

DT # 46525 QA-NA 12/12/2005

MOL.20060508.0050



OCRWM Office of Science and Technology and International

*Center for Electrochemical
Science and Engineering*



University of Illinois

Computational Modeling of Crevice Corrosion Stability of Wetted SS316L

Presented to:
208th ECS Meeting

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October 16, 2005

This presentation has been funded in whole or in part by the U.S. Department of Energy

Acknowledgements

- Support by the Office of Science and Technology 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
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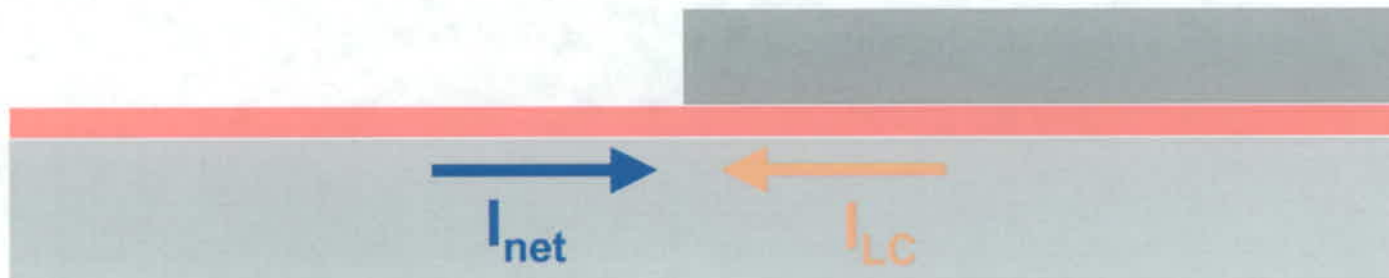
Introduction

