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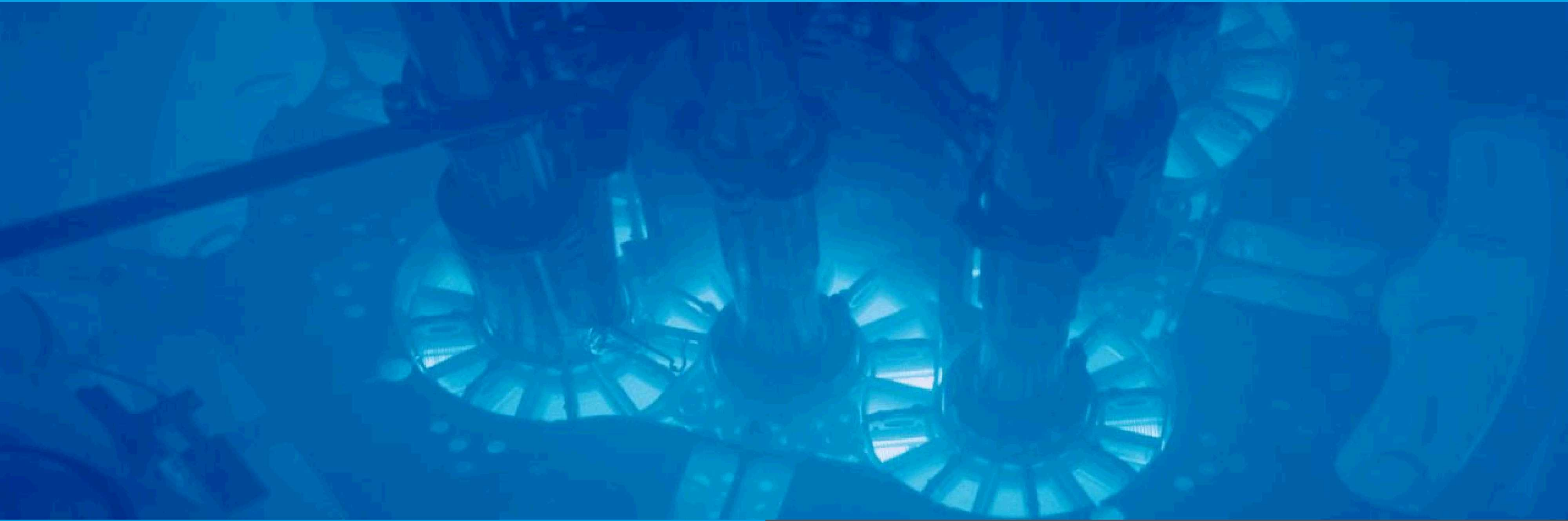

SNF Storage Canister Corrosion: Current Research at Sandia National Labs

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EPRI ESCP Fall Meeting

Charlotte, SC

November 6, 2019

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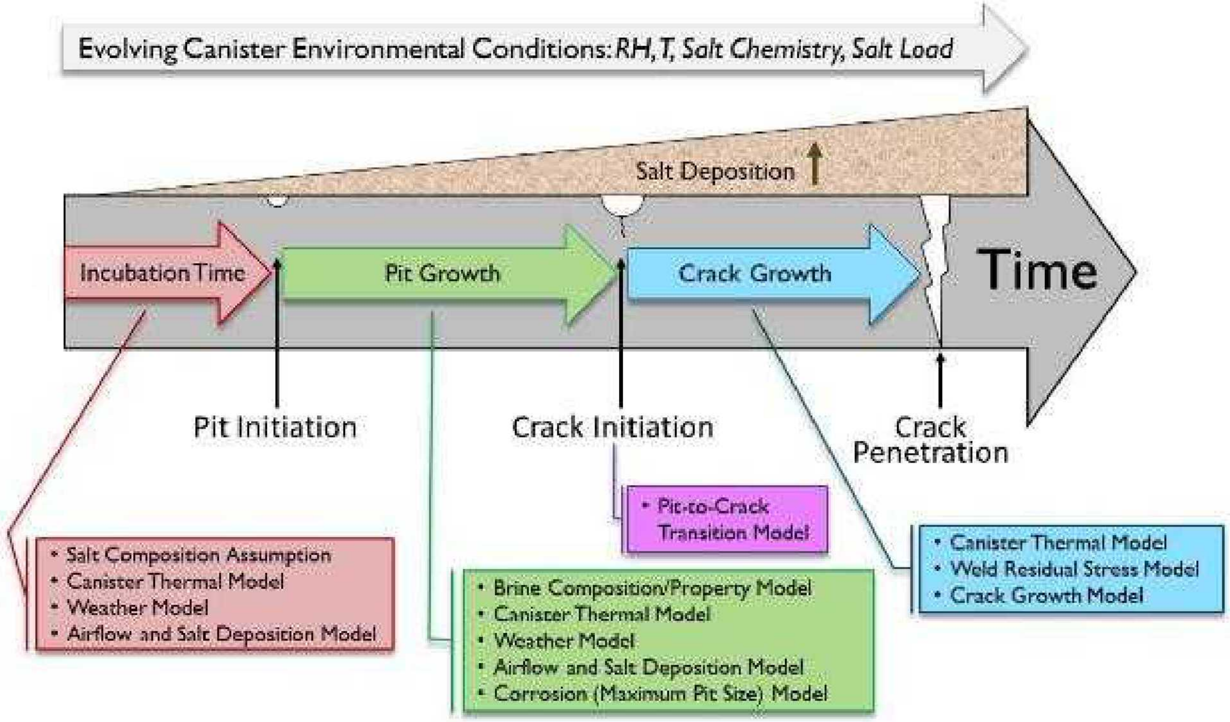
SNL Objectives

Overall objective: Improve the ability to predict timing and location of potential canister penetration by SCC cracks

- Improve understanding of electrolyte (deliquescent brine) physical and chemical characteristics
  - Effects of brine/atmosphere reactions
  - Effects of corrosion
- Understand the relationship between surface environment and damage (pitting/SCC) distributions and rates
  - Temperature and RH
  - Salt surface load and spatial distribution
- Develop quantitative understanding of the effects of variability in material properties and mechanical environment on corrosion.
  - Weld/HAZ/base metal material properties (sensitization, texture, mineralogy)
  - Tensile stress intensity and depth profile

SNL Stress Corrosion Cracking Studies

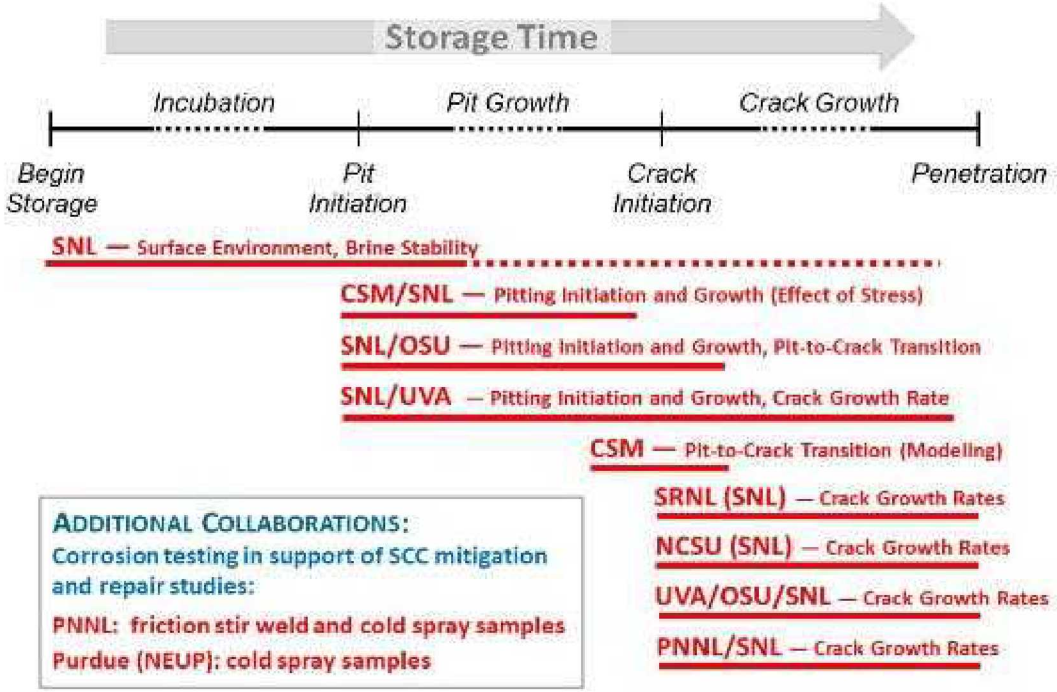


INTEGRATED MECHANISTIC/PROBABILISTIC MODEL FOR CANISTER SCC

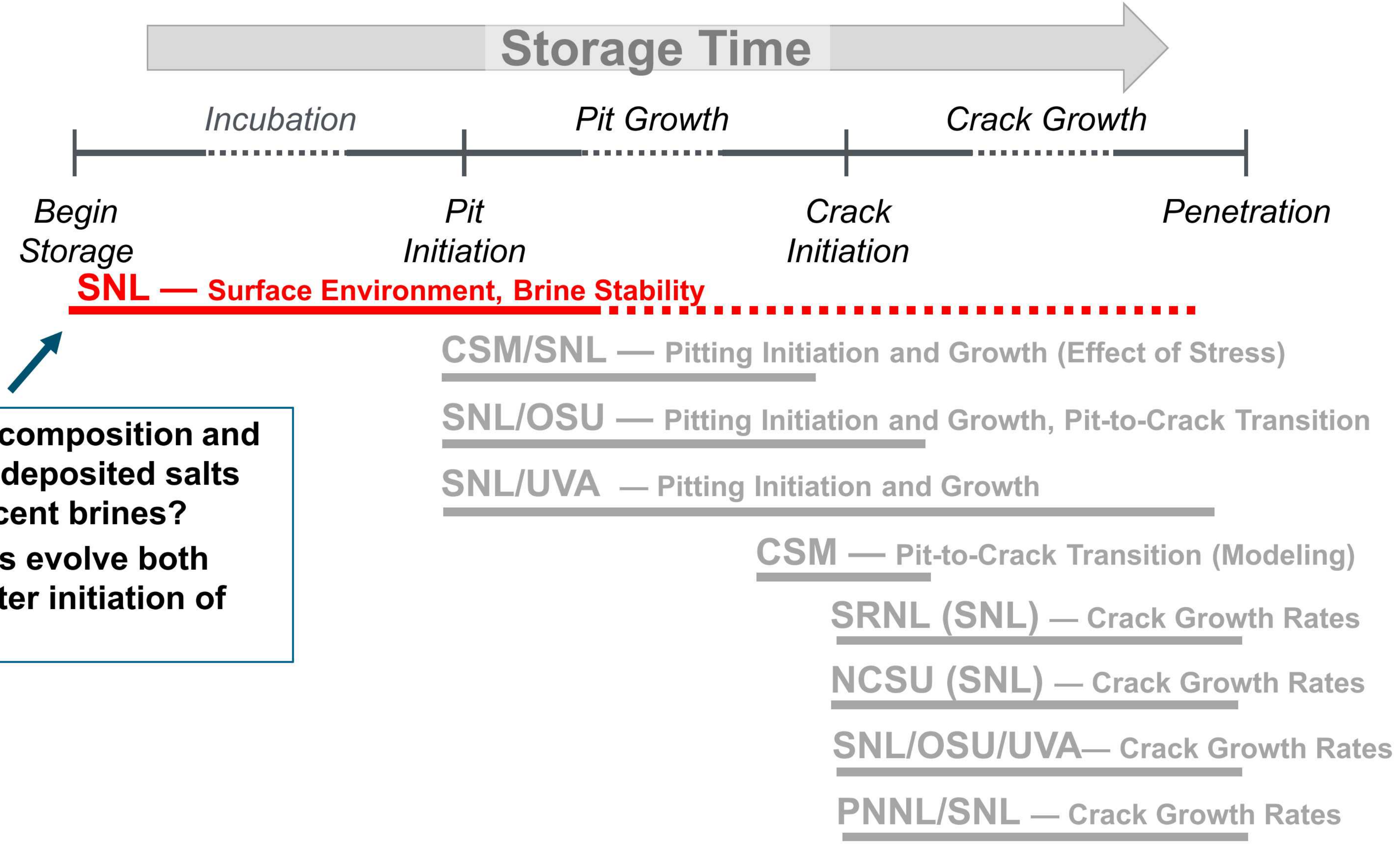
Goal: Improve the ability to predict timing and location of potential canister penetration by SCC cracks

COLLABORATIVE EFFORT

- Determine electrolyte *(deliquescent brine)* compositions and evolution with time
- Determine the relationship between surface environment *(T, RH, salt load/distribution)* and damage *(pitting/SCC)* distributions/rates
- Determine the effects of material properties *(microstructure)* and mechanical environment *(residual stress intensity and depth profile)* on corrosion distributions and rates



Canister SCC: Corrosion Testing



- **What are the composition and properties of deposited salts and deliquescent brines?**
- **How do brines evolve both before and after initiation of corrosion**

Canister Surface Environment: Evaluation of Sea-Salt Brine Stabilities

Focus on $Mg\text{-}Cl_2$ brine, that strongly control deliquescence RH and potentially brine corrosiveness

Experimental Evaluation of Magnesium Chloride Brine Stability

Previous Experiments:

80°C, 35% RH test:

- Chloride loss
- Conversion to Mg-hydroxychloride

48°C, 40% RH test:

- Chloride loss
- Reaction with atmospheric CO_2; conversion to Mg-carbonate
- Degree of reaction limited by low air flow, limited duration

Current Experiment (in progress)

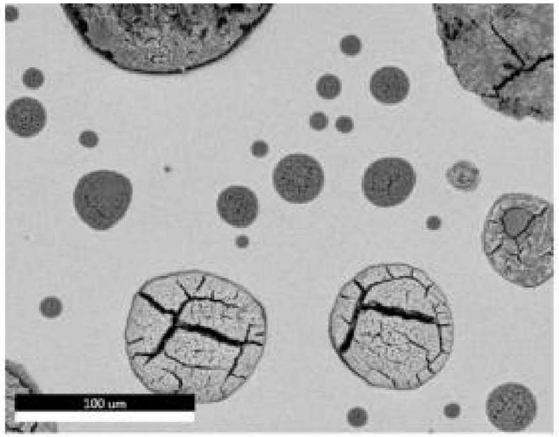
48°C, 40% RH test:

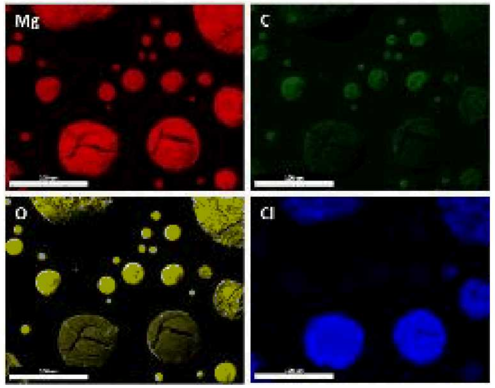
- High air flow, longer duration

Future work: Reactions with other atmospheric gases

- SO_x, NO_x

SEM Image of $MgCl_2$ droplets on wafer surface

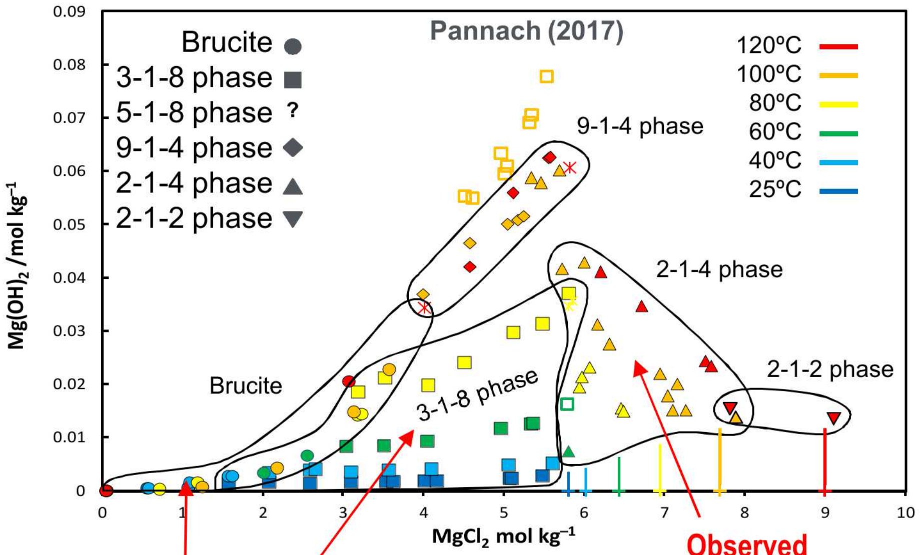




EDS element maps showing depletion of chloride in small droplets of $MgCl_2$. due to chloride degassing.

