CENT
SCIENCE AND ENGINEERING
Department of Materials Science and Engineering

University of Virginia Engineering

SAND2020-9900C

# Finite Element Modeling of SS316 Pit Stability, with respect to Geometry Parameters, Under Atmospheric Conditions

R. Skelton Marshall[1], R. M. Katona[1,2], M. A. Melia[2], R. G. Kelly[1]

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*C06-1306: Atmospheric and Marine Corrosion, PRIME ECS 2020, Virtual, 10/5/2020 from 10:40 to 11am HST*

Presenter email: rjs2wu@virginia.edu

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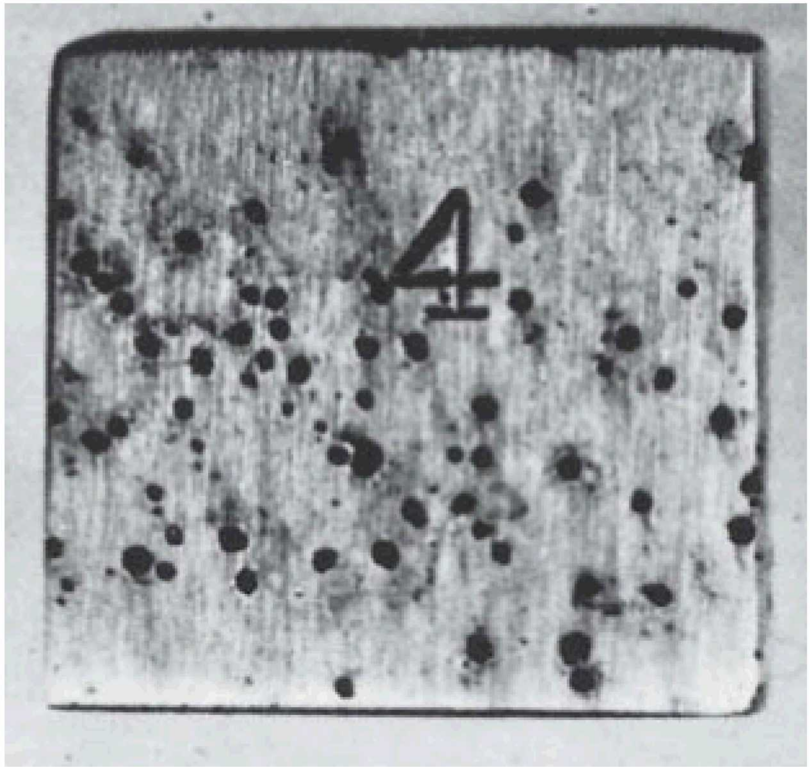
SAND2020-XXXXX

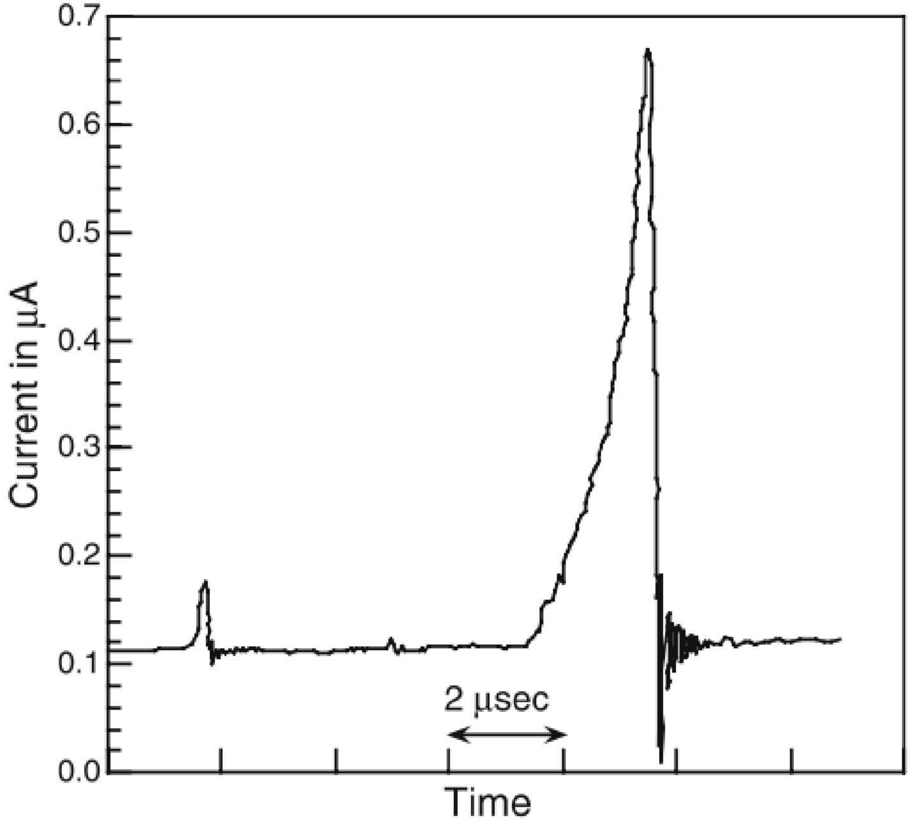
# Pitting on Stainless Steels

Pitting on SS304



M. G. Fontana, Corrosion Engineering, 3rd edition. 1986 by McGraw-Hill Book Company

Pit Repassivation on SS302

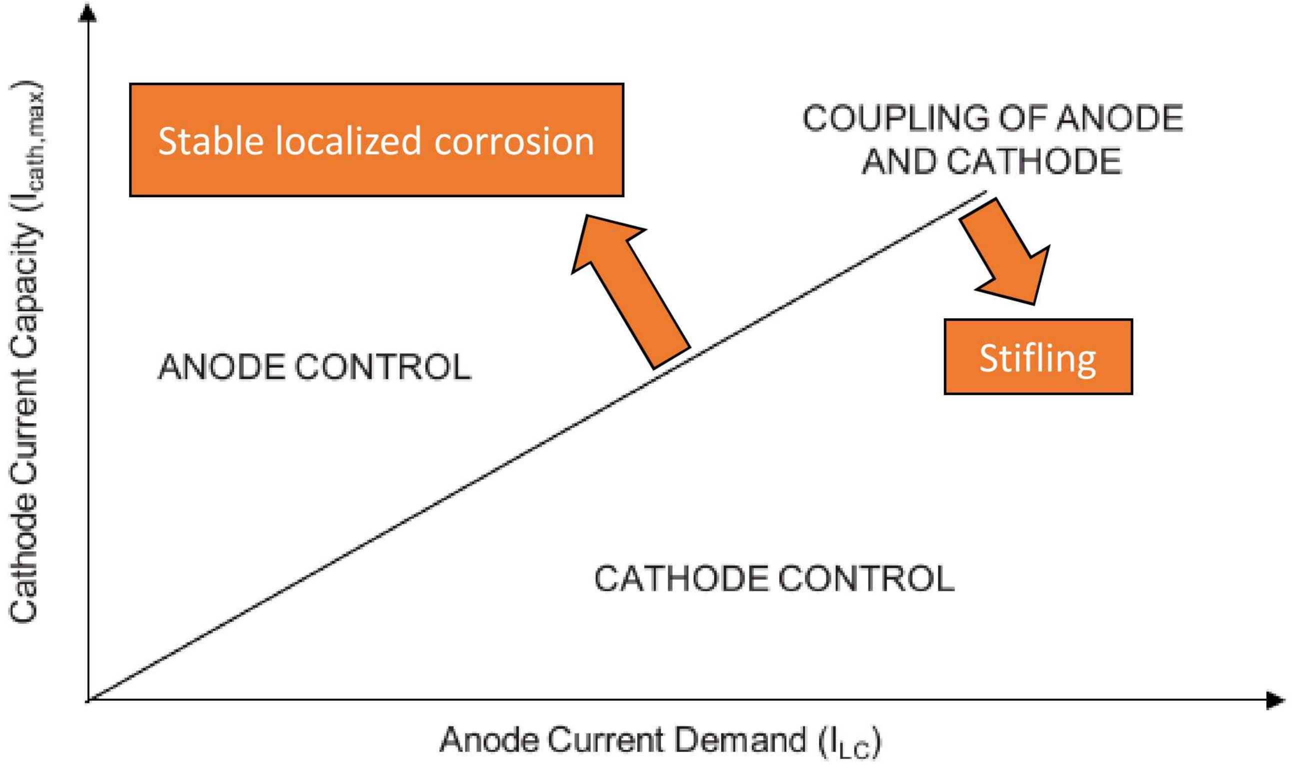



E. McCafferty, Introduction to corrosion science, Springer, 2010.

# Pit Stability Background

$$I_c = I_a$$

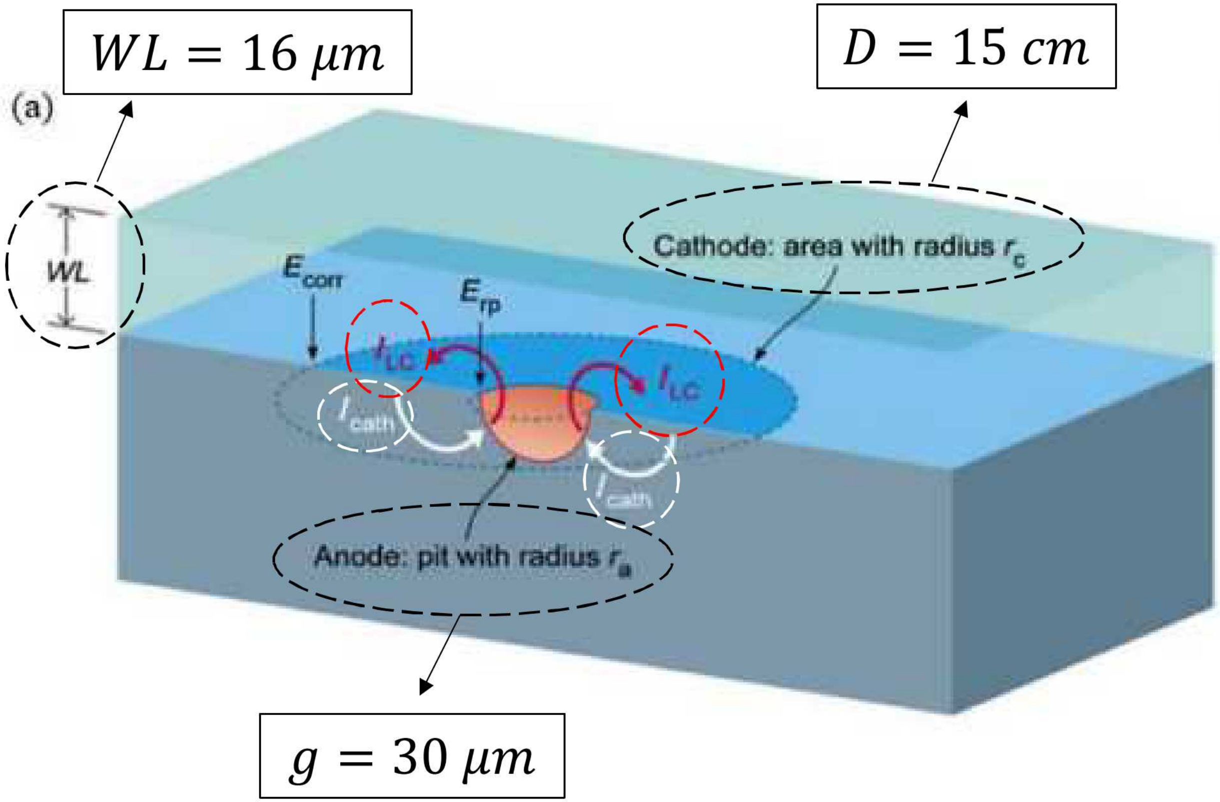
Determined through cathode kinetics and environmental factors

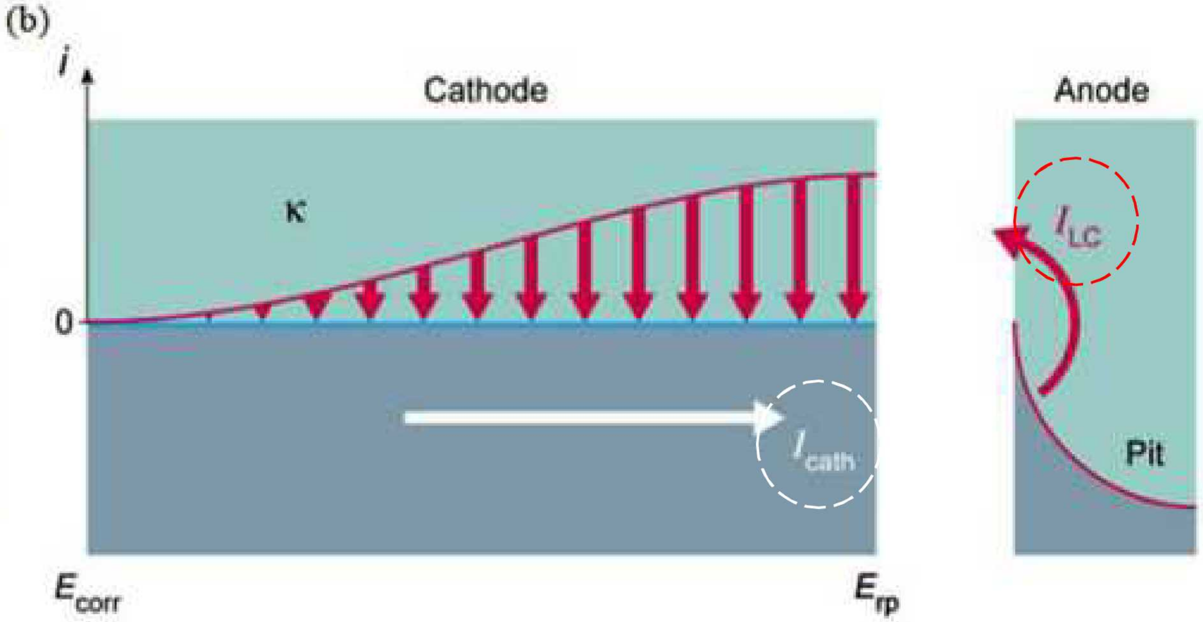



Determined through size of the pit, and pit stability product

Z.Y. Chen, R.G. Kelly (2009)

