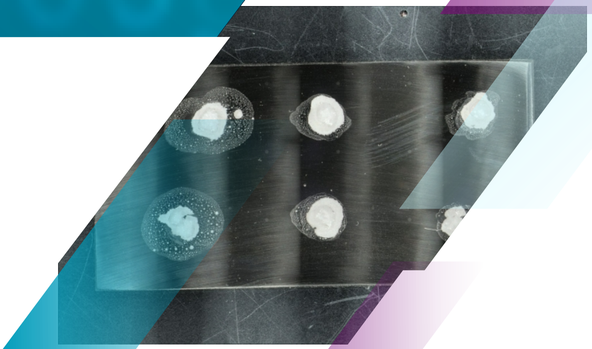
SAND2022-14136C

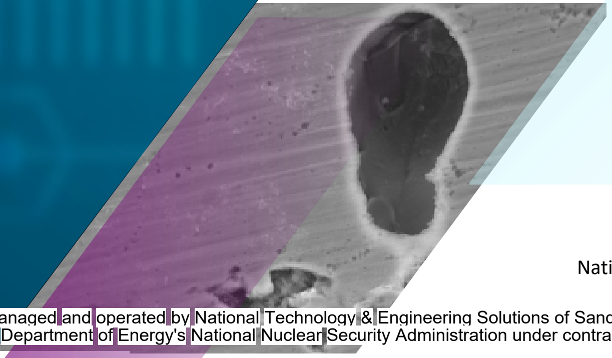
Sandia National Laboratories

Evaluating Localized Corrosion Susceptibility of Austenitic Stainless Steels Exposed to Varying Nitrate to Chloride Ratio Droplets



The Electrochemical Society Meeting, Atlanta, Georgia

October 10th-14th, 2022 | Ryan Katona



T. J. Montoya[2], J. Snow[1], M. Maguire[1], C. R. Bryan[1], and R. F. Schaller[1]

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

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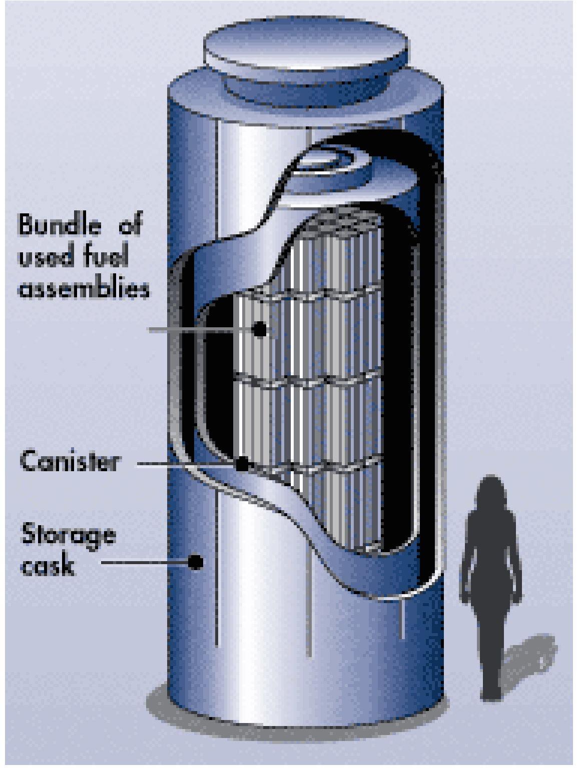
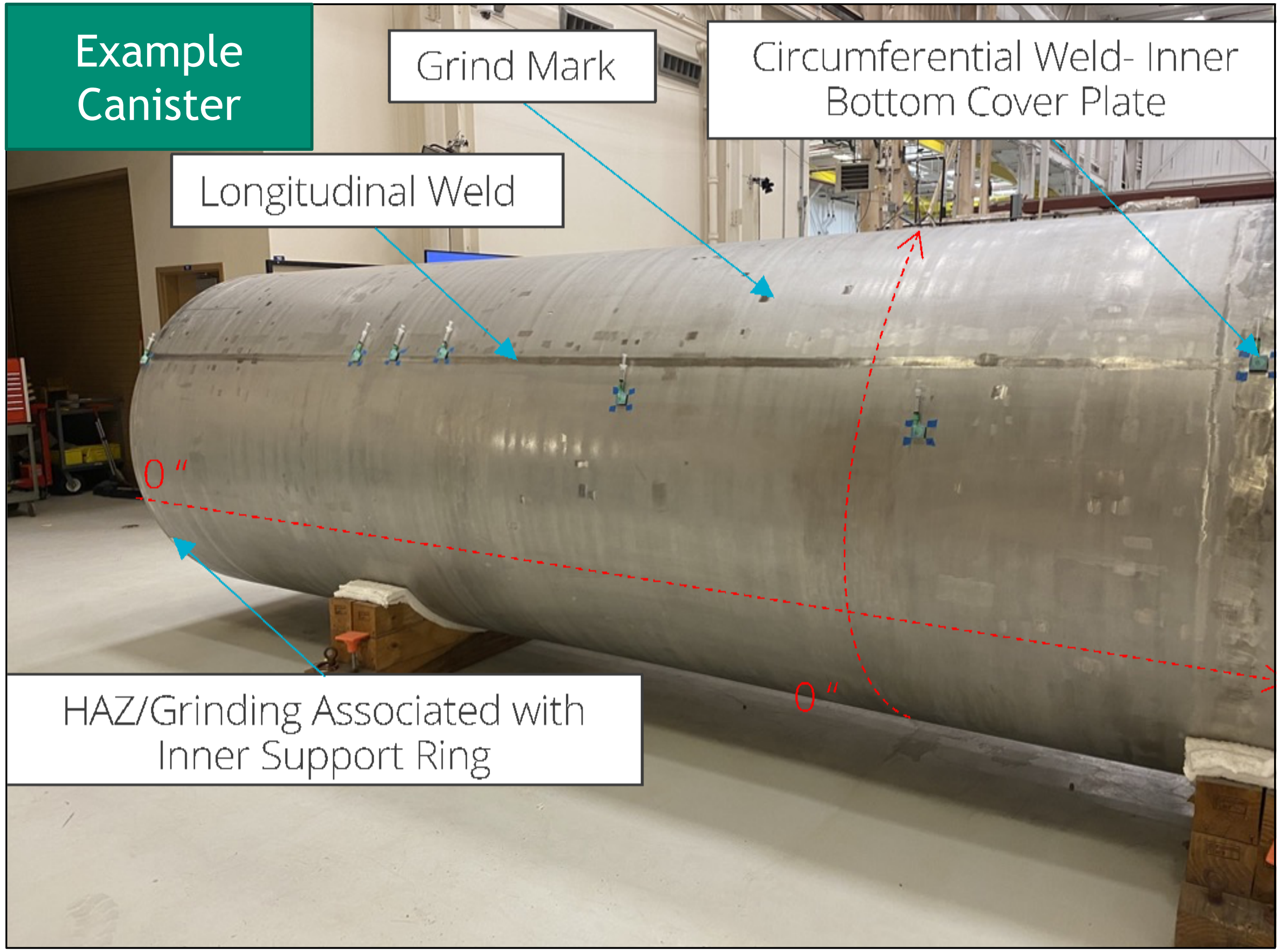
Background – SNF and SCC

- SNF is stored in
  - Welded austenitic stainless steel canisters





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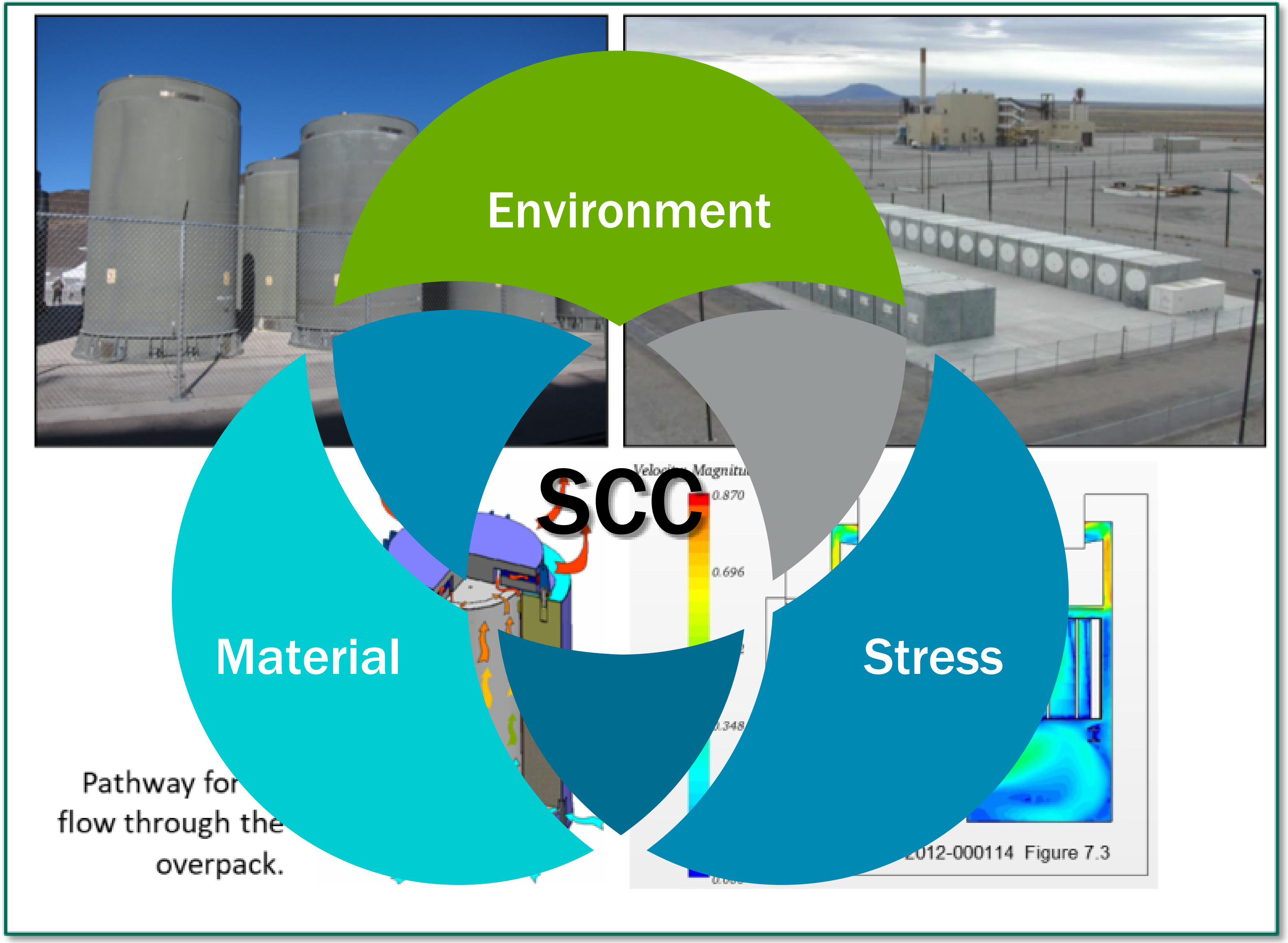
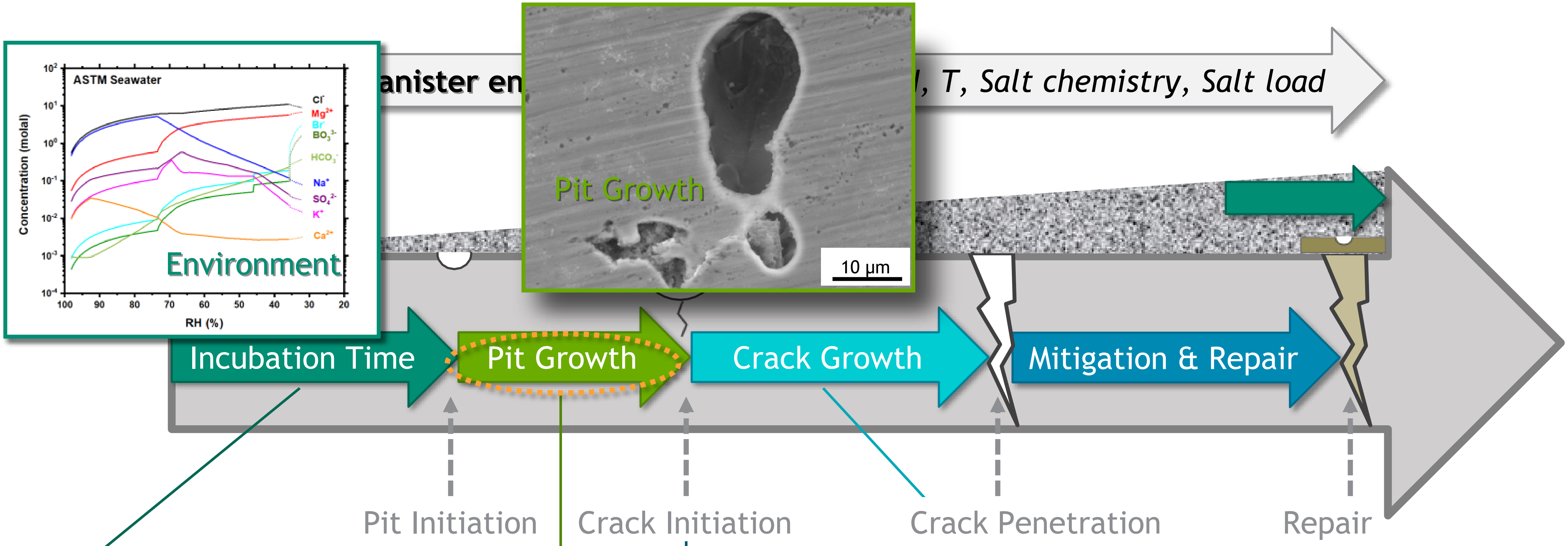
- SNF is stored in
  - Welded austenitic stainless steel canisters
  - Passively-ventilated overpacks
  - Accumulate surface dust over time
  - Deliquescence of chloride-rich salts