Characterization of Mg-hydroxychloride Hydrates:

- Observed in several experiments
- Controls on deliquescence RH, brine composition and properties



Observed in rotating disc electrode experiments, split electrode experiment (low T)

Observed 80°C, 35% RH

Canister Surface Environment: Dust Sampling and Analysis

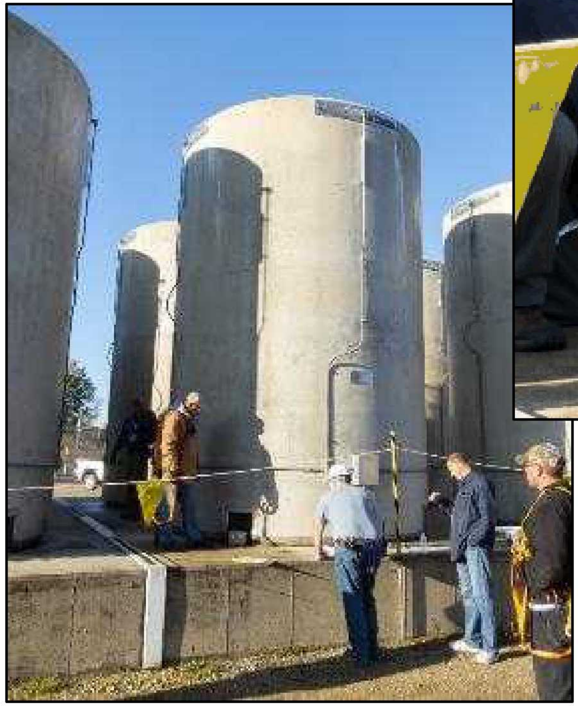
Maine Yankee Sampling

MAINE YANKEE SAMPLING, OCTOBER, 2019

- Samples placed in inlet and outlet vents of four storage systems (SNF canisters) by CSM in 2017; transferred to SNL ownership with end of CSM IRP.
- Locations (8 total): high and low heat flow, sheltered and exposed inlet and outlet vent locations
- At each location:
  - 1 large 4-pt bend specimen, with attached dust collection coupons.
  - 3 small 4-pt bend specimens (varying surface finishes and stress levels)

Specimens examined, all 8 dust collection coupons collected and replaced, two small 4-pt bend samples collected.

Samples characterized by SEM/EDS and chemical analysis.



Sampling at Maine Yankee ISFSI, October, 2017

Maine Yankee Sampling

General Impressions

- Samples tethered to vent screens, close to the screens
- Samples dirty with wind-blown dust and plant debris, and spider webs and other insect debris; inlet samples much dirtier (in general) than outlet samples
- Much lower deposition on vertical surfaces *(tension surface of large 4-point bend)*
- Many samples show evidence of wetting—rain spatter, condensation(?), or accumulation of wet fog(?) (rings or droplet patterns in the dust; rust under dust collector)

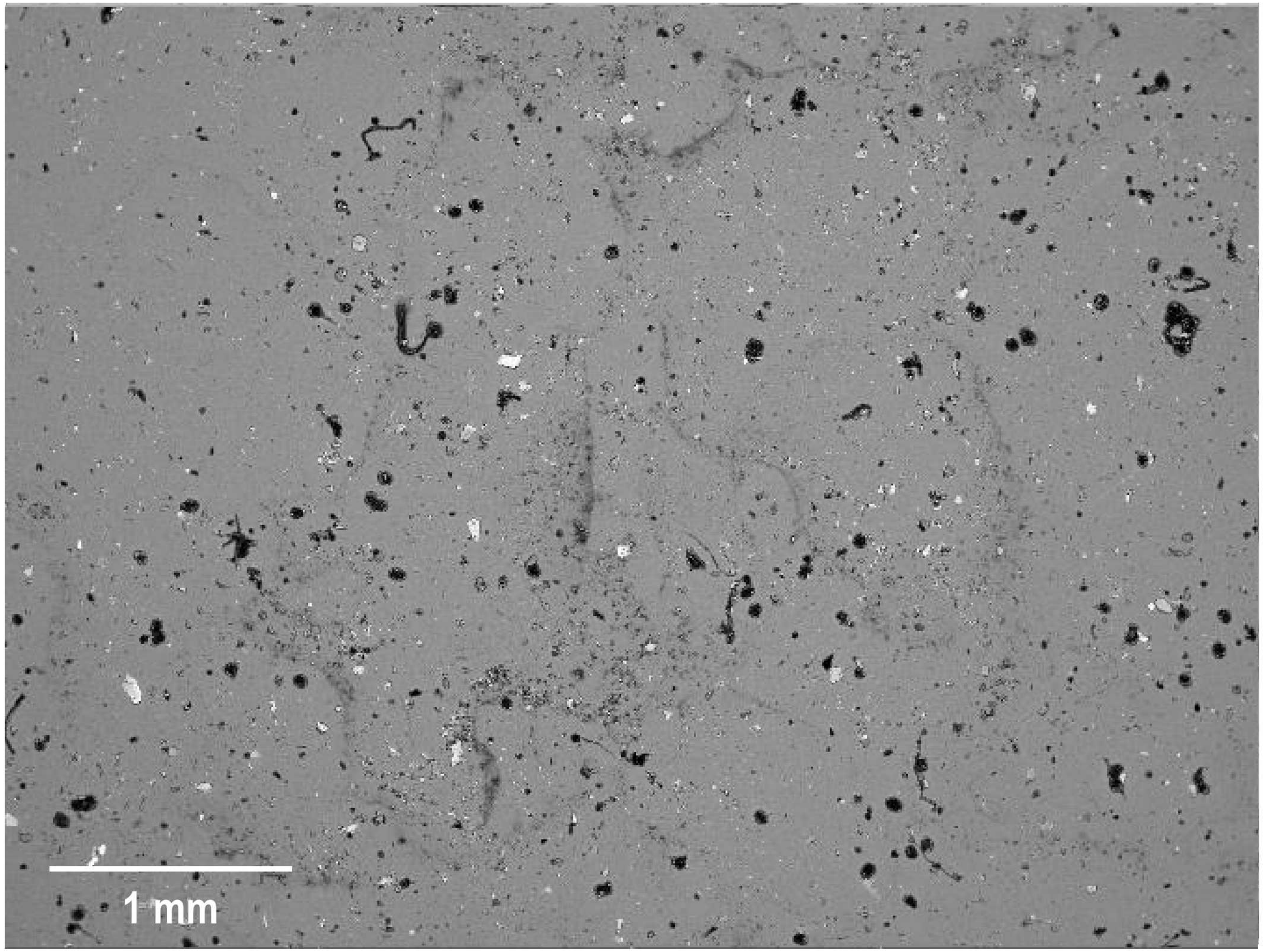
Important to note that these samples are **not representative** of the canister surface environment (exposure to wetting, ambient T and RH, horizontal orientation leads to heavy dust loads). But they do provide some information on salt compositions, and potentially, on salt corrosiveness.

Maine Yankee Sampling

SEM/EDS Analysis

Dust analyzed as deposited, on silica wafer dust collectors:

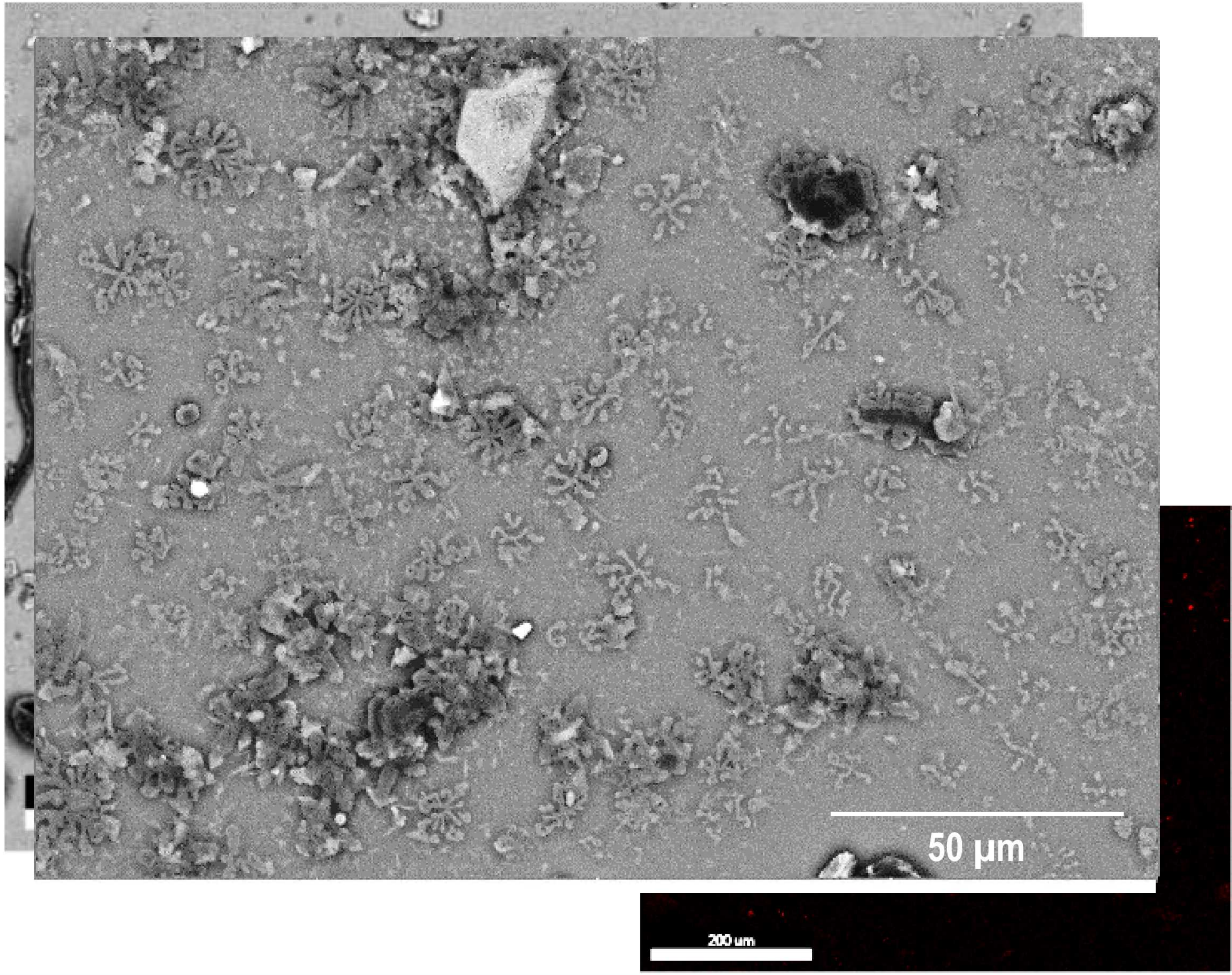
- Organic materials
  - Pollen
  - Stellate trichomes, plant fibers
  - Cobwebs, insect parts
- Mineral Phases
  - Dominantly silicate minerals—mica, quartz, feldspars (Si-Al-silicates)
  - Salt phases



Maine Yankee Sampling
SEM/EDS Analysis

<u>Salt phases: Composition and distribution</u>

- Individual salt aerosols—generally tiny particles of NaCl, associated with mineral, pollen grains
- Sea-salts? Dried sea-fog droplets?
- Salts associated with pollen and plant matter
- Redistributed salts due to wafer wetting



Maine Yankee Sampling

SEM/EDS Analysis

Chemical Analyses: Soluble Salts

Salts consist of a mixture of marine (Na, Cl, Mg, SO_4) and continental (Ca, K, NO_3, SO_4) salts

Salts are somewhat more chloride-rich than salts previously recovered from the Maine Yankee canister surfaces

Sample #	**Na^+**	**NH_4^+**	**K^+**	**Mg^{+2}**	**Ca^{+2}**	**F^-**	**Cl^-**	**NO_2^-**	**NO_3^-**	**PO_4^{3-}**	**SO_4^{2-}**
VCC-18 inlet	1.853	0.021	0.500	0.190	0.478	–	0.675	0.027	0.273	0.020	0.120
VCC-18 outlet	0.350	0.026	0.080	0.041	0.120	–	0.969	0.033	0.879	0.007	0.221
VCC-37 inlet	2.368	0.016	0.398	0.232	0.494	0.019	0.989	–	0.364	0.033	0.208
VCC-37 outlet	0.152	0.019	0.029	0.012	0.039	–	0.178	0.017	0.168	–	0.065
VCC-42 inlet	0.963	0.016	0.479	0.089	0.263	–	0.373	0.017	0.128	–	0.085
VCC-42 outlet	2.339	0.018	1.109	0.183	0.981	–	0.872	0.033	1.528	–	0.292
VCC-56 inlet	0.669	0.012	0.500	0.063	0.285	–	0.272	0.017	0.111	–	0.077
VCC-56 outlet	0.373	0.018	0.358	0.045	0.334	–	0.139	–	0.053	–	0.027

Maine Yankee Summary

Sampled 4 storage systems (inlets & outlets), ~2 years exposure. Corrosion test samples examined, dust coupons collected and replaced.