- 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

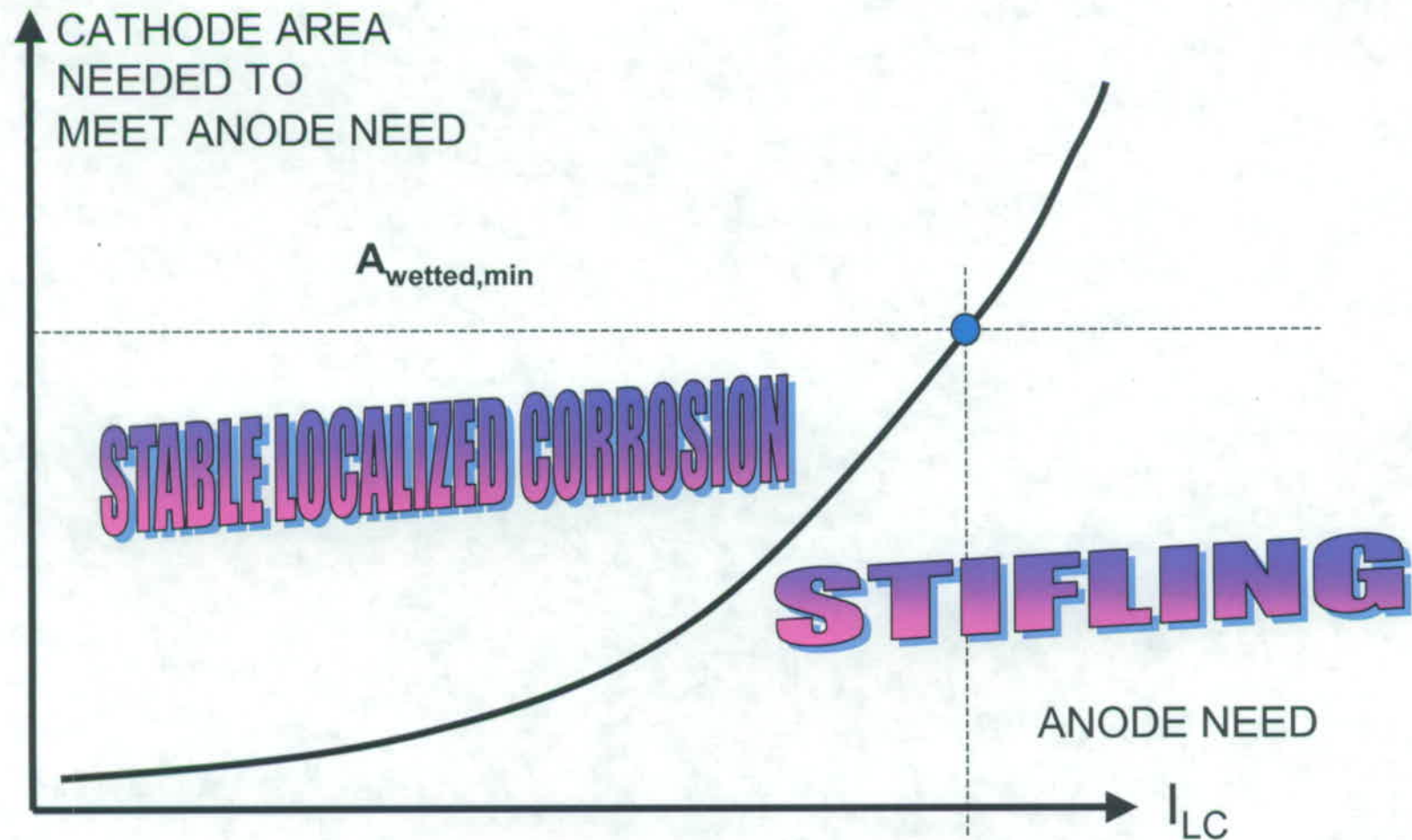
Stability of Localized Corrosion

Crevice with Thin Layer External Cathode

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

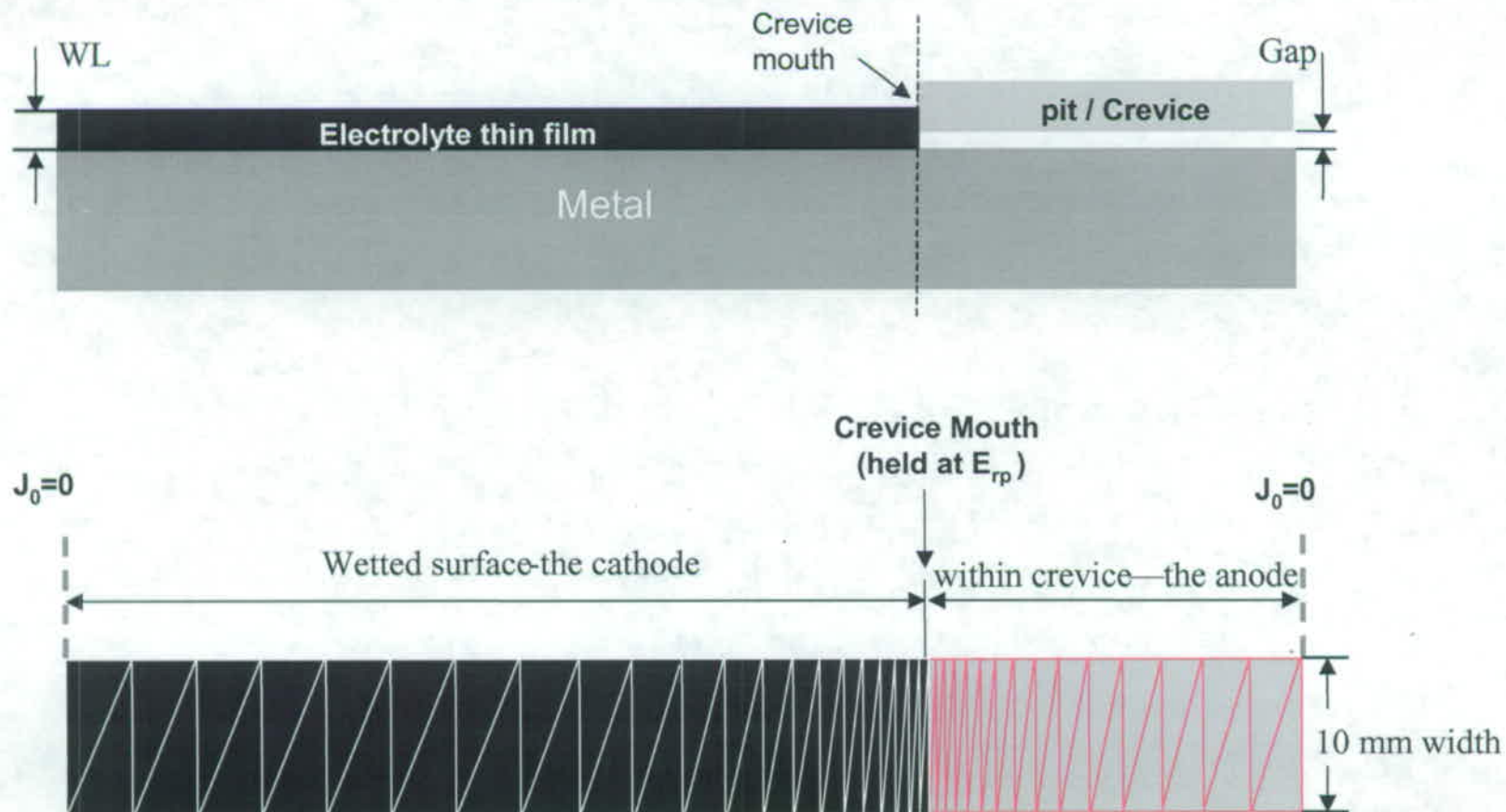


Stability Requires Cathode Current Capacity Meets Anode Current Demand

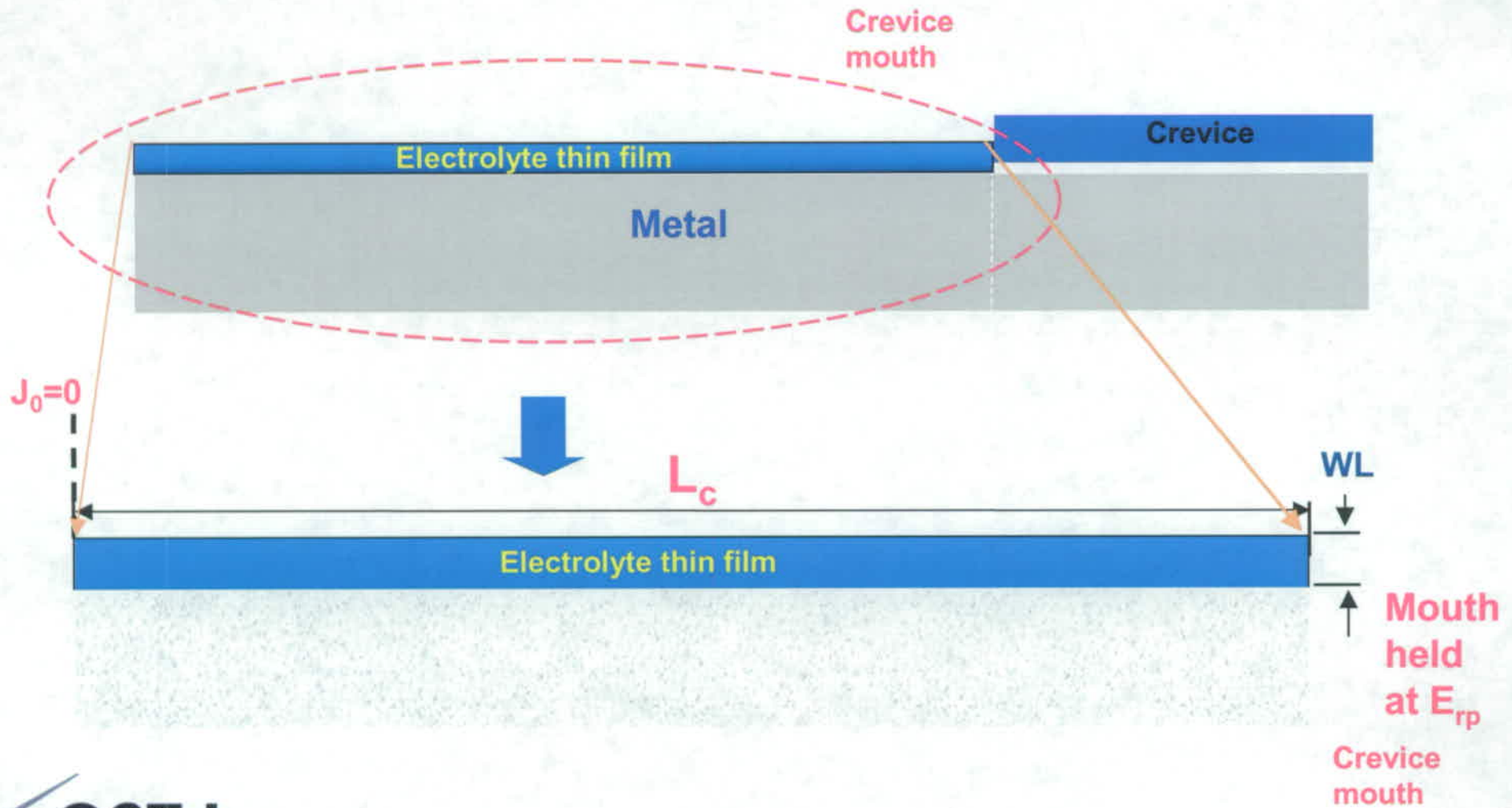


Approach

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



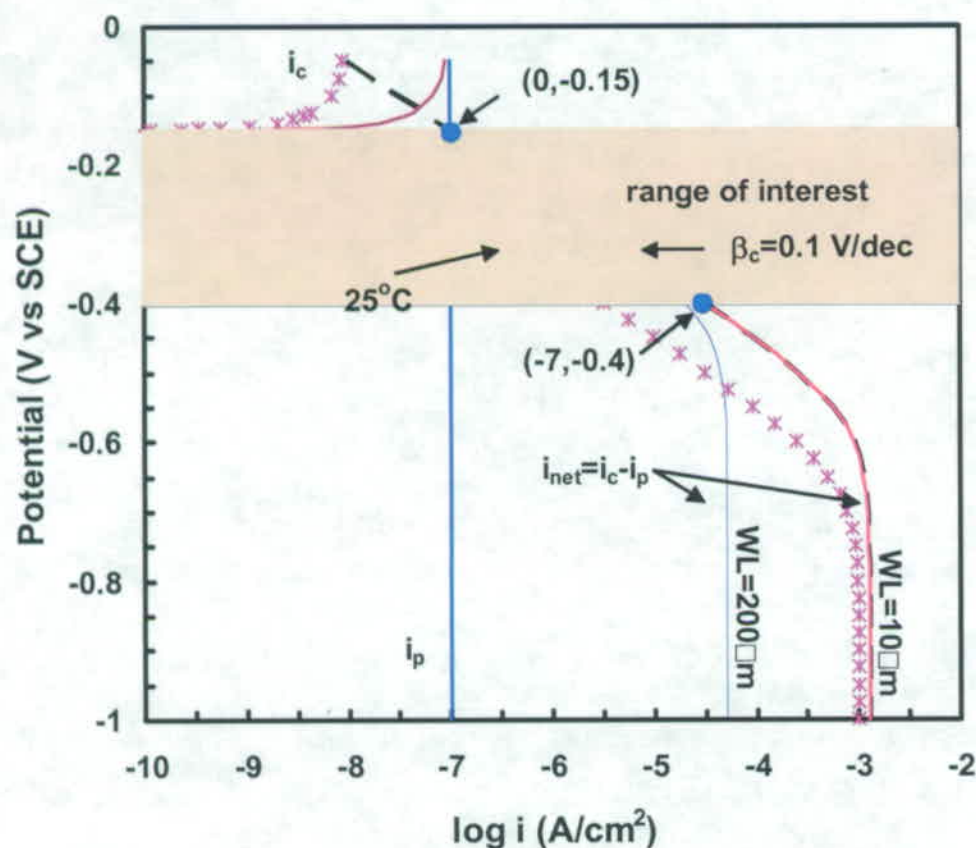
Cathode Modeling



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 3³ factorial design
 - > Effect of T
 - >> 95 vs 25°C
 - > Effect of kinetic parameters
 - >> ($i_{o,c}$, b_c , E_{rp} and i_p) (full factorial of [Cl⁻] and Lc)