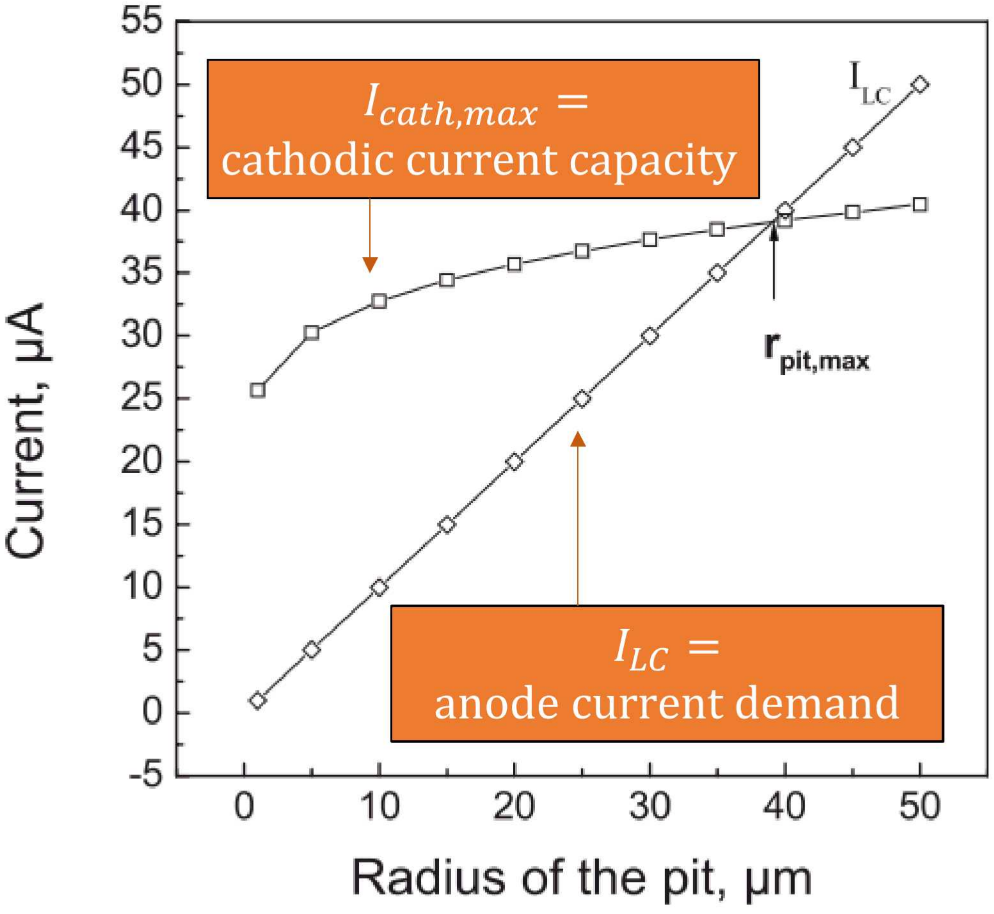
# Pit Stability Background



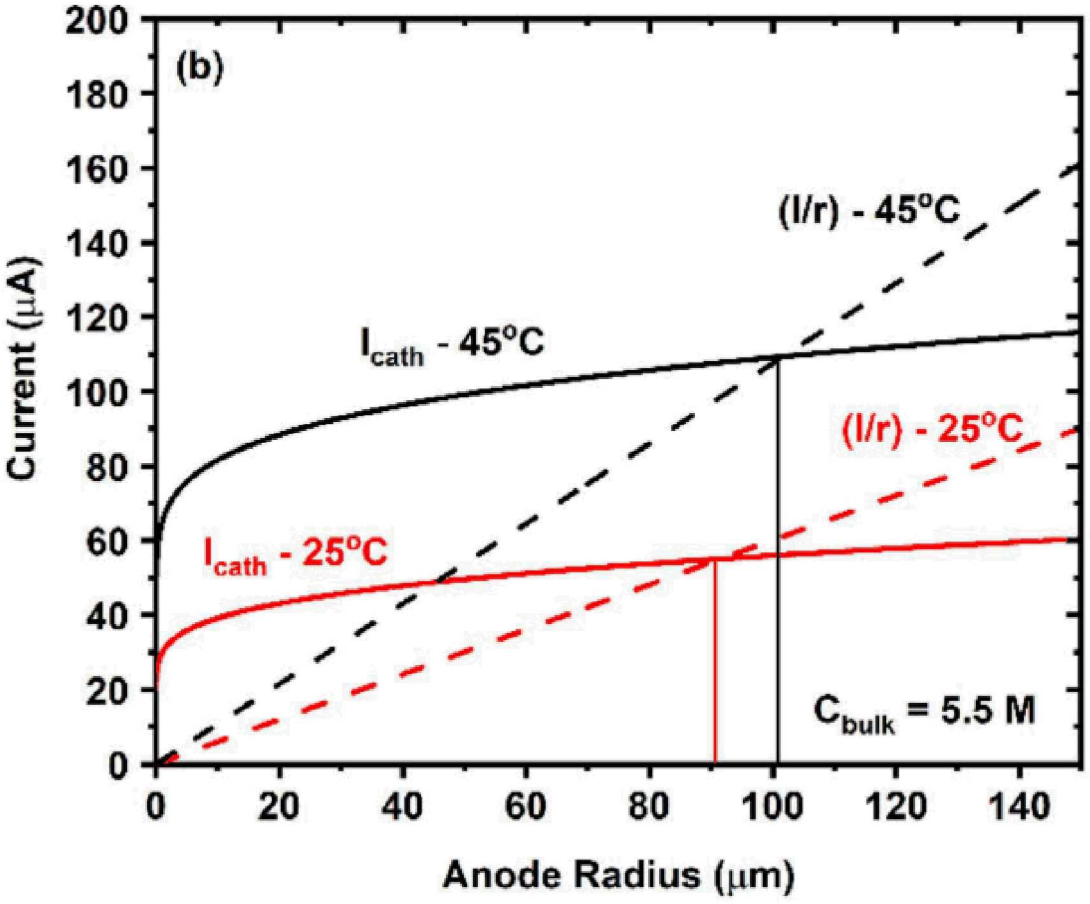




R.M. Katona, J. Carpenter, E.J. Schindelholz, R.G. Kelly (2019)

# Pit Stability Background




Z.Y. Chen, R.G. Kelly (2009)



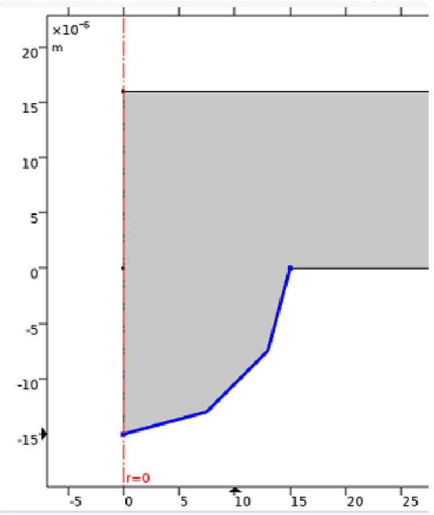

R.M. Katona, J. Carpenter, E.J. Schindelholz, R.G. Kelly (2019)

# Motivation and Goals

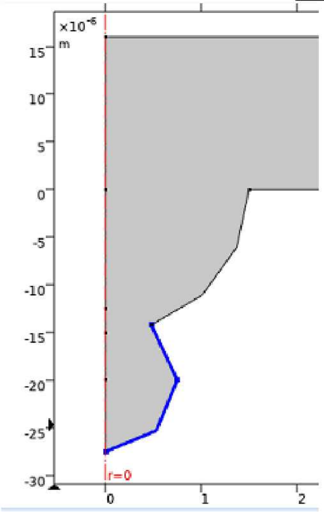
- Maximum pit model provides size bound, but
  - No time dependence
  - No pit geometry dependence
  - No insights into effects of cathodes smaller than maximum cathode
- Next step is time dependence of chemistry in a pitting system
  - Still must couple pit with external cathode
  - Apply pit stability criteria
  - Must implement potential-dependent pit kinetics and transport of species
- Current presentation
  - Initial development of modeling framework and application to a range of pit geometries and WL

# Different Pit Geometries

- Consider three pit shapes:
  - Hemisphere (simple)
  - Double and undercutting pits (complex)
  - *Under what conditions will these pits grow or repassivate?*
- $I_{cath,max}$ impact on stability
  - Water layer thickness change
- $I_{LC}$ impact on stability
  - Pit geometry/size

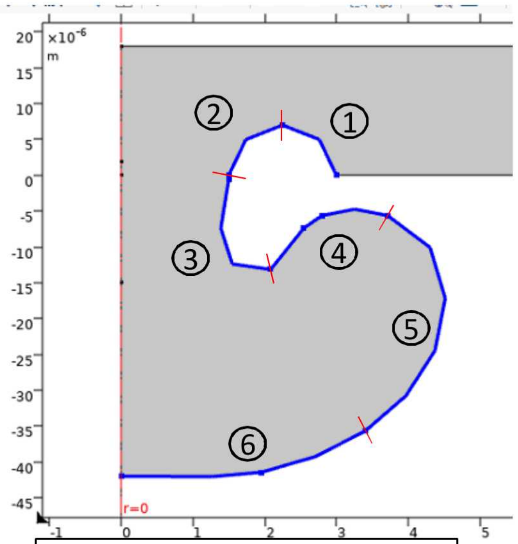



Hemispherical Pit




Double Pit

Represents active pit growing on "old" repassivated pit



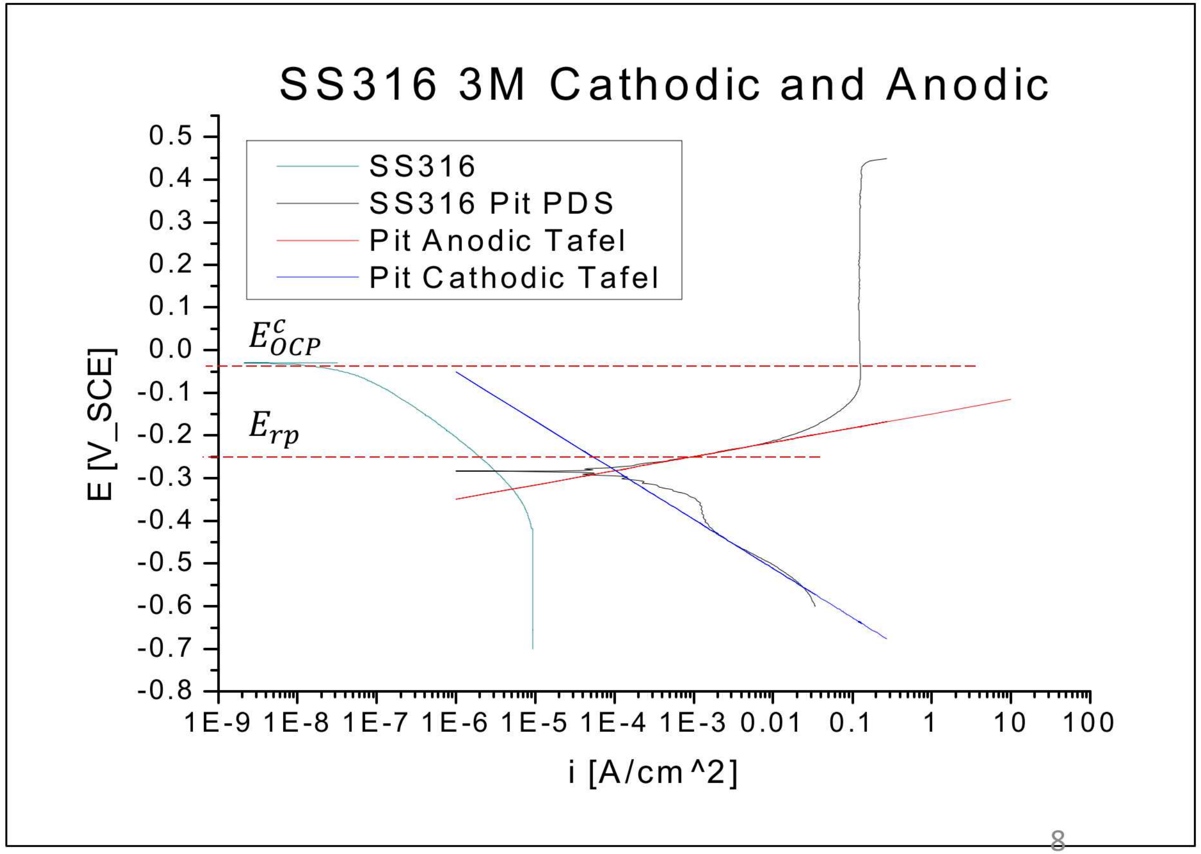

Undercutting Pit

Represents undercut pit with corrosion product built up at pit mouth

# Pit Stability Criteria

If Inequality is True, Then Pit Will Grow

1. $\mathrm{E_{mouth}} > \mathrm{E_{rp}}$ → Criteria for all pits
2. $\left(\frac{\mathrm{I}}{\mathrm{r}}\right)_{\mathrm{FEM,anode}} > \left(\frac{\mathrm{I}}{\mathrm{r}}\right)_{\mathrm{max\ pit\ model}}$
   - $\left(\frac{\mathrm{I}}{\mathrm{r}}\right)^{\mathrm{3M}}_{\mathrm{max\ pit\ model}} = 0.8\,\frac{\mathrm{A}}{\mathrm{m}}$
3. $[M^{+}]_{FEM} > [M^{+}]_{\mathrm{critical}}$
   - $[Ni^{2+}]_{\mathrm{critical}} = 2048.84\ \left[\frac{mol}{m^3}\right]$
   - $[Cr^{3+}]_{\mathrm{critical}} = 3213\ \left[\frac{mol}{m^3}\right]$
   - $[Fe^{2+}]_{\mathrm{critical}} = 13{,}622.02\ \left[\frac{mol}{m^3}\right]$