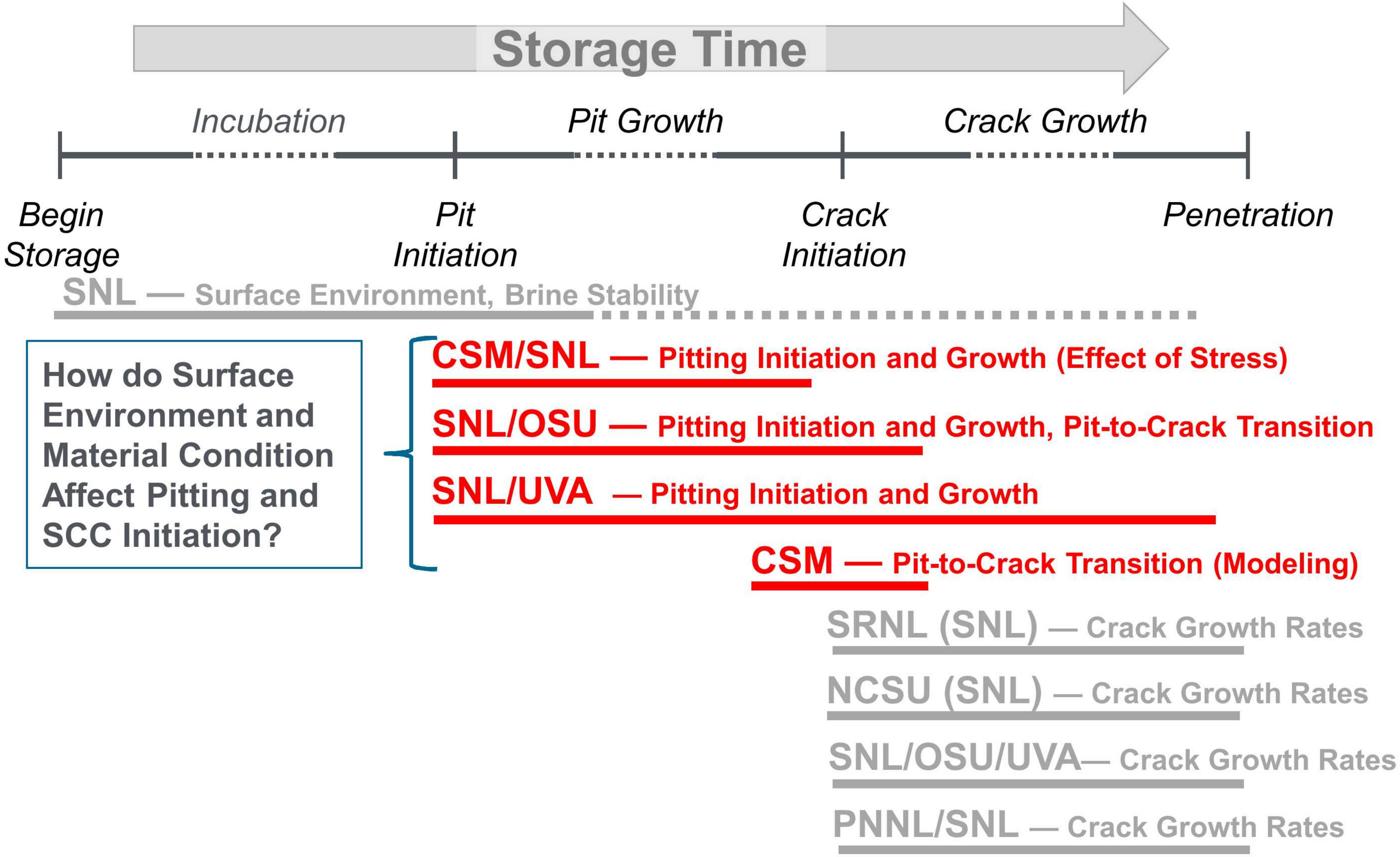
Results

- Samples were close to vent screens, had heavy dust loads
- Dust primarily silicate minerals and biologicals
- Soluble salts a mixture of sea salts and continental salts
  - Sea-salt (sea fog?) particles observed
  - Soluble salts relatively chloride-rich; more chloride observed than in dust previously collected from canister surfaces
- Salts occurred as tiny aerosol particles, frequently attached to pollen or mineral grains. Salt redistribution on coupons wetted by rain.
  - Chloride wicked into organic materials during drying.
  - Recrystallized as coarser salt crystals or as more extensive, finely crystalline surface coatings.

Impact:

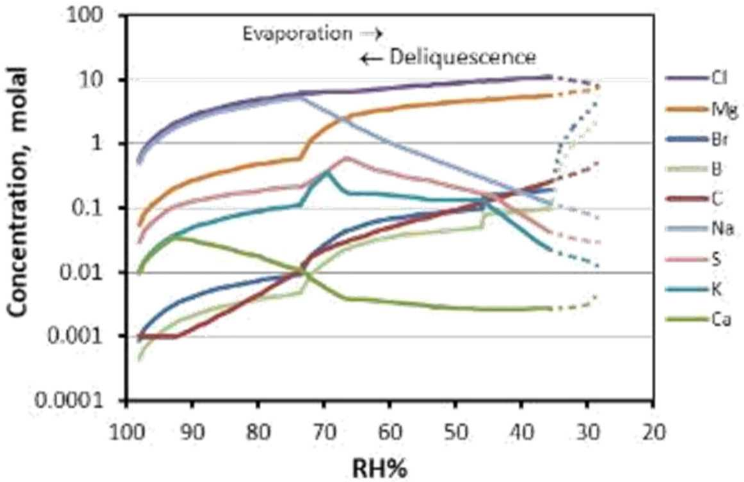
- Wetting results in salt redistribution and recrystallization—coarser crystals or coatings over larger areas. Relevance to cleaning canisters for inspection?

Canister SCC: Corrosion Testing

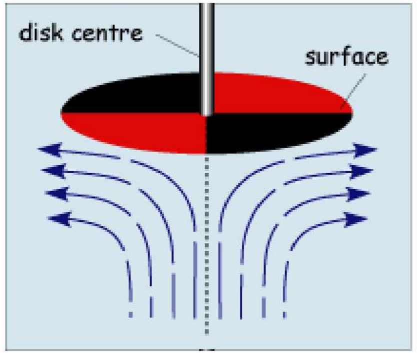


Prediction of Maximum Pit Size from Brine Characteristics and Electrochemical Kinetics

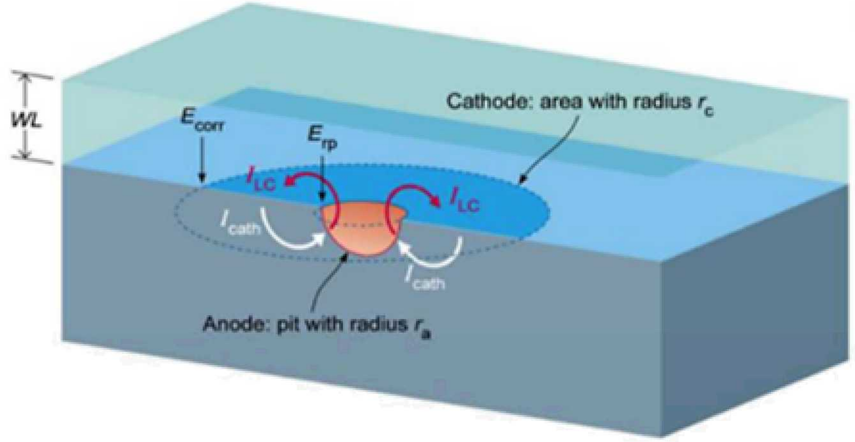
Challenge: Information on ***electrochemical parameters lacking*** for expected canister brine conditions (W_L and chemistry)

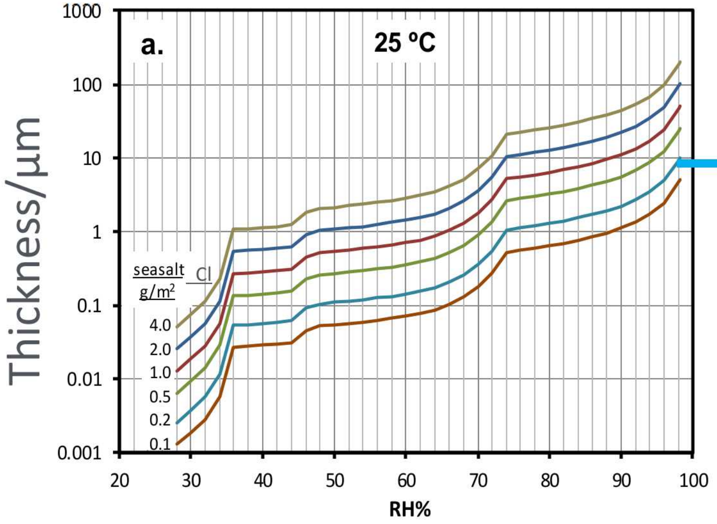


Rotating disc electrode



Simulate $W_L > 1$ µm





Cathodic polarization curves

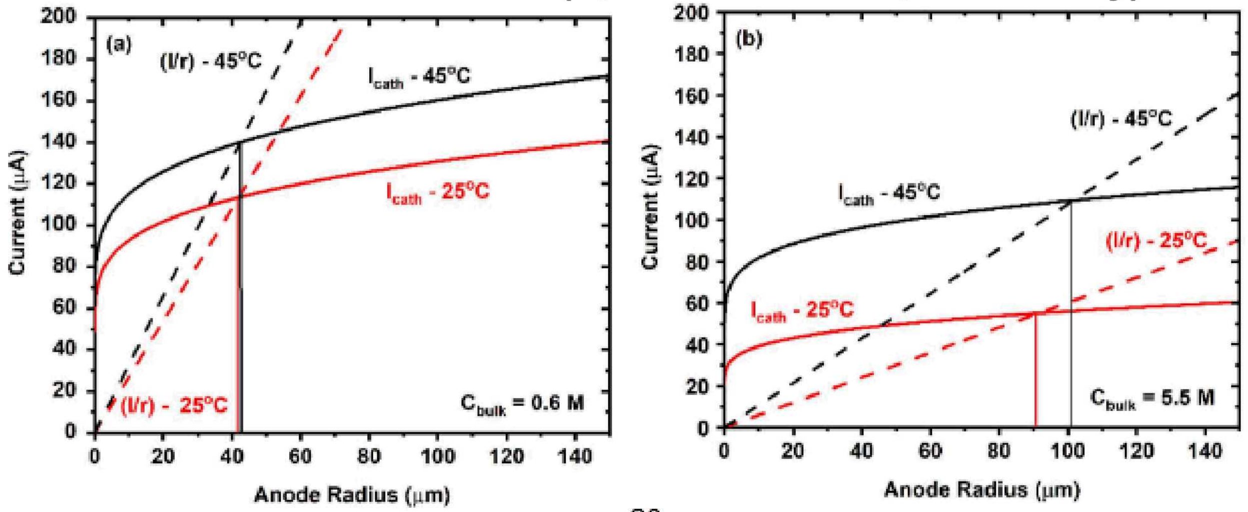
$$\ln I_{c,max} = \frac{4\pi k W_L \Delta E_{max}}{I_{c,max}} + ln\left[\frac{\pi e r_a^2 \int_{E_{corr}}^{E_{rp}} (I_c - I_p)\, dE}{\Delta E_{max}}\right]$$

Anodic polarization curves

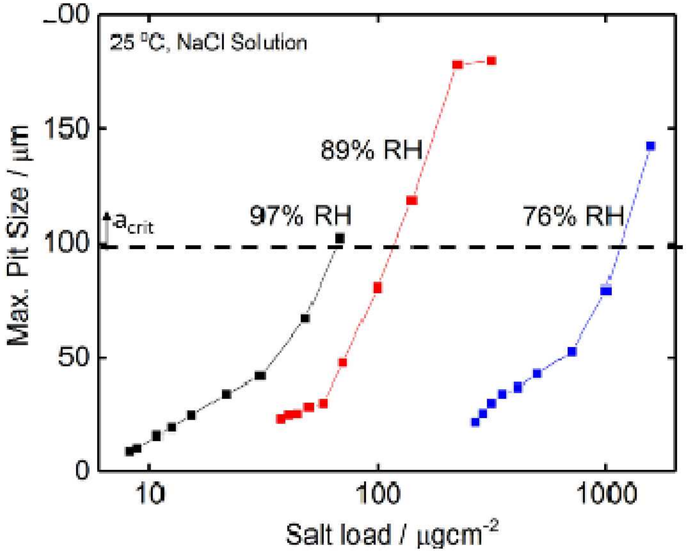
$$d = \frac{A}{nF\rho}\int_0^t i\, dt$$

Maximum Pit Size Predictions: Canister Relevant Conditions

Predictions as f (**T, RH, Salt Load, Chemistry)**



Example:
K_{ISCC} = 5 Mpa·m$^{1/2}$
σ= 500 MPa



Current Status:

- **Predicted max pit size includes the following assumptions:**
  1. *Continuous brine layer*
  2. *Hemispherical pit*
  3. *Kinetics independent of t (fixed electrolyte)*
- **JECS 2019 paper**
- **Journal article in progress.**

Important results

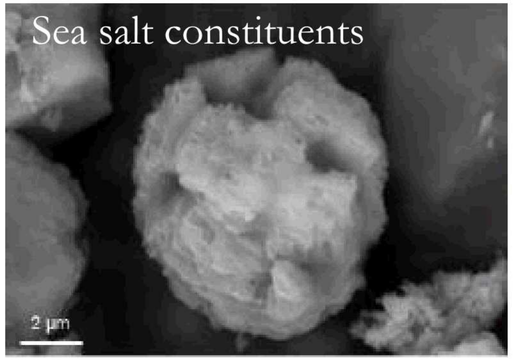
- ***Kinetic parameters determined for canister relevant conditions to implement maximum pit size model***

Role of Surface Environment on Pitting Damage and Pit-to-Crack Transition

Samples

SS304H

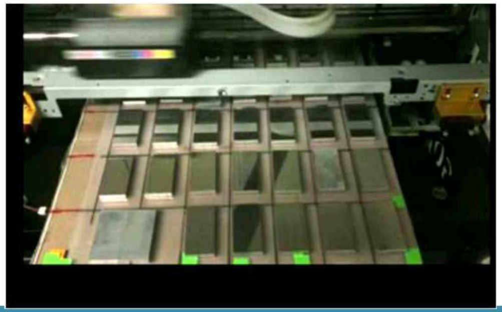
Mirror, R_a = 0.05 µm
Ground, R_a = 2.83 µm

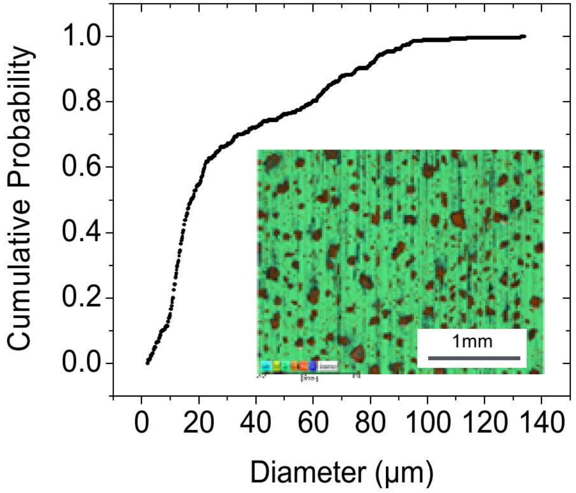


Salt	g/L	DRH
NaCl	24.53	75%
$MgCl_2$	5.2	32%

Salt Load

Inkjet Deposition





Exposure Conditions

%RH	Temperature (°C)			
76	35			
70	35			
65	35			
60	35			
55	35	40		
50	35	40		
45	35	40	45	
40	35	40	45	
35	35	40	45	50
30	35	40	45	50