Conditions for Stress Corrosion Cracking (SCC) may exist



Background – Overall Goals



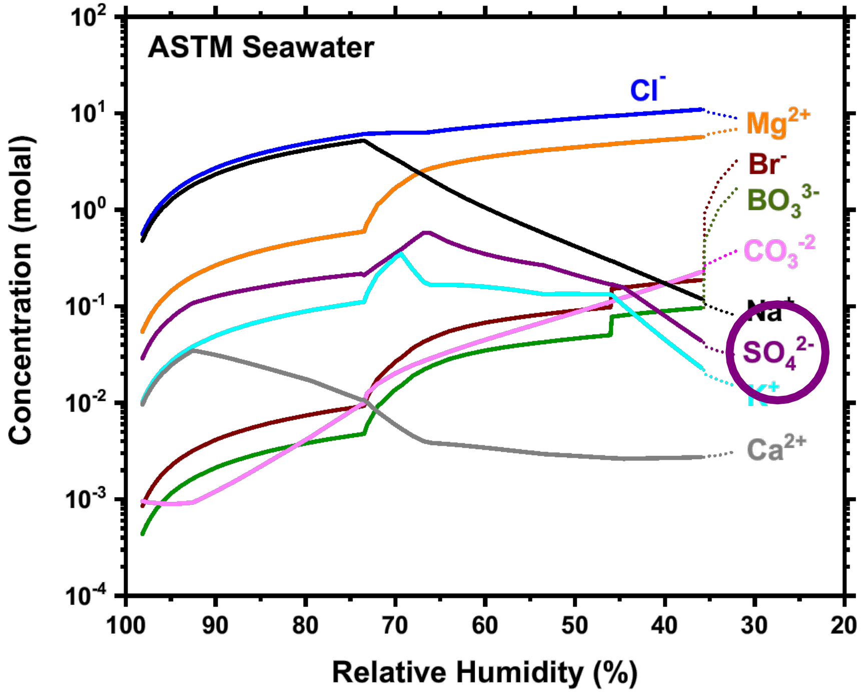
- Salt Composition Assumption
- Canister Thermal Model
- Weather Model
- Airflow and Salt Deposition Model

- Pit-to-Crack Transition Model

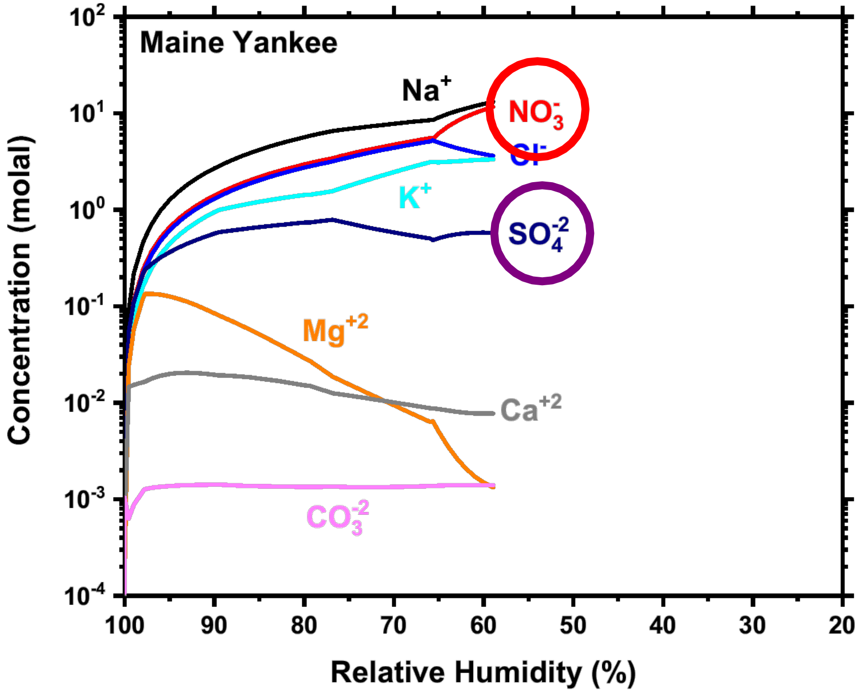
- Canister Thermal Model
- Weld Residual Stress Model
- Crack Growth Model

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

Observed Salt Chemistry on Canister Surfaces

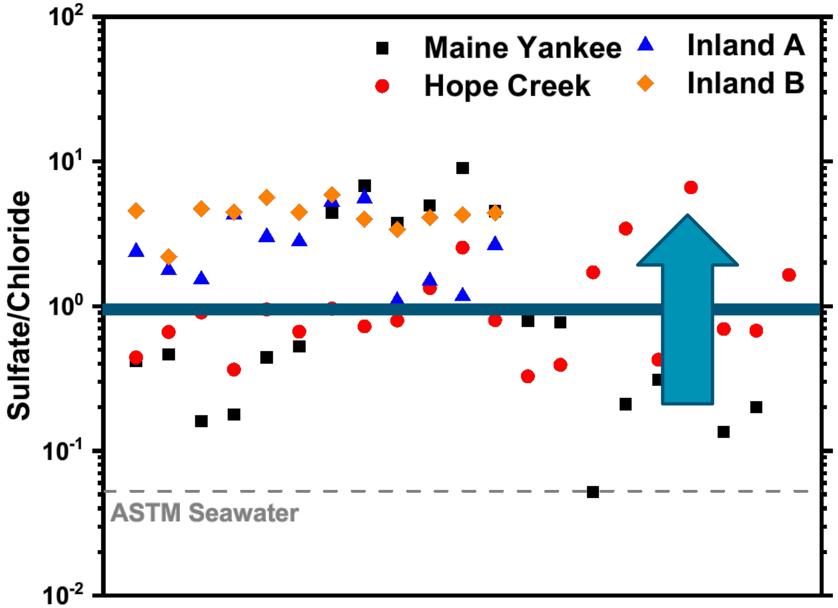


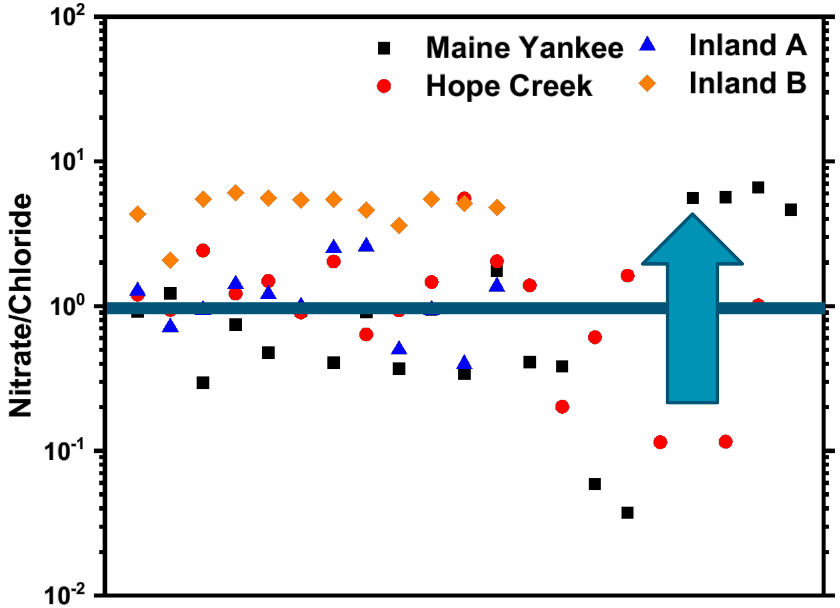
C.R. Bryan, A.W. Knight, R.M. Katona, A. Sanchez, E.J. Schindelholz, R.F. Schaller, Science of the total environment. 824 (2022) 19.



- ASTM Seawater originally assumed to be representative of canister salts
- Field sampling of near-marine canisters indicates bulk salt composition differs from sea-salts
  - Higher DRH (lower Mg)
  - Differences in passivating species

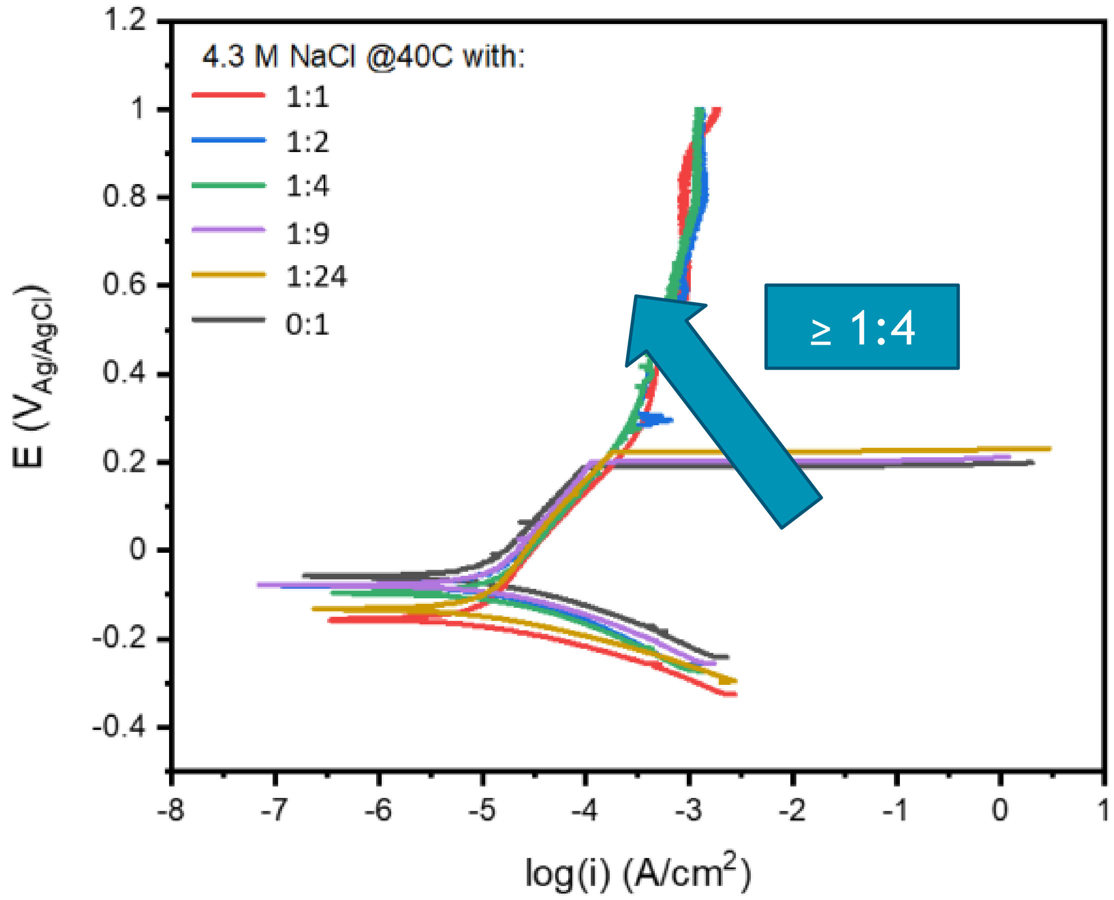
Presence of Passivating Species on Canister Surfaces

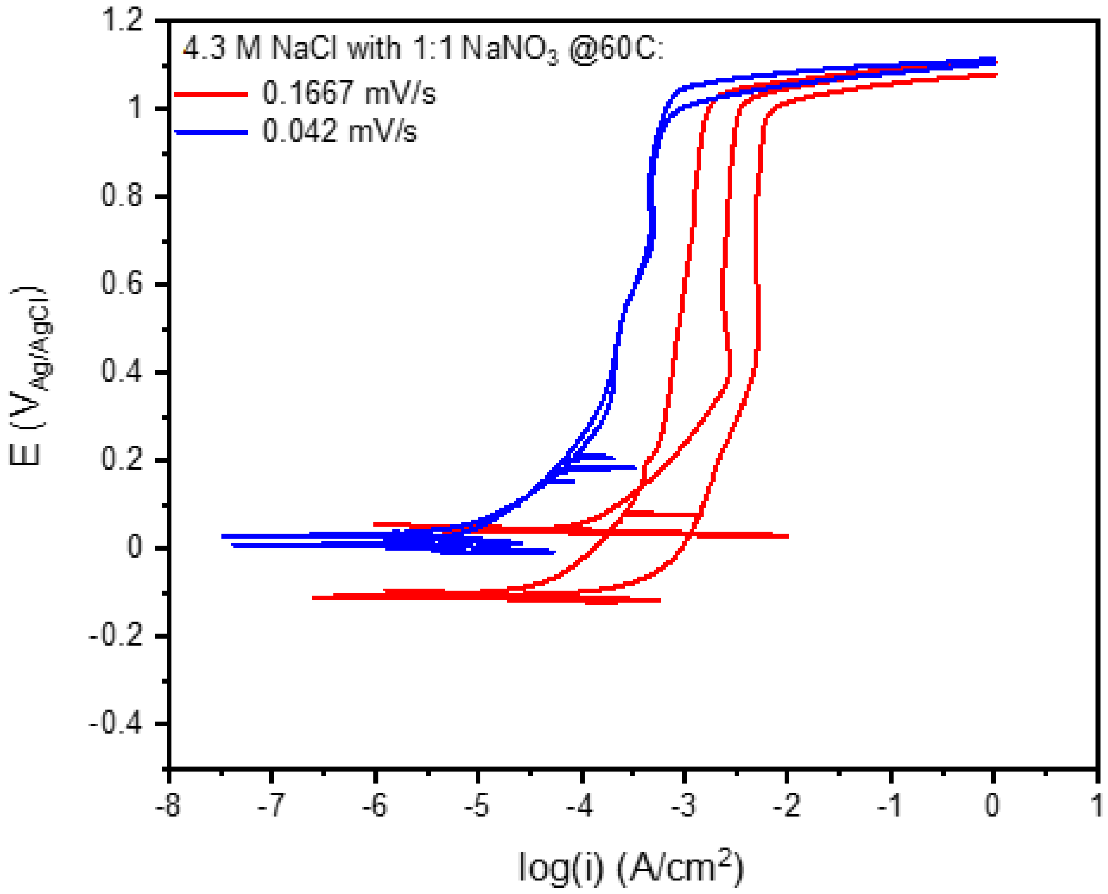




- Significant concentrations of sulfate on canister surface (ratio above one)
- Observed nitrate : chloride ratio above one for most samples
  - No nitrate in ASTM Seawater

