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Sandia National Laboratories

Accelerated Relevant Atmospheric Corrosion Testing of Austenitic Stainless Steel for SNF Storage Environments

International High-Level Radioactive Waste Management Conference, Phoenix, AZ

November 14th, 2022 | Rebecca Schaller[1]

Andrew Knight[1], Ryan Katona[1], Jason Taylor[1], Timothy Montoya[2], Erin Karasz[1], and Charles Bryan[1]

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[2]*University of Virginia*

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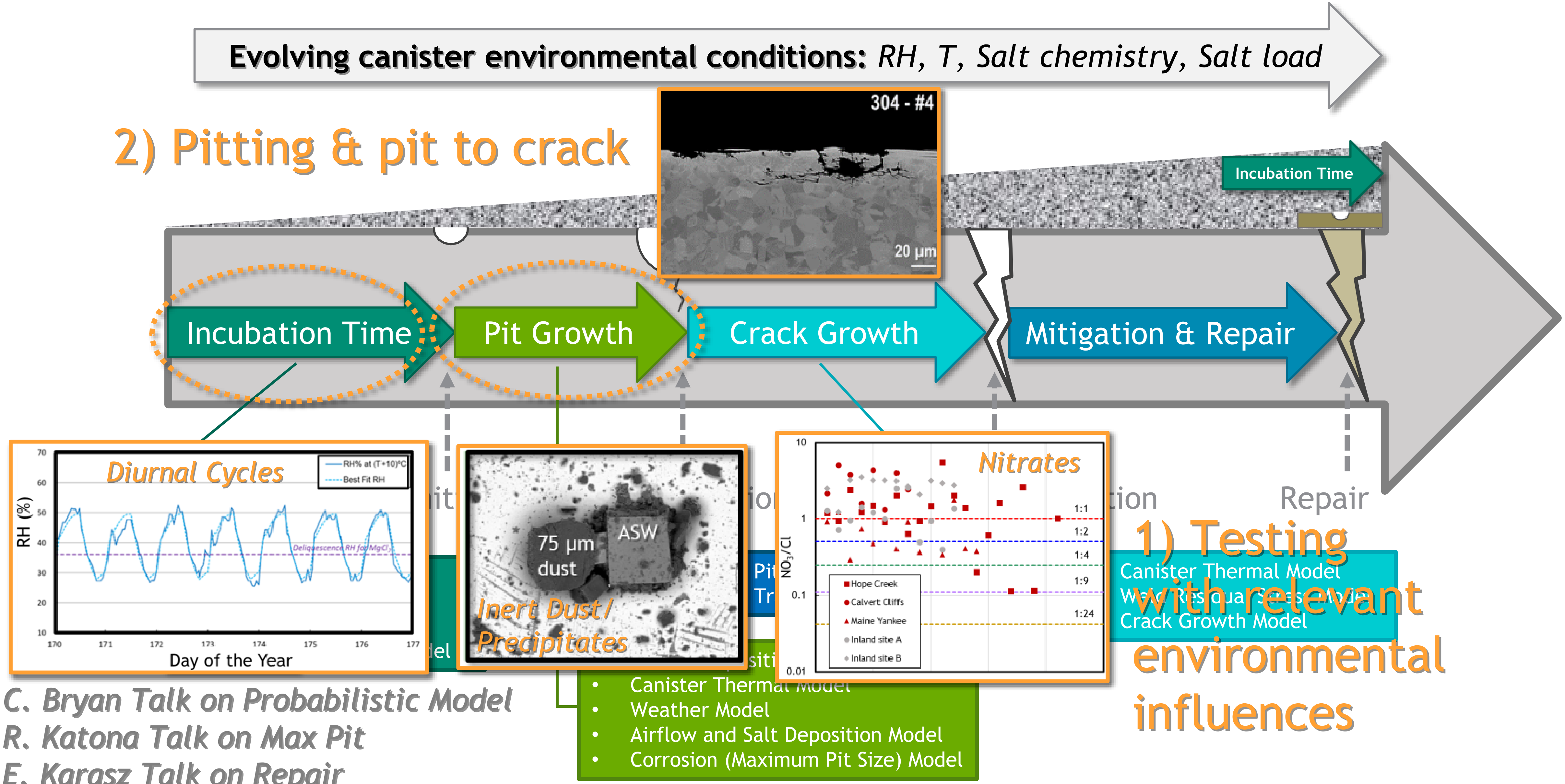
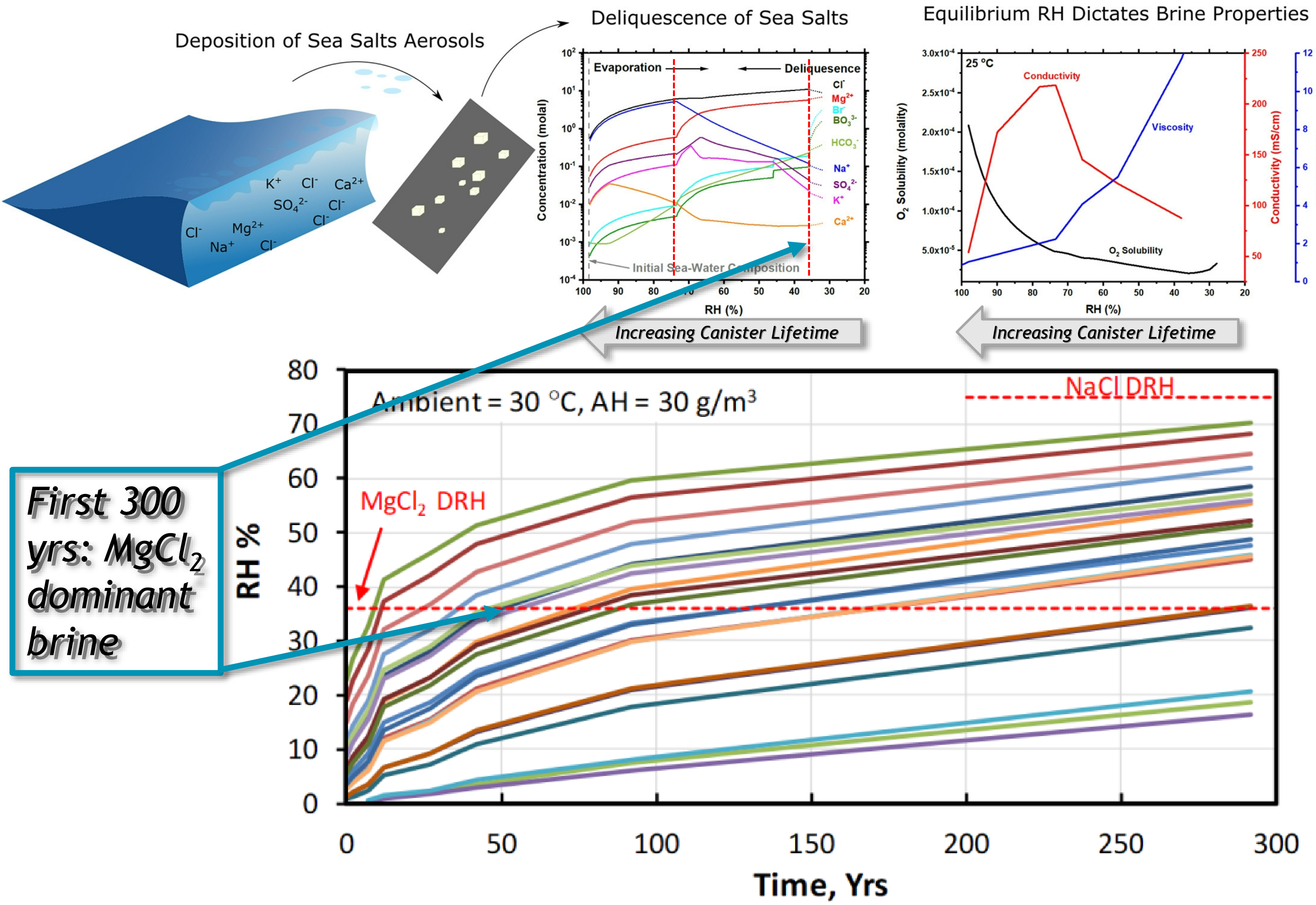
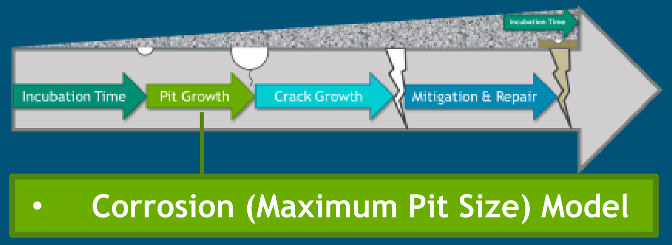
Background – SNF and SCC



C. Bryan Talk on Probabilistic Model
R. Katona Talk on Max Pit
E. Karasz Talk on Repair

Environment – Brine formation





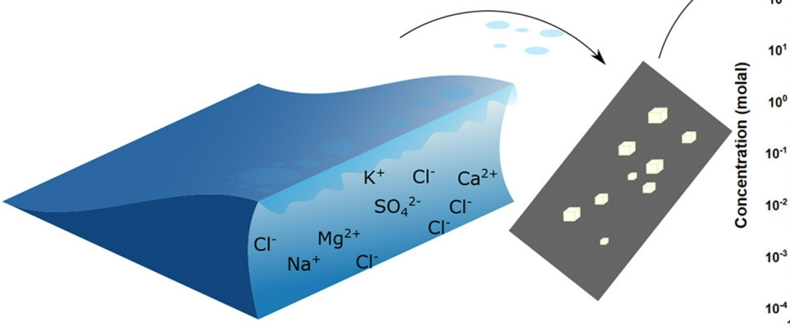
Corrosion Damage:

- Function of brine chemistry
- Function of Deposition
- *What about factors influencing/governing morphology?*

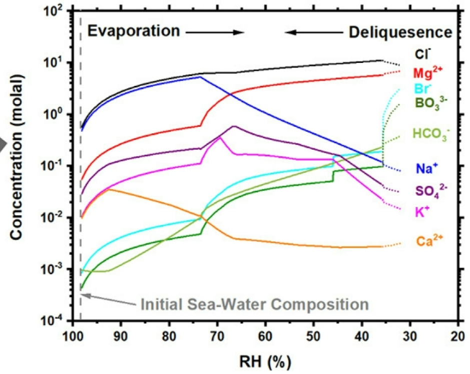
Bryan, C. R., Knight, A. W., Katona, R. M., Sanchez, A. C., Schindelholz, E. J., & Schaller, R. F. (2022). Physical and chemical properties of sea salt deliquescent brines as a function of temperature and relative humidity. *Science of the Total Environment*, *824*, 154462.

Environmental Influences

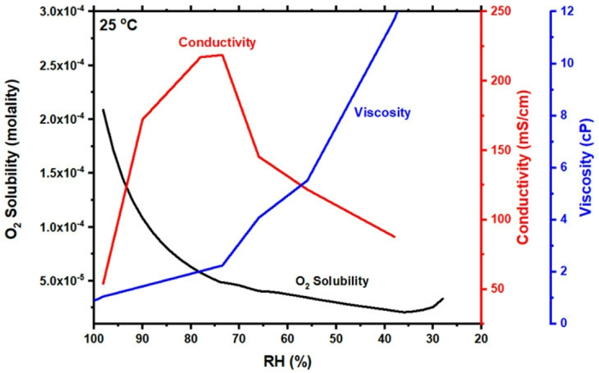
Deposition of Sea Salts Aerosols

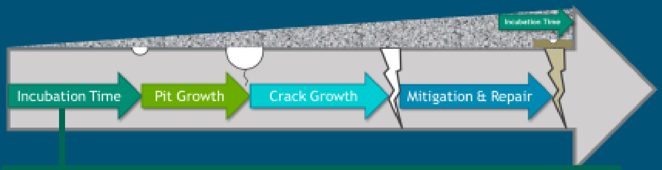


Deliquescence of Sea Salts



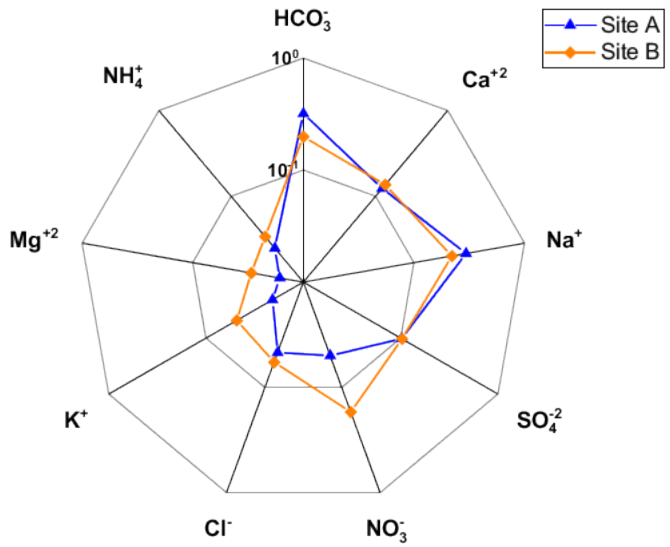
Equilibrium RH Dictates Brine Properties



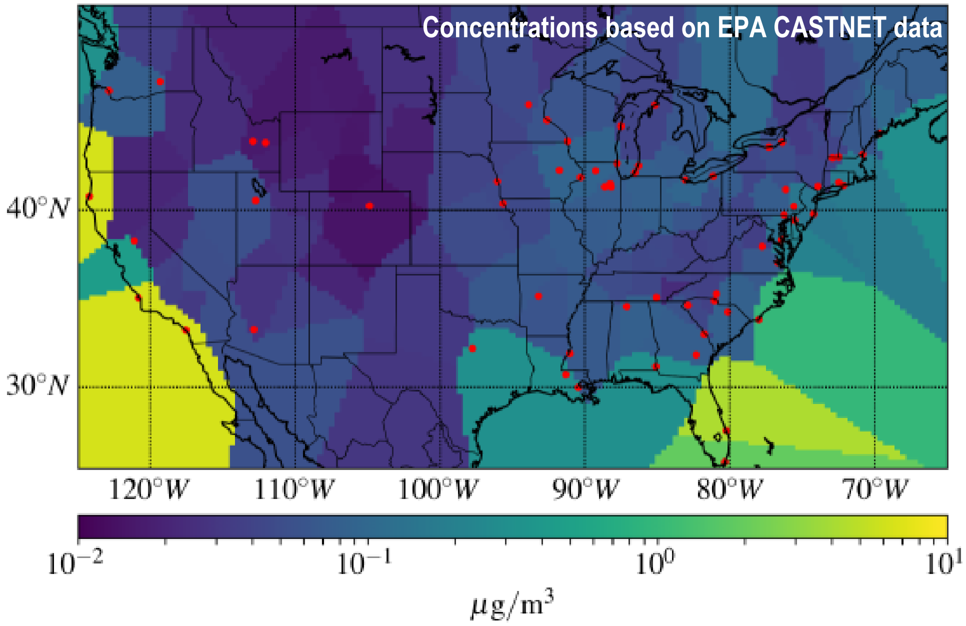


- Salt Composition Assumption
- Canister Thermal Model
- Weather Model
- Airflow and Salt Deposition Model

Composition varies per site



Deposition varies per site



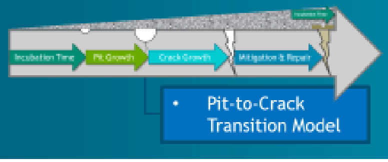
Brine composition controlled by environment

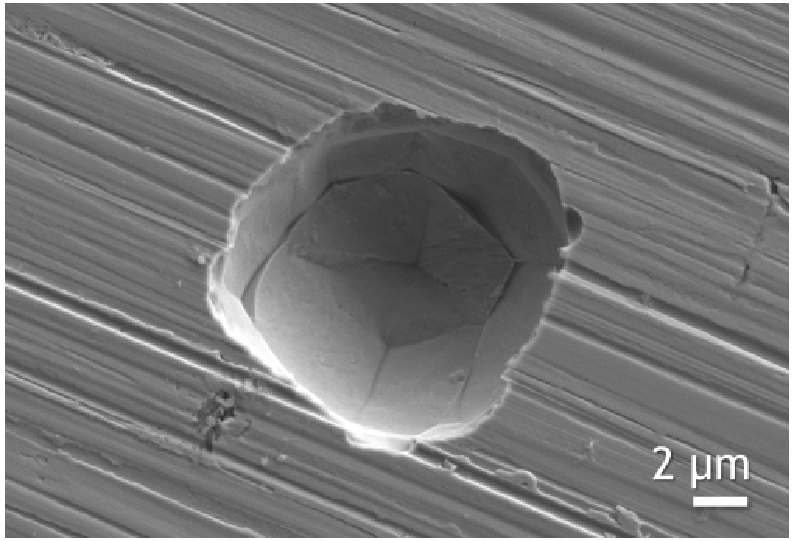
Varies across locations:

- *Composition*
- *Deposition density*

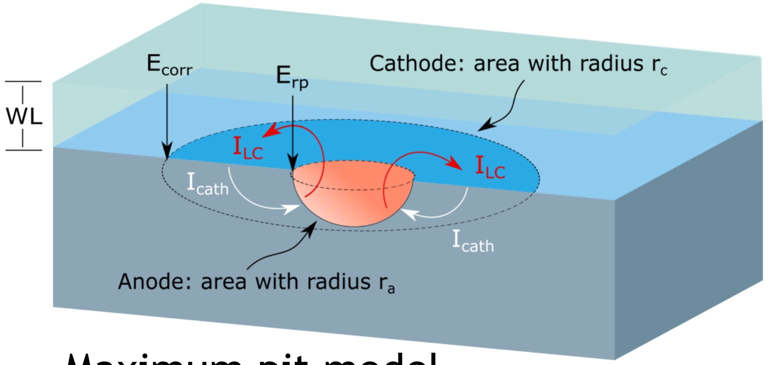
Bryan, C. R., Knight, A. W., Katona, R. M., Sanchez, A. C., Schindelholz, E. J., & Schaller, R. F. (2022). Physical and chemical properties of sea salt deliquescent brines as a function of temperature and relative humidity. Science of the Total Environment, 824, 154462.

Why care about pitting?



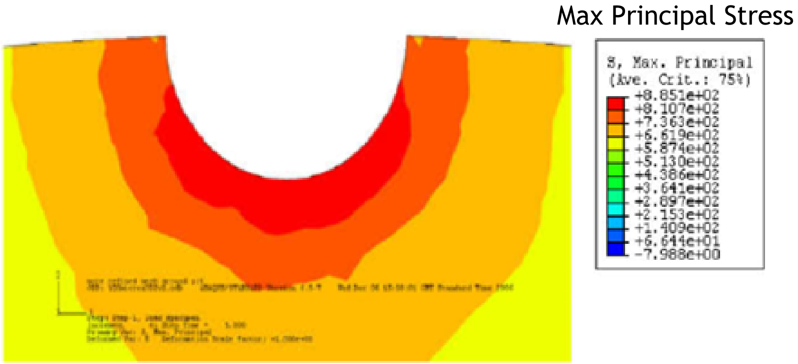


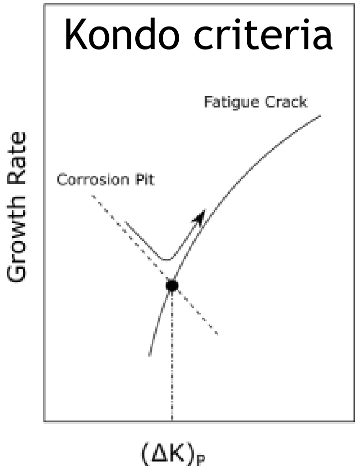
Pit to crack transition



Maximum pit model

Pit → stress/strain concentrator

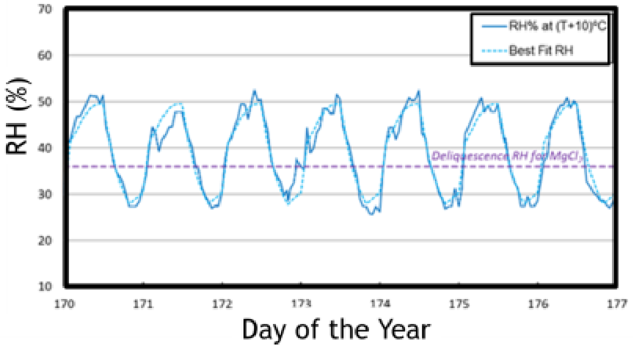




Chen, Z. Y., & Kelly, R. G. (2009). Computational modeling of bounding conditions for pit size on stainless steel in atmospheric environments. *Journal of the Electrochemical Society*, *157*(2), C69.
Turnbull, A., Wright, L., & Crocker, L. (2010). New insight into the pit-to-crack transition from finite element analysis of the stress and strain distribution around a corrosion pit. *Corrosion Science*, *52*(4), 1492-1498.
Kondo, Y. Prediction of fatigue crack initiation life based on pit growth. *Corrosion* **45**, 7-11, doi:10.5006/1.3577891 (1989).
Mai, W., & Soghrati, S. (2017). A phase field model for simulating the stress corrosion cracking initiated from pits. *Corrosion Science*, *125*, 87-98.

