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Sandia National Laboratories

Factors Impacting Atmospheric Pitting Morphologies

242nd ECS Meeting, Atlanta, Georgia

October 13th, 2022 | Ryan Katona[1]

SAND####

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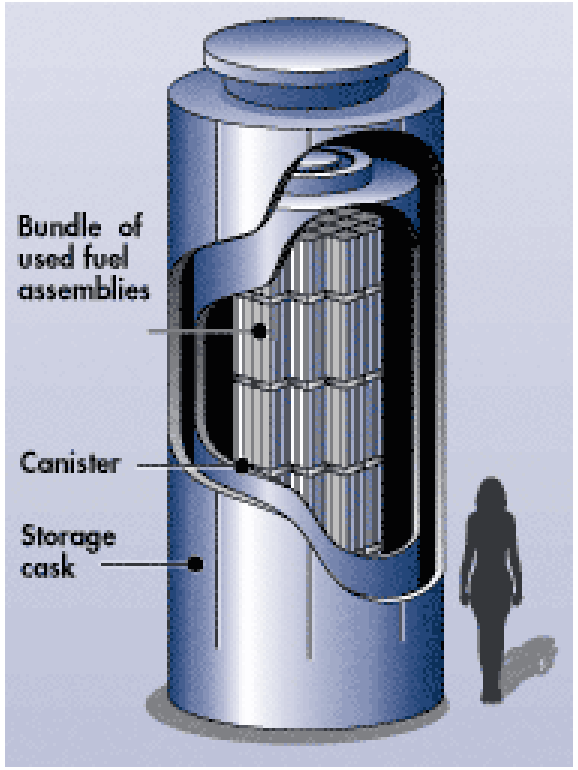
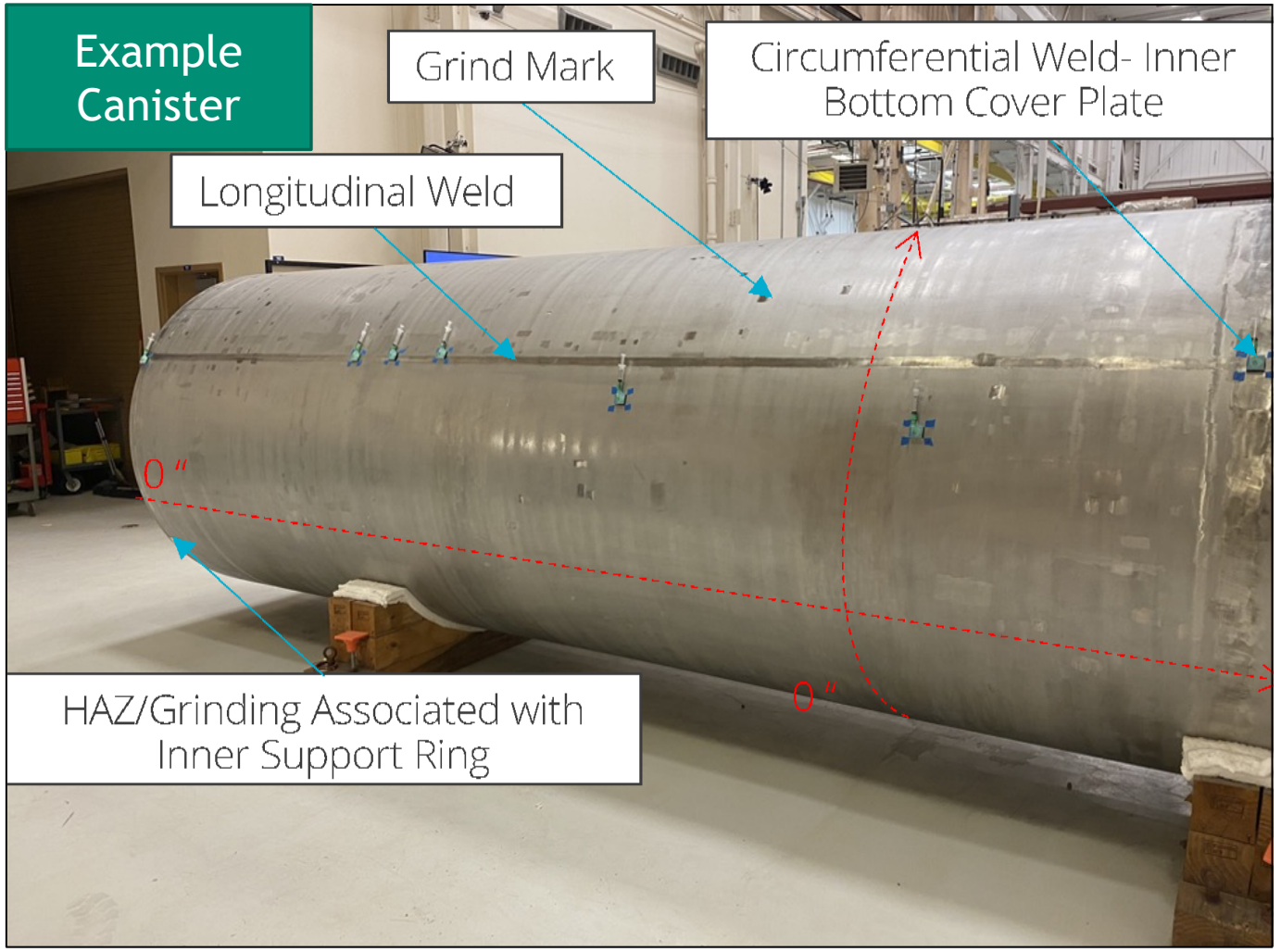
Background – SNF and SCC

- SNF is stored in
  - Welded austenitic stainless steel canisters





Background – SNF and SCC

Evolvi **nental conditions:** *RH, T, Salt chemistry, Salt load*

Incubation Time

Incubation Time | Pit Growth | Crack Growth | Mitigation & Repair

Pit Initiation | Crack Initiation | Crack Penetration | Repair

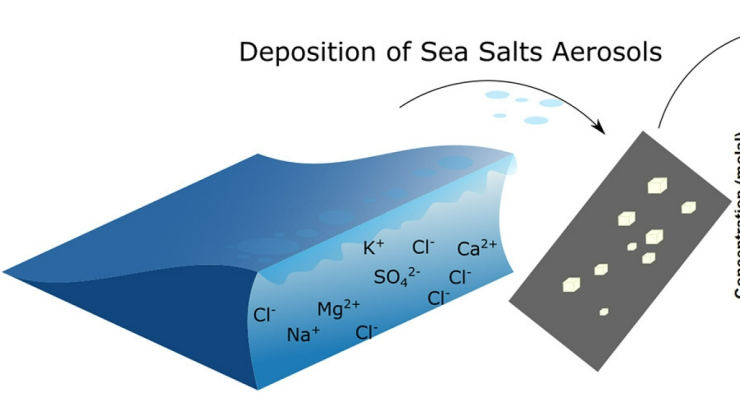
- Salt Composition Assumption
- Canister Thermal Model
- Weather Model
- Airflow and Salt Deposition Model

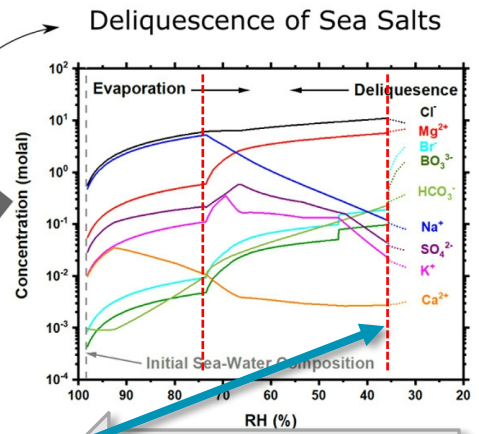
- Pit-to-Crack Transition Model

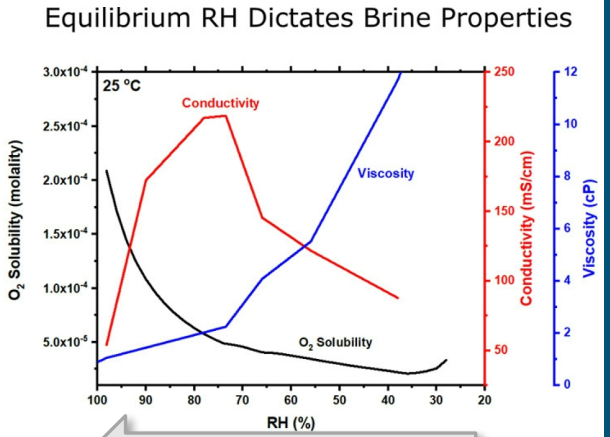
- Brine Composition/Property Model
- Canister Thermal Model
- Weather Model
- Airflow and Salt Deposition Model
- Corrosion (Maximum Pit Size) Model

- Canister Thermal Model
- Weld Residual Stress Model
- Crack Growth Model

Environment – Brine formation

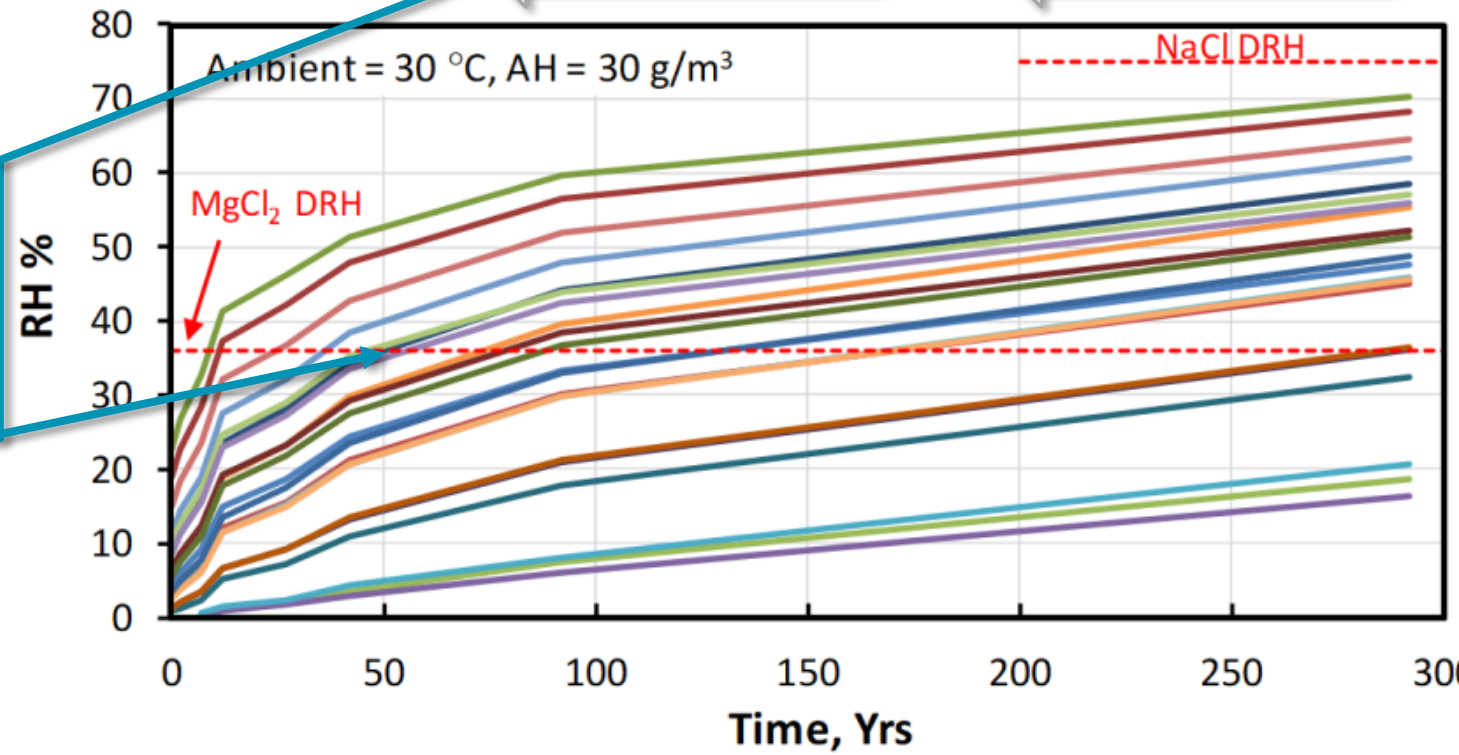




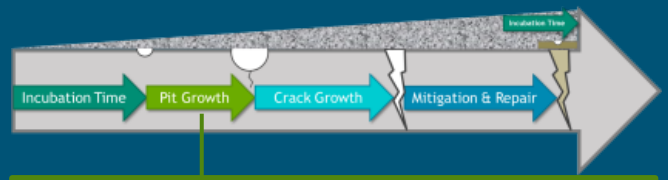


Increasing Canister Lifetime

Increasing Canister Lifetime



First 300 yrs: $MgCl_2$ dominant brine



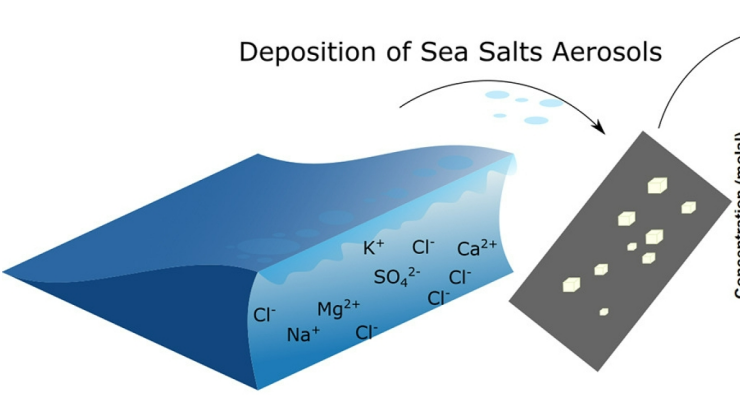
- **Corrosion (Maximum Pit Size) Model**

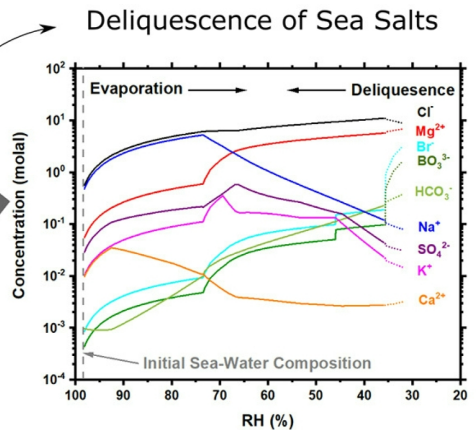
Corrosion Damage:

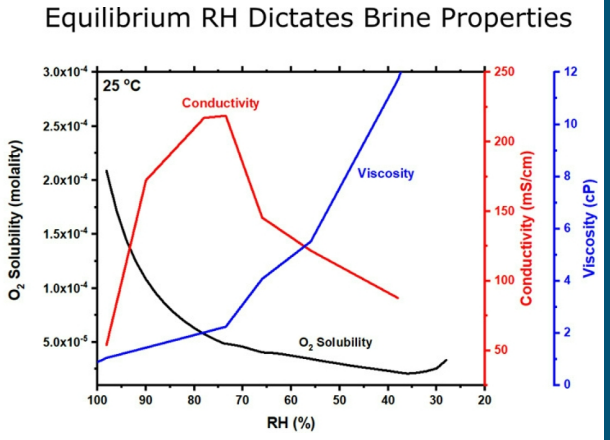
- Function of brine chemistry
- Function of Deposition
- *What about factors influencing/governing morphology?*

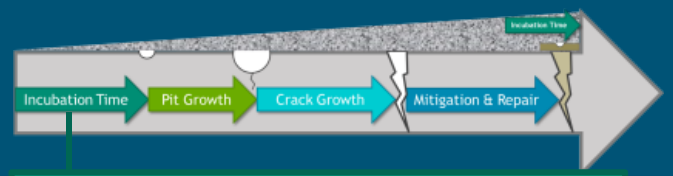
Bryan, C. R., Knight, A. W., Katona, R. M., Sanchez, A. C., Schindelholz, E. J., & Schaller, R. F. (2022). Physical and chemical properties of sea salt deliquescent brines as a function of temperature and relative humidity. *Science of the Total Environment*, *824*, 154462.