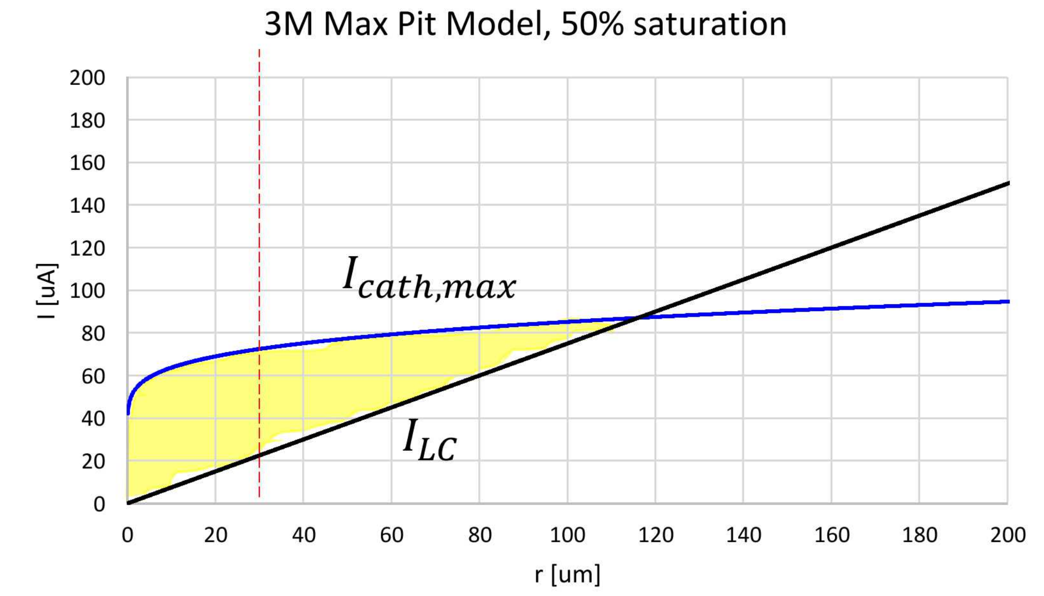
# Pit Stability Criteria

If Inequality is True, Then Pit Will Grow

1. $E_{mouth} > E_{rp}$
2. $\left(\frac{I}{r}\right)_{FEM,anode} > \left(\frac{I}{r}\right)_{max\ pit\ model}$
   - $\left(\frac{I}{r}\right)^{3M}_{max\ pit\ model} = 0.8\,\frac{A}{m}$
3. $[M^+]_{FEM} > [M^+]_{critical}$
   - $[Ni^{2+}]_{critical} = 2048.84\ \left[\frac{mol}{m^3}\right]$
   - $[Cr^{3+}]_{critical} = 3213\ \left[\frac{mol}{m^3}\right]$
   - $[Fe^{2+}]_{critical} = 13{,}622.02\ \left[\frac{mol}{m^3}\right]$

- Dashed lines represent constant pit size, $g = 30um$
- Highlighted region represents satisfied pit stability

Criteria for hemisphere-like pits



# Pit Stability Criteria

If Inequality is True, Then Pit Will Grow

1. $E_{\text{mouth}} > E_{\text{rp}}$

2. $\left(\frac{I}{r}\right)_{\text{FEM,anode}} > \left(\frac{I}{r}\right)_{\text{max pit model}}$

   - $\left(\frac{I}{r}\right)^{3M}_{\text{max pit model}} = 0.8\,\frac{A}{m}$

3. $[M^{+}]_{FEM} > [M^{+}]_{\text{critical}}$

   - $[Ni^{2+}]_{\text{critical}} = 2048.84\ \left[\frac{mol}{m^3}\right]$
   - $[Cr^{3+}]_{\text{critical}} = 3213\ \left[\frac{mol}{m^3}\right]$
   - $[Fe^{2+}]_{\text{critical}} = 13{,}622.02\ \left[\frac{mol}{m^3}\right]$

Criteria for time-dependent pits

# Stationary Pit Stability Criterion

Summary: No differences between pits are seen in $E > E_{rp}$ criteria; always satisfied. Minimal differences between pits are seen in $\frac{I}{r}$ criterion

# Finite Element Modeling Setup

<u>Input Parameters:</u>

Concentration NaCl $= 3M$ (RH $= 88.321$)

WL = 10 – 1000 $\mu m$ (for LD = 1.8 – 180 g/m$^2$)

$$g = 30\ \mu m; D = 15\ cm$$

$$\kappa = 19.7\ \left[\frac{S}{m}\right]$$

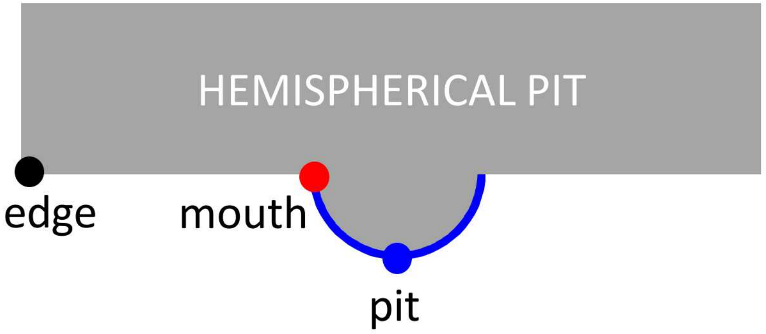
<u>Assumptions:</u>

Laplace as governing equation (constant conductivity)

WL = water layer thickness

g = pit diameter

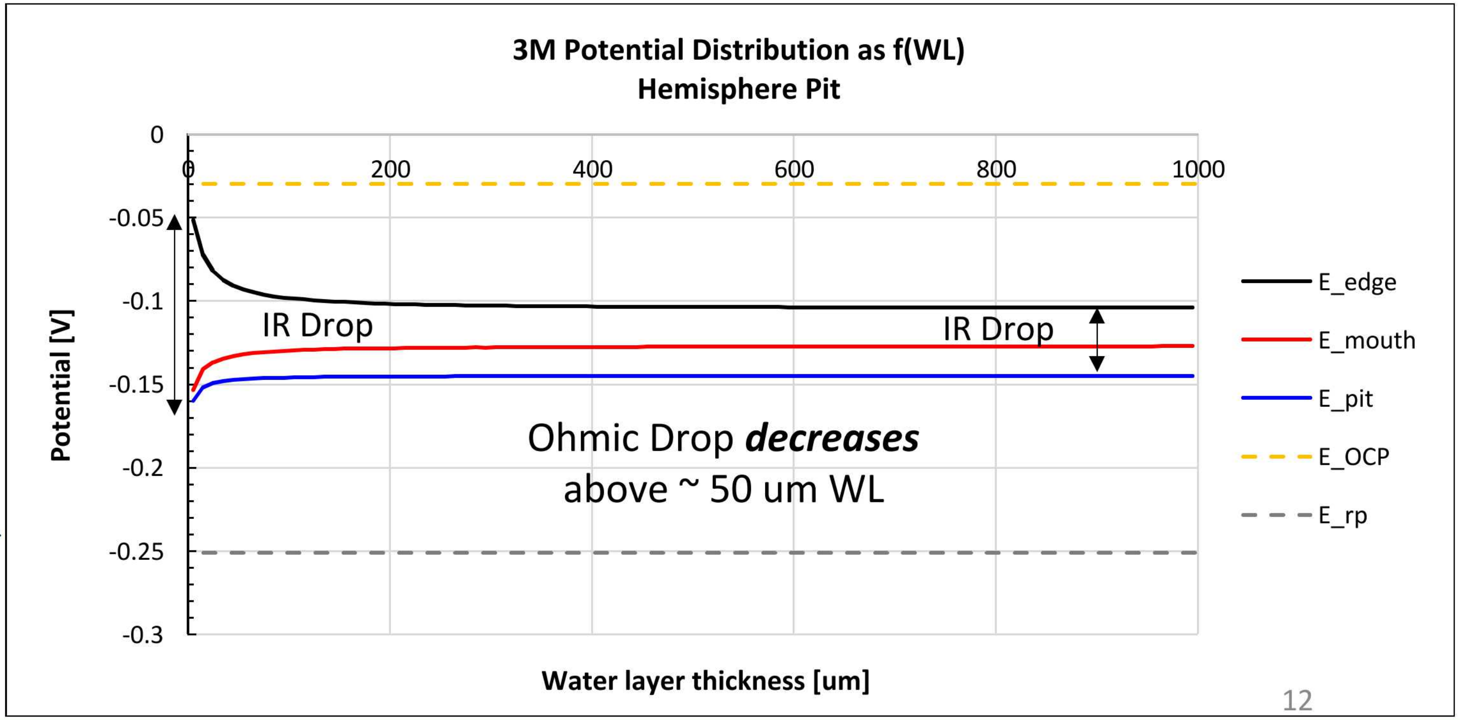
D = cathode diameter




<u>Comparison of stability criterion:</u>

$$E_{FEM} > E_{rp}$$

$$\left(\frac{I}{r}\right)_{FEM} > \left(\frac{I}{r}\right)_{max\ pit}$$



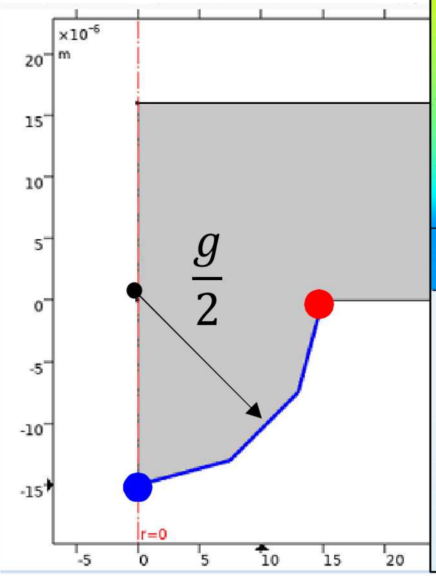
# Hemisphere Pit

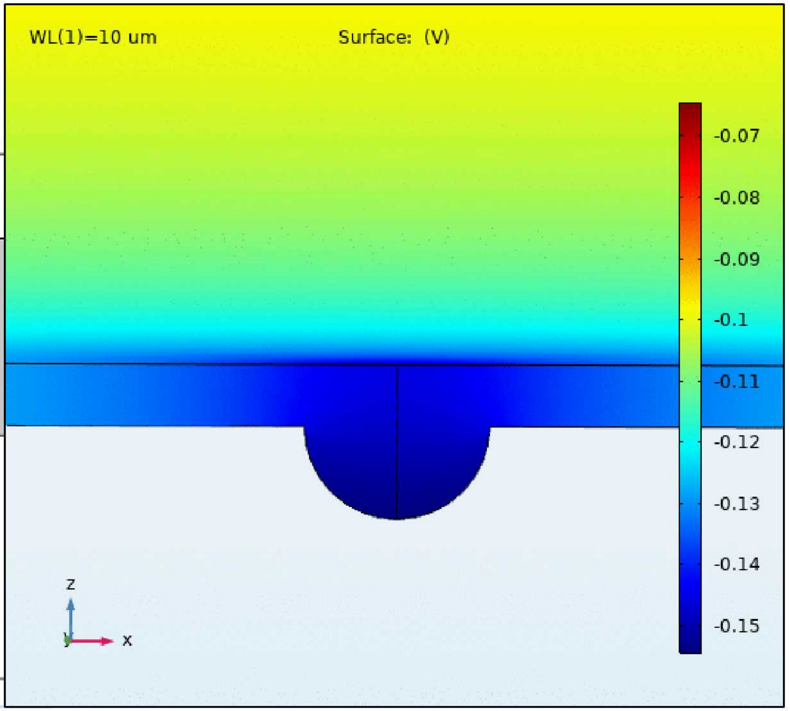
- $\frac{I}{r}$ satisfied for $WL > 10.5\ um$
- $E_{pit} > E_{rp}$ for $ALL\ WL's$