Static Polarization Scans Show Passivating Behavior

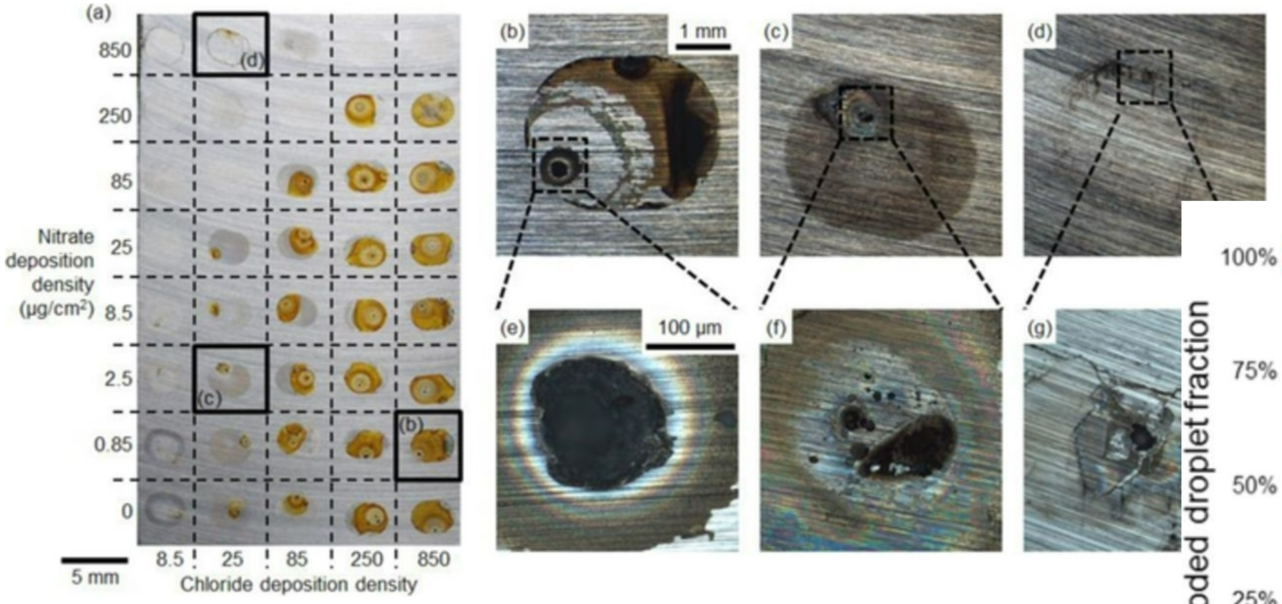




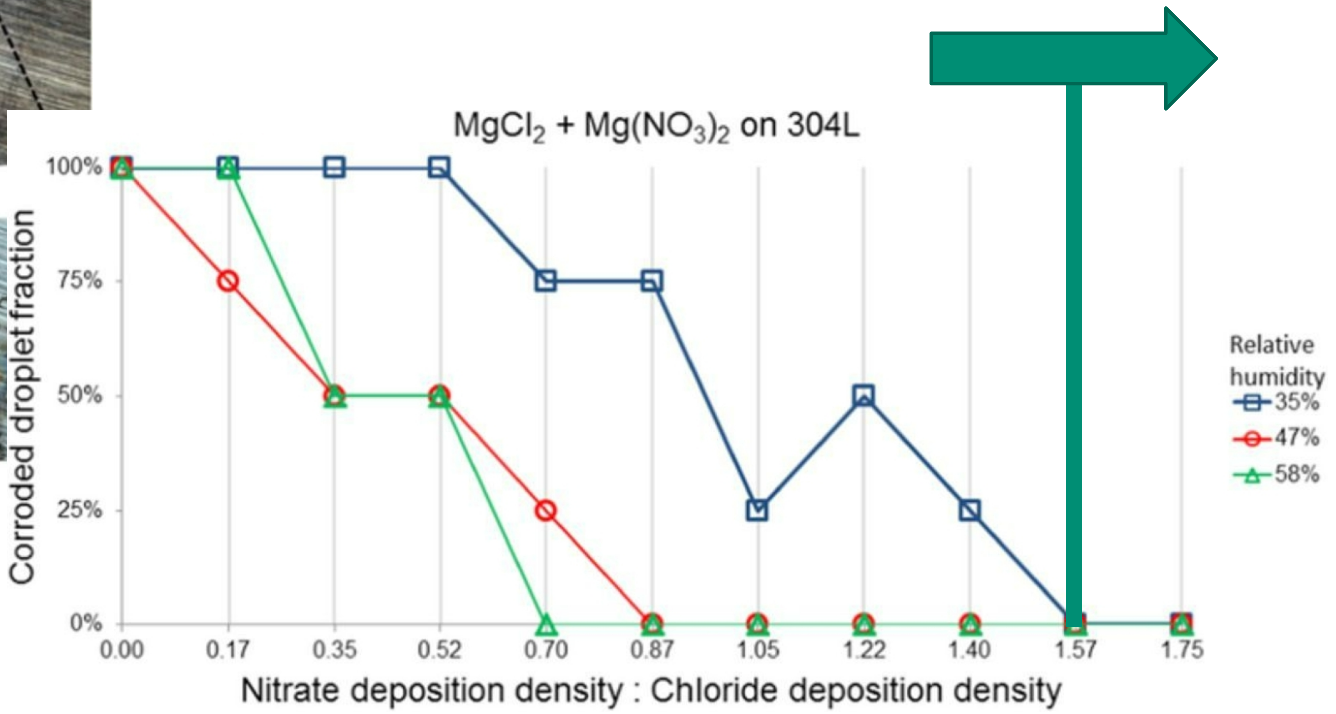
- Polarization scans are indicative of passivating behavior at higher ratios of nitrate : chloride at 40 ˚C
- Slower scan rates indicate that this may be a time dependent process
- 1:1 nitrate : chloride passive even at higher temperatures (60 ˚C) and slower scan rates

Inhibiting Nature of Nitrates Exhibited in $MgCl_2$ Droplets

No corrosion above 1.57:1 Nitrate : Chloride

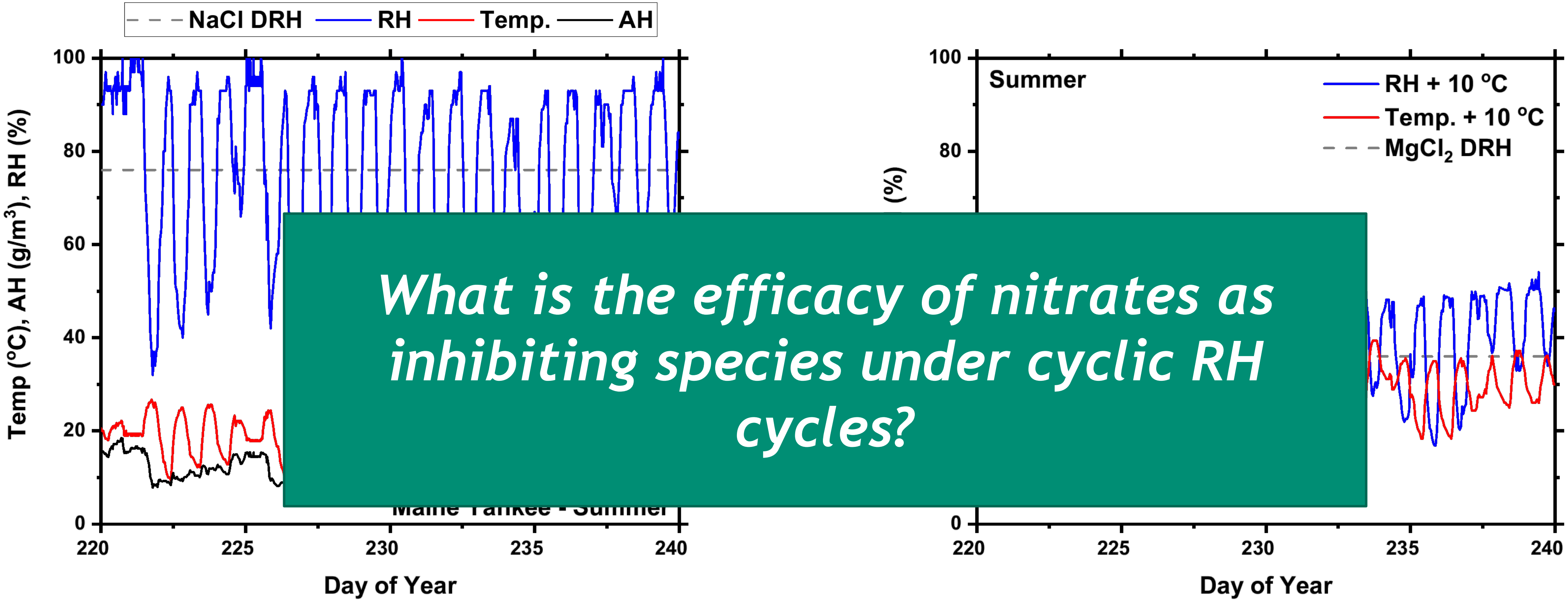


A.J.M.C. Cook, C. Padovani, A.J. Davenport, Effect of Nitrate and Sulfate on Atmospheric Corrosion of 304L and 316L Stainless Steels, Journal of The Electrochemical Society, 164 (2017) C148-C163.



- Varying levels of inhibition exhibited in $MgCl_2$ solutions based on exposure RH and Nitrate:Chloride deposition
- Performed under ***static relative humidity*** conditions

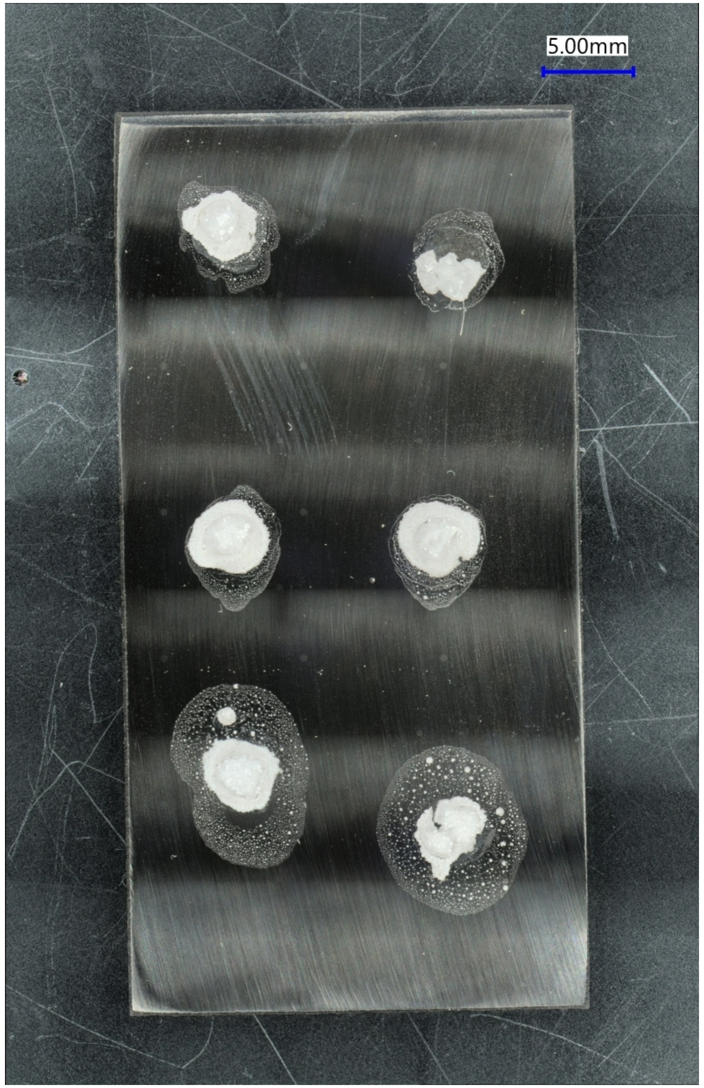
Realistic Relative Humidity and Temperature

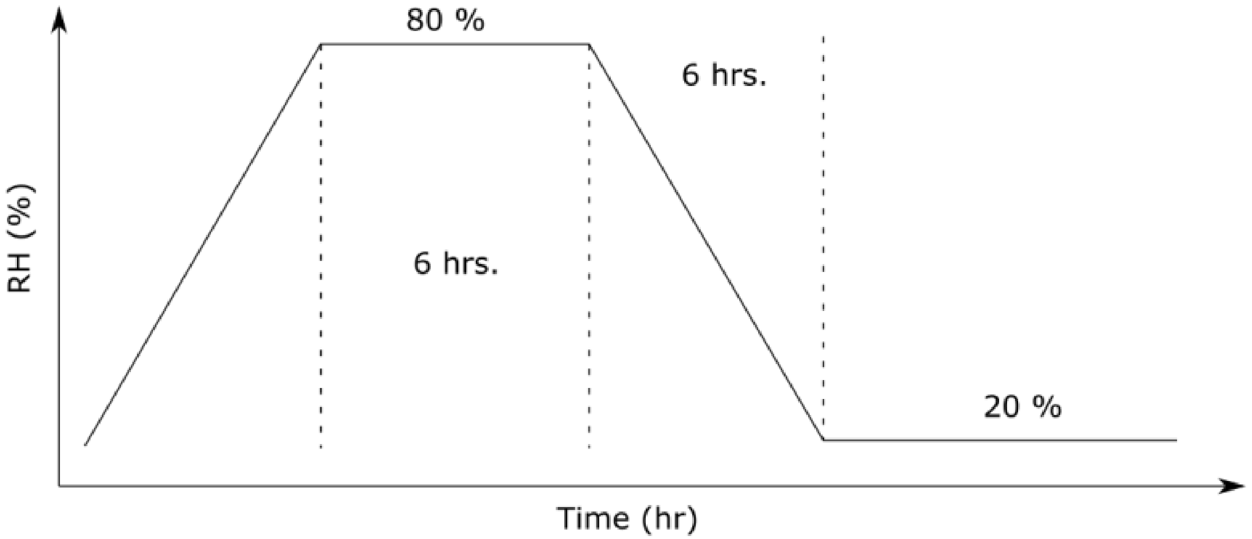


What is the efficacy of nitrates as inhibiting species under cyclic RH cycles?