Time

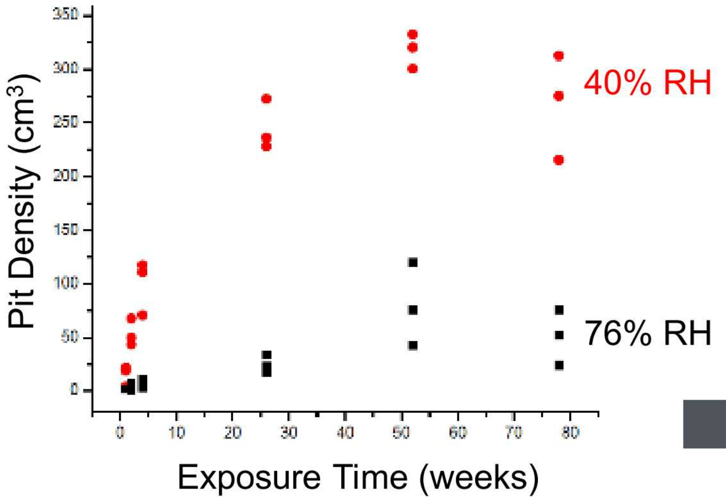
I week to 2 years

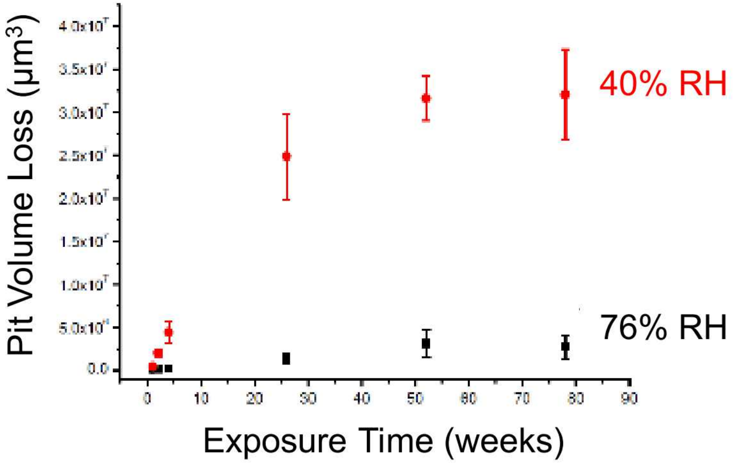
Effect of Humidity on Pitting and Cracking

ENVIRONMENT, F(t)
RH, T, seasalt, 10 μg/cm^2 and 300 μg/cm^2

MATERIAL
304H (unsensitized)

MATERIAL CONDITION
ground



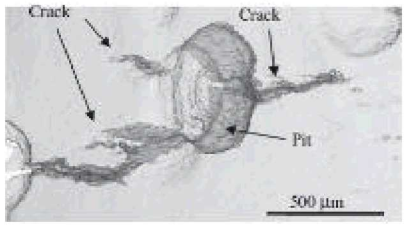


K = f(pit depth, σ), assuming hemispherical pits

Turnbull, 2010

$K > K_{ISCC}$?

Crack initiation?



Horner, 2011

Current Status:

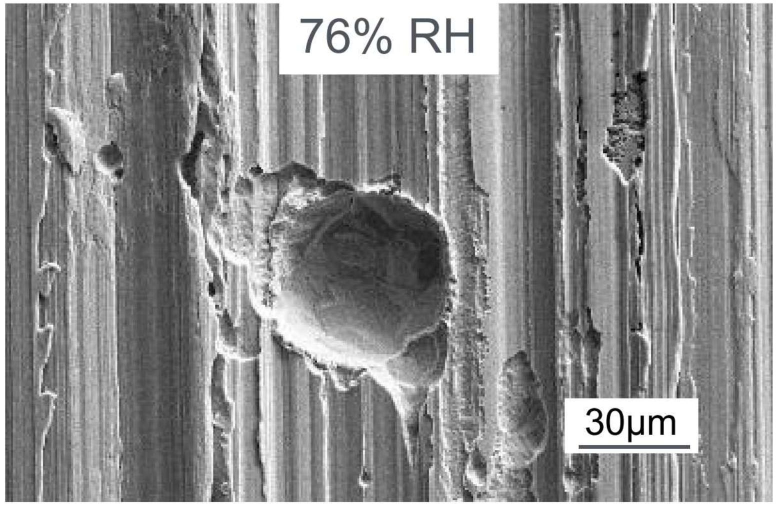
- ***Similar depth distribution, but diameters and shape RH dependent***
- **Maximum pit size model validated by atmospheric exposure with critical assumptions**
- **JECS 2019 paper**

Important results

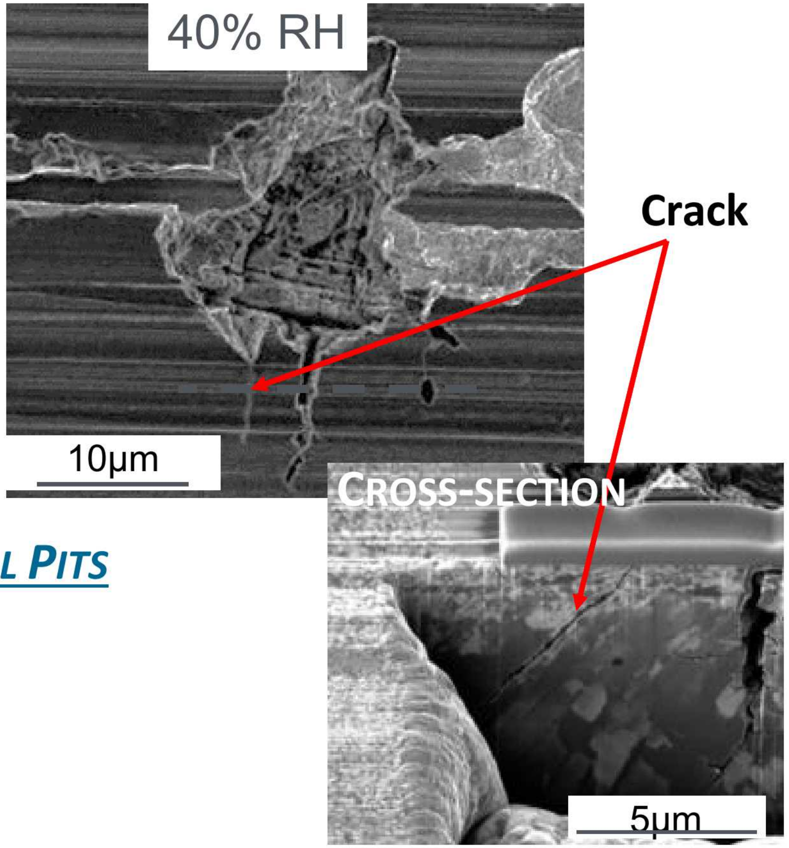
- ***Maximum pit size model bounds results at 76% RH, but when/where is it valid?***

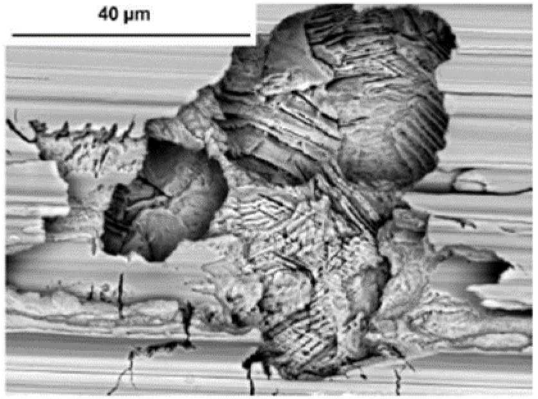
Humidity Controls Pit Morphology and Cracking

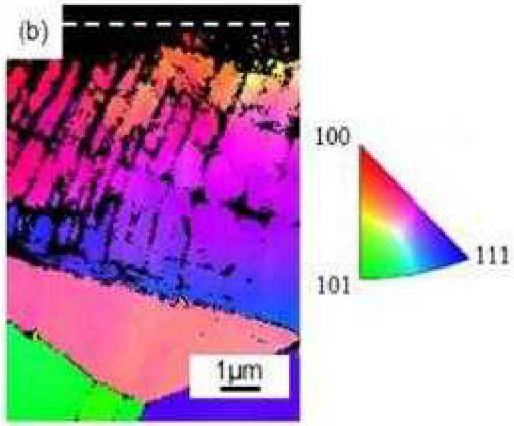
HIGH RH: NaCl RICH BRINE



LOW RH: $MgCl_2$ RICH BRINE







CURRENT MODEL ASSUMPTION: ***HEMISPHERICAL PITS***

- DEFORMATION FROM GRINDING MAY BE RESPONSIBLE FOR *MORPHOLOGY AT LOW RH* AND *SUSCEPTIBILITY TO CRACKING*

Cathodic Kinetics Controlling Pit Morphology
f (T, RH, Salt Load, Chemistry)

RH Effects Brine Characteristics and Pit Morphologies

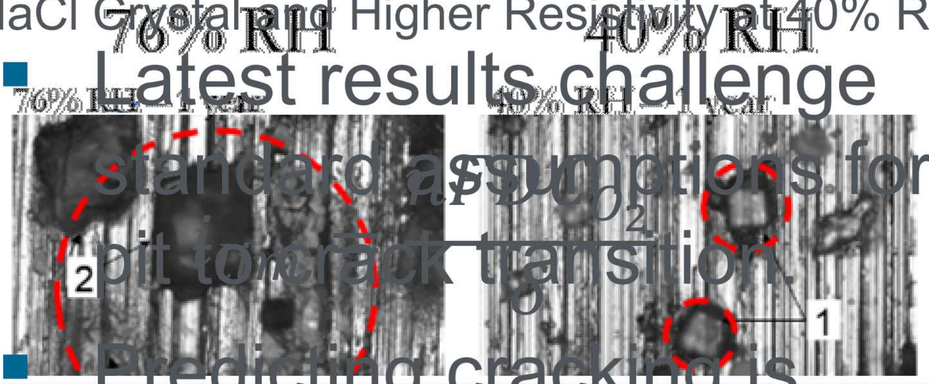
1) The ***available area*** surrounding a pit that can serve as a cathode.

2) Ohmic drop between the corroding pit areas and the surrounding cathode.

3) Electrolyte properties ***control cathodic kinetics*** (diffusion controlled and charge transfer controlled)

Current Status:

NaCl Crystal and Higher Resistivity at 40% RH



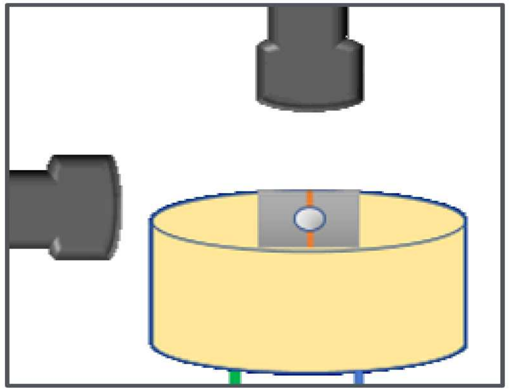
- Latest results challenge standard assumptions for pit to crack transition.
- Predicting cracking is more complicated.
- Current work focused on understanding factors for crack initiation

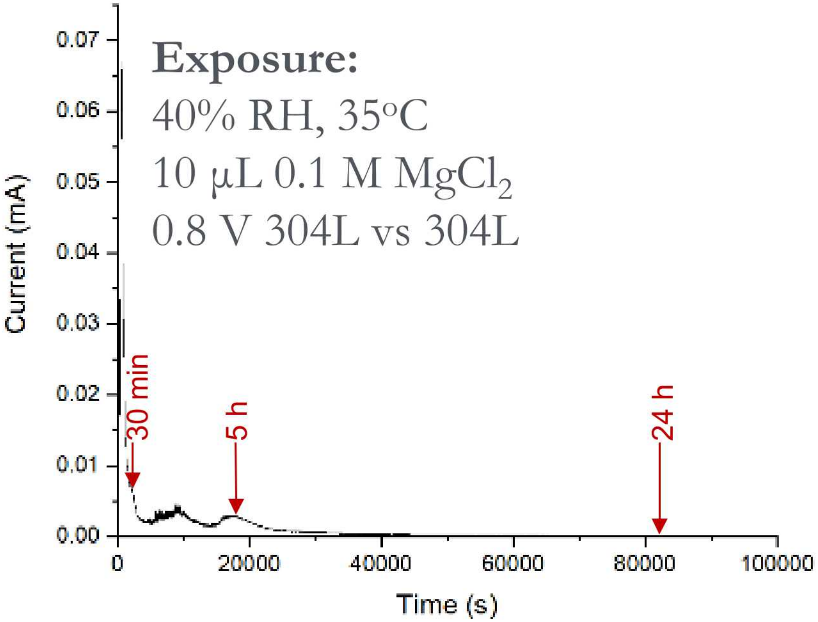
Properties of evaporated sea salt brine at 35°C

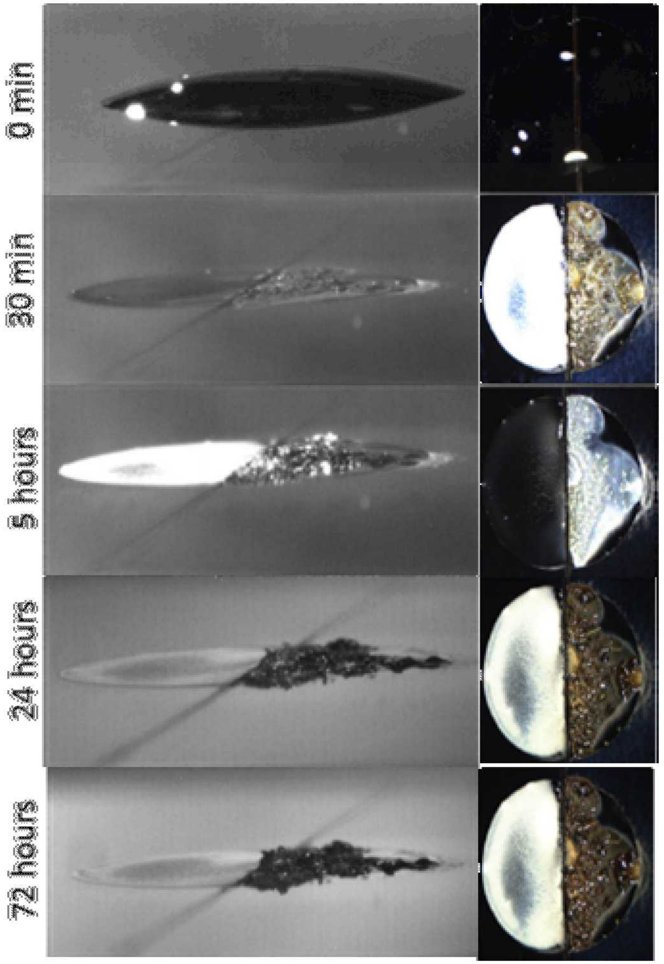
RH / %	$[O_2]$ / molal	[η] / cP	$[D_{O2}]$ / m^2/s	[κ] / mS/cm	[ρ] / Kg/m^3
40	[illegible]	8.31	[illegible]	[illegible]	1.33
76	[illegible]	1.65	[illegible]	[illegible]	1.20