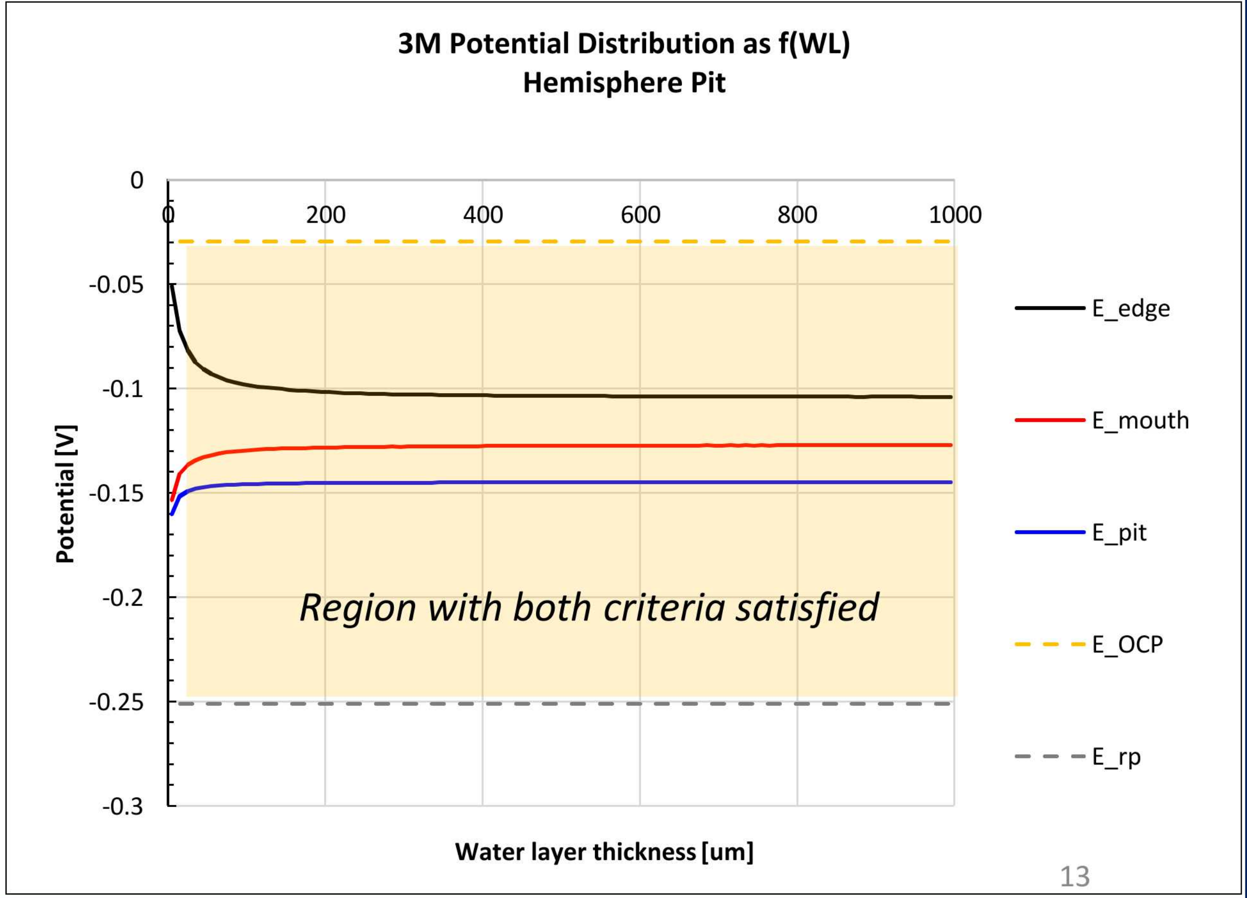
Geometric Parameters:

*water layer varied*

$$WL = 10\text{–}1000\ \mu m, g = 30\ \mu m, D = 15\ cm$$



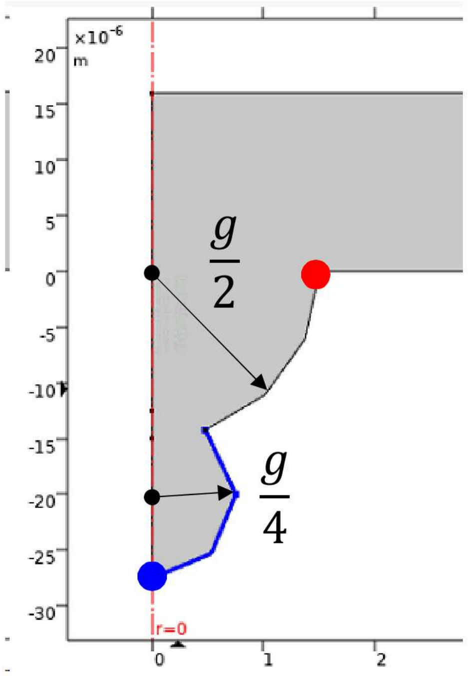
# Double Pit

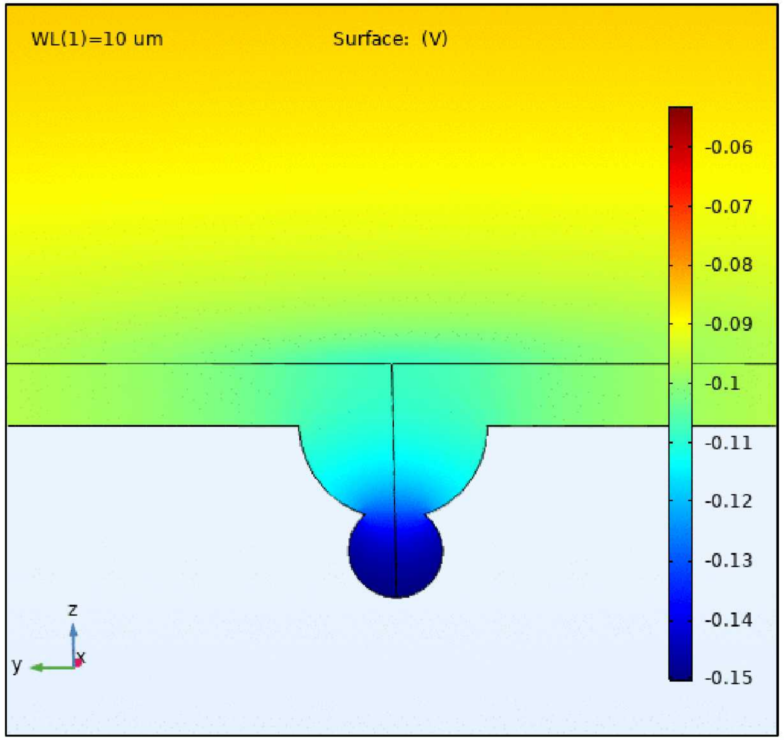
- $\frac{I}{r}$ satisfied for $WL > 50\ um$
- $E_{pit} > E_{rp}$ for $ALL\ WL's$

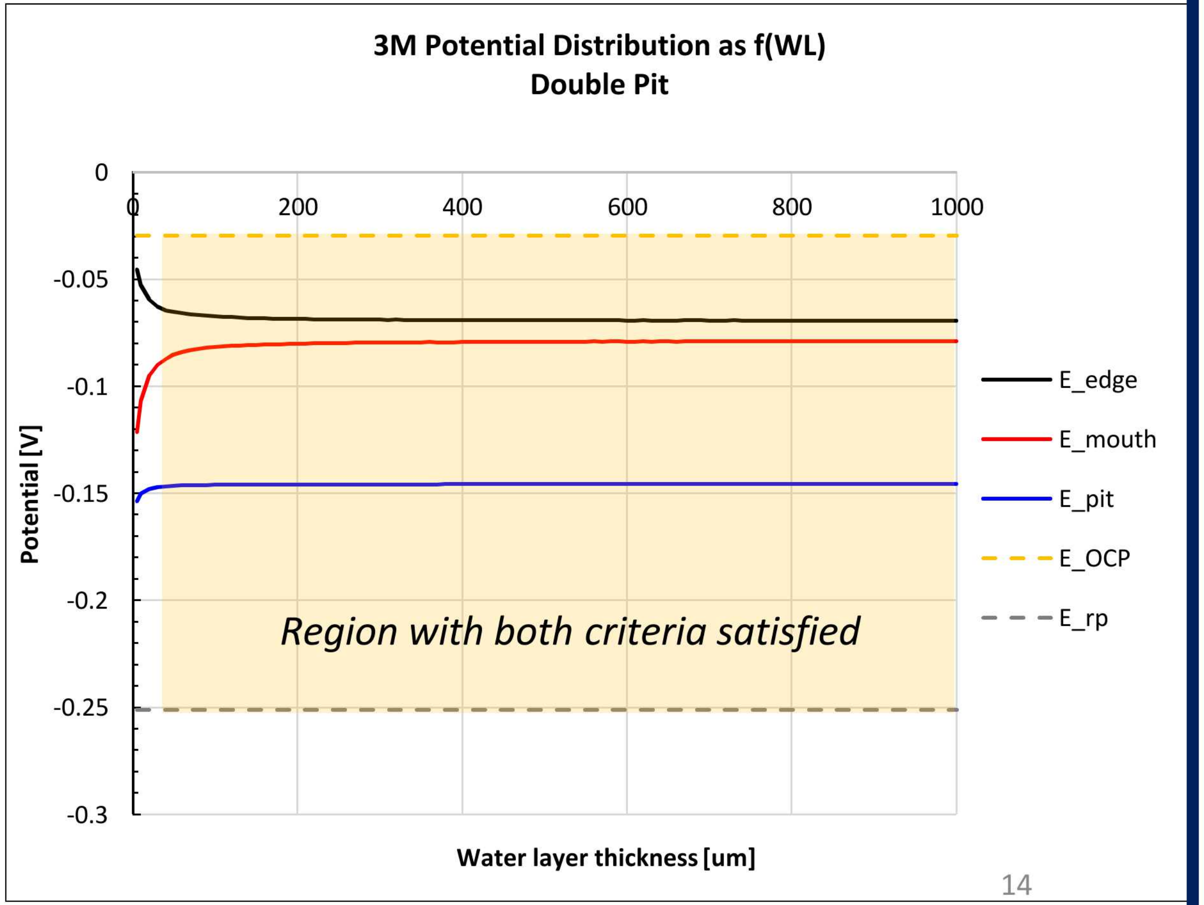
Geometric Parameters:

*water layer varied*

$$WL = 10\text{–}1000\ \mu m, g = 30\ \mu m, D = 15\ cm$$



# Undercut Pit

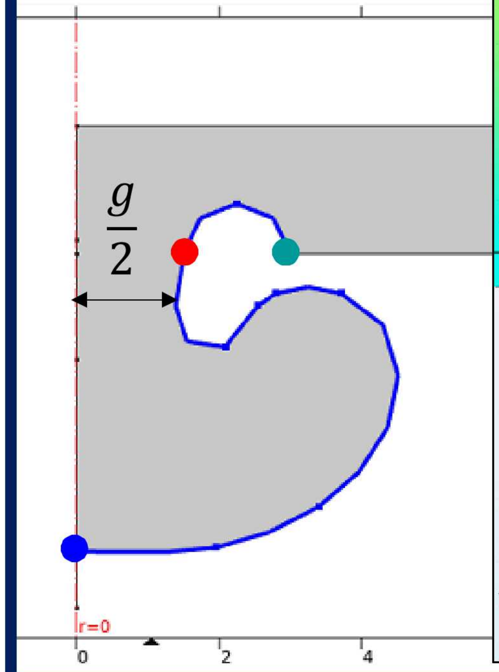
Geometric Parameters:

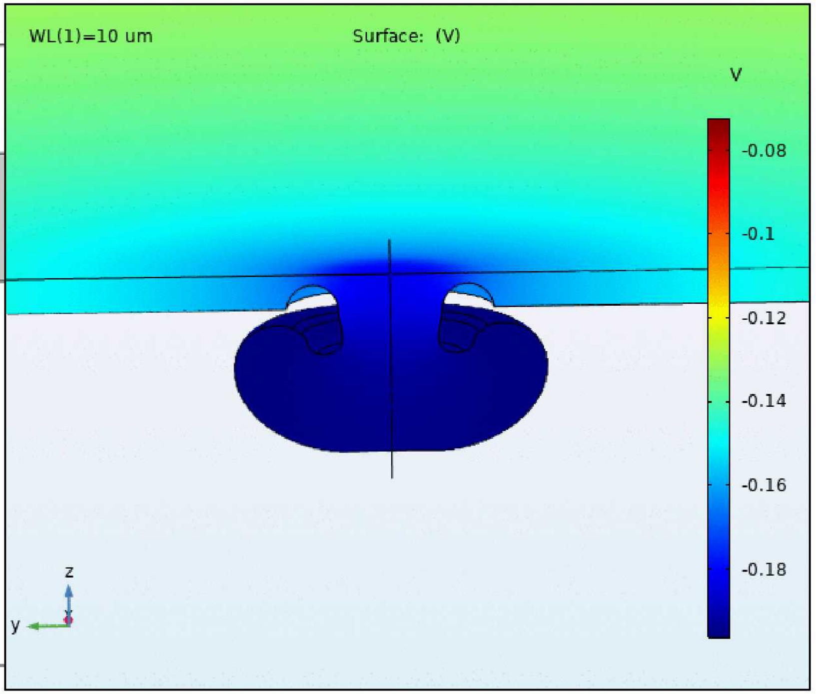
*water layer varied*

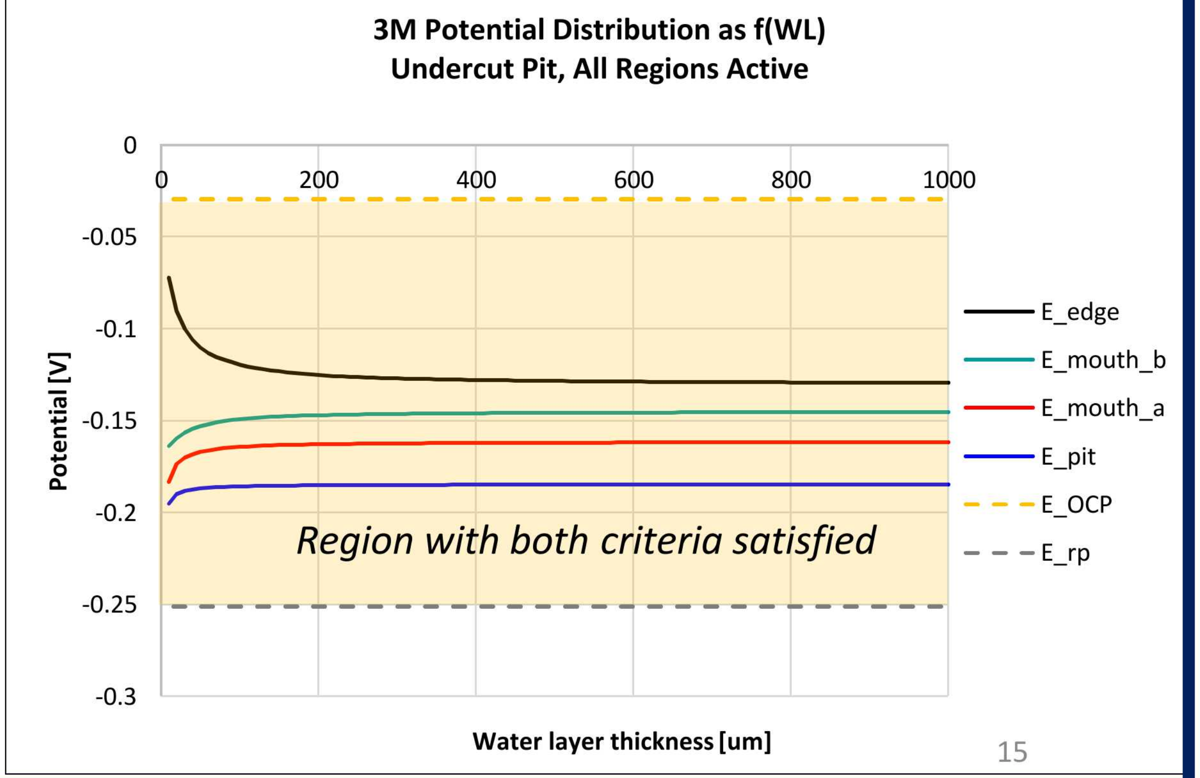
$\mathrm{WL} = 10\text{–}1000\ \mu\mathrm{m}, \mathrm{g} = 30\ \mu\mathrm{m}, \mathrm{D} = 15\ \mathrm{cm}$