Development of Relevant Lab Exposures:
Environmental influences

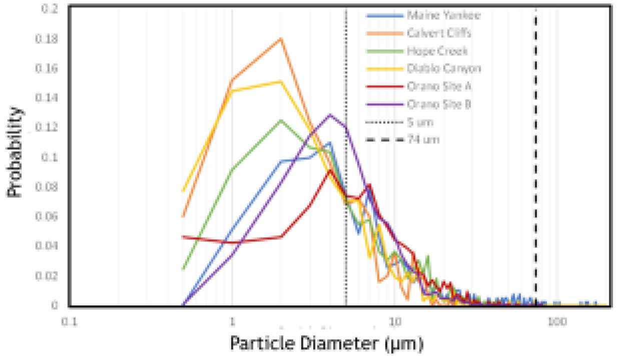
Diurnal Cycles

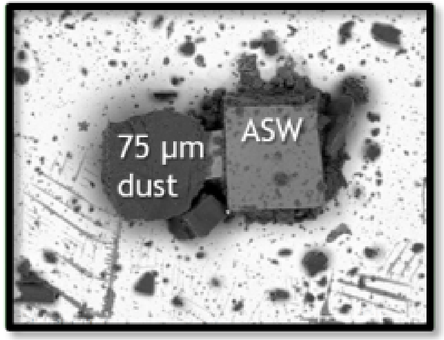


Cycle Conditions:

- Based on ISFSI weather data
- ΔT imposed mimic canister surface

Dust/Precipitates

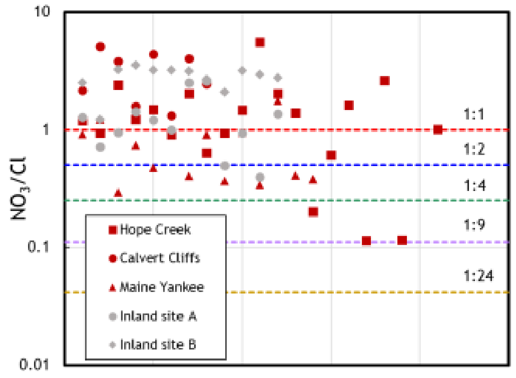




Dust Conditions:

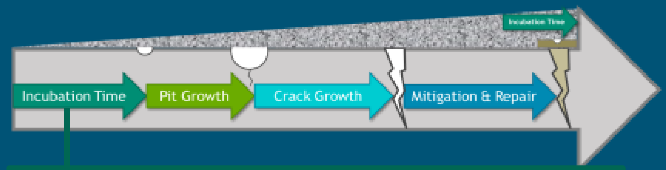
- Dust size based on ISFSI site collection
- Co-deposition of ASW with SIL-CO-SIL® 75 or MIN-U-SIL® 10

Chemistry



Electrochemical:

- NO_3:Cl ratios representative of ISFSI sites
- Varied NO_3:Cl ratios in NaCl, $MgCl_2$, Seawater



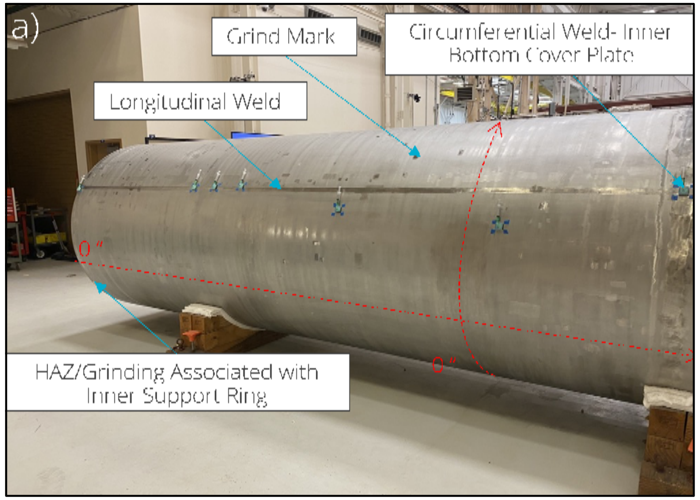
- Salt Composition Assumption
- Canister Thermal Model
- Weather Model
- Airflow and Salt Deposition Model

- Is pitting behavior influenced by SNF conditions? *i.e. higher T, more concentrated brines*
- Explore influences of:
  - Diurnal Cycles
  - Dust
  - Chemistry

A. Knight Talk on Environment

Development of Relevant Lab Exposures:
Material influences

Example Horizontal Canister

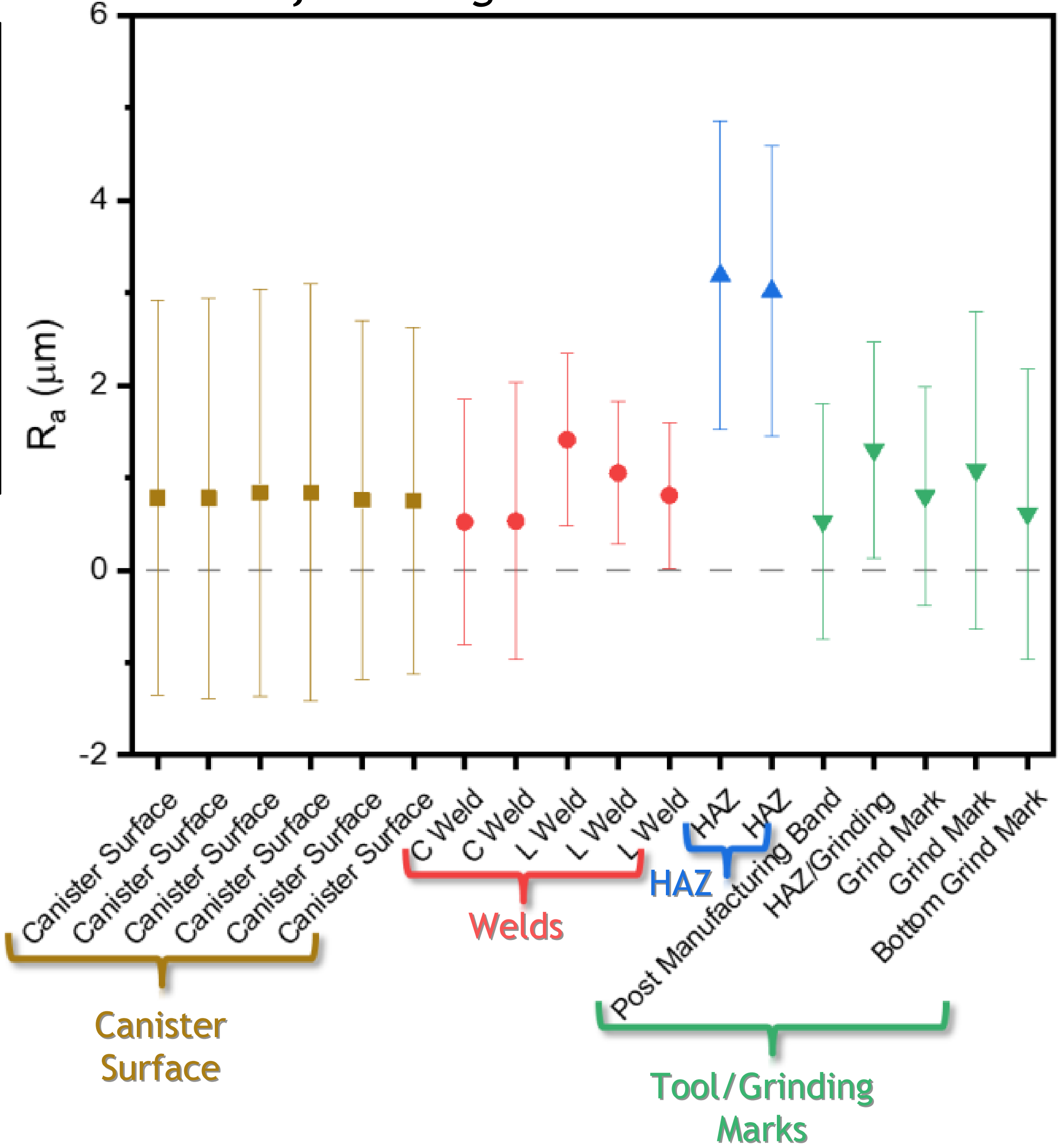


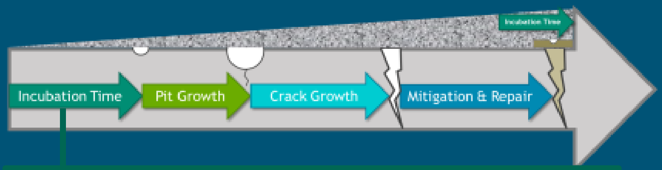
<u>*Canister Alloy Composition:*</u>

Austenitic Stainless Steels

- *304*
- *304L*
- *316L*

Surface Roughness Characterization





- Salt Composition Assumption
- Canister Thermal Model
- Weather Model
- Airflow and Salt Deposition Model

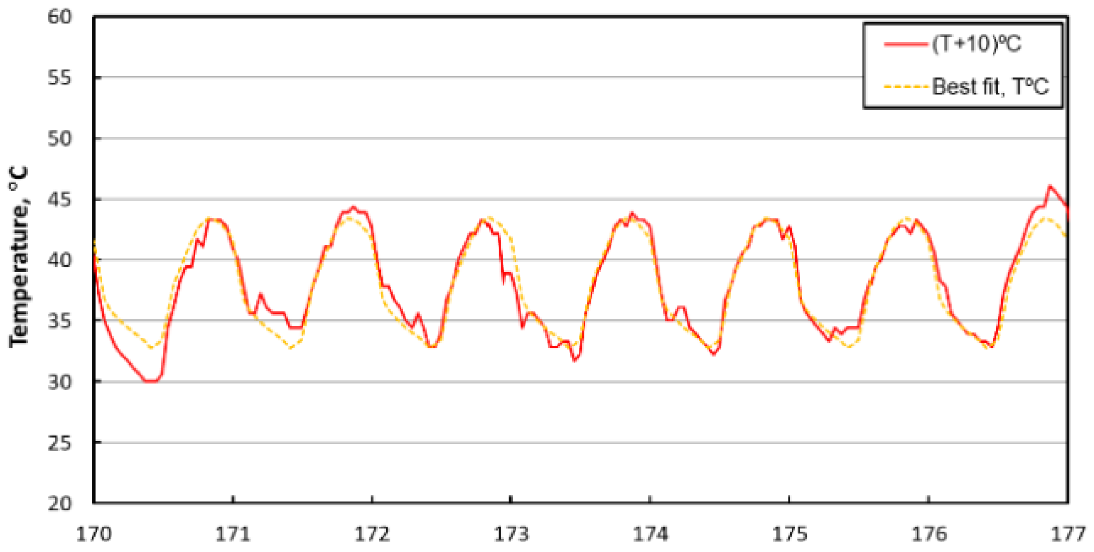
Material <u>surface finish</u> varies across canister surface

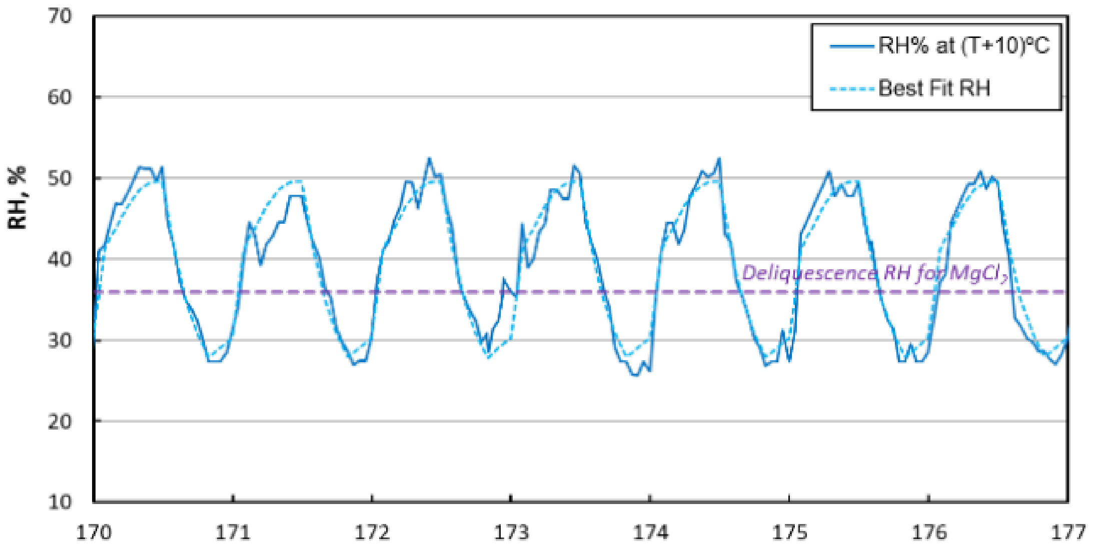
- *Mill finish*
- *Welds*
- *Surface prep to remove tooling marks*

Material <u>composition</u> varies per canister manufacturer/date of manufacturing

Initial results of Relevant Lab Exposures: ***Diurnal Cycling***

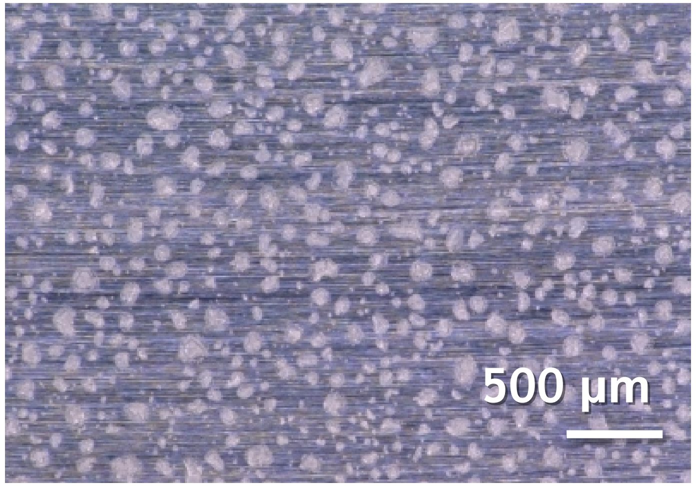
Diurnal Cycles





Cycle Conditions:

- Storage site weather data
- ΔT: heated canister
- Fine distribution of artificial seawater (300 μg/cm²)
- SS304, SS304H, SS316L
- Rough grind, 600 grit, and mirror finish

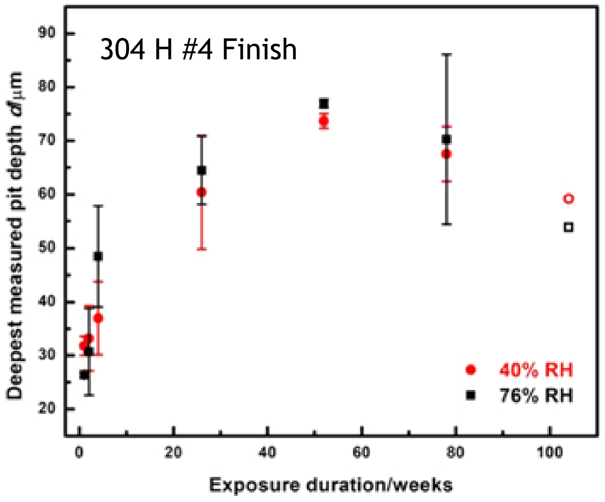


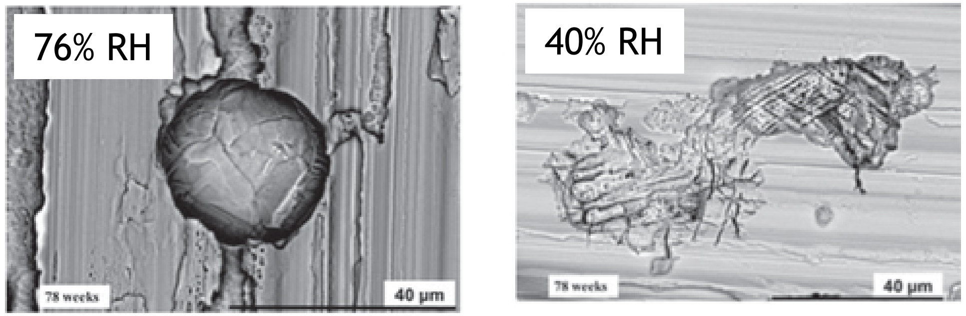
- Corrosion (Maximum Pit Size) Model

- Explore influences of:
  - **Diurnal Cycles**
  - Dust
  - Chemistry

Influence of diurnal cycling on pitting

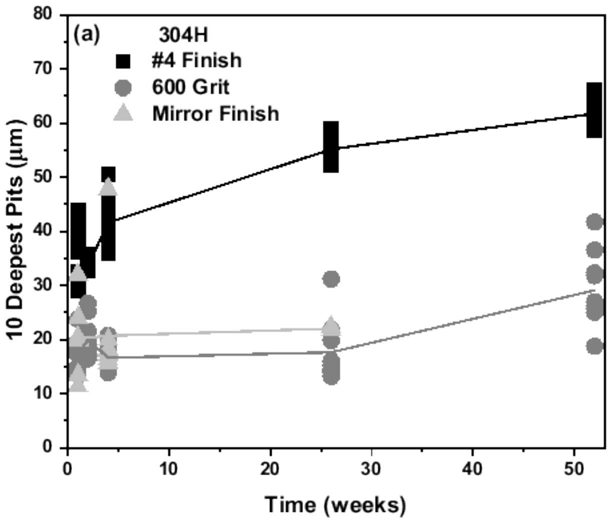
Constant RH



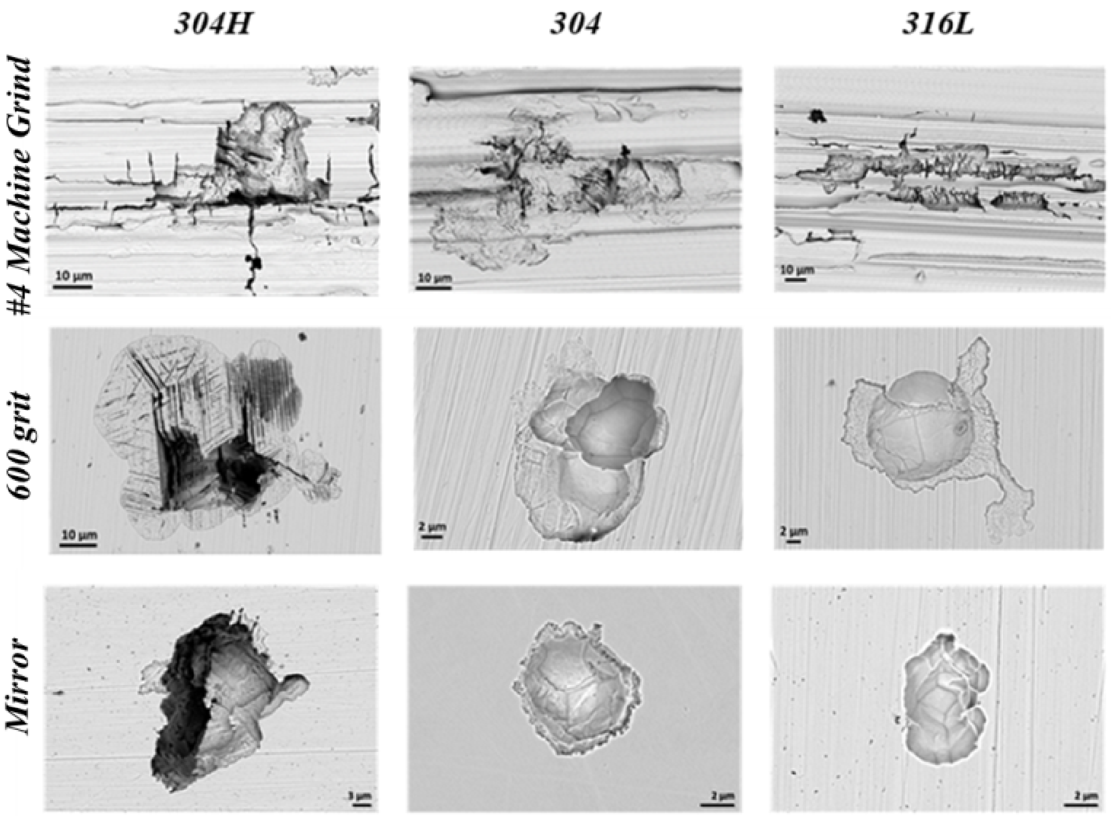


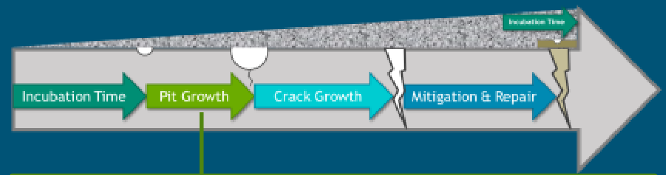
Diurnal Cycles

Profilometry comparison across material finish for 304H coupons



Diurnal Cycles





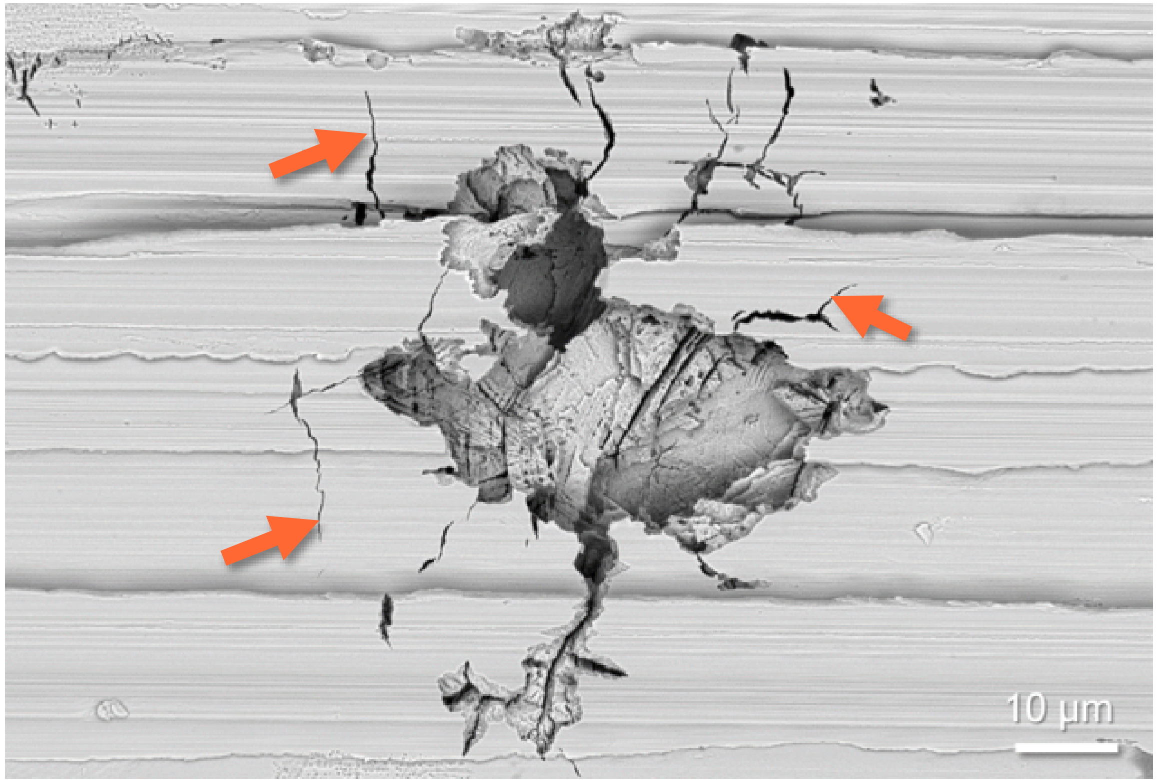
- Corrosion (Maximum Pit Size) Model

- Understanding pit growth under SNF relevant conditions:
  - Higher T
  - More concentrated brines
  - Material composition and finish