Environmental Influences





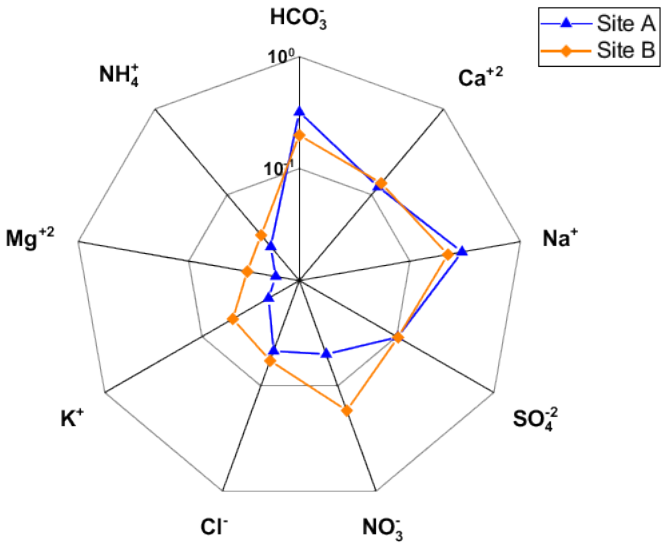




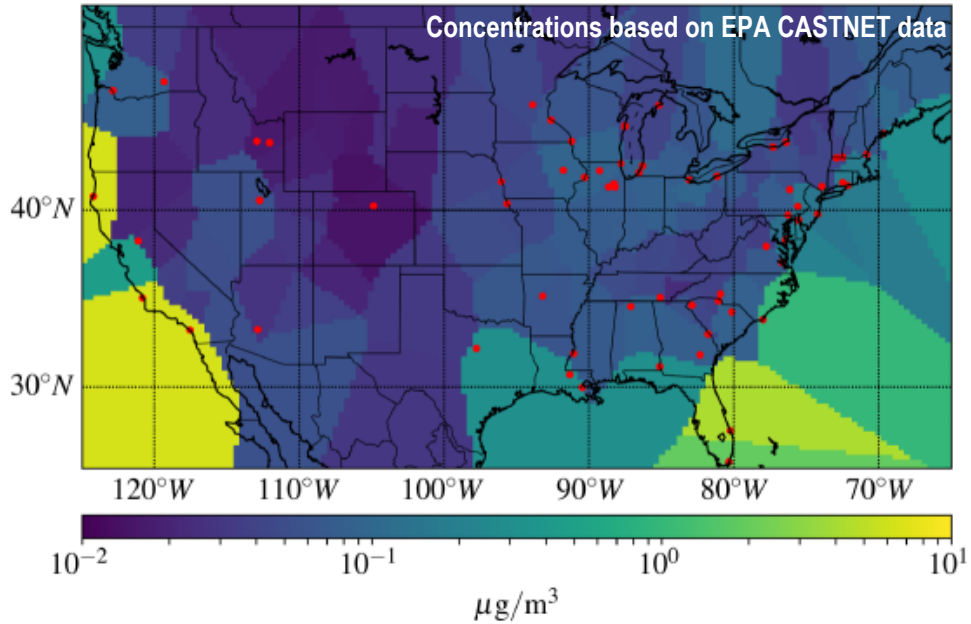
- Salt Composition Assumption
- Canister Thermal Model
- Weather Model
- Airflow and Salt Deposition Model

Brine composition controlled by environment

Composition varies per site



Deposition varies per site

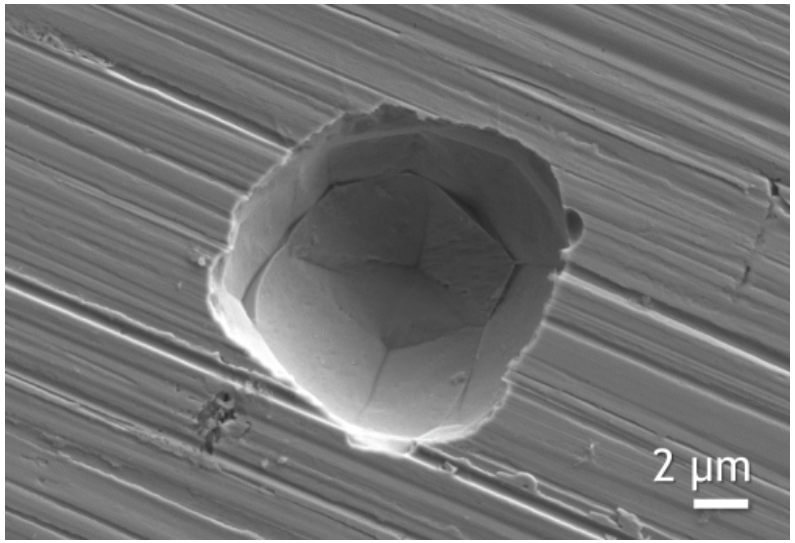


Varies across locations:

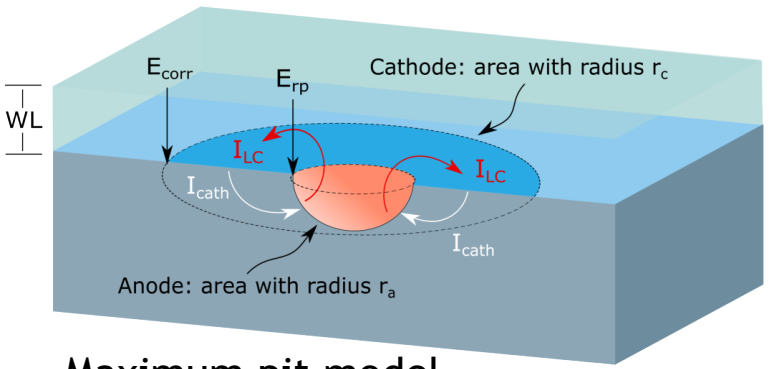
- *Composition*
- *Deposition density*

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?

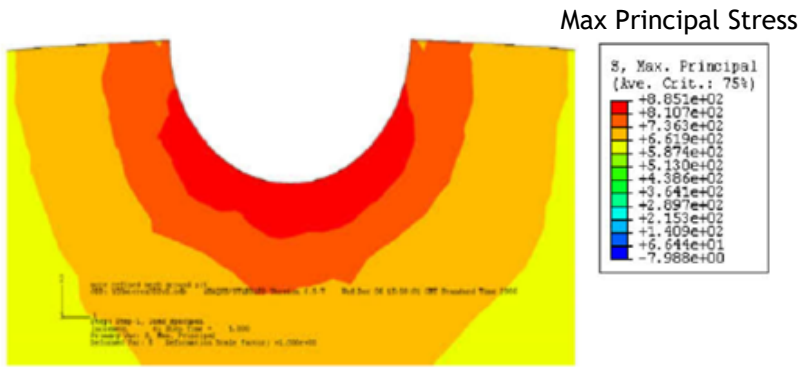


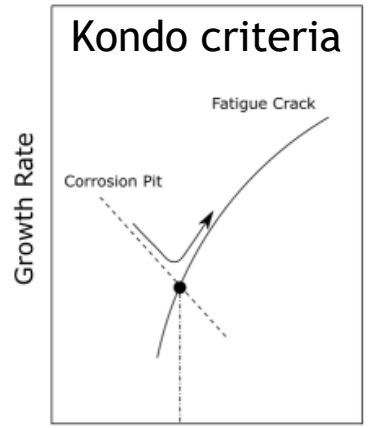
Pit to crack transition



Maximum pit model

Pit → stress/strain concentrator

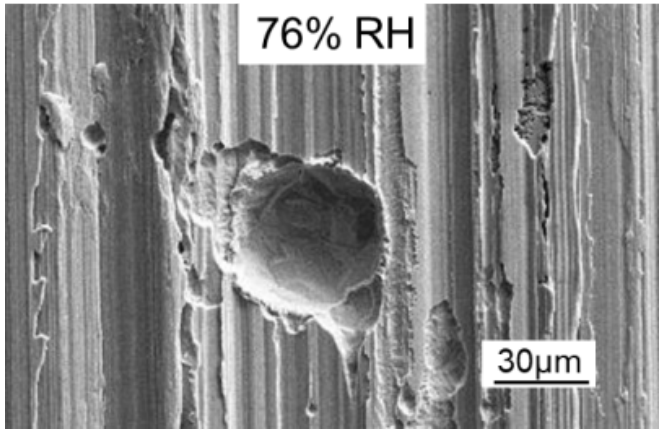




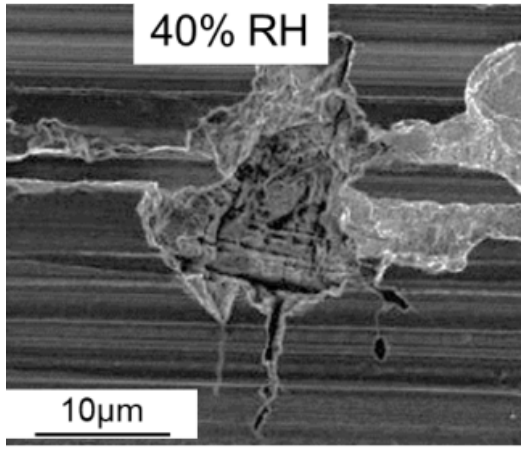
Chen, Z. Y., & Kelly, R. G. (2009). Computational modeling of bounding conditions for pit size on stainless steel in atmospheric environments. *Journal of the Electrochemical Society*, *157*(2), C69.
Turnbull, A., Wright, L., & Crocker, L. (2010). New insight into the pit-to-crack transition from finite 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.

Why is brine composition (RH) significant?

HIGH RH: NaCl RICH BRINE

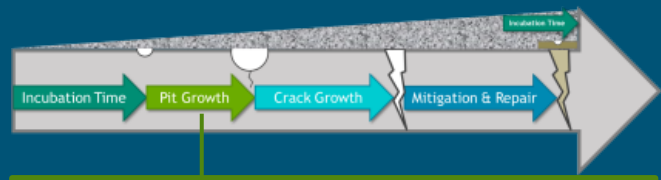


LOW RH: $MgCl_2$ RICH BRINE



- 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)

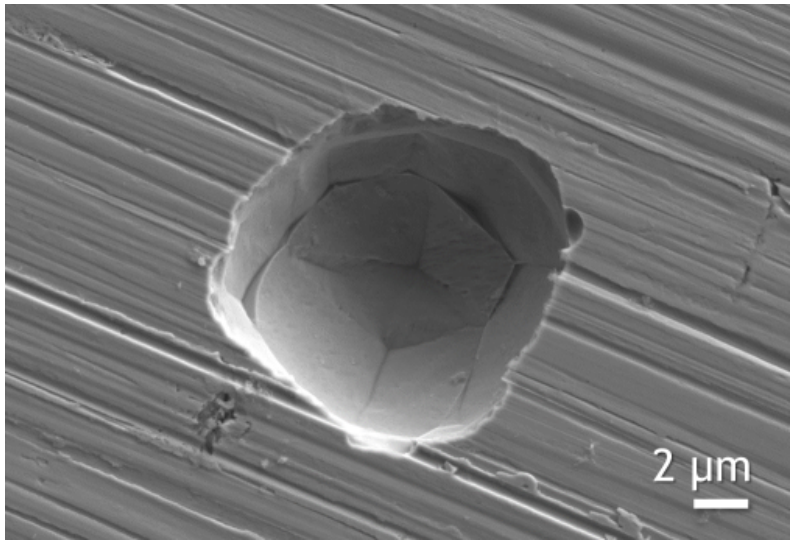


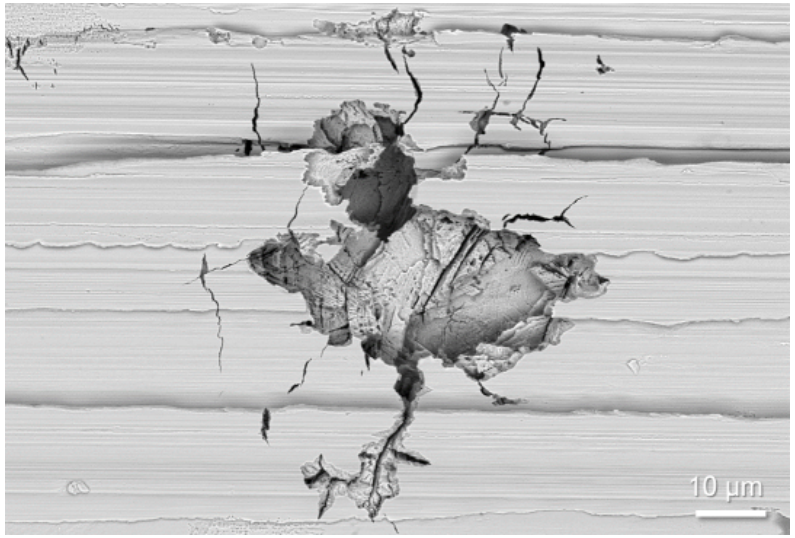
- **Corrosion (Maximum Pit Size) Model**

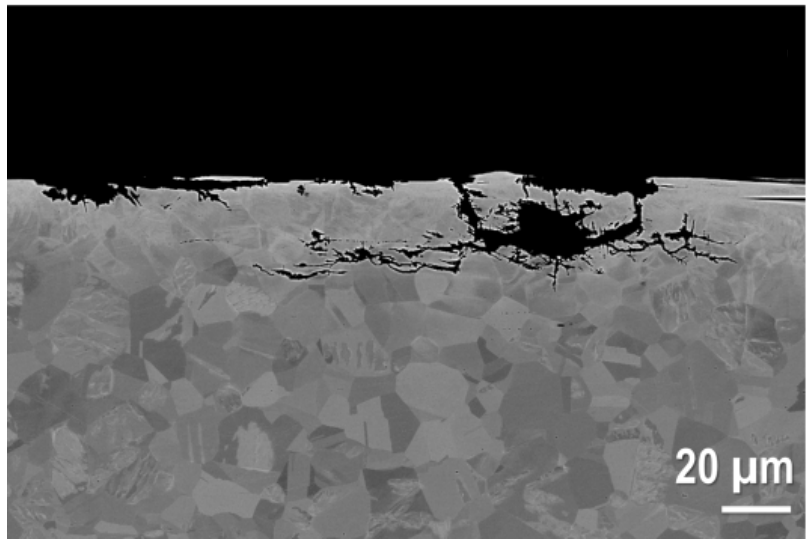
- Is there a link between morphology and exposure RH?
  - Lower RH dominated by $MgCl_2$
  - Is it influences of HER? Precipitates?

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.

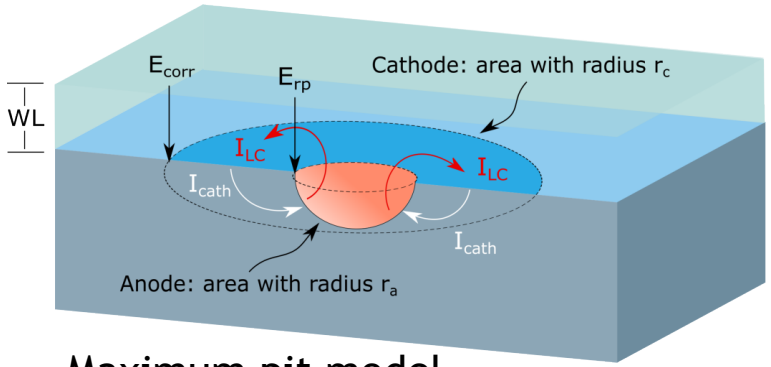
Why care about pit morphology?







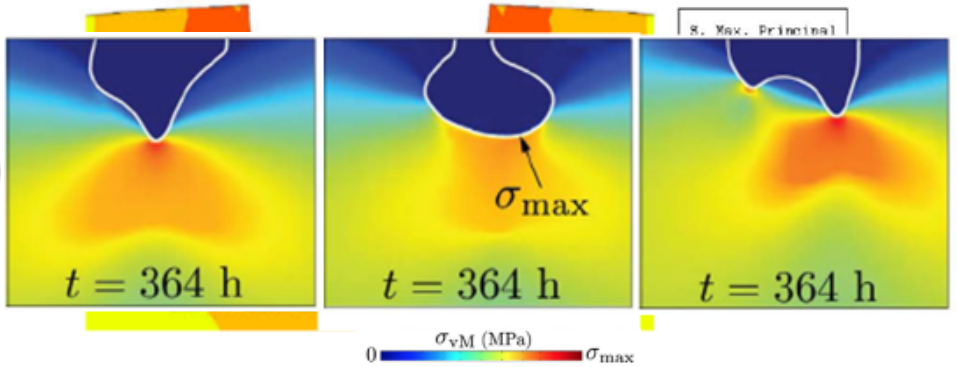
Are these irregular geometries significant? For pitting…pit to crack…CGR?

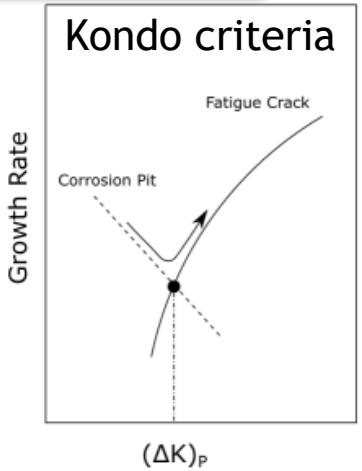


Maximum pit model

Pit → stress concentrator

Max Principal Stress





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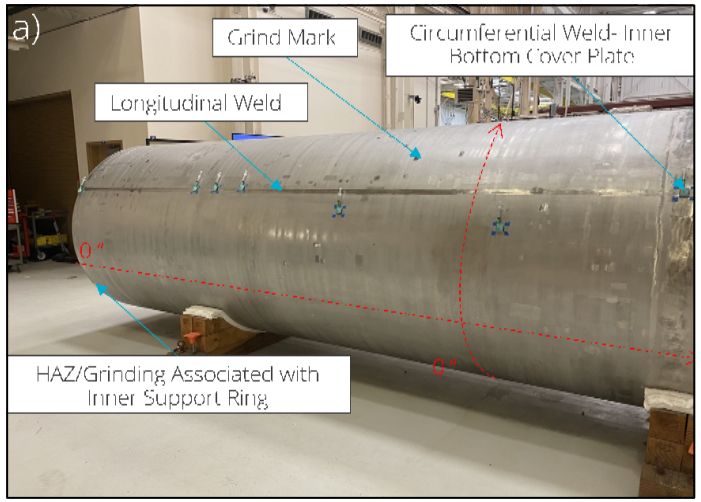
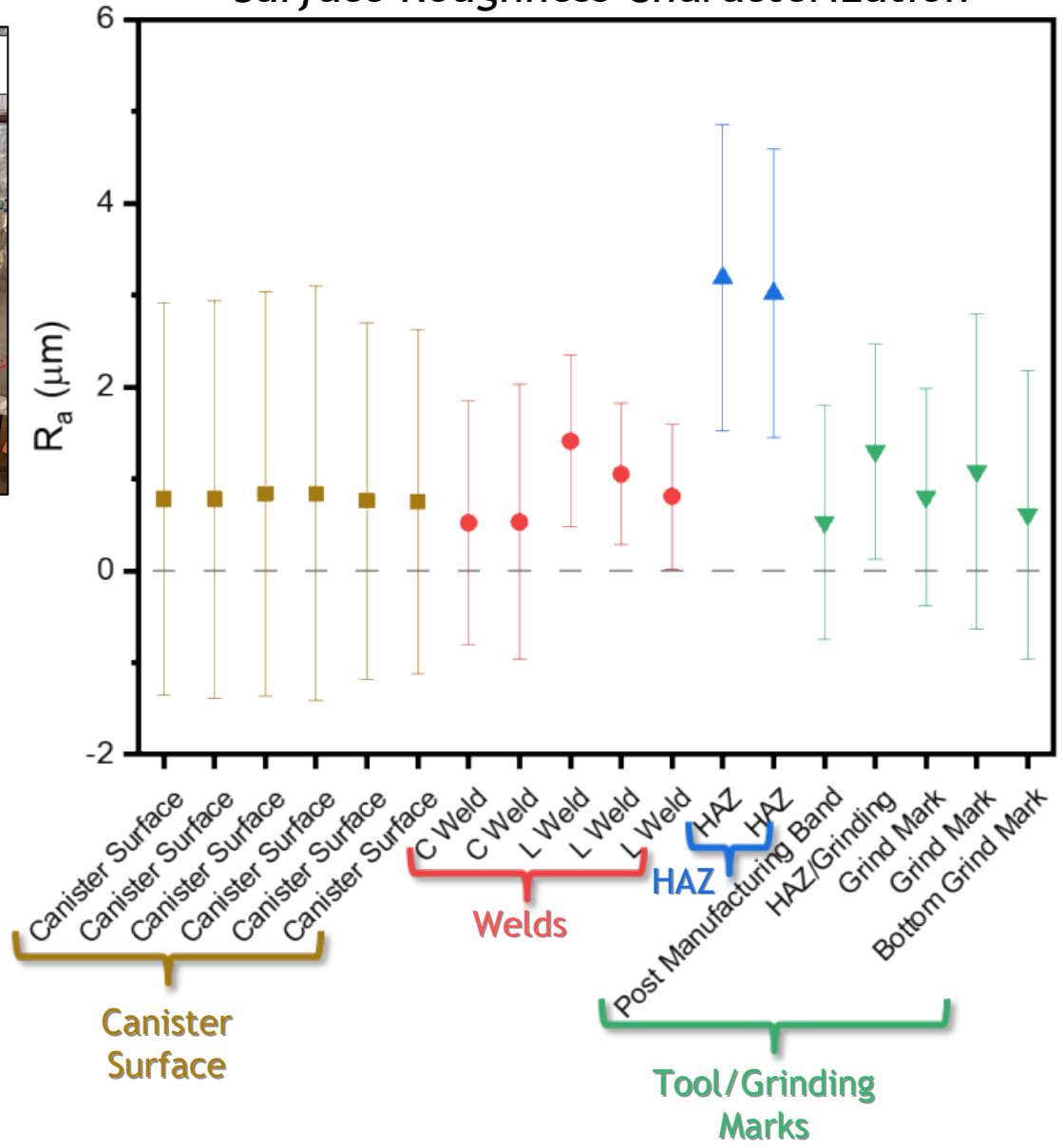
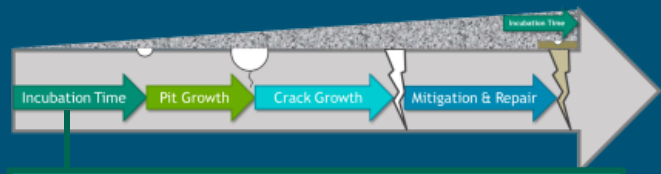
Material Influences – Surface Finish & Composition