Electrochemical Kinetics Used for Cathode

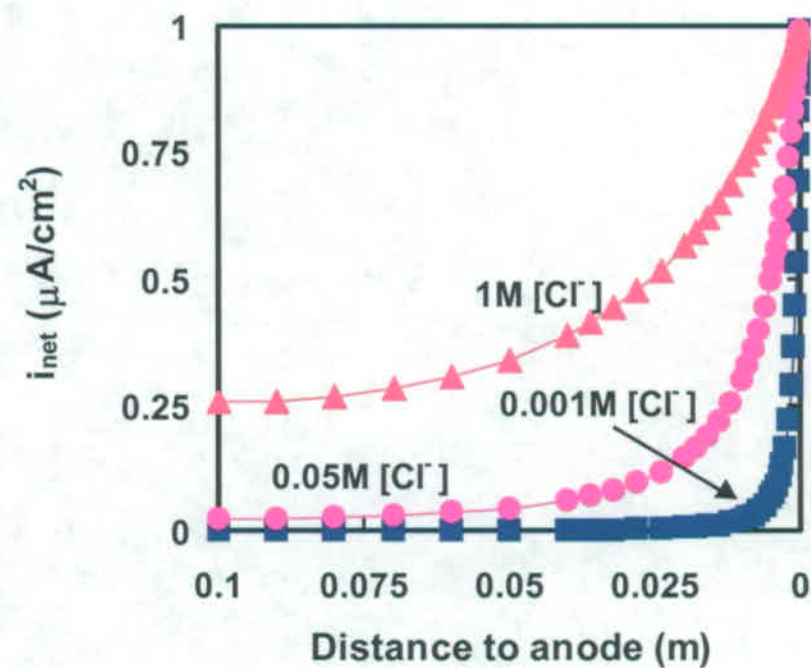
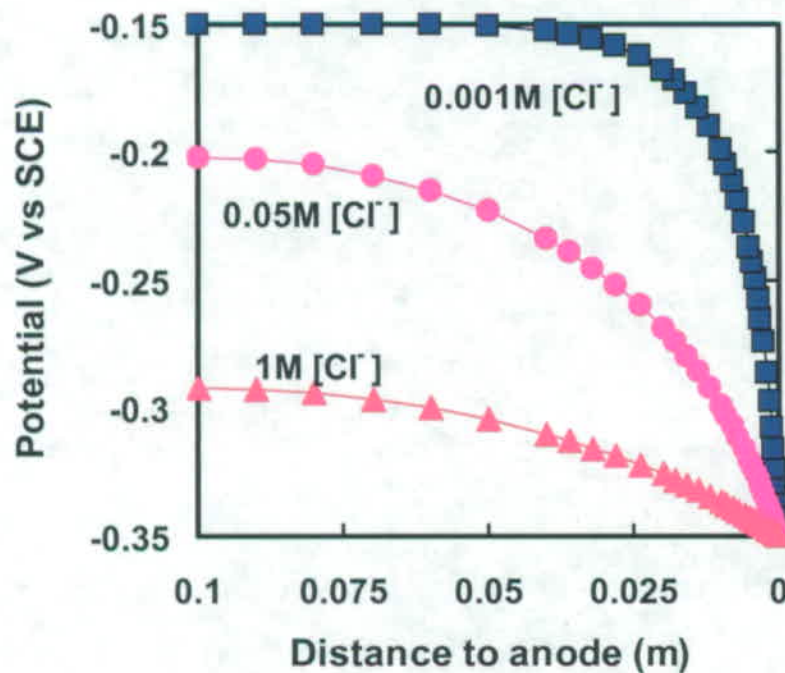


Base Case
 $E_{\text{corr}} = -0.15 \text{ V}$
 $E_{\text{o,c}} = -0.05 \text{ V}$
 $E_{\text{rp}} = -0.4 \text{ V}$
 $i_{\text{o,c}} = 10^{-8} \text{ A/cm}^2$
 $i_{\text{p}} = 10^{-7} \text{ A/cm}^2$
 $B_{\text{c}} = 100 \text{ mV/dec}$
 $i_{\text{lim}} = nFDC_{\text{o}_2}/WL$
 $T = 95^\circ\text{C}$

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

Typical Model Outputs

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



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
$WL \times L_c$	0.60
$WL \times Cl$	0.24
$Cl \times L_c$	1.28
$WL \times L_c \times Cl$	0.36
Total	

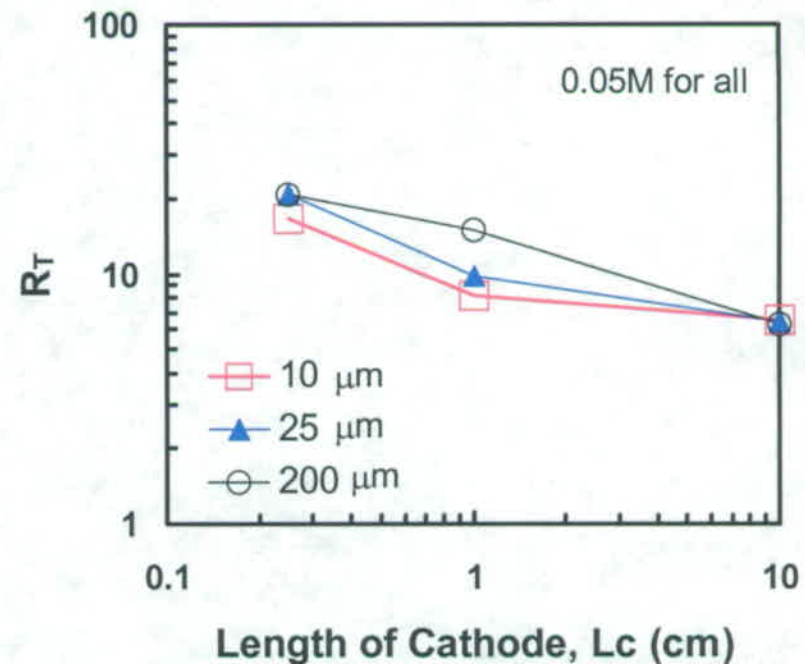
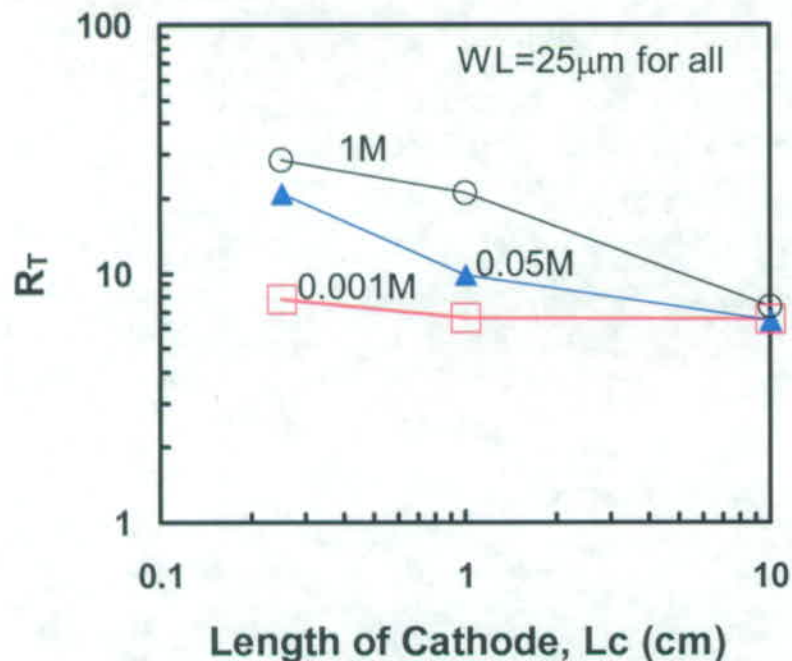
For Cathode Area = 0.01 cm^2
($10 \text{ cm} \times 10 \mu\text{m}$)