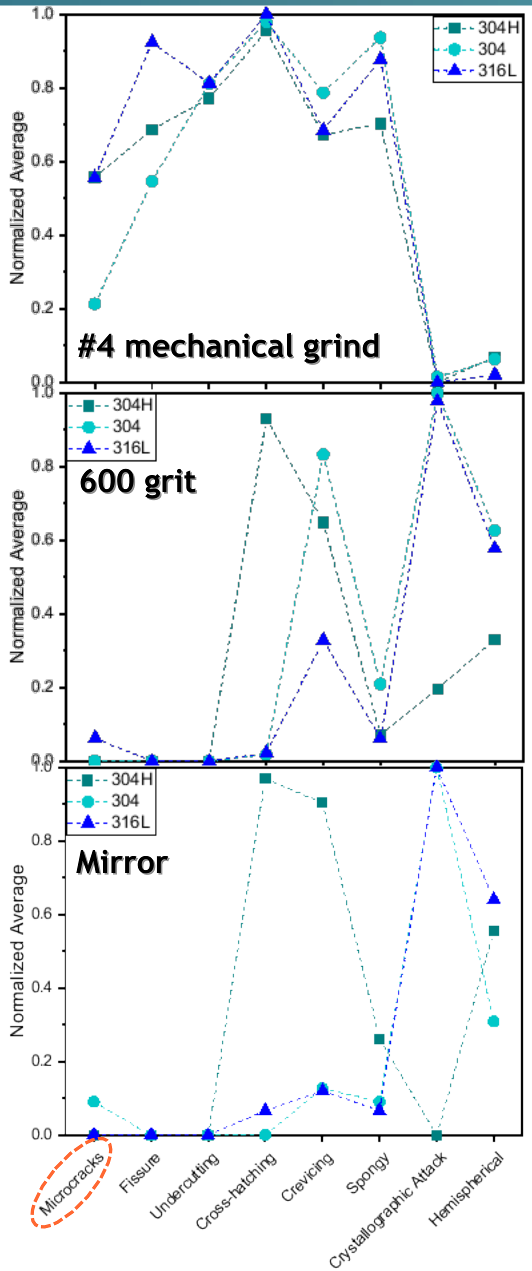
Srinivasan, J., Weirich, T.D., Marino, G.A., Annerino, A.R., Taylor, J.M., Noell, P.J., Griego, J.J.M., Schaller, R.F., Bryan, C.R., Locke, J.S. and Schindelholz, E.J., 2021. Long-term effects of humidity on stainless steel pitting in sea salt exposures. *Journal of the Electrochemical Society*, *168*(2), p.021501.

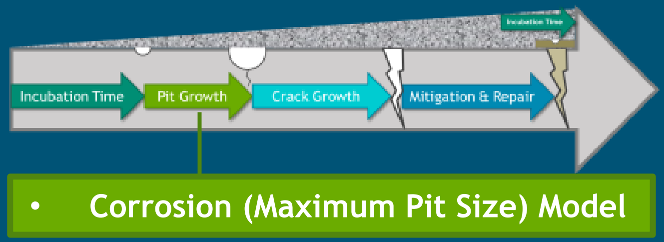
What influences pit morphology?

Cycle Conditions:
- 6 month diurnal cycle exposure (all below 52% RH)
- 304, 304H, and 316L
- #4 (~120 grit), 600 grit, mirror



Microcracking

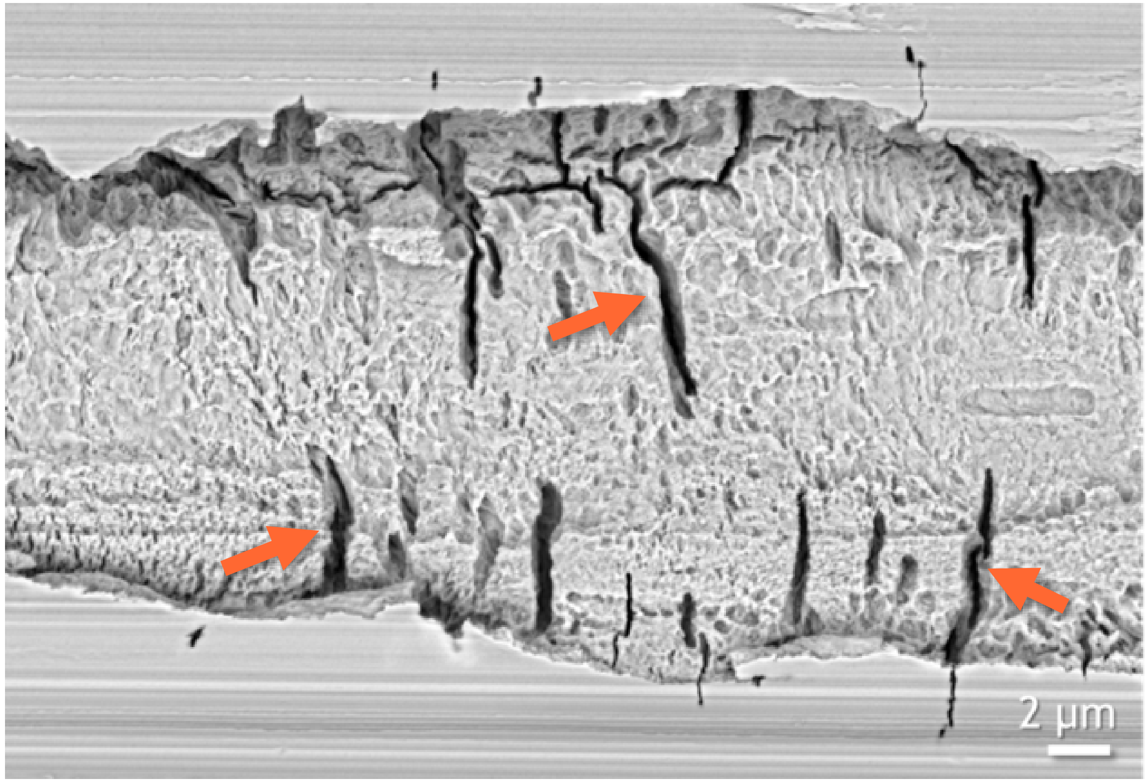




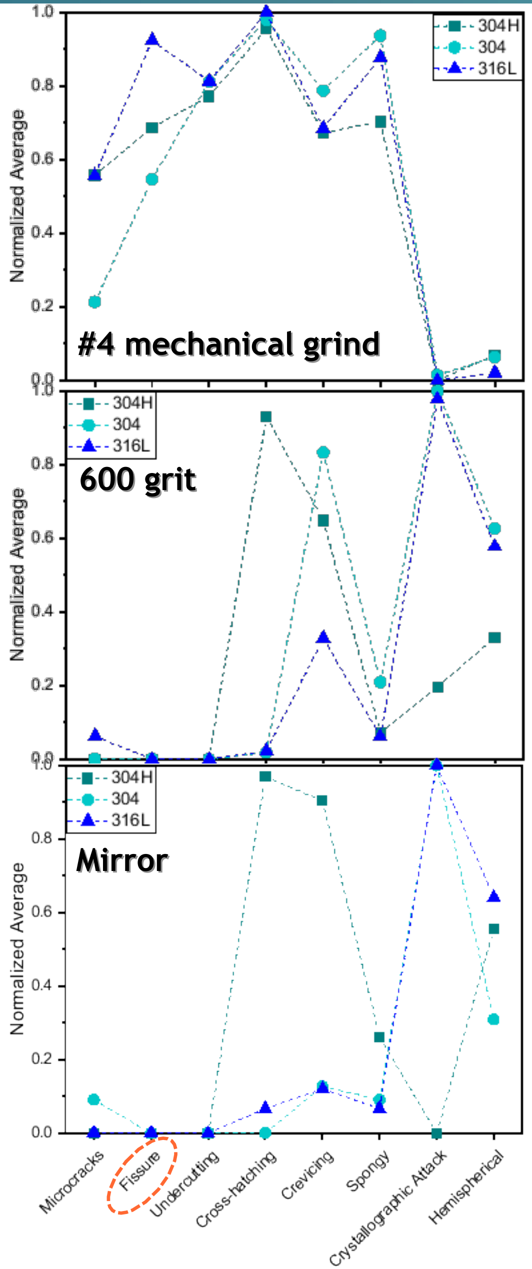
Qualitative pit characterization

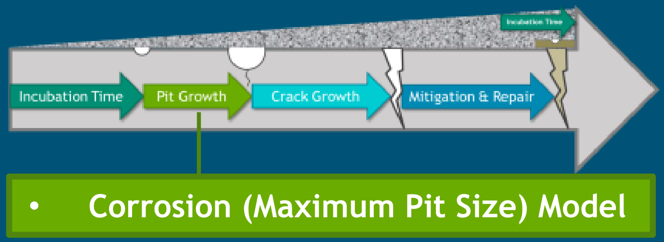
- *Initial attempt to obtain quantitative metrics*
  - *Identify dominant pit features governed by exposure, material, surface finish, etc.*

What influences pit morphology?



Fissures





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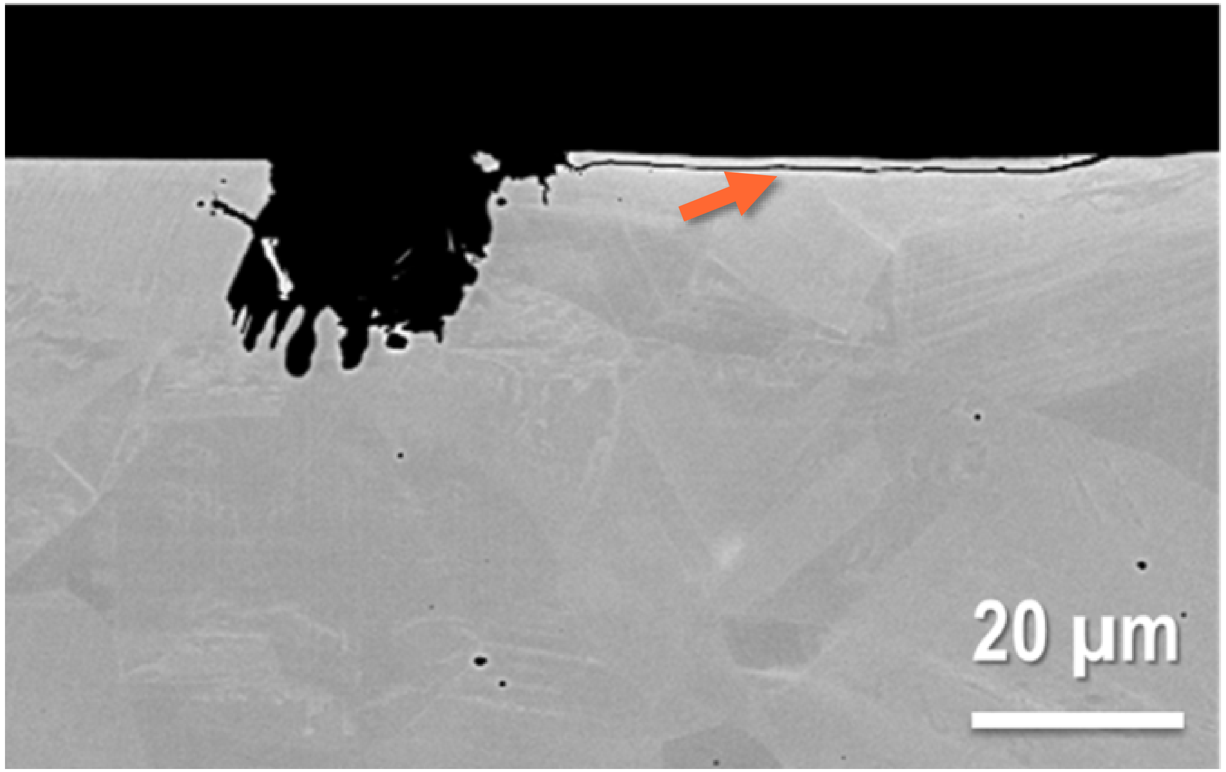
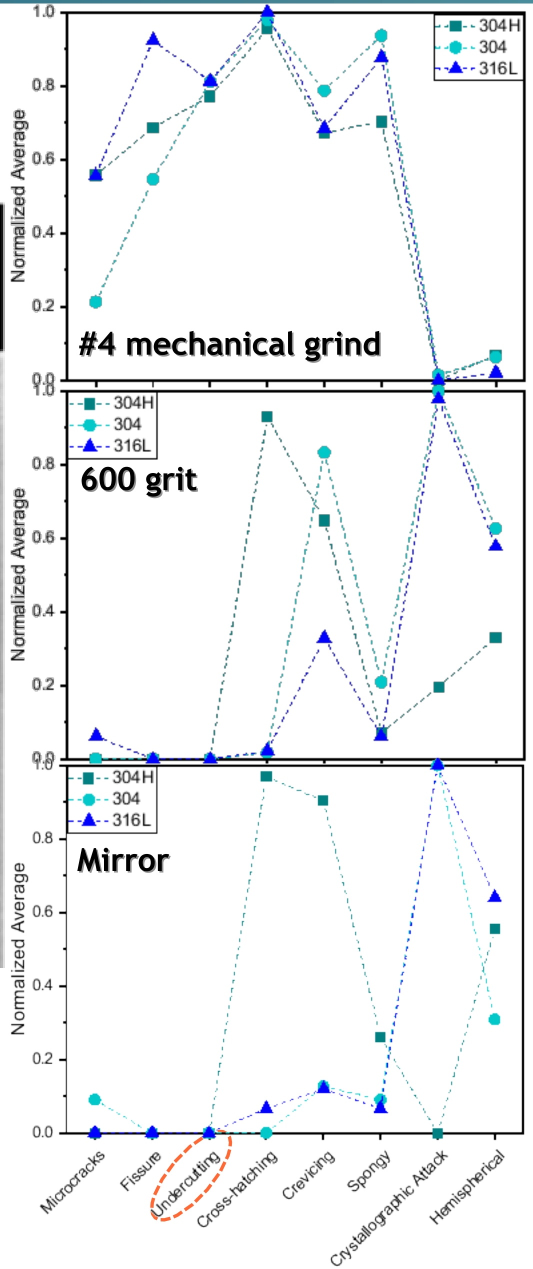
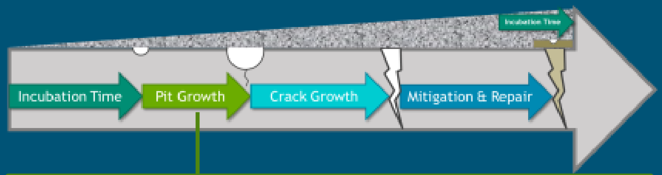


Undercutting





- Corrosion (Maximum Pit Size) Model

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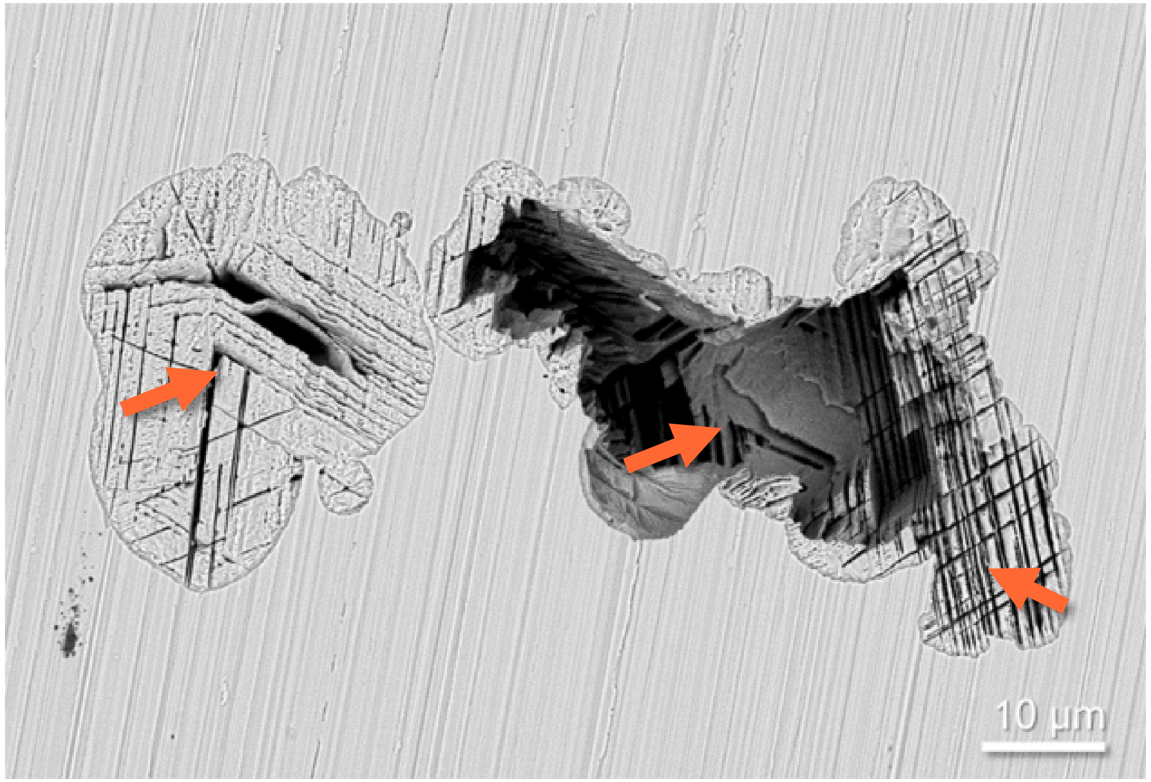
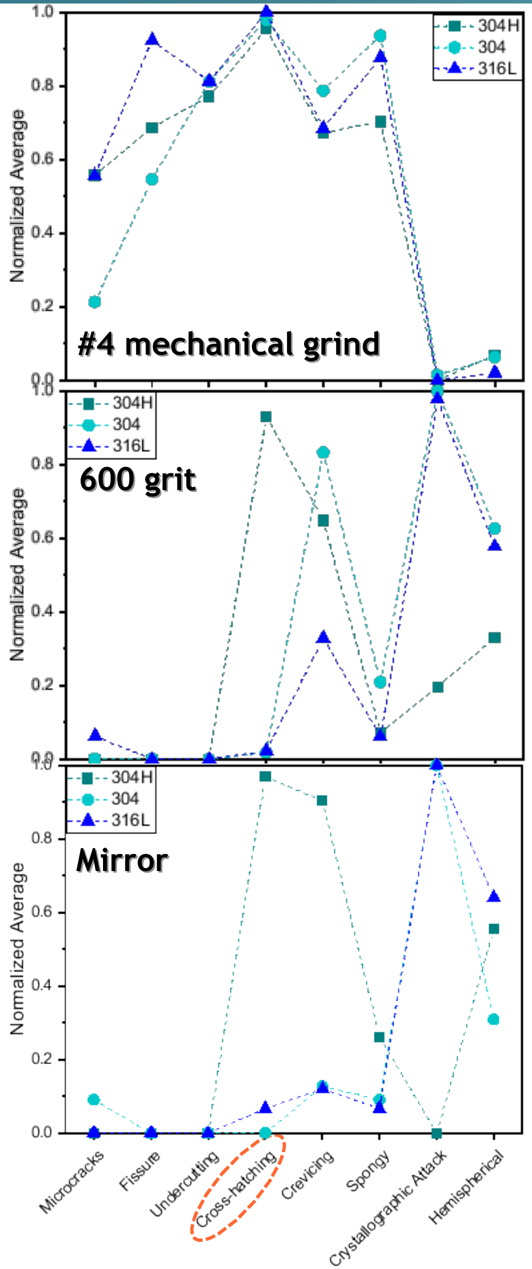
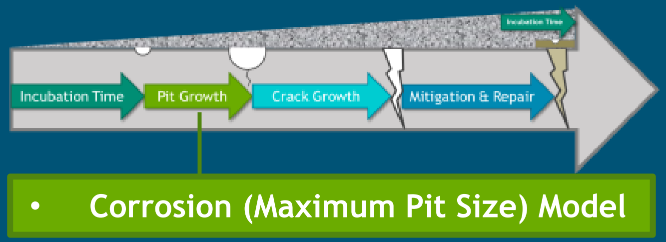


