



# SNF Storage Canister Pitting and SCC: Current Research at Sandia National Labs

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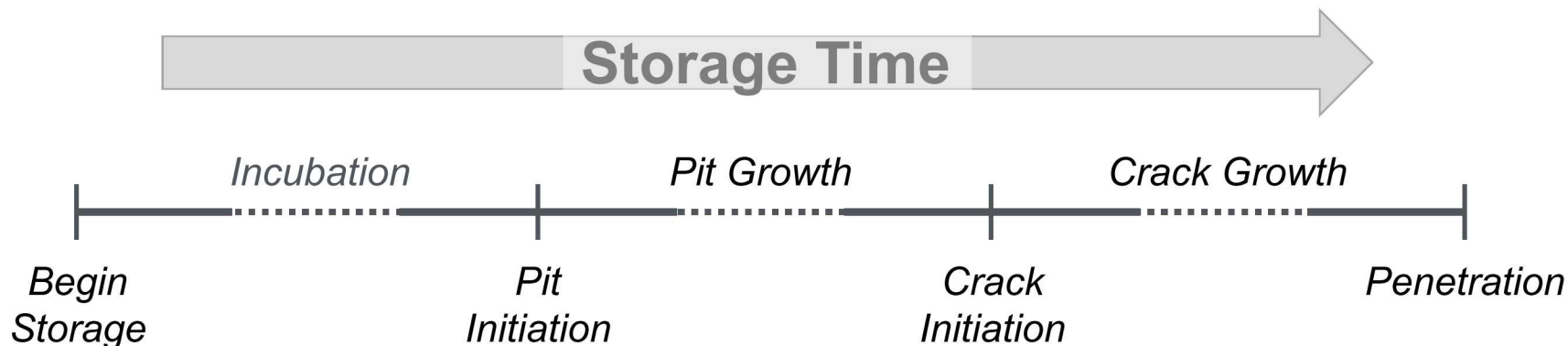
EPRI Extended Storage Collaboration Program  
November 7, 2018

# SNL Objectives

## **Overall objective: Improve 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 load and 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

# Canister SCC: Collaborations



**SNL** — Surface Environment, Brine Stability

**CSM/SNL** — Pitting Initiation and Growth (Effect of Stress)

**SNL/OSU** — Pitting Initiation and Growth, Pit-to-Crack Transition

**SNL/UVA** — Pitting Initiation and Growth, Crack Growth Rate

**CSM** — Pit-to-Crack Transition (Modeling)

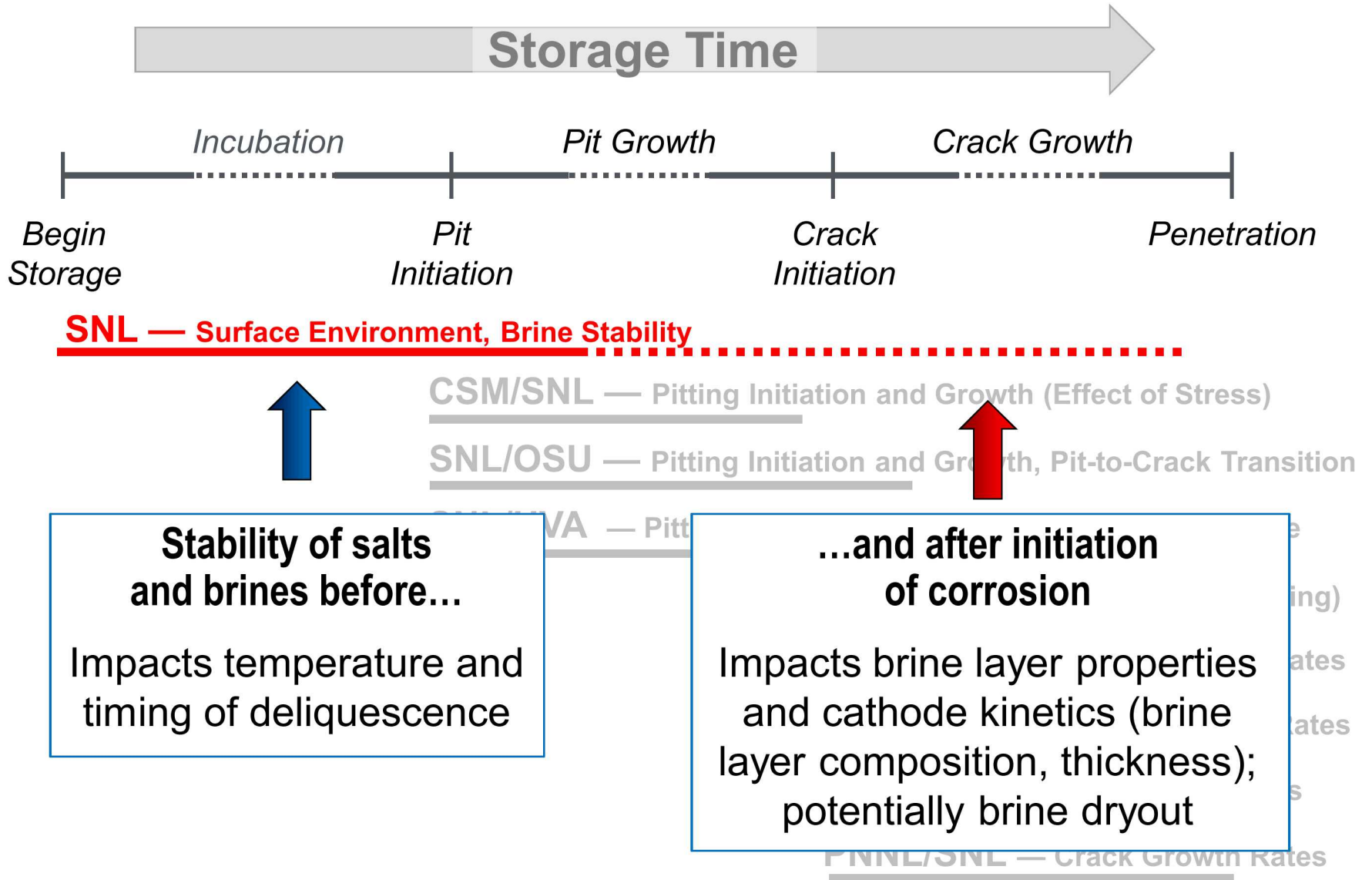
**SRNL (SNL)** — Crack Growth Rates

**NCSU (SNL)** — Crack Growth Rates

**OSU/SNL** — Crack Growth Rates

**PNNL/SNL** — Crack Growth Rates

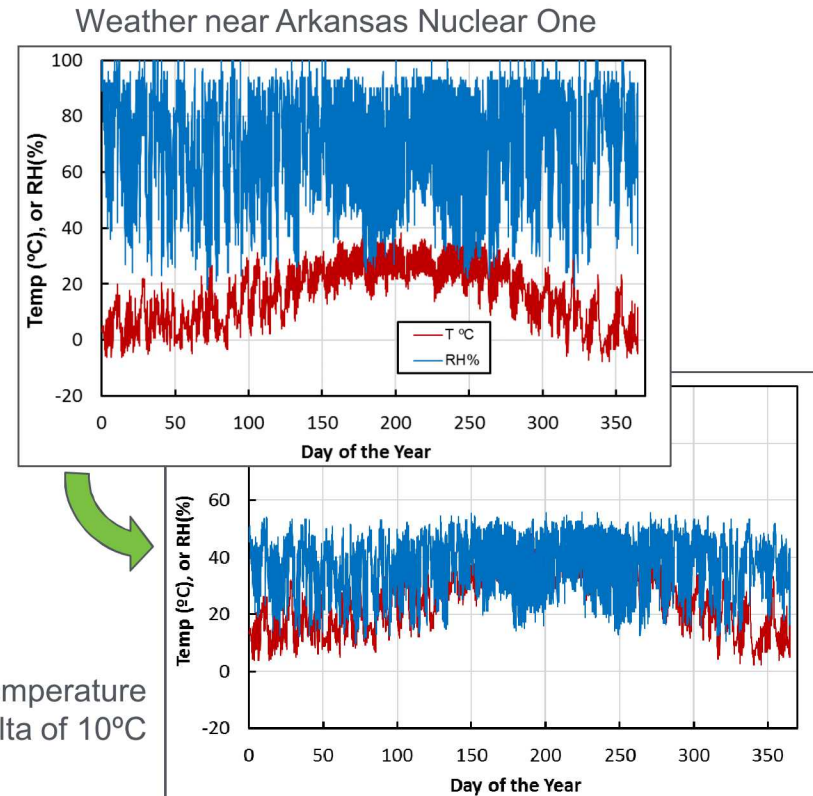
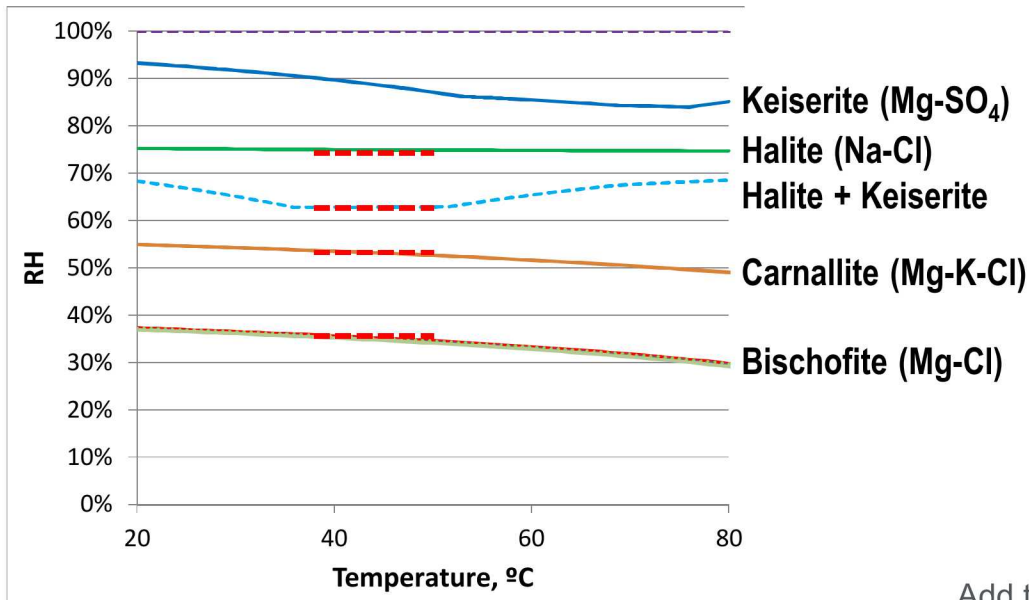
# Canister SCC: Surface Environment



# Stability of Mg-Cl brines

## Why Study MgCl<sub>2</sub> Brines?

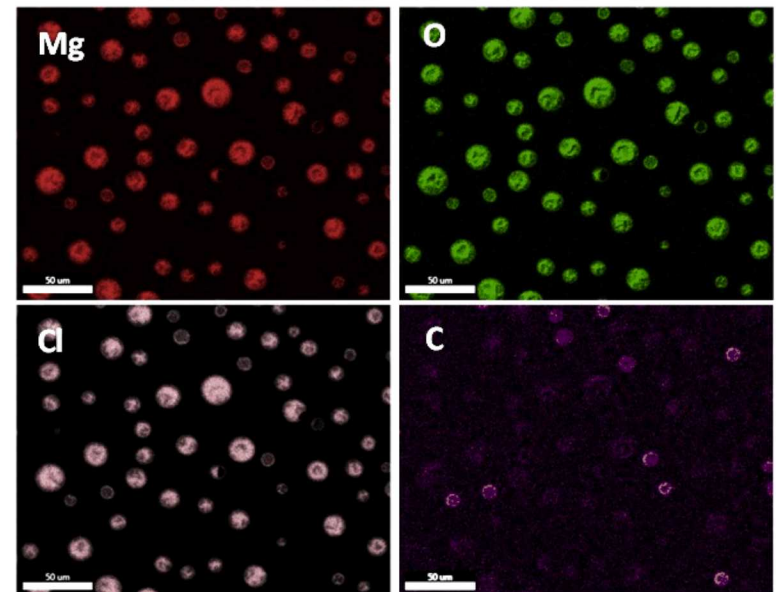
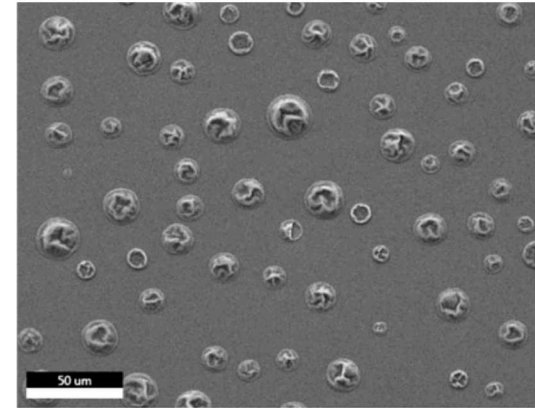
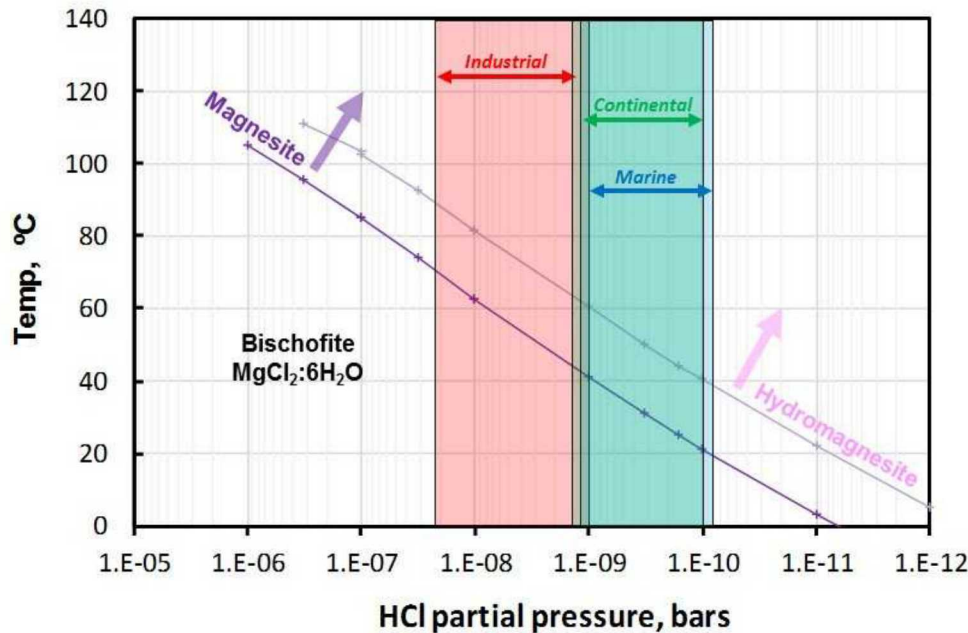
- As temperatures drop and sea-salts deliquesce, MgCl<sub>2</sub> brines are the first to form—lowest deliquescence RH.
- If MgCl<sub>2</sub> brines are not stable, deliquescence RH is much higher, delaying corrosion until temperatures drop to much lower levels.