Example Horizontal Canister



Surface Roughness Characterization





- Salt Composition Assumption
- Canister Thermal Model
- Weather Model
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Material surface finish varies across canister surface

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

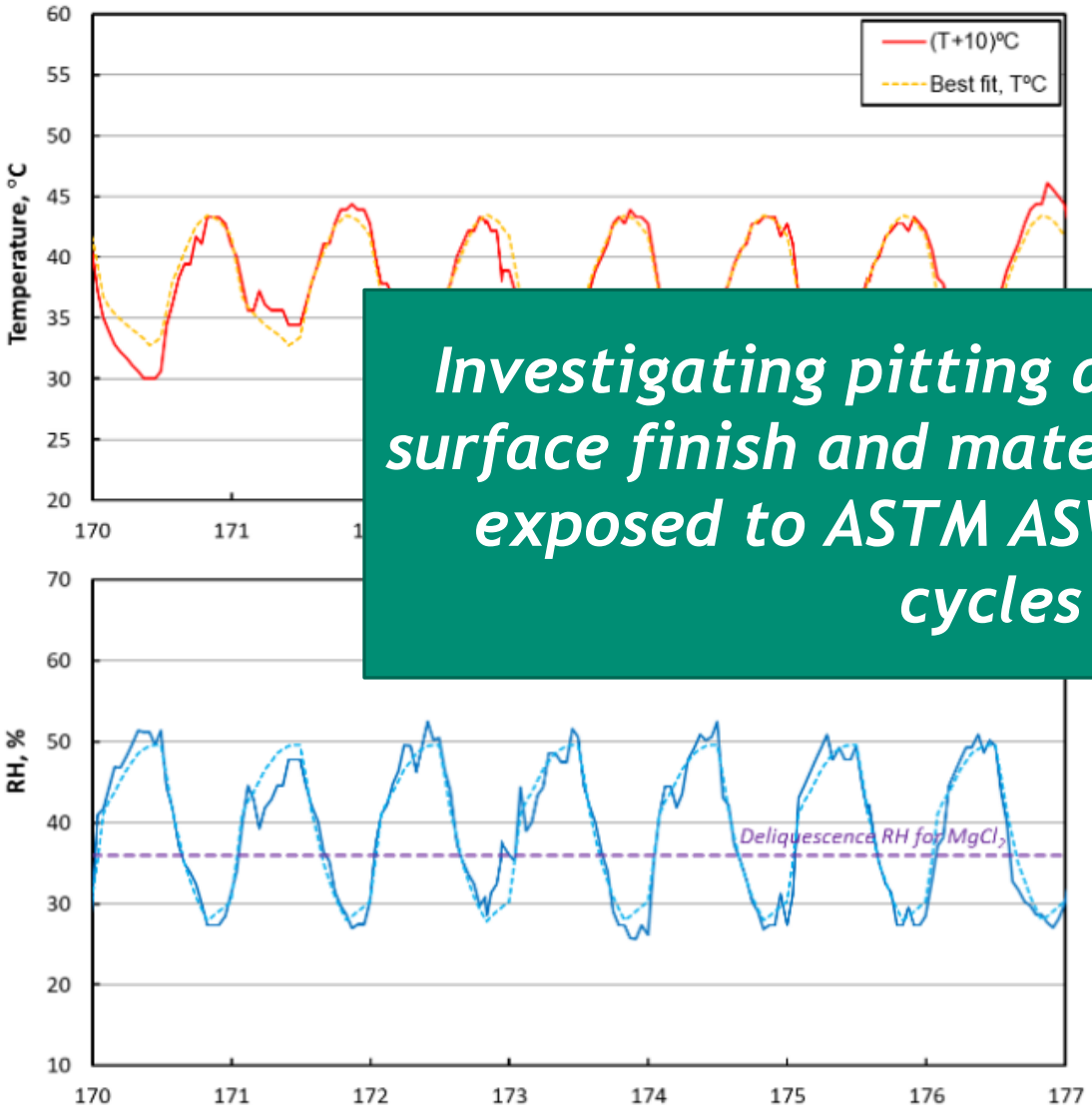
Material composition varies per canister manufacturer/date of manufacturing

Canister Composition:
Austenitic Stainless Steels

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

Development of Relevant Lab Exposures - Diurnal

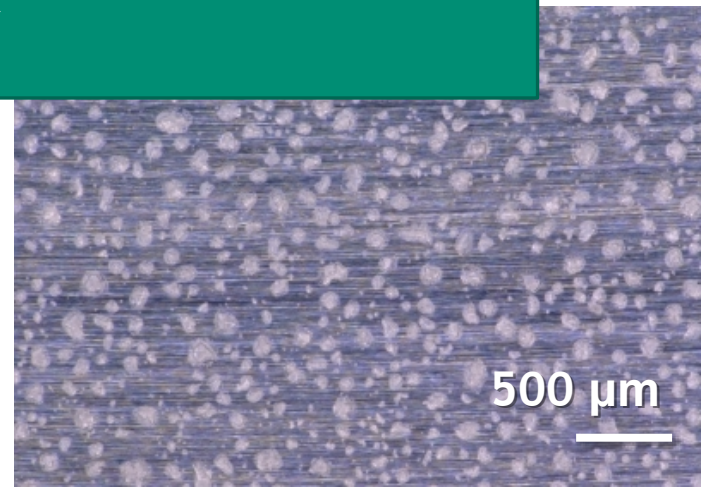
Diurnal Cycles

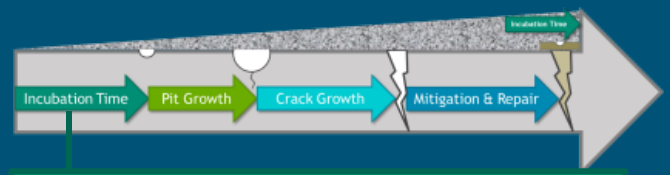


Cycle Conditions:

- Based on storage site weather data
- ΔT imposed to mimic
- ace
- 300

Investigating pitting as a function of surface finish and material composition exposed to ASTM ASW and diurnal cycles





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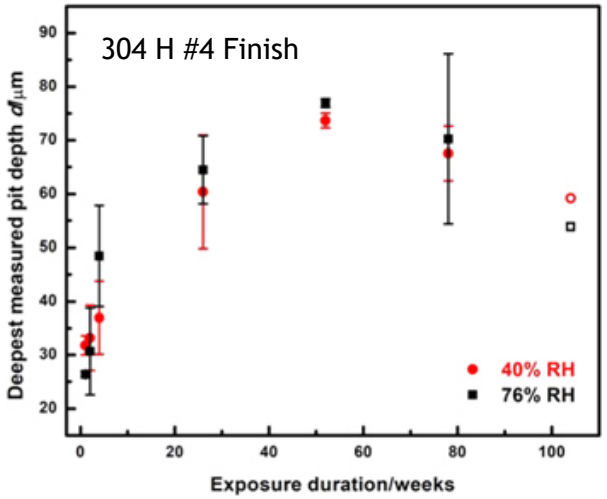
- Is pitting behavior influenced by SNF conditions? *i.e. higher T, more concentrated brines*
- Explore influences of:
  - **Diurnal Cycles**
  - Dust
  - Chemistry

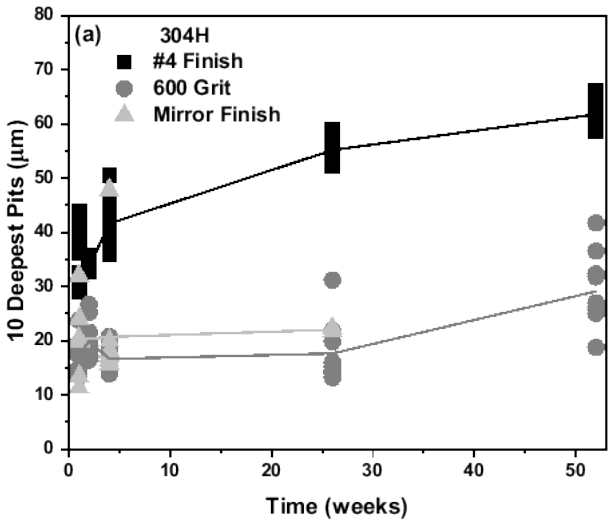
Influence of more relevant environments on pitting

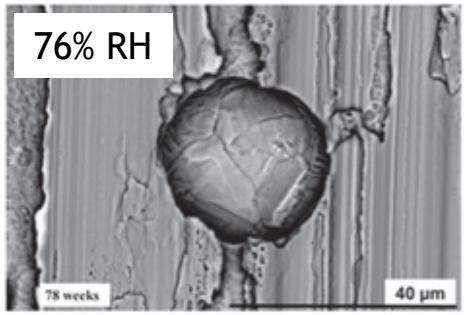
Constant RH

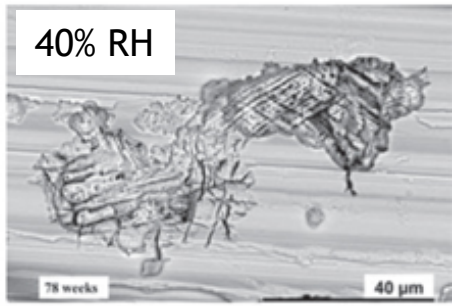


Diurnal Cycles

Profilometry comparison across material finish for 304H coupons







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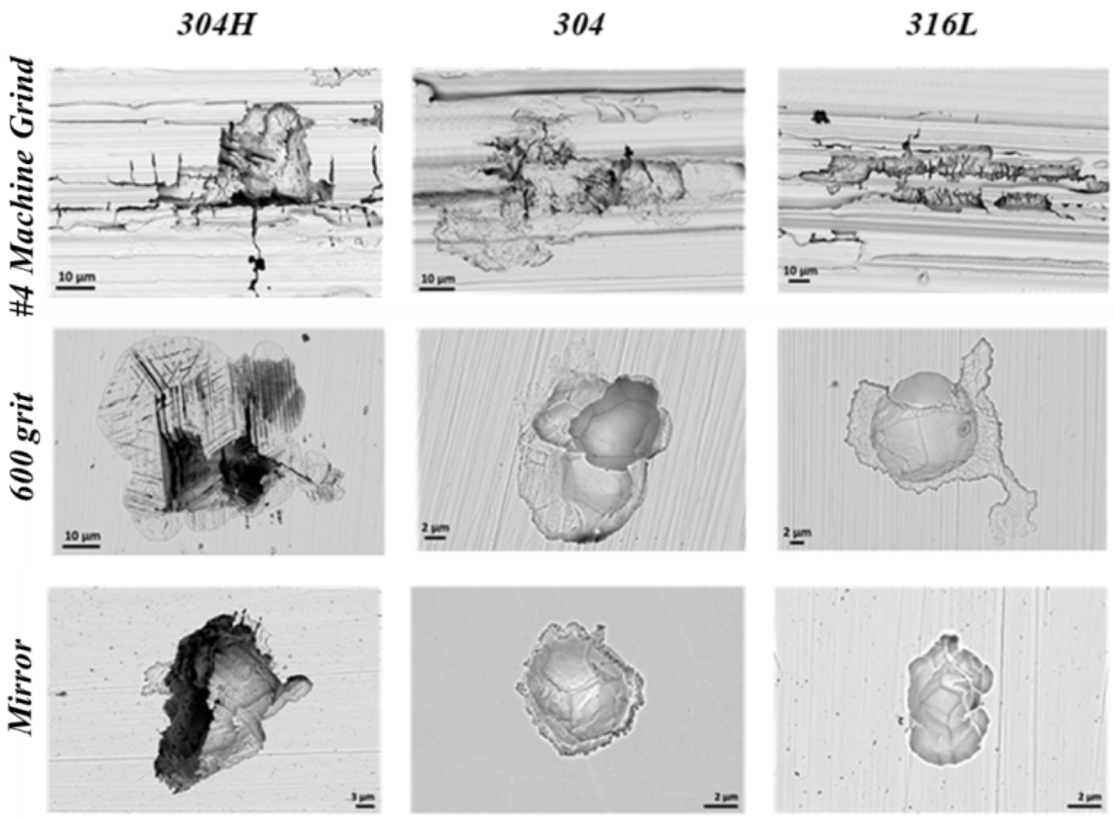
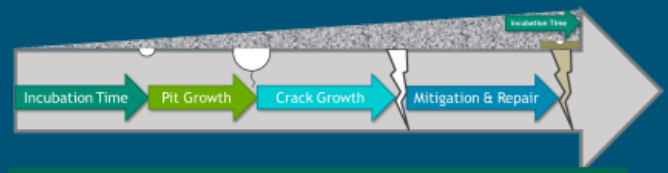




- Salt Composition Assumption
- Canister Thermal Model
- Weather Model
- Airflow and Salt Deposition Model

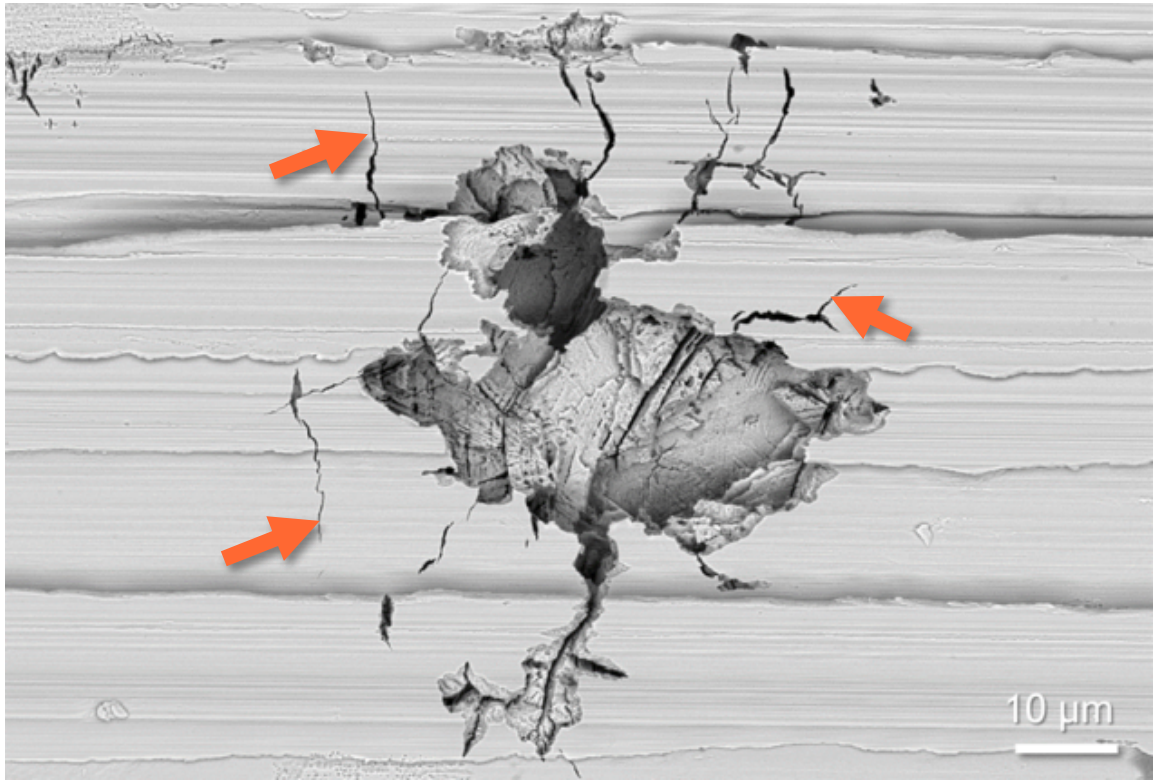
- Understanding pit growth under SNF relevant conditions:
  - Higher T
  - More concentrated brines
  - Material composition and finish

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.