- Daily and seasonal variations in ambient humidity (AH), RH, and temperature
- Influence of heated canister surface decreases RH fluctuations

Droplet Study

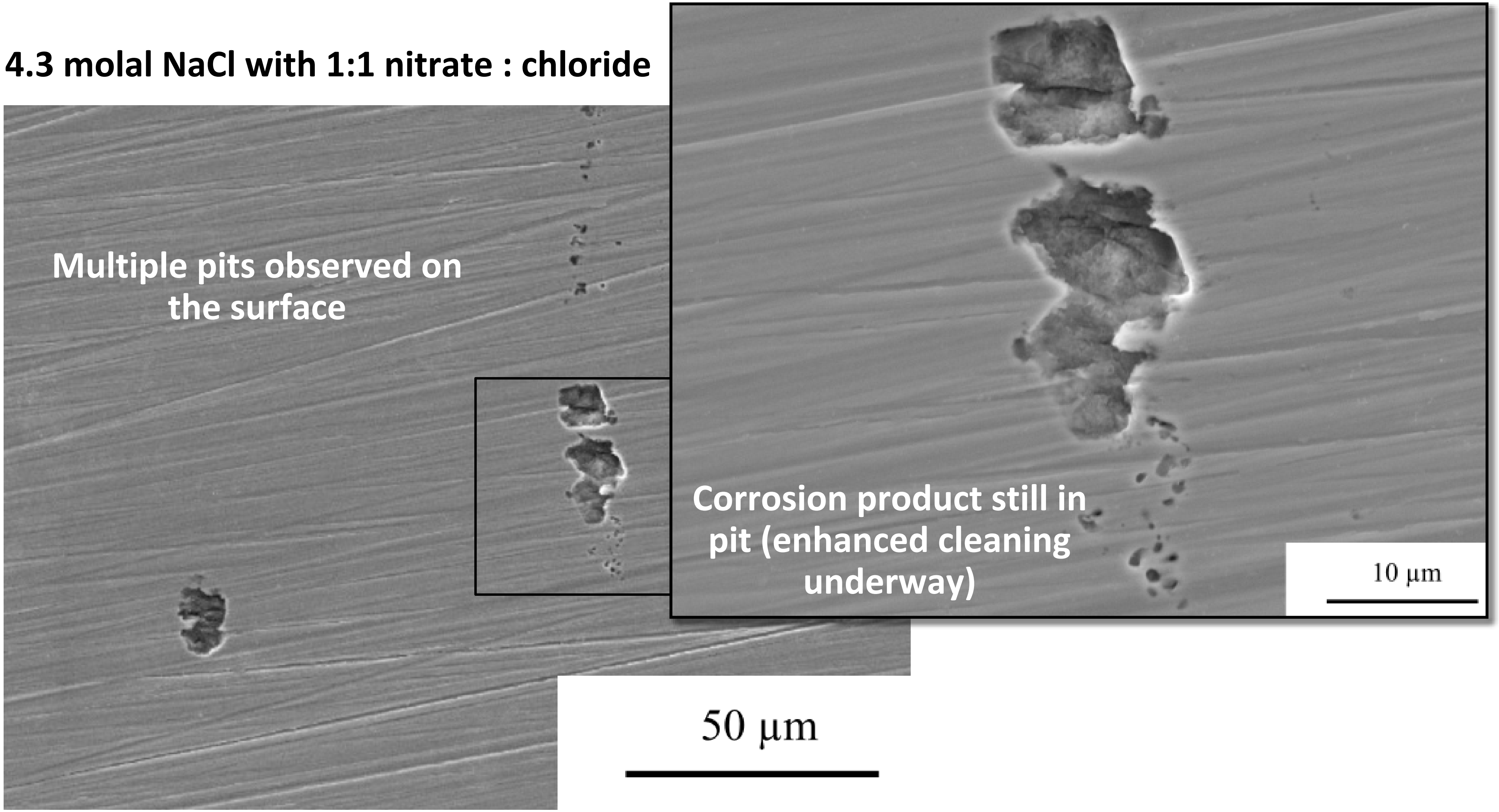




- NaCl/$NaNO_3$ droplets of various sizes deposited in 3 x 2 arrays on SS304 coupon
- Varied the following parameters:
  - Chloride concentration (4.3 to 1.075 molal)
  - Droplet size (4 to 1 μL)
  - Nitrate : chloride ratio
- Simplified RH profile at a constant temperature of 35 ˚C

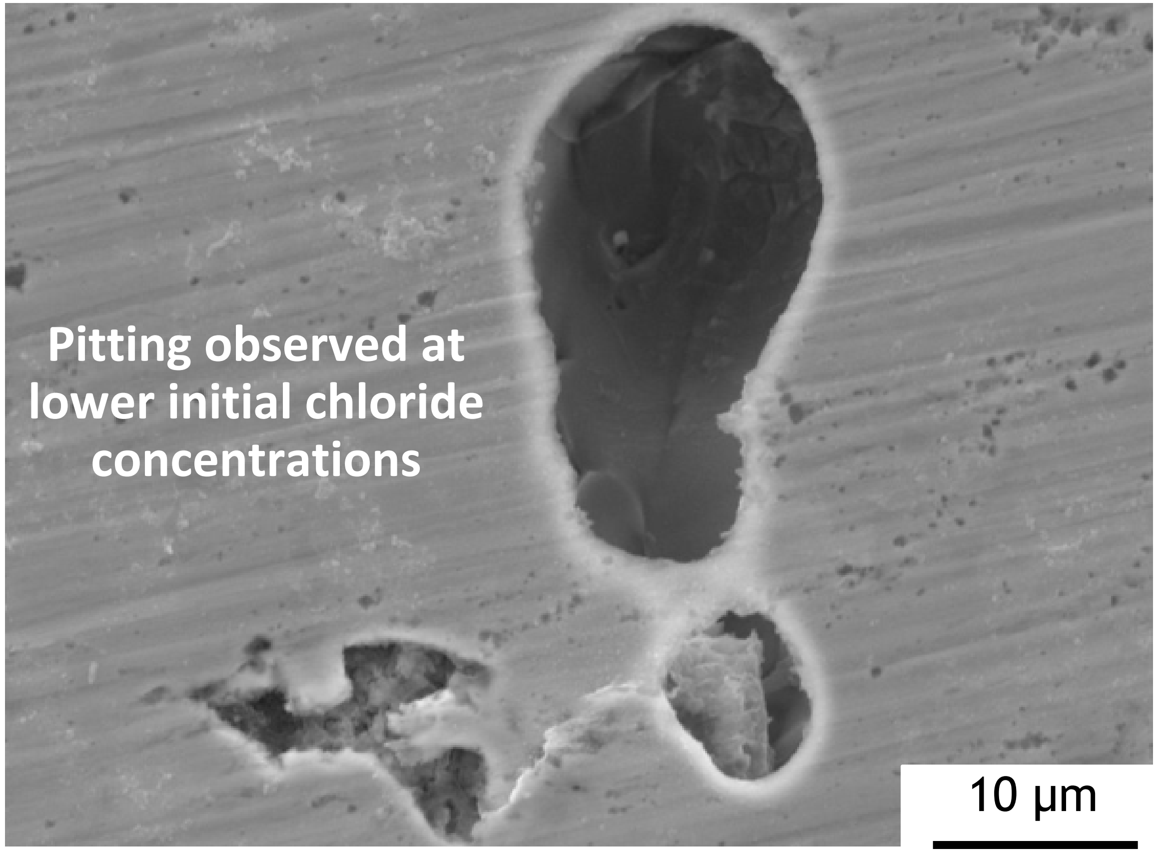
Corrosion observed with high chloride concentrations

4.3 molal NaCl with 1:1 nitrate : chloride



Crystallographic pitting morphologies observed

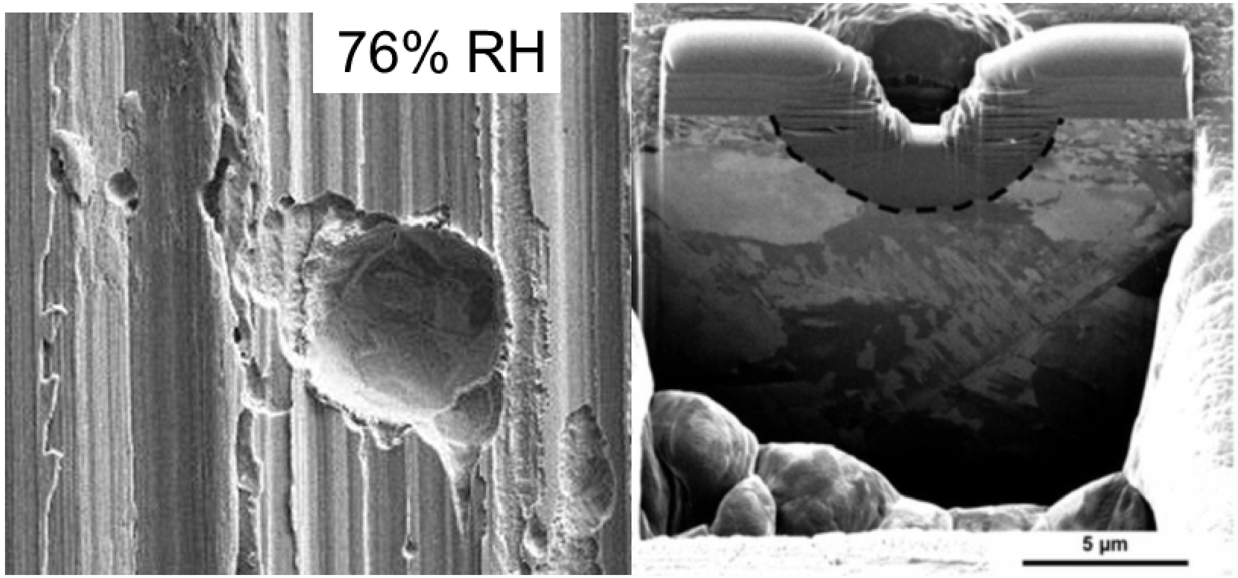
2.15 m NaCl with 1:1 nitrate : chloride



Similar pitting morphologies to previous studies

76 % (35 ˚C): crystallographic pitting significant of pitting under stable salt film

HIGH RH: NaCl RICH BRINE



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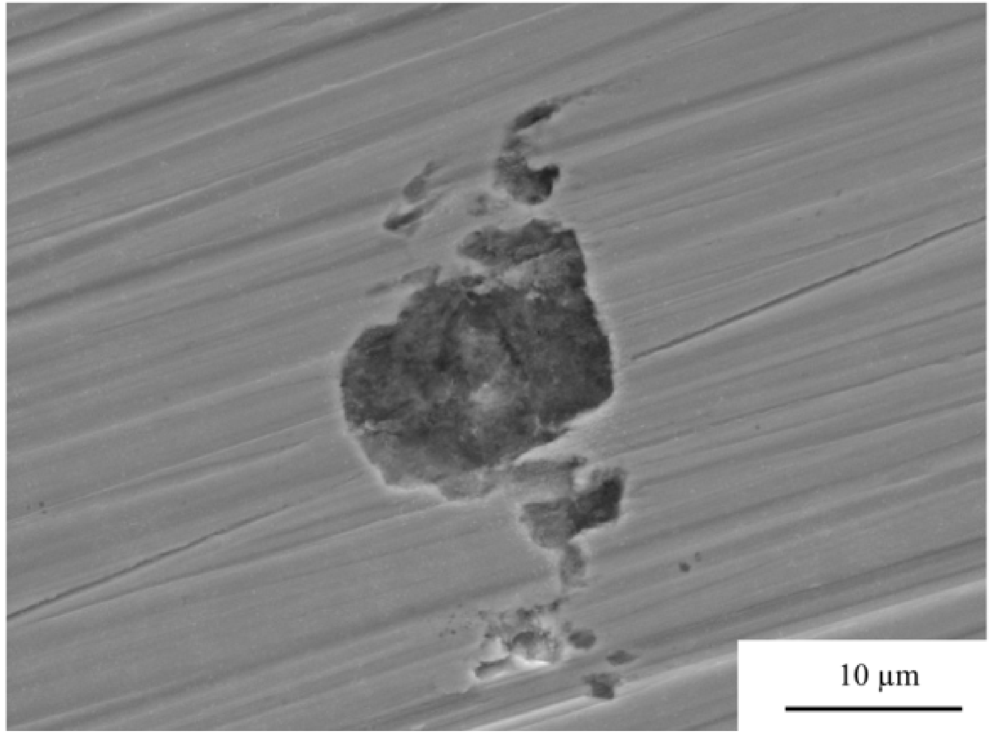
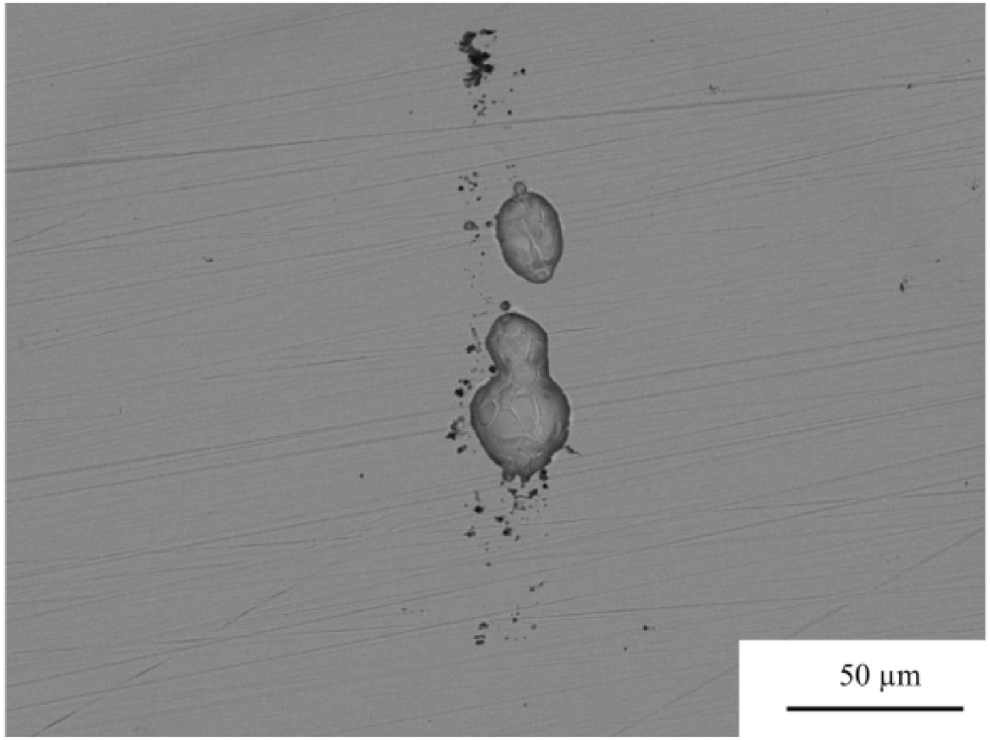
Corrosion observed with low chloride concentrations

