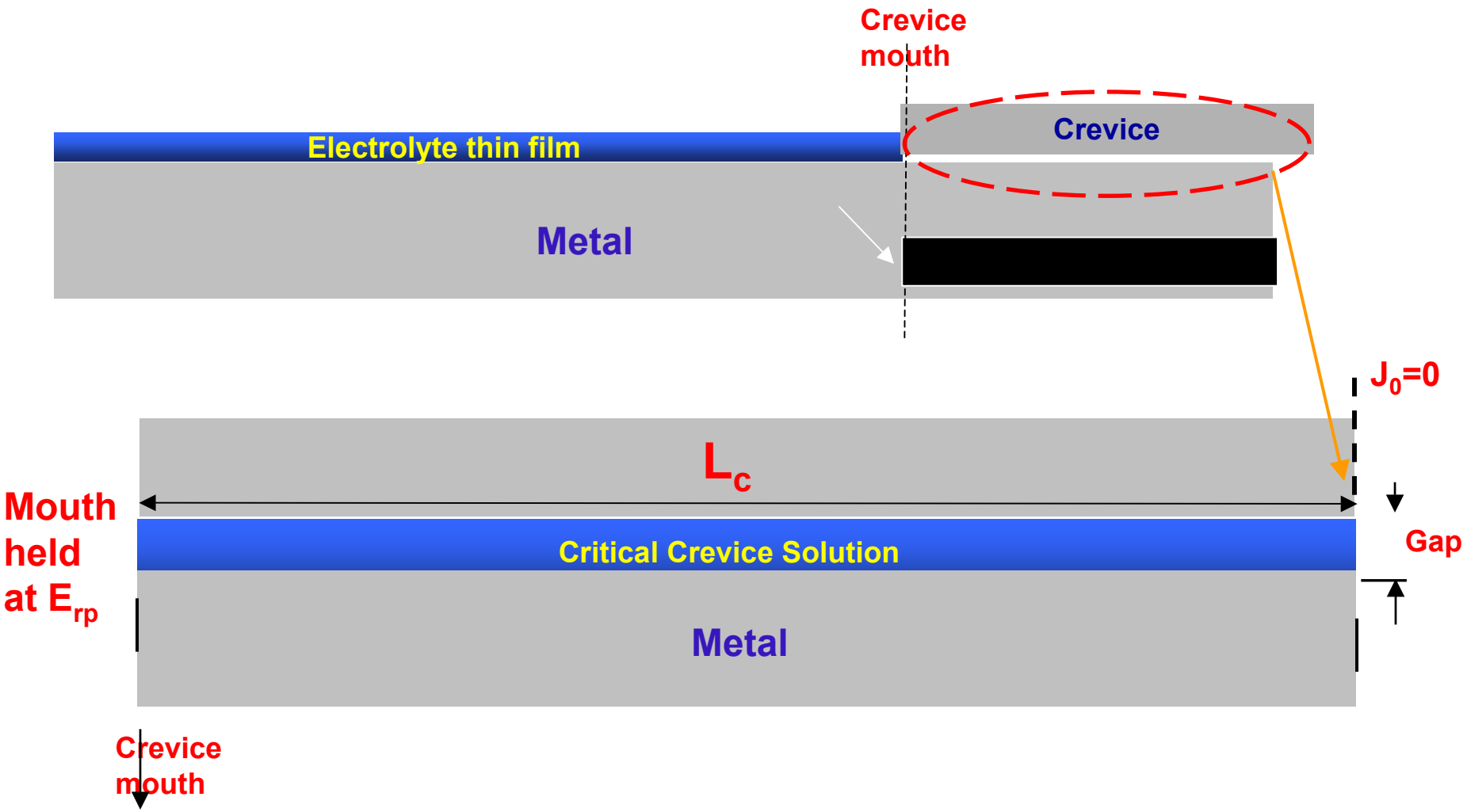
WL μm	10	10	10	25	25	25	200	200	200
$[Cl^-]$ M	0.001	0.05	1	0.001	0.05	1	0.001	0.05	1
L_c (cm) needed for 98% I_{max}	0.25	1	4	0.25	4	10	1	10	15
98% I_{max} (A)	$6.6 \cdot 10^{-10}$	$4.6 \cdot 10^{-9}$	$1.9 \cdot 10^{-8}$	$1.0 \cdot 10^{-9}$	$7.3 \cdot 10^{-9}$	$3.0 \cdot 10^{-8}$	$2.6 \cdot 10^{-9}$	$1.9 \cdot 10^{-8}$	$7.5 \cdot 10^{-8}$