Add temperature delta of 10°C

# Brine Stability Prior to Corrosion: Previous Work

MgCl<sub>2</sub> brine stability near the max. temp. at which deliquescence can occur on a canister



48°C, 40% RH (8 weeks of exposure)

- Partial conversion to non-deliquescent Mg-carbonate
- Low air flow rates in experimental system limited conversion

# Brine Stability:

## MgCl<sub>2</sub> Brines at Elevated Temperatures

Why study MgCl<sub>2</sub> brine stability at higher temperatures?

- Because experiments are frequently carried out under “accelerated” (high temperature) conditions.
- Interpreting those experiments requires understanding brine stability

Current Experiment: MgCl<sub>2</sub> brine stability at 80°C and 35% RH

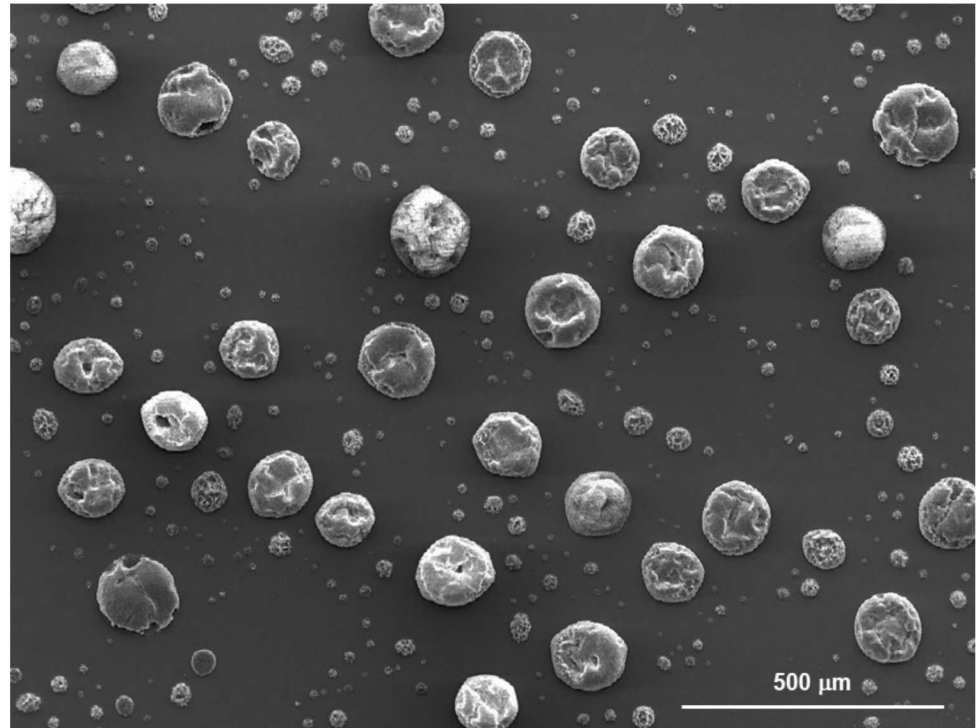
- Conditions for “big-plate corrosion” experiment by SNL
- Conditions for CRIEPI SCC experiments
- Will experimental brines (Mg-Cl or seawater) dry out?

# Brine Stability: $\text{MgCl}_2$ brine at 85°C and 35% RH

## Experimental conditions:

- 85°C, 35% RH
- Inert substrate (Si wafer)
- 300  $\mu\text{g}/\text{cm}^2$   $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (1520  $\mu\text{g}/\text{sample}$ ): 105  $\mu\text{g}/\text{cm}^2$  Cl (530  $\mu\text{g}/\text{sample}$ )
- Deposited using inkjet printer (droplets ~10 to 150  $\mu\text{m}$  in diameter)
- Airflow rate 2 liters/minute
- Sampled after 2/4/8 weeks.

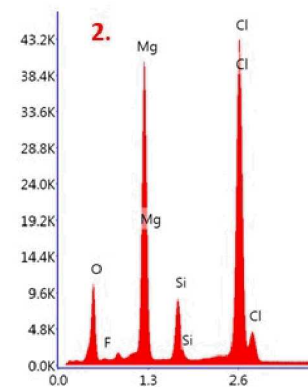
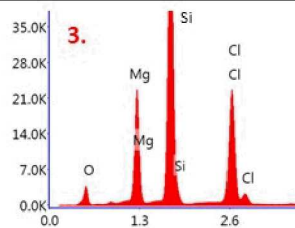
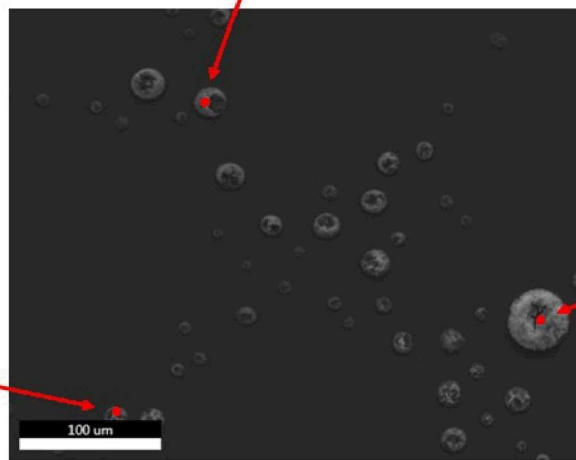
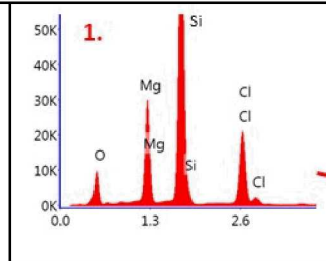
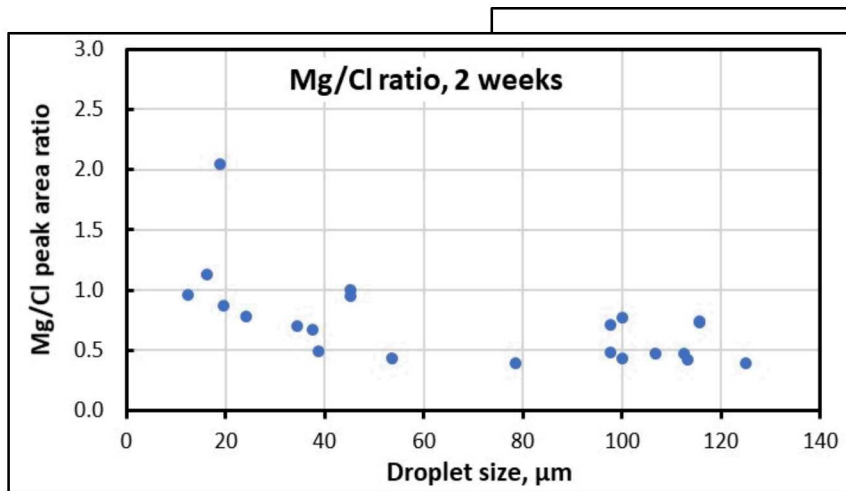
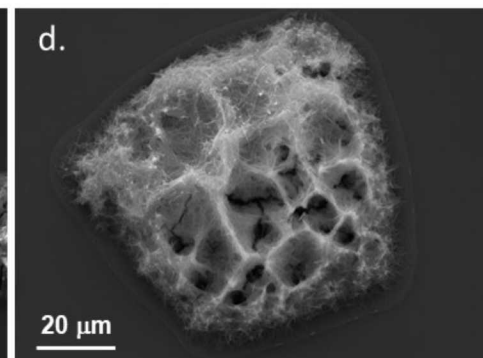
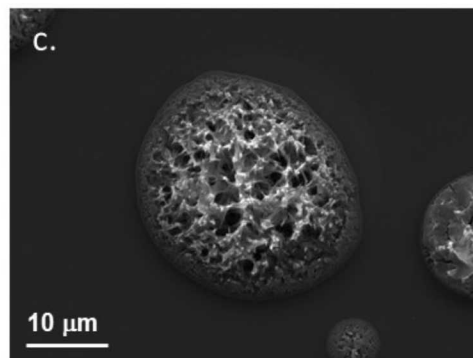
SEM photo:  $\text{MgCl}_2$  brine droplets on silicon wafer



# Mg-Cl Brine Stability: 2-Week Samples

## Results

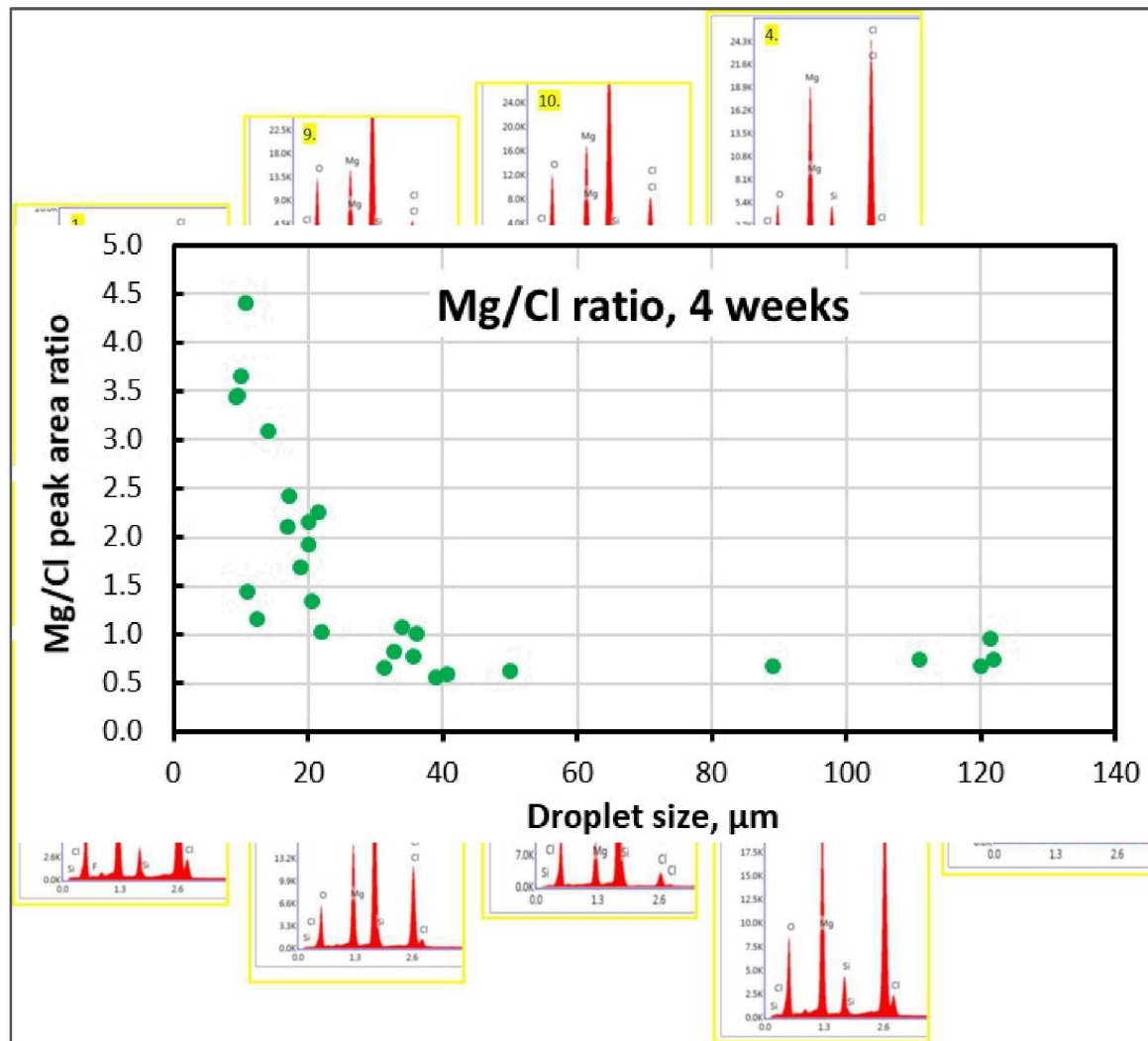
- Large droplets remain smooth, but smaller droplets change texture (fibrous).
- Possible slight increase in Mg-Cl ratio in smaller droplets?