1.075 m NaCl with 1:1 nitrate : chloride

4 µL



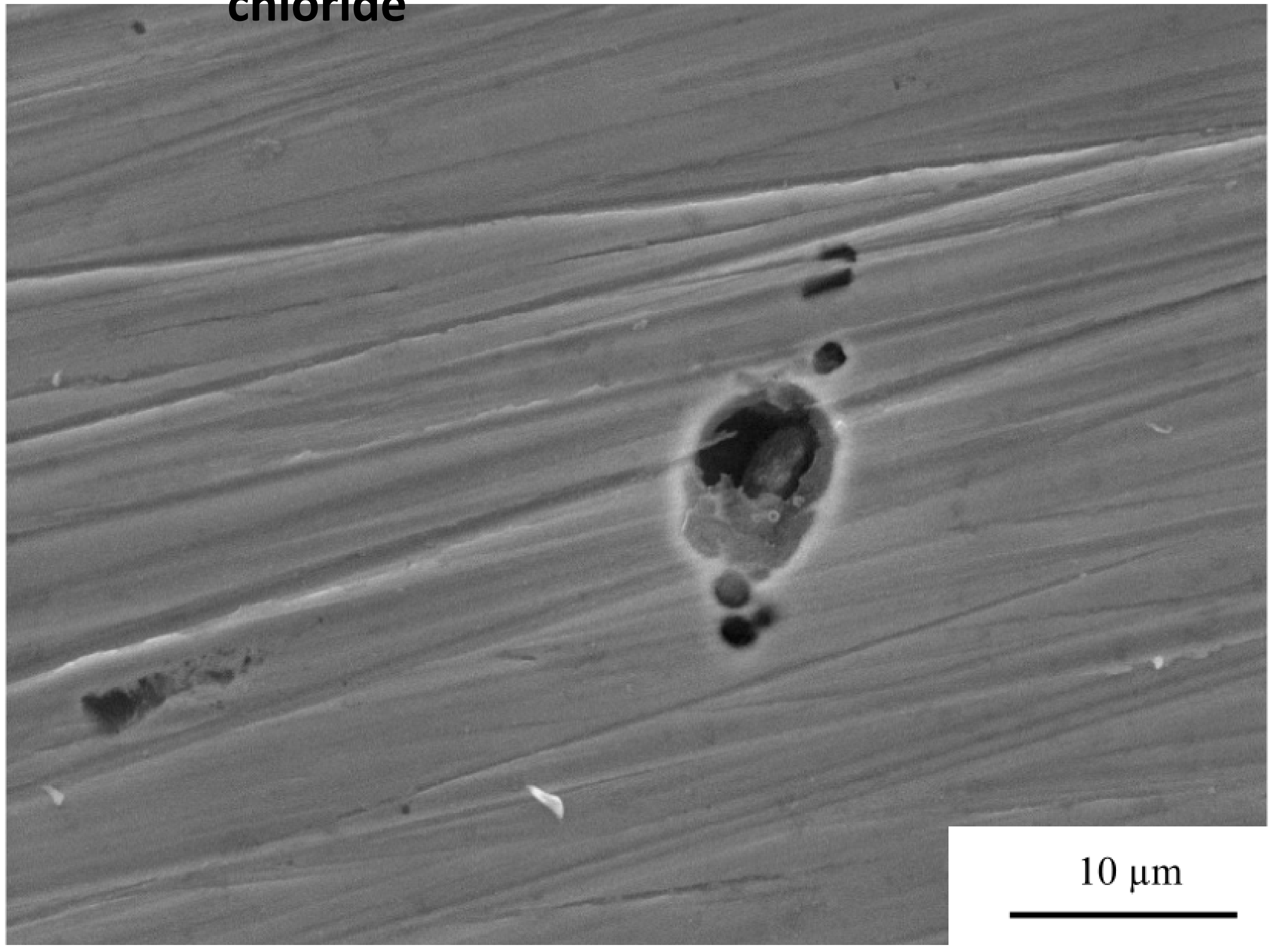
3 µL



- Pitting still observed at low chloride concentrations with 1:1 nitrate : chloride ratios
- Initial droplet size does not significantly influence pitting or morphology for sizes tested

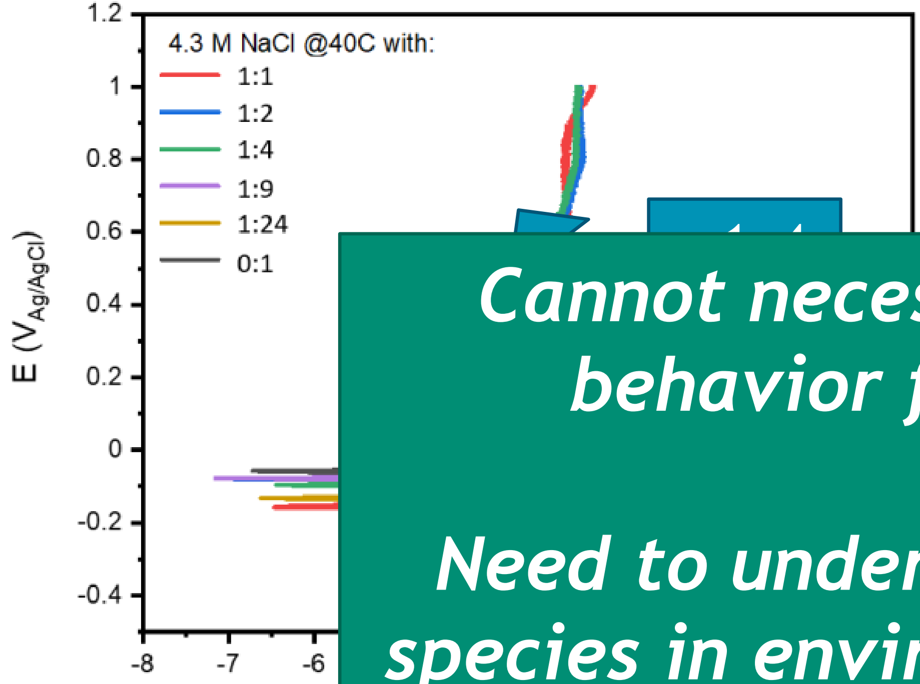
Pitting observed with high nitrate concentrations

1.075 m NaCl with 4:1 nitrate : chloride

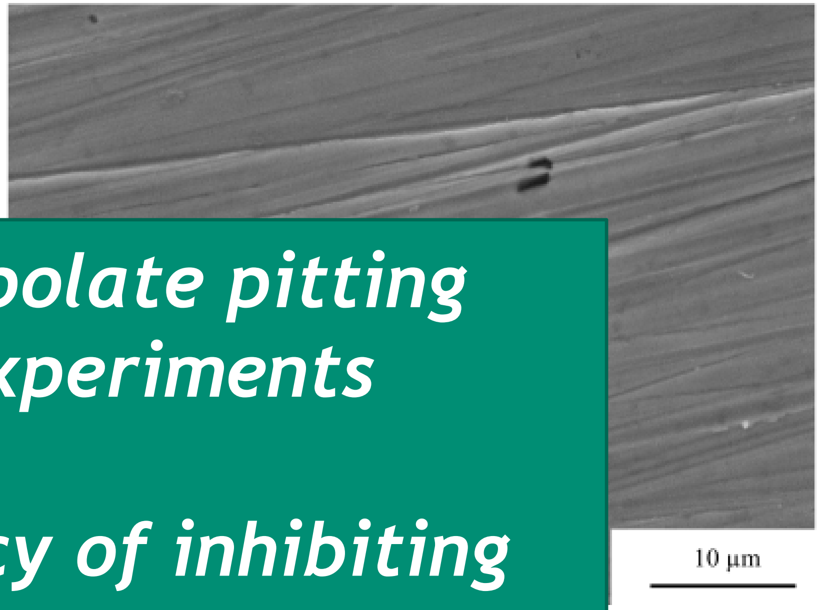


- Pitting still observed even when ***4 times*** the amount of nitrate present than chloride

Polarization scans unrepresentative of dynamic environments

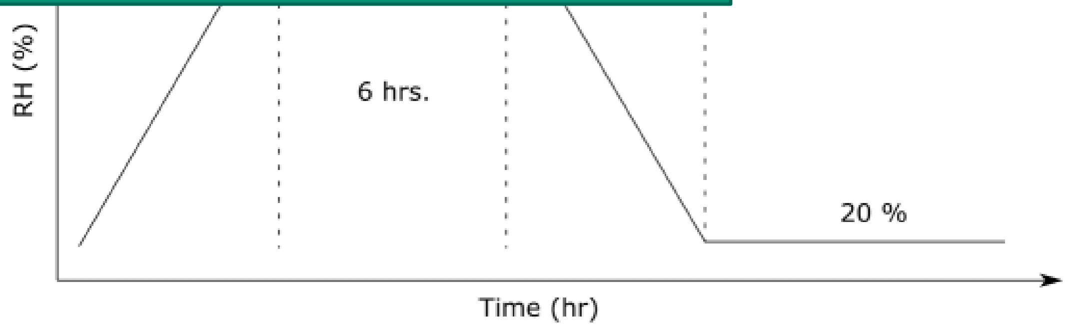


1.075 m NaCl with 4:1 nitrate : chloride



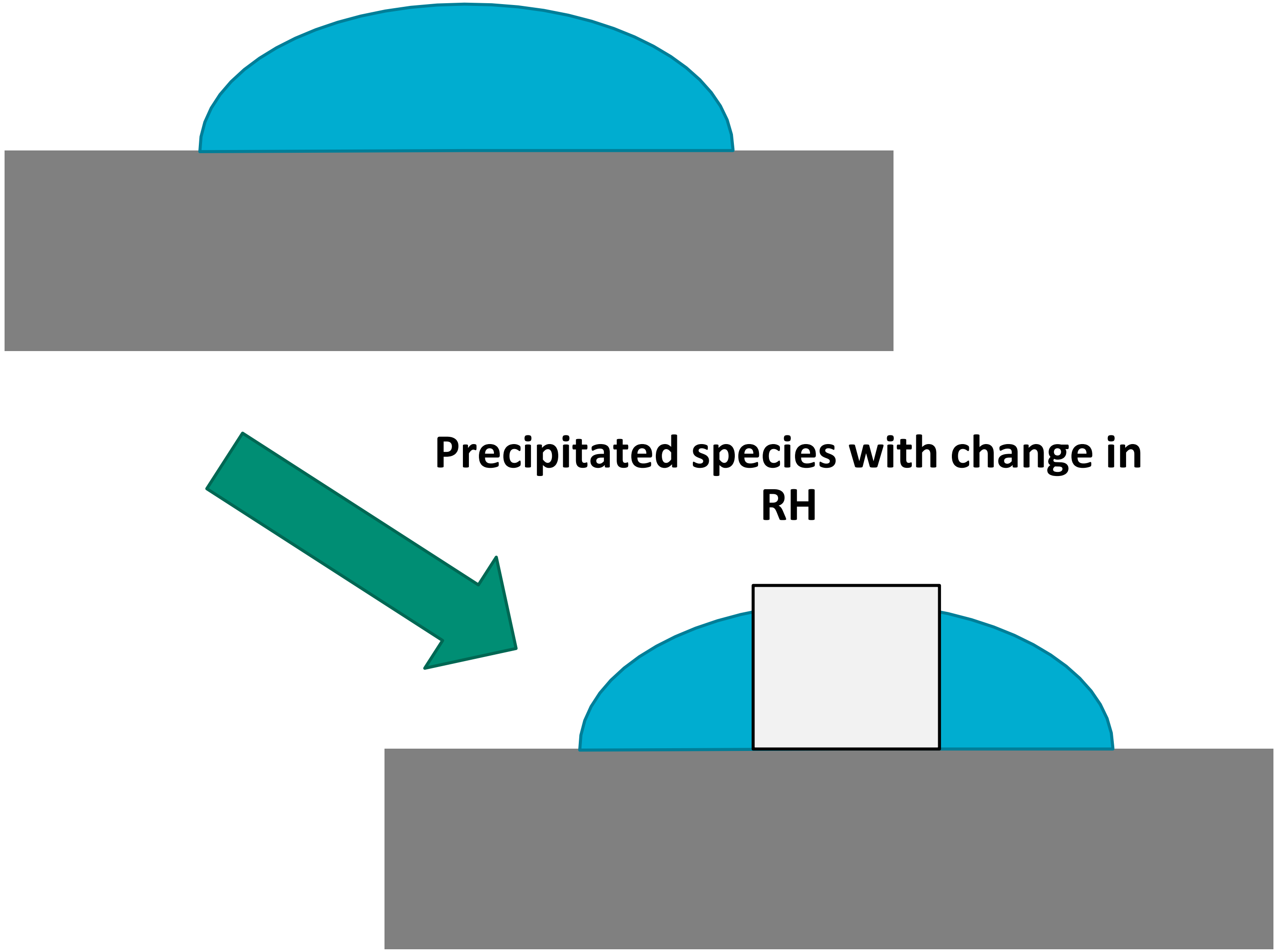
Cannot necessarily extrapolate pitting behavior from static experiments