$6.6 \times 10^{-10} < I_{\text{total}} < 7.2 \times 10^{-8} \text{ (A)}$

Significant interactions between $L_c \times Cl$; None of the three effects include WL

Effect of Temperature (95 vs 25° C)

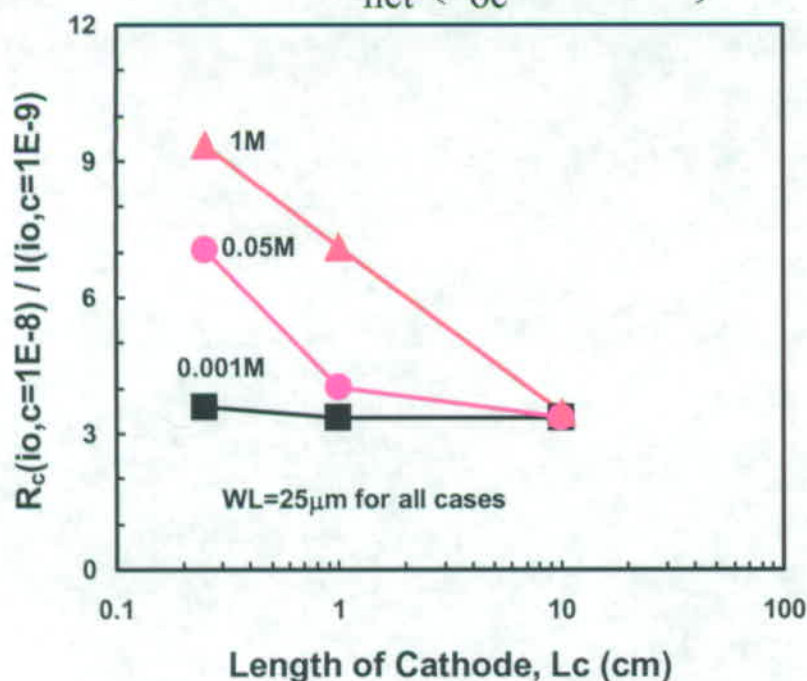
$$R_T = \frac{I_{\text{net}}(T = 95^\circ\text{C})}{I_{\text{net}}(T = 25^\circ\text{C})}$$



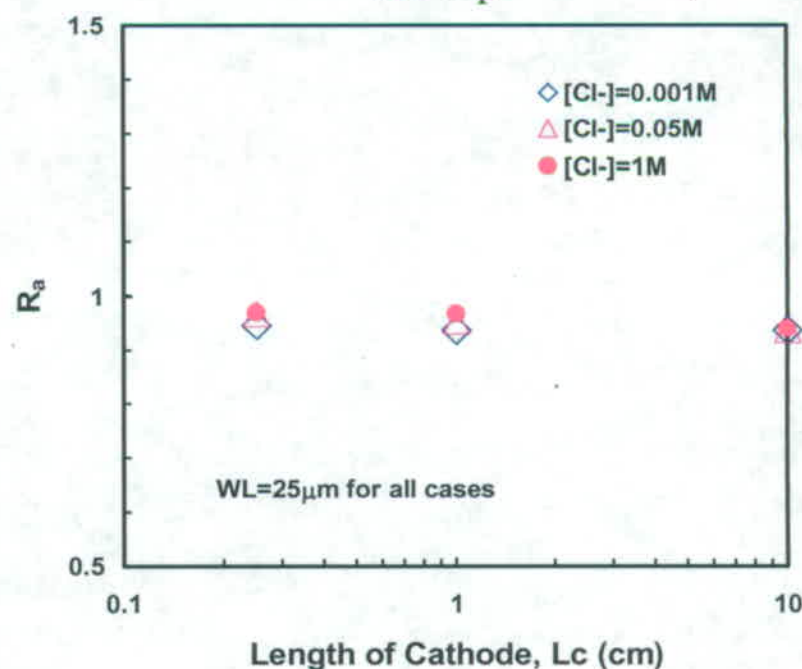
- Total net cathodic current increased at least 5.5 times
- R_T decrease with L_c

Effect of Kinetic Parameters

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



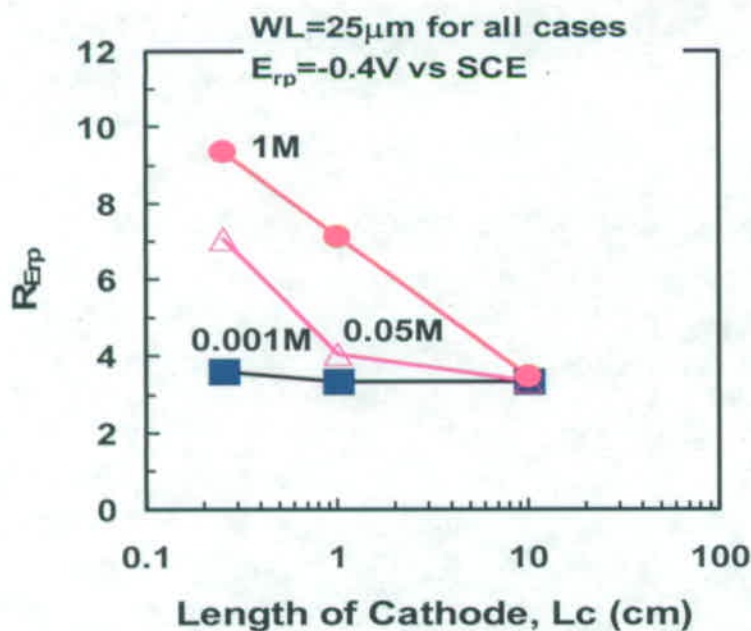
$$R_a = \frac{I_{\text{net}}(i_p = 10^{-6})}{I_{\text{net}}(i_p = 10^{-7})}$$



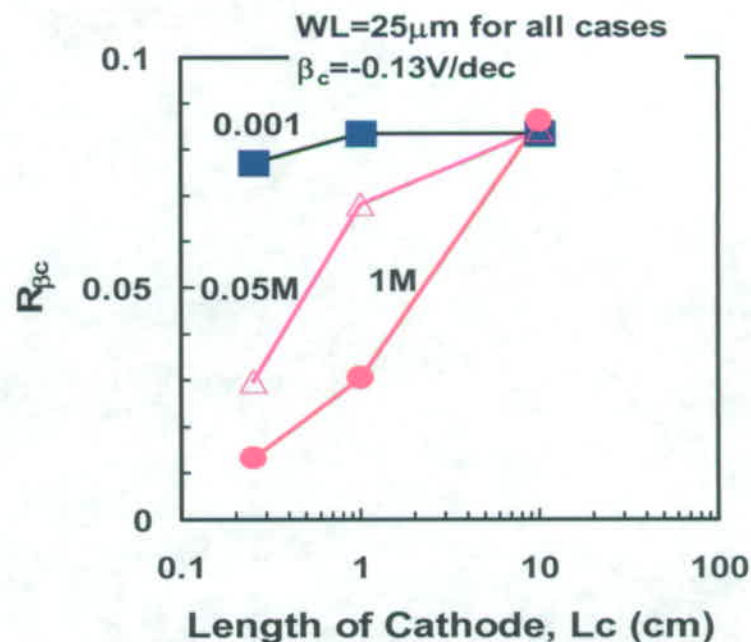
- i_{oc} has significant effect while i_p has very small effect;
- R_c approach a constant at large L_c

Effect of Kinetic Parameters (continued)