# Mg-Cl Brine Stability: 4-Week Samples

## Results

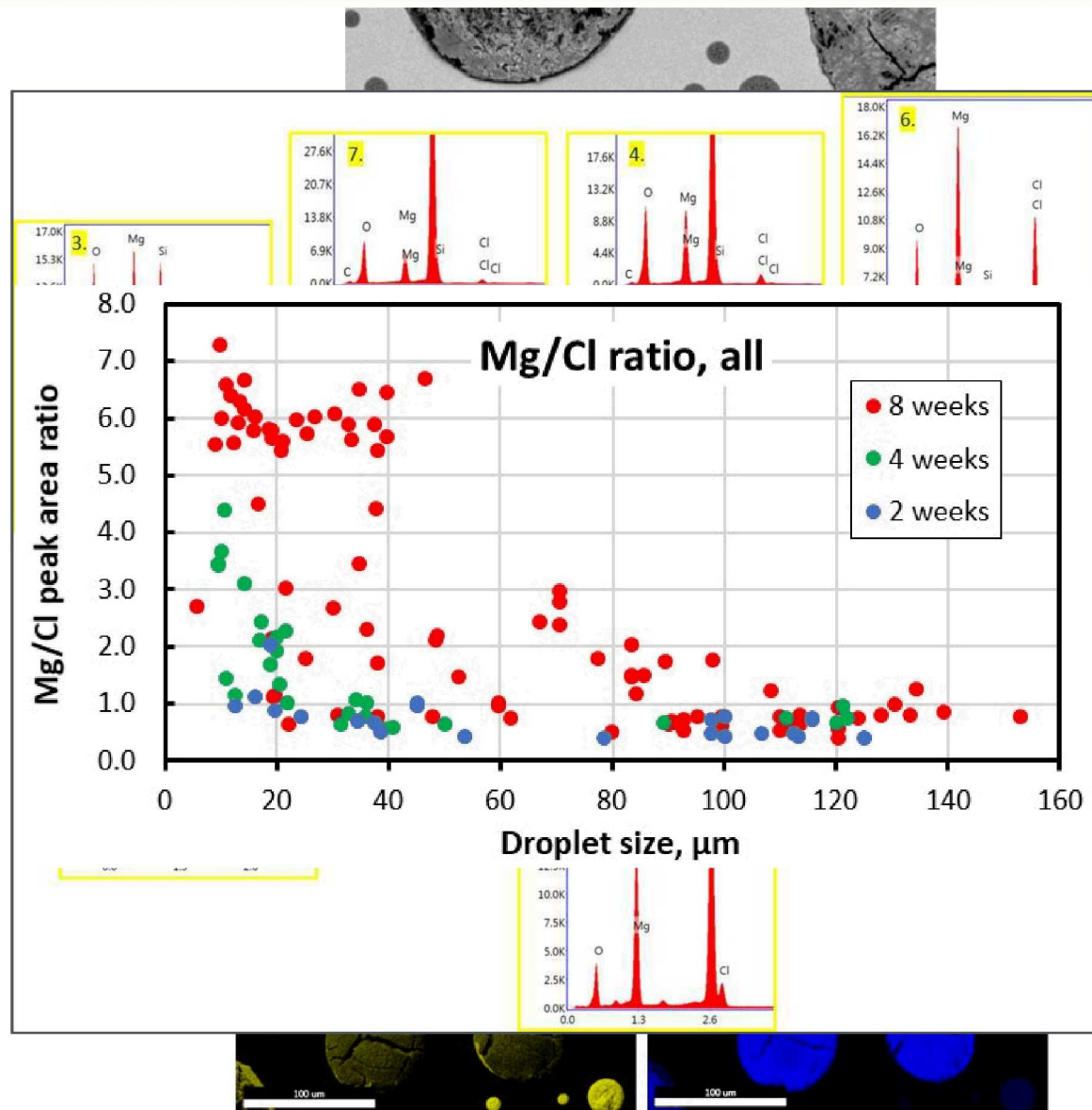
- In SEM BSE images, smaller droplets now appear darker—lower average atomic number (suggests chloride loss)
- Significant increase in measured Mg/Cl peak area ratios in smaller droplets



# Mg-Cl Brine Stability: 8-Week Samples

## Results

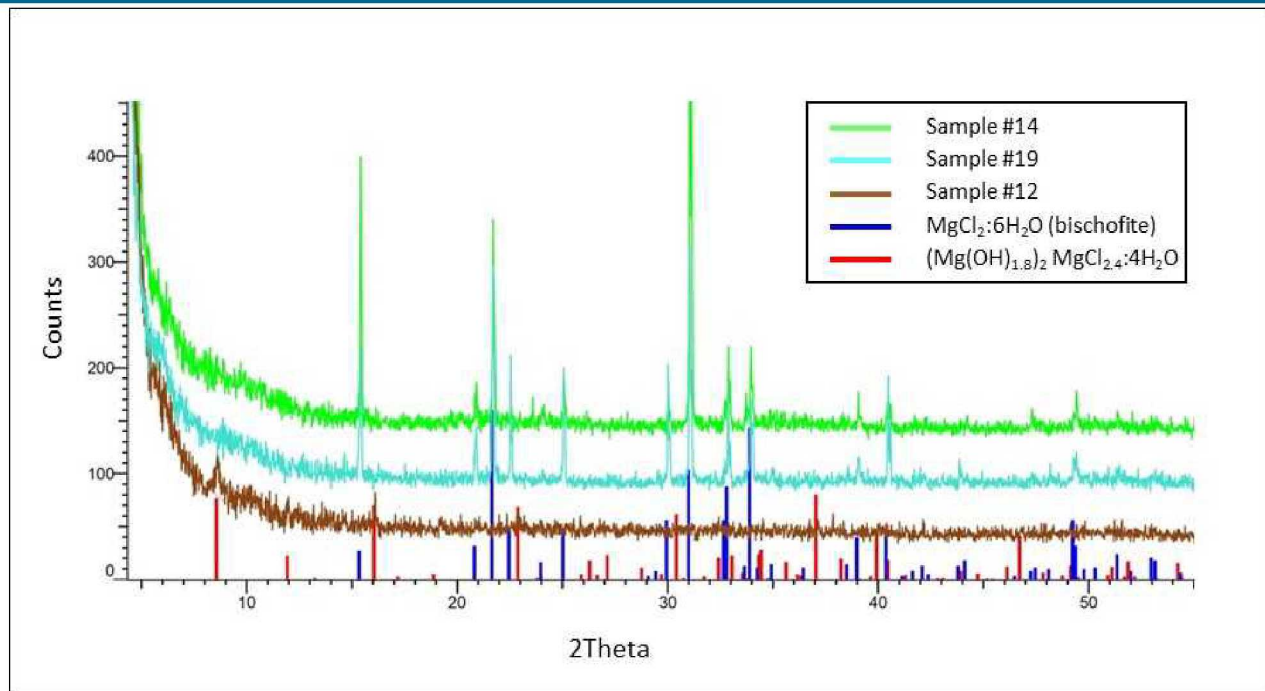
- In SEM BSE images, smaller droplets and some larger droplets appear darker. SEM EDS maps indicate chloride loss, oxygen gain, and minor carbon gain.
- Significant increase in measured Mg/Cl peak area ratios in small and medium-sized droplets



# Mg-Cl Brine Stability: What Formed?

## X-Ray diffraction (XRD) of 8-week samples

- Rapid scan to avoid deliquescence
- Samples 14,19: only bischofite observed
- Sample 12: Inadvertently allowed to deliquesce. A crystalline phase remained.
- Identified as “phase 2” Mg-hydroxychloride.



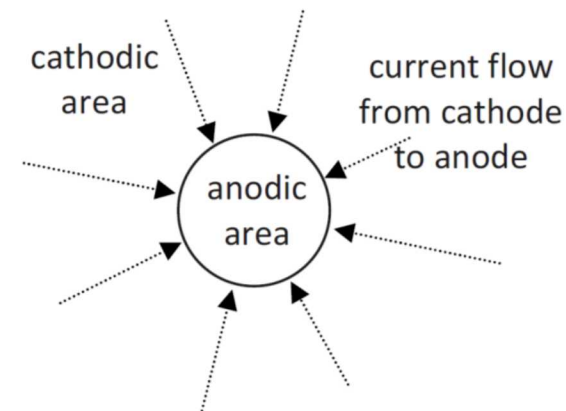
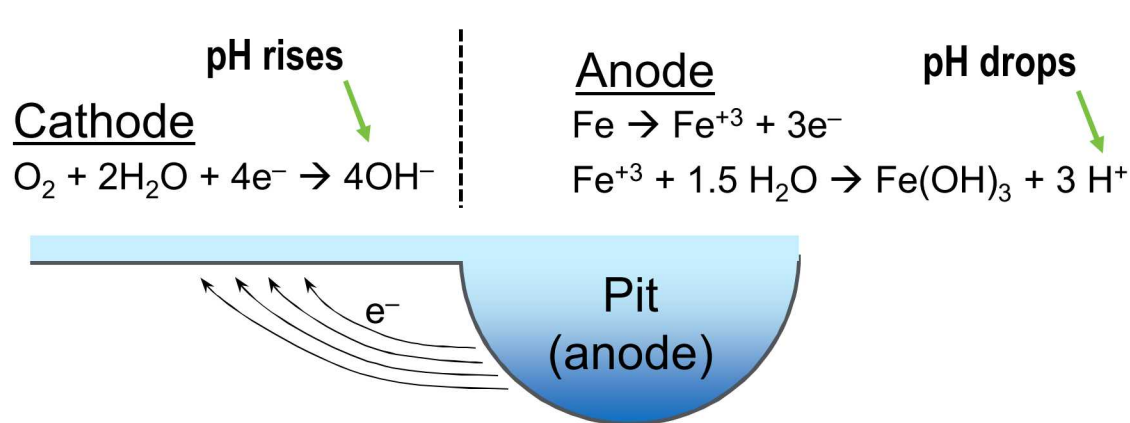
**Mg-Cl brine ( $Mg:Cl = 1:2$ ) converts to less deliquescent  $(Mg(OH)_2)_2MgCl_2 \cdot 4H_2O$  ( $Mg:Cl = 3:2$ )**

## Conclusion:

**Elevated temperatures promote HCl degassing, resulting in pH rise and Mg-hydroxychloride precipitation, potentially leading to brine dryout.**

# Effects of Corrosion on Brine Stability

## Corrosion cell



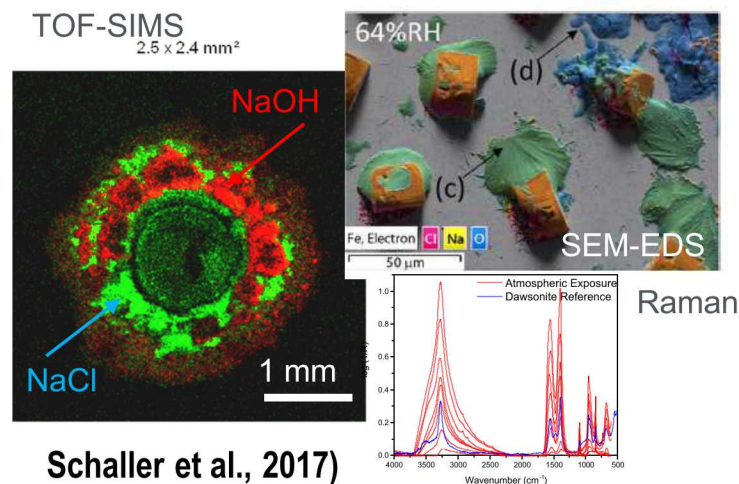
## Corrosion reactions may affect brine stability

### Cathode:

- Changes in brine chemistry may affect cathode kinetics by changing brine composition and volume
- Elevated pH may result in hydroxyl or carbonate precipitation. E.g., Al corrosion: high pH promotes  $CO_2$  absorption, precipitation of carbonates and dryout (Schaller et al., 2017).