Cross-hatching





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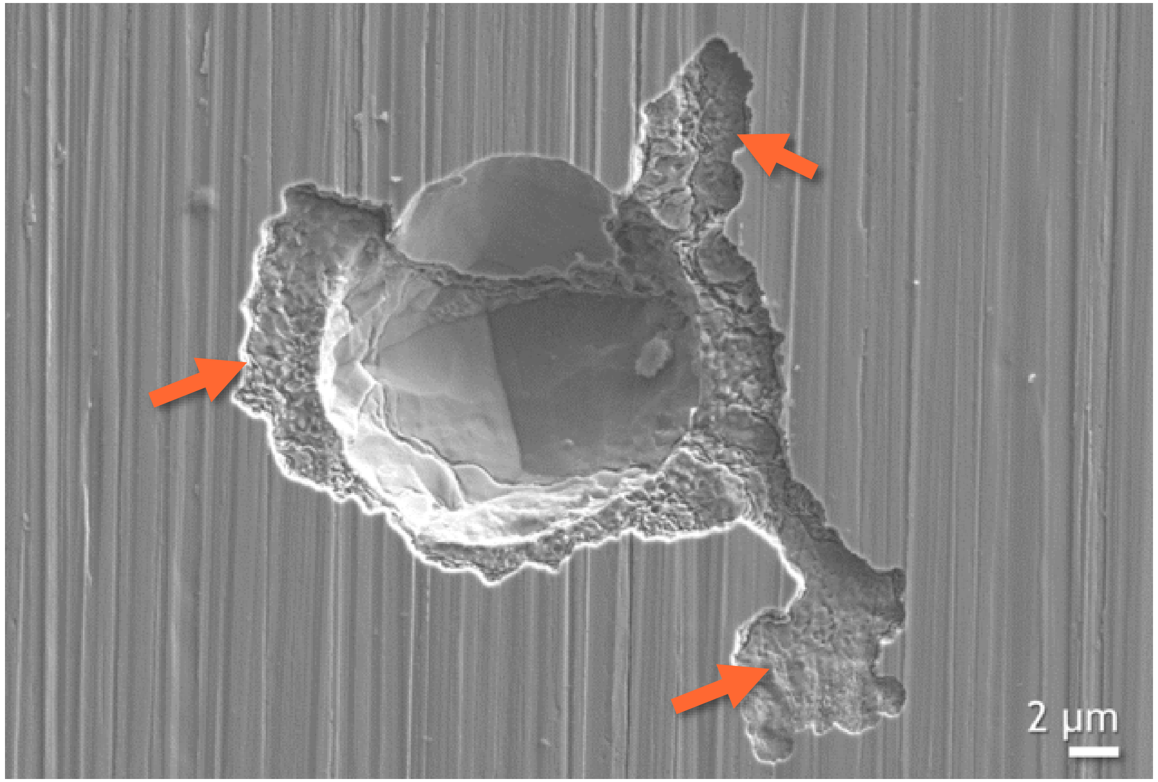
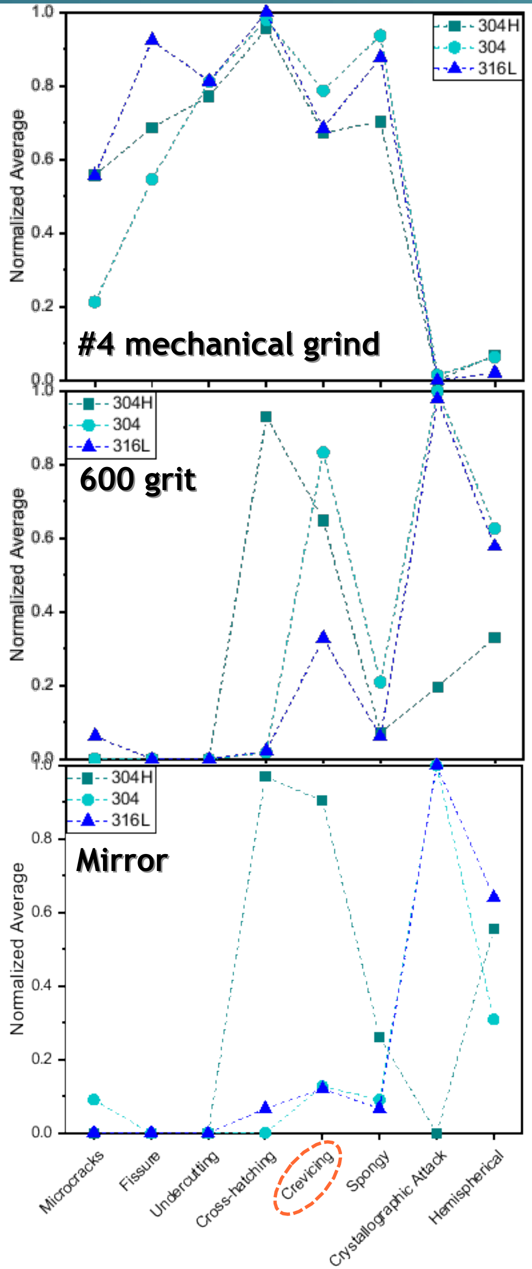
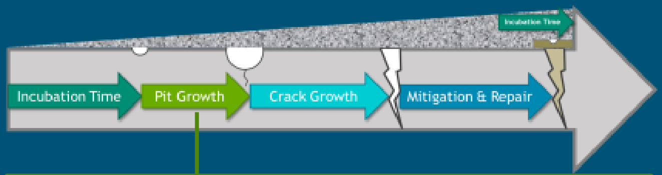


Crevicing





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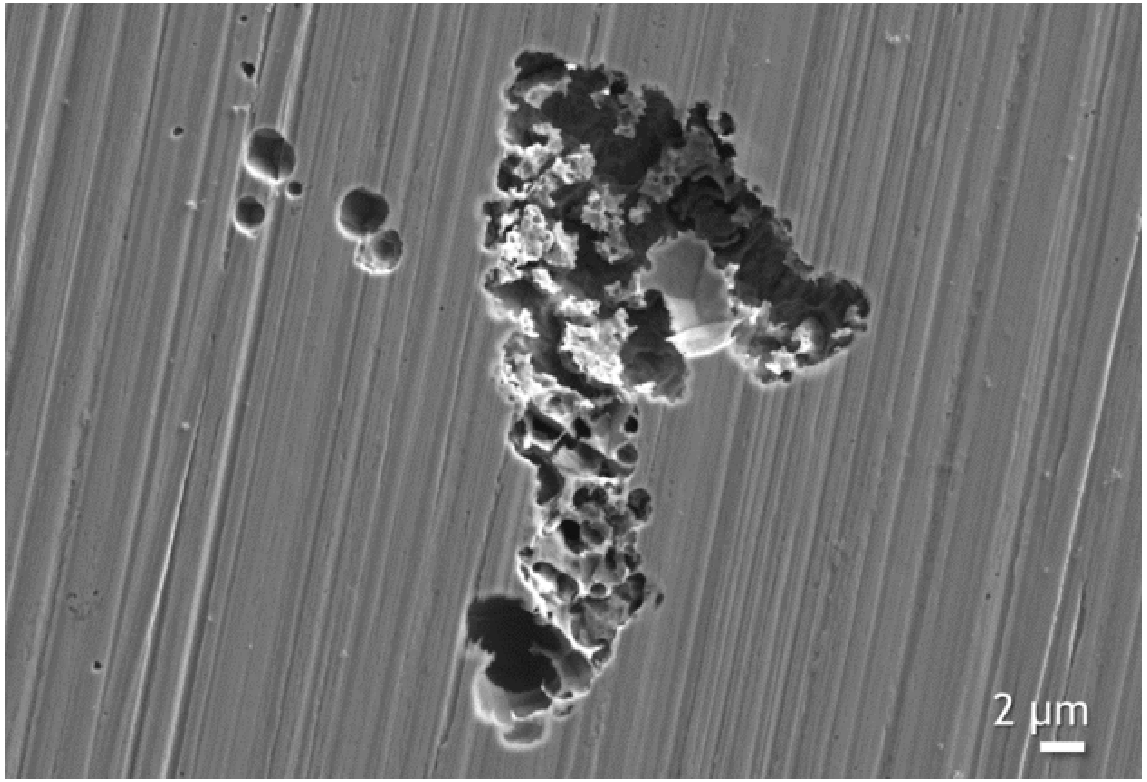
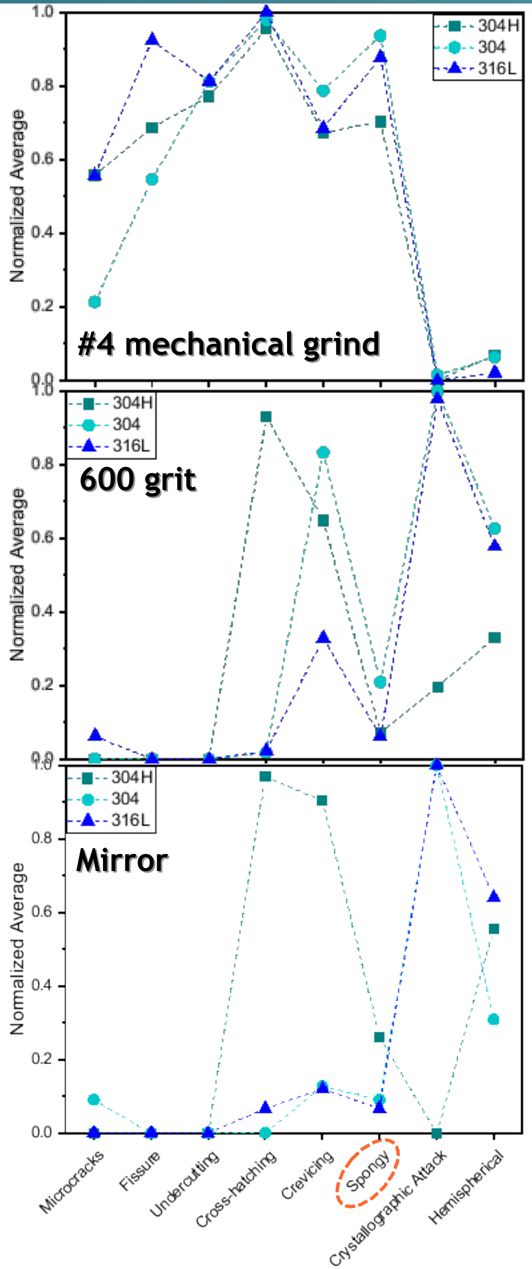
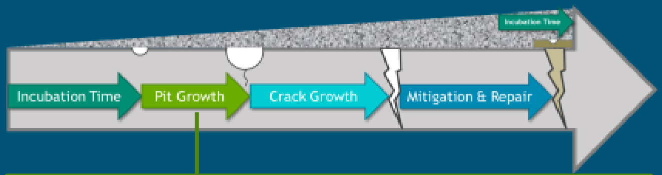


Spongy





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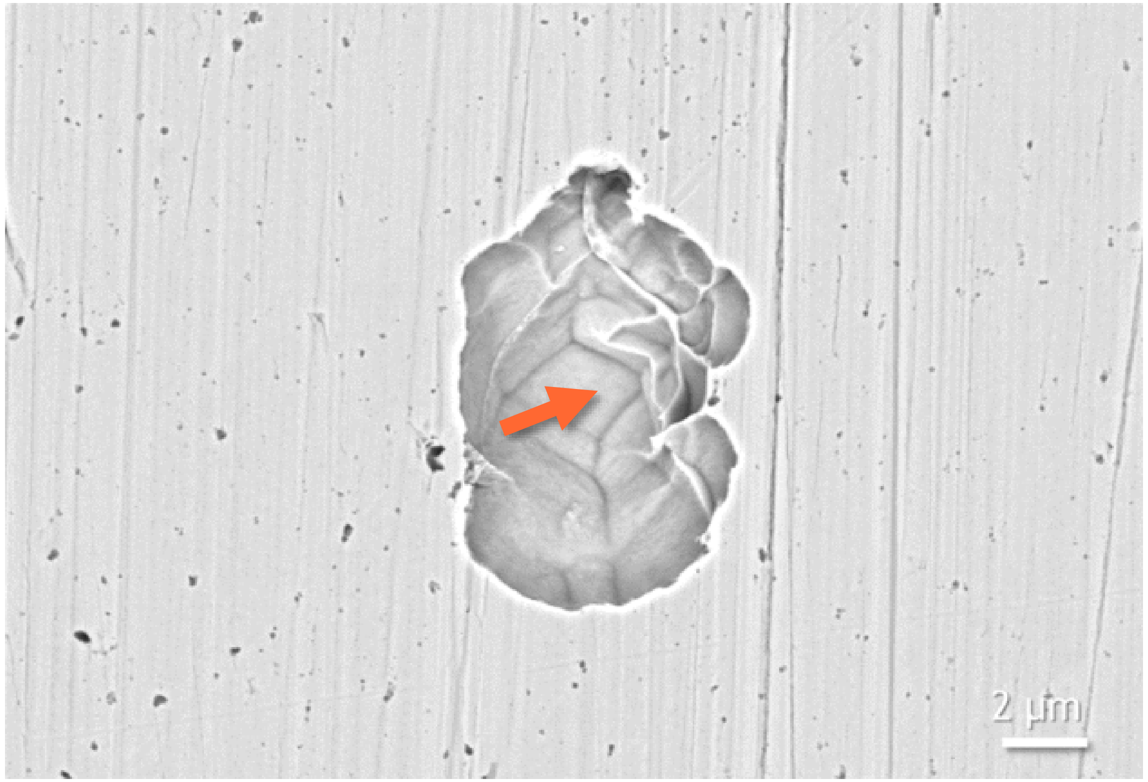
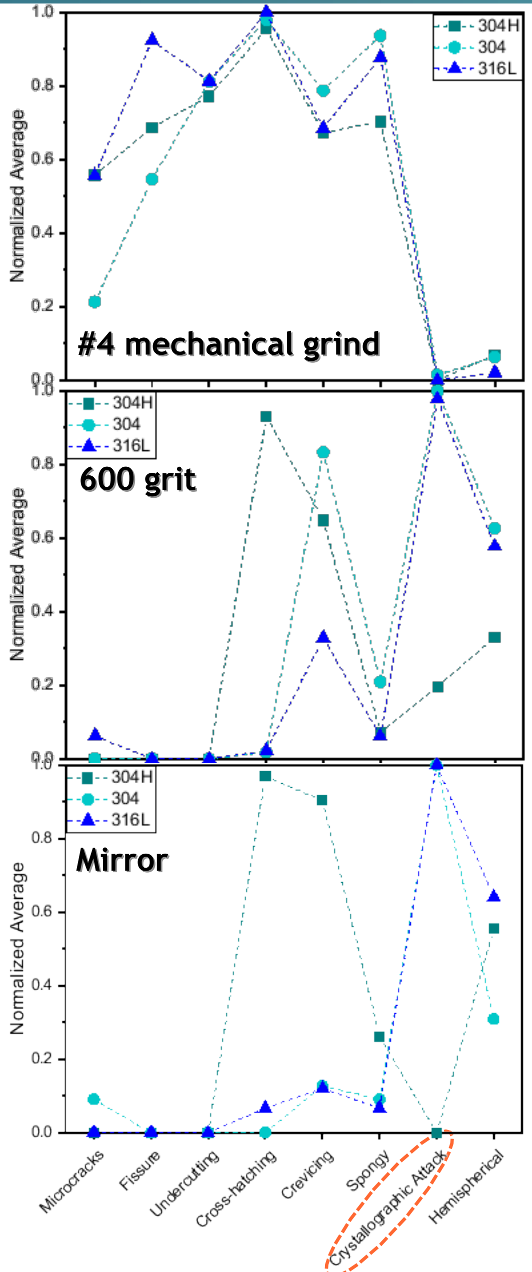
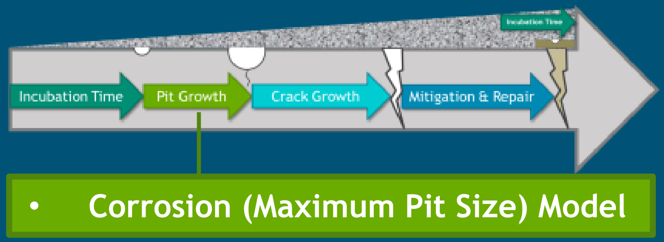


Crystallographic attack





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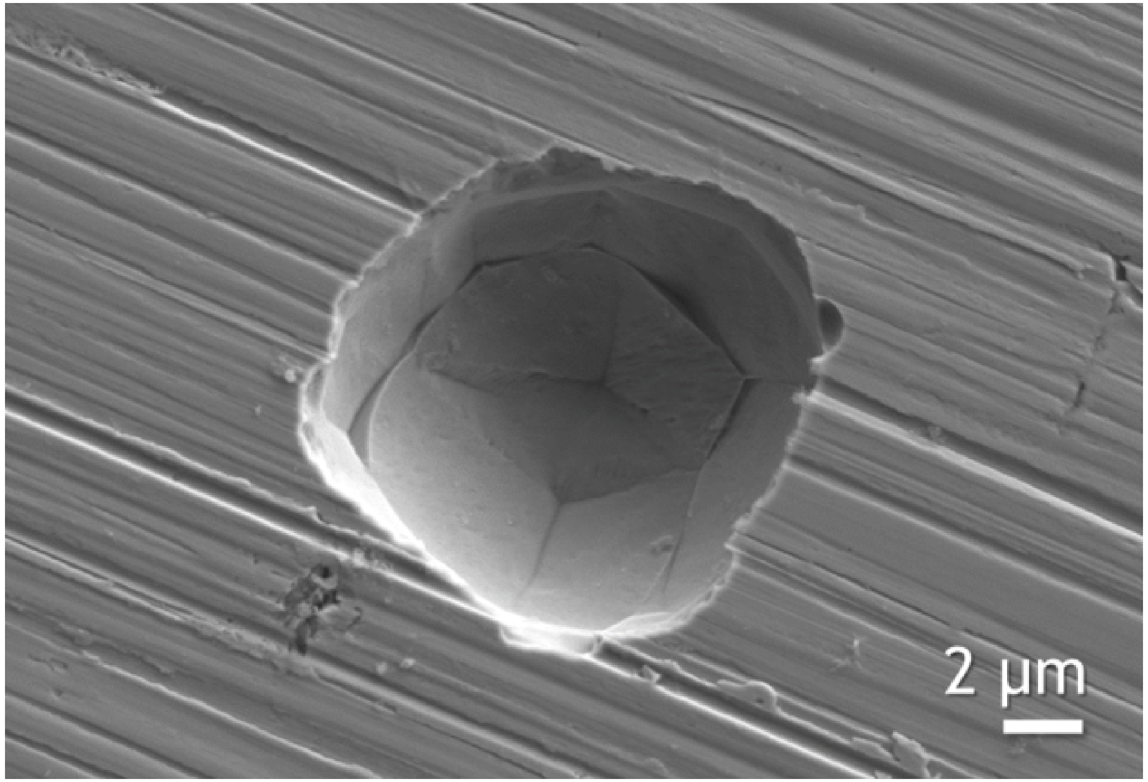