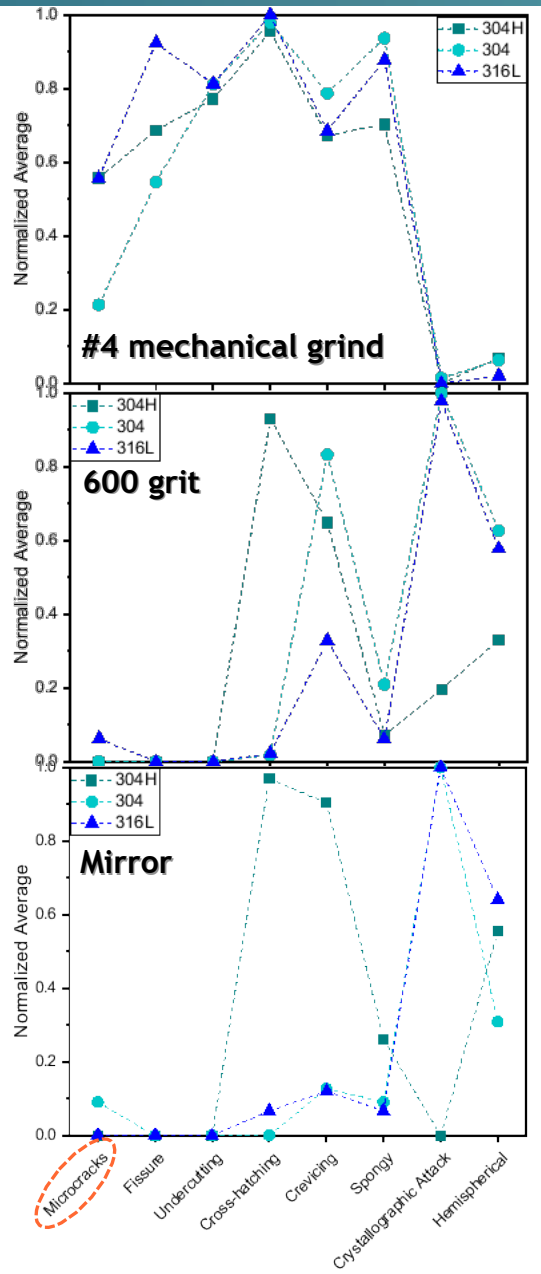
What influences pit morphology?

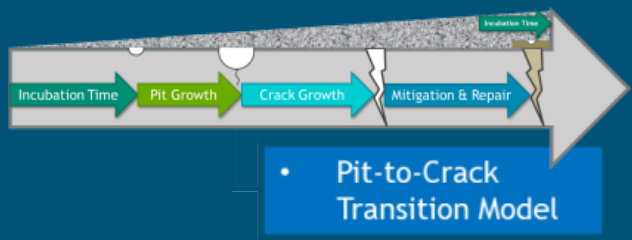
Cycle Conditions:

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



Microcracking

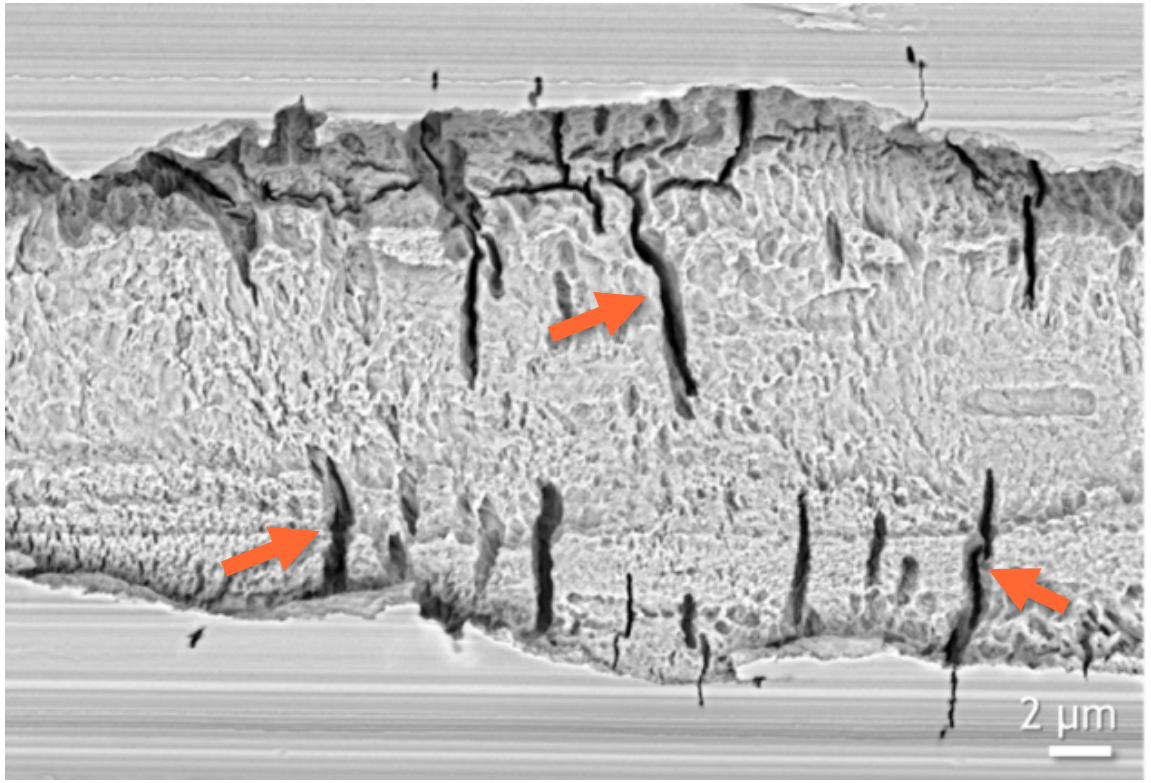




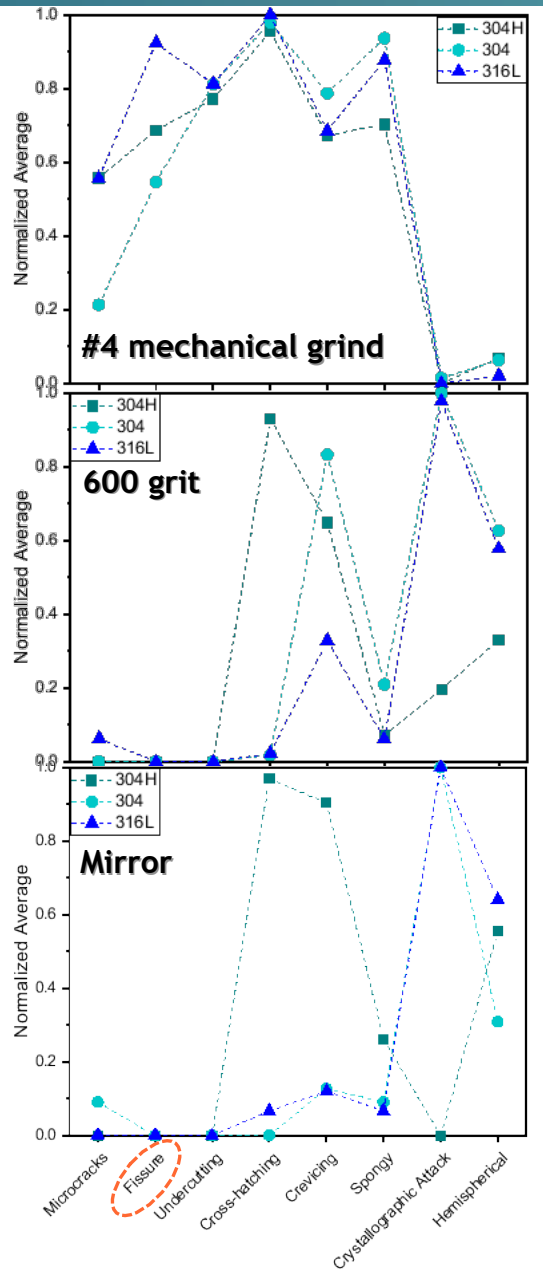
Qualitative pit characterization

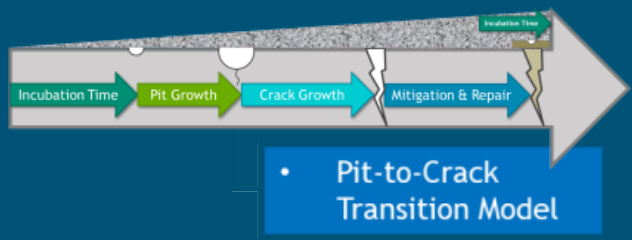
- *Initial attempt to obtain quantitative metrics*
  - *Identify dominant pit features governed by exposure, material, surface finish, etc.*

What influences pit morphology?



Fissures





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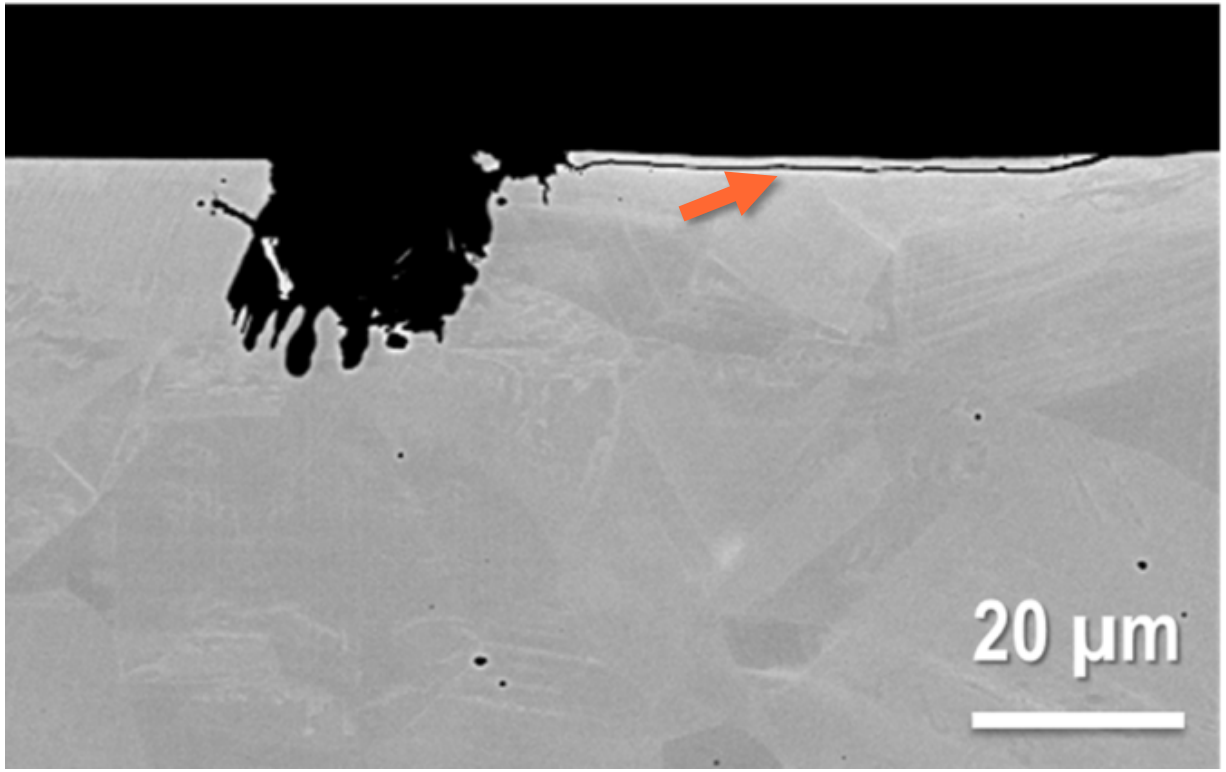
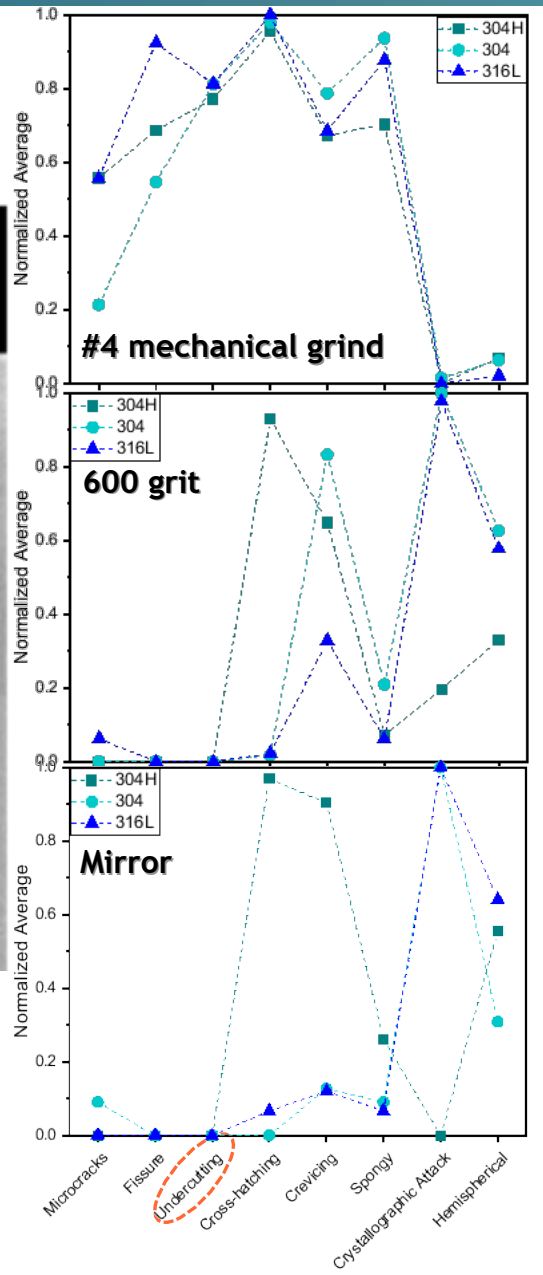


Undercutting



- Pit-to-Crack Transition Model

Qualitative pit characterization

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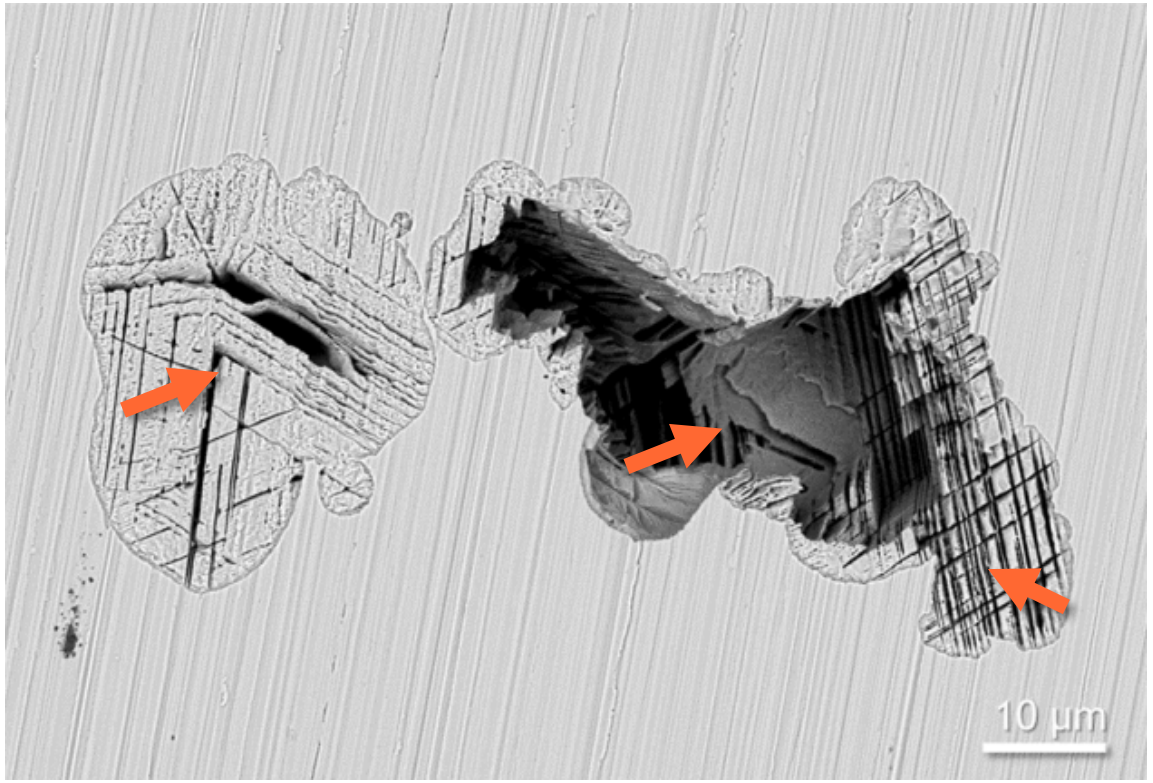
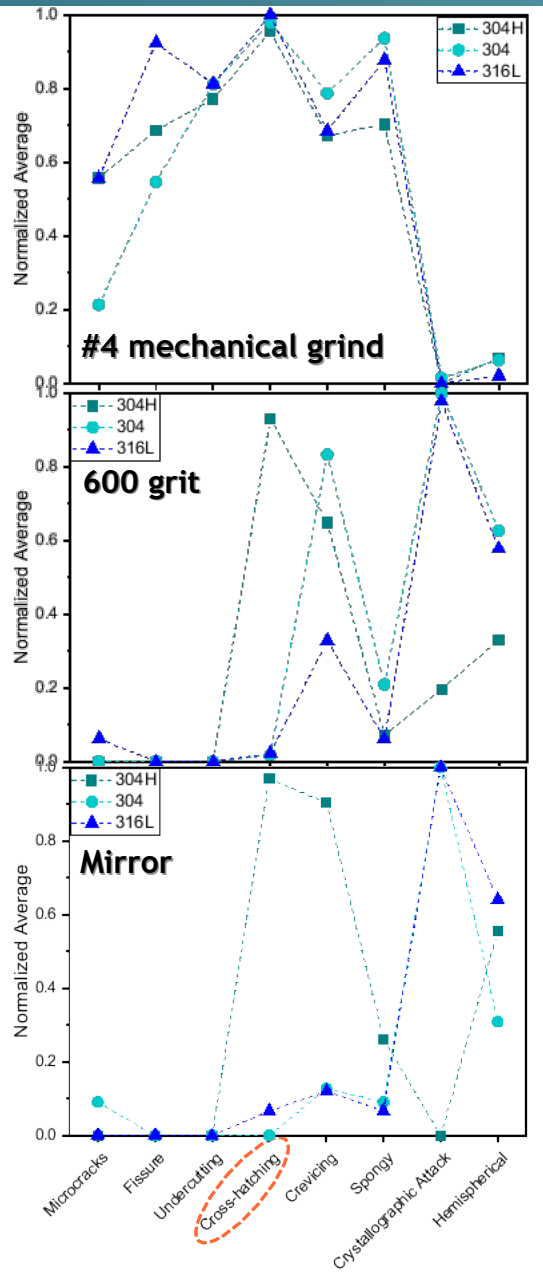
  - *Identify dominant pit features governed by exposure, material, surface finish, etc.*

What influences pit morphology?