### Anode:

- Low pH promotes acid degassing?



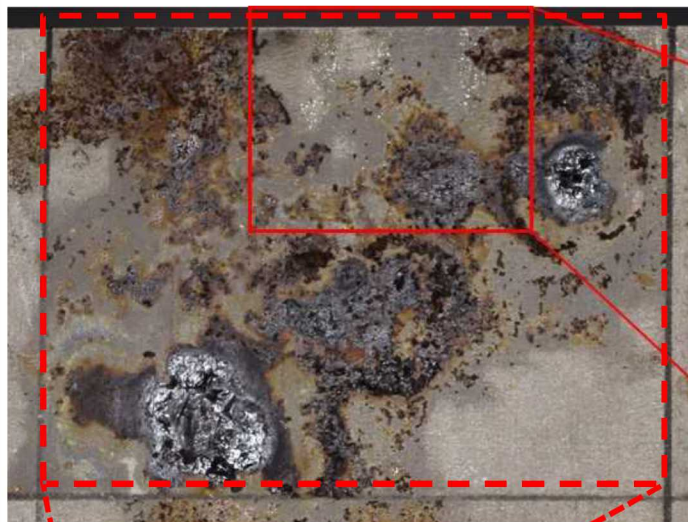
# Effects of Corrosion on Brine Stability:

What about on stainless steel?

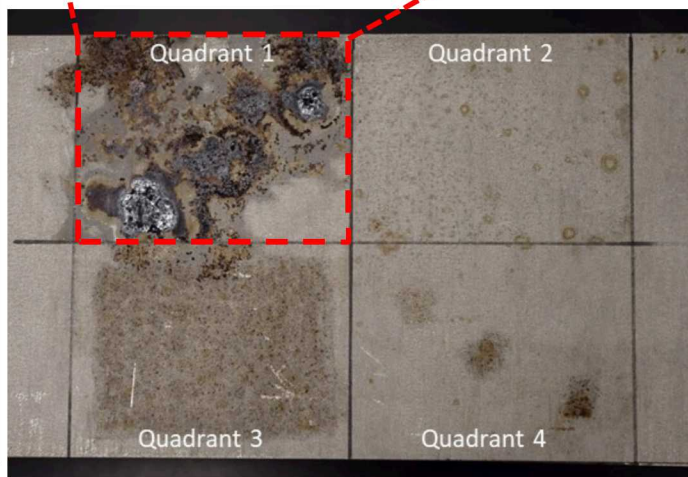
4-Point bend test with 4” wide test beam







80°C, 35% RH

- Different deposited salts, with salt loads and distributions
- Heavy corrosion around Mg-Cl brine droplets
- White precipitate observed around corroded areas
- Must be less deliquescent than bischofite, since above the deliquescence RH for that mineral.



White precipitate



Sat. MgCl <sub>2</sub> droplets	 5 μl	Ink-jet deposited NaCl
 10 μl	 20 μl	
Pool of sea-water	 5 μl	Sea-water droplets
	 10 μl	 20 μl

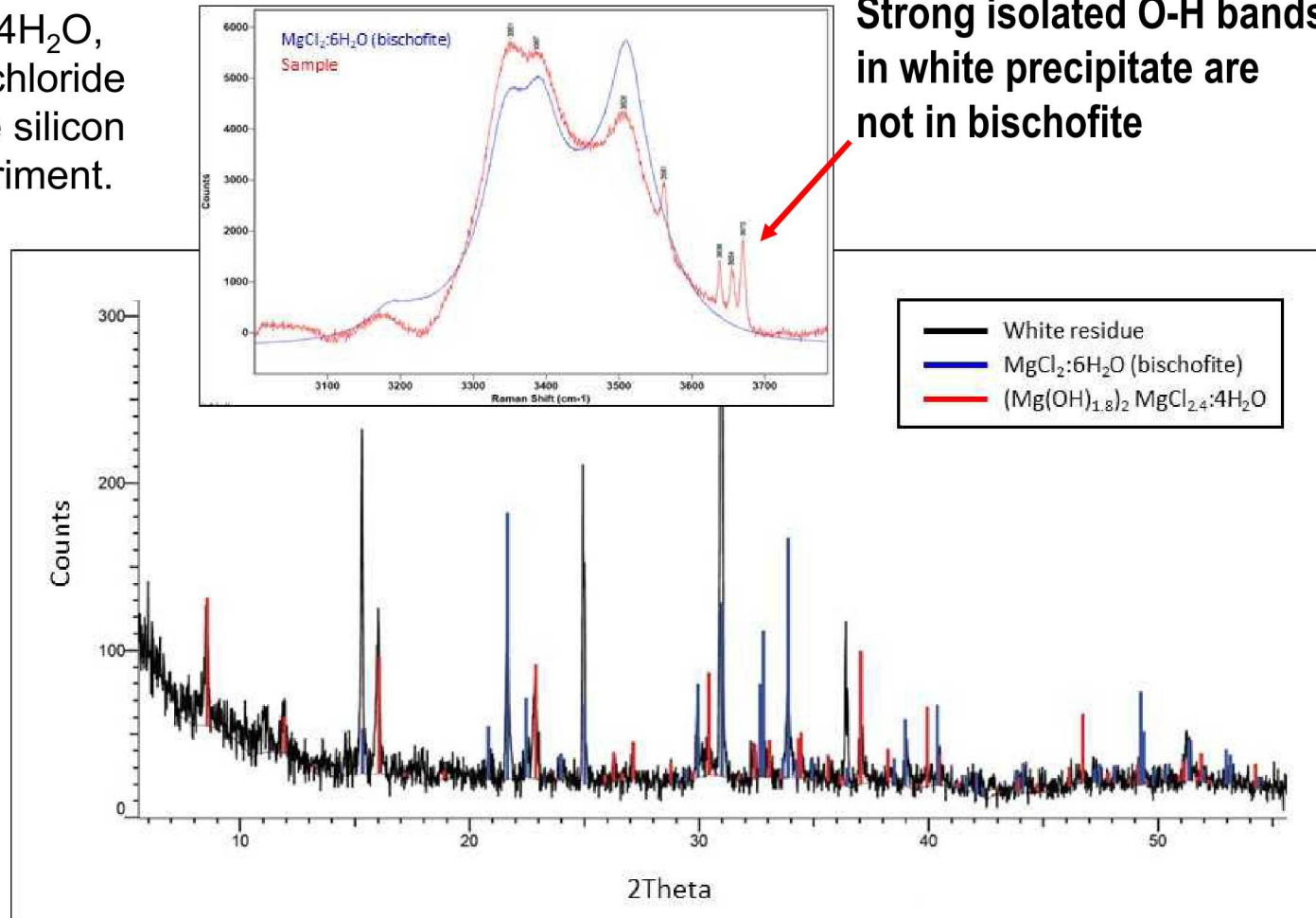
# White Precipitate on 4-Point Bend

## XRD analysis

- Sample consists of bischofite and  $(\text{Mg}(\text{OH})_2)_2\text{MgCl}_2 \cdot 4\text{H}_2\text{O}$ , the same Mg-hydroxychloride seen previously on the silicon wafer degassing experiment.

**At any given RH (brine concentration), Mg-hydroxychloride species is determined by temperature?**

**Raman Spectroscopy**  
**Strong isolated O-H bands in white precipitate are not in bischofite**



# Mg-hydroxychlorides

precipitate when base is added to Mg-Cl containing brines

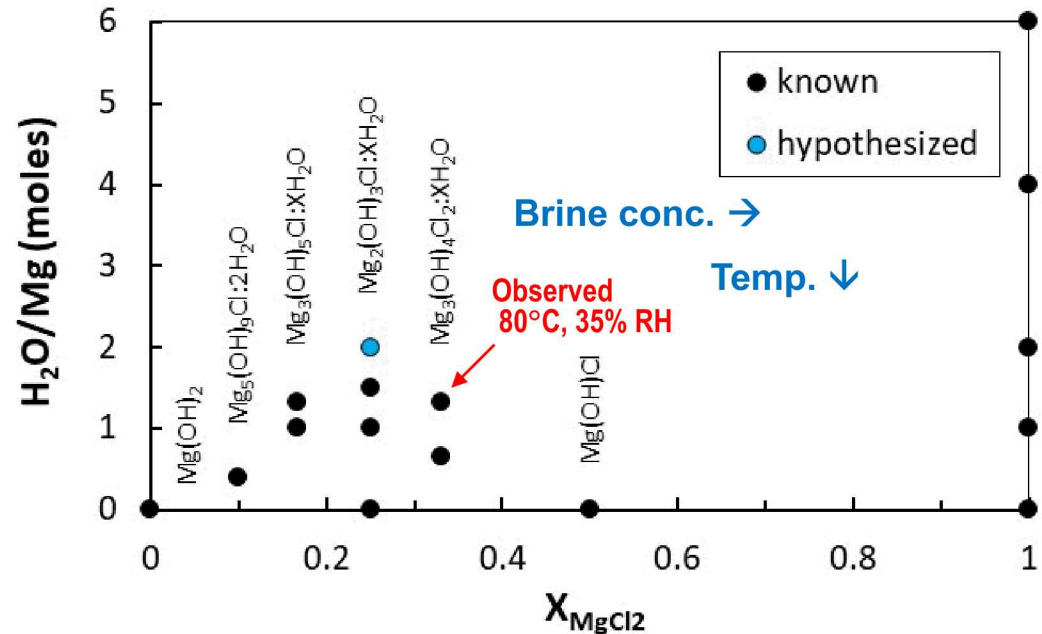
## System $\text{MgCl}_2\text{-Mg(OH)}_2\text{-H}_2\text{O}$

### Many species:

- (OH):Cl ratios 1:1, 2:1, 3:1, 5:1, 9:1.
- Variable waters of hydration

### Species that forms is controlled by environment:

- Brine concentration
- Temperature



### Questions:

- Which phases form under conditions of interest?
- Deliquescence properties
- Kinetic effects? (e.g., carbonate vs hydroxychloride?)

Future work will address these

# Maine Yankee Dust Analyses

In-service storage system opened and dust samples collected from the canister surface in July, 2018.

## Samples collected for Sandia

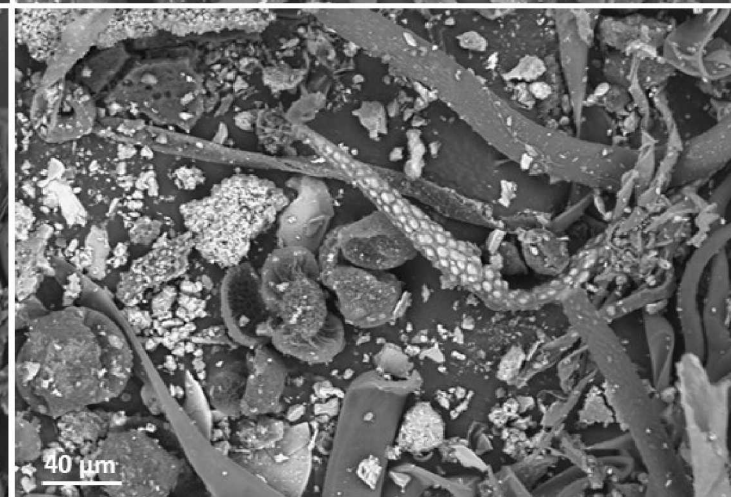
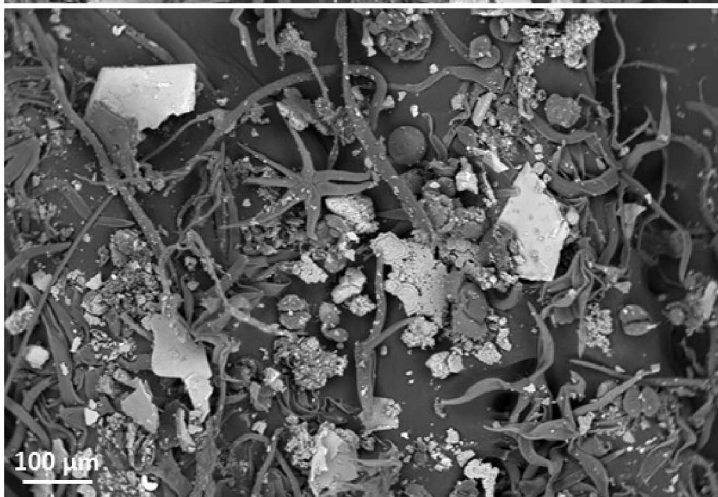
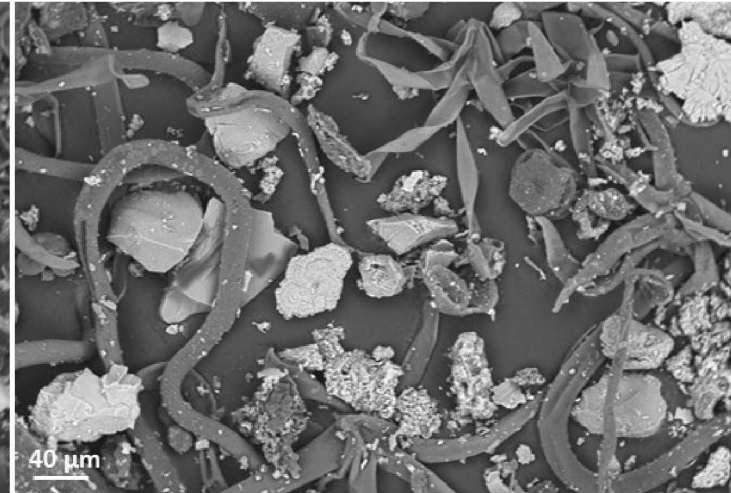
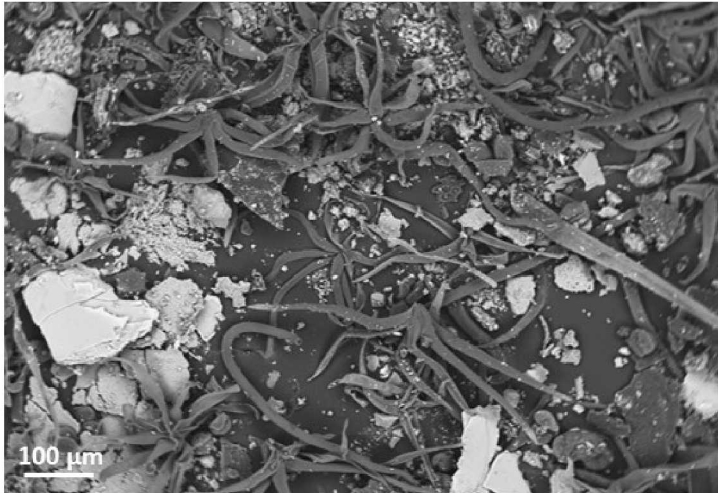
- Dry dust samples—Scotch-Brite™ pads (several samples, unnumbered)
  - Analyzed by SEM/EDS
- Wet samples for soluble salts (damp sponge)—quantitative:
  - 6 samples, sampled area 36 cm<sup>2</sup> each
  - Analyzed by ion chromatography