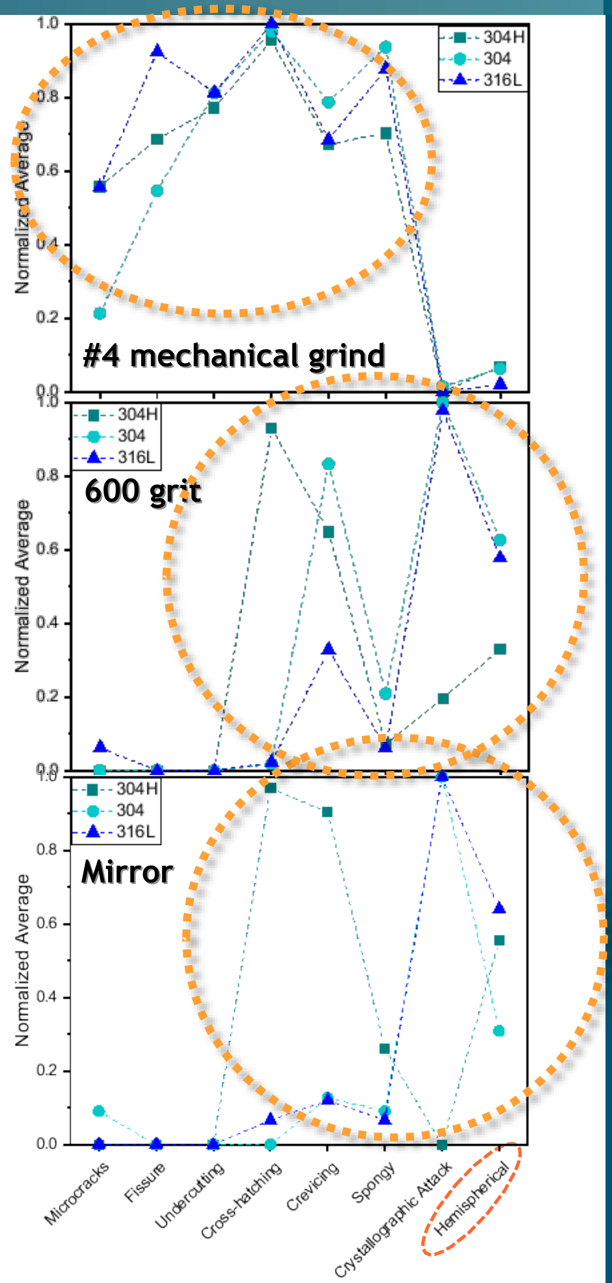

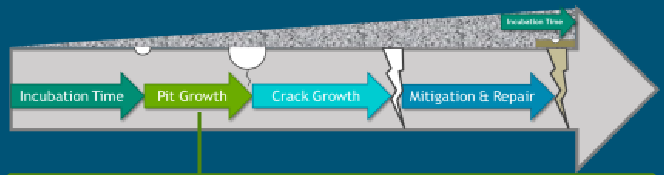

- Corrosion (Maximum Pit Size) Model

Hemispherical

Pit morphology: function of brine but also material and surface finish

Qualitative pit characterization

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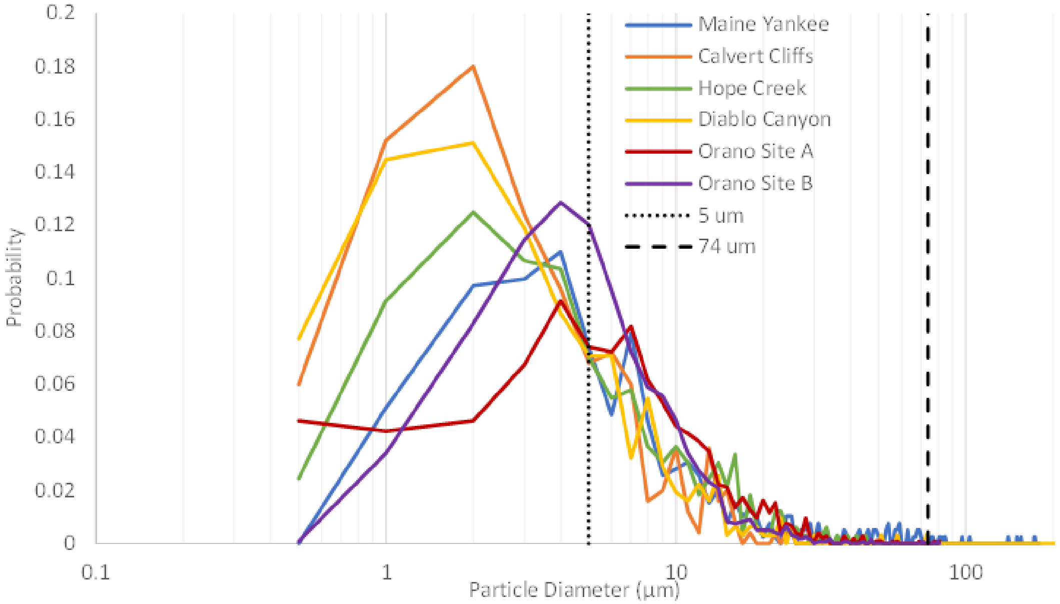
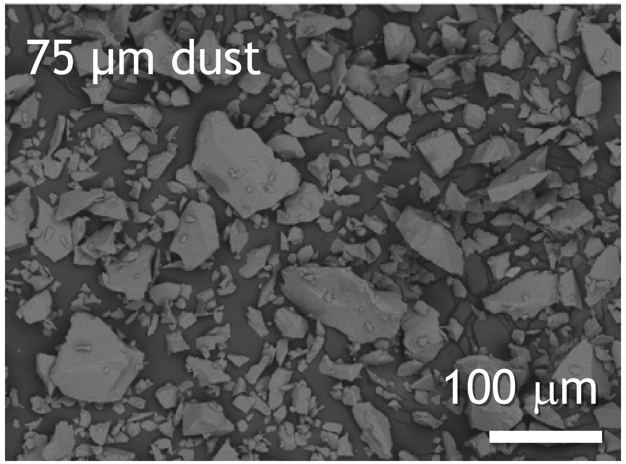
Initial results of Relevant Lab Exposures: ***Inert Dust***

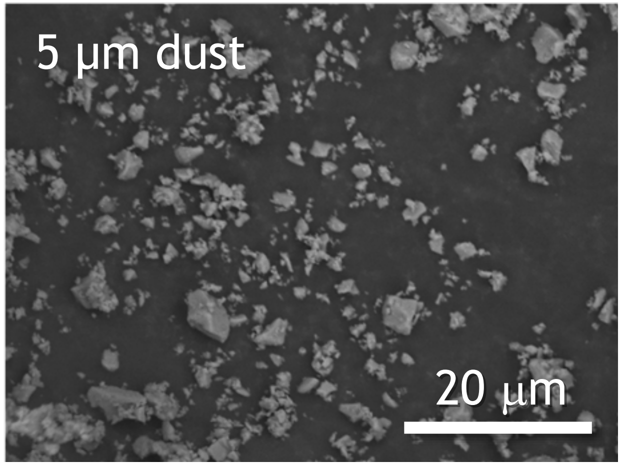
Particle Size

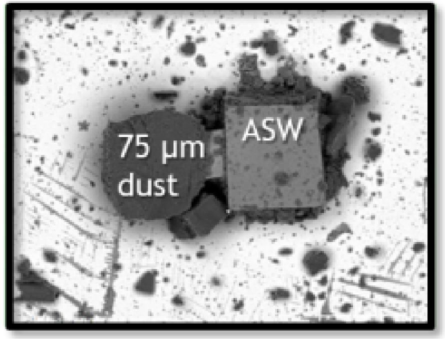


<u>Dust Exposures:</u>

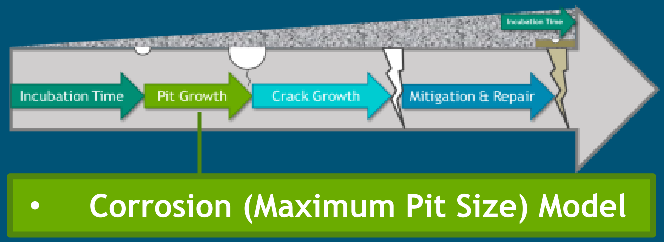
- Small (5 μm), large (75 μm) co-deposited with 300 $\mu g/cm^2$ ASW
- Exposed: Cyclic and static 75 and 40% RH at 50 ^oC







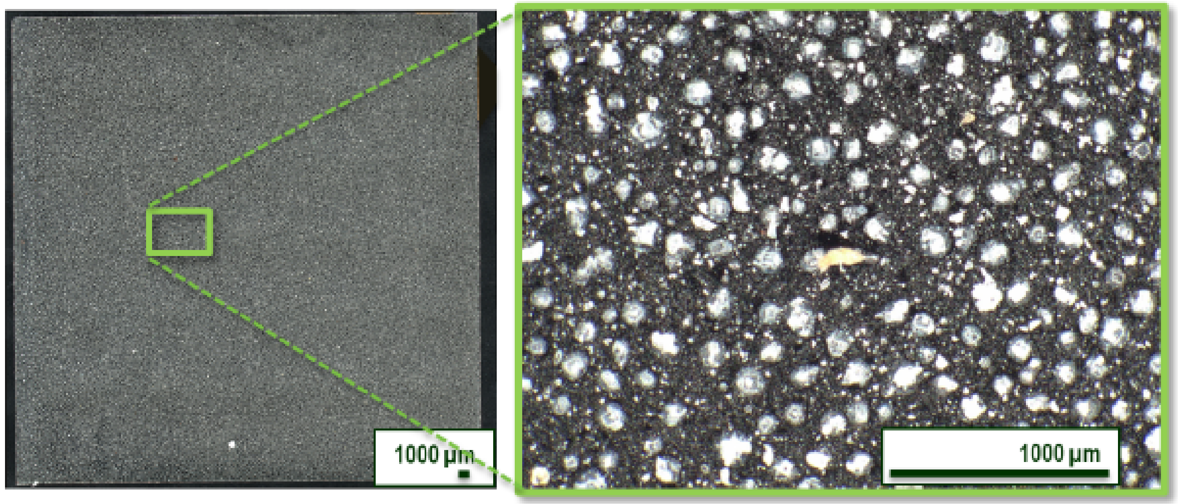
Dust co-deposited with ASW



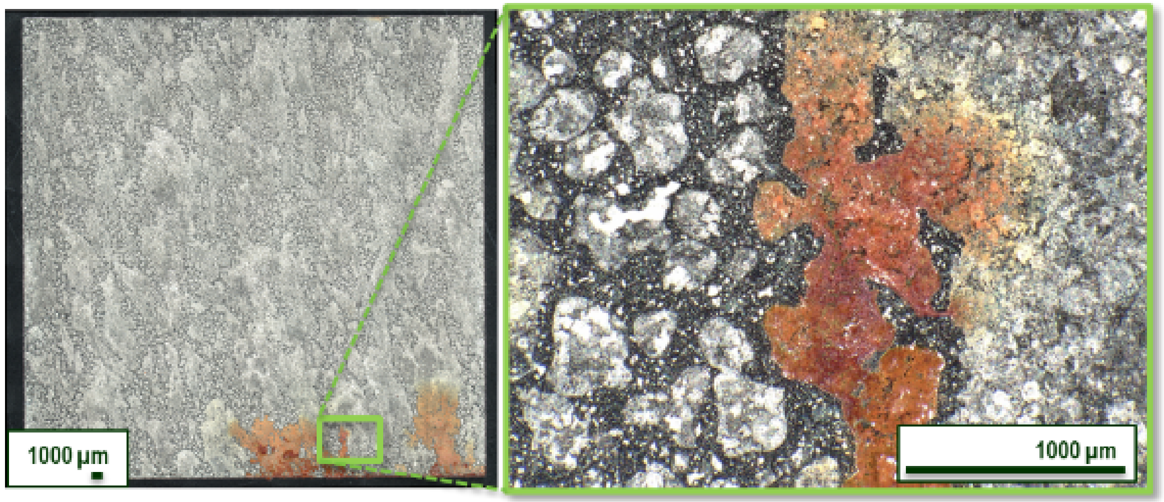
- Explore influences of:
  - Diurnal Cycles
  - <u>**Dust**</u>
  - Chemistry

Influence of inert dust on pitting

Static 40 % RH

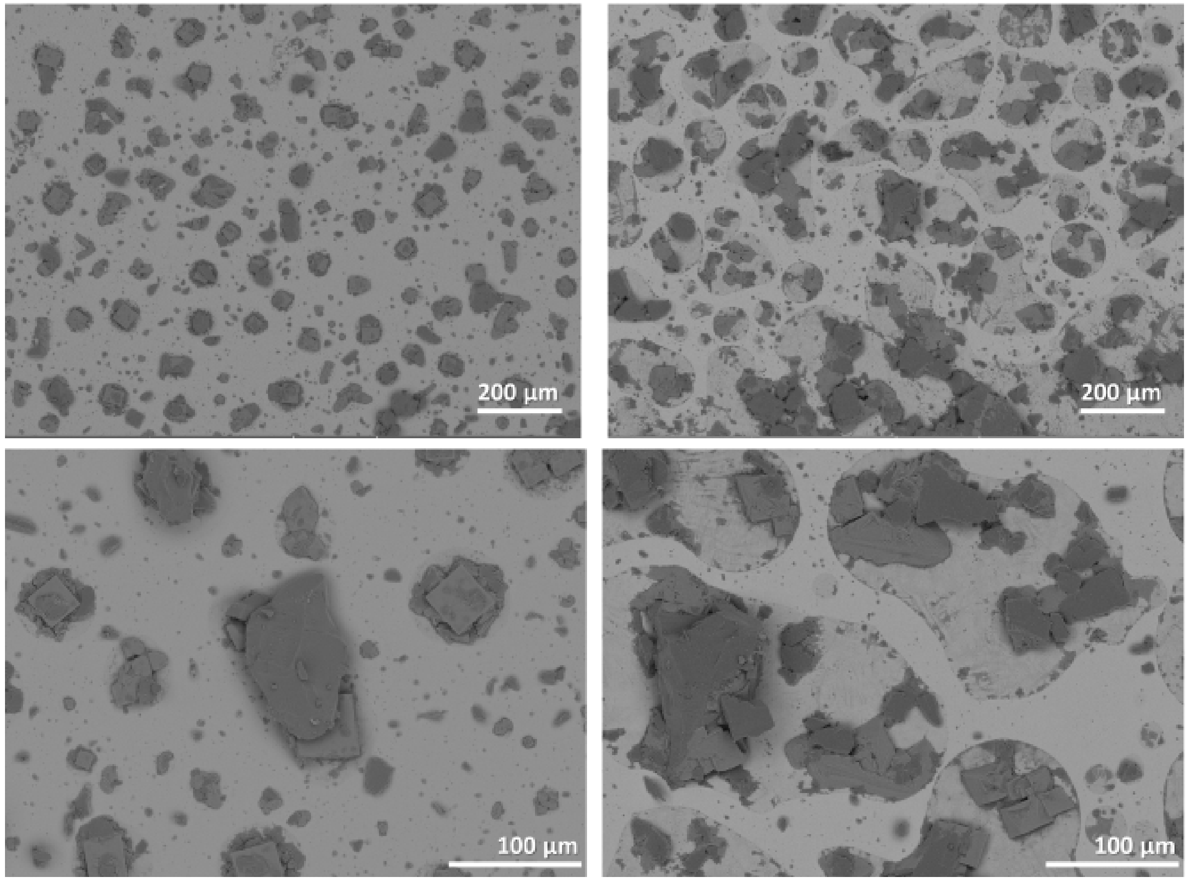


Static 75 % RH



Optical Imaging: Post 1 month exposure for coupons with 75 μm dust co-deposited with ASW

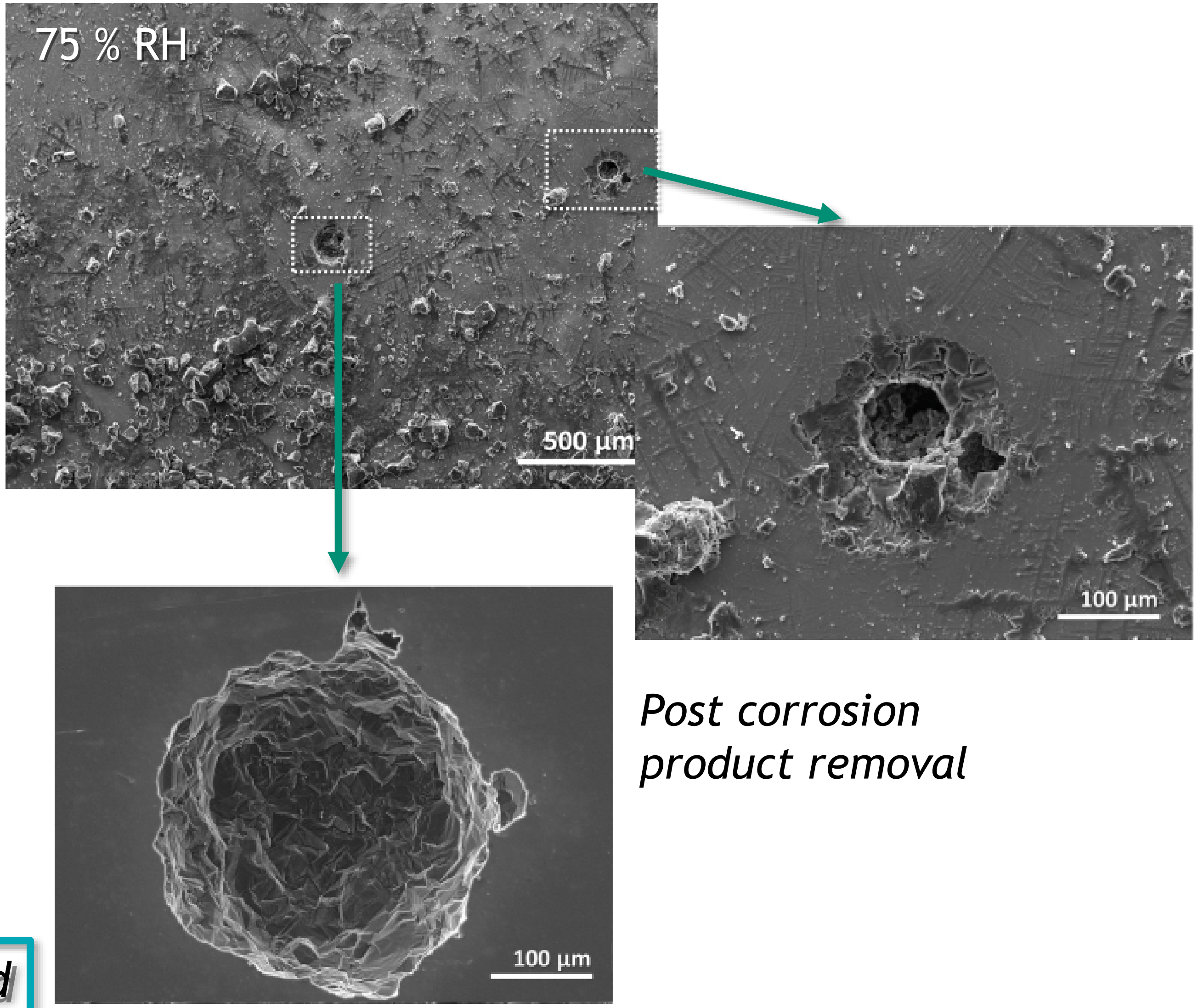
Influence of inert dust on pitting



SEM Imaging: Post 1 month exposure for coupons with 75 µm dust co-deposited with ASW

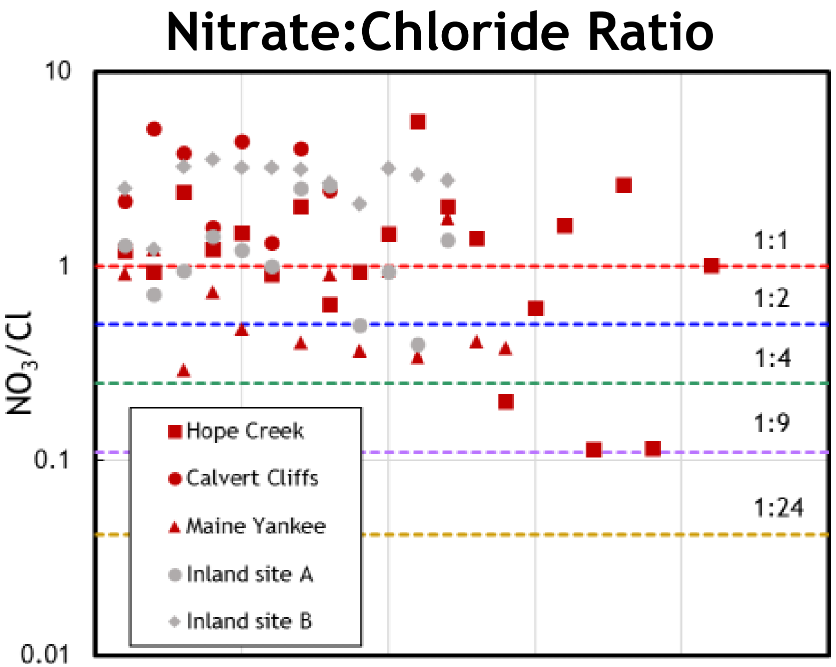
Pitting may be influenced by brine spreading and crevice environments due to presence of dust

SEM of Corrosion



Post corrosion product removal

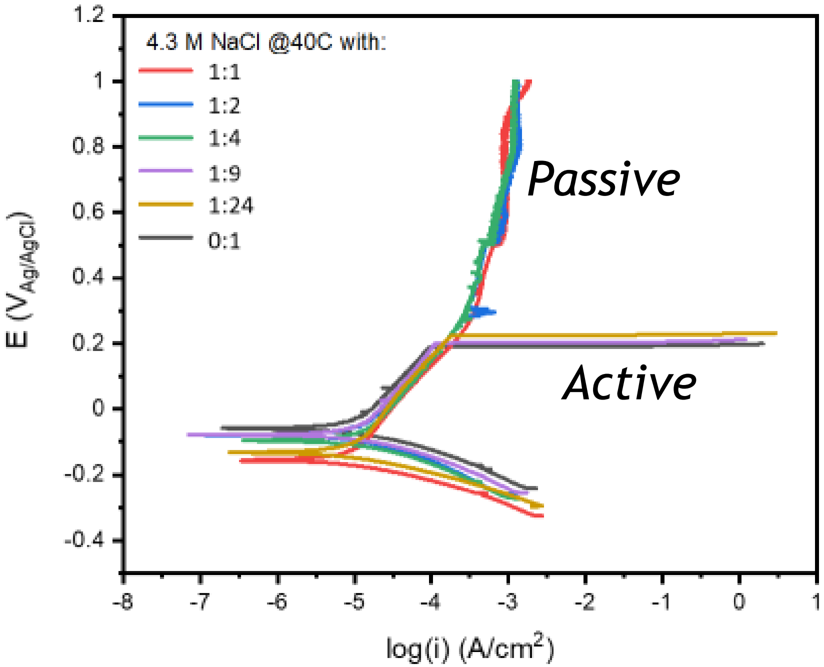
Initial results of Relevant Lab Exposures: Chemistry