Cross-hatching



- Pit-to-Crack Transition Model

Qualitative pit characterization

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

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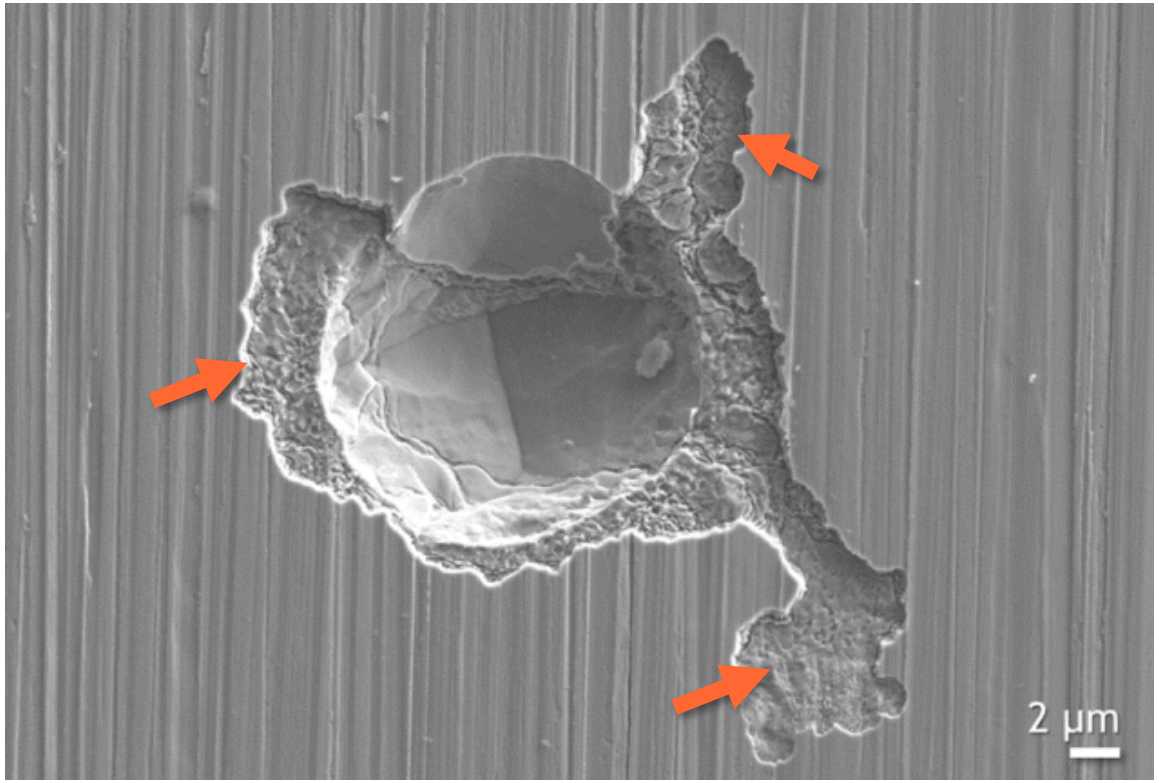
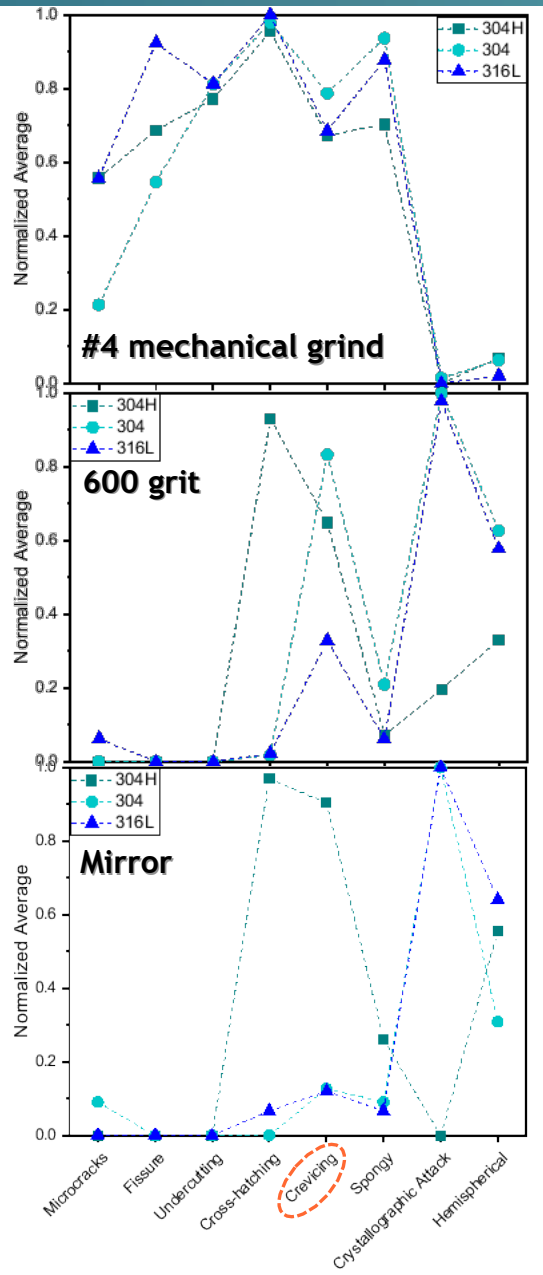
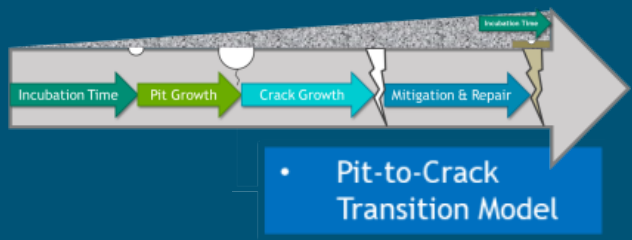


Crevicing





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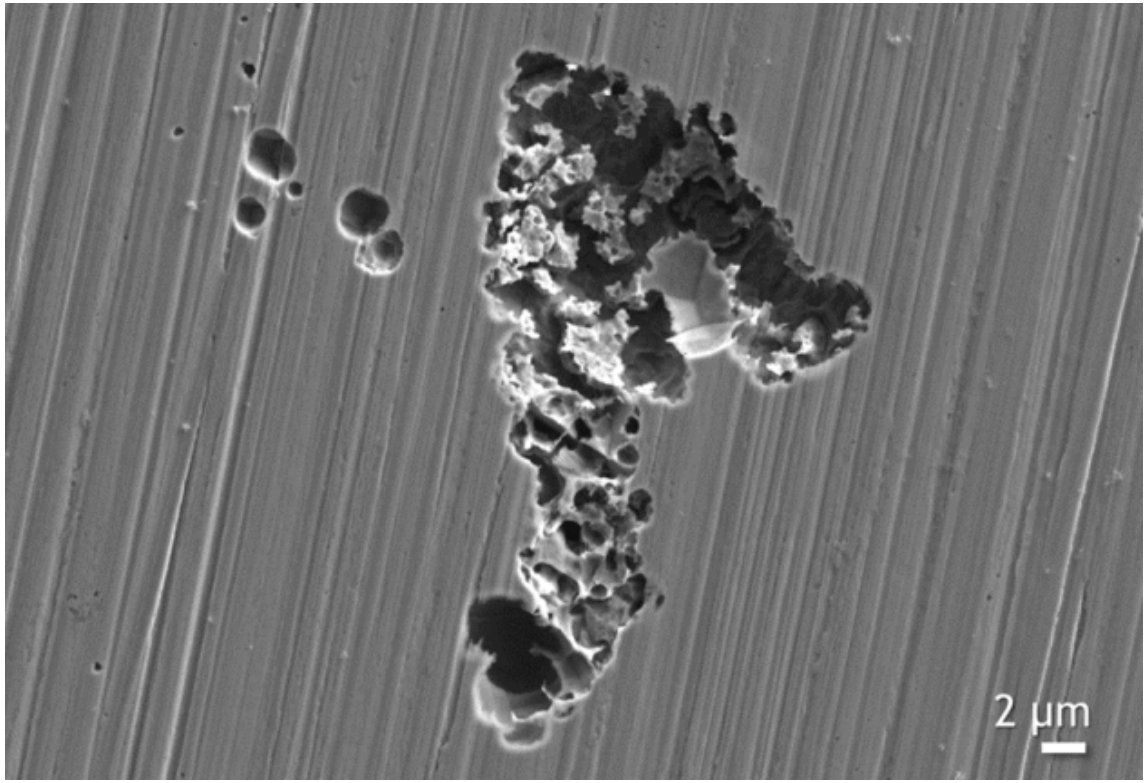
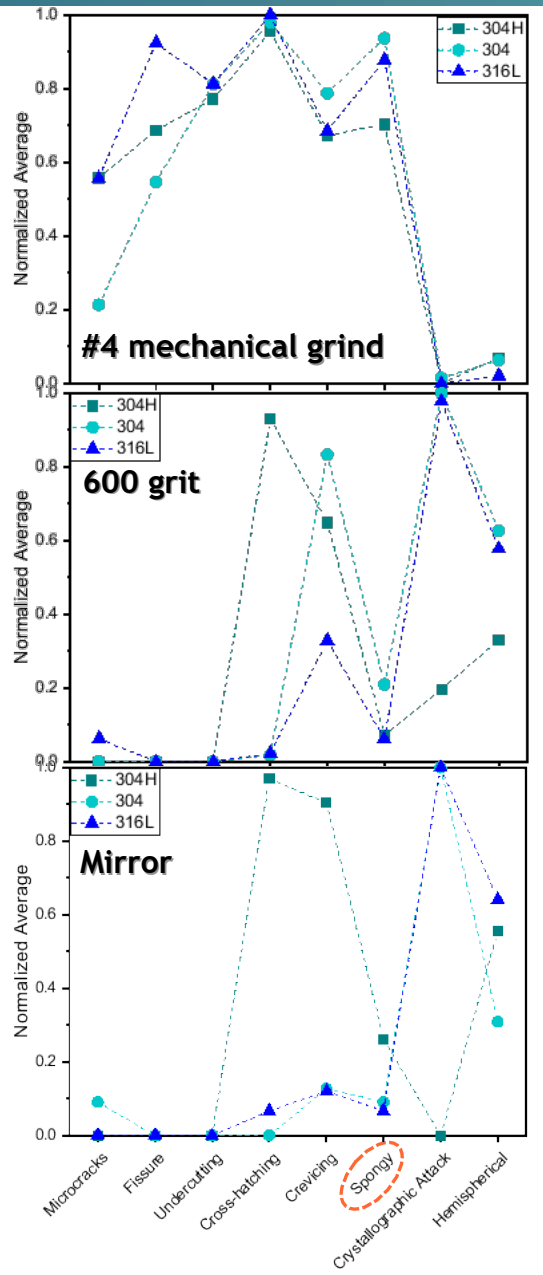
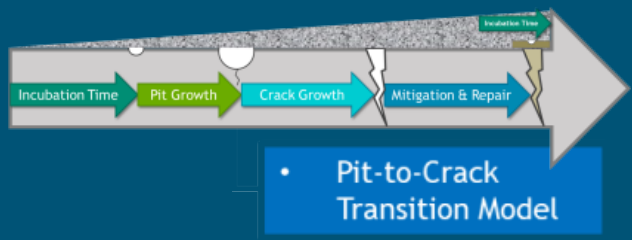


Spongy





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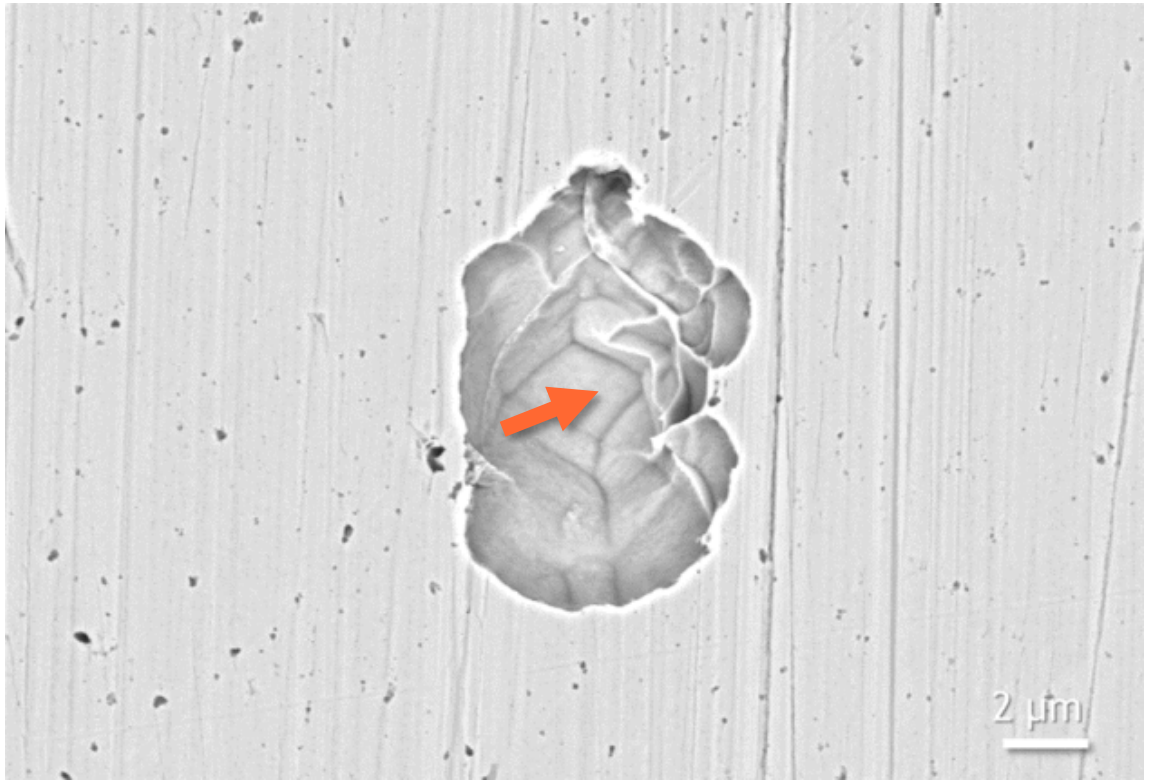
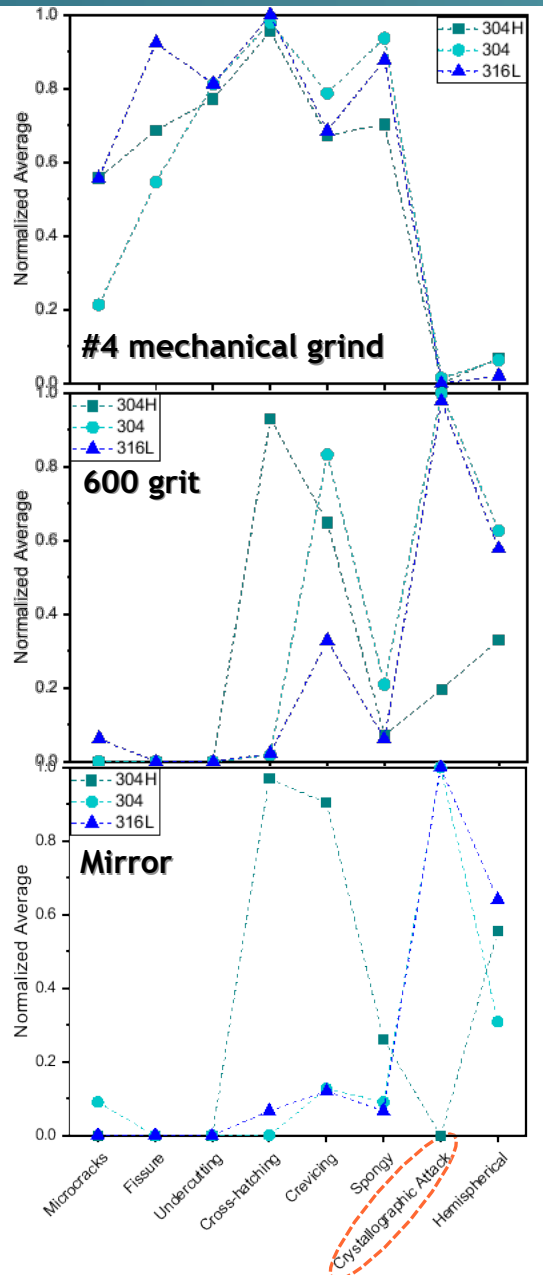
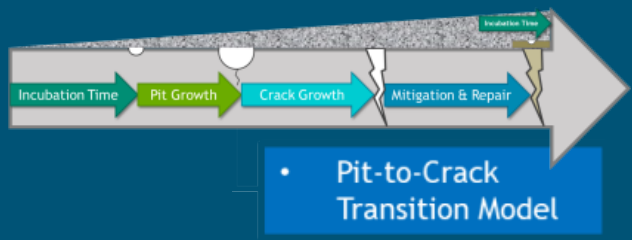