Base Case

E_{corr}=-0.15 V, $E_{o,c}$=-0.05 V, E_{rp}=-0.4 V, $i_{o,c}=10^{-8}$ A/cm^2, $i_p=10^{-7}$ A/cm^2

B_c=100 mV/dec, $i_{lim}=nFDC_{o2}/WL$, T=95°C

Anode Modeling

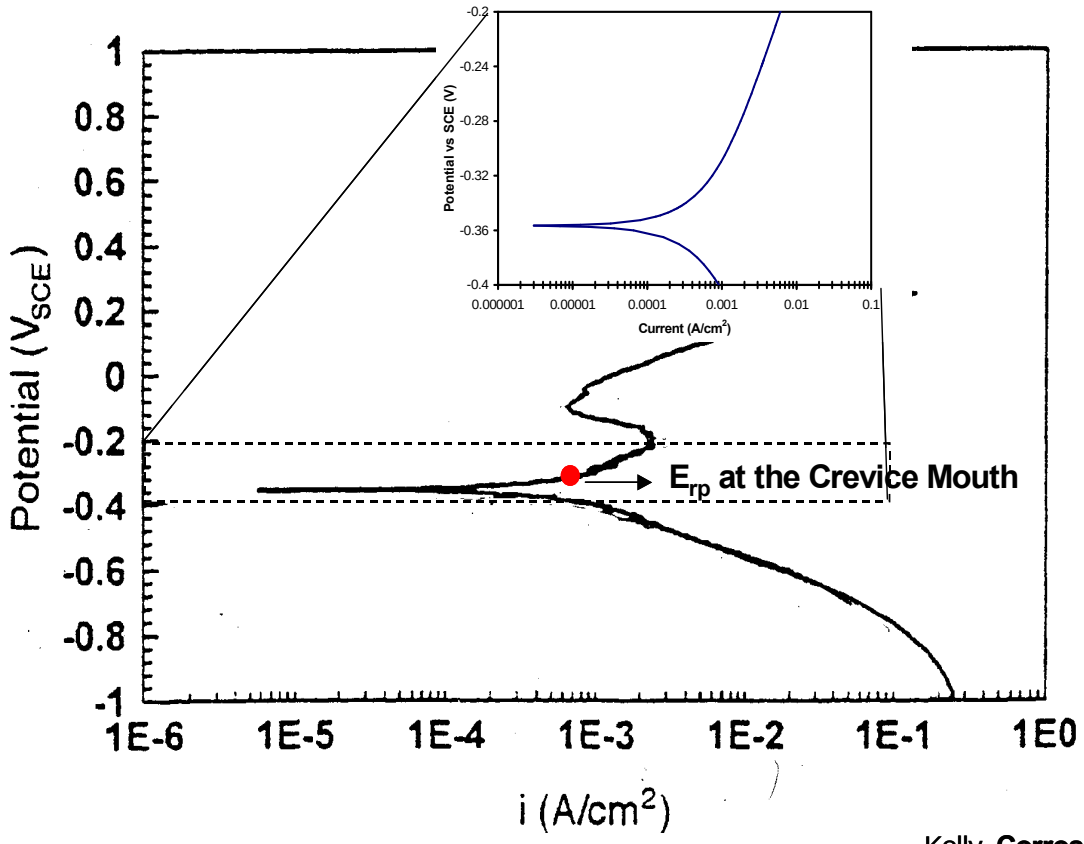


Modeling on the SS316L Crevice (anode)

- Assume constant crevice chemistry, E_{rp} at mouth
- Calculate potential and current distribution
  - Variables: Gap, L (Crevice Depth)
  - Constants: Anodic kinetics (E_{rp}, E-Log i) from literature
  - Room T