# Maine Yankee Dust Samples

## SEM analysis: Dominant Species

### Dominant materials:

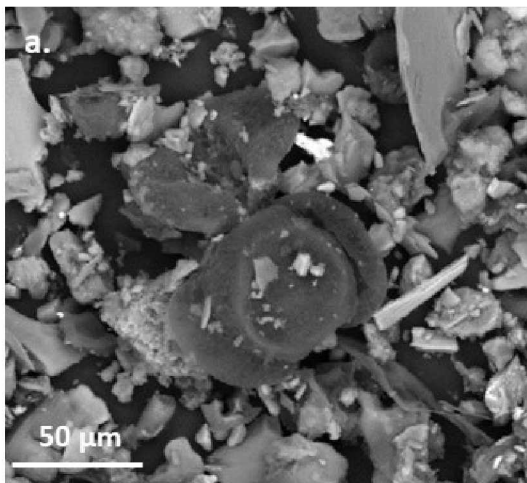
- Detrital mineral grains (biotite, feldspars, quartz, clay aggregates)
- Plant material (pollen, stellate trichomes, plant fibers)



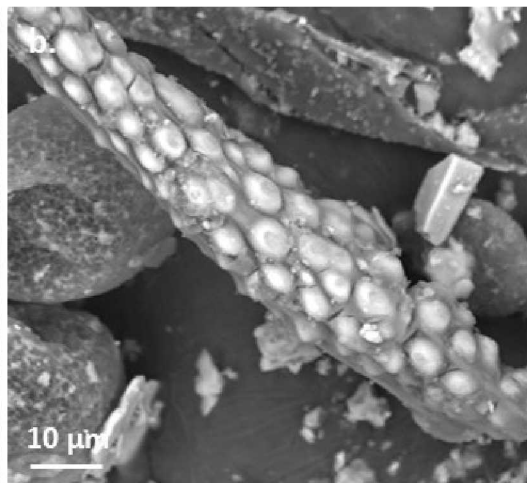
# Maine Yankee Dust Samples

SEM analysis: Close-ups

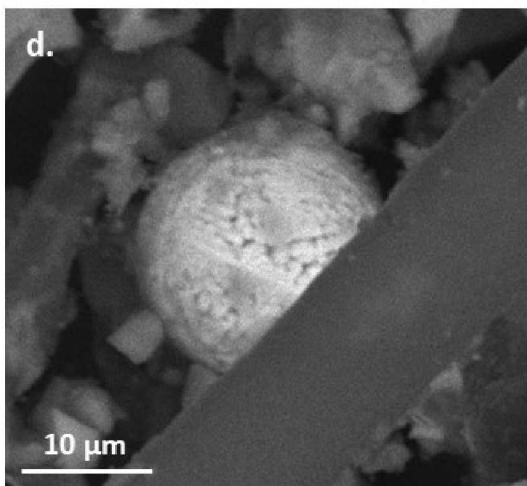
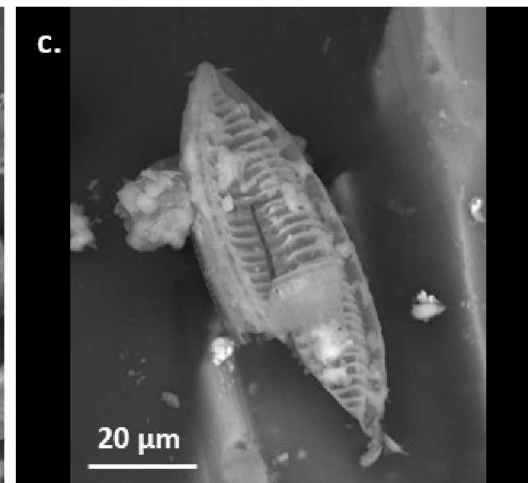
**Pollen**



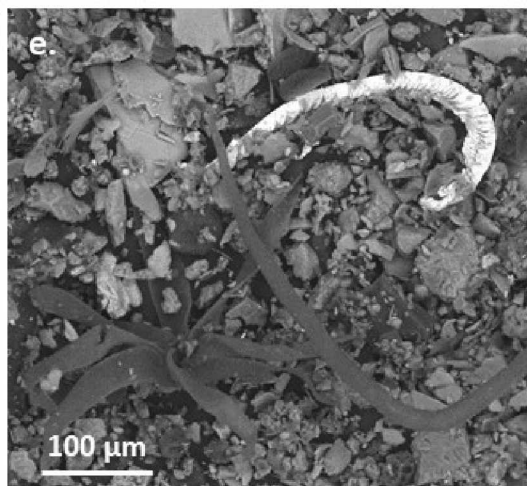
**Chitinophosphatic material**



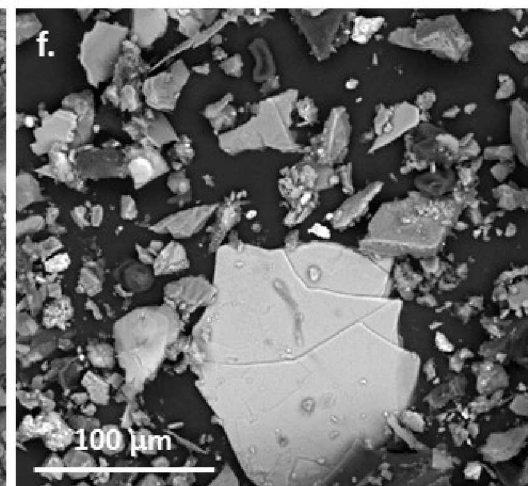
**Diatom**



**Fe-Cr Oxide Sphere  
(welding spatter)**



**Stellate trichomes,  
steel shaving**

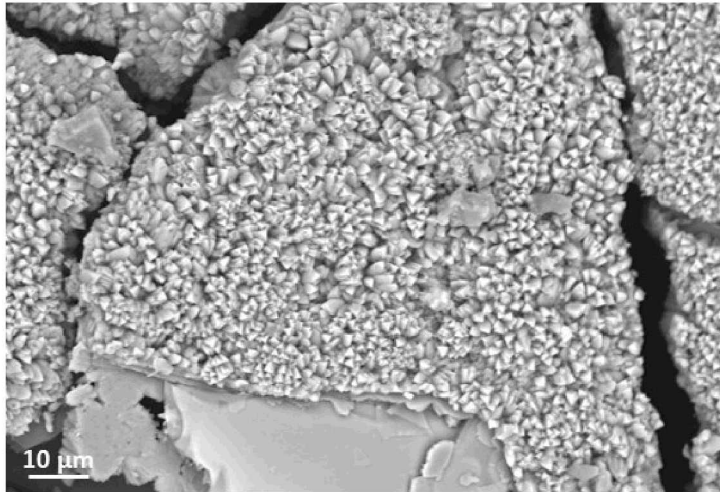


**Mineral grains (large  
one is biotite)**

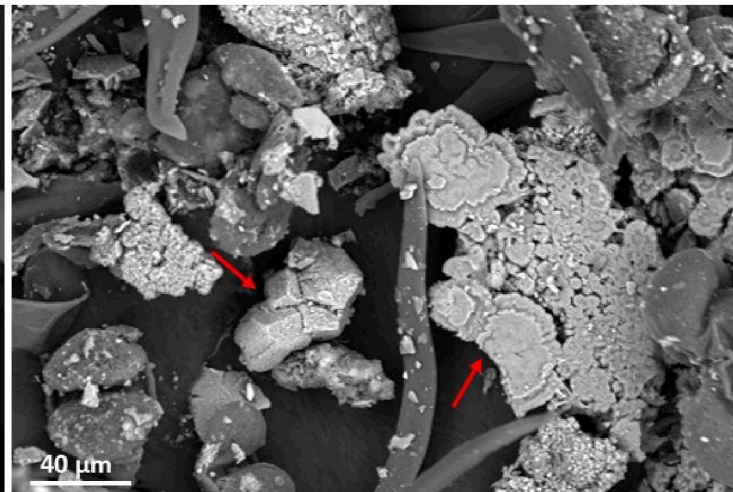
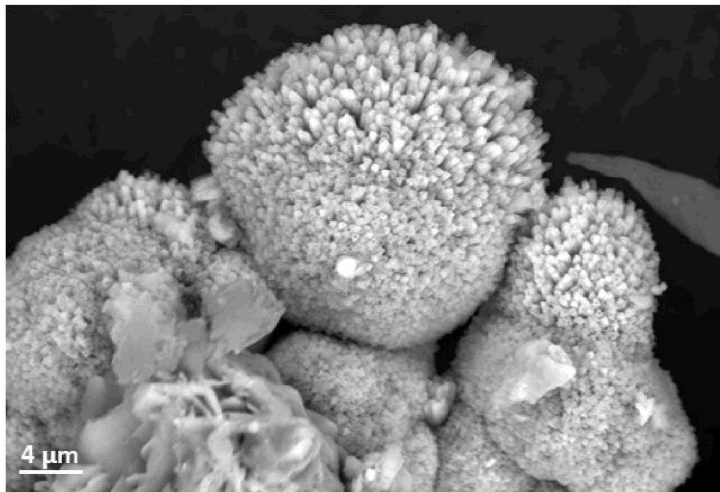
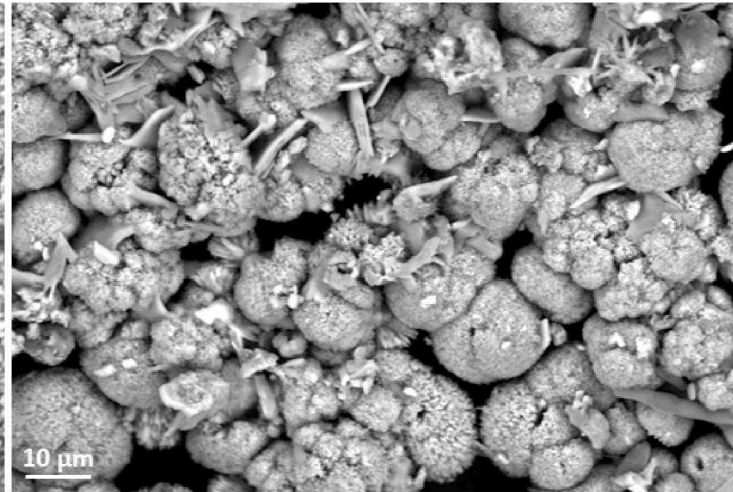
# Maine Yankee Dust Samples