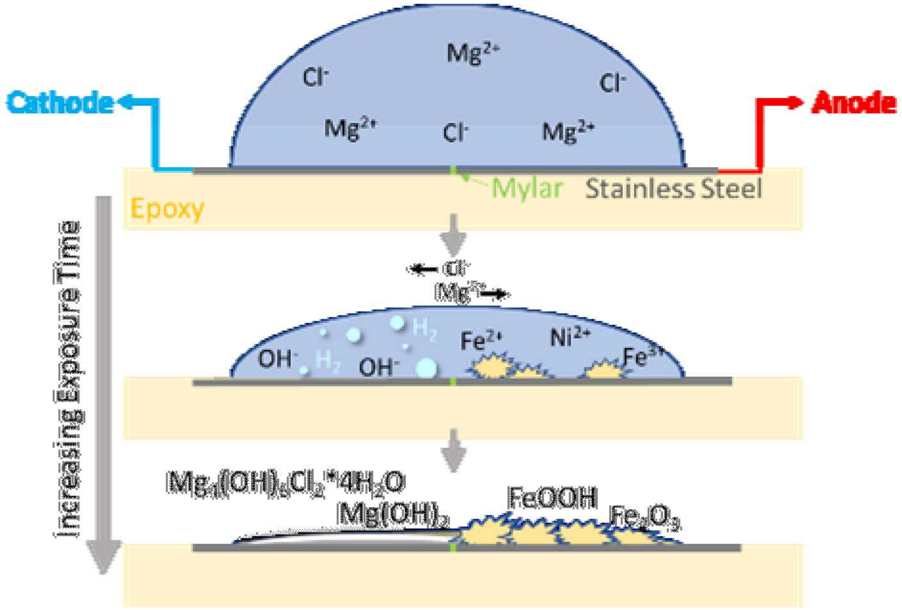
Brine Interaction with Corrosive Environment
f (T, RH, Salt Load, Chemistry) ?

Dual Electrode Exposure







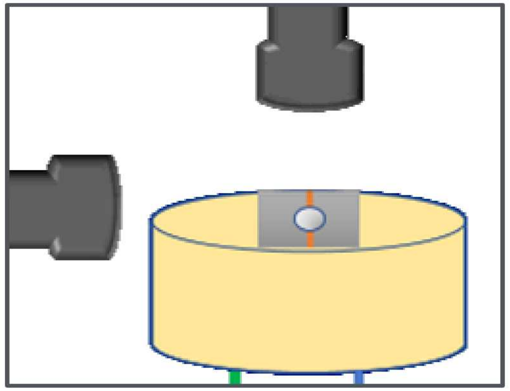


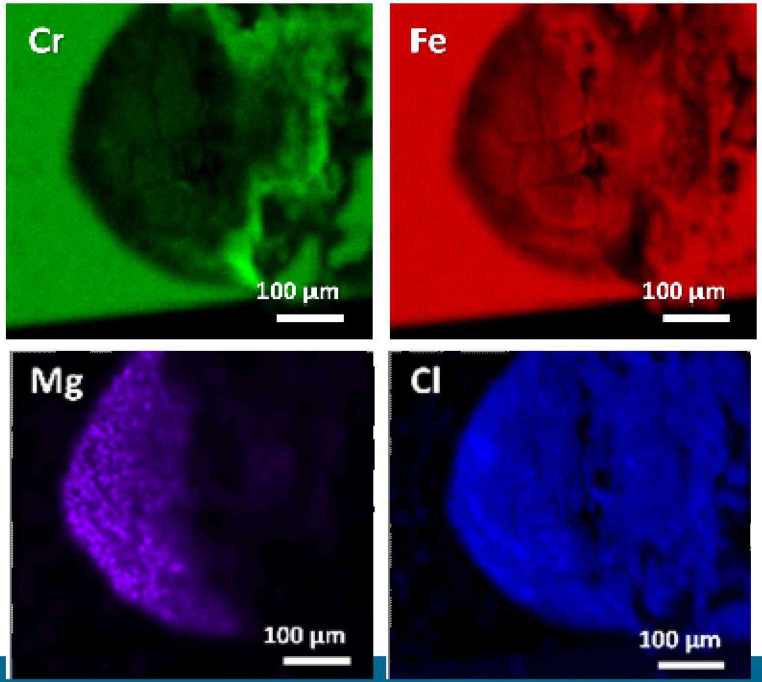
Current Status:

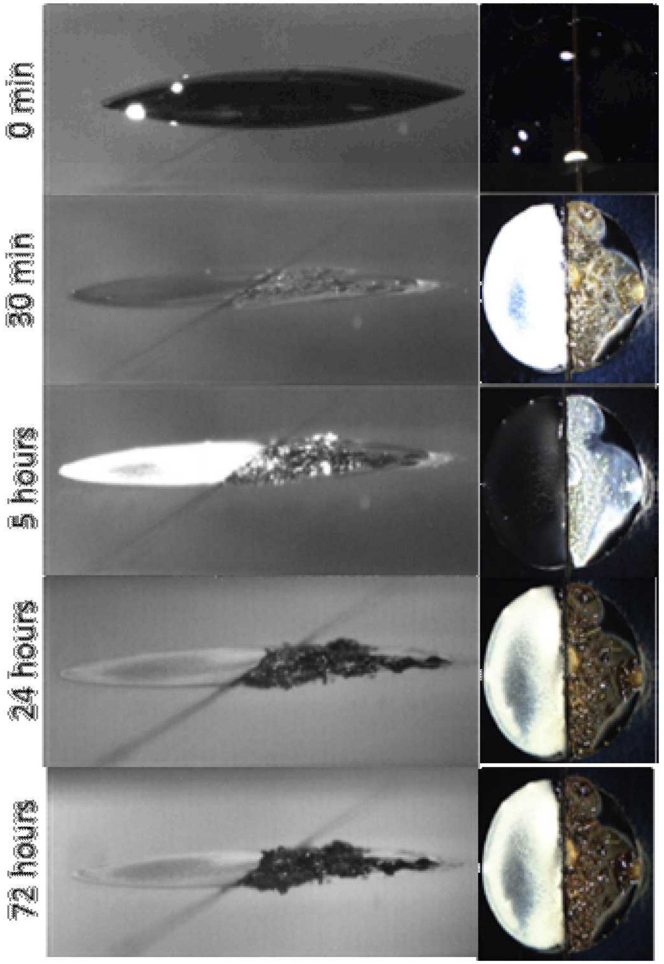
- Brine evolution during corrosion
- Correlate extent of corrosion with brine conditions?

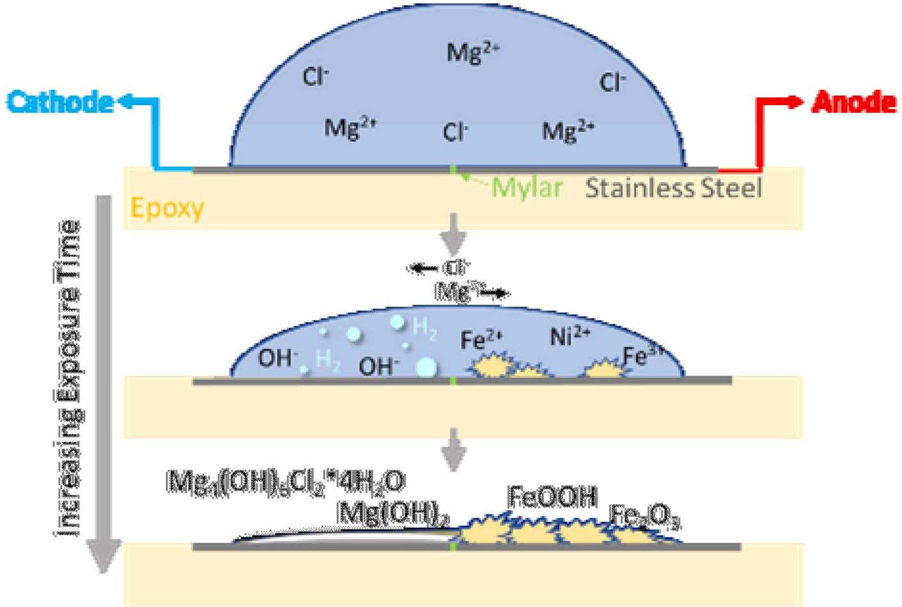
Brine Interaction with Corrosive Environment
f (T, RH, Salt Load, Chemistry) ?

Dual Electrode Exposure









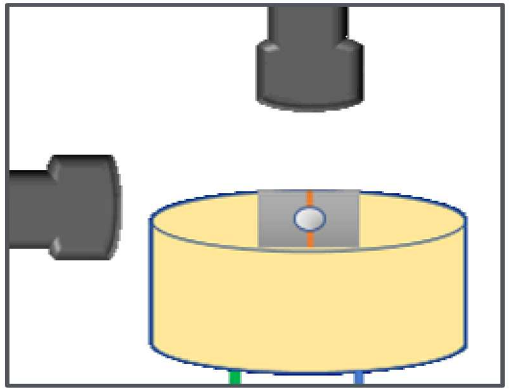
Current Status:

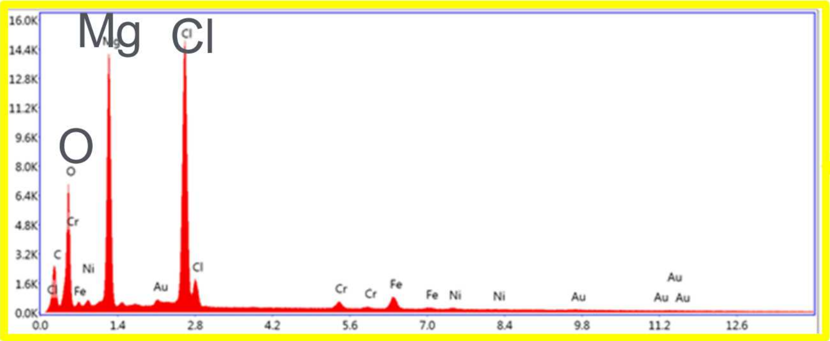
- Brine evolution during corrosion
- Correlate extent of corrosion with brine conditions?

← EDS maps Post-corrosion

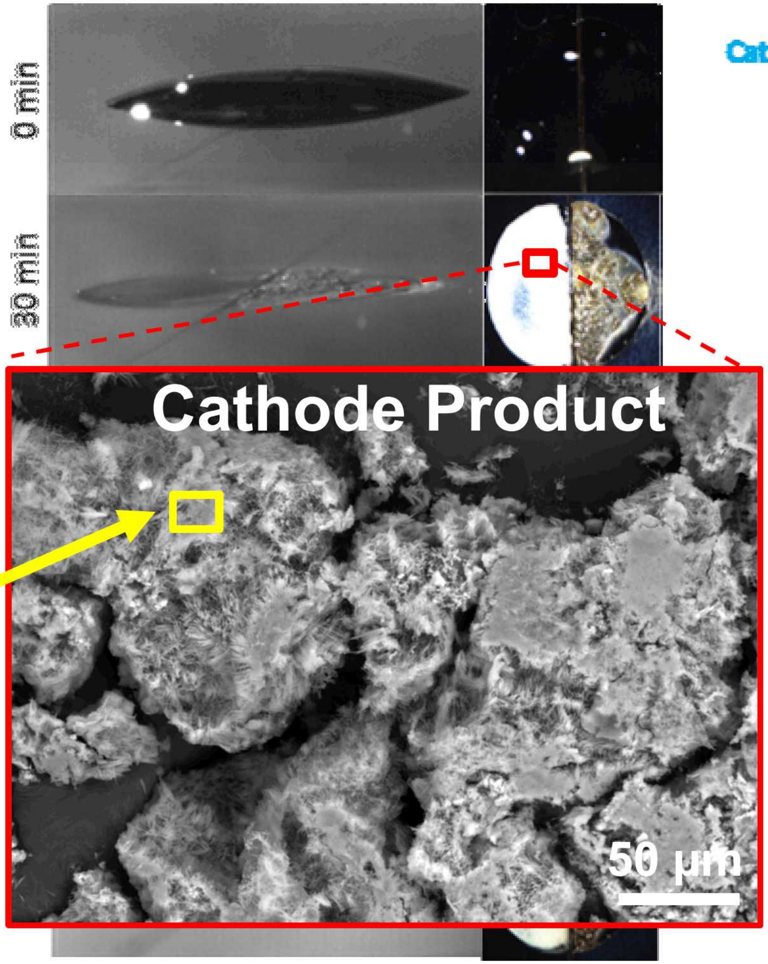
Brine Interaction with Corrosive Environment
f (T, RH, Salt Load, Chemistry) ?

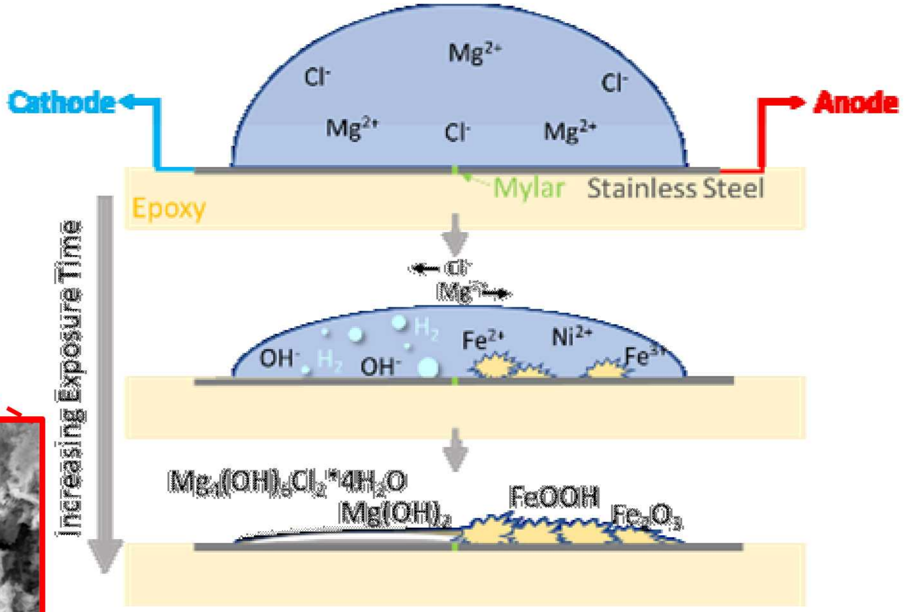
Dual Electrode Exposure





Mg/Cl/O rich bladed materials, likely magnesium hydroxychlorides





Current Status:

- Brine evolution during corrosion
- Correlate extent of corrosion with brine conditions?