Need to understand efficacy of inhibiting species in environments of interest and how RH influences brine composition



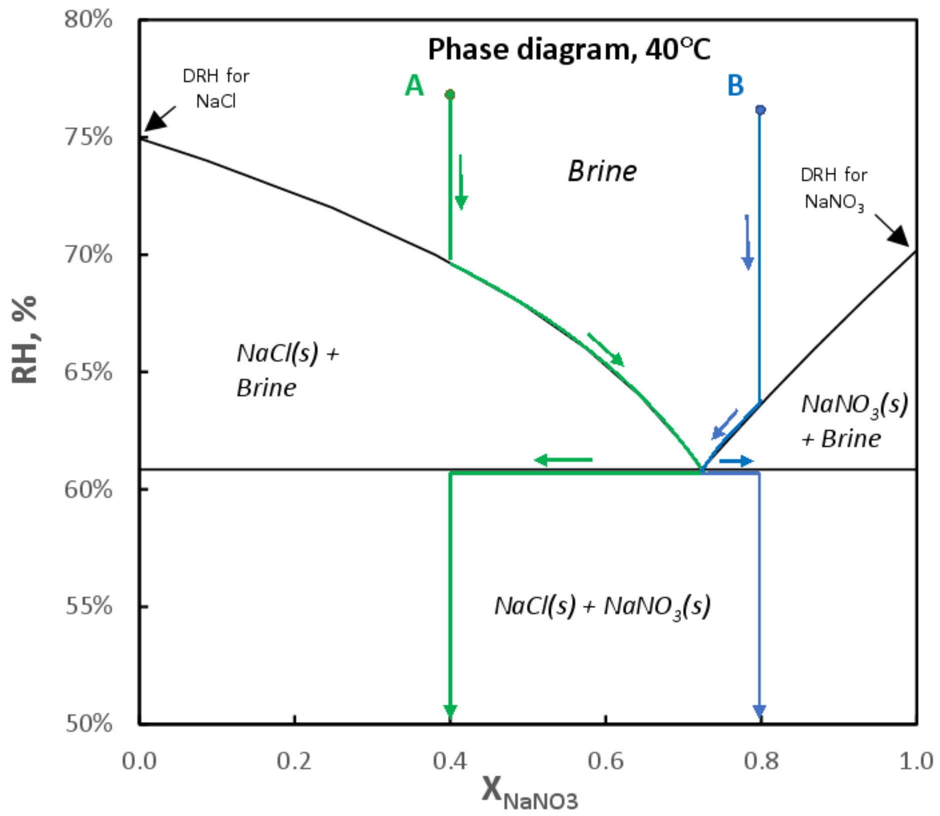
- Polarizations indicated passive behavior at nitrate ratios greater than 1:4
- Pitting observed under higher ratios of nitrate to chloride (explored up to 4:1) under cyclic exposure

Changes in bulk and micro-environments could influence pitting



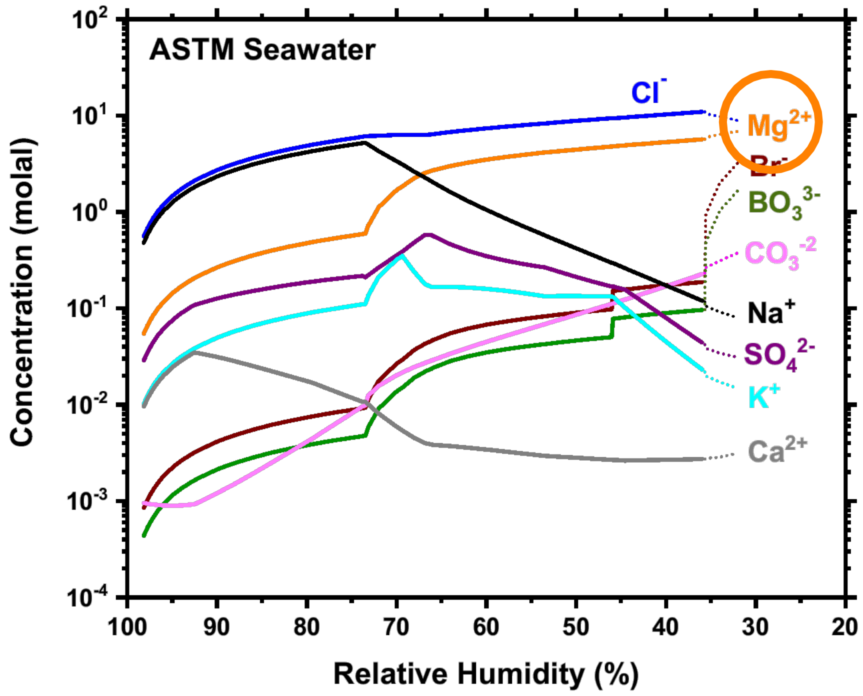
Precipitated species with change in RH

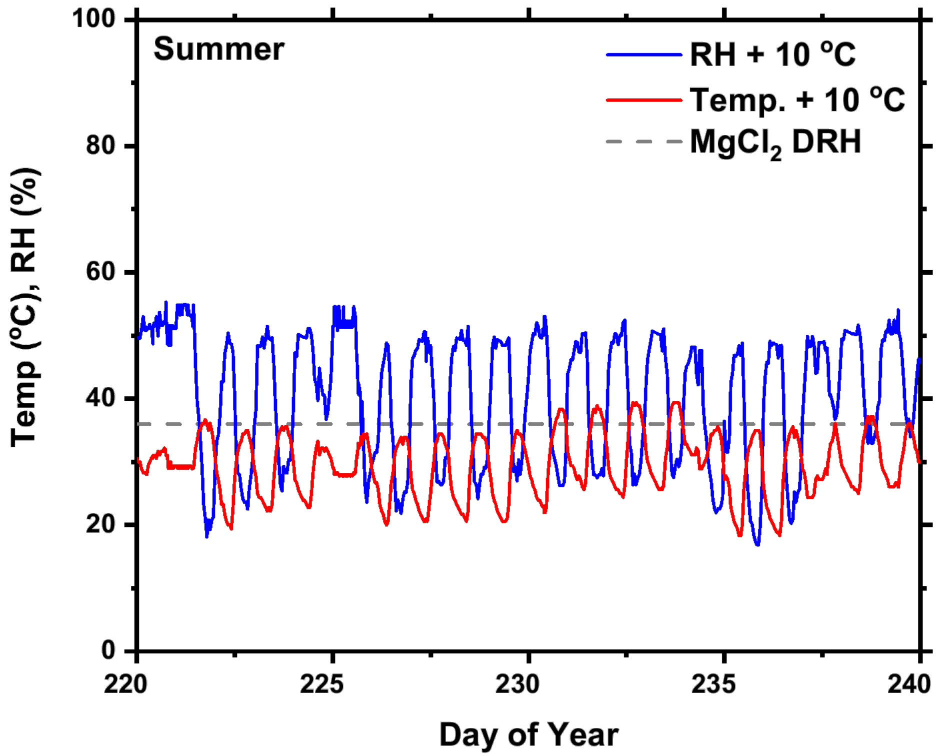
Possibility for crevices to form with different chemistry from bulk solution



Brine thickness and concentration change over exposure RH change

Future Work





- Further SEM and profilometry for quantitative pit analysis
- Influence of nitrates on corrosion behavior in $MgCl_2$ and seawater solutions
- Realistic diurnal cycles for a heated sheltered surface

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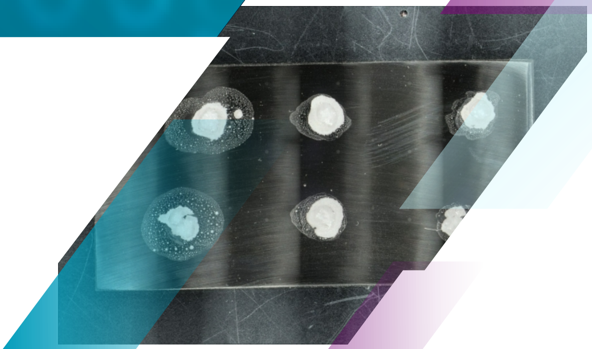

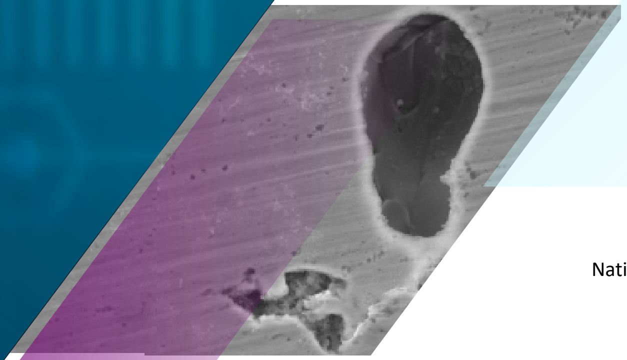

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Extras

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  - Welded stainless steel (304 SS) canisters
  - Passively-ventilated overpacks
  - Accumulate surface dust over time
  - Deliquescence of chloride-rich salts

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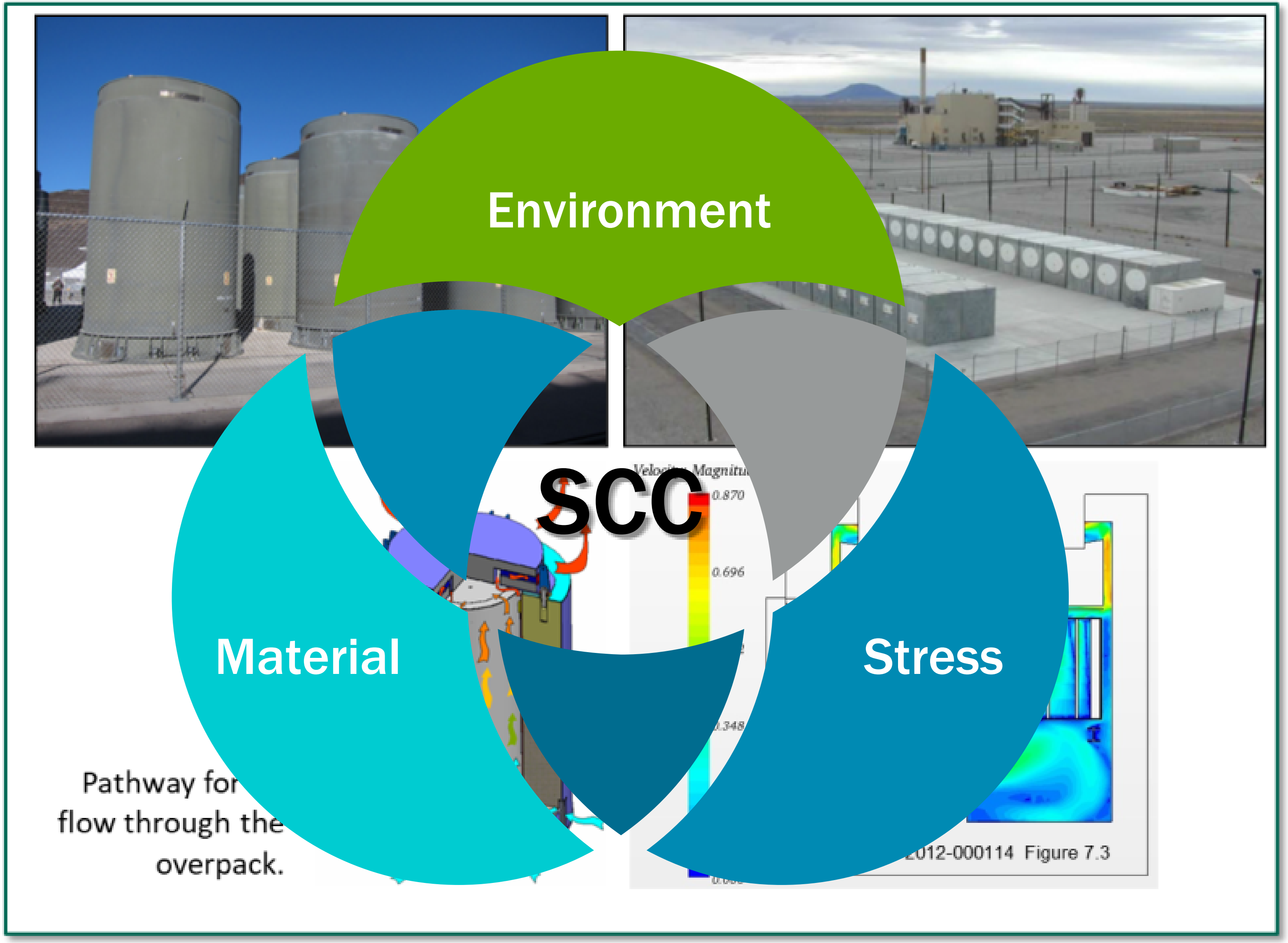
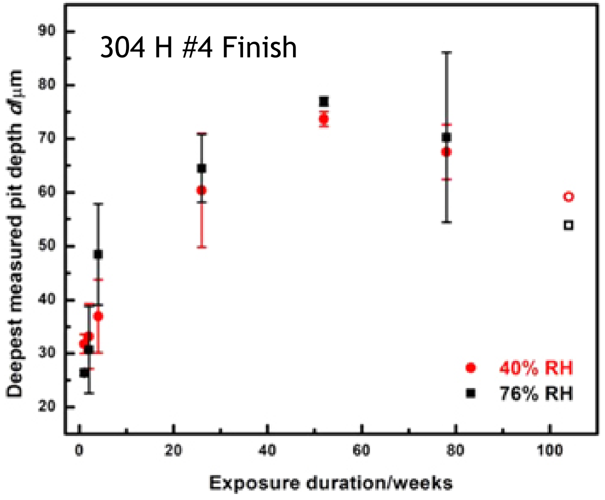
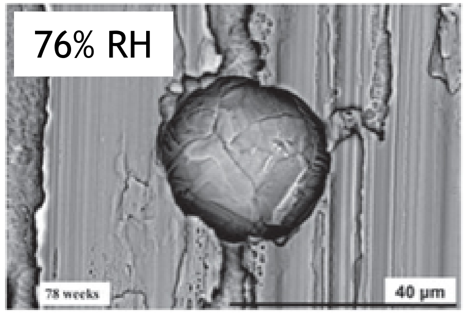
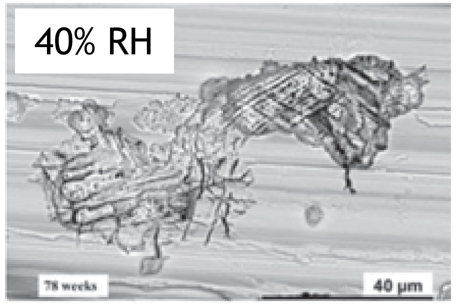