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

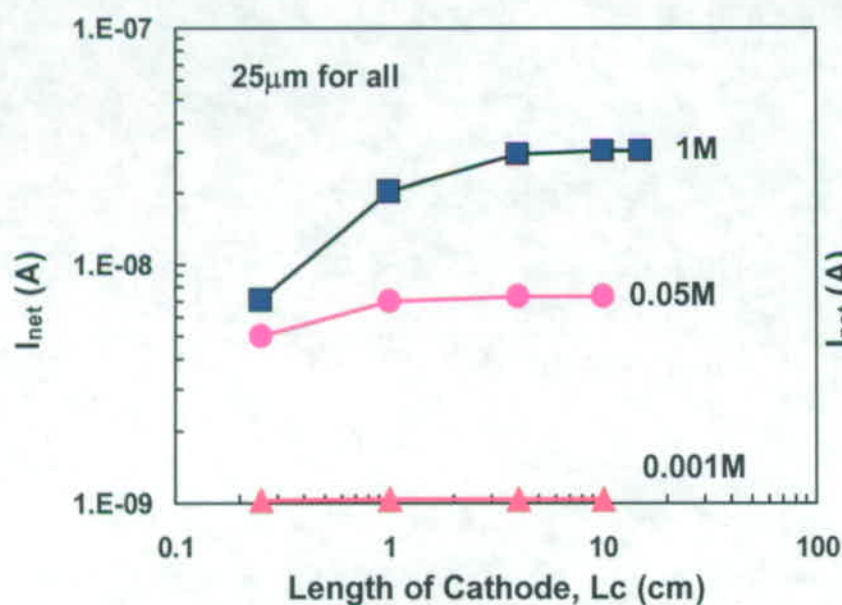


$$R_{\beta_c} = \frac{I_{net}(\beta_c = 0.1V/dec)}{I_{net}(\beta_c = 0.06V/dec)}$$



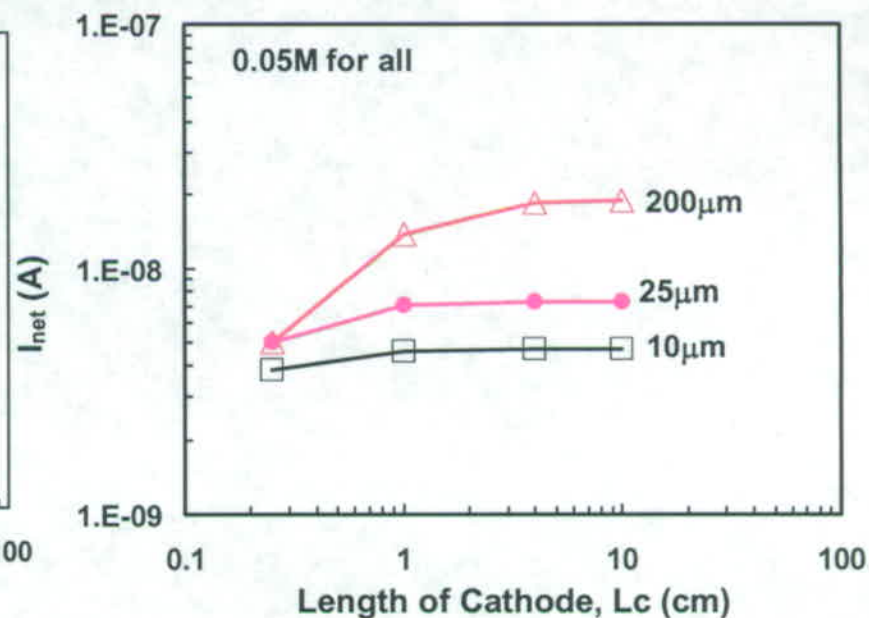
- E_{rp} and β_c both have significant effects on I_{net}
- R values approach to a constant value at large L_c

Total Current from Cathode Saturates



($WL=25mm$)

For anode = $1 \times 10 \mu m$



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

WL increases I_{net} more significantly at larger cathodes

Model Projections for Cathode Size at Saturation

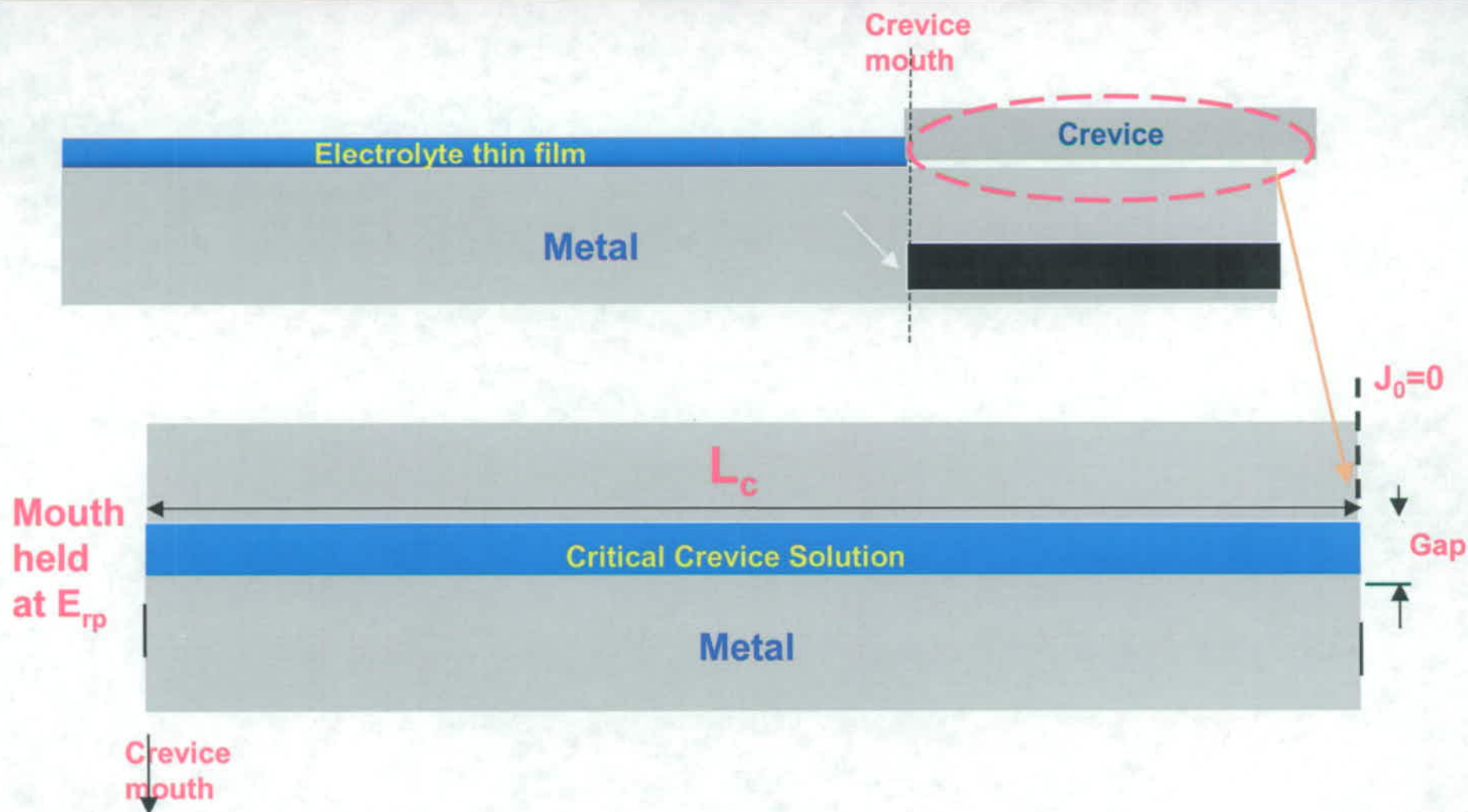
WL μm	10	10	10	25	25	25	200	200	200
[Cl ⁻] M	0.001	0.05	1	0.001	0.05	1	0.001	0.05	1
L_c (cm) needed for 98% I_{max}	0.25	1	4	0.25	4	10	1	10	15
98% I_{max} (A)	$6.6 \cdot 10^{-10}$	$4.6 \cdot 10^{-9}$	$1.9 \cdot 10^{-8}$	$1.0 \cdot 10^{-9}$	$7.3 \cdot 10^{-9}$	$3.0 \cdot 10^{-8}$	$2.6 \cdot 10^{-9}$	$1.9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