SEM analysis: Concrete efflorescence

**Ca-carbonate**



**Calcium carbonate + Ca sulfate (blades)**



**Ca-carbonate + Ca-silicate, Ca-Si silicate**

**Ca-carbonate**

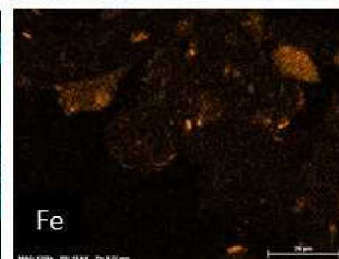
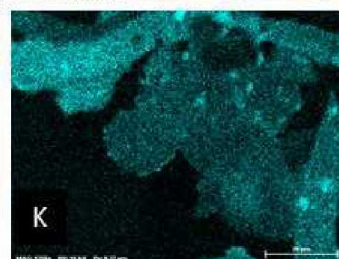
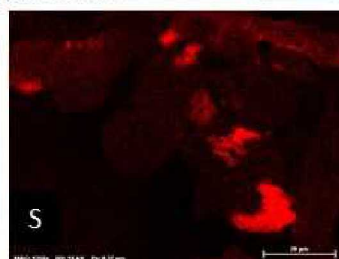
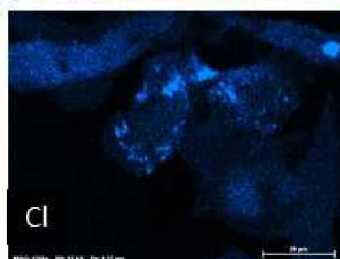
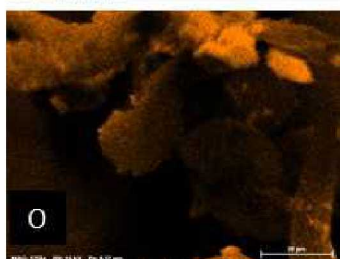
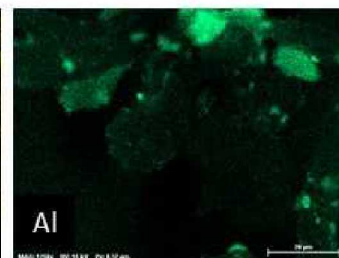
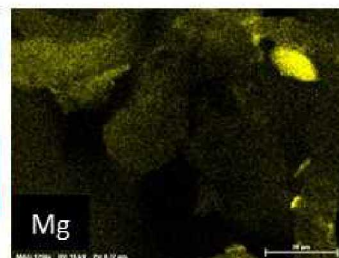
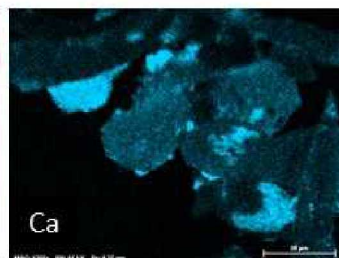
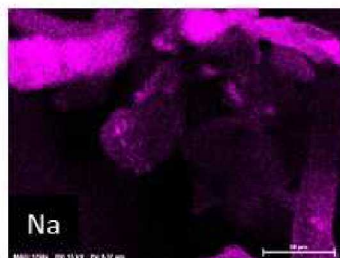
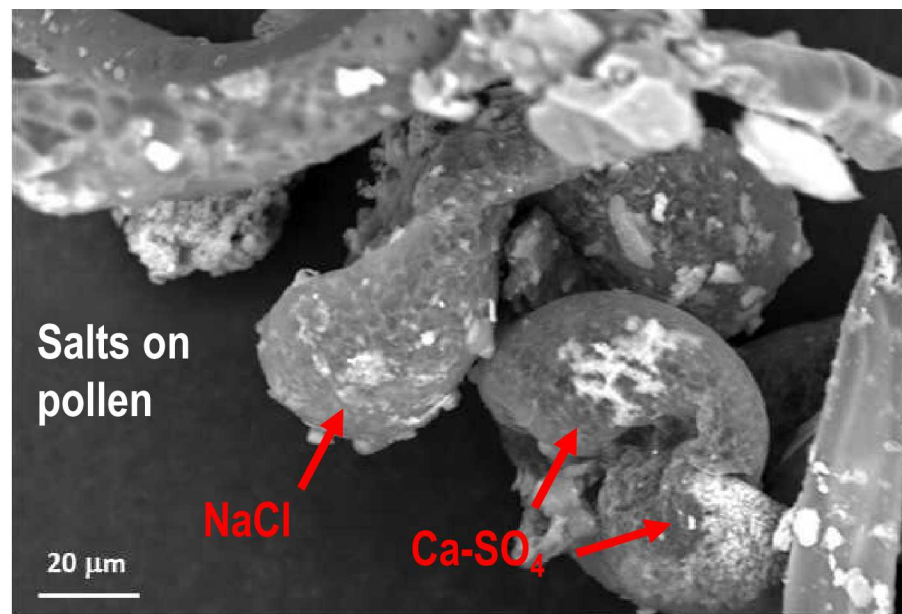
# Maine Yankee Dust Samples

## SEM analysis: Salt Minerals

Most common soluble salts calcium carbonate, calcium sulfate.

Chloride salts: NaCl, minor KCl

Ubiquitous association with organic material (pollen, plant fibers).

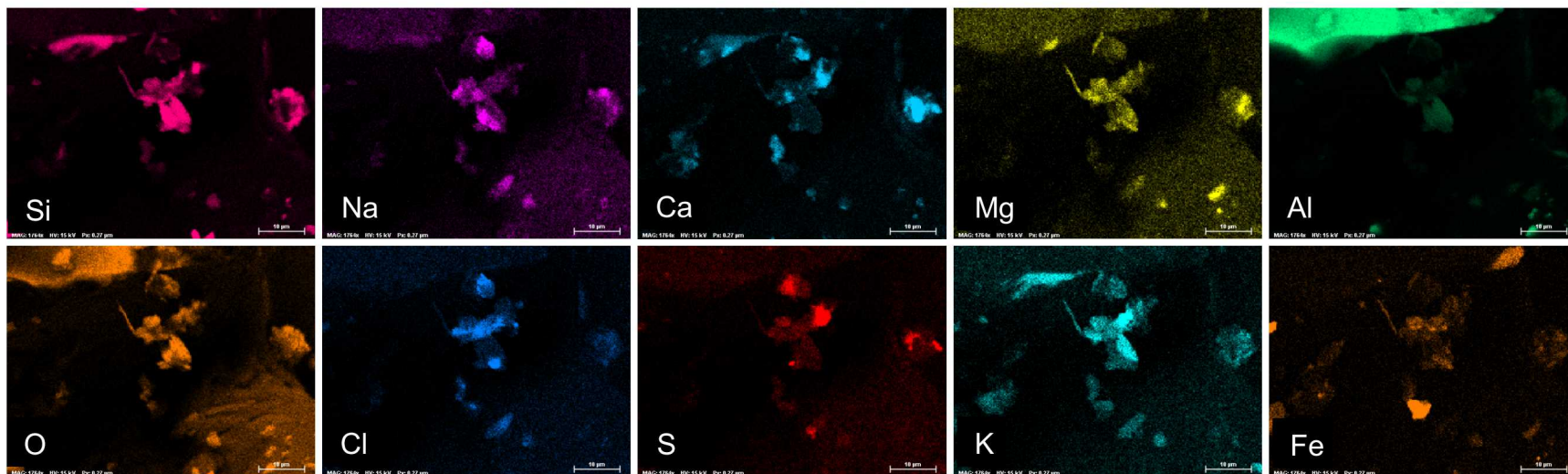
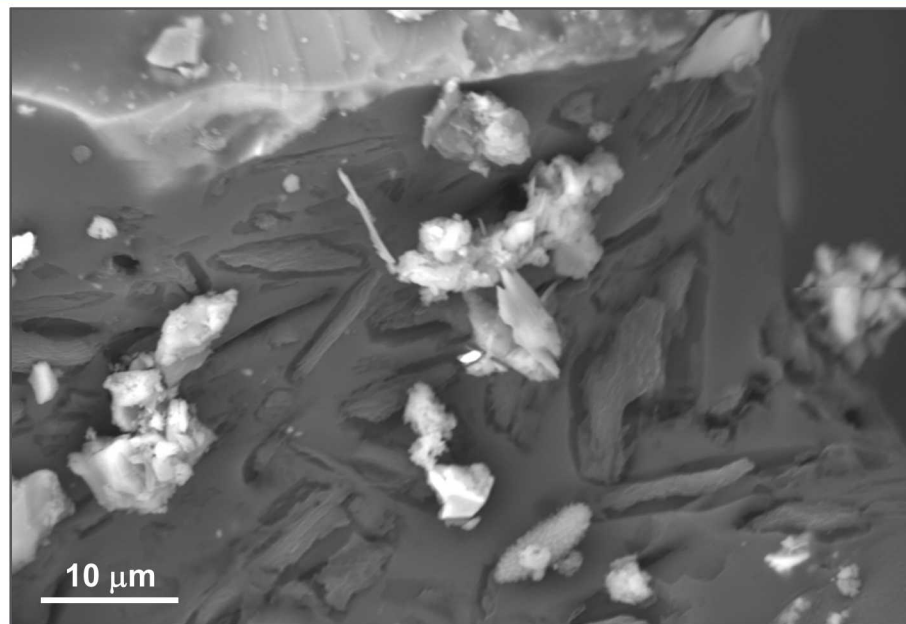


# Maine Yankee Dust Samples

## SEM analysis: Salt Minerals

Chloride also frequently associated with fine-grained clay aggregates.

Salt association with other particles suggests that salts are usually transported as deliquesced droplets, contacting and adhering to other atmospheric aerosol particles (before or during suspension)... Important to consider during modeling of salt transport and deposition.



# Maine Yankee Dust Samples

## Chemical analysis of soluble salts

### Soluble Salts

- **Cations:**

- ☐  $\text{Ca} \gg \text{Na} > \text{K}, \text{Mg}$

- ☐ K/Na, Mg/Na ratios are much larger than in seawater.

- **Anions**

- ☐  $\text{SO}_4^{2-} > \text{NO}_3^- , \text{Cl}^-$

- ☐ Huge anion deficiency indicates something unmeasured (carbonate and/or organic ligands?) are dominant cations.

Soluble Ion Concentrations in Maine Yankee Dust Samples,  $\mu\text{g}/\text{sample}$ .

Sample #	Na <sup>+</sup>	NH <sub>4</sub> <sup>+</sup>	K <sup>+</sup>	Mg <sup>2+</sup>	Ca <sup>2+</sup>	F <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	SO <sub>4</sub> <sup>2-</sup>
MY-1	173	n.d.	91.6	26.7	699	14.4	130	260	7.5	199
MY-2	168	2.1	92.7	20.4	808	30.5	102	296	5.0	187
MY-3	28.5	n.d.	3.8	8.2	162	12.4	20.9	7.6	n.d.	27.6
MY-4	42.0	n.d.	17.5	n.d.	107	11.0	20.3	62.1	n.d.	30.8
MY-5	117	n.d.	56.2	22.3	421	29.3	114	108	n.d.	193
MY-6	355	n.d.	228	48.5	746	33.4	268	485	13.1	450

# Maine Yankee Dust Samples

## Chloride Surface Loads

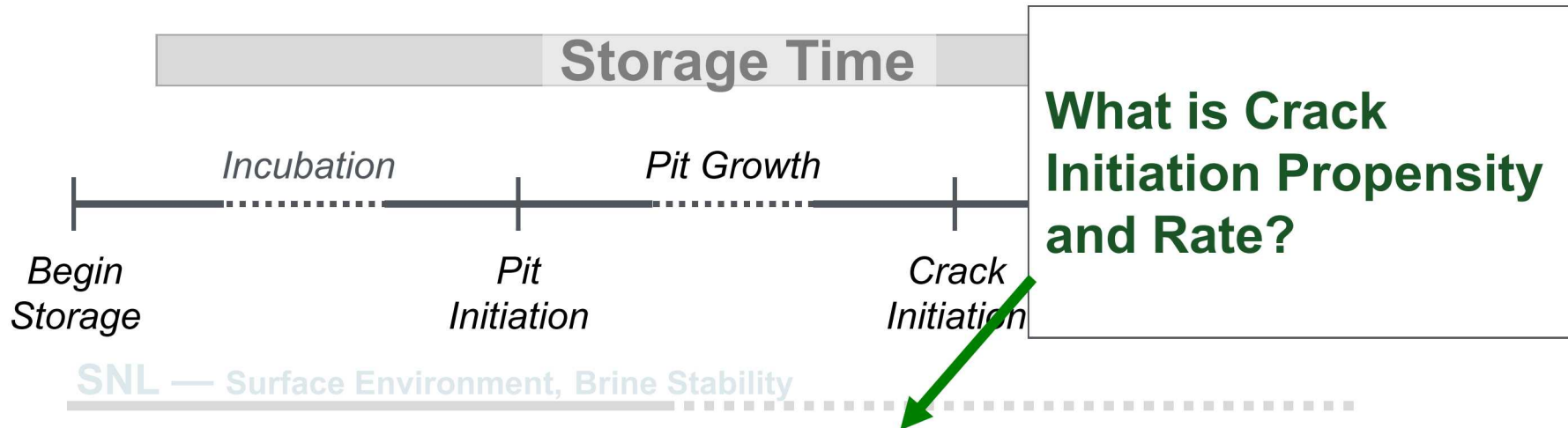
Chloride surface loads are mostly similar to those measured by site M&O (Paul Plante et al.); the highest sample is a little higher. But all chloride loads are still less than 0.1 g/m<sup>2</sup>.