Influence of more relevant environments on pitting

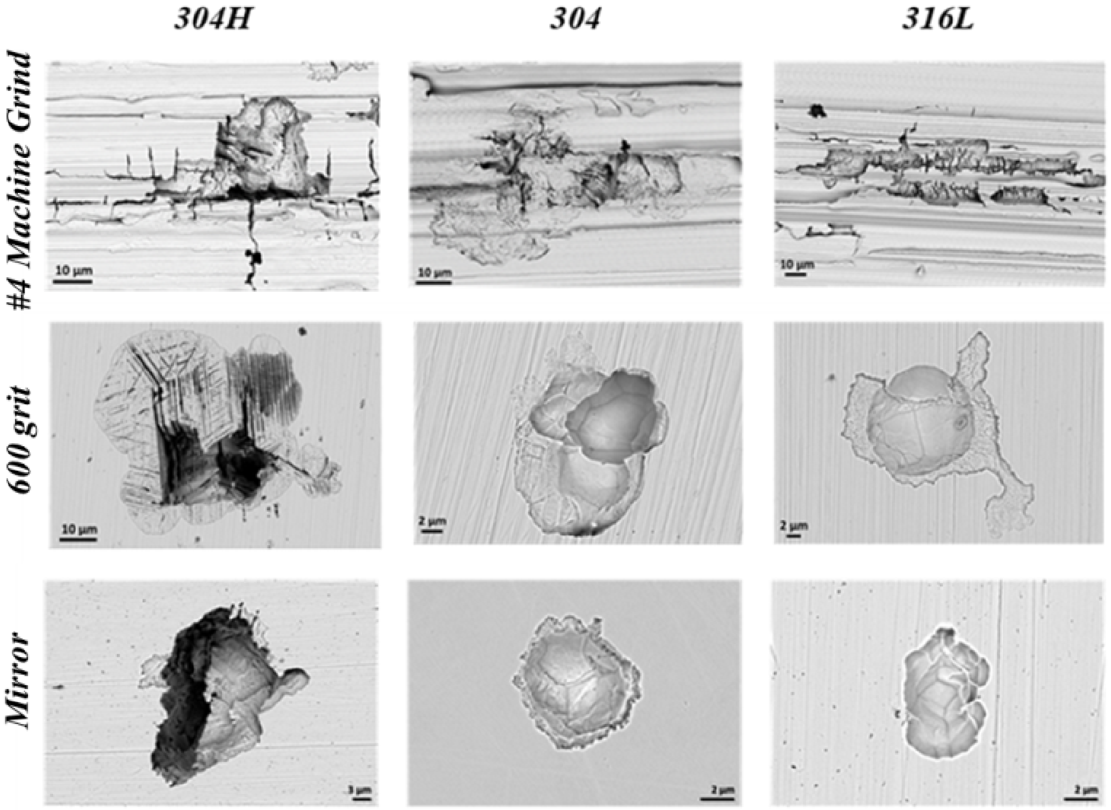
Constant RH





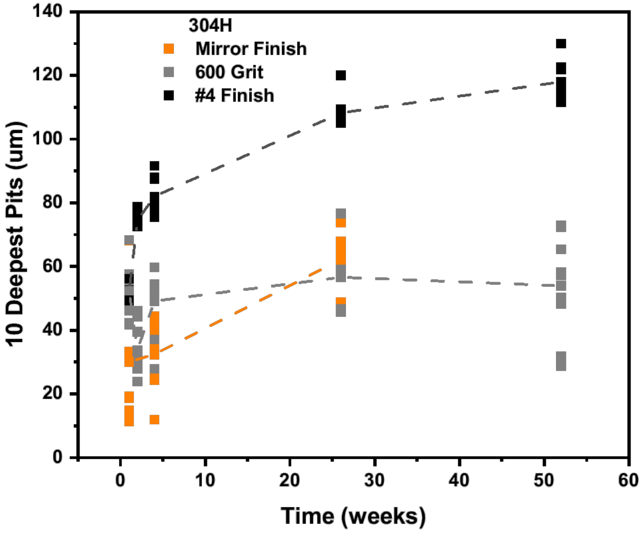


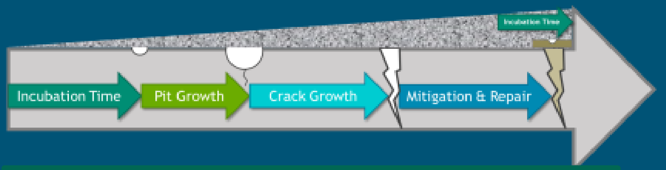
Diurnal Cycles



Diurnal Cycles

Profilometry comparison across material finish for 304H coupons





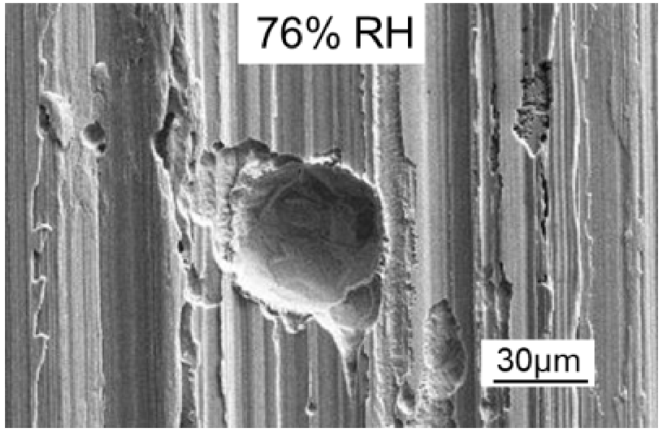
- Salt Composition Assumption
- Canister Thermal Model
- Weather Model
- Airflow and Salt Deposition Model

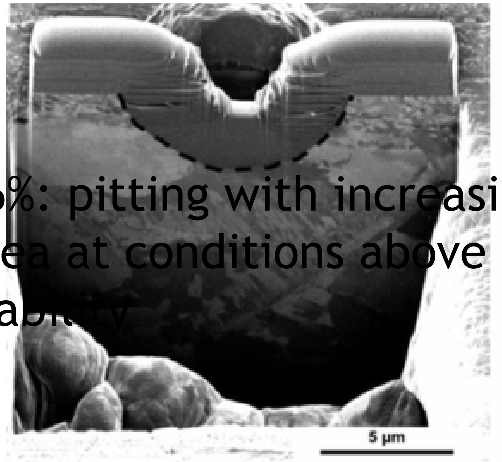
- Understanding pit growth under SNF relevant conditions:
  - Higher T
  - More concentrated brines
  - Material composition and finish

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.

RH (brine composition) influences morphology

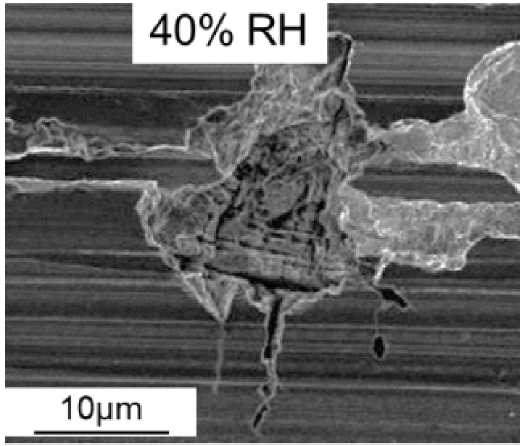
HIGH RH: NaCl RICH BRINE

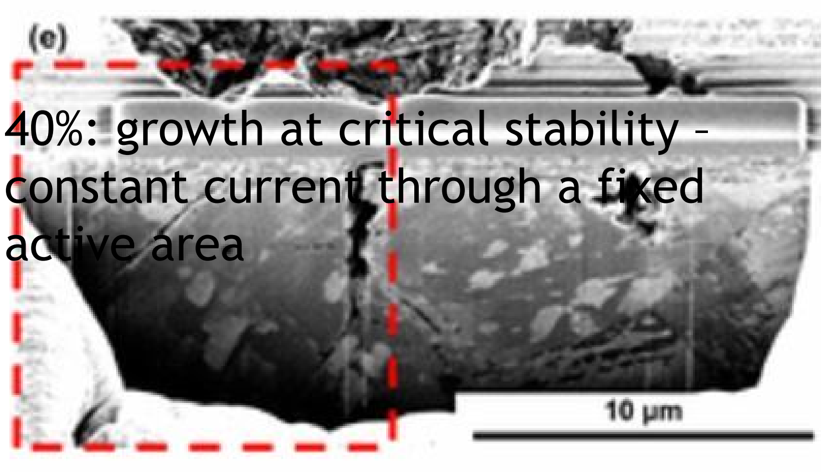




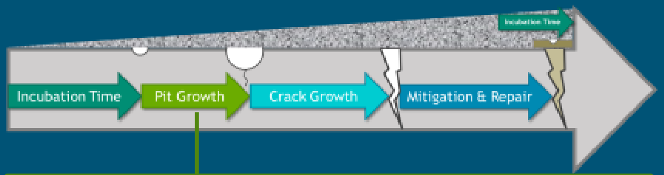
76%: pitting with increasing active area at conditions above critical stability

LOW RH: $MgCl_2$ RICH BRINE





40%: growth at critical stability – constant current through a fixed active area



- Corrosion (Maximum Pit Size) Model

- *Cathodic kinetics are influenced by brine evolution but what about the anode?*
- What influences pit morphology?
- Originally linked this to RH of exposure:
  - Lower RH dominated by $MgCl_2$
  - Is it influences of HER? Precipitates?

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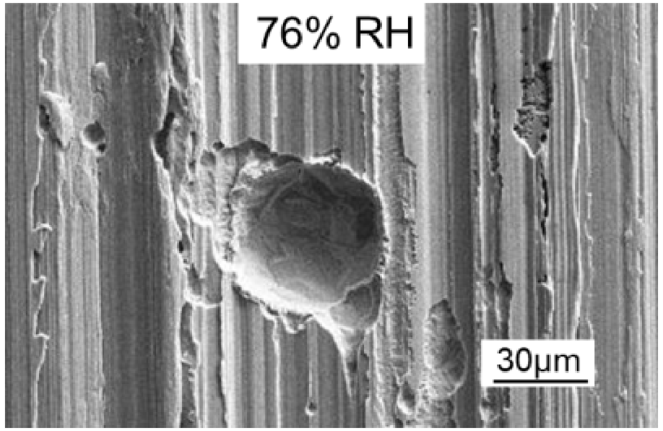

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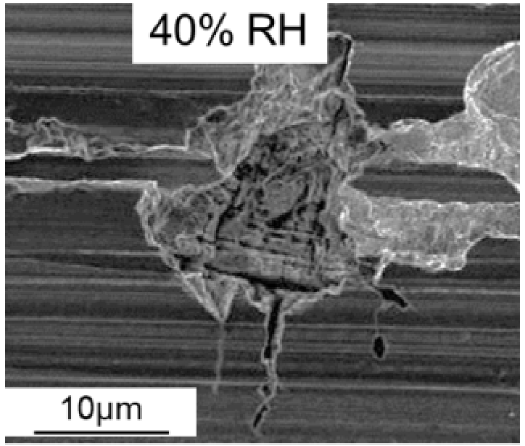
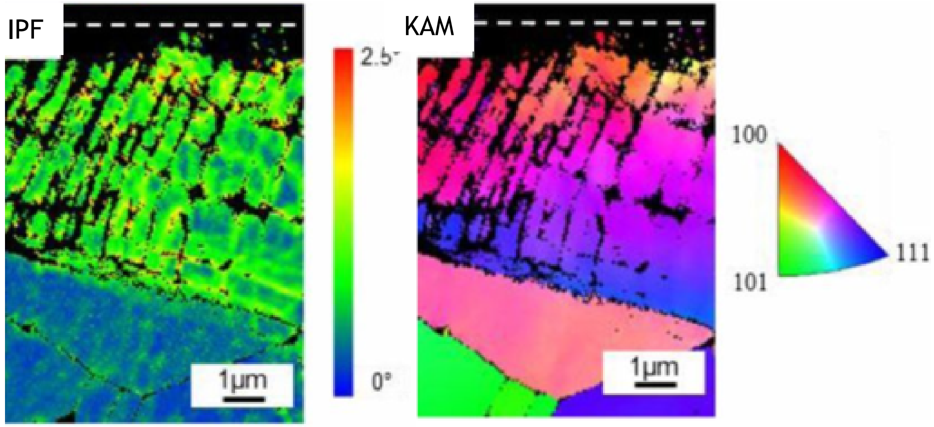
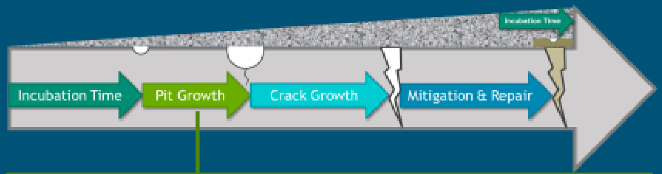




Preferential attack due to residual stress?