Crystallographic attack





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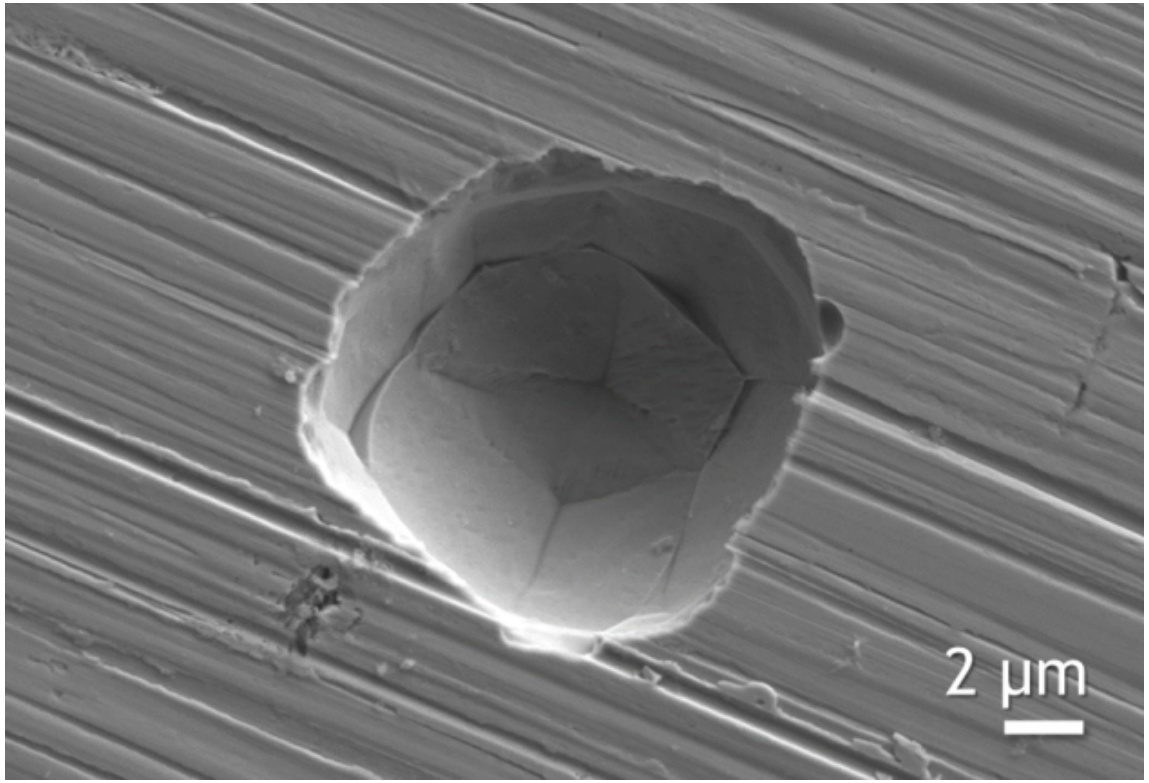
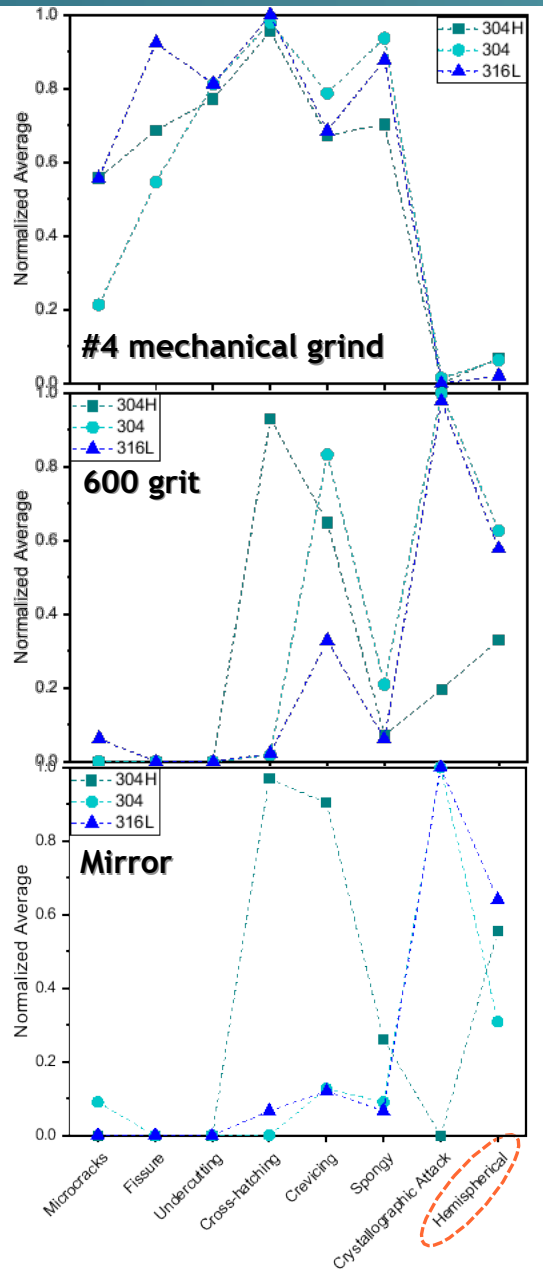
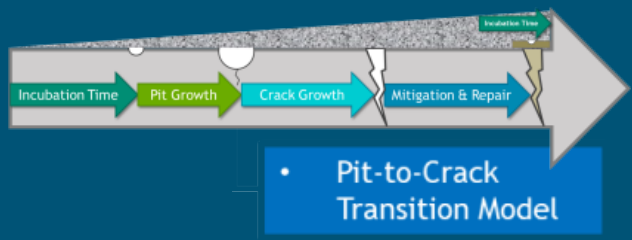


Hemispherical

Pit morphology: function of <u>brine</u> but also material and surface finish





Qualitative pit characterization

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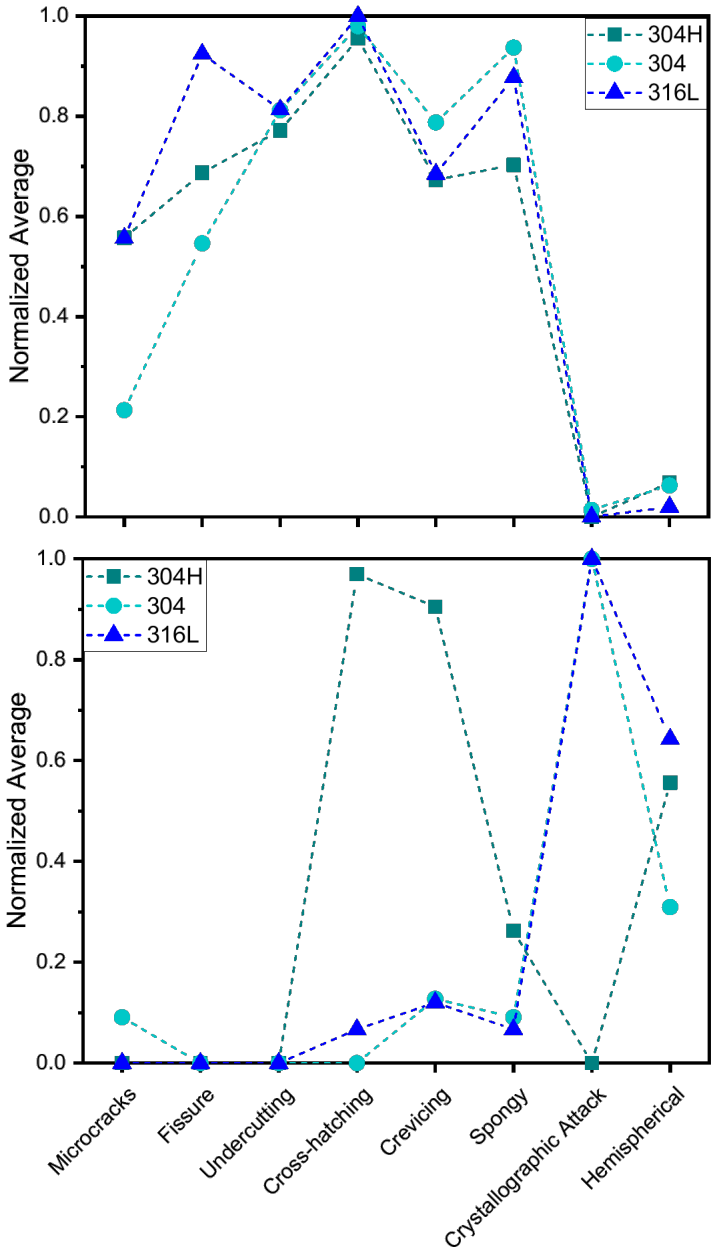
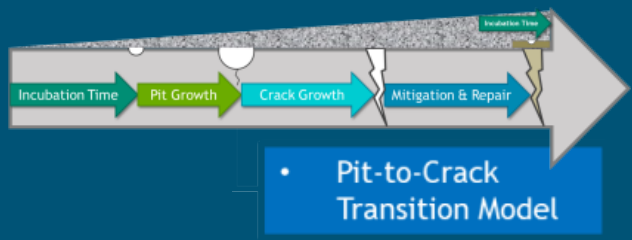
What influences pit morphology?

#4 mechanical grind

Mirror





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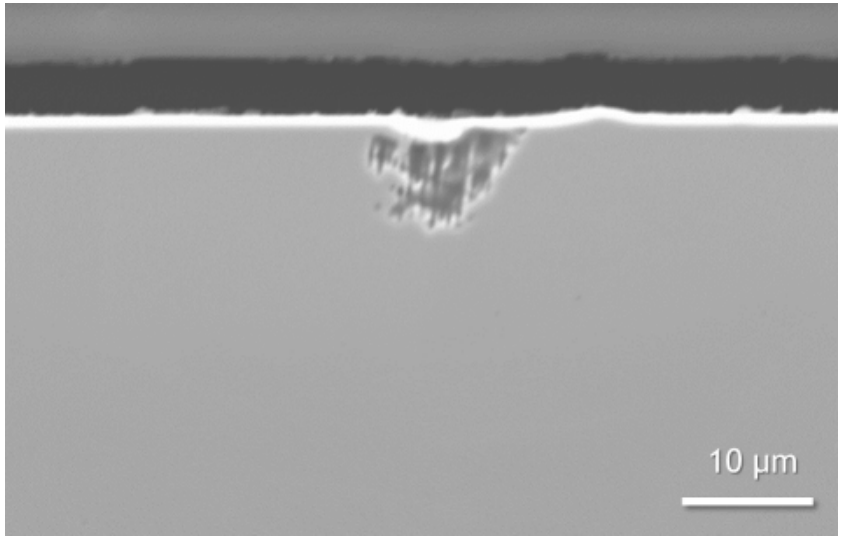
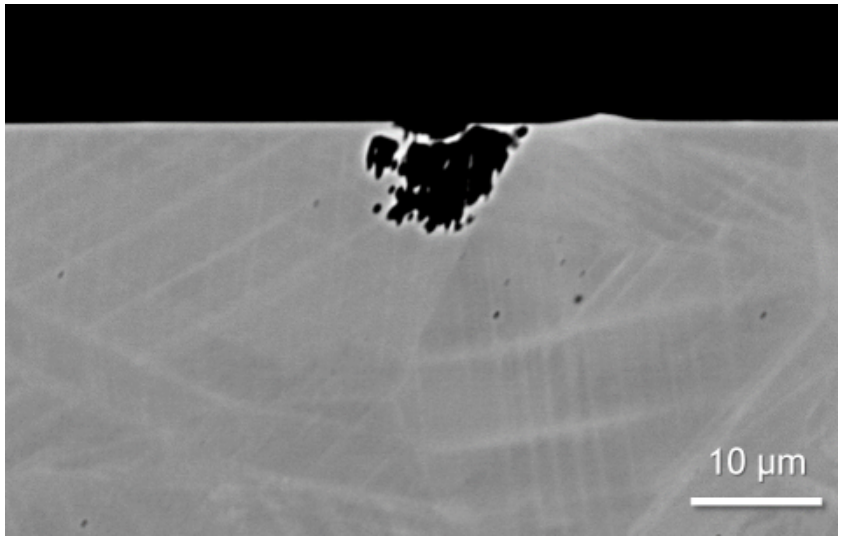
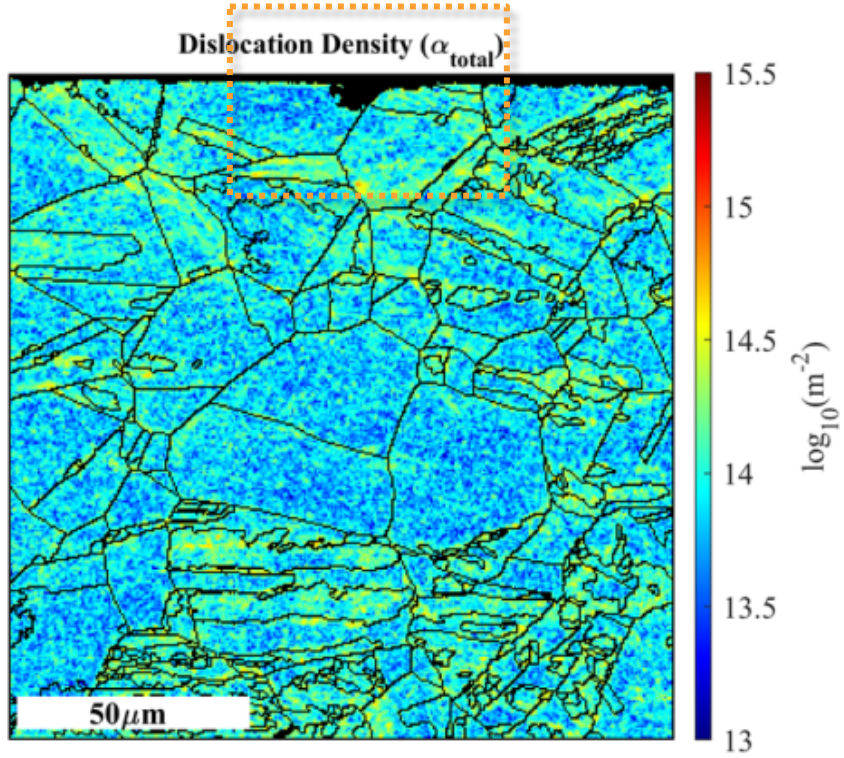
Surface finish residual stress influences pitting

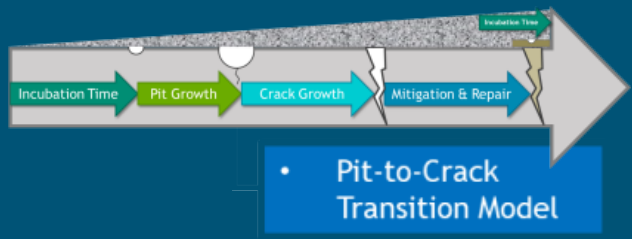




1 month diurnal cyclic exposure



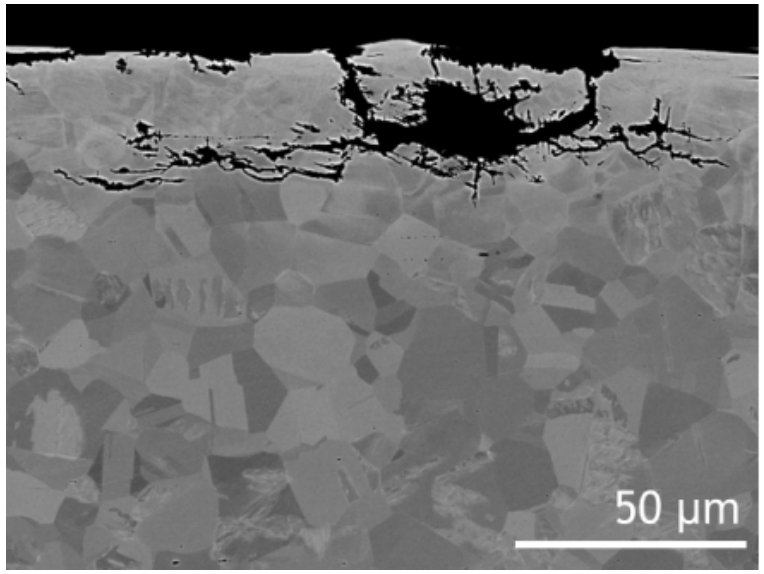
304H – **mirror finish**

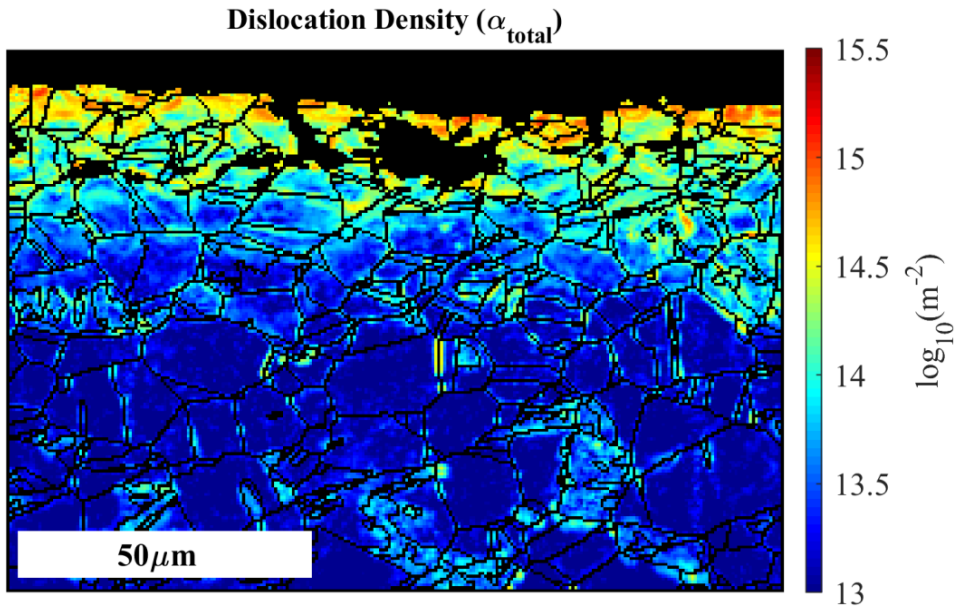


Material influences

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

Surface finish residual stress influences pitting

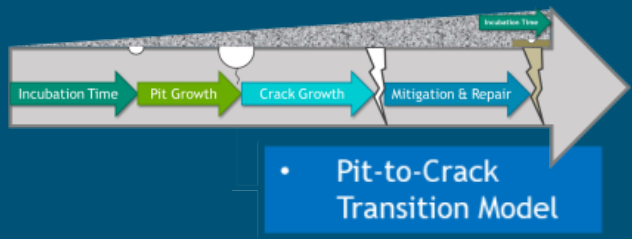




304L - #4 mechanical grind

1 month diurnal cyclic exposure

Is pit growth/morphology influenced by the dislocation density?



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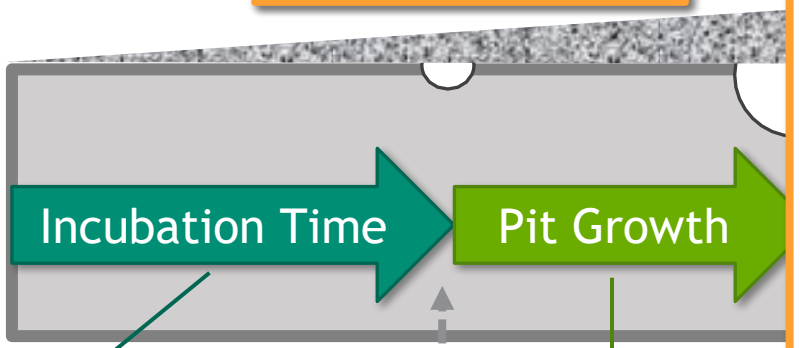
Pathway Forward



- Can we develop an understanding of the relevant environmental and material parameters' effects on localized corrosion?
  - What influences pit size, shape, etc. under SNF relevant exposures?
- Do we care?
  - How does this influence pit to crack transition?