Electrochemical Kinetics

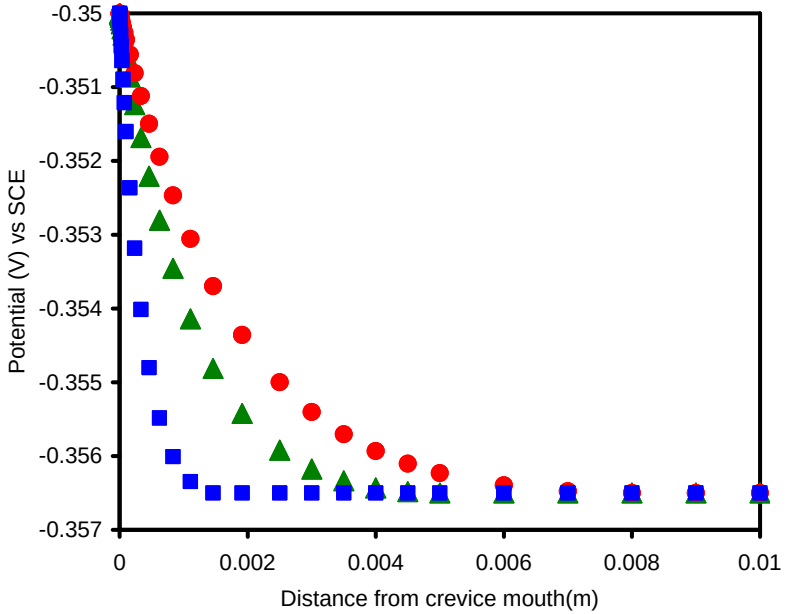
- **Extracted from literature from measurements in Critical Crevice Solution**