Base Case

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

$$B_c = 100 \text{ mV/dec}, i_{\text{lim}} = nFDC_{\text{O}_2}/\text{WL}, T = 95^\circ\text{C}$$

Anode Modeling

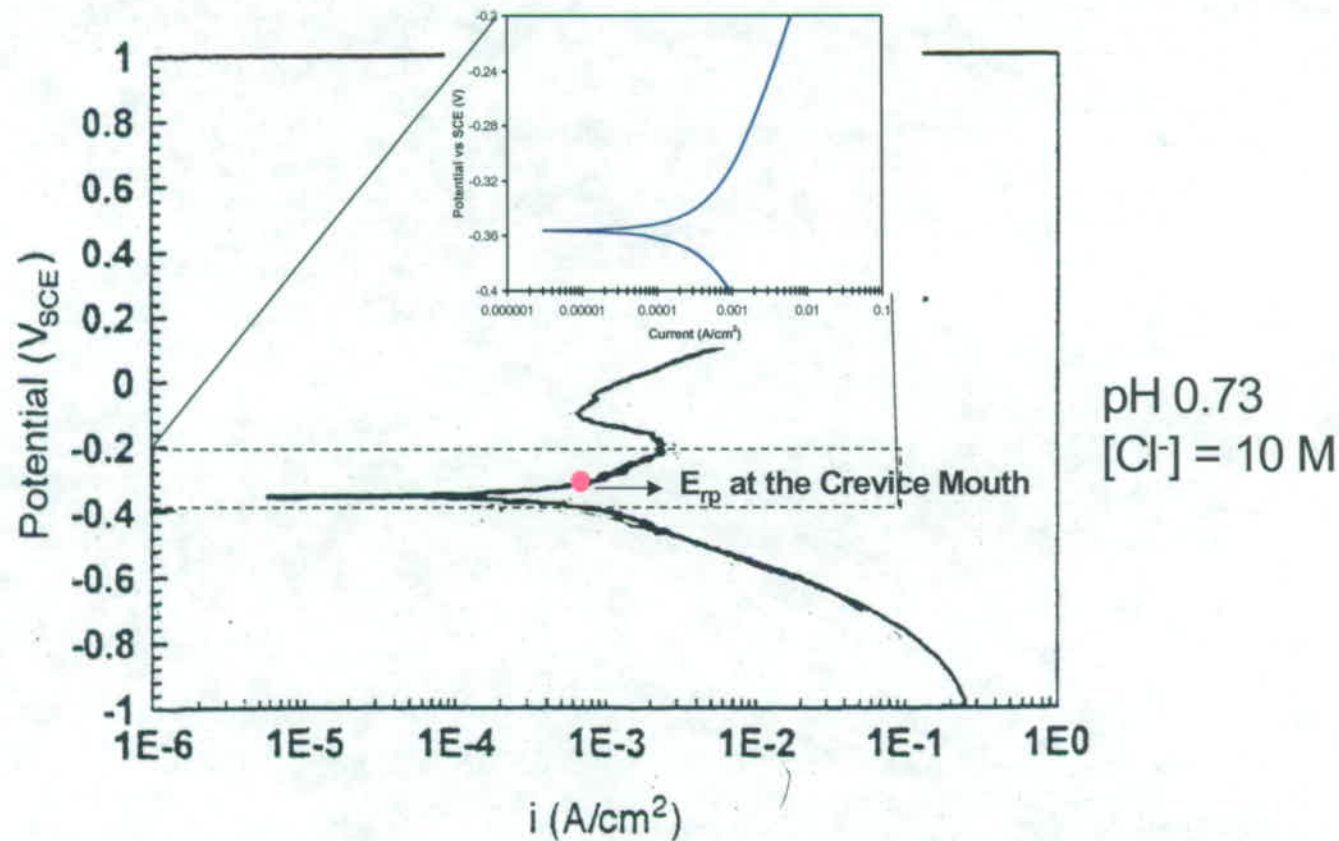


Modeling on the SS316L Crevice (anode)

- 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

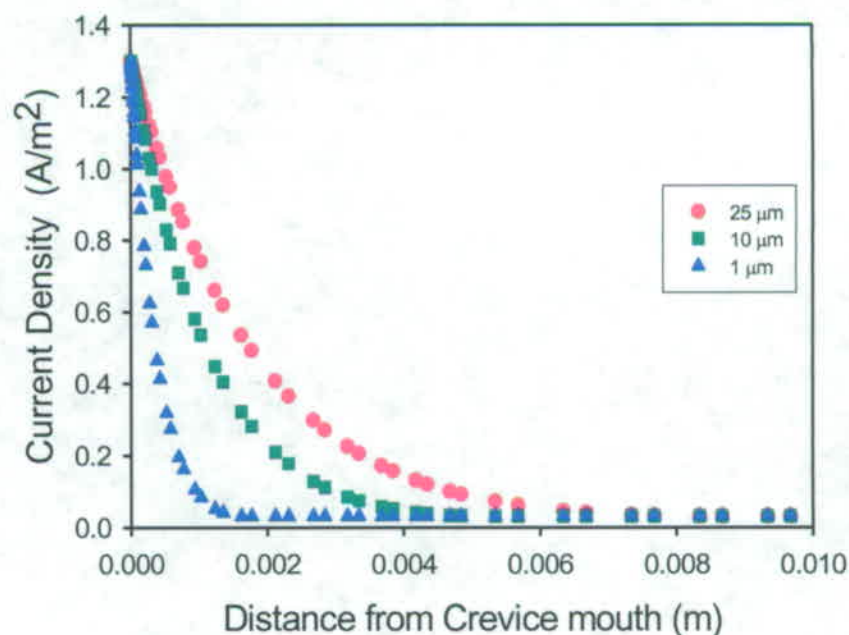
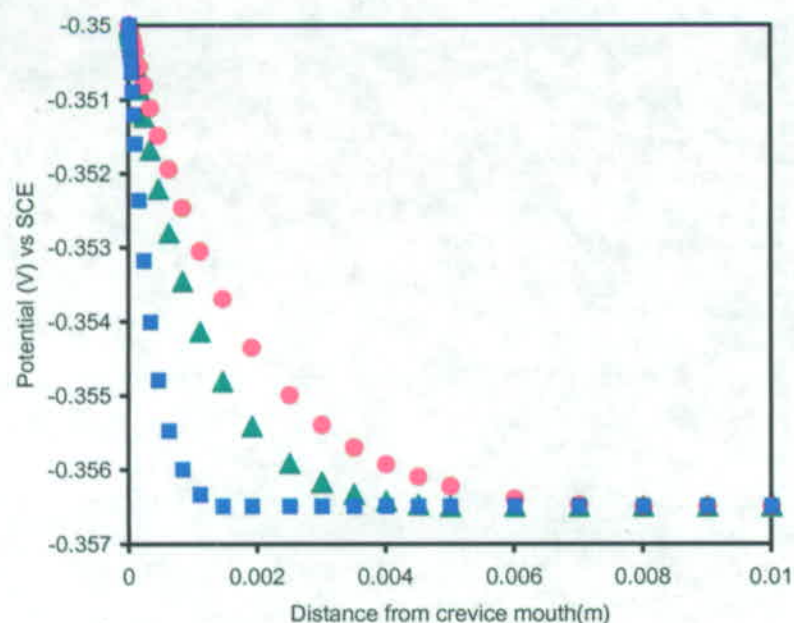
Electrochemical Kinetics