Pit Initiation

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

Crack Initiation

- Pit-to-Crack Transition Model

Crack Penetration

- Canister Thermal Model
- Weld Residual Stress Model
- Crack Growth Model

Repair

- Brine Composition/Property Model
- Canister Thermal Model
- Weather Model
- Airflow and Salt Deposition Model
- Corrosion (Maximum Pit Size) Model

Acknowledgements

DoE Collaborations:

Dr. Ned Larson

Dr. Charles Bryan, Dr. Andrew Knight, Jason Taylor, Brendan Nation, Dr. Erin Karasz, Dr. Ryan Katona, Makeila Maguire, Timothy Montoya, Jason Snow, Sara Dickens, Dr. Tim Ruggles, Derek Wichhart, Scott Sanborn, and Sylvia Saltzstein.

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

Sandia National Laboratories

Factors Impacting Atmospheric Pitting Morphologies

242nd ECS Meeting, Atlanta, Georgia

October 13th, 2022 | Ryan Katona[1]

SAND####

Erin Karasz[1], Timothy Montoya[2], Jason Taylor[1], Charles Bryan[1], and Rebecca Schaller[1]

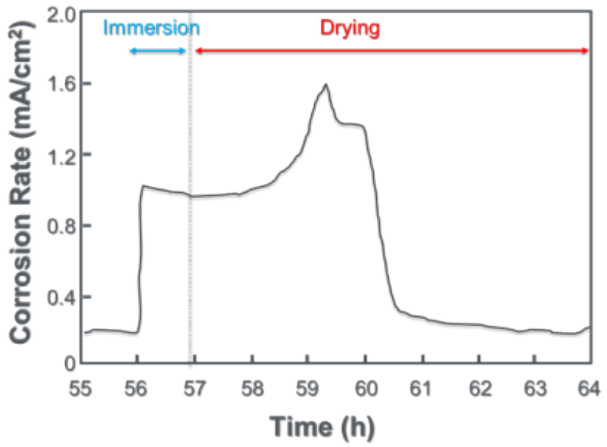
[1]Sandia National Laboratories
[2]University of Virginia

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and 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.

EXTRAS

What brine is really present on SNF canisters?

Diurnal Cycles

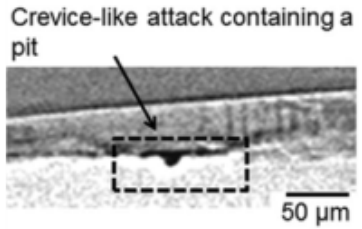


Changes in the corrosion rate, i_{corr}, and potential during a wet/dry cycle of carbon steel.[1]

Corrosion rate increases upon initial drying (highly concentrated brine)

Dust/Precipitates

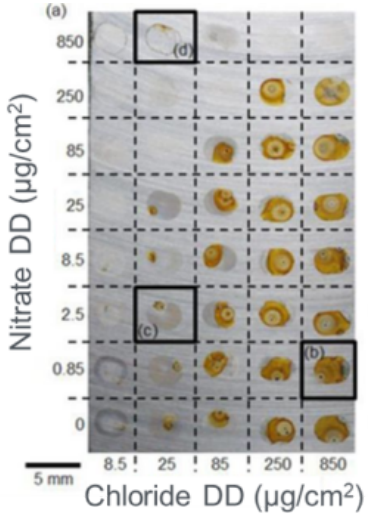
Electrolyte spreading due to capillary action



Observation of crevice-like on a SS304 sample with surface deposits[2]

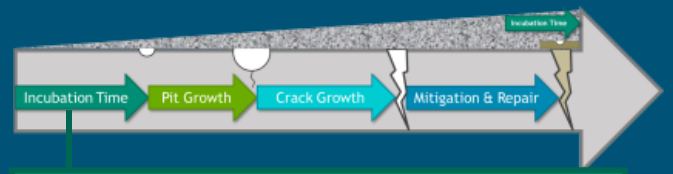
Dust may act to spread water layer and/or as cervices former

Chemistry



304L plate with mixed droplets of $MgCl_2$ + $Mg(NO_3)_2$.[3]

Certain chemistries may mitigate corrosion



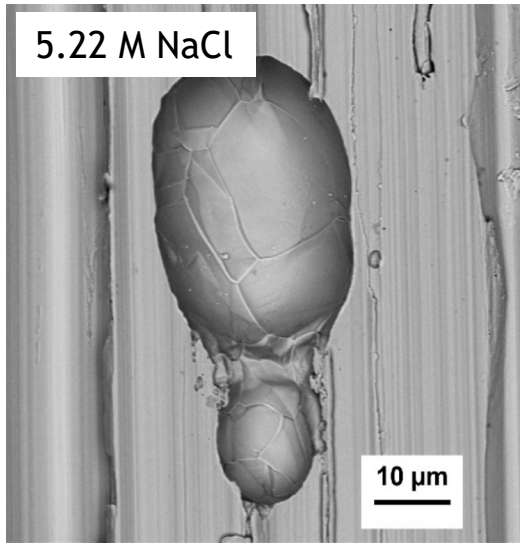
- Salt Composition Assumption
- Canister Thermal Model
- Weather Model
- Airflow and Salt Deposition Model

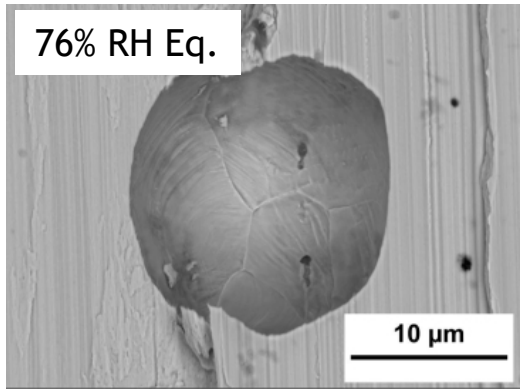
Need a better understanding of the local environment and significant influences on corrosion:

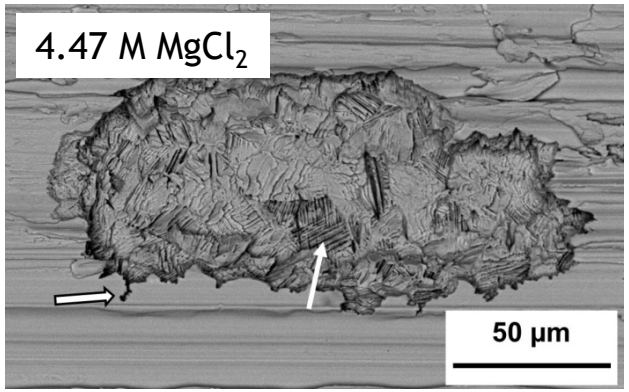
1) **Develop relevant atmospheric testing**
2) **Examine relevant materials/conditions**

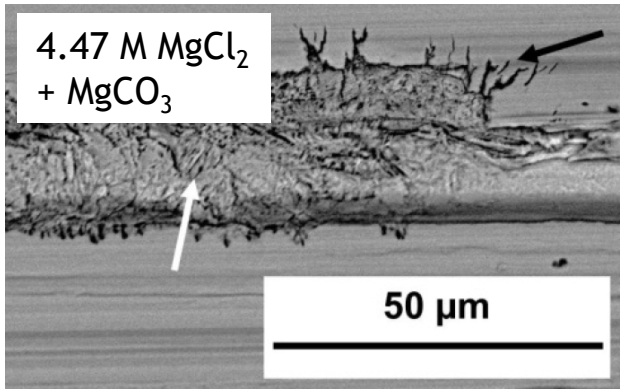
[1] Nishikata, A., Yamashita, Y., Katayama, H., Tsuru, T., Tanabe, K., & Mabuchi, H. (1995). *Corrosion science*, *37*(12), 2059-2069.
[2] Guo, L., Mi, N., Mohammed-Ali, H., Ghahari, M., Du Plessis, A., Cook, A., ... & Davenport, A. J. (2019).
[3] Cook, A. J., Padovani, C., & Davenport, A. J. (2017). *Journal of The Electrochemical Society*, *164*(4), C148.

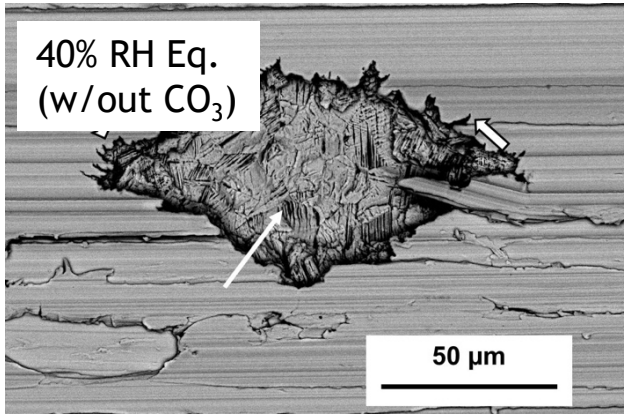
Is there a controlling species in the brine?

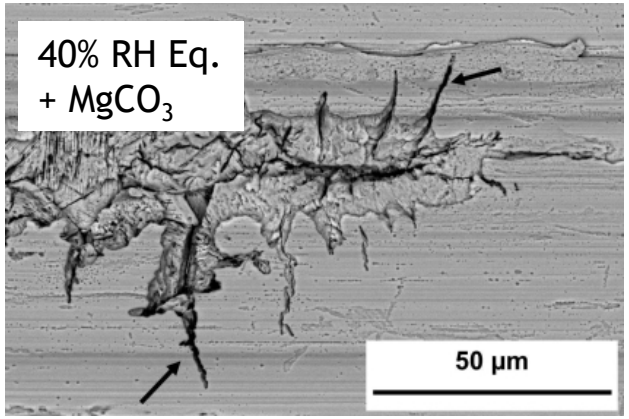






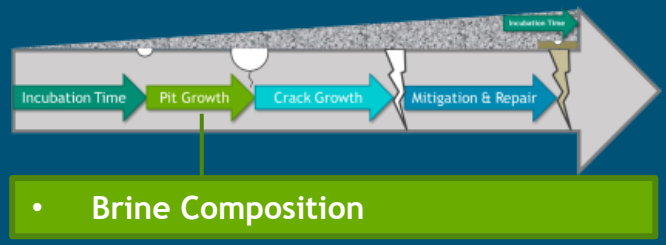






Are microcracks enhanced due to formation of $MgCO_3$?

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).

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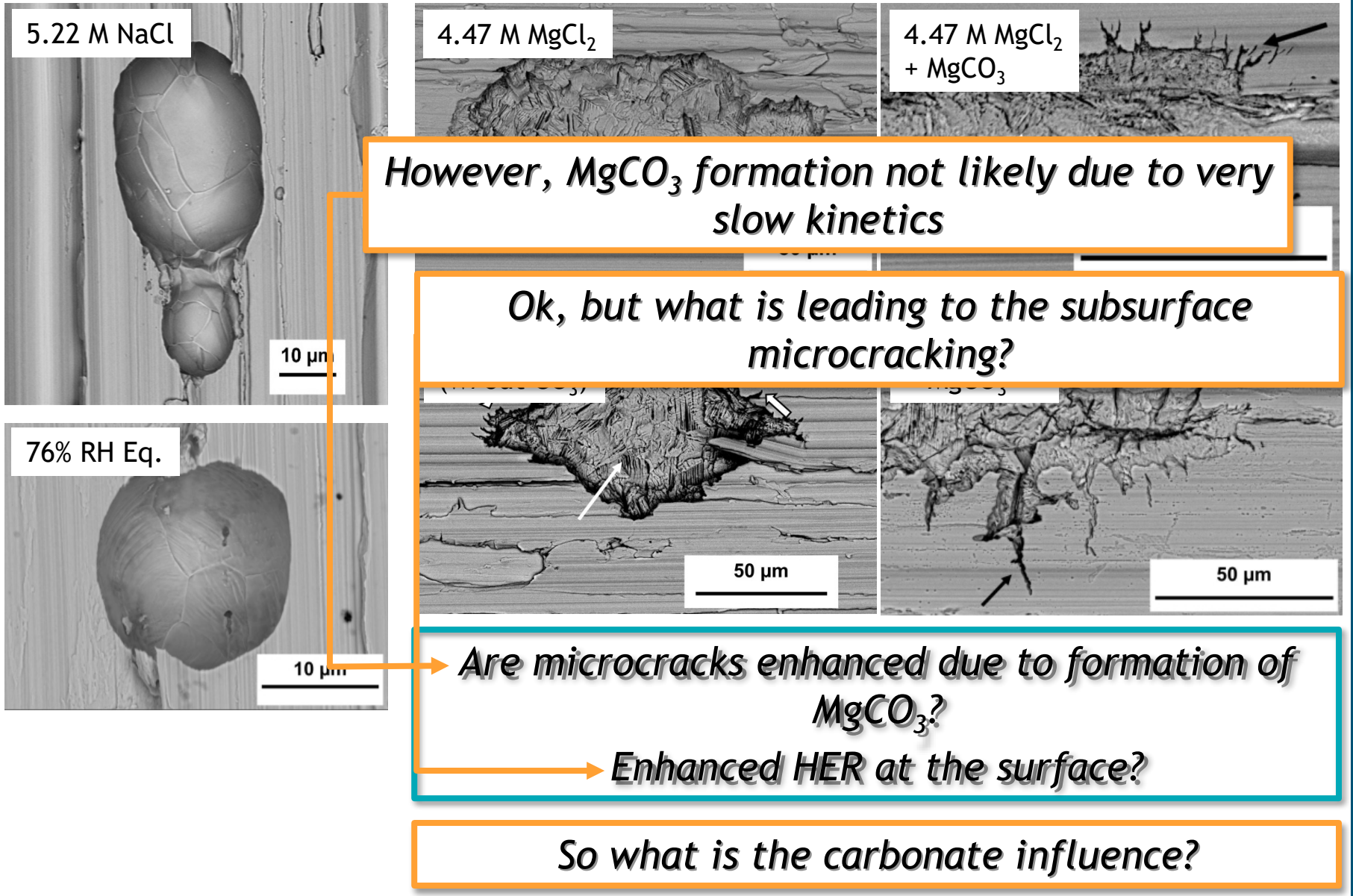


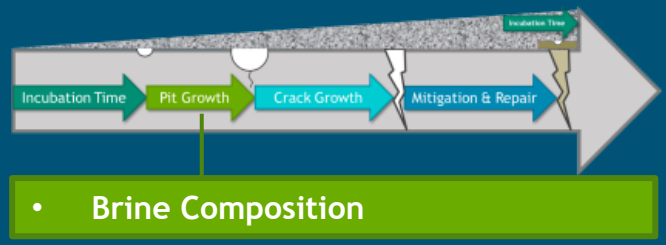
However, $MgCO_3$ formation not likely due to very slow kinetics

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?



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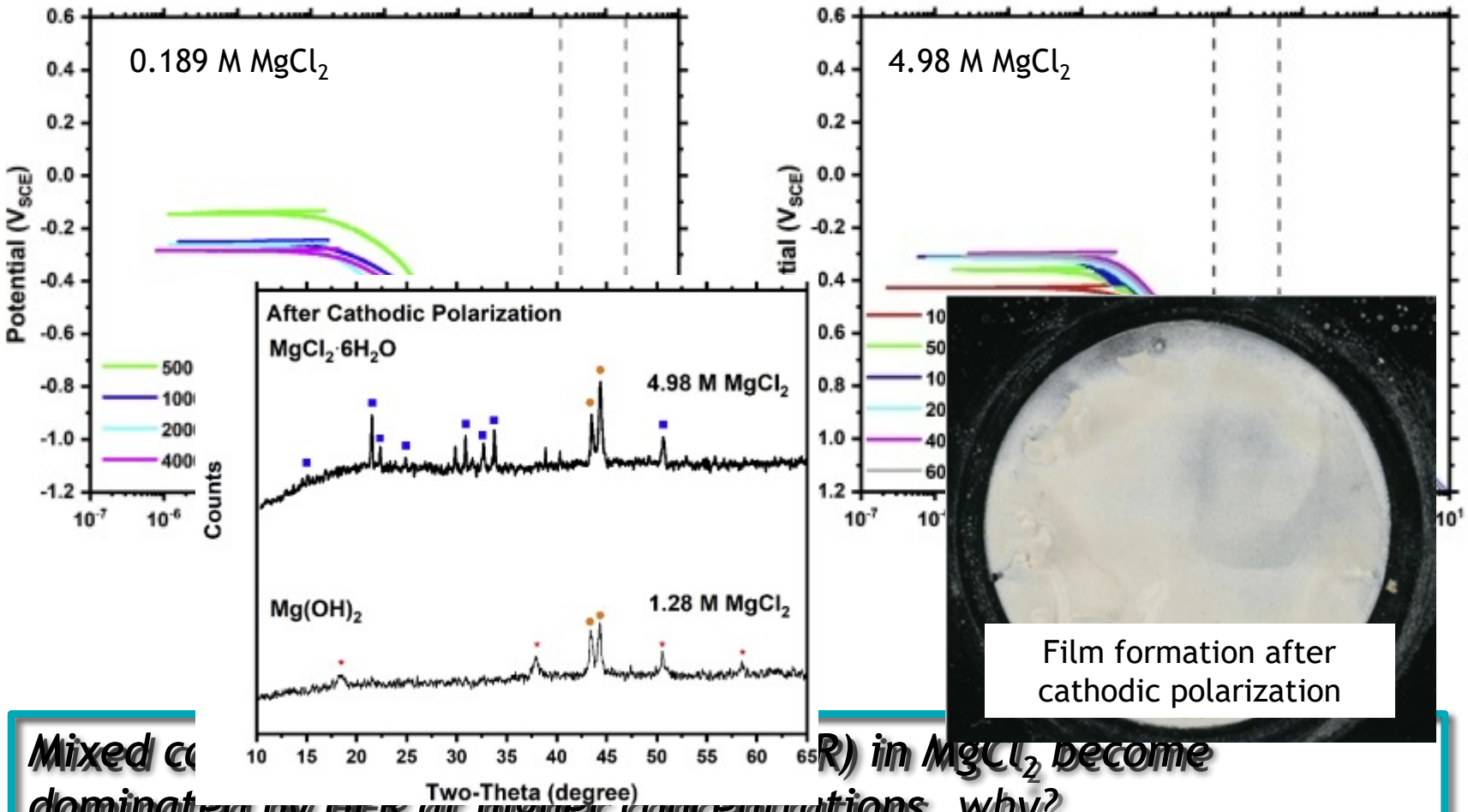
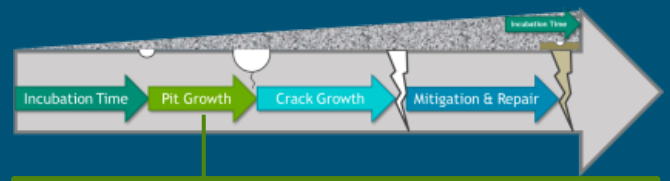
Salt composition & deposition influences



Film formation after cathodic polarization

Mixed co R) in $MgCl_2$ become dominated by HER at higher concentrations...why?