**All Regions Active**

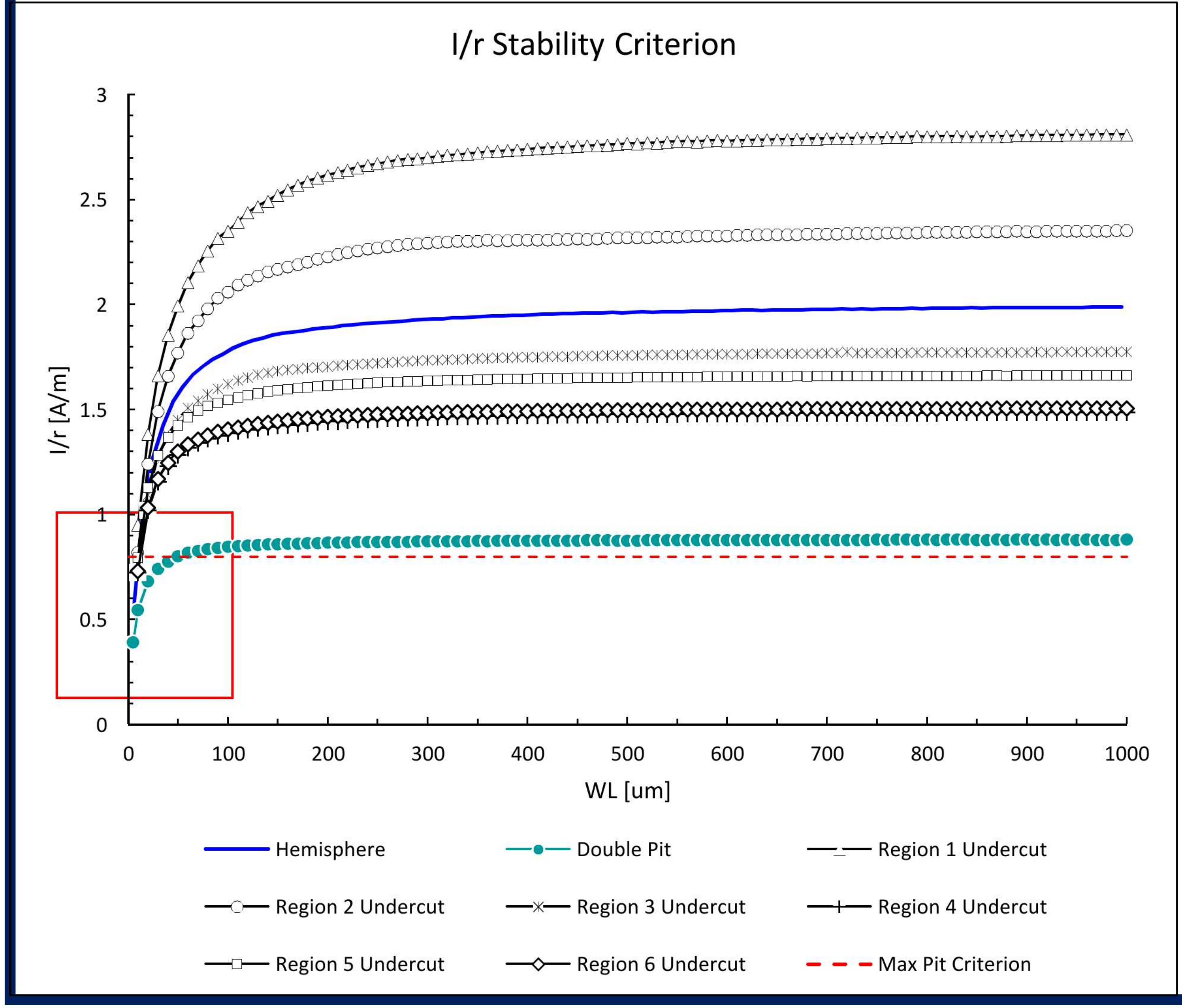
- $\frac{I}{r}$ satisfied for $ALL\ WL's$
- $E_{pit} > E_{rp}$ for $ALL\ WL's$

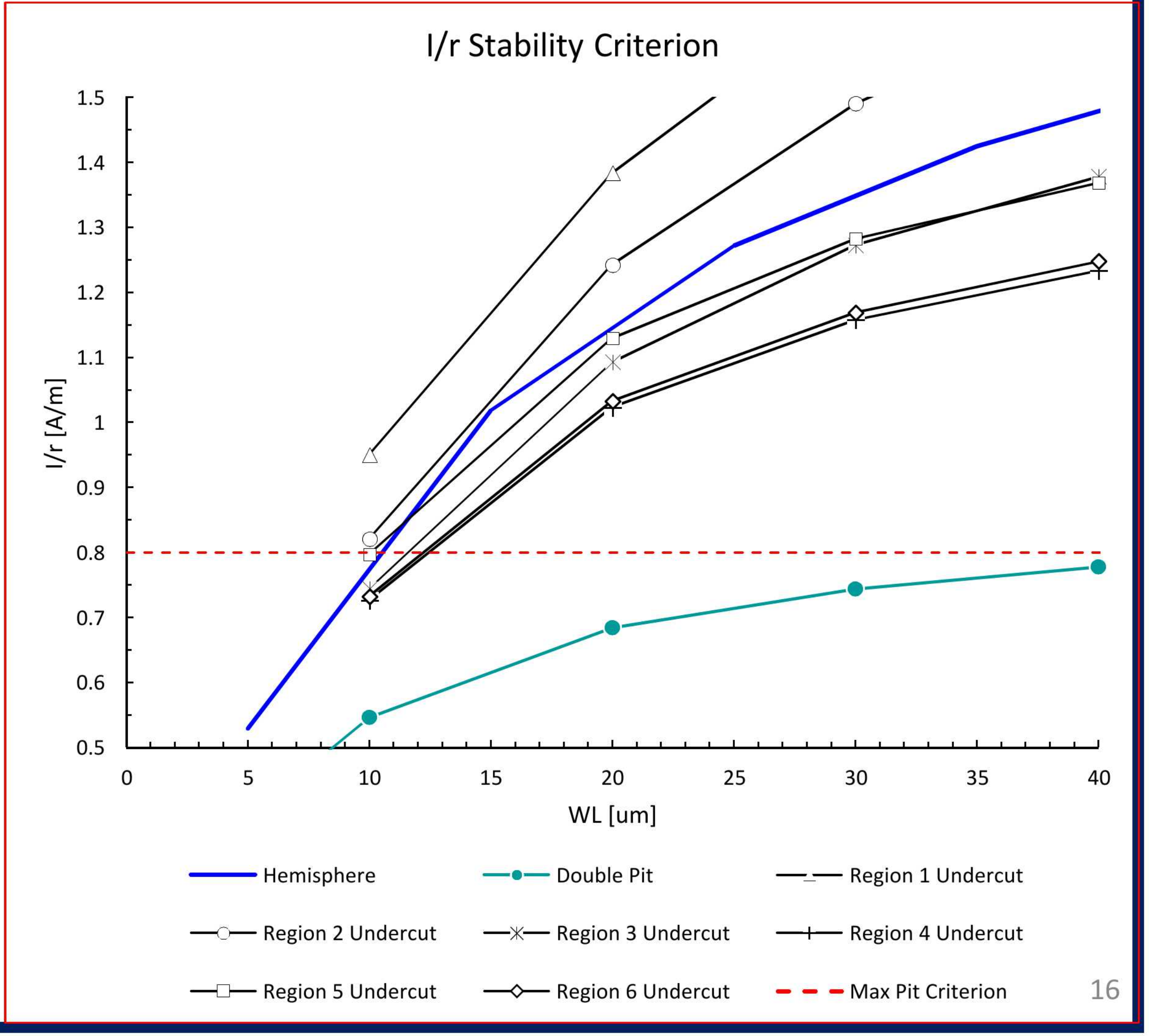


# Plotting I/r Stability Criterion for Hemisphere-Based Pits



# Conclusions for Steady-State Modeling

- All pits satisfy $E_{FEM} > E_{rp}$ criteria for geometries and environmental factors considered
- Water layer changes $> 100\ \mu m$ do not have a large impact on stability, indicating that pit size/geometry (*i.e.* $I_{LC}$) is *more important* to stability than environmental factors (*i.e.* $I_{cath,max}$)
- Complex hemisphere-like pits behave *similarly to a hemisphere pit* in both $E_{FEM} > E_{rp}$ and $\left(\frac{I}{r}\right)_{FEM} > \left(\frac{I}{r}\right)_{max\ pit}$ criteria
  - Indicates that using "hemispherical pit" for simplicity is not a bad assumption
- "Double Pit" is less stable than hemisphere and undercutting pit

Does the concentration profile of metal ions agree with these statements?

# Time-Dependent Pit Stability Criterion

Summary: Concentrations of $Ni^{2+}$, $Cr^{3+}$, and $Fe^{2+}$ all increase with time, and all satisfy critical concentration criteria before reaching steady-state

# Time-Dependent FEM Setup

<u>Input Parameters:</u>

Concentration NaCl $= 3M$ (RH $= 88.321$)

$$D_{Ni} = 4.01x10^{-10} \left[\frac{\mathrm{m}^2}{\mathrm{s}}\right]$$

$$D_{Fe} = 4.03x10^{-10} \left[\frac{\mathrm{m}^2}{\mathrm{s}}\right]$$

$$D_{Cr} = 3.23x10^{-10} \left[\frac{\mathrm{m}^2}{\mathrm{s}}\right]$$

$$\kappa = 19.7 \left[\frac{S}{m}\right]$$

<u>Assumptions:</u>

Laplace as governing equation (constant conductivity)

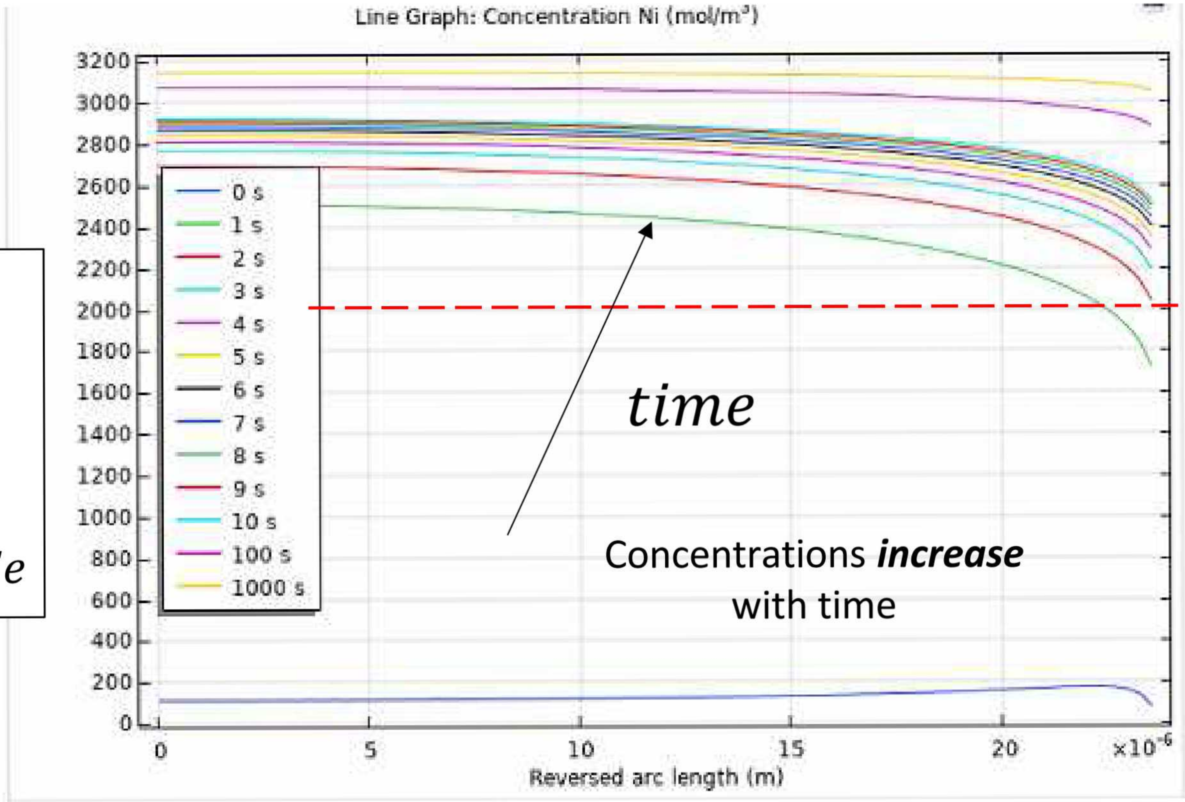
Dilute solution (Nernst-Einstein equation)