- Extracted from literature from measurements in Critical Crevice Solution



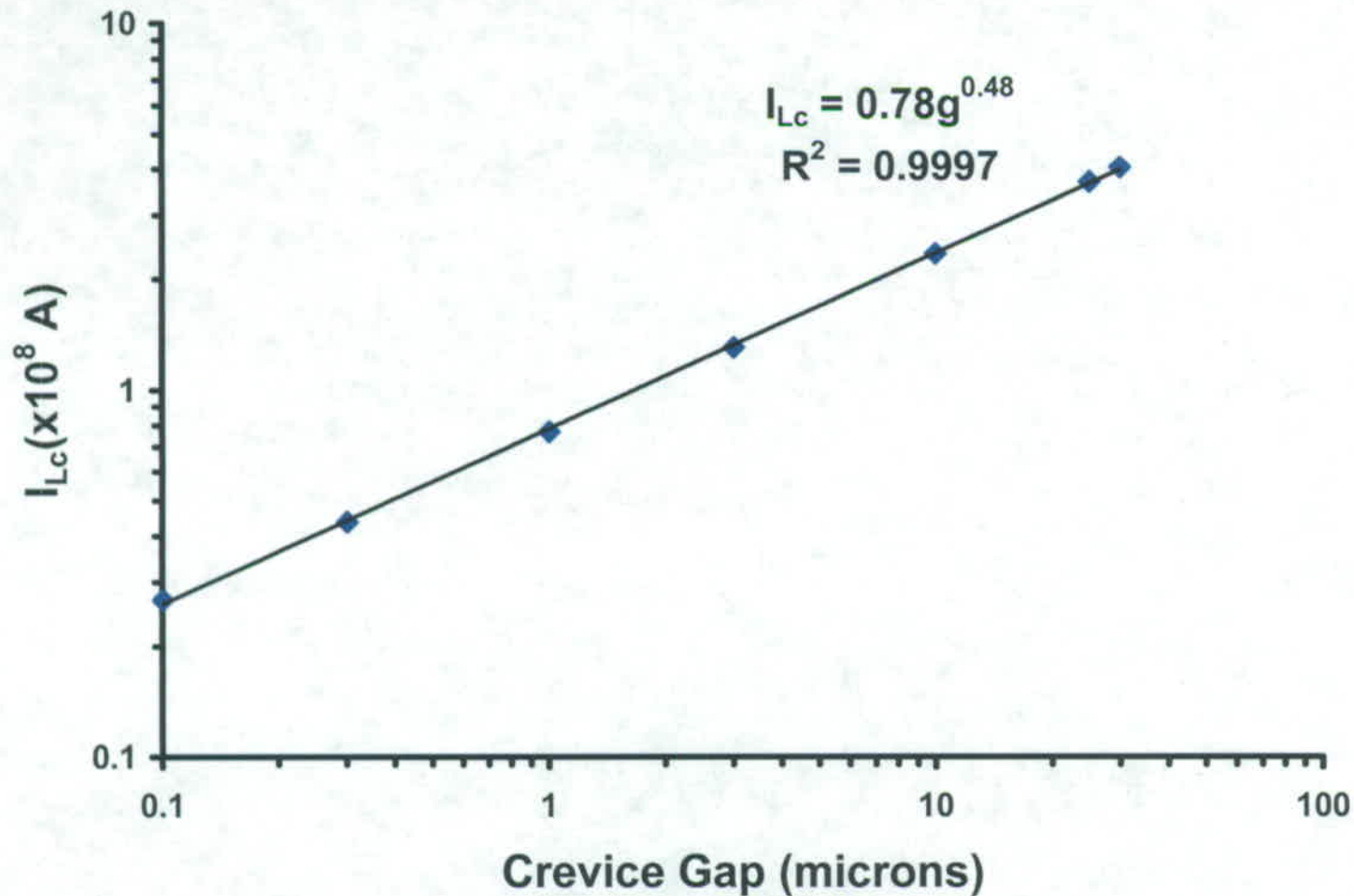
Kelly, Corrosion 51,11,p832

Typical Model Outputs



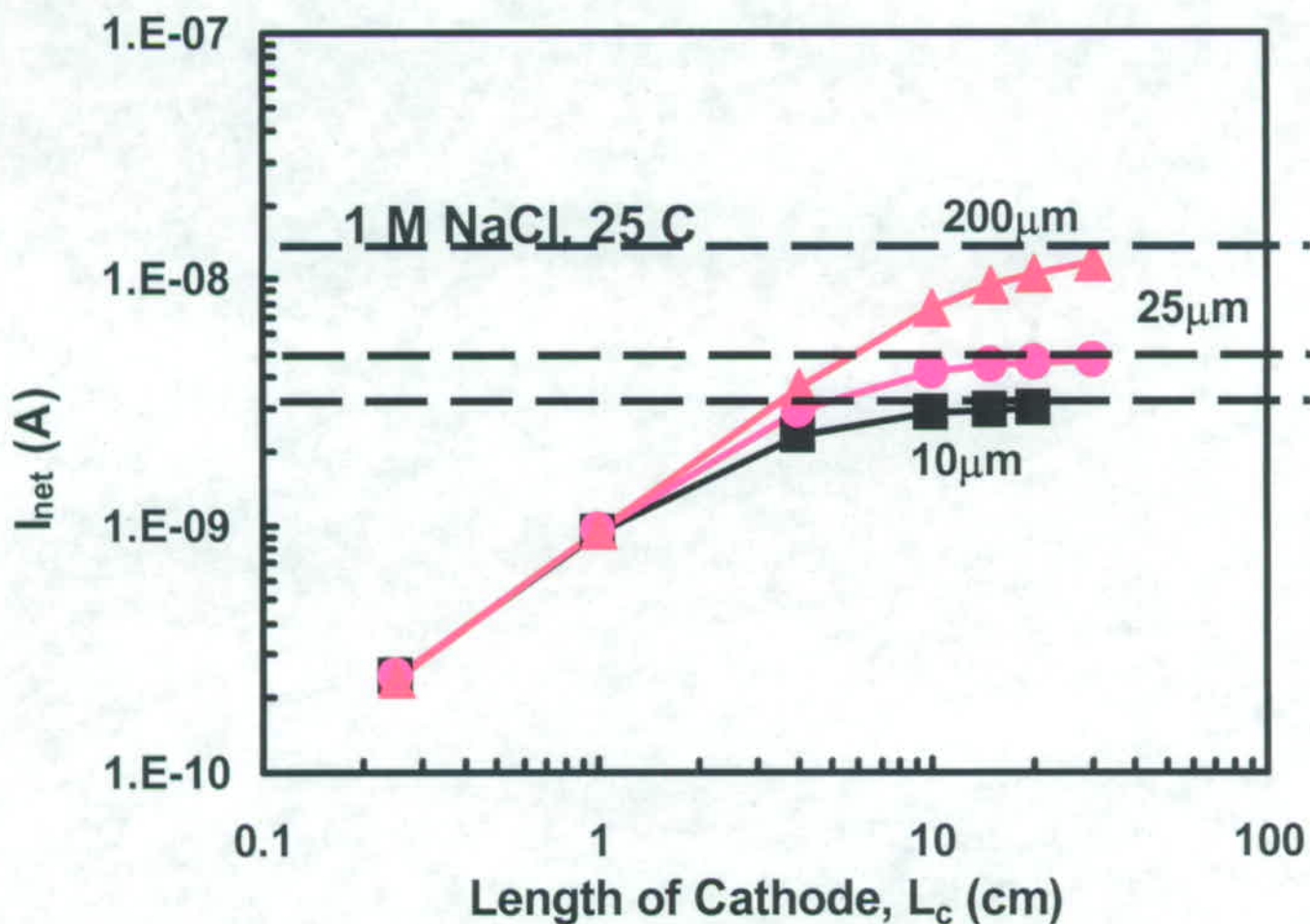
Potential and i decreased with depth into crevice