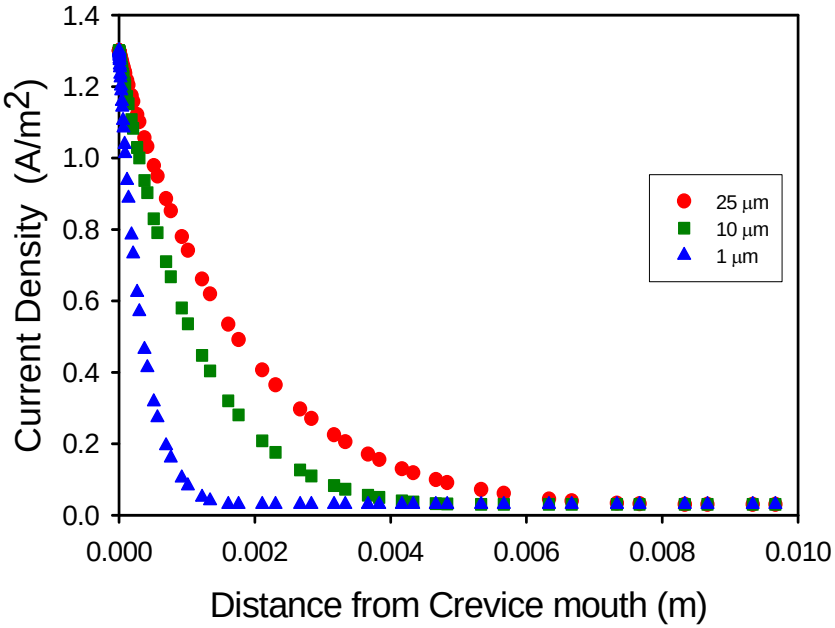


pH 0.73
$[Cl^-]$ = 10 M

Kelly, **Corrosion 51**,11,p832

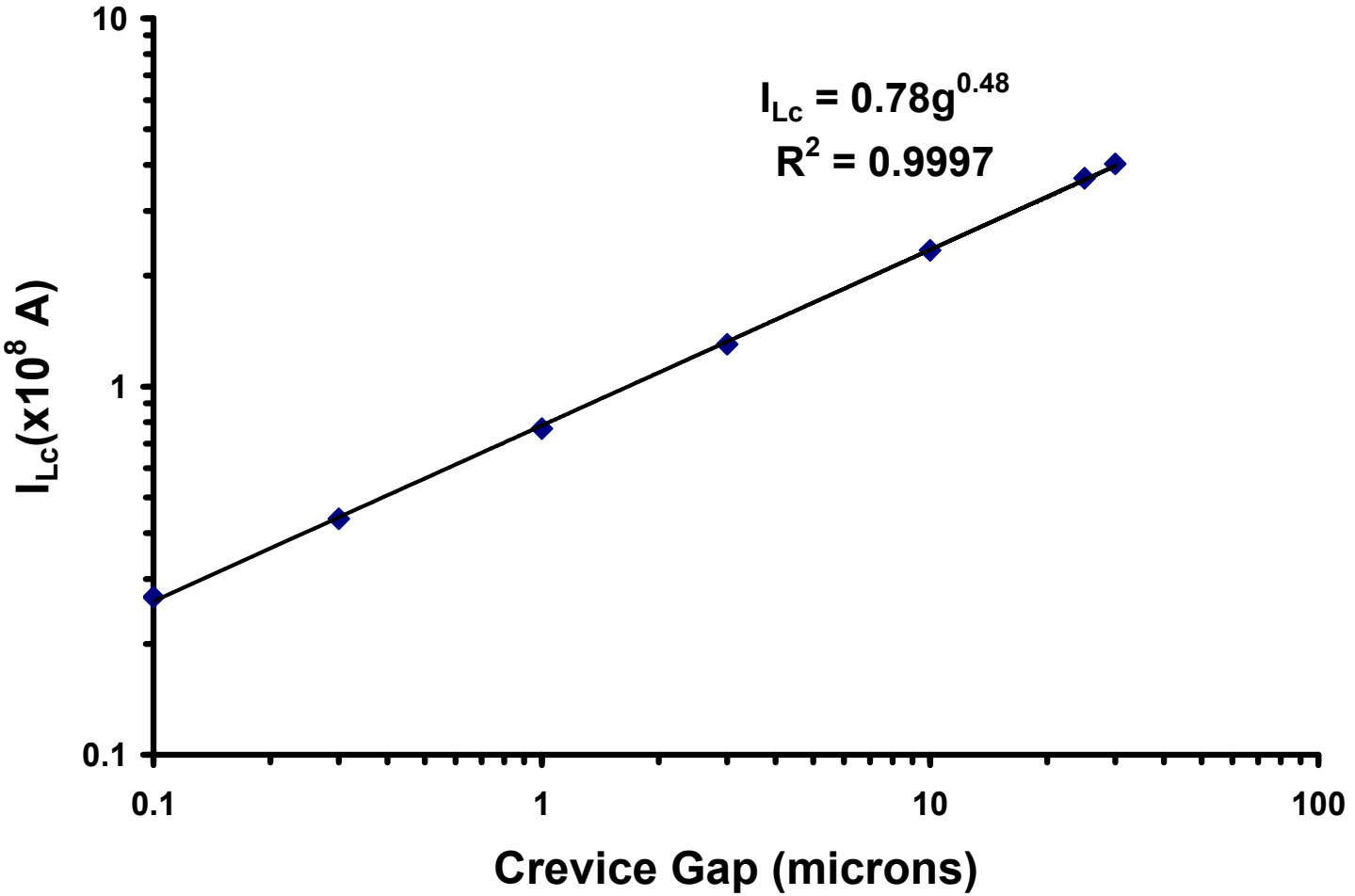