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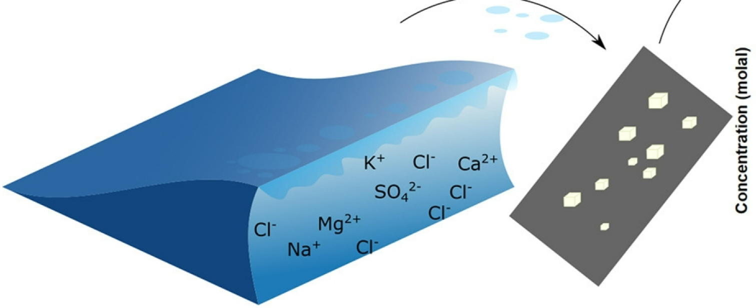
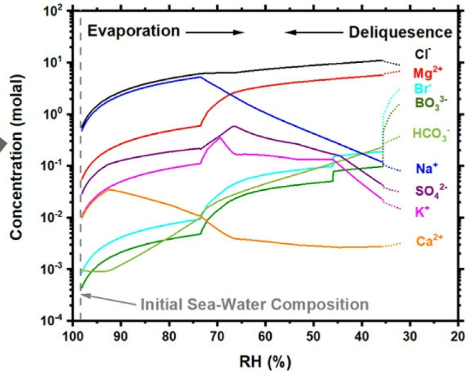
Model Parameterization: Salt inputs

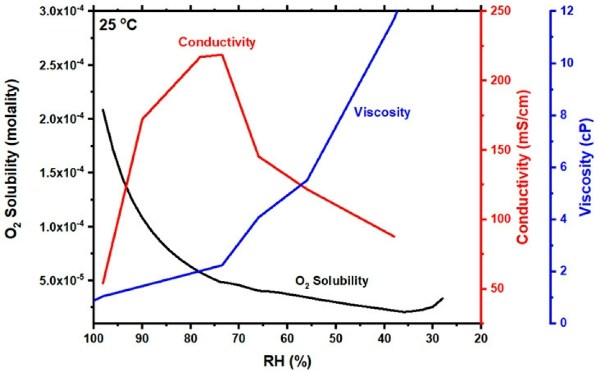
Deposition of Sea Salts Aerosols

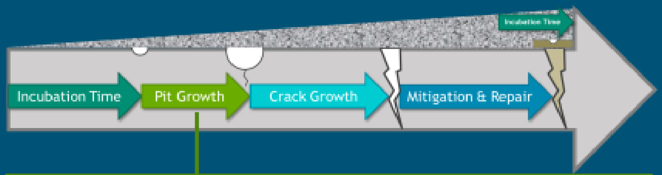


Deliquescence of Sea Salts



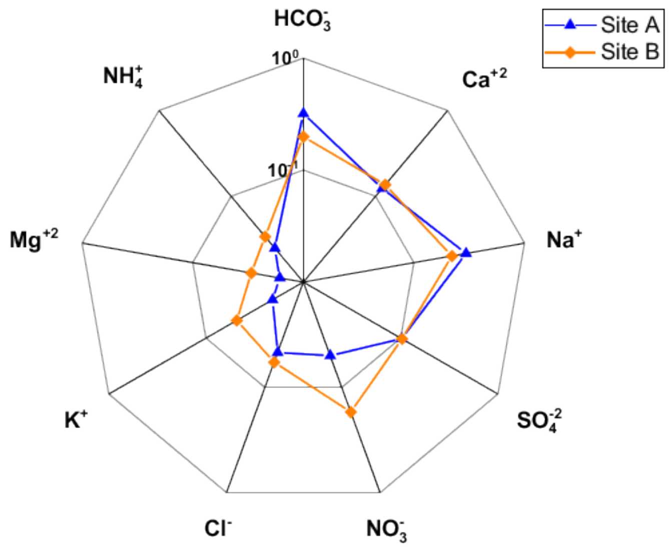
Equilibrium RH Dictates Brine Properties





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

Composition varies per site



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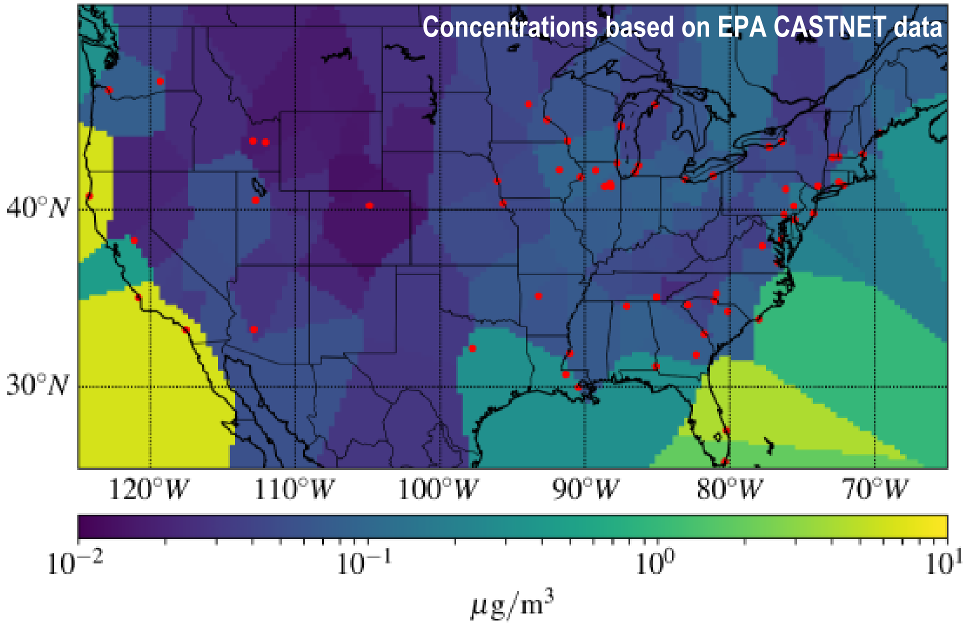


Salt Inputs:

Composition: Currently assumes chloride is deposited as sea-salt aerosols

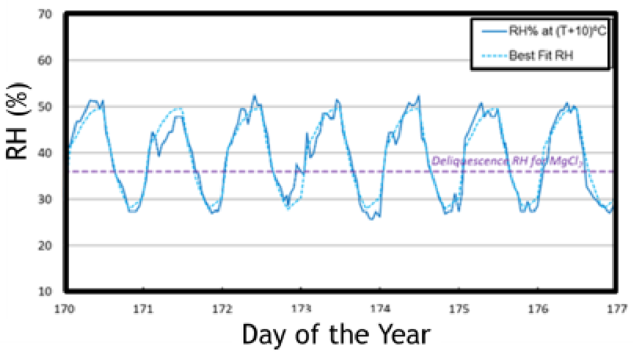
Deposition: Current (unvalidated) model grossly overpredicts salt deposition

Therefore maximum pit size results based on **constant salt deposition**

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.

Development of Relevant Lab Exposures

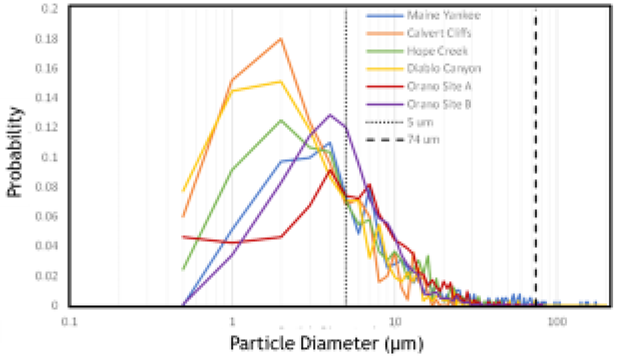
Diurnal Cycles

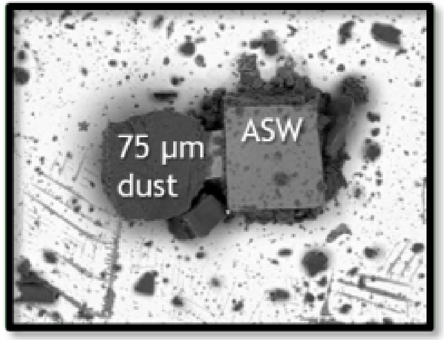


Cycle Conditions:

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

Dust/Precipitates

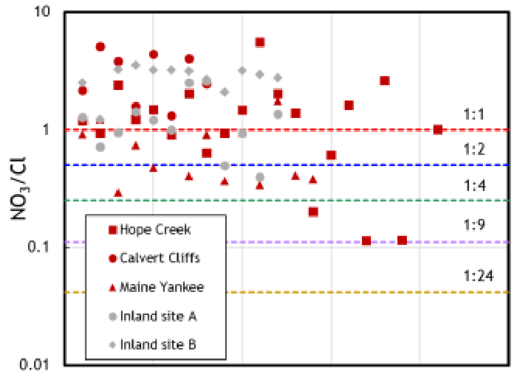




Dust Conditions:

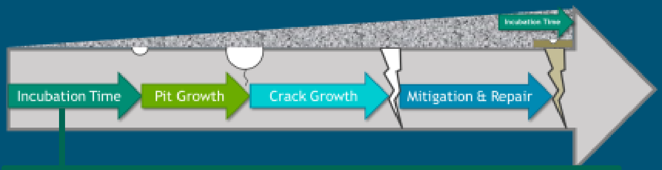
- Dust size based on ISFSI site collection
- Co-deposition of SIL-CO-SIL® 75 and MIN-U-SIL® 10 with ASW

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

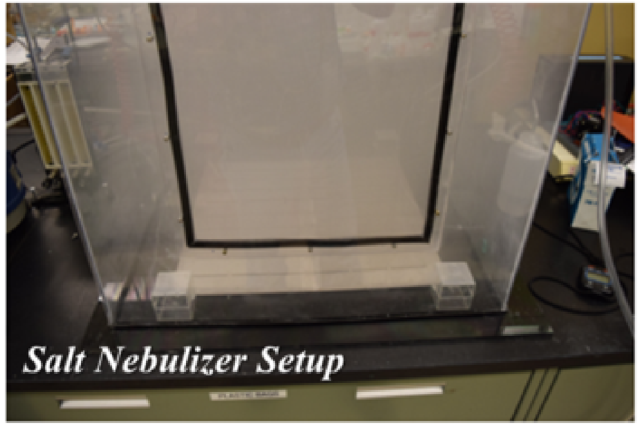
Cold Spray: Canister Relevant Conditions

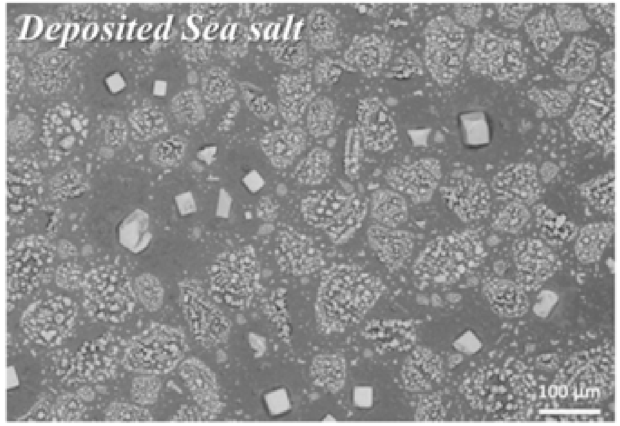
Atmospheric Exposure in Relevant Conditions:

Deposited 300 µg/cm2 of Artificial Sea Water on CS Surface

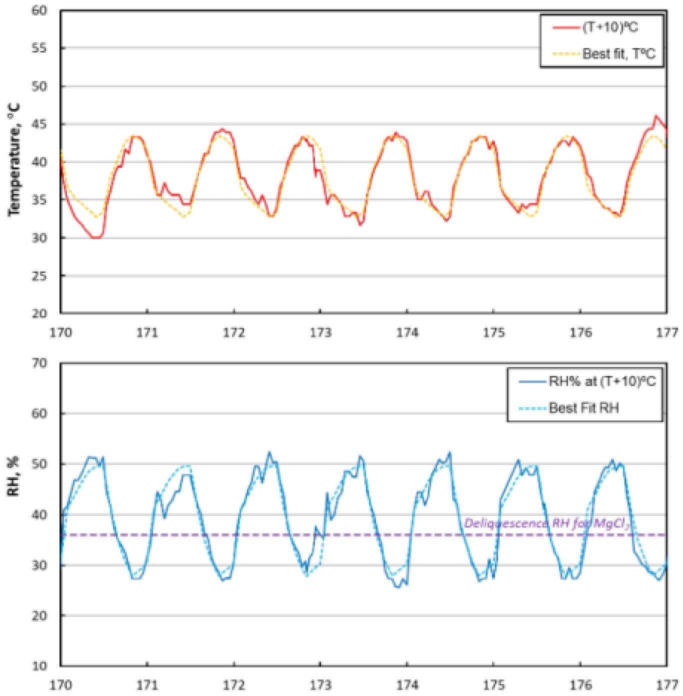
Three Atmospheric Exposure Conditions

1. *Static 40% RH; 35 °C*
2. *Static 75% RH; 35 °C*
3. *Cyclic – at right*





** Note: Exposure conditions 1 and 3 < NaCl deliquescence RH, 2 is > NaCl deliquescence RH*



Cyclic atmospheric conditions developed from Arkansas Nuclear 1 ISFSI (SNL 2021 M2)