<b>Sample #</b>	<b>Cl<sup>-</sup>, mg/m<sup>2</sup></b>
MY-1	36.0
MY-2	28.3
MY-3	5.8
MY-4	5.6
MY-5	31.8
MY-6	74.4

### Important conclusions, Maine Yankee dust analyses:

- Chloride loads are light.
- Chloride is strongly associated with organic debris (pollen and plant fibers). Transport/deposition properties may be different that expected.

# Canister SCC: Corrosion Experimental Work



**What is Crack Initiation Propensity and Rate?**

**CSM/SNL — Pitting Initiation and Growth (Effect of Stress)**

**SNL/OSU — Pitting Initiation and Growth, Pit-to-Crack Transition**

**SNL/UVA — Maximum Pit Size, Crack Growth Rate**

CSM — Pit-to-Crack Transition (Modeling)

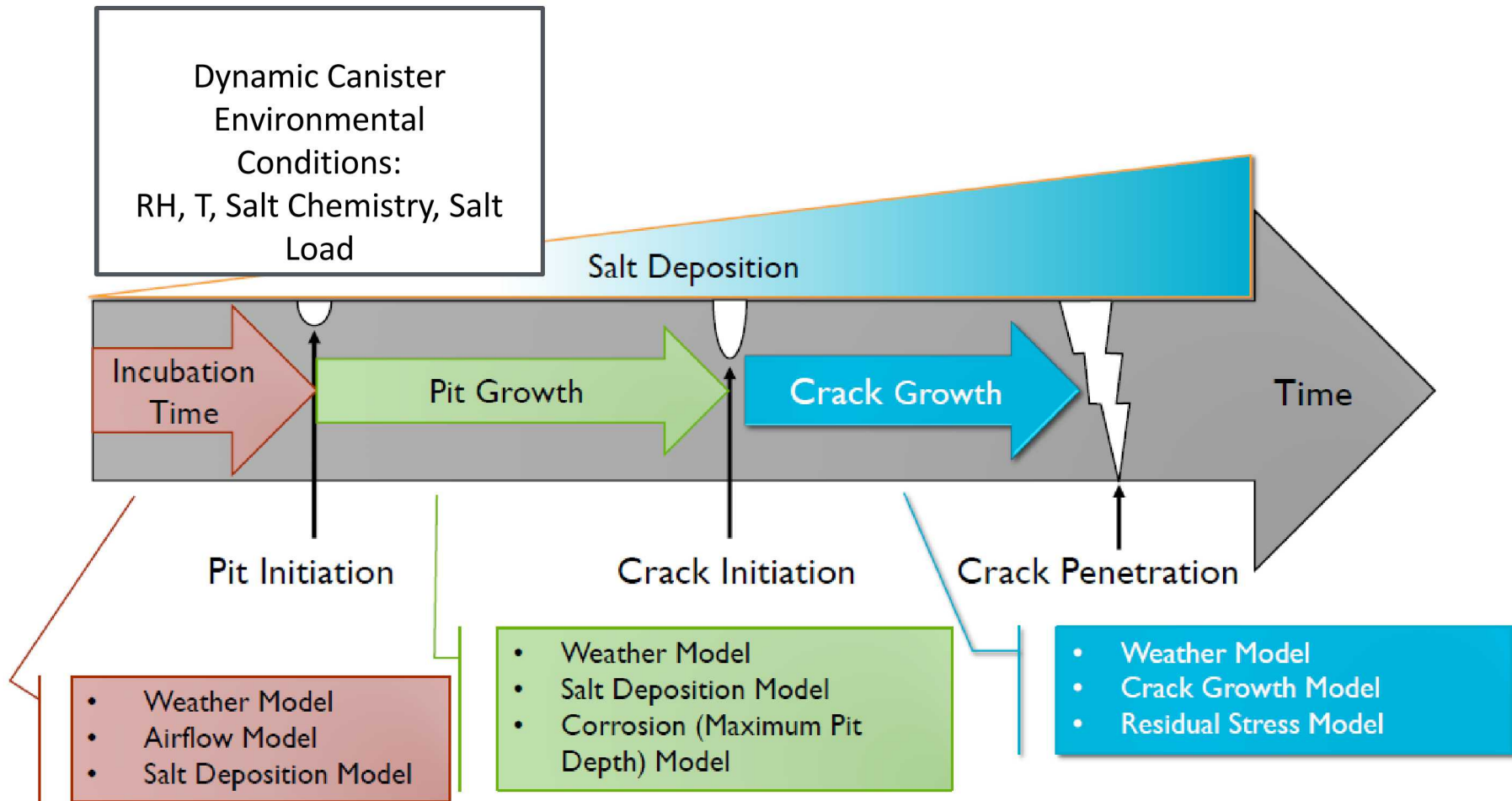
SRNL (SNL) — Crack Growth Rates

NCSU (SNL) — Crack Growth Rates

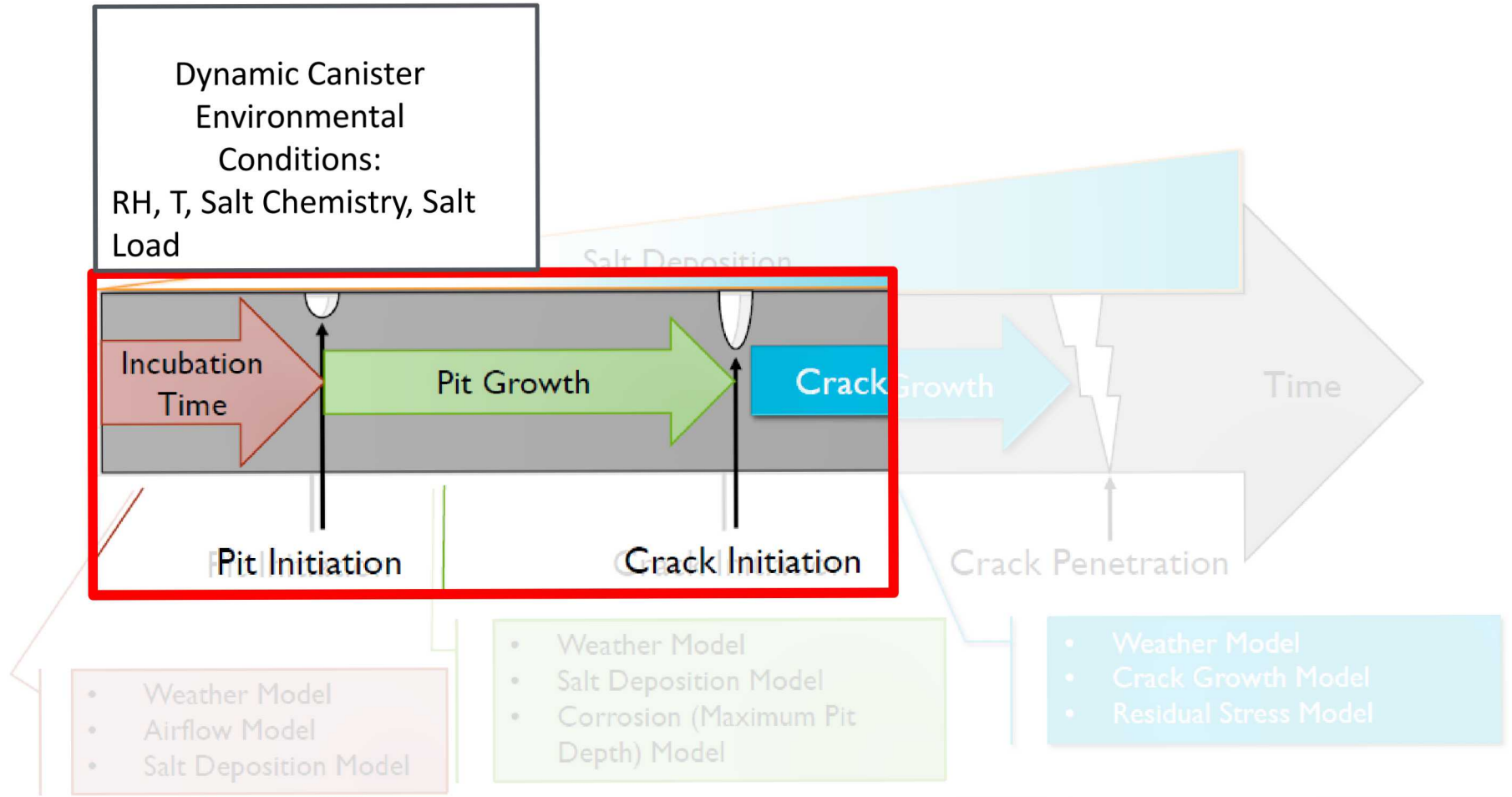
OSU/SNL — Crack Growth Rates

PNNL/SNL — Crack Growth Rates

# Integrated Model for Atmospheric SCC



# Holistic Model for Atmospheric SCC



# How do Surface Environment and Material Condition Affect SCC Onset?

## Environment, $f(t)$

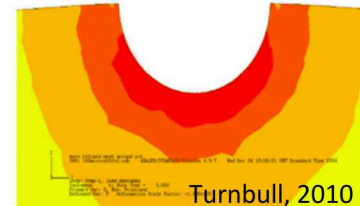
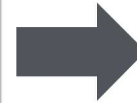
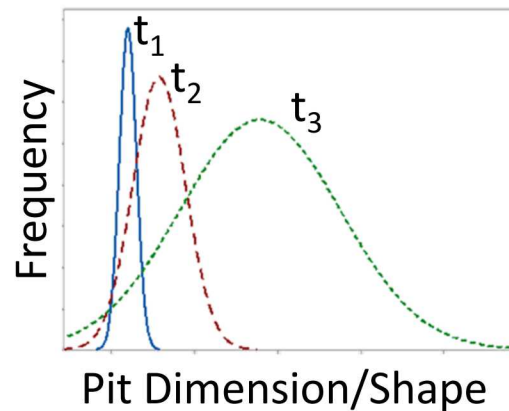
RH, T, Salt  
Chemistry, Salt  
Load

## Material

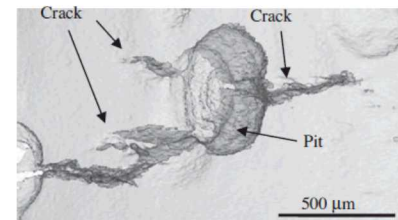
304H, 304L,  
316L

## Material Condition

Nominal  
stress/strain,  
microstructure,  
surface finish



Stress intensity,  
weakest link  
features?



Crack initiation

# How do Surface Environment and Material Condition Affect SCC Onset?

## Goals

1. Quantify relationship between environment and pitting damage distributions and rates
2. Identify prevalent damage pathways leading to SCC initiation
3. Extend and validate maximum pit size model and pit shape/size factor approach as tool for canister SCC susceptibility ranking

## Current Approach

1. Generate temporal pitting damage datasets as function of RH, T, salt load and surface finish for SS304H (unsensitized)
2. Identify hierarchal weakest link pitting damage features leading to crack initiation via marker band SCC tests.