Characterization of SCC in Canister-Relevant Weld Regions

"Big Plate" Sandia Mockup Exposure Samples

- 8 g/m^2 $MgCl_2$
  - Exposure: 80ºC, 35 % RH, 12 months
  - 3 % Potassium Tetrathionate, pH =1, 6 mo. (3 mo. 40ºC)
- Analysis
  - Composition of brine and corrosion products
  - NDE inspections for SCC
    - Fluorescent Dye Penetrant
    - UT Phased Array & Eddy Current Array
- Goals
  - Determine orientation and location of SCC around canister welds
  - Evaluate brine evolution under corrosion

80ºC, 35 % RH

Circumferential Weld

80ºC, 35 % RH

Longitudinal Weld

80ºC, 35 % RH

4-point bend specimen

Potassium Tetrathionate

Circumferential Weld

Characterization of SCC in Canister-Relevant Weld Regions

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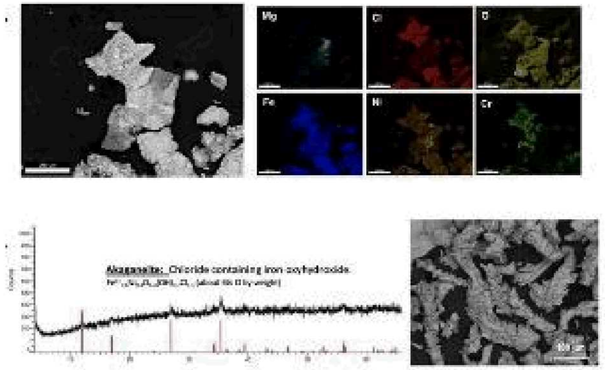


SEM/EDS and XRD of Corrosion products

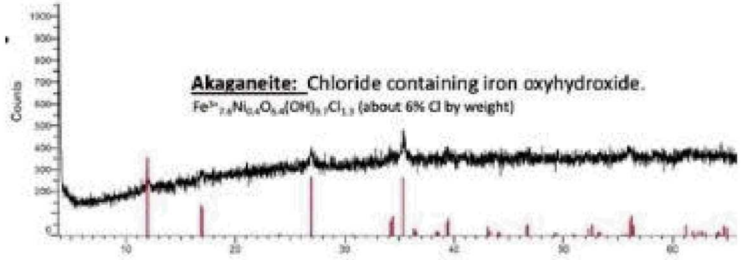
Fluorescent Dye Penetrant

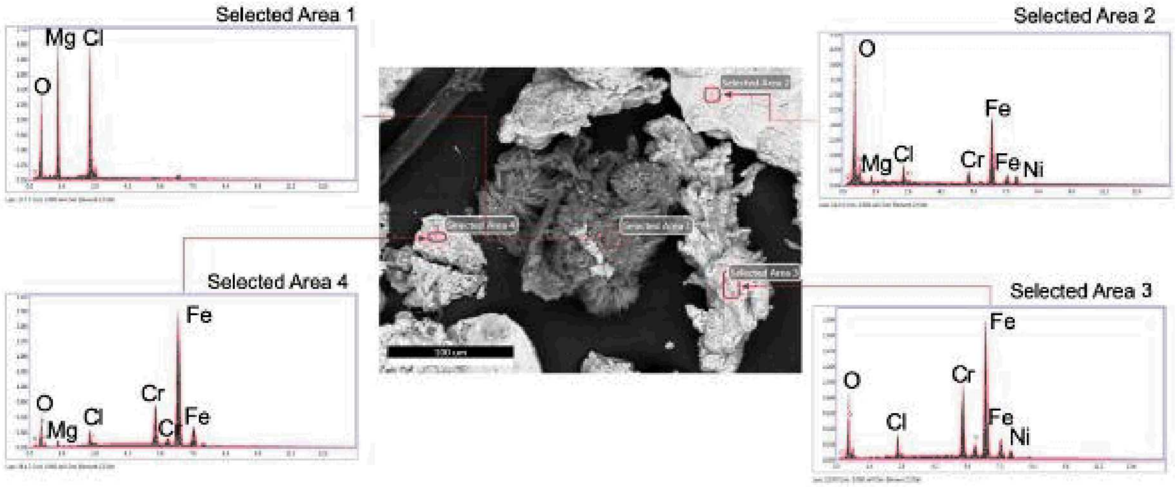
Eddy Current Array

UT Phased Array

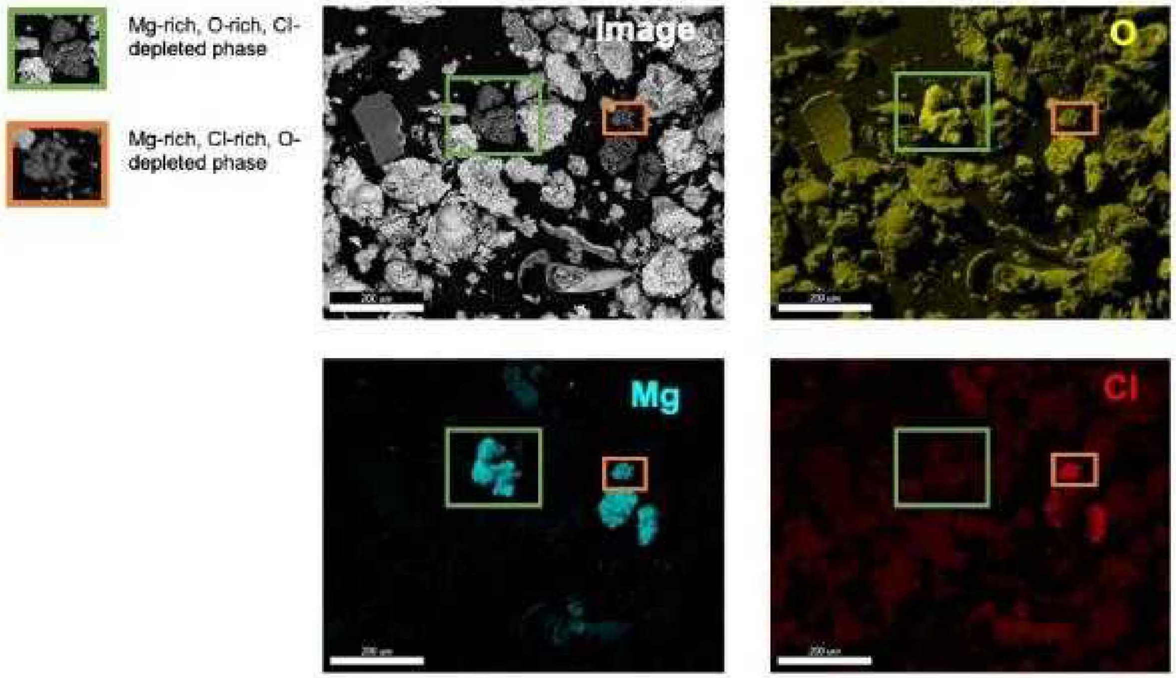
Chemical Composition of Brine and Corrosion Products

- Corrosion Products
  - Iron containing corrosion products were largely amorphous
    - Akageneite was identified by XRD





- Brine Evolution
  - Distinct Mg containing phases were found
    - O-rich/Cl-depleted: Likely mg-hydroxychloride (2-1-4 phase)
    - Cl-rich: Likely bischofite



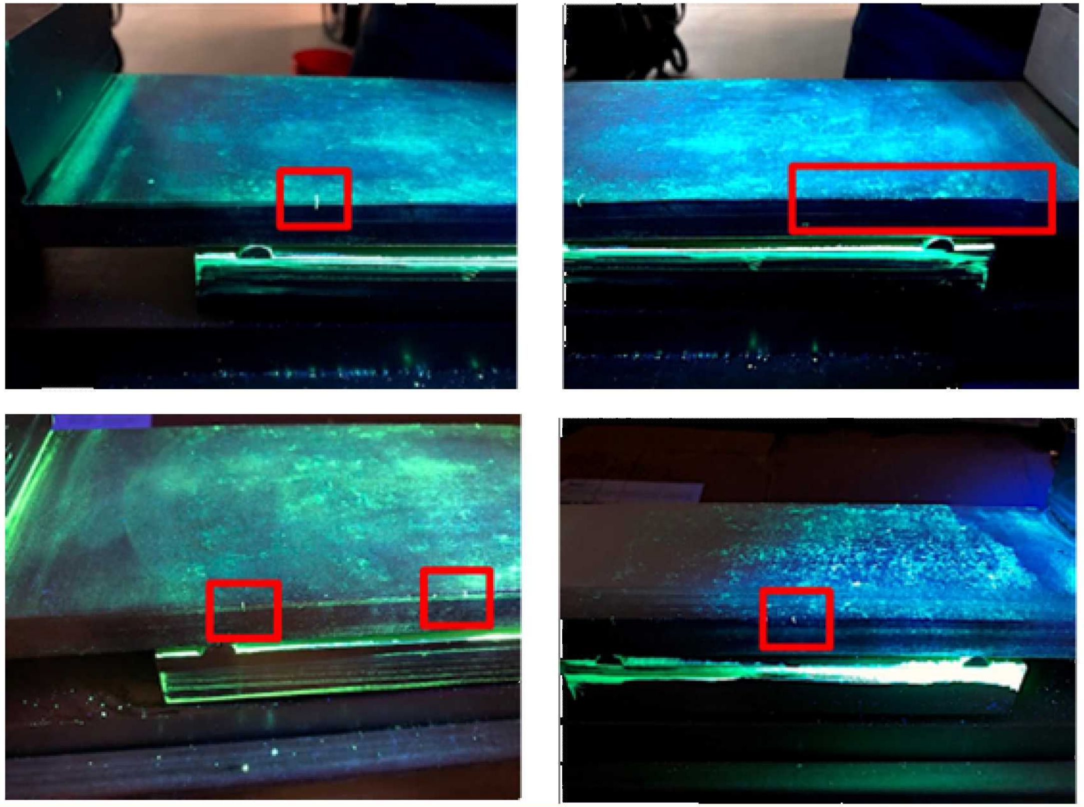
Dye Penetrant Analysis

- Presence of cracks on the edge of the 4-point bend specimen
- No crack indications found in mock up welded plates

→ Mockup plate samples were subsequently analyzed by *Eddy current & Phased Array*

Part Inspected	Exposure	Crack Indications	Notes
Circumferential Weld	80 C, 35% RH	No	
Longitudinal Weld	80 C, 35% RH	No	High background due to corroded surface
Circumferential Weld	Potassium Tetrathionate	No	
4 Point Bend Specimen	80 C, 35% RH	Yes	

4-point bend specimen



Eddy Current and Phased Array

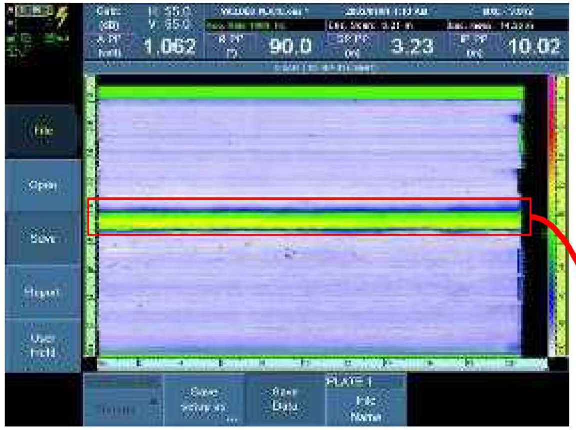
– Flaws were identified
  - Most likely caused from manufacturing
– No crack indications detected in any mockup plate sample

Current Status:

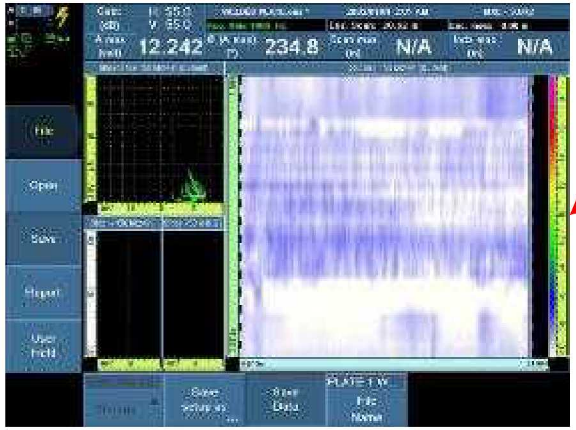
- Further analysis through SEM/EBSD to inspect corrosion damage/ identify if microcracks formed

Circumferential weld, 80 C, 35 % RH

Eddy Current



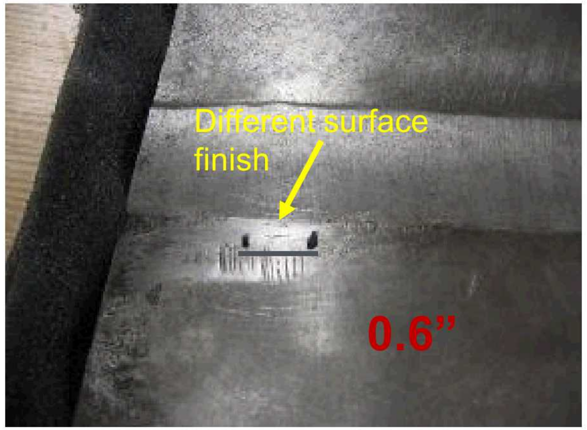
Top: No flaw indications.



Top scan of weld: No flaw indications.