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

$$Cr \rightarrow Cr^{3+} + 3e^-$$

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

$16\%\ Cr; 10\%\ Ni; 74\%\ Fe$




<u>Comparison of stability criterion:</u>

$$[M^+]_{FEM} > [M^+]_{\mathrm{critical}}$$

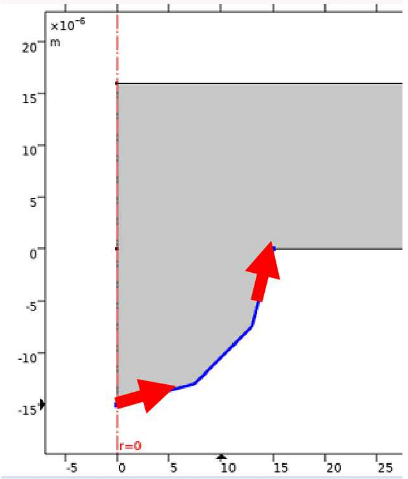
# Hemisphere Pit

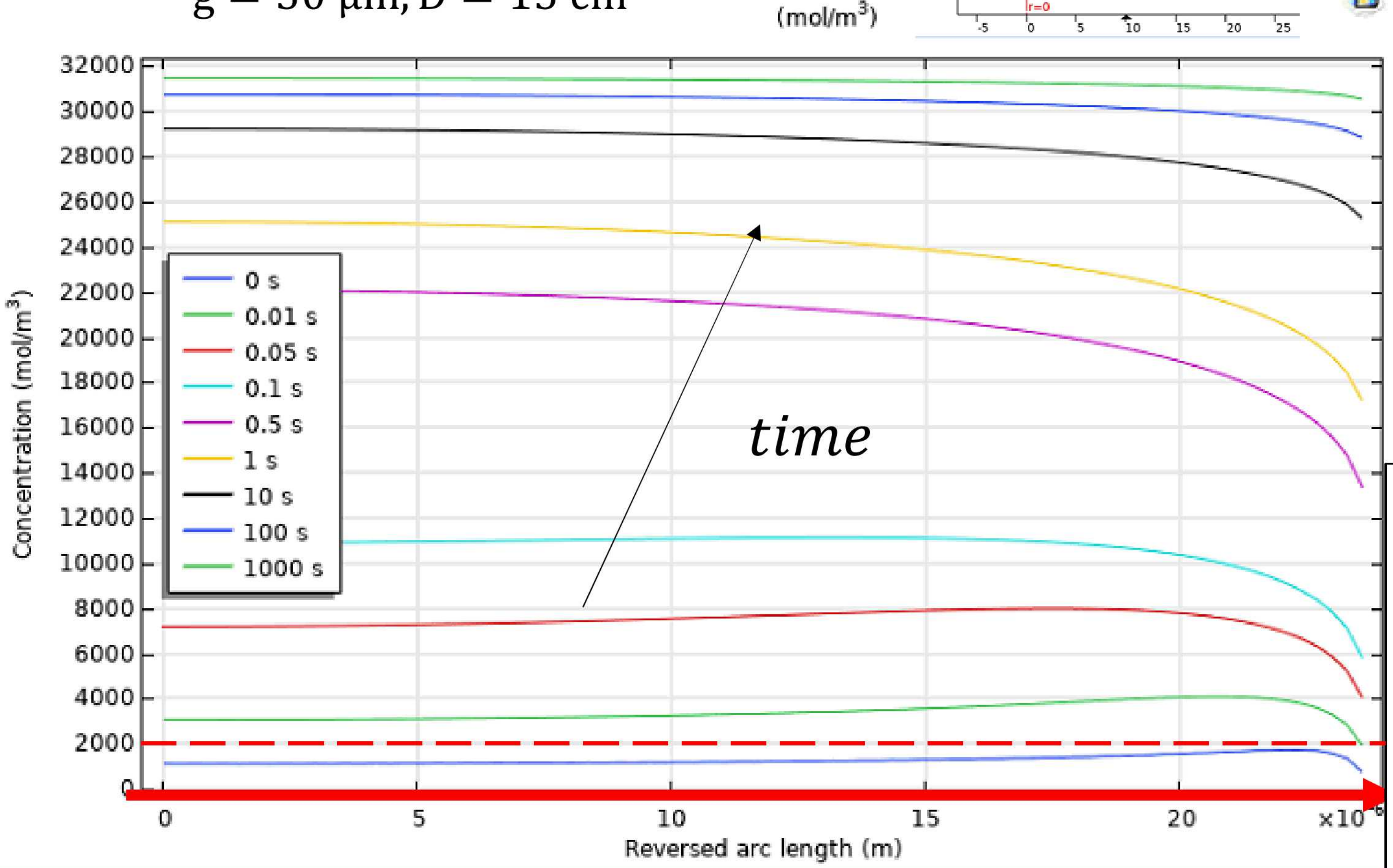
**Geometric Parameters:**

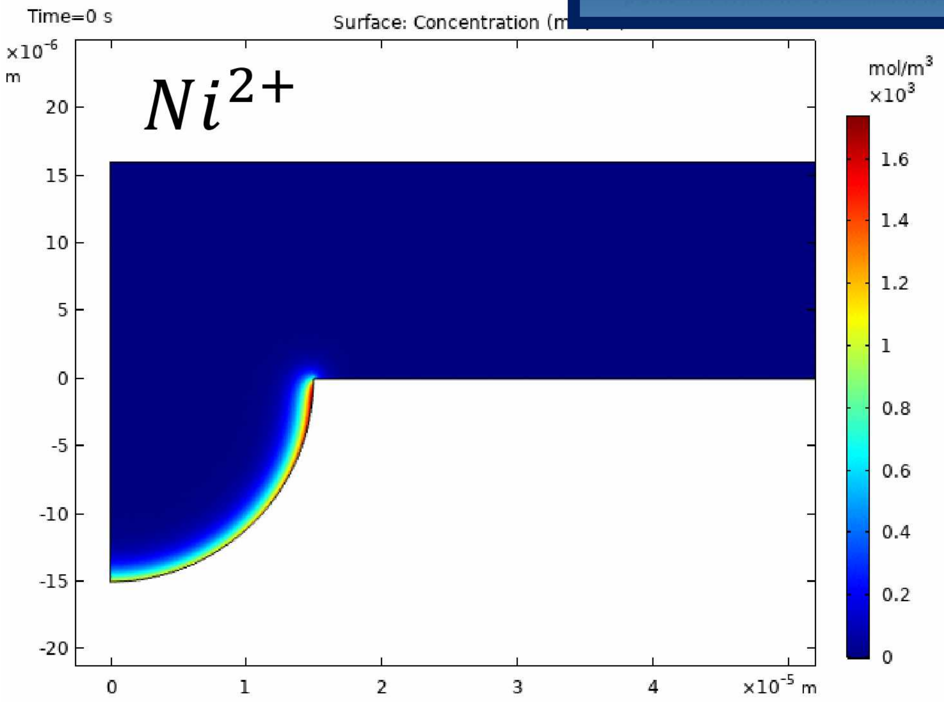
*Time varied*

$t = 0\text{–}1000\ s, WL = 16\ \mu m,$

$g = 30\ \mu m, D = 15\ cm$




Critical concentration $\left[\frac{mol}{m^3}\right]$ at BASE of pit satisfied for:

$[Ni^{2+}] > \mathbf{2048.84}$ **after** $\mathbf{0 < t < 0.01}$ ***seconds***

$[Cr^{3+}] > 3213$ after $0 < t < 0.01$ *seconds*

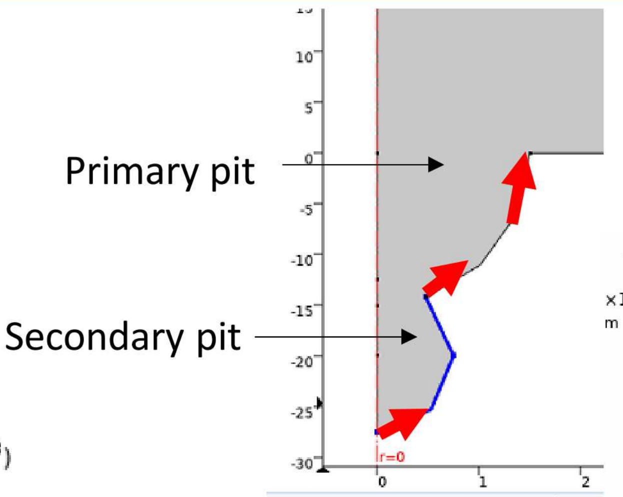
$[Fe^{2+}] > 13{,}622.02$ after $0 < t < 0.01$ *seconds*

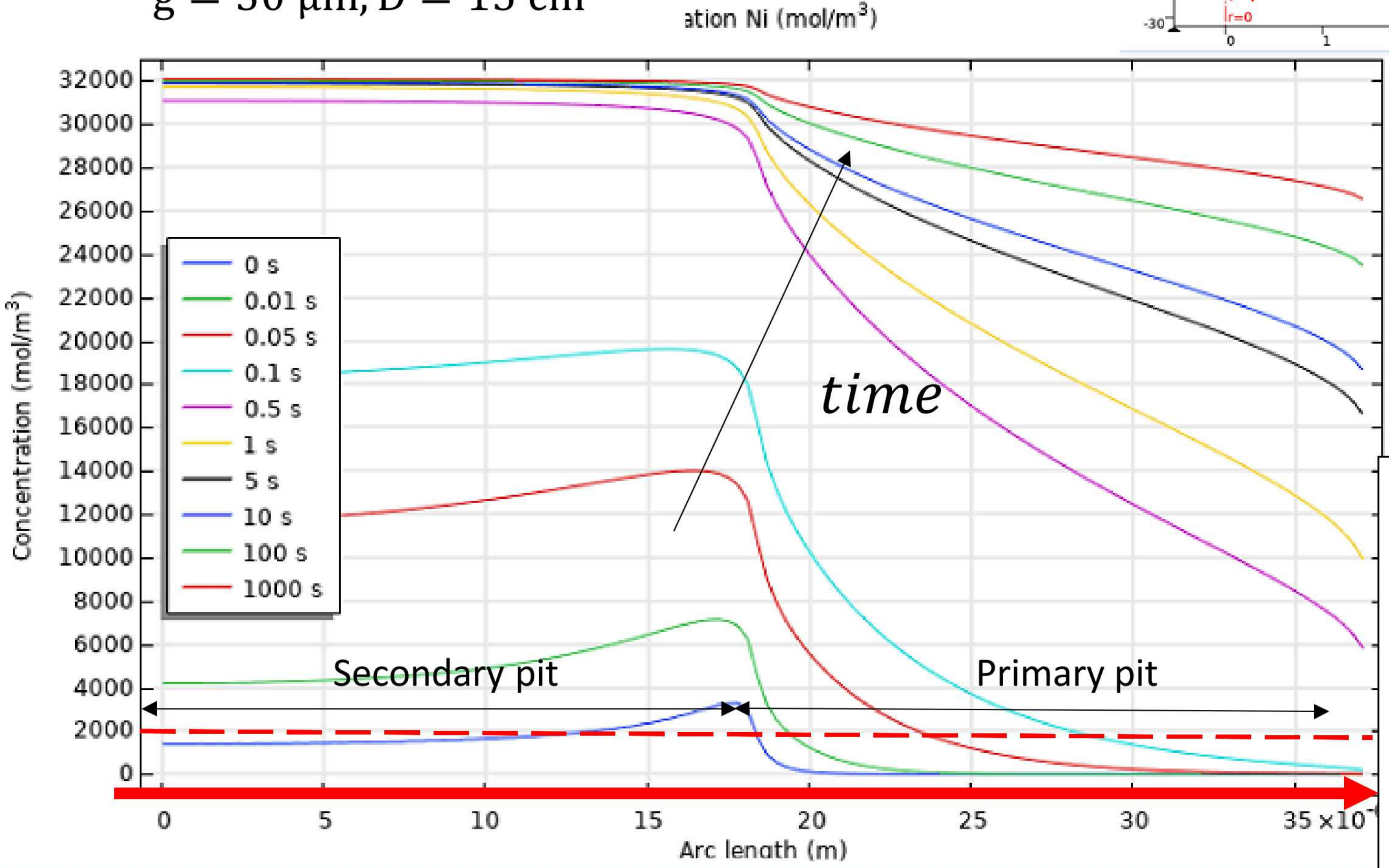
# Double Pit

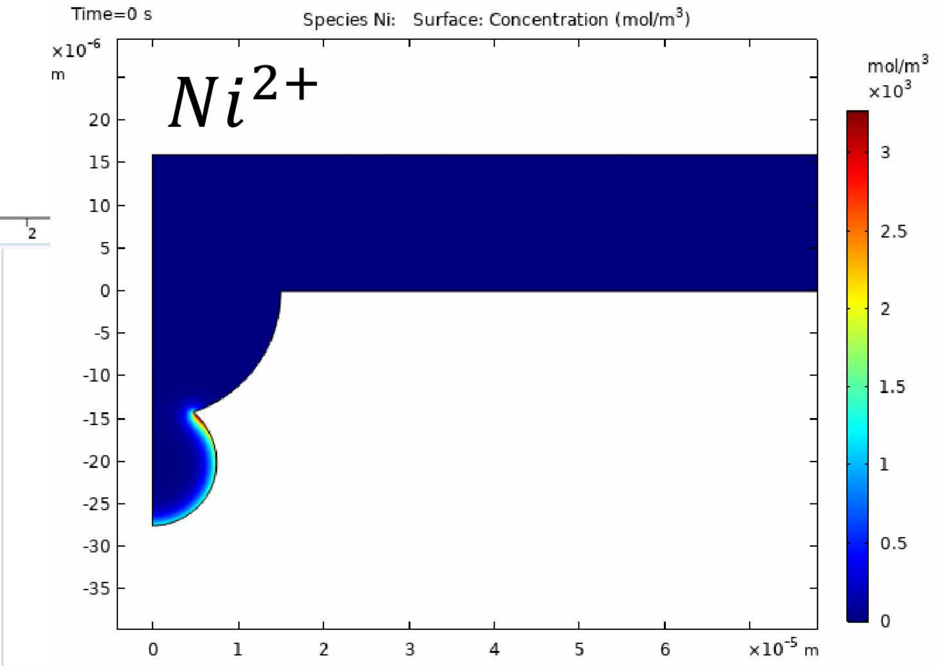
**Geometric Parameters:**

*Time varied*

$t = 0\text{–}1000\ \text{s}, \text{WL} = 16\ \mu\text{m},$
$g = 30\ \mu\text{m}, D = 15\ \text{cm}$