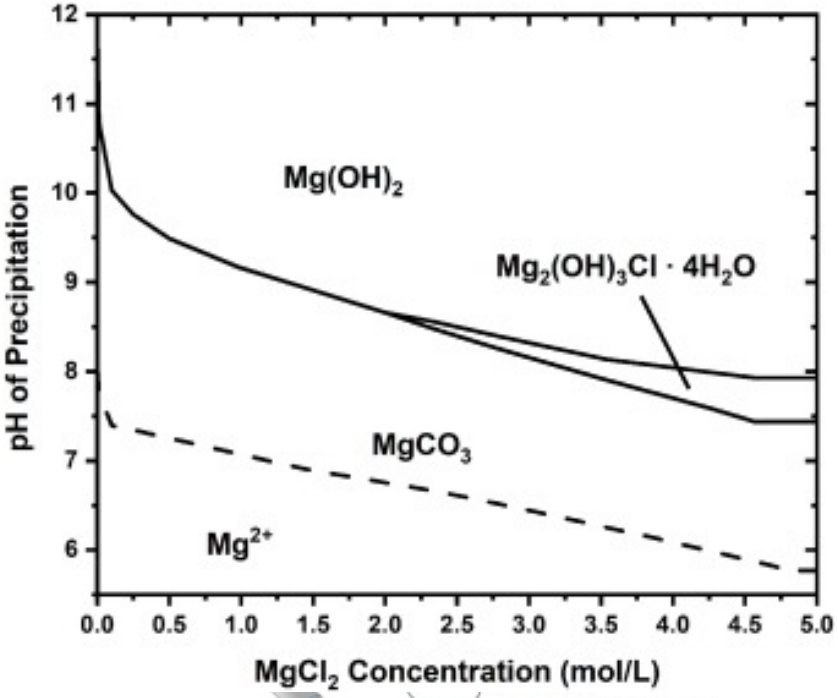


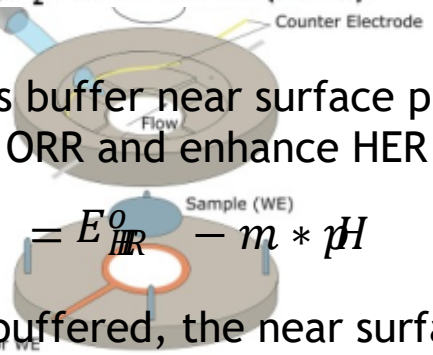
- **Corrosion (Maximum Pit Size) Model**

- *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

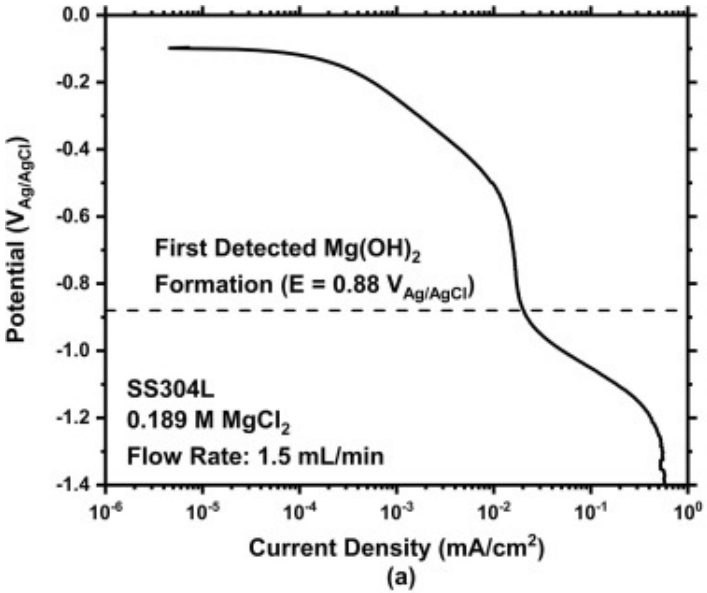


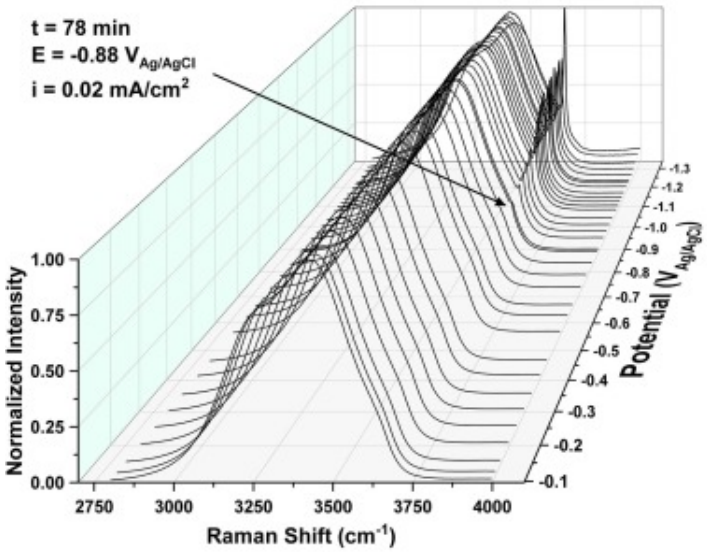


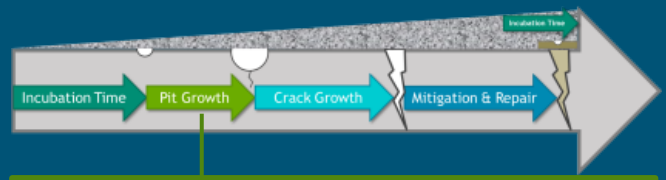
Precipitates buffer near surface pH, suppress ORR and enhance HER

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

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







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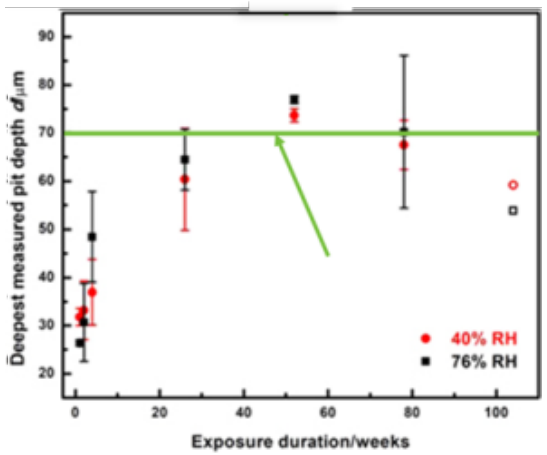
Why care about brine influences?

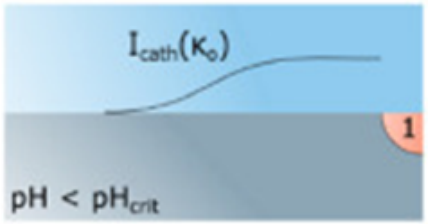
Maximum pit depths:
Measured from static atmospheric laboratory exposures

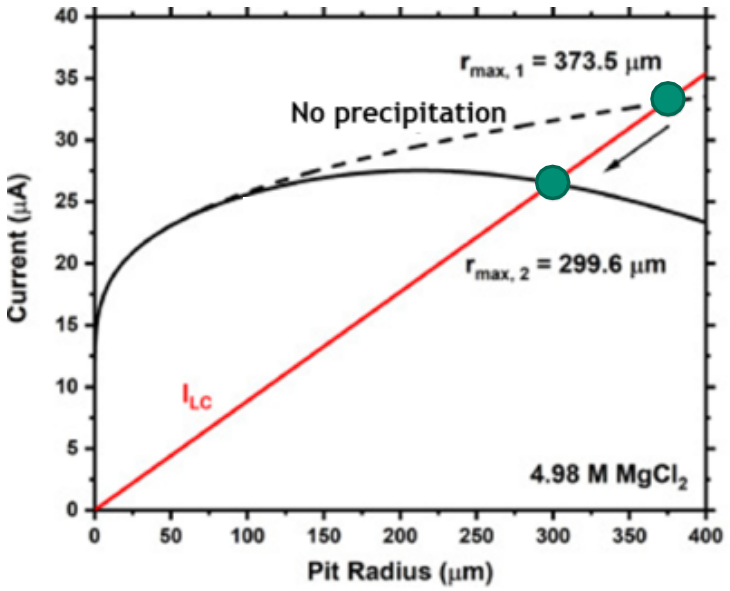
Maximum pit sizes: with precipitation are ***directly inline for 40% RH***

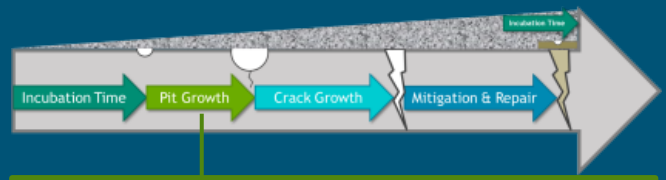
Maximum pit sizes: 1.5 X higher from conservative predictions



Precipitation influences cathodic limitation







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

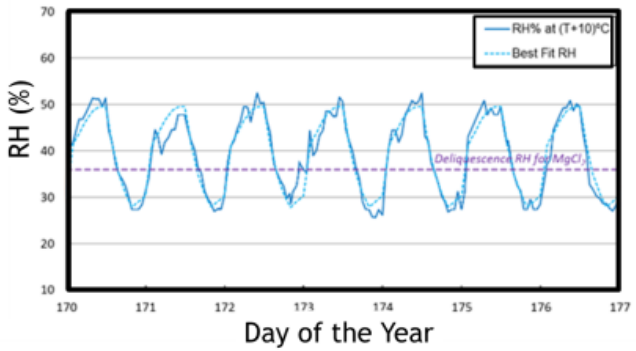
- *Dilute Chloride Solutions*
  - ORR dominant cathodic reaction
  - Diffusion limited at negative potentials
  - Cathodic rates predicted through Levich analysis
- Cathodic kinetics in concentrated brines

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.

Development of Relevant Lab Exposures

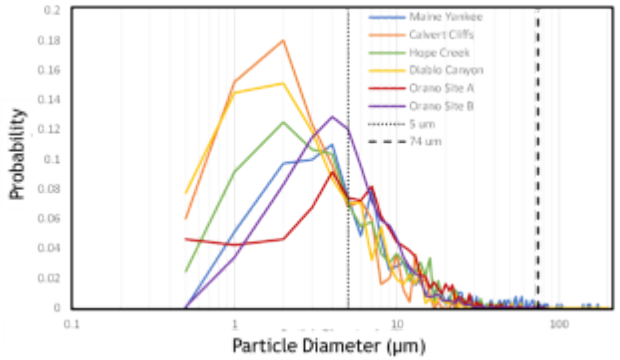
Diurnal Cycles

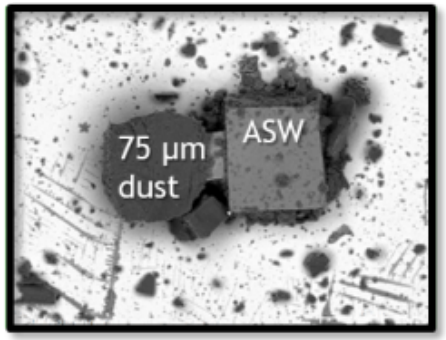


Cycle Conditions:

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

Dust/Precipitates

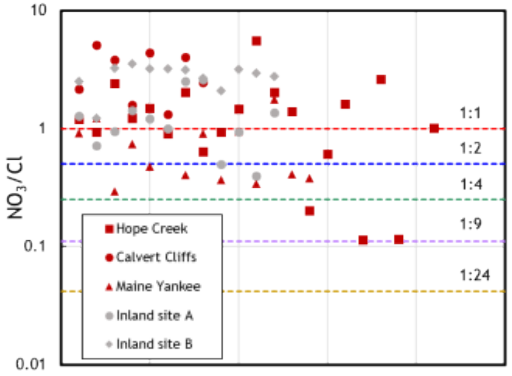




Dust Conditions:

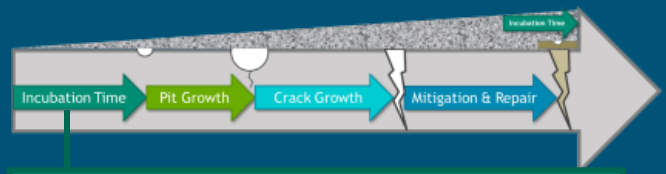
- Dust size based on ISFSI site collection
- Co-deposition of SIL-CO -SIL® 75 and MIN-U-SIL® 10 with ASW

Chemistry



Electrochemical:

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



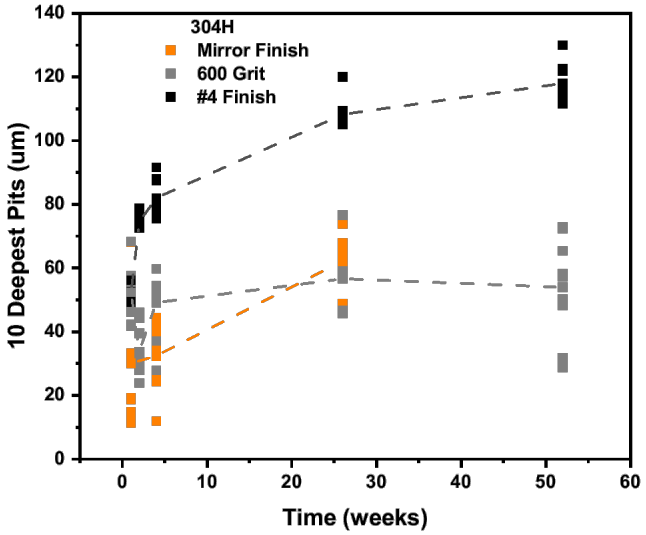
- Salt Composition Assumption
- Canister Thermal Model
- Weather Model
- Airflow and Salt Deposition Model

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

Environment: Relevant Lab Exposures

Diurnal Cycles

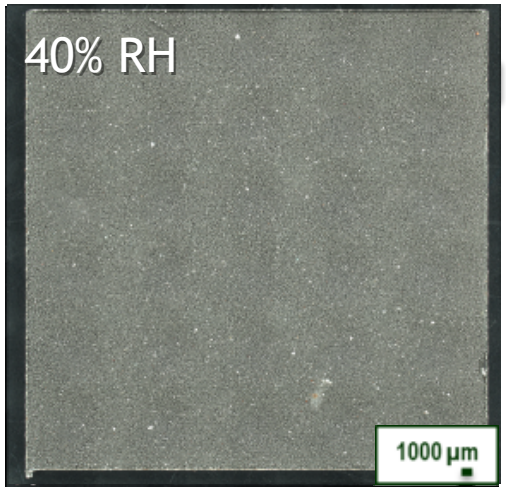
Comparison across material finish for 304H coupons

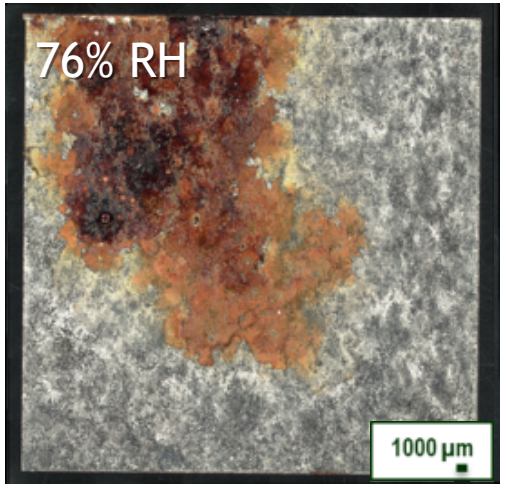


Profilometry: assumes hemispherical pits

Dust/Precipitates

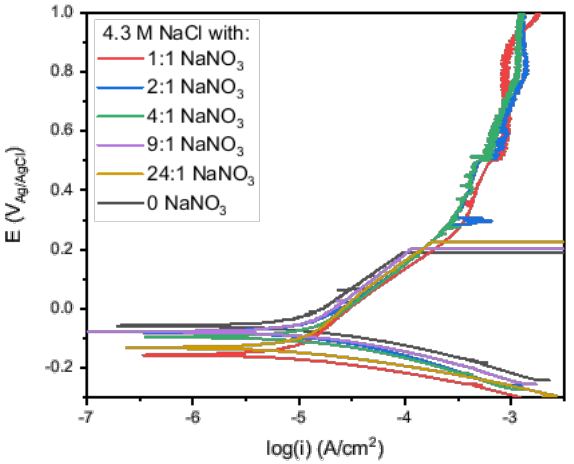
6 month static exposure

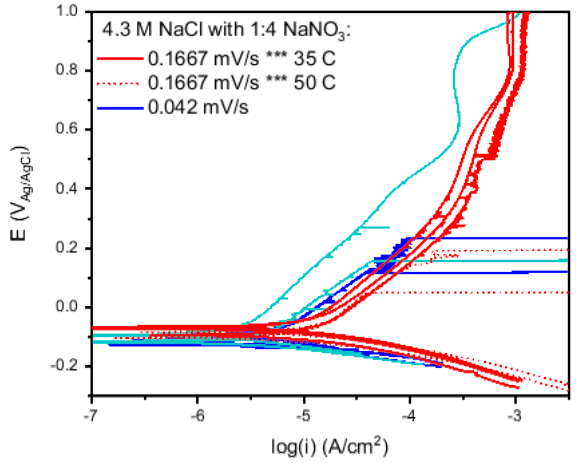




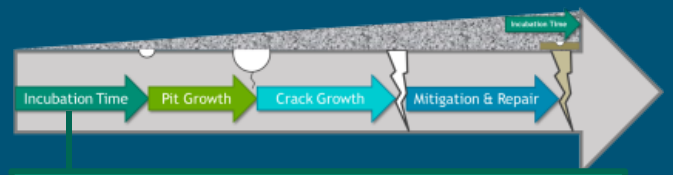
Chemistry

Nitrate:Chloride influence





Time (scan rate) dependent



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

- Building large datasets of pitting statistics to validate maximum pit size model for SNF relevant conditions
- ***Need to understand model assumptions when applying this data!***