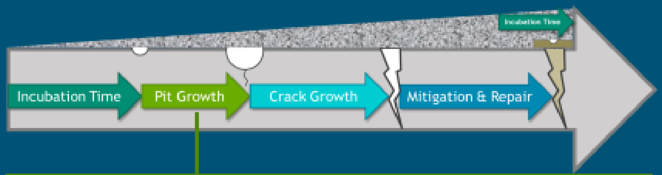


Observed influence of nitrate to chloride ratio on corrosion behavior

Initial Chemistry Exposures:

- Accelerated electrochemical testing:
  - Full immersion
  - 24 h open circuit potential
  - Anodic polarization



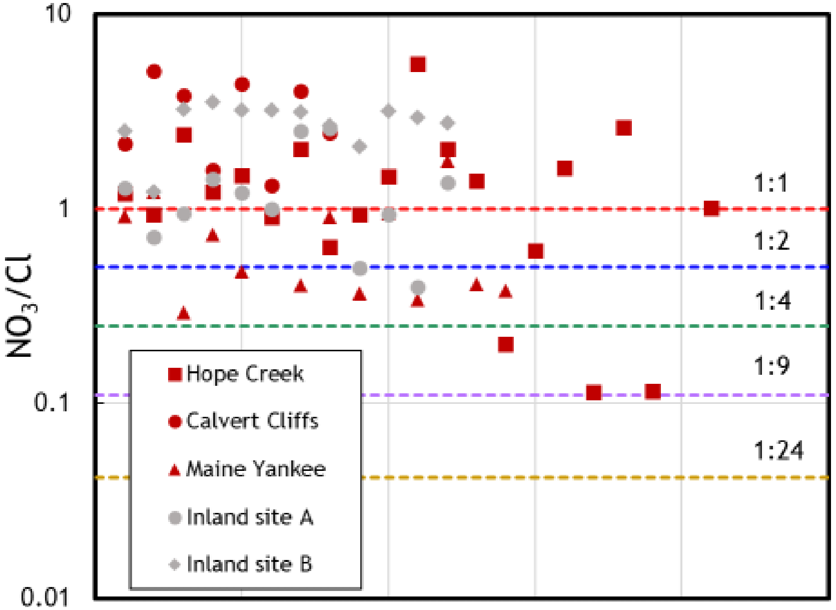


- Corrosion (Maximum Pit Size) Model

- Explore influences of:
  - Diurnal Cycles
  - Dust
  - **Chemistry**

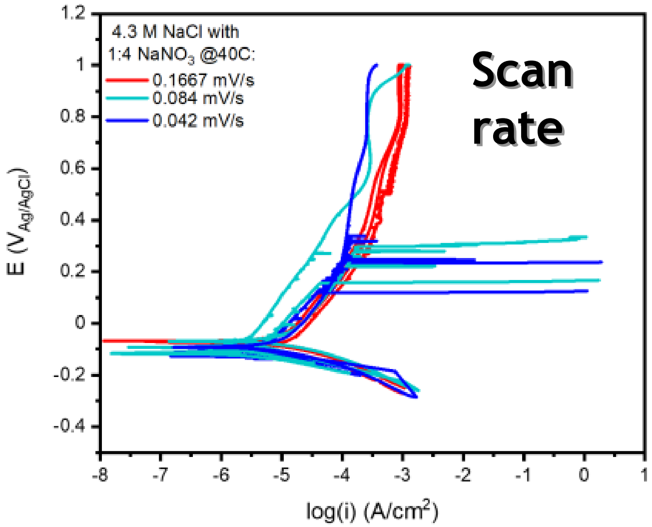
Initial results of Relevant Lab Exposures: ***Chemistry***

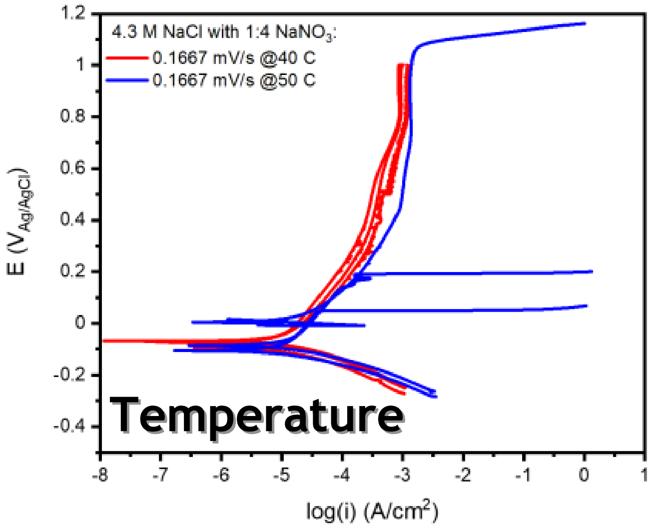
Nitrate:Chloride Ratio



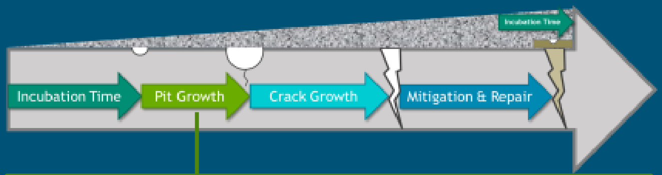
Initial Chemistry Exposures:

- Accelerated electrochemical testing:
  - Full immersion
  - 24 h open circuit potential
  - Anodic polarization





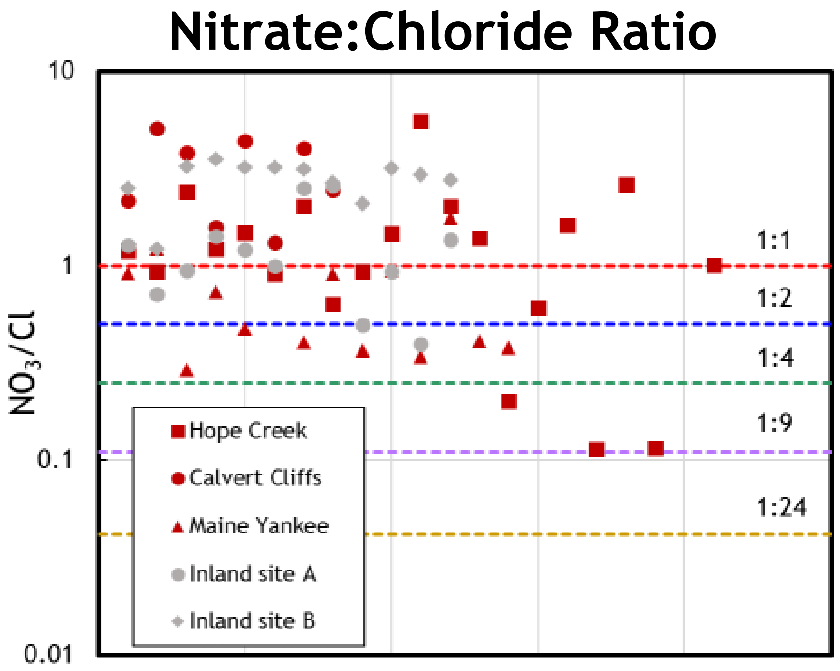
Influences at ratio of 1:4
Behavior stochastic as scan rate and T increased



- Corrosion (Maximum Pit Size) Model

- Explore influences of:
  - Diurnal Cycles
  - Dust
  - **Chemistry**

Initial results of Relevant Lab Exposures: ***Chemistry***



Initial Chemistry Exposures:

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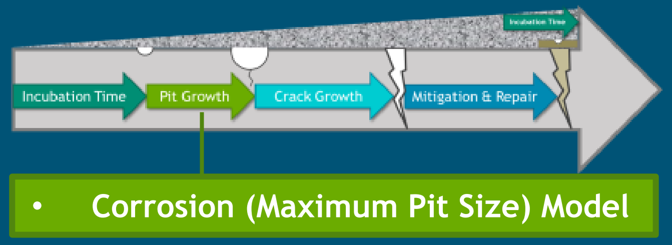
  - 24 h open circuit potential
  - Anodic polarization



- Explore influences of:
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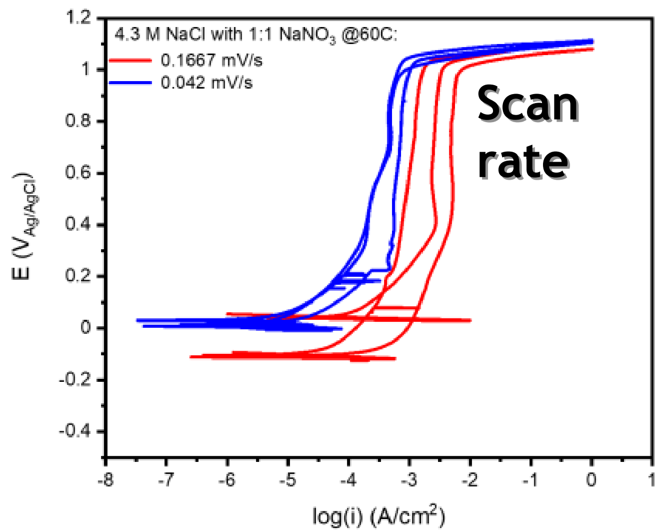
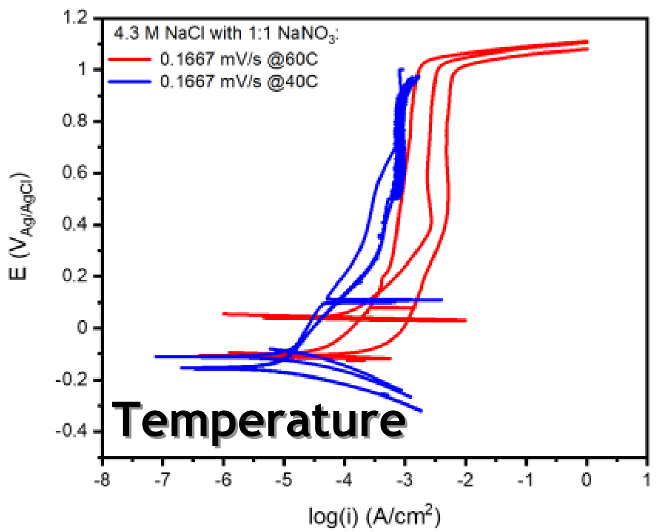
  - Dust
  - **Chemistry**

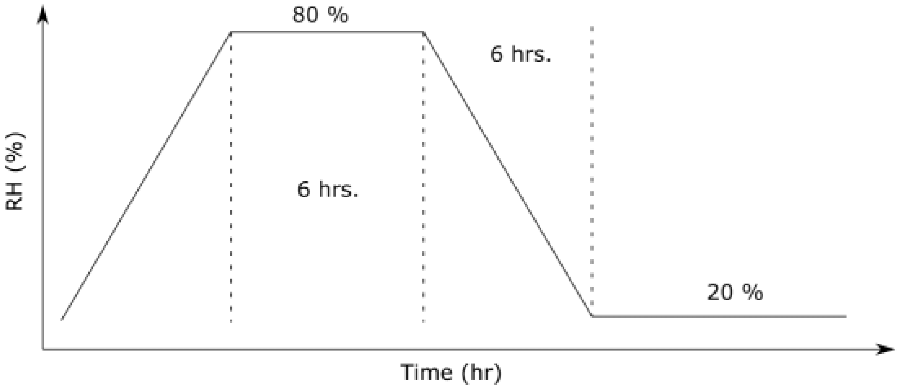




Influences at ratio of 1:1
Behavior unaffected by scan rate and T examined

Initial results of Relevant Lab Exposures: <u>Chemistry</u>

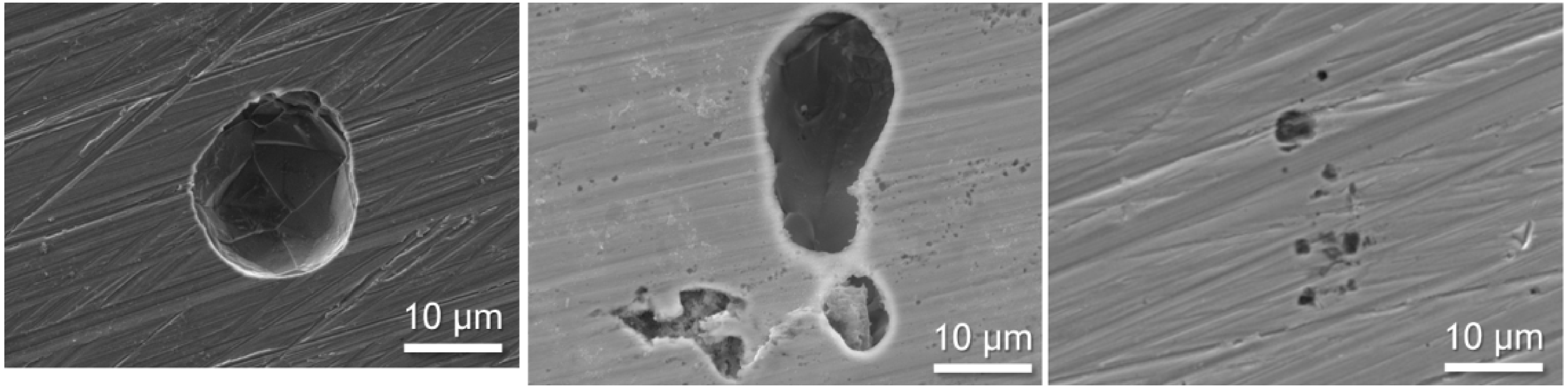
Nitrate:Chloride Ratio
Atmospheric Exposure Cycle 55°C



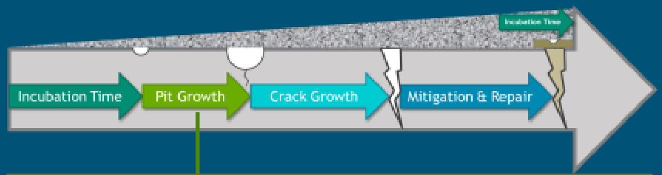
<u>Droplet Exposures:</u>

- Nitrate: Chloride Ratio:
  - Range of 0:1 to 4:1
  - Sizes 1 to 4 μL
  - Composition 1.075 to 4.3 m NaCl
  - Time 1 week

0:1 **1:1** **4:1**



Corrosion observed across all Nitrate:Chloride ratios and droplet sizes examined

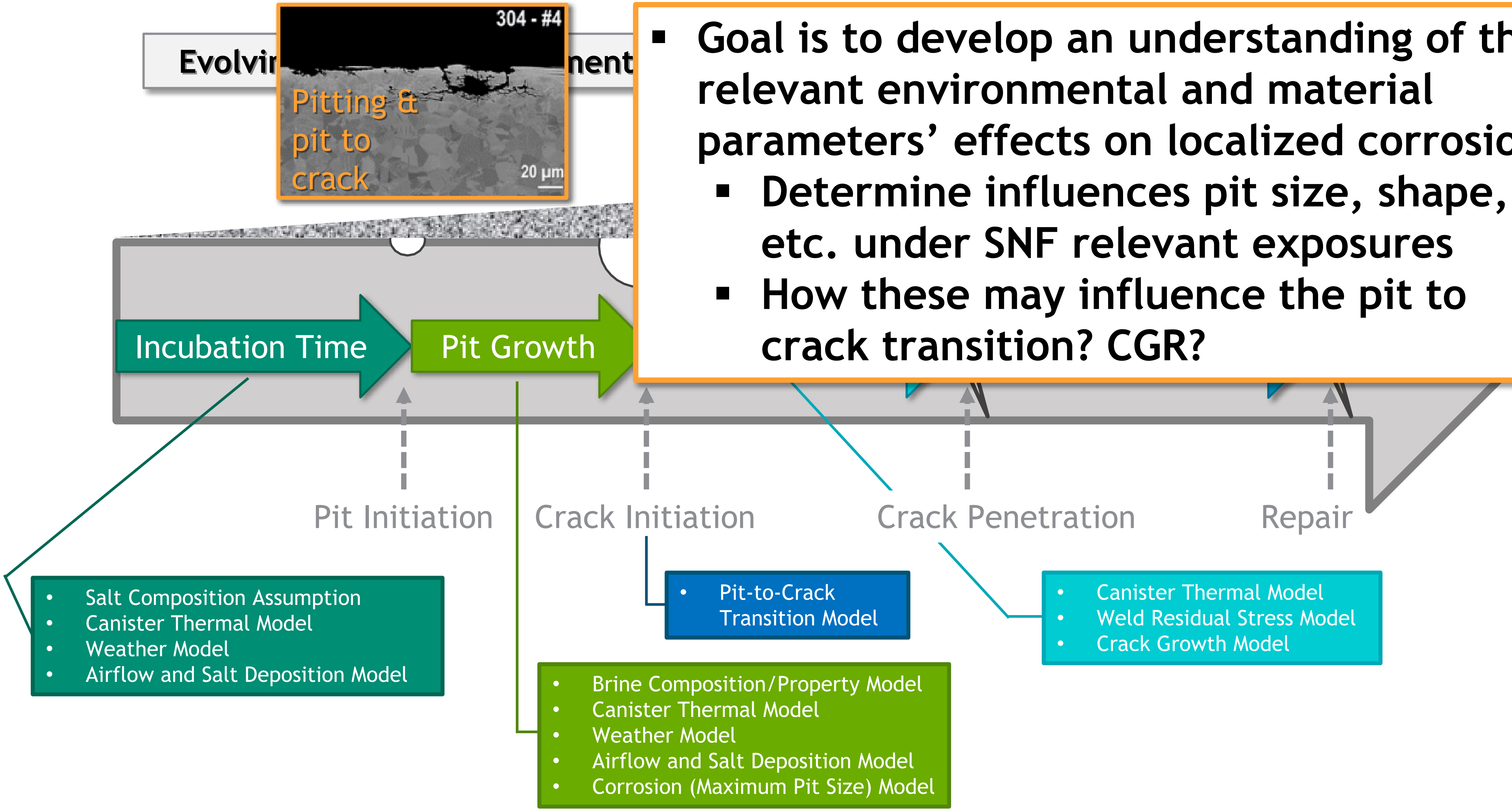


- Corrosion (Maximum Pit Size) Model

- Explore influences of:
  - Diurnal Cycles
  - Dust
  - **<u>Chemistry</u>**

Pathway Forward

- Goal is to develop an understanding of the relevant environmental and material parameters' effects on localized corrosion
  - Determine influences pit size, shape, etc. under SNF relevant exposures
  - How these may influence the pit to crack transition? CGR?



Sandia National Laboratories

Accelerated Relevant Atmospheric Corrosion Testing of Austenitic Stainless Steel for SNF Storage Environments

International High-Level Radioactive Waste Management Conference, Phoenix, AZ

November 14th, 2022 | Rebecca Schaller[1]

Andrew Knight[1], Ryan Katona[1], Jason Taylor[1], Timothy Montoya[2], Erin Karasz[1], and Charles Bryan[1]

[1]*Sandia National Laboratories*
[2]*University of Virginia*

U.S. DEPARTMENT OF ENERGY NNSA

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EXTRAS

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Ken Ross, Dr. Mychailo Toloczko, Dr. Jim Fort, Dr. Sara Suffield

Dr. Bob Sindelar and Dr. Andrew Duncan

University Collaborations:

Dr. Rob Kelly
Dr. Jimmy Burns

Dr. Jenifer Locke
Dr. Eric Schindelholz
Dr. Jayendran Srinivasan

Dr. Janelle Wharry
Haozheng Qu

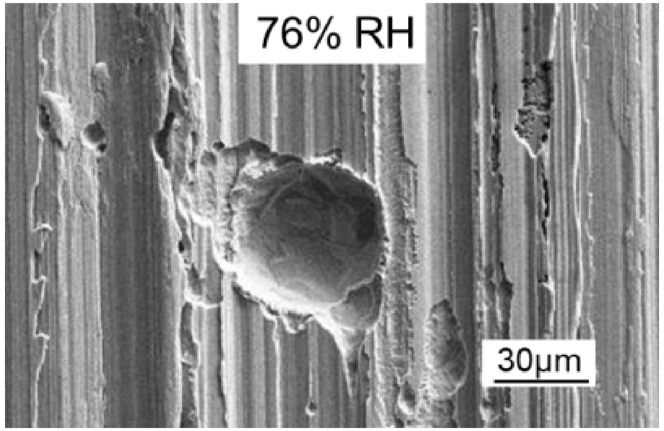
Dr. Fernando Garzon
Dr. John Plumley

Industry Collaborations:

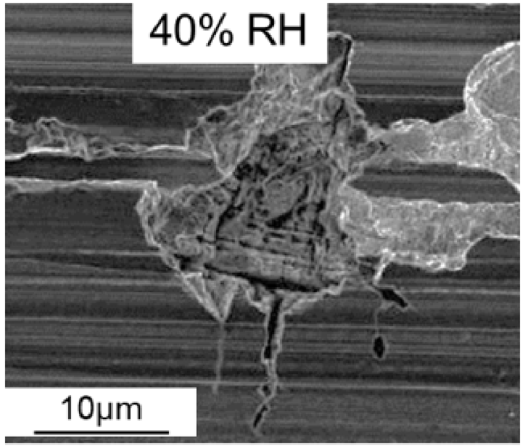
Ramgopal Thodla

Why is brine composition (RH) significant?