Typical Model Outputs





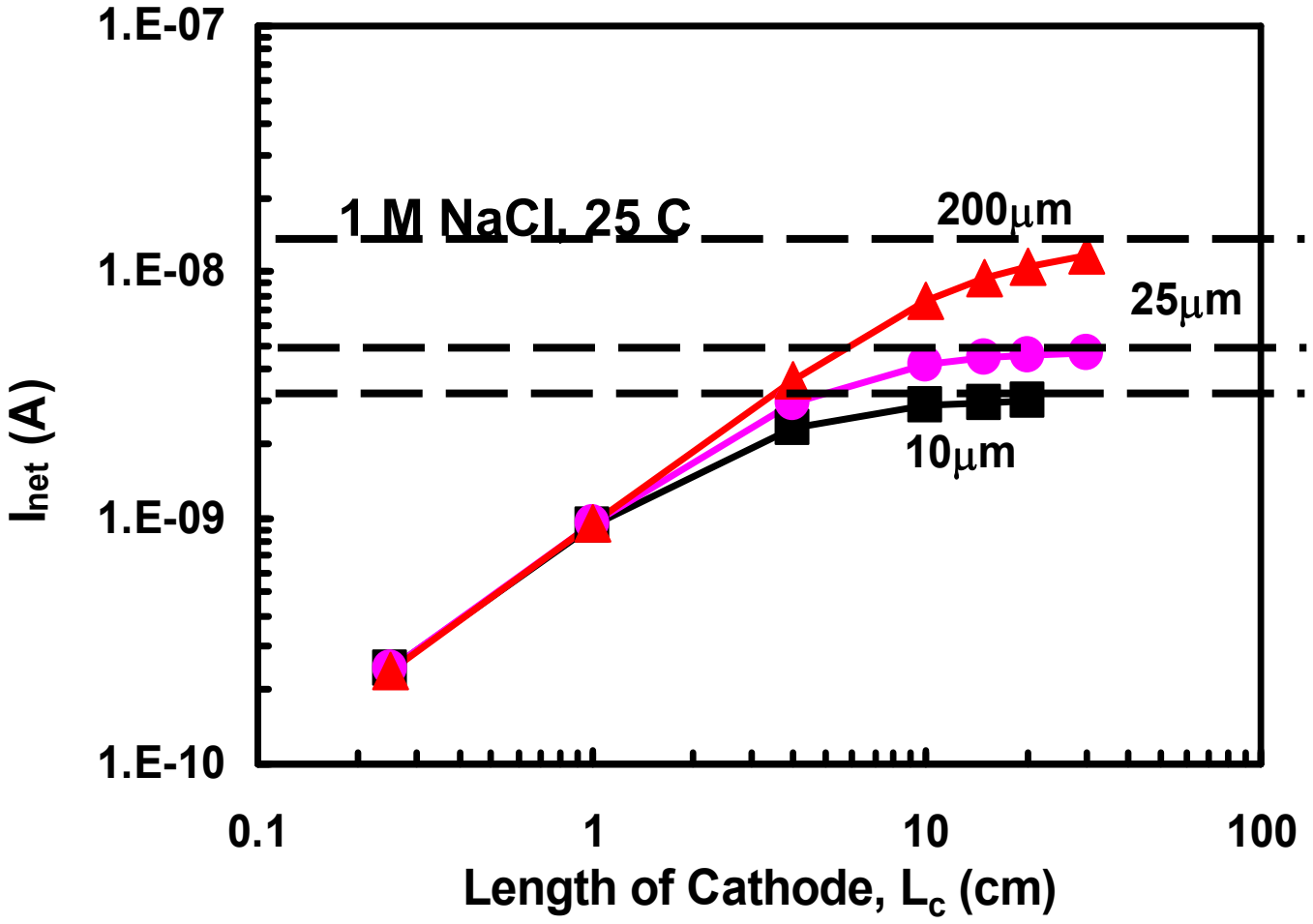
Potential and i decreased with depth into crevice