Phased Array

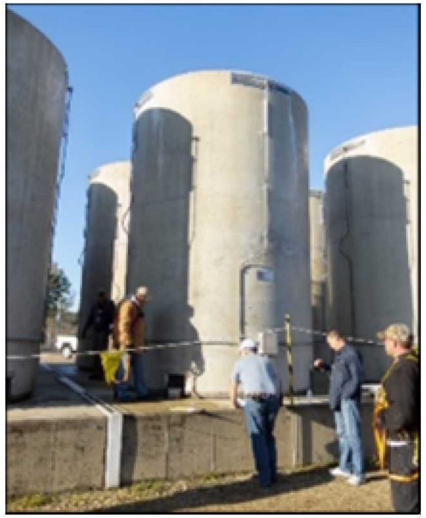
Indication seen

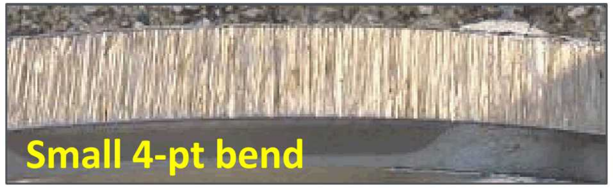


Indication marked on surface of plate to

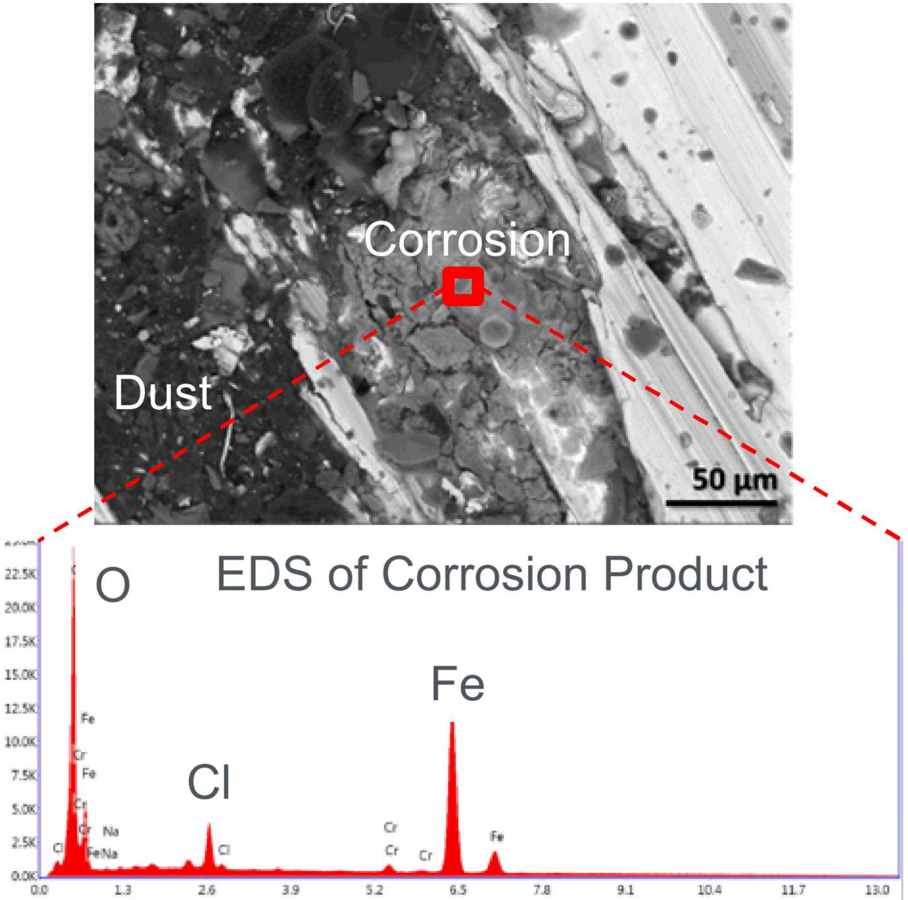
Characterization of corrosion under field conditions

Maine Yankee ISFSI Sampling, Aug. 2017 - Oct. 2019

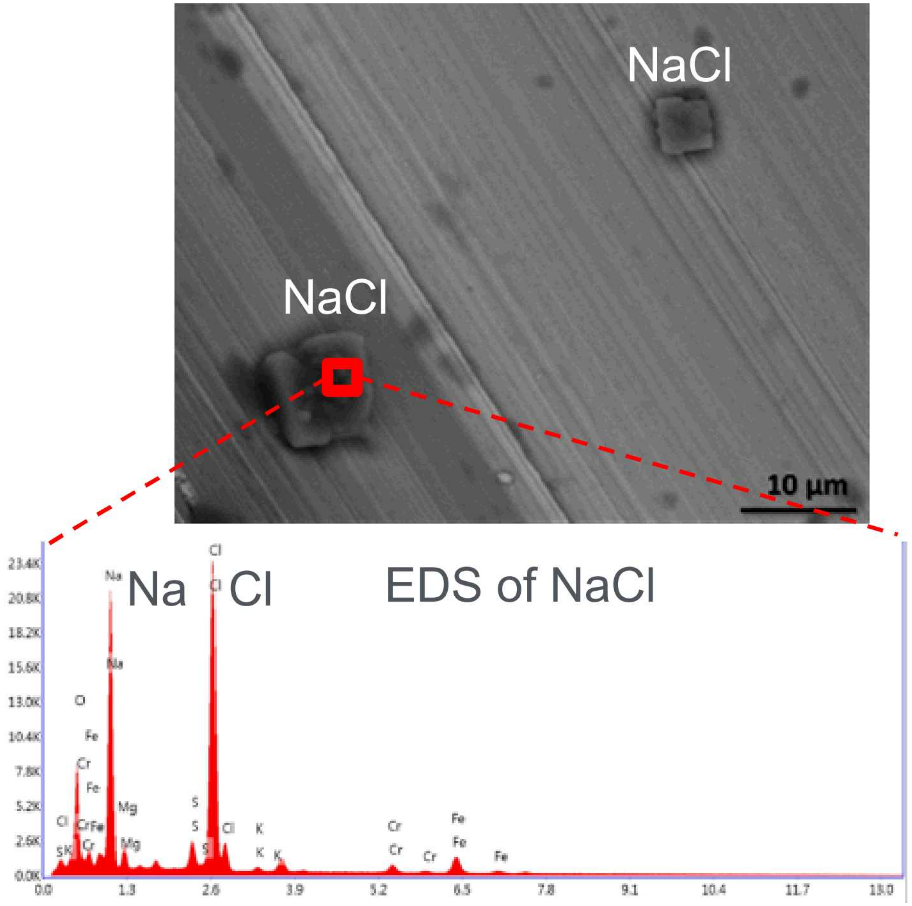




Small 4 Pt Bend: Outlet Location



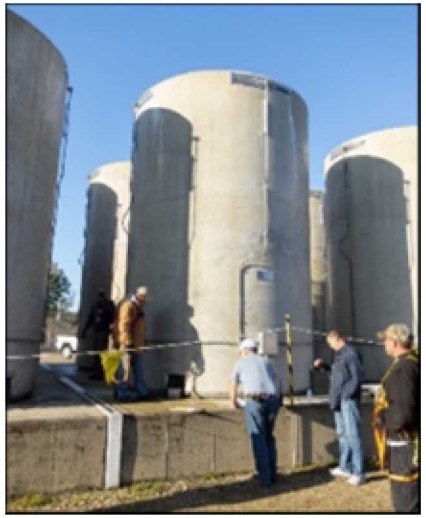
Small 4 Pt Bend: Outlet Location

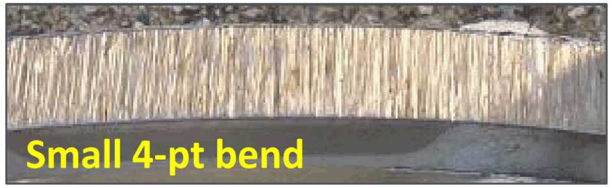


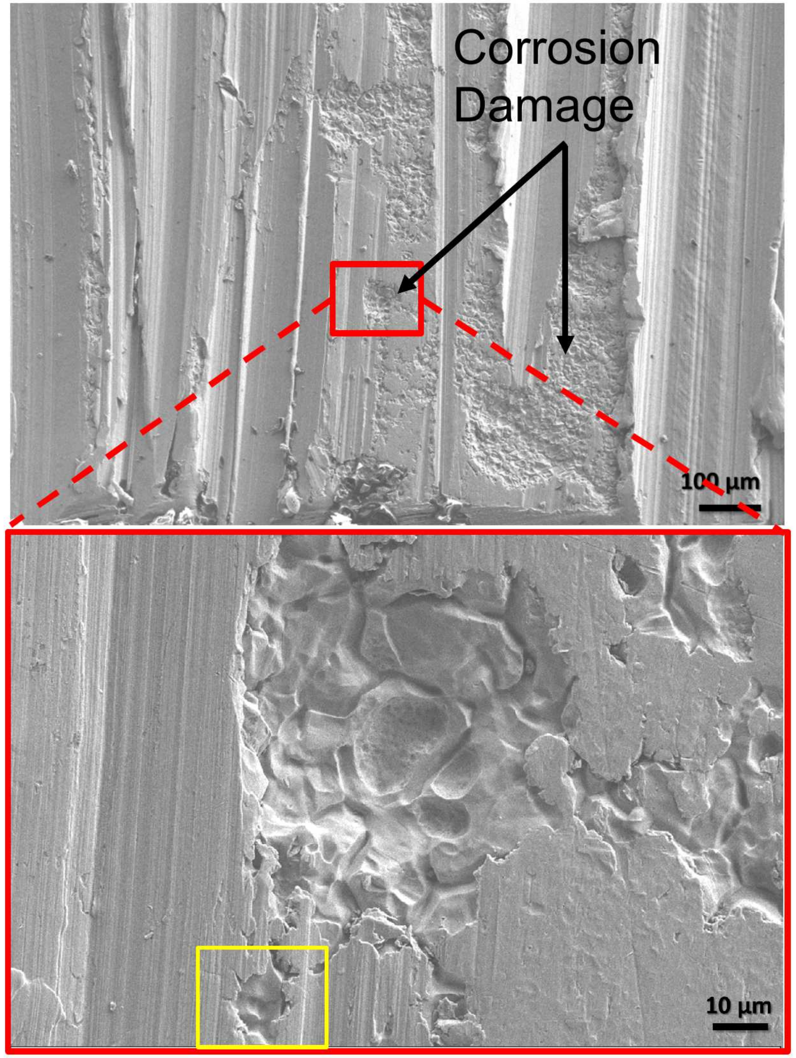
Sample from VCC 42 High heat load, outlet in prevailing wind

Characterization of corrosion under field conditions

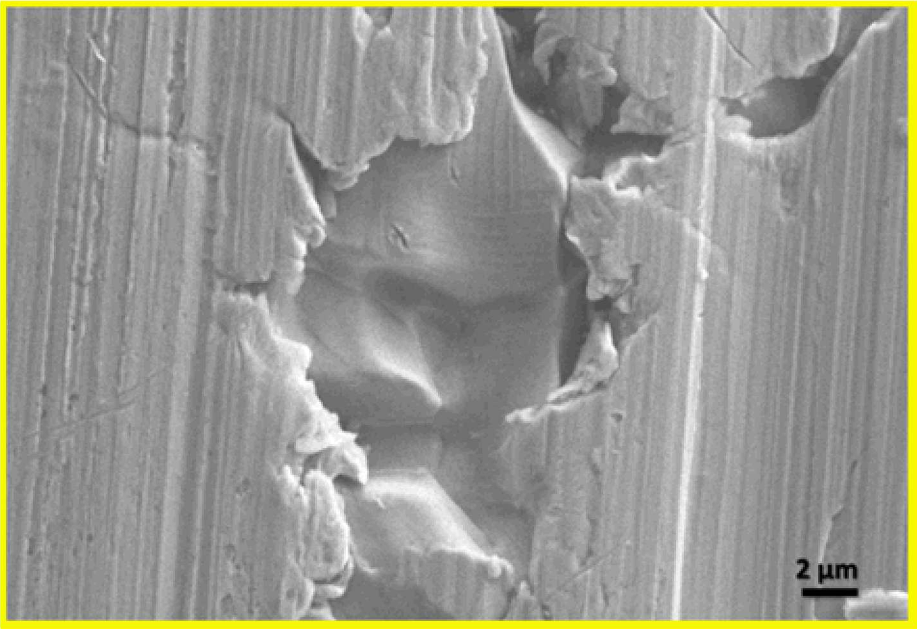
Maine Yankee ISFSI Sampling, Aug. 2017 - Oct. 2019







Small 4 Pt Bend: Outlet Location



Current Status:

- Corrosion damage observed under field exposure after 2 years
- Continued exposure of large 4 pt bends, small 4 pt bends, and dust collectors for another 2 year time period

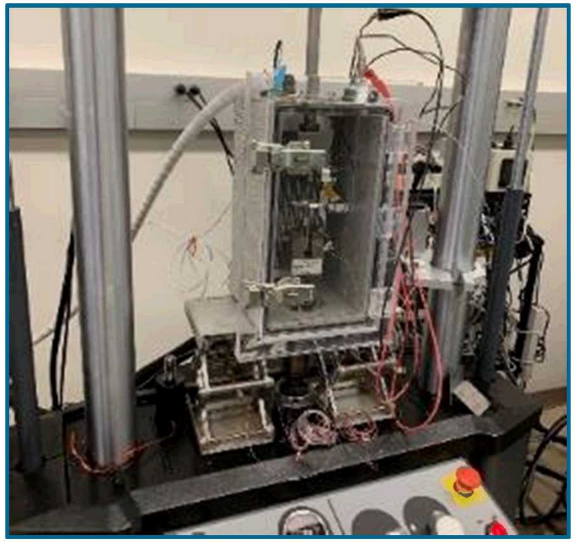
Initial SCC Testing for Canister Relevant Conditions

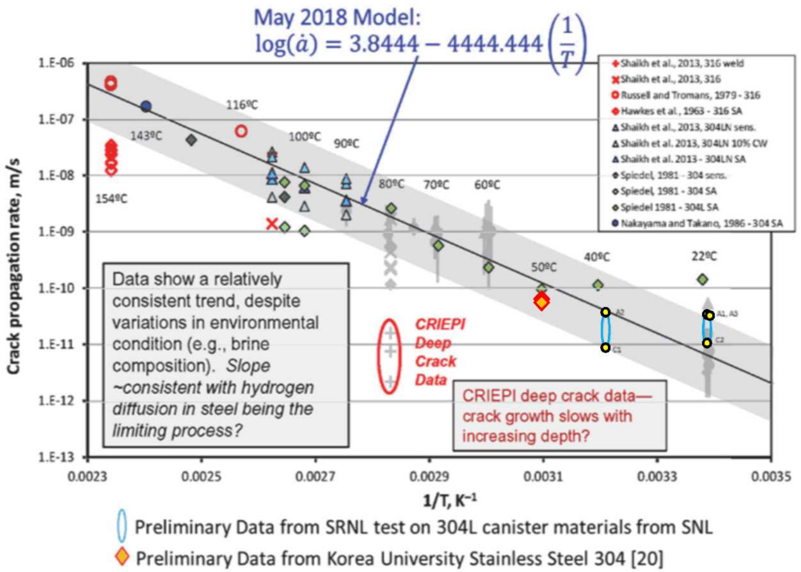
KNOWLEDGE GAPS

CGR data for austenitic SS in relevant atmospheric environments is lacking

GOALS

1) Quantify SCC behavior of SS via CGR vs. K in atmospheric conditions
2) Validation and development of SCC models





Current Status:

Pit to crack-

- With OSU, developed a method for periodic loading
- FY19, generated data for sample under atmospheric salt load
- Characterization of features controlling pit-to-crack transition underway.