HIGH RH: NaCl RICH BRINE

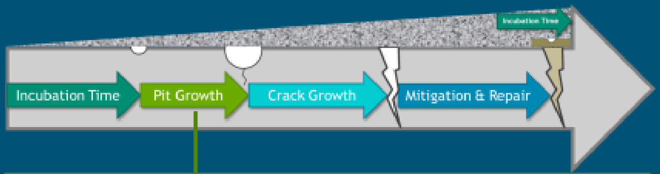


LOW RH: $MgCl_2$ RICH BRINE



- 76% RH: pitting with increasing active area at conditions above critical stability
- 40% RH: growth at critical stability – constant current through a fixed active area

Observed link between morphology and exposure RH (i.e., brine chemistry)

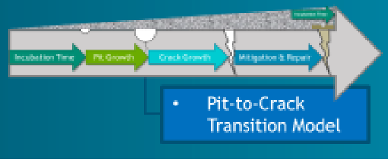


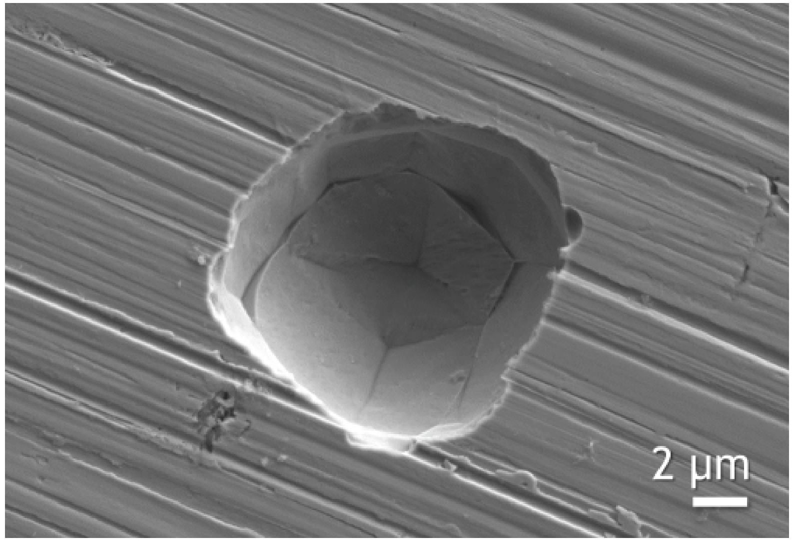
- Corrosion (Maximum Pit Size) Model

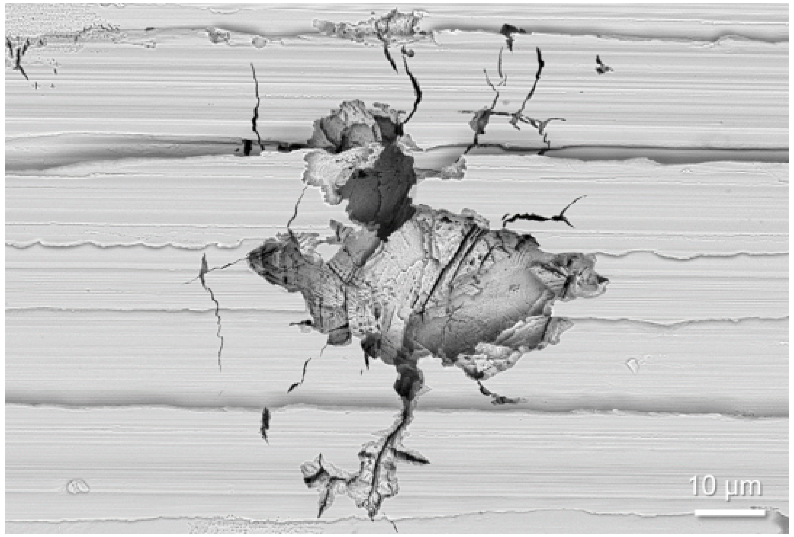
- Is there a link between morphology and exposure RH?
  - Lower RH dominated by $MgCl_2$
  - Is it influences of HER? Precipitates?

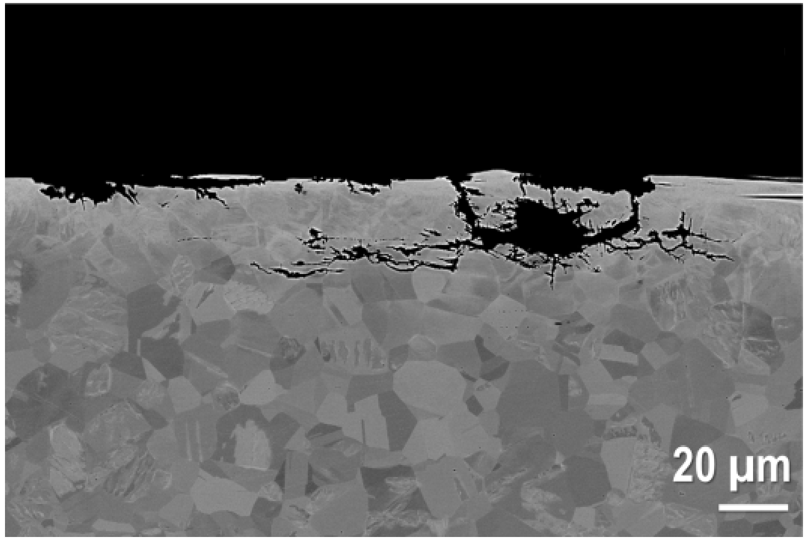
Weirich, T. D., Srinivasan, J., Taylor, J. M., Melia, M. A., Noell, P. J., Bryan, C. R., … & Schindelholz, E. J. (2019). Humidity effects on pitting of ground stainless steel exposed to sea salt particles. *Journal of The Electrochemical Society*, *166*(11), C3477.

Why care about pit morphology?

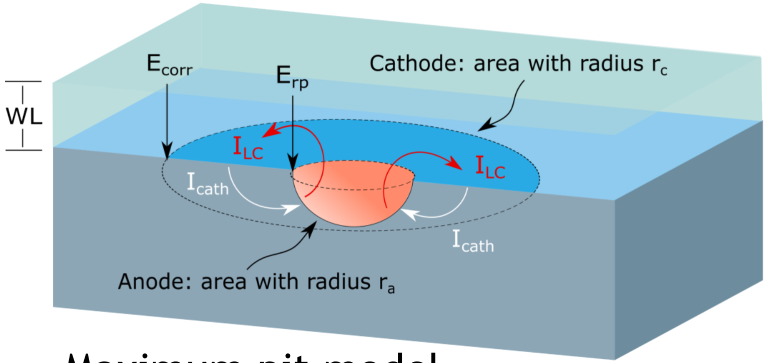






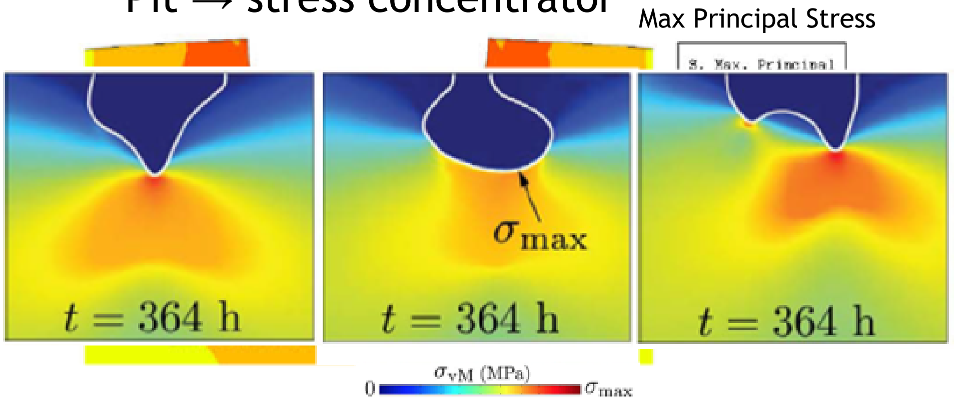


Are these irregular geometries significant? For pitting…pit to crack…CGR?

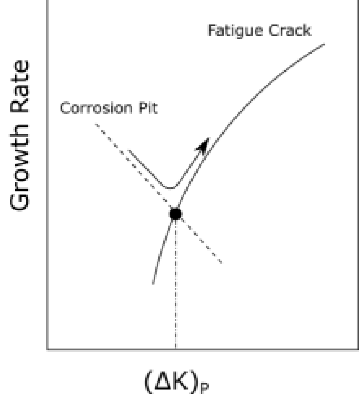


Maximum pit model

Pit → stress concentrator

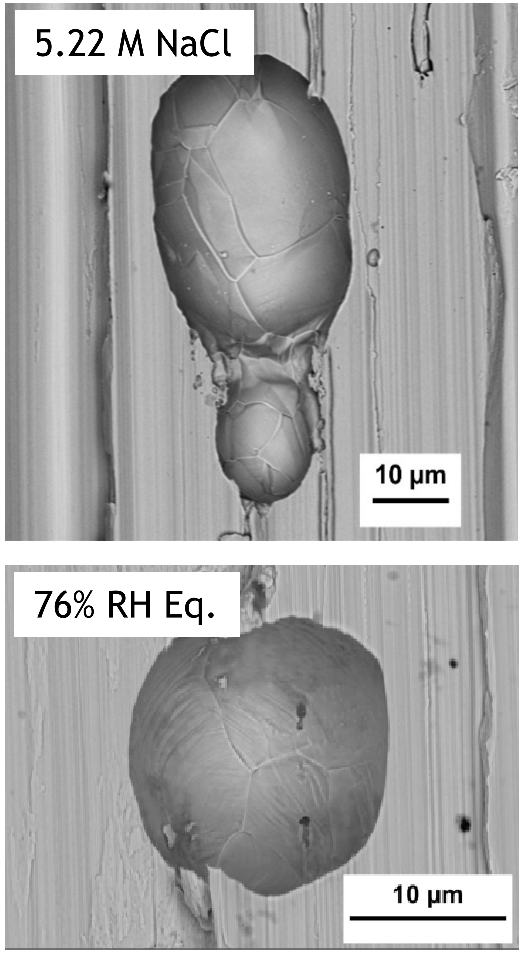


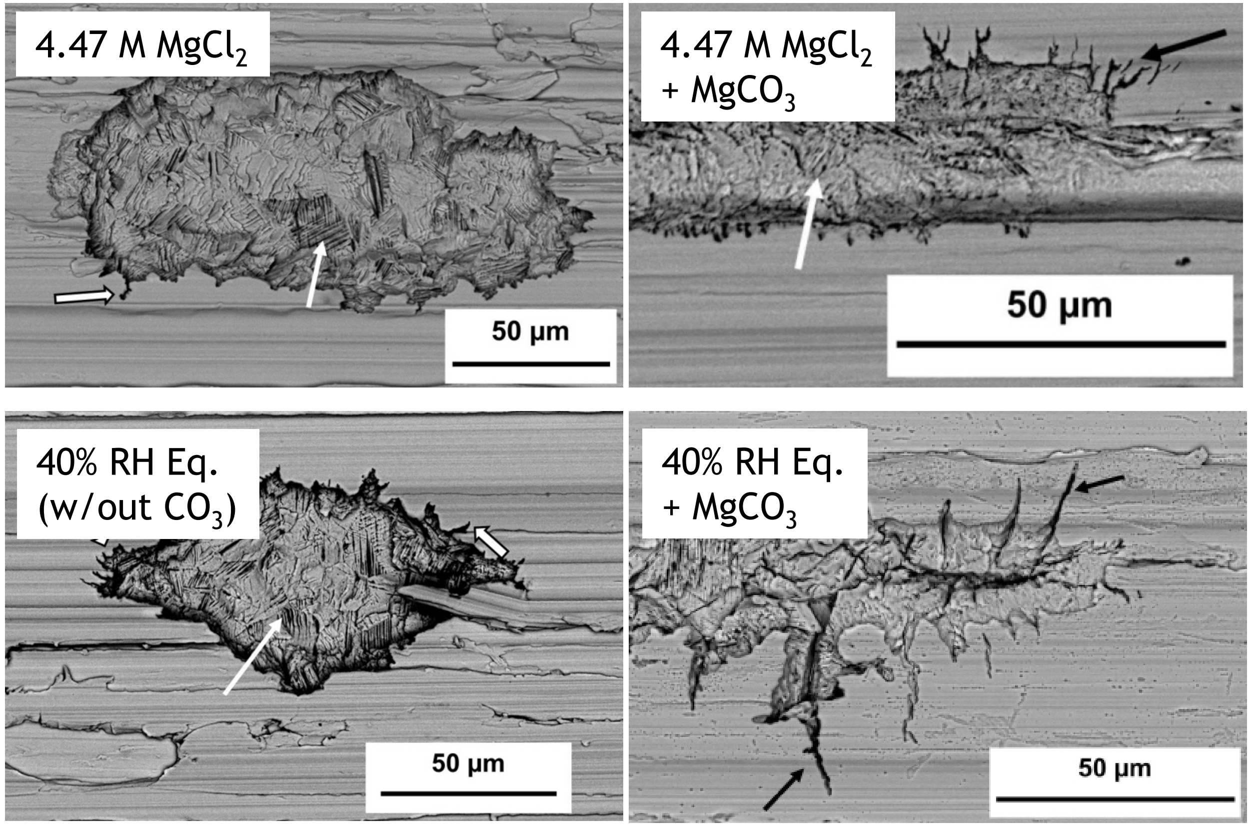
Kondo criteria



Chen, Z. Y., & Kelly, R. G. (2009). Computational modeling of bounding conditions for pit size on stainless steel in atmospheric environments. *Journal of the Electrochemical Society*, *157*(2), C69.
Turnbull, A., Wright, L., & Crocker, L. (2010). New insight into the pit-to-crack transition from finite element analysis of the stress and strain distribution around a corrosion pit. *Corrosion Science*, *52*(4), 1492-1498.
Kondo, Y. Prediction of fatigue crack initiation life based on pit growth. *Corrosion* **45**, 7-11, doi:10.5006/1.3577891 (1989).
Mai, W., & Soghrati, S. (2017). A phase field model for simulating the stress corrosion cracking initiated from pits. *Corrosion Science*, *125*, 87-98.

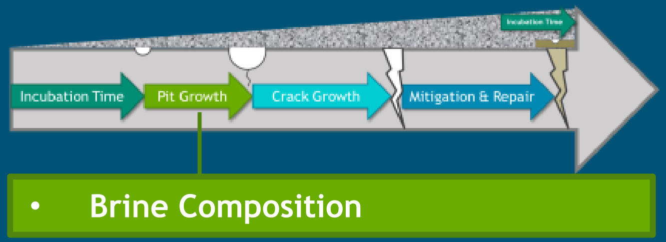
Is there a controlling species in the brine?





Are microcracks enhanced due to formation of $MgCO_3$?

Enhanced HER at the surface?

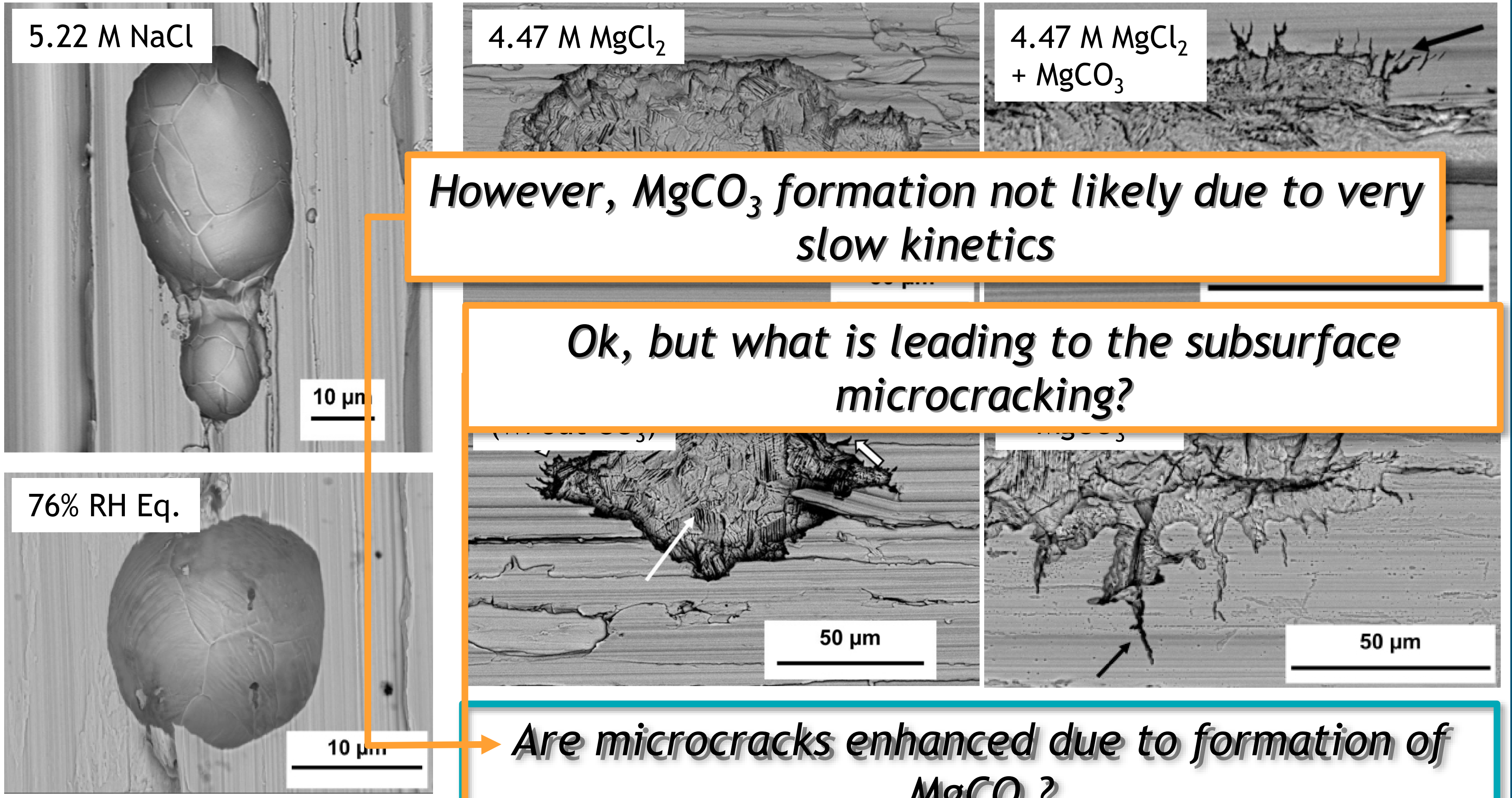


Qualitative pit characterization

- *Dependence of morphology on brine composition*
- *Possible influence of carbonates?*

Srinivasan, et al., Correlation of Stainless Steel Pit Morphology to Humidity Specific Sea Salt Brine Constituents. submitted to *Corrosion*,(2022).

Is there a controlling species in the brine?



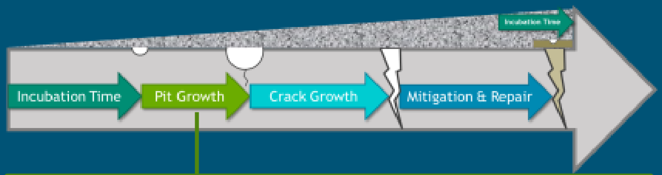
However, $MgCO_3$ formation not likely due to very slow kinetics

Ok, but what is leading to the subsurface microcracking?

Are microcracks enhanced due to formation of $MgCO_3$?

Enhanced HER at the surface?

So what is the carbonate influence?