Crevice Current Demand ~ $g^{1/2}$

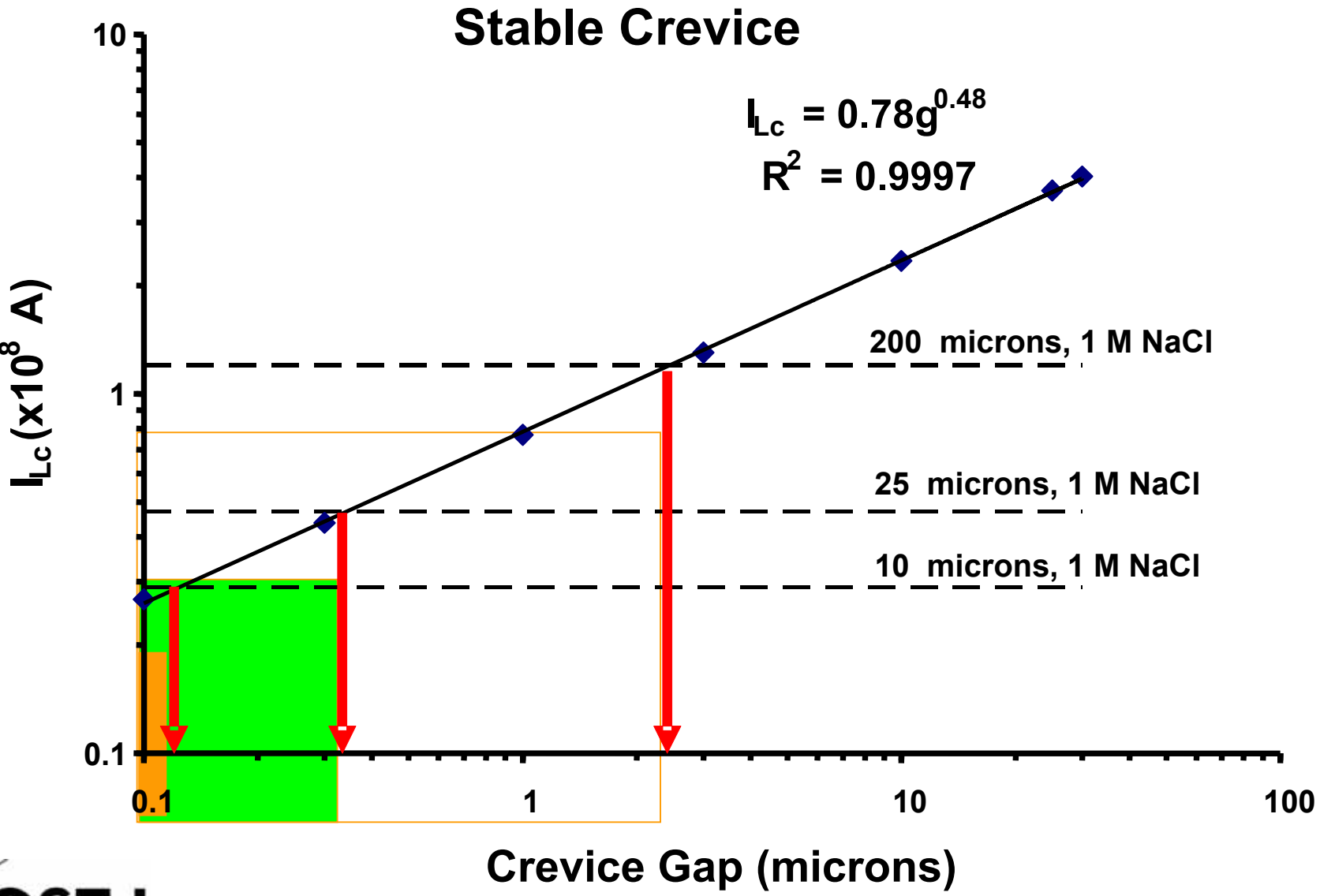


Only gaps smaller than arrows can stabilize

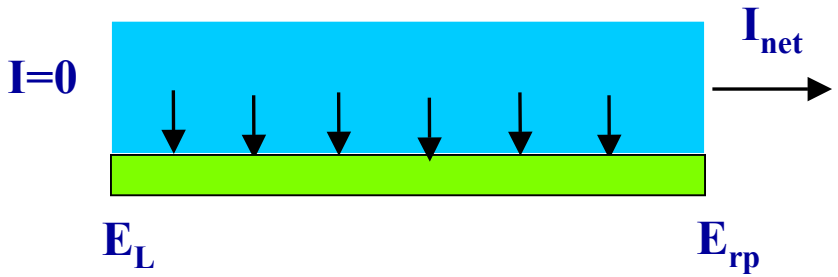
Recall that the I_{net} Saturates at High L_c



When Anode Demand = Cathode Capacity



Analytic Expression for Total Current from Wetted Surface



- Consider a surface with a thin electrolyte layer
- Fixed potential at one end (E_{rp}), other end has a zero flux
- Current sinks/sources along the length
- Assume:

$$I_{net} = i_{eq} \cdot L_{eq} \cdot W \quad \text{with} \quad i_{eq} = \frac{\int_{E_L}^{Erp} (i_c - i_p) \cdot dE}{E_L - E_{rp}} = \frac{\int_{E_L}^{Erp} (i_c - i_p) \cdot dE}{\Delta E}$$