SCC-

- 4 new load frames procured
- Load frame and sample development for atmospheric SCC testing underway: SENT vs. CT sample, pre-cracked and ground

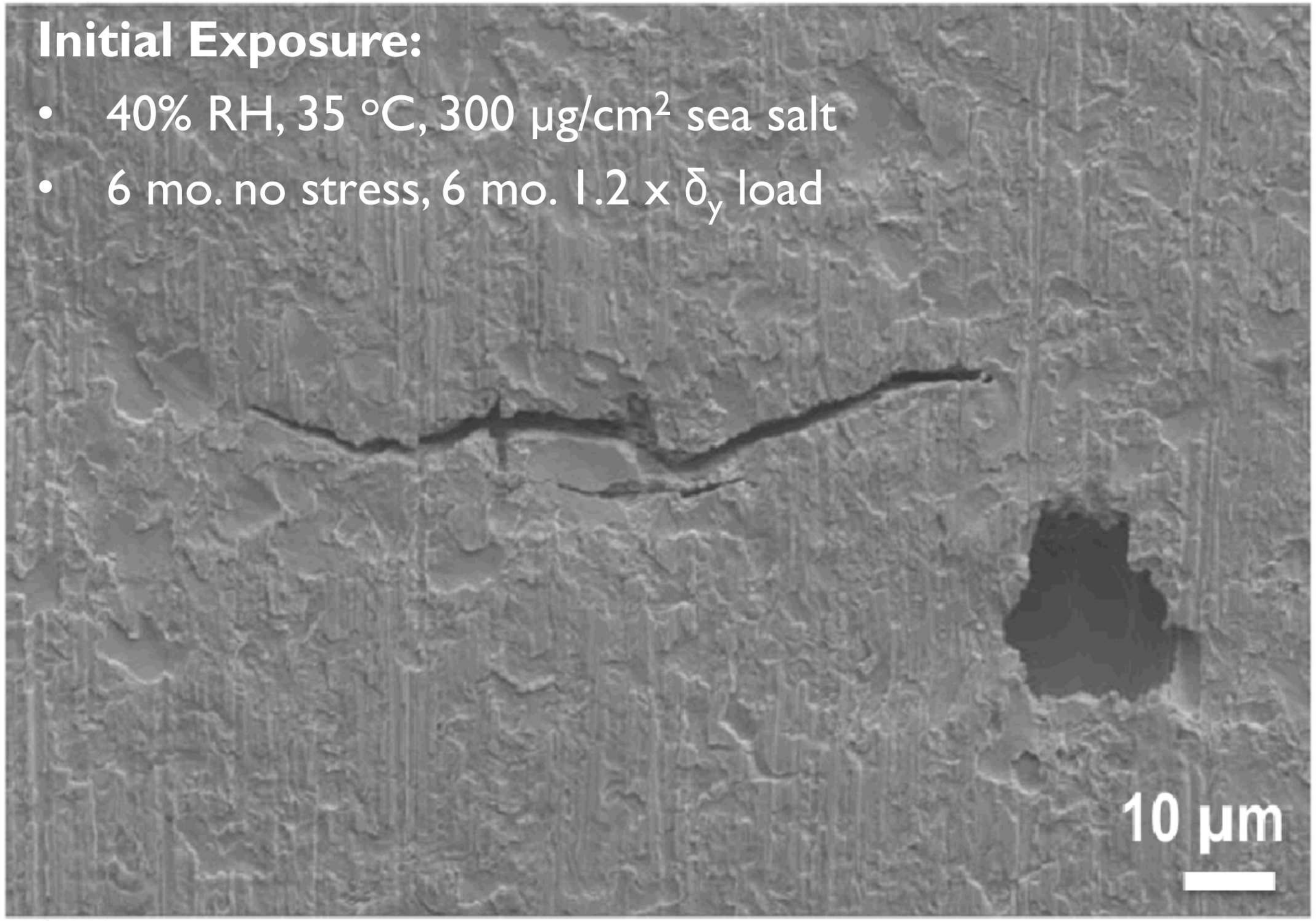
Initial SCC Testing for Canister Relevant Conditions

Knowledge Gaps

CGR data for austenitic SS in relevant atmospheric environments is lacking

Goals

1) Quantify SCC behavior of SS via CGR vs. K in atmospheric conditions
2) Validation and development of SCC models



Cracks observed associated with pits

- *Unclear if cracks formed during exposure or while under load*

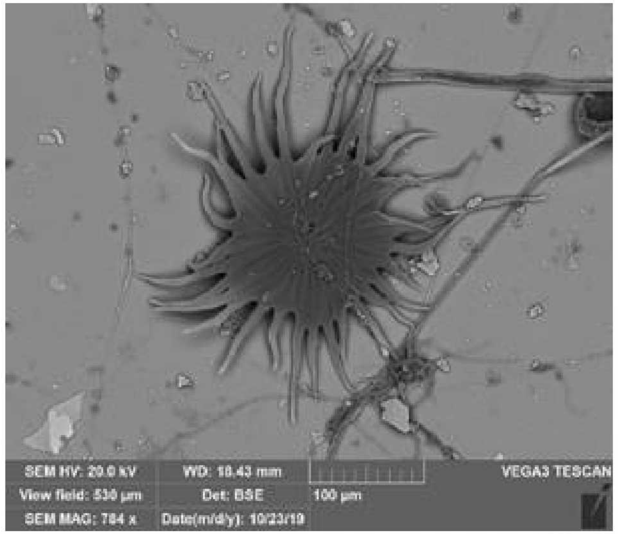
Summary and Next Steps

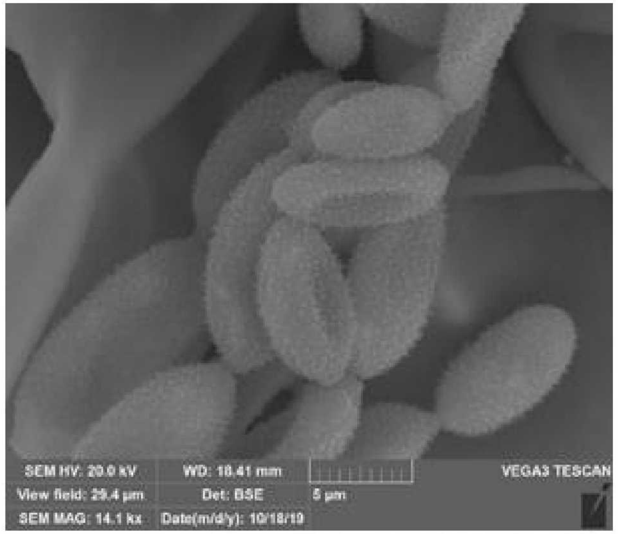
- Experimental Results:
  - Large scale atmospheric exposures displayed dependence of pitting and morphology as a *f(Environment)*
  - SCC atmospheric weld exposures displayed very few detectable cracks
  - Corrosion field exposures displayed small amounts of corrosion after two year exposures

- *Implications: SCC Model Assumptions may be challenged by:*
  - *f(environment)*
  - Material microstructure
  - Brine evolution during corrosion processes

- Next steps:
  - Determine validity of SCC model assumptions with respect to ***pitting, pit-to-crack, and crack growth*** as a ***f(Environment and material)***
    - *What is the primary factor that governs pit morphology?*
    - *Is pit-crack transition influenced by f(Environment) and pit morphology?*
    - *Is crack growth rate a f(Environment)?*

Questions?


SEM HV: 20.0 kV
WD: 18.43 mm
VEGA3 TESCAN
View field: 530 µm
Det: BSE
100 µm
SEM MAG: 784 x
Date(m/d/y): 10/23/19


SEM HV: 20.0 kV
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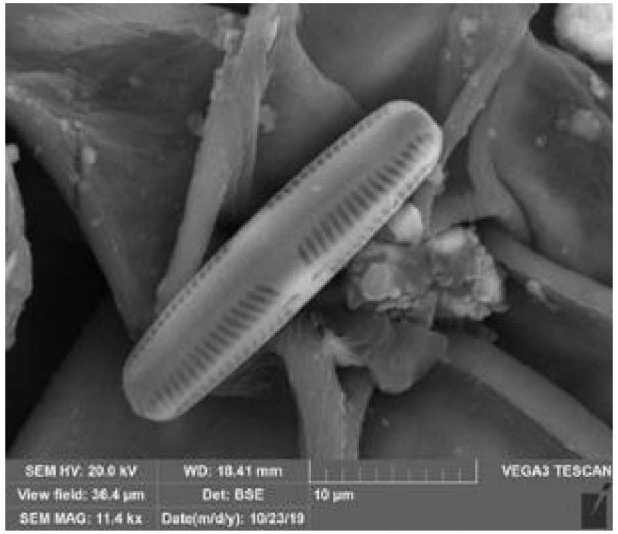
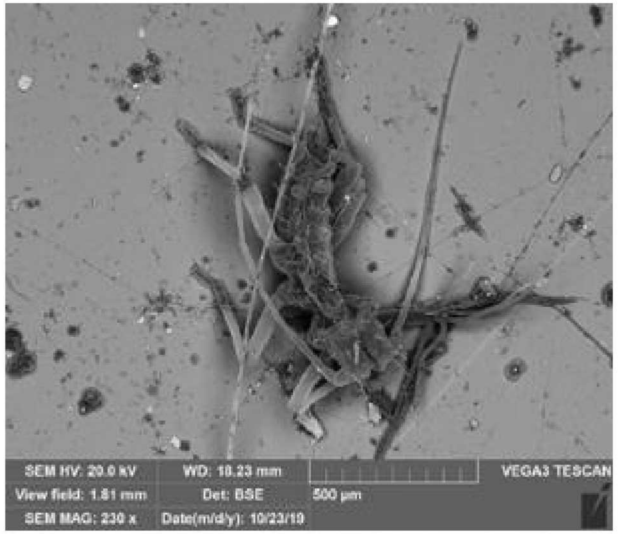
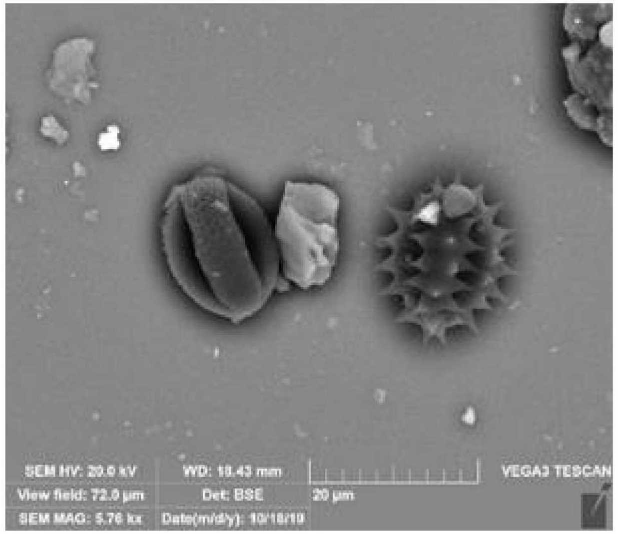
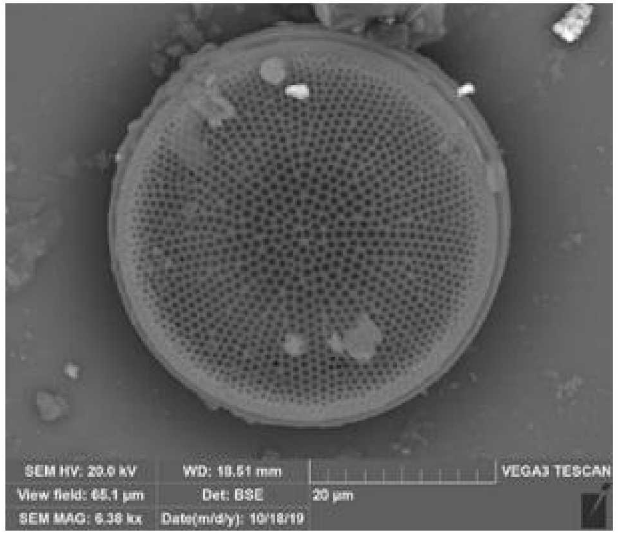
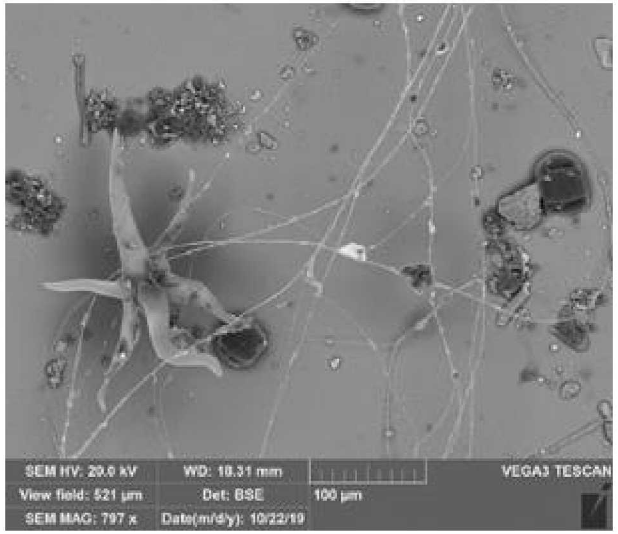
VEGA3 TESCAN
View field: 29.4 µm
Det: BSE
5 µm
SEM MAG: 14.1 kx
Date(m/d/y): 10/18/19

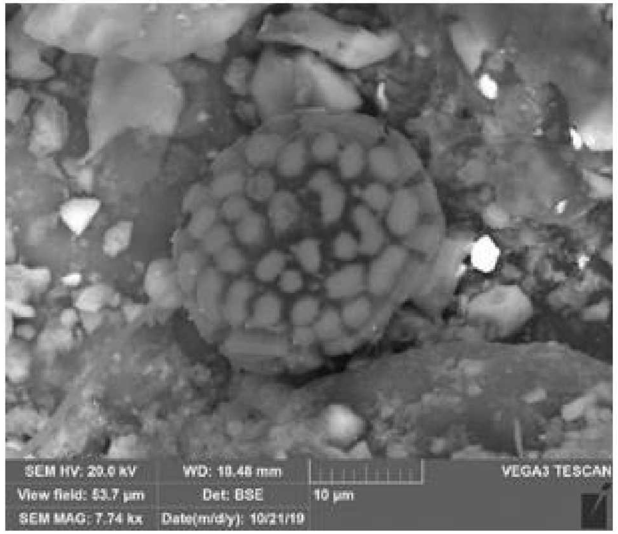

SEM HV: 20.0 kV
WD: 18.41 mm
VEGA3 TESCAN
View field: 36.4 µm
Det: BSE
10 µm
SEM MAG: 11.4 kx
Date(m/d/y): 10/23/19


SEM HV: 20.0 kV
WD: 18.23 mm
VEGA3 TESCAN
View field: 1.81 mm
Det: BSE
500 µm
SEM MAG: 230 x
Date(m/d/y): 10/23/19


SEM HV: 20.0 kV
WD: 18.43 mm
VEGA3 TESCAN
View field: 72.0 µm
Det: BSE
20 µm
SEM MAG: 5.76 kx
Date(m/d/y): 10/18/19


SEM HV: 20.0 kV
WD: 18.51 mm
VEGA3 TESCAN
View field: 65.1 µm
Det: BSE
20 µm
SEM MAG: 6.38 kx
Date(m/d/y): 10/18/19


SEM HV: 20.0 kV
WD: 18.31 mm
VEGA3 TESCAN
View field: 521 µm
Det: BSE
100 µm
SEM MAG: 797 x
Date(m/d/y): 10/22/19


SEM HV: 20.0 kV
WD: 18.48 mm
VEGA3 TESCAN
View field: 53.7 µm
Det: BSE
10 µm
SEM MAG: 7.74 kx
Date(m/d/y): 10/21/19