- **Brine Composition**

Qualitative pit characterization

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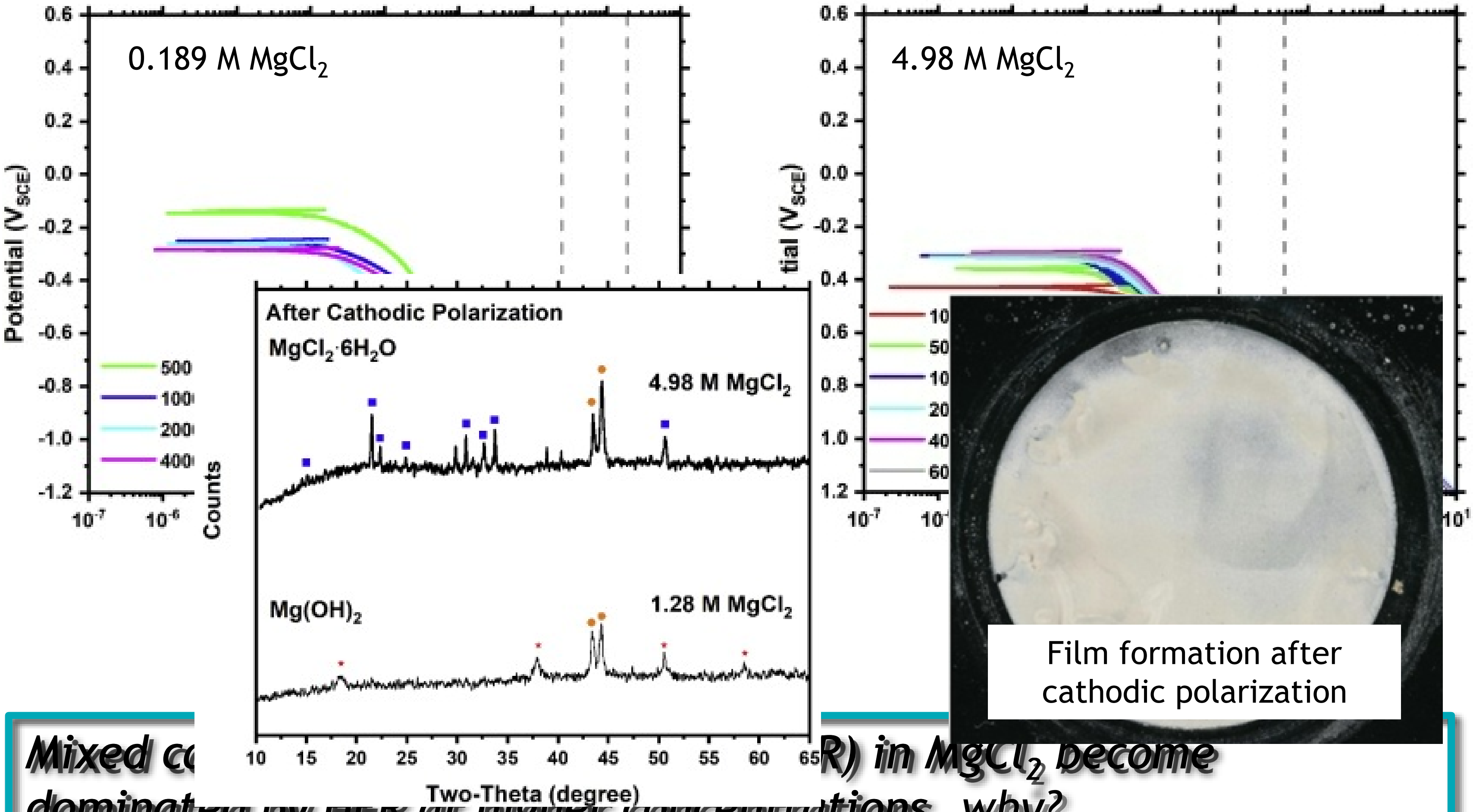
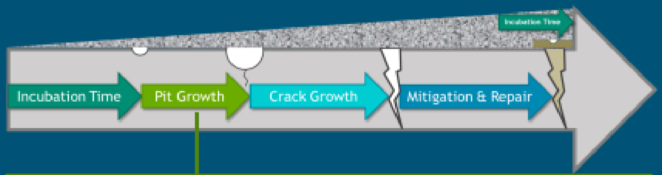
Srinivasan, et al., Correlation of Stainless Steel Pit Morphology to Humidity Specific Sea Salt Brine Constituents. submitted to *Corrosion*,(2022).

Salt composition & deposition influences



Film formation after cathodic polarization

Mixed c… R) in $MgCl_2$ become dominated by HER at higher concentrations…why?

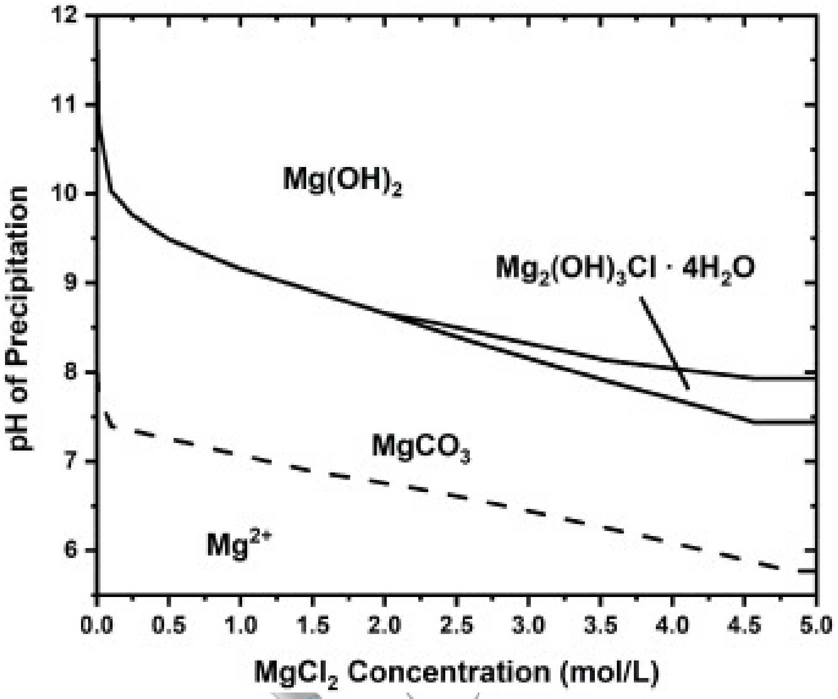


- **Corrosion (Maximum Pit Size) Model**

- *Dilute Chloride Solutions*
  - ORR dominant cathodic reaction
  - Diffusion limited at negative potentials
  - Cathodic rates predicted through Levich analysis
- Cathodic kinetics in concentrated brines

Katona, R. M., Carpenter, J. C., Knight, A. W., Bryan, C. R., Schaller, R. F., Kelly, R. G., & Schindelholz, E. J. (2020). Importance of the hydrogen evolution reaction in magnesium chloride solutions on stainless steel. *Corrosion Science*, *177*, 108935.

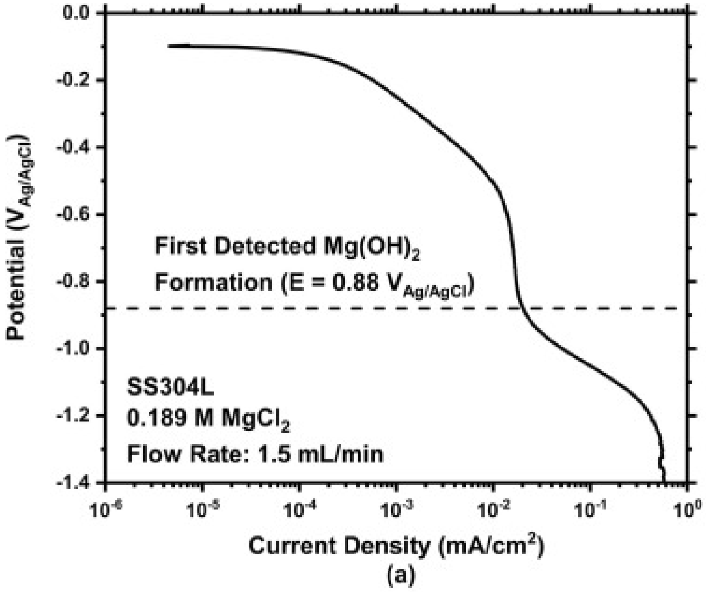
Salt composition & deposition influences

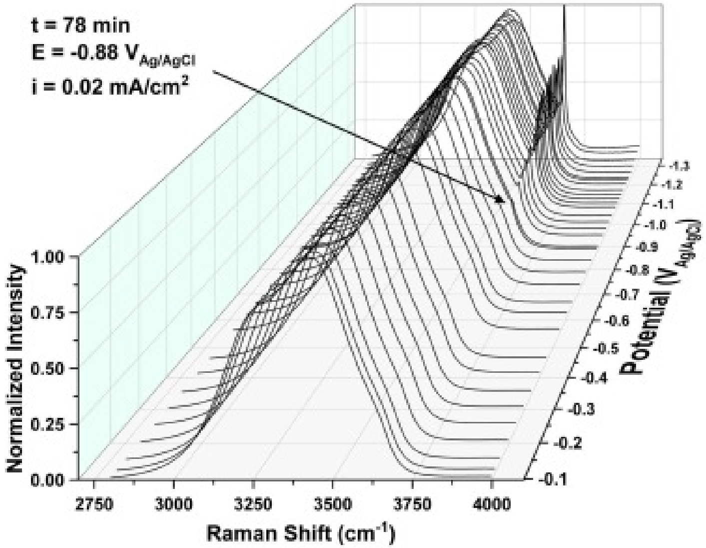


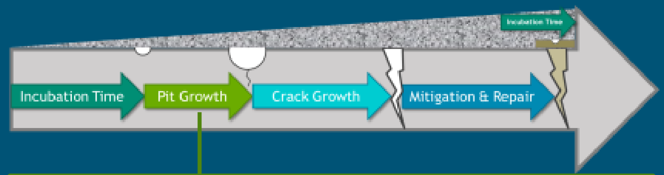
Precipitates buffer near surface pH, suppress ORR and enhance HER

$$E_{HER} = E^{o}_{HER} - m * pH$$

When pH is buffered, the near surface pH remains constant, and decreases the overpotential for HER







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Katona, R. M., Kelly, R. G., Bryan, C. R., Schaller, R. F., & Knight, A. W. (2020). Use of in situ Raman spectroelectrochemical technique to explore atmospheric corrosion in marine-relevant environments. *Electrochemistry Communications*, *118*, 106768.

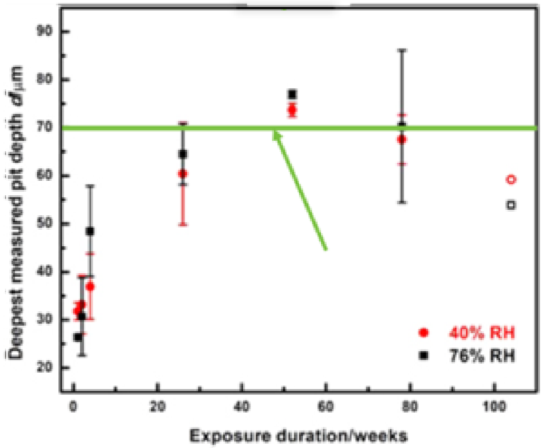
Why care about brine influences?

Maximum pit depths:

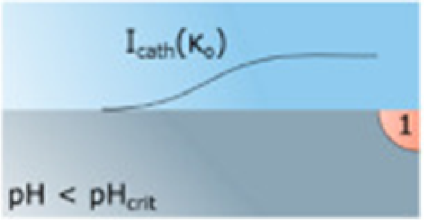
Measured from static atmospheric laboratory exposures

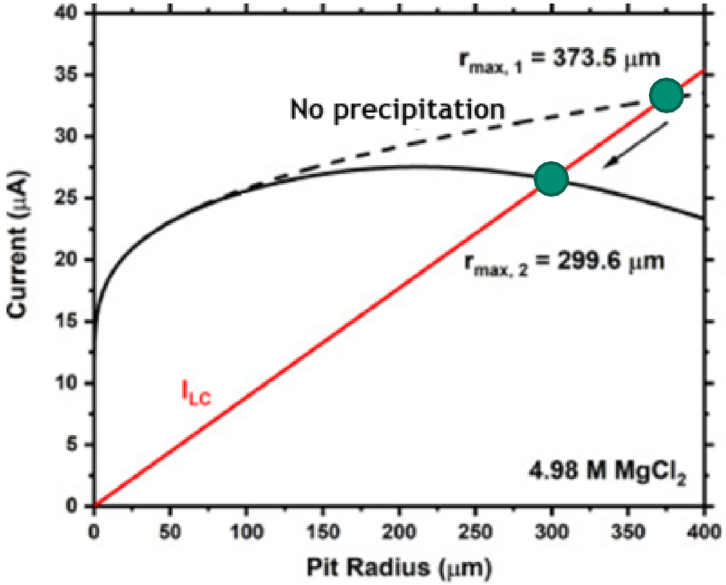
Maximum pit sizes: with precipitation are ***directly inline for 40% RH***

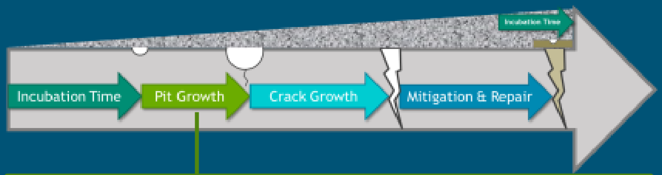
Maximum pit sizes:
1.5 X higher from conservative predictions



Precipitation influences cathodic limitation







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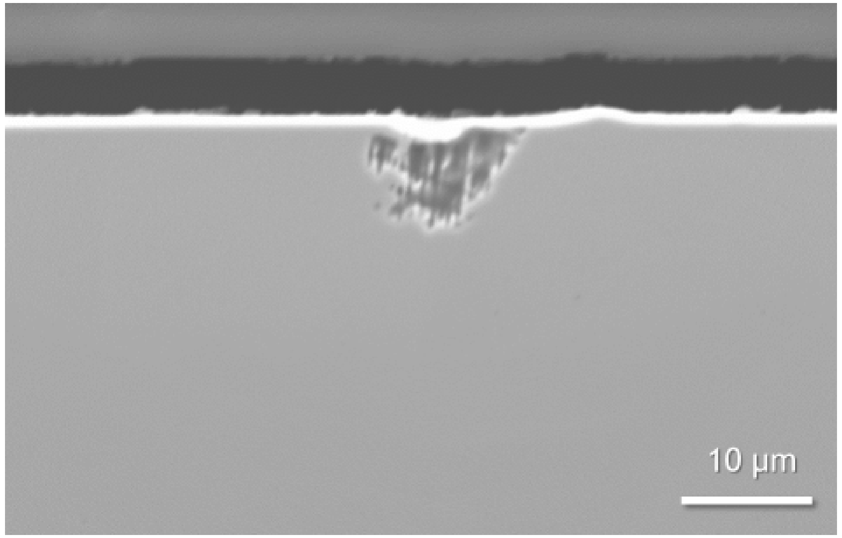
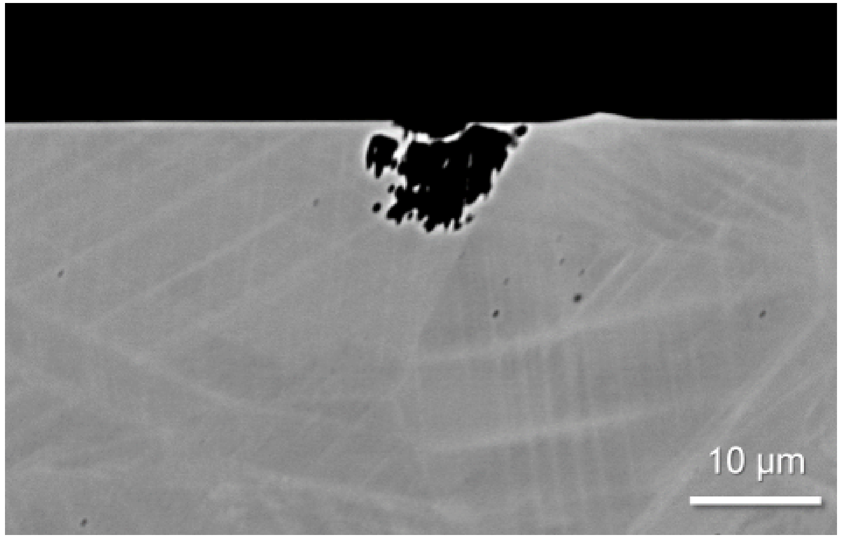
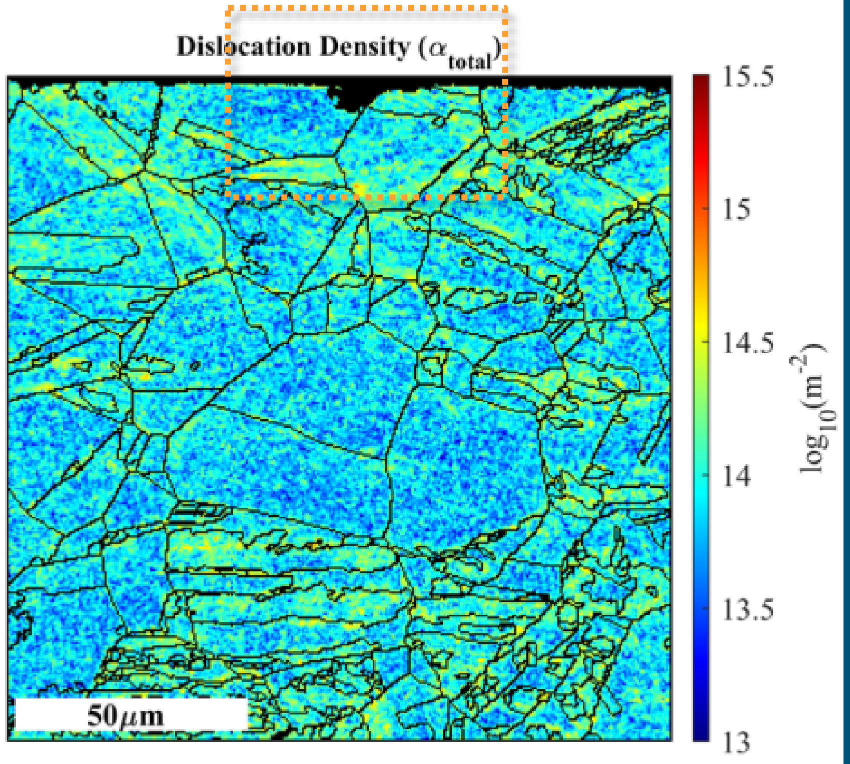
Srinivasan, J., Weirich, T.D., Marino, G.A., Annerino, A.R., Taylor, J.M., Noell, P.J., Griego, J.J.M., Schaller, R.F., Bryan, C.R., Locke, J.S. and Schindelholz, E.J., 2021. Long-term effects of humidity on stainless steel pitting in sea salt exposures. *Journal of the Electrochemical Society*, *168*(2), p.021501.

Katona, R. M., Knight, A. W., Schindelholz, E. J., Bryan, C. R., Schaller, R. F., & Kelly, R. G. (2021). Quantitative assessment of environmental phenomena on maximum pit size predictions in marine environments. *Electrochimica Acta*, *370*, 137696.

Surface finish residual stress influences pitting







304H – **mirror finish**

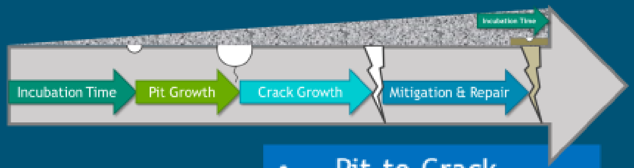
1 month diurnal cyclic exposure

- Pit-to-Crack Transition Model

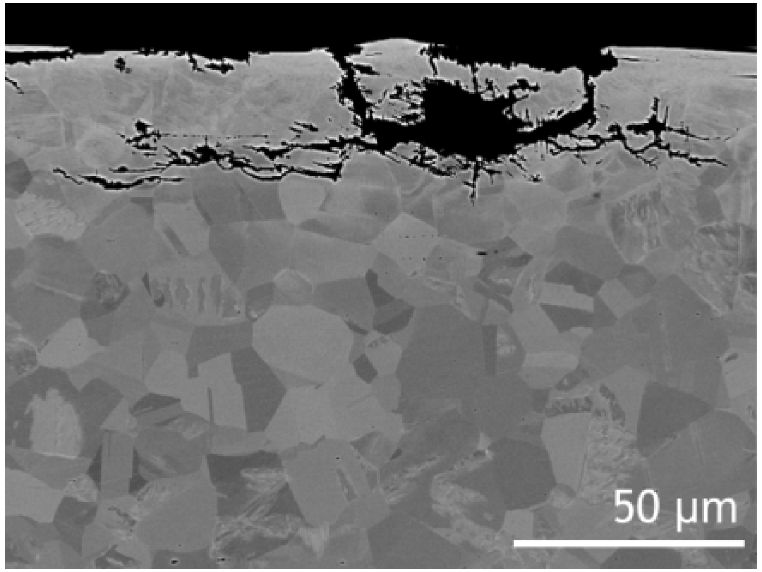
Material influences

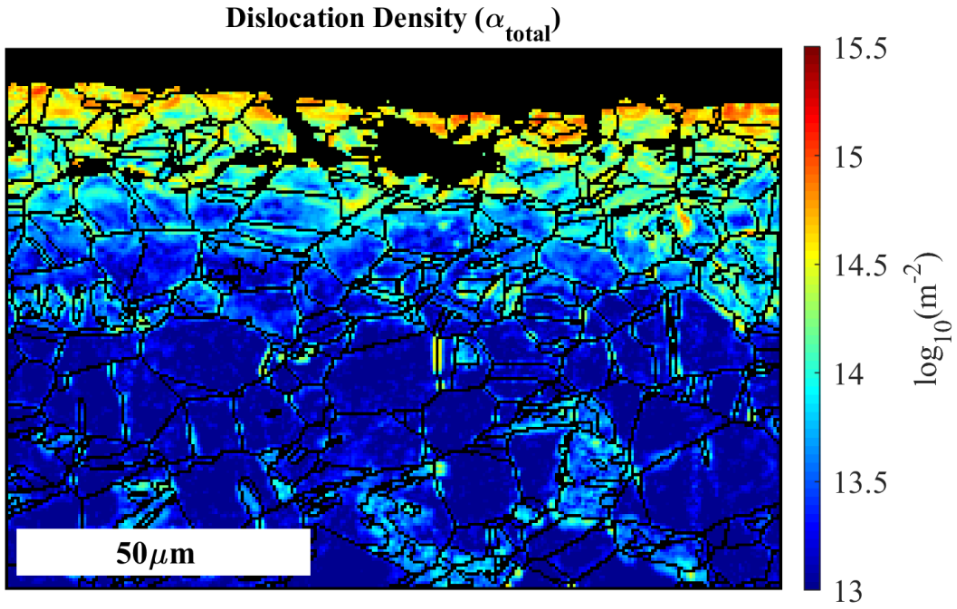
- *Surface finish effects near surface dislocation density, may be the cause for irregular shaped pits and microcracking*

Surface finish residual stress influences pitting



- Pit-to-Crack Transition Model





304L - #4 mechanical grind

1 month diurnal cyclic exposure

Is pit growth/morphology influenced by the dislocation density?

Material influences

- *Surface finish effects near surface dislocation density, may be the cause for irregular shaped pits and microcracking*