Considering Secondary Current Distribution

- **Total Resistance of Electrolyte can be shown to be:**

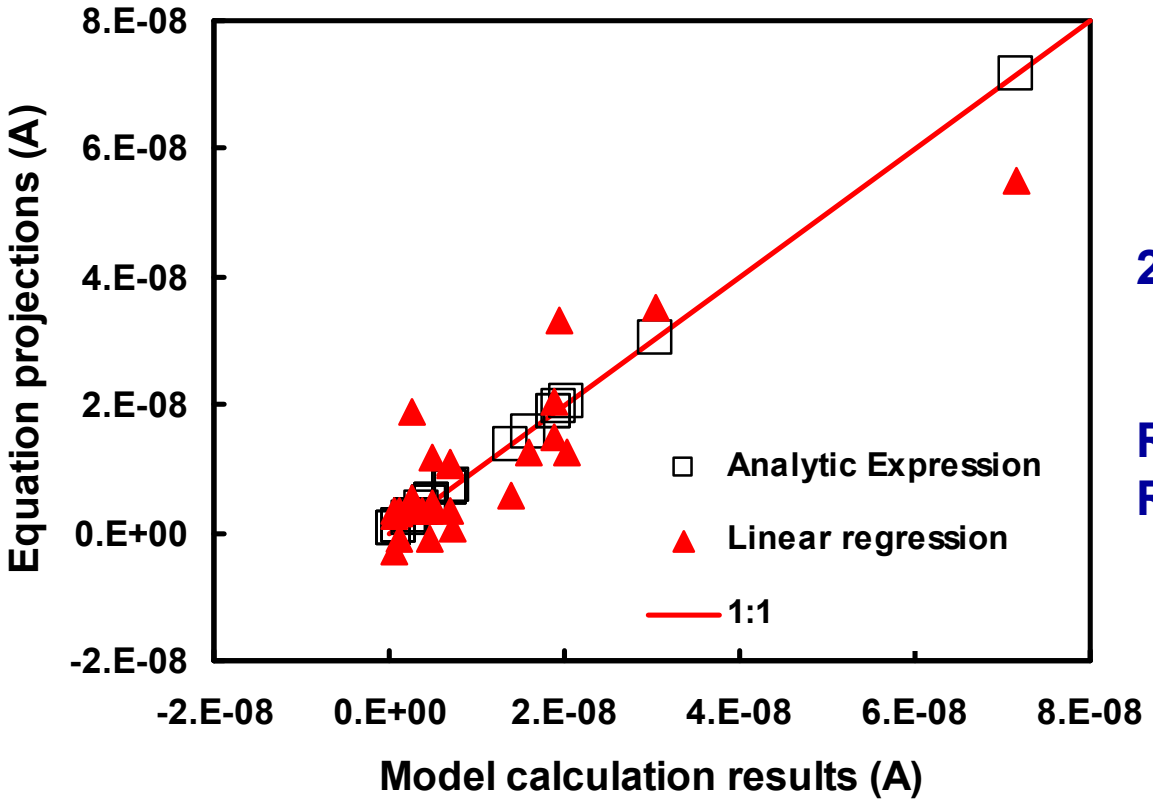
$$R = \frac{L_{eq}}{2 \cdot \sigma \cdot WL \cdot W}$$

- **Ohmic Potential Drop:**

$$\Delta E = E_L - E_{rp} = I_{net} \cdot R = \frac{I_{net} \cdot L_{eq}}{2 \cdot \sigma \cdot WL \cdot W}$$

$$\mathbf{I_{net} = W \cdot \sqrt{2 \cdot \sigma \cdot WL \cdot \int_{E_L}^{E_{rp}} (i_c - i_p) \cdot dE}}$$

Analytic Expression vs. Linear Regression



26 cases varying:
L_c, i_{oc}, T, β, σ, WL

R^2 (Analytic) = 1.0
R^2(Linear Regression) = 0.8

Expression reproduces observed effects of physiochemical and kinetic parameters

Conclusions

- Computationally separating the anode and cathode of wetted SS316L allowed effects of parameters on crevice corrosion stability by comparing I_{net} and I_{Lc}
  - Used to determine critical gap needed for stable crevice
- <u>Cathode</u>:
  - All physicochemical and kinetic parameters studied except i_p were found to have significant effect on I_{net}.
  - The I_{net} was found to reach I_{max} as L_c increased
- <u>Anode</u>:
  - Total current demand increased with $g^{1/2}$
- Analytic expression developed for total current from restricted geometry