Critical concentration $\left[\frac{mol}{m^3}\right]$
at BASE of pit satisfied for:

$[Ni^{2+}] > \mathbf{2048.84\ after\ 0 < t < 0.01}\ \boldsymbol{seconds}$

$[Cr^{3+}] > 3213$ after $0 < t < 0.01$ *seconds*

$[Fe^{2+}] < 13{,}622.02$ after $0 < t < 0.01$ *seconds*

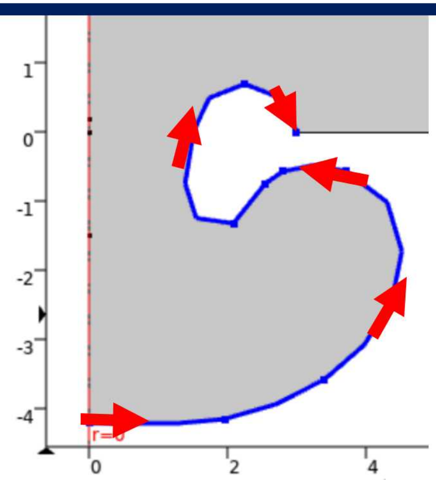
# Undercut Pit

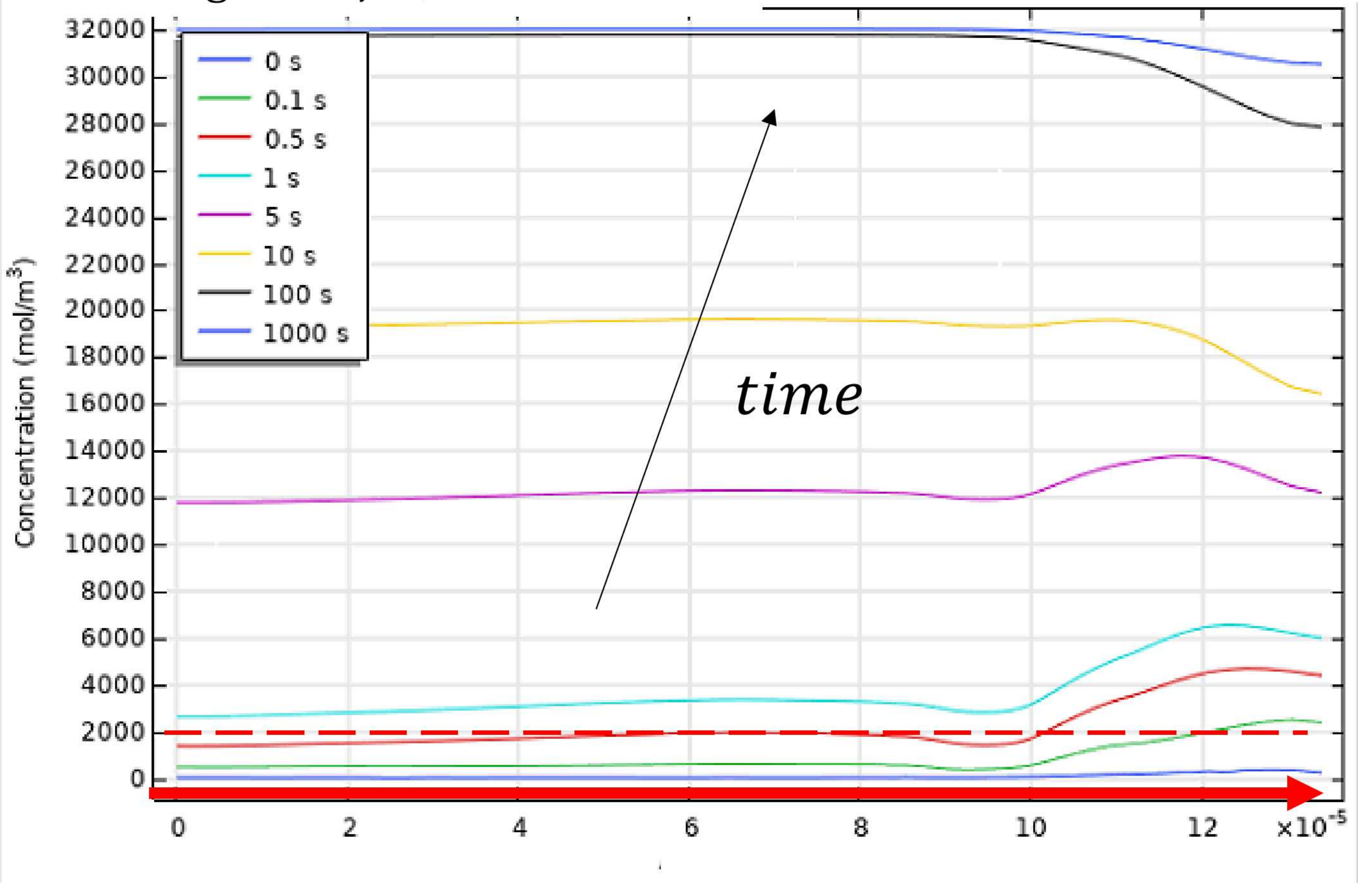
Geometric Parameters:

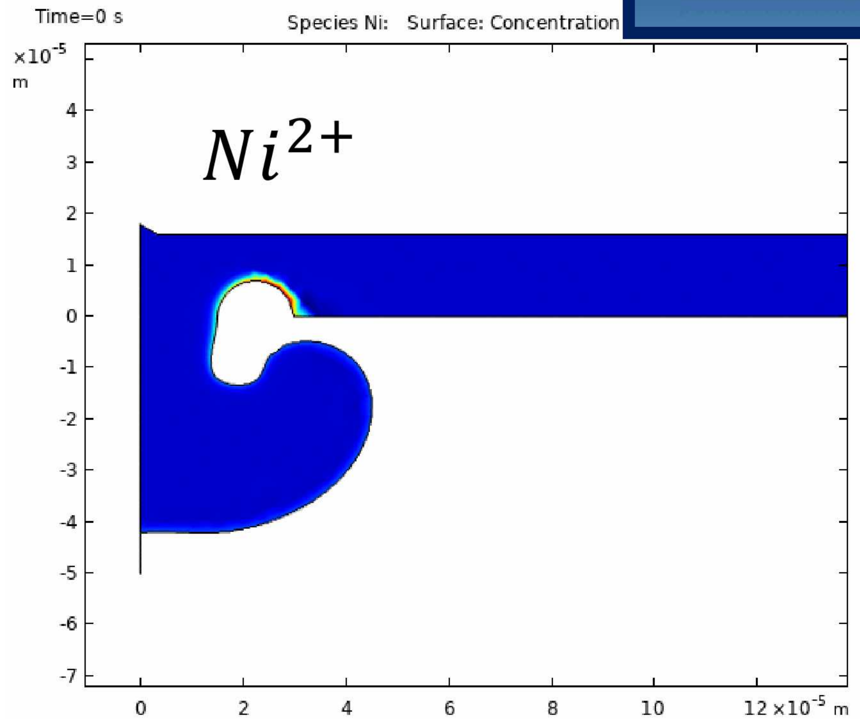
*Time varied*

$t = 0\text{–}1000\ s, \mathrm{WL} = 16\ \mu\mathrm{m},$

$g = 30\ \mu\mathrm{m}, \mathrm{D} = 15\ \mathrm{cm}$






Critical concentration $\left[\frac{mol}{m^3}\right]$ at BASE of pit satisfied for:

$[Ni^{2+}] > \mathbf{2048.84}$ **after** $\mathbf{0.5 < t < 1}$ ***seconds***

$[Cr^{3+}] > 3213$ after 1 *second*

$[Fe^{2+}] > 13{,}622.02$ after 0.5 *seconds*

# Conclusions for Time-Dependent Modeling

- At the edge of the pit, it is more difficult to satisfy the critical concentration criteria (due to easier diffusion)
- In all pit geometries, all metal ions satisfy the critical concentration criteria *before reaching steady state*
- The Double Pit reached stability the *quickest,* but was also the quickest to *loose stability* via easy diffusion out of the pit

- Both steady-state and time-dependent results indicate that with the current set of pit geometries, all pits will actively corrode
    - Note that these pits are all fairly small, so it is not surprising that they are stable.
    - In the future we will explore pit size to find size at which external cathode cannot support pit growth

# Disclaimer and Acknowledgements


- Any opinions, findings and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of Sandia National Laboratory
- Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525
- This work was supported through a DOE funded ACT program
- Discussions with other members of CESE at the University of Virginia are gratefully acknowledged

CENTER FOR ELECTROCHEMICAL SCIENCE AND ENGINEERING
Department of Materials Science and Engineering
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# Finite Element Modeling of SS316 Pit Stability, with respect to Geometry Parameters, Under Atmospheric Conditions

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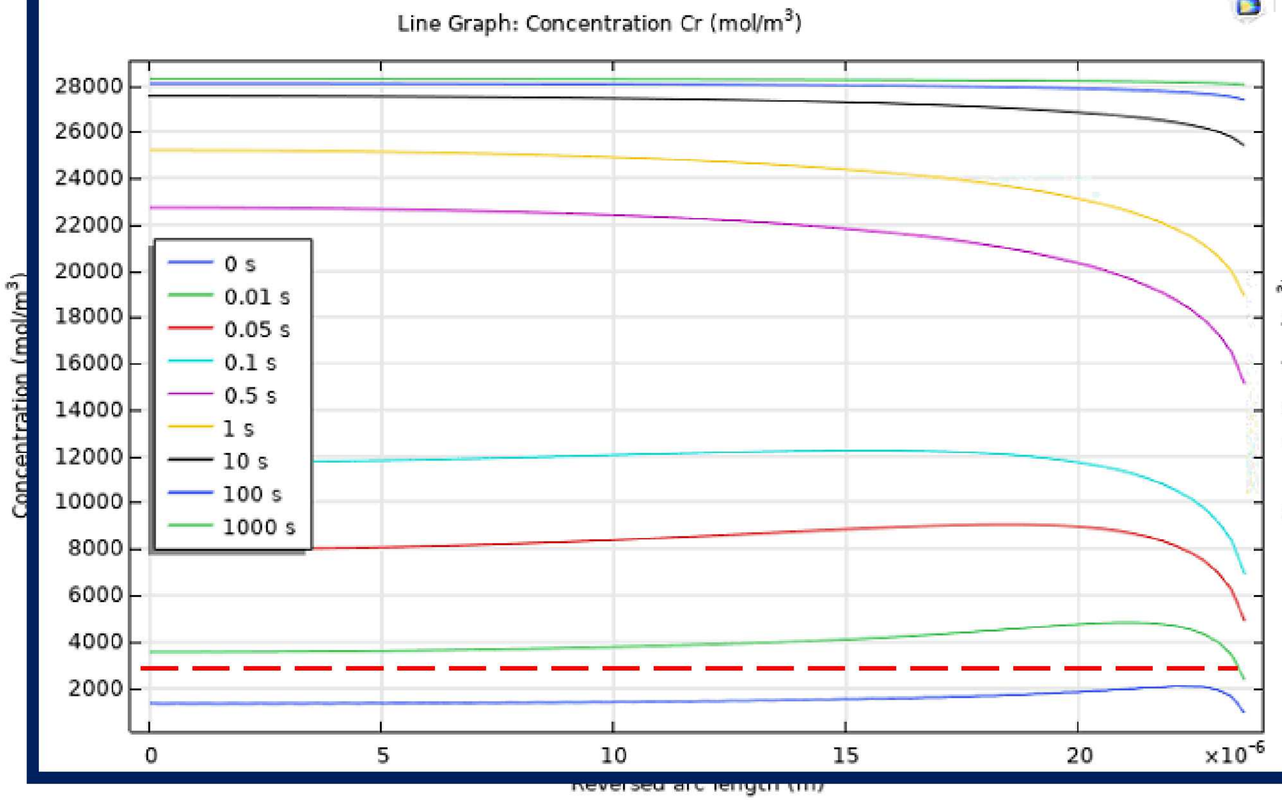
*C06-1306: Atmospheric and Marine Corrosion, PRIME ECS 2020, Virtual, 10/5/2020 from 10:40 to 11am HST*