Crevice Current Demand $\sim g^{1/2}$

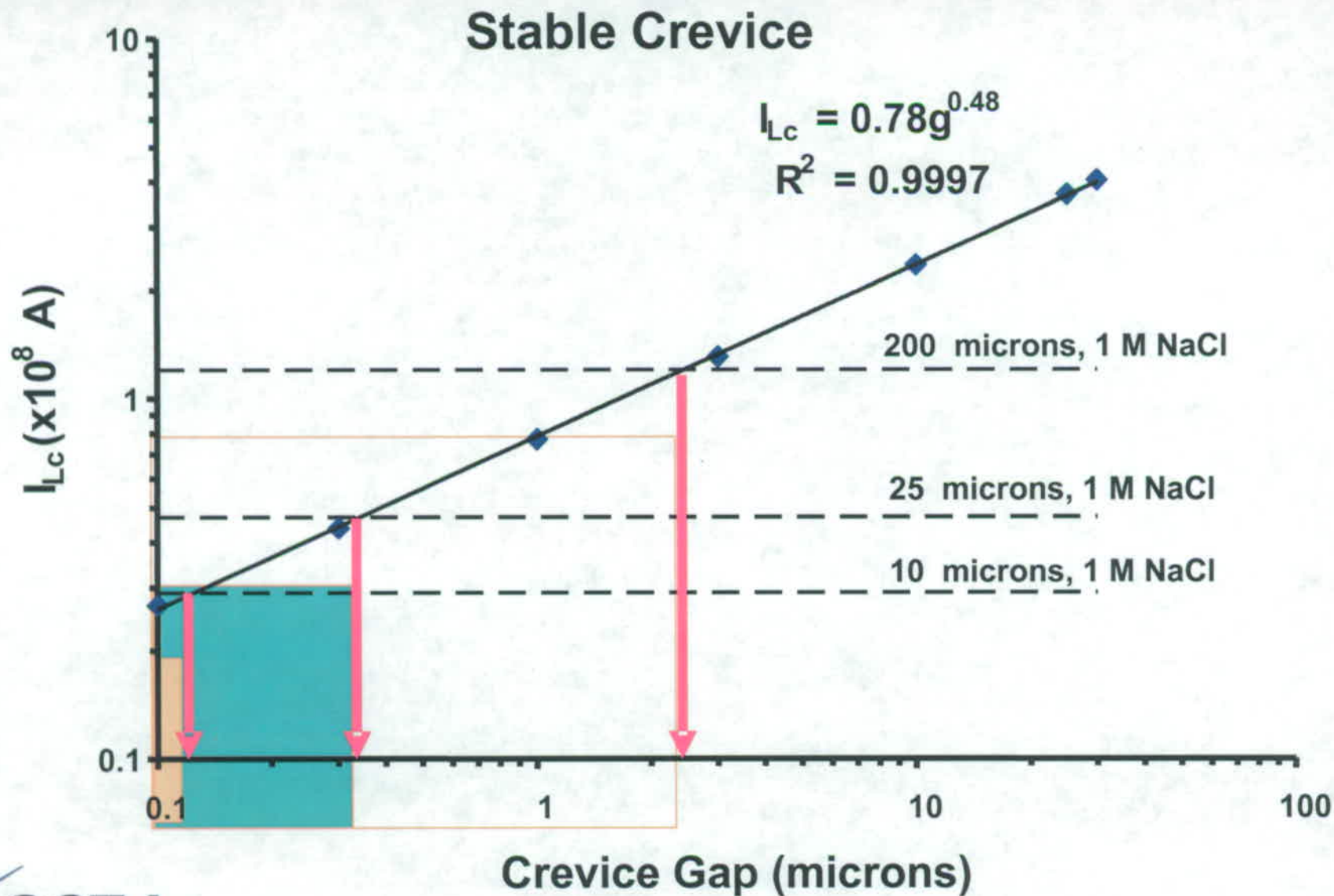


Only gaps smaller than arrows can stabilize

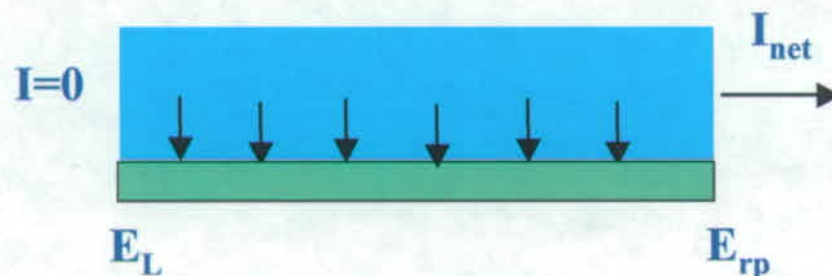
Recall that the I_{net} Saturates at High L_c



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:

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

Considering Secondary Current Distribution

- Total Resistance of Electrolyte can be shown to be:

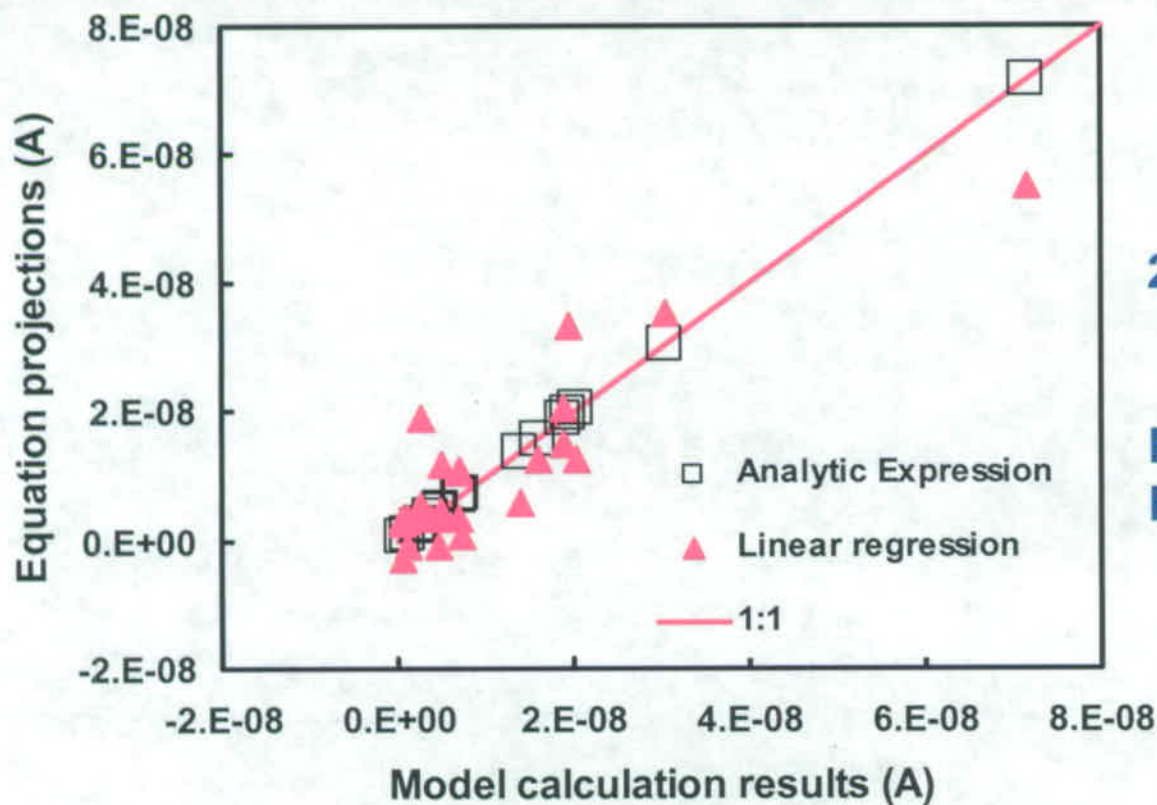
$$R = \frac{L_{eq}}{2 \cdot \sigma \cdot WL \cdot W}$$

- Ohmic Potential Drop:

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

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

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
- Cathode:
 - > 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
- Anode:
 - > Total current demand increased with $g^{1/2}$
- Analytic expression developed for total current from restricted geometry