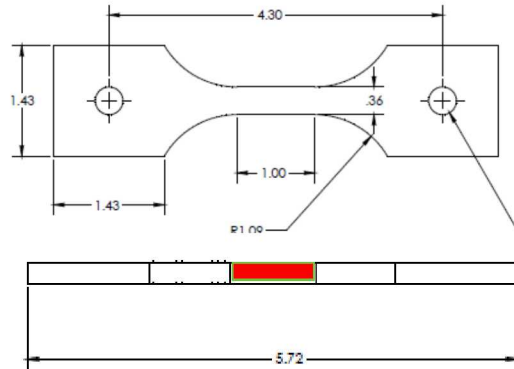
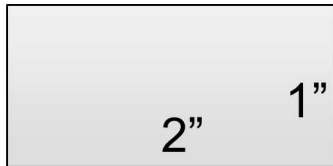
## Impact

1. **Datasets** and understanding **for** development/validation of **damage function models**
2. Relevance and role of environment and material on crack initiation probability and rates  
→ **identify red flag SCC conditions**
3. **Development of tool for risk-based ranking**

# How do Surface Environment and Material Condition Affect SCC Onset? – Baseline Study

## Samples

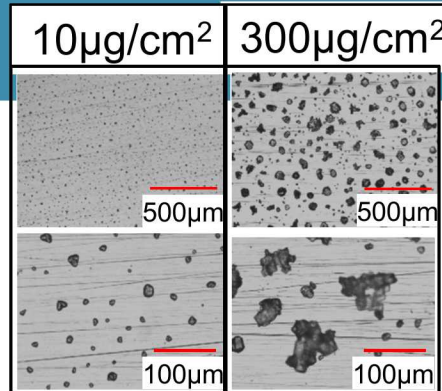
SS304H



Mirror,  $R_a = 0.05 \mu\text{m}$   
Ground,  $R_a = 2.83 \mu\text{m}$

## Salt Load

Inkjet Deposition



ASTM D-1141 sea salt

## Exposure Conditions

%RH	Temperature (°C)			
75	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

1 week to 2 years

# 300 $\mu\text{g}/\text{cm}^2$ Salt Loading After Exposure

Mirror 35°C, 40%RH Rough

Mirror 35°C, 75%RH Rough

1 Week

1 Week

2 Weeks

2 Weeks

1 month

1 month

6 months

6 months

1 Year

1 Year

1cm

1cm

1cm

1cm

1cm

1cm

1cm

1cm

1cm

1cm

1cm

1cm

1cm

1cm

1cm

1cm

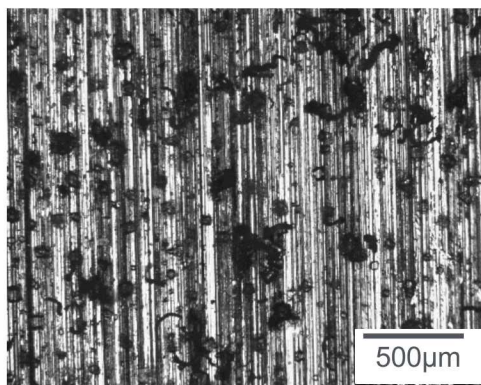
1cm

1cm

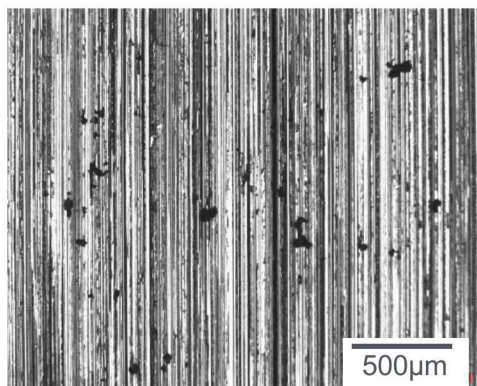
1cm

1cm

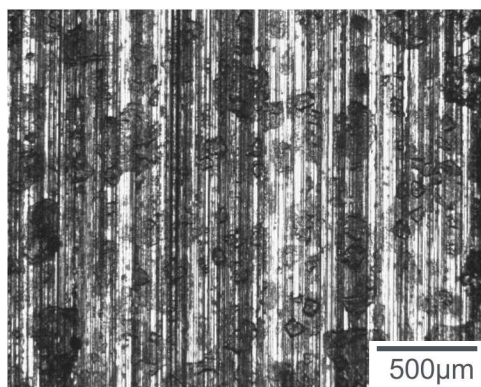
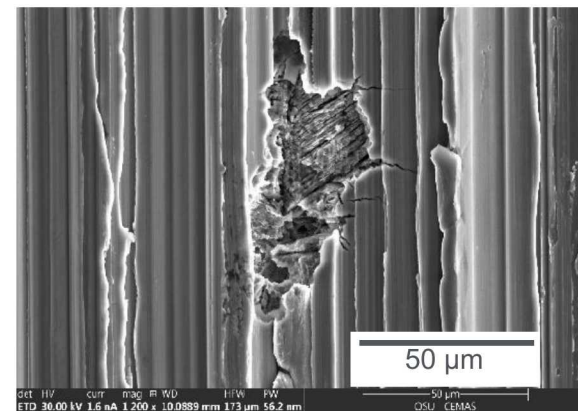
# Removal of Rust Reveals Varied Pit Distributions and Morphologies



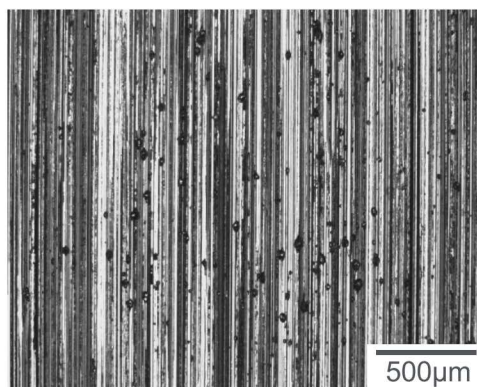
**300 $\mu\text{g}/\text{cm}^2$ , 40%RH, 1 Year  
Before Cleaning**



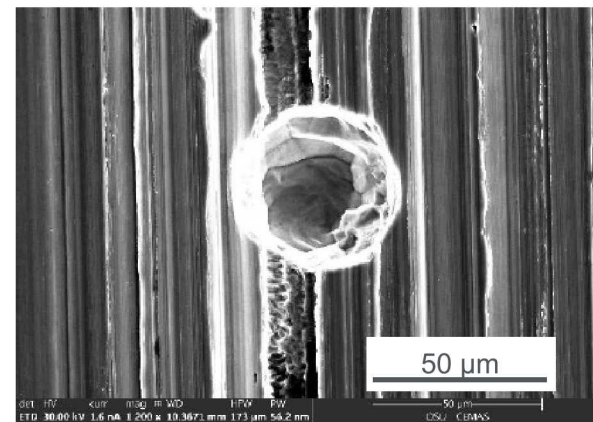
**300 $\mu\text{g}/\text{cm}^2$ , 40%RH, 1 year  
After Cleaning**



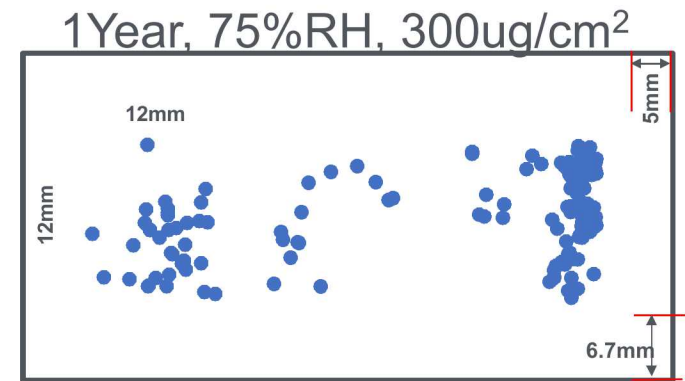
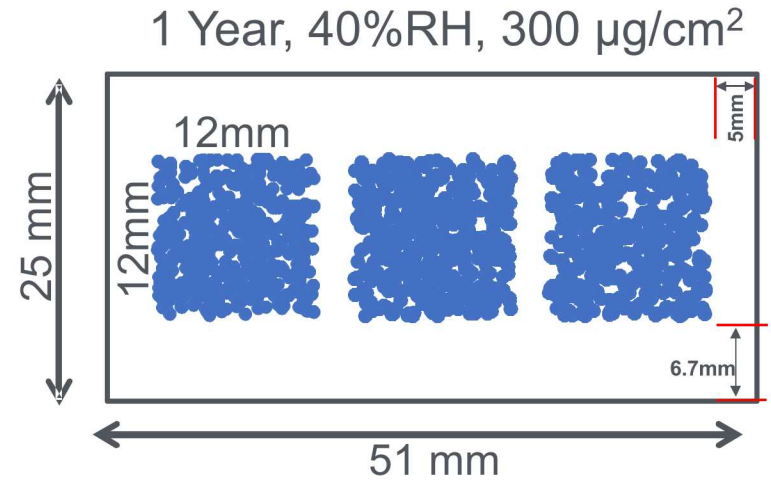
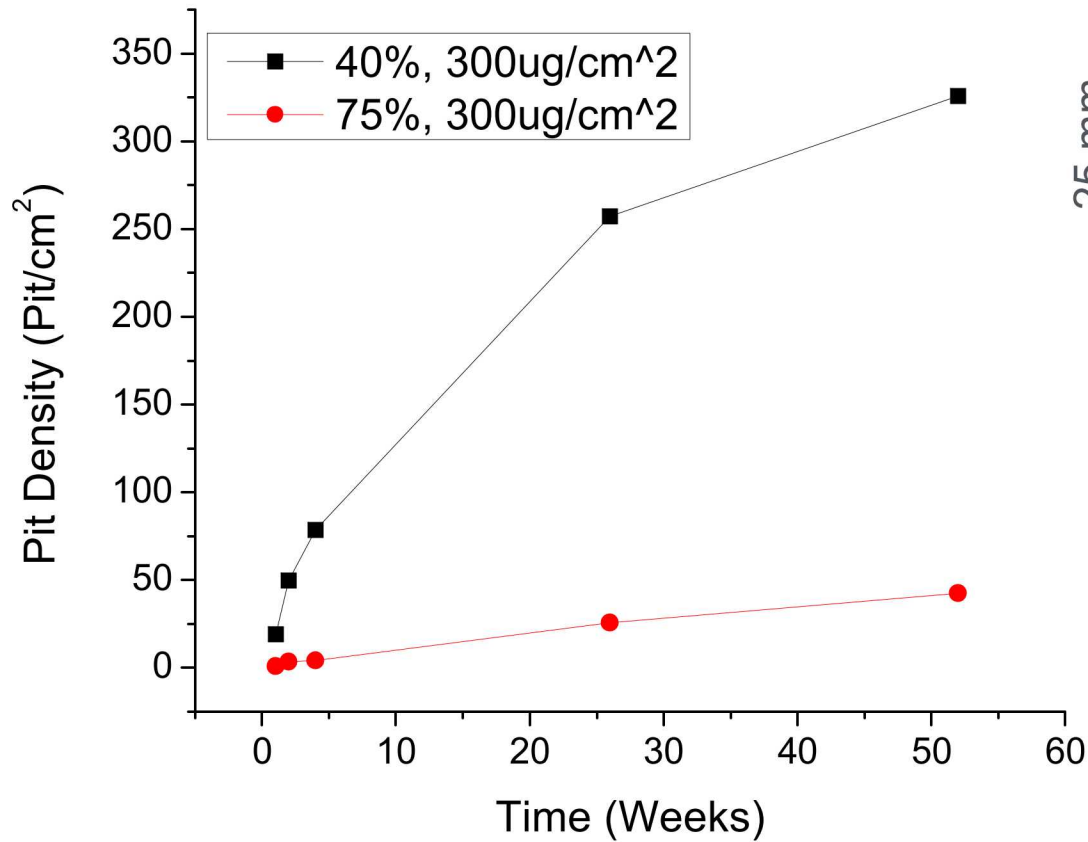
**300 $\mu\text{g}/\text{cm}^2$ , 75%RH, 1 Year  
Before Cleaning**



**300 $\mu\text{g}/\text{cm}^2$ , 75%RH, 1 Year  
After Cleaning**

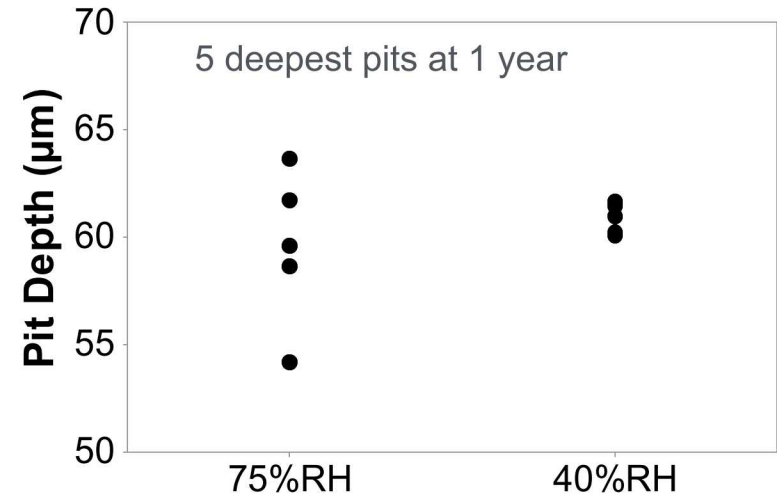
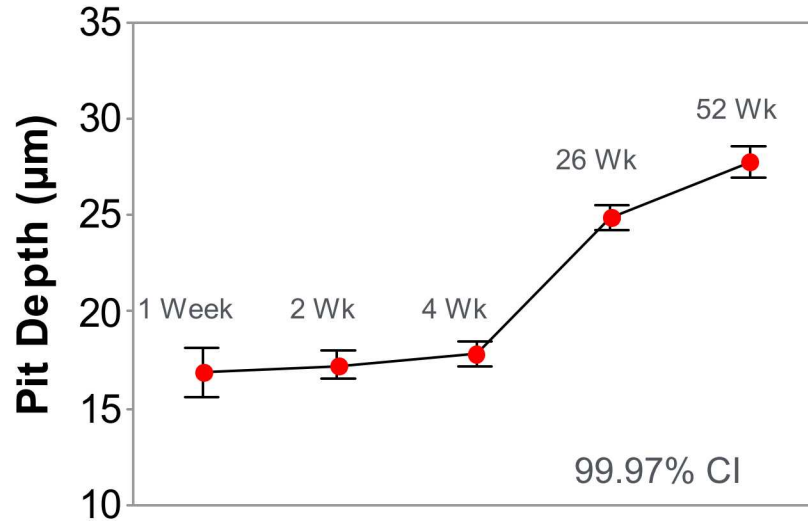


# Pit Number Density is Strongly Dependent on RH