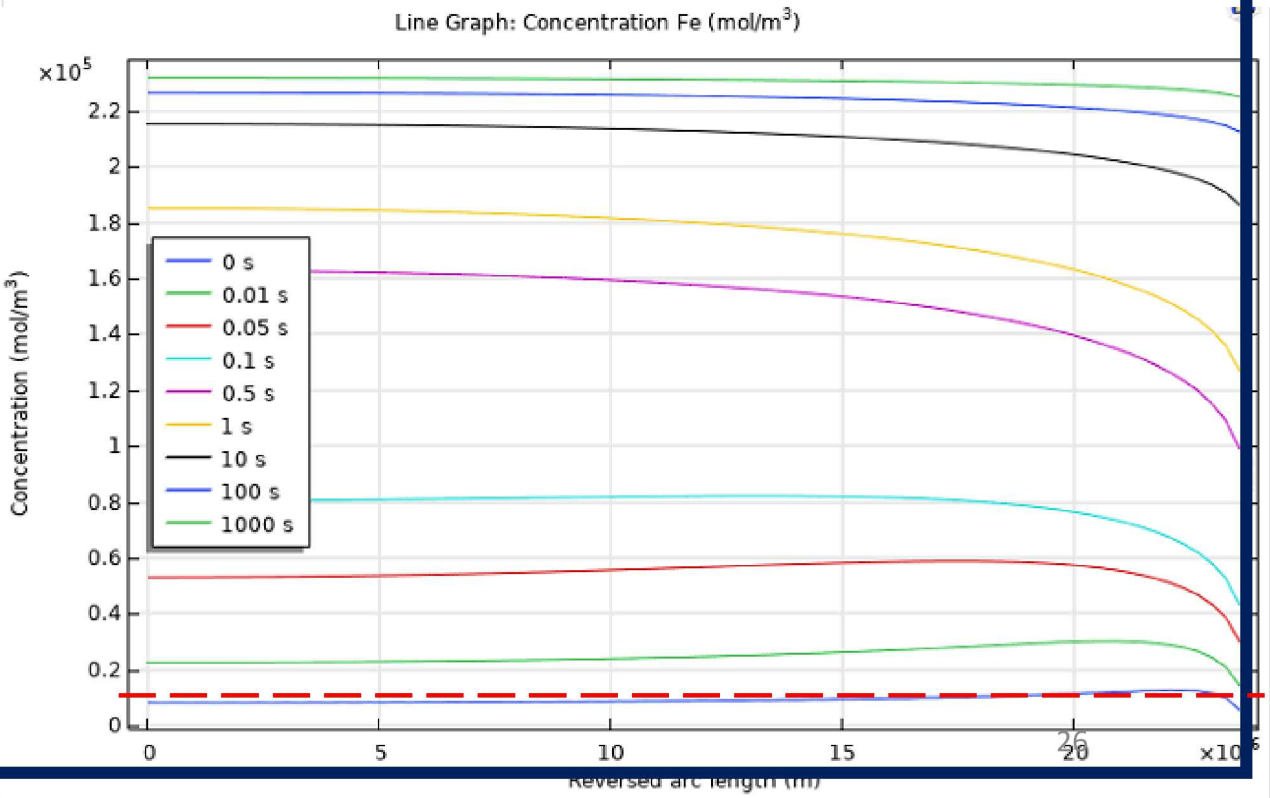
Presenter email: rjs2wu@virginia.edu

# Hemisphere Pit

$Cr^{3+}$

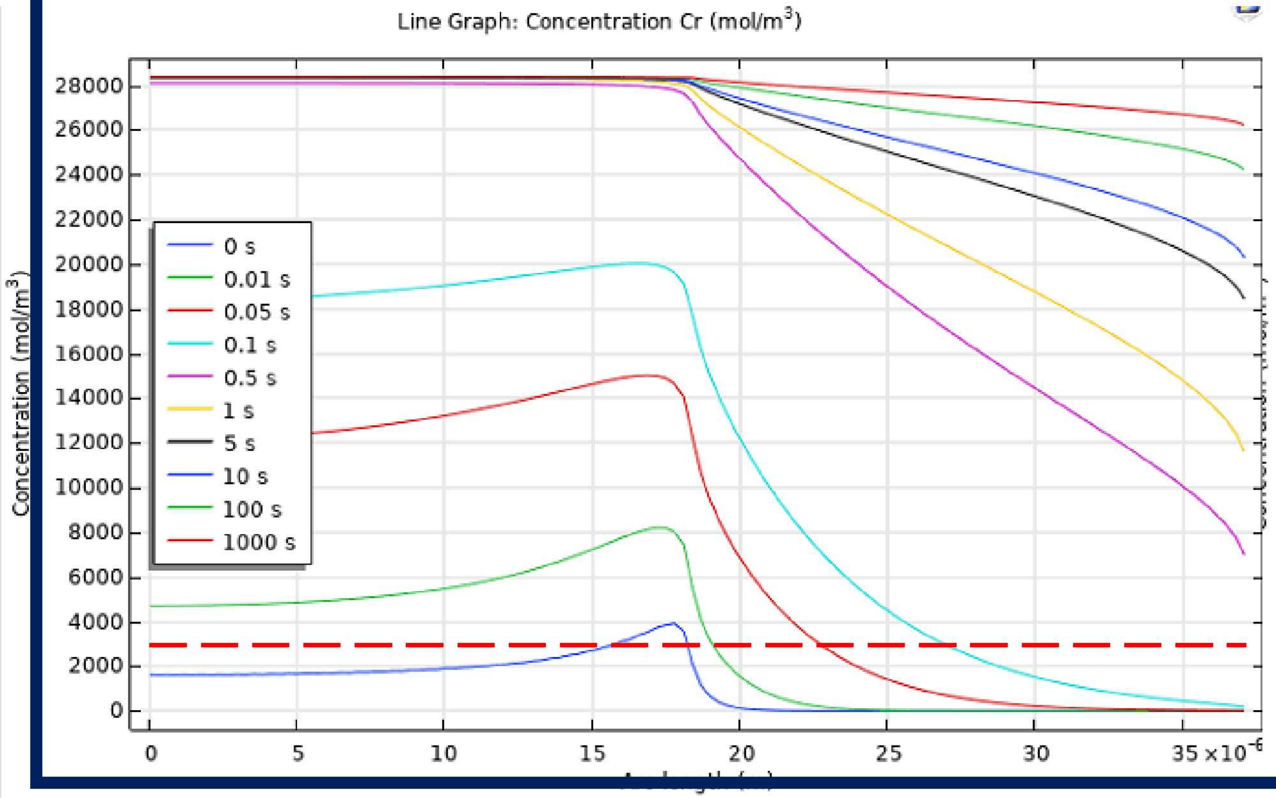



$Fe^{2+}$

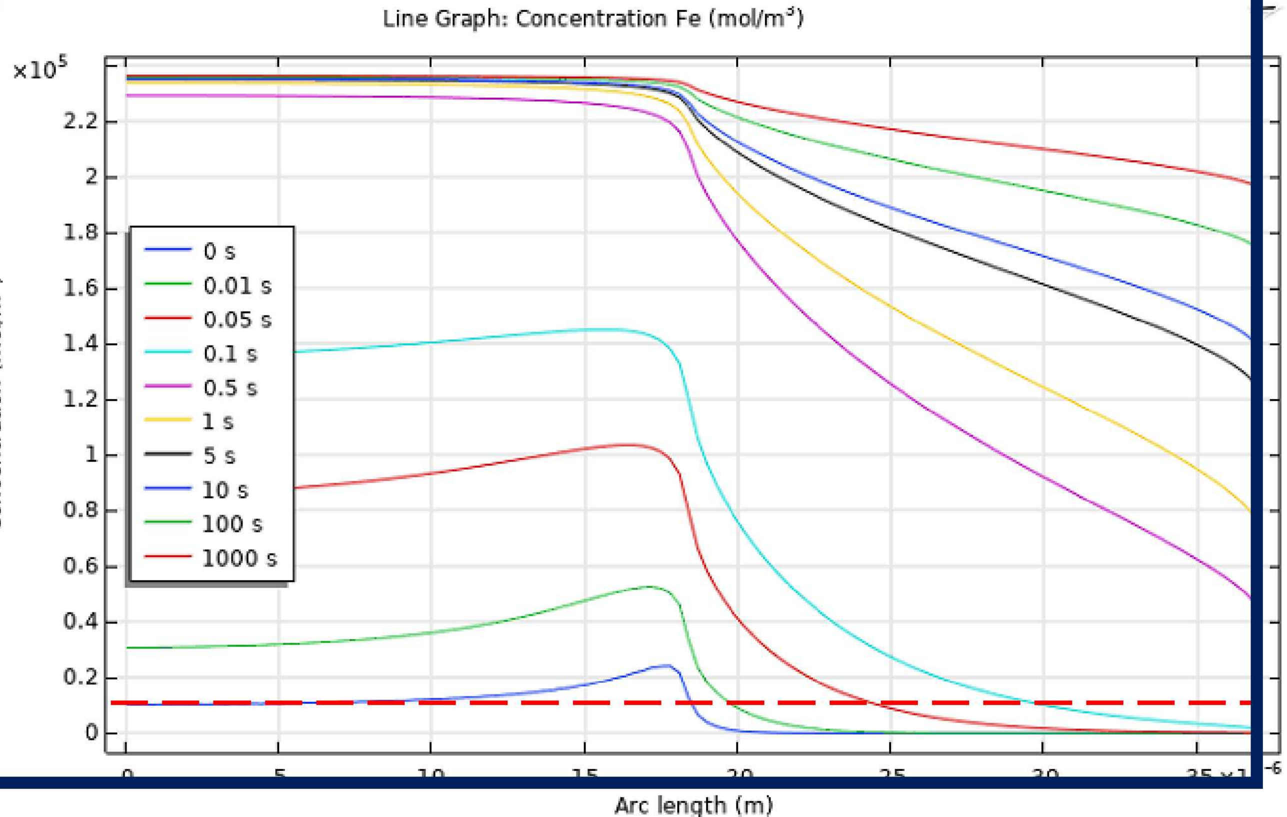


# Double Pit

$Cr^{3+}$

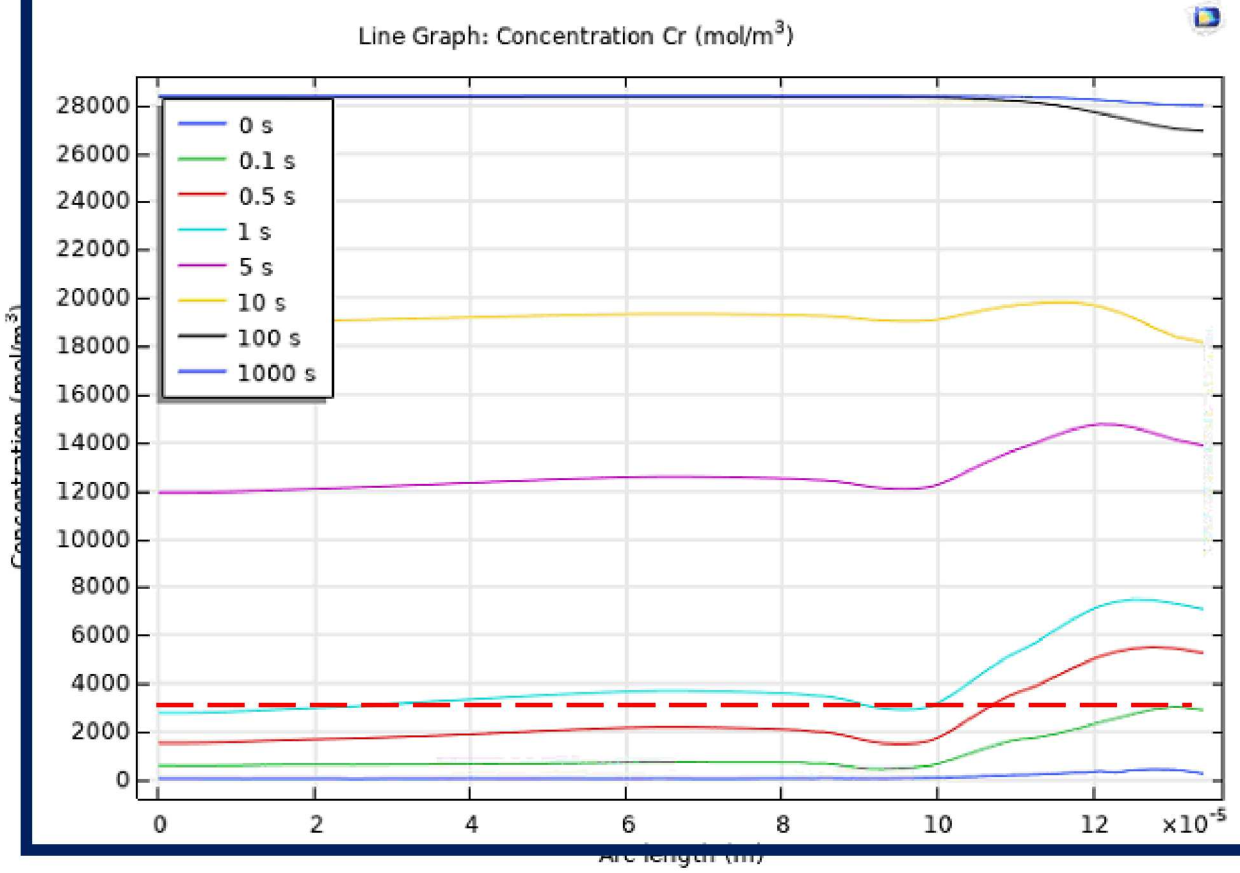



$Fe^{2+}$



# Undercut Pit

$Cr^{3+}$




$Fe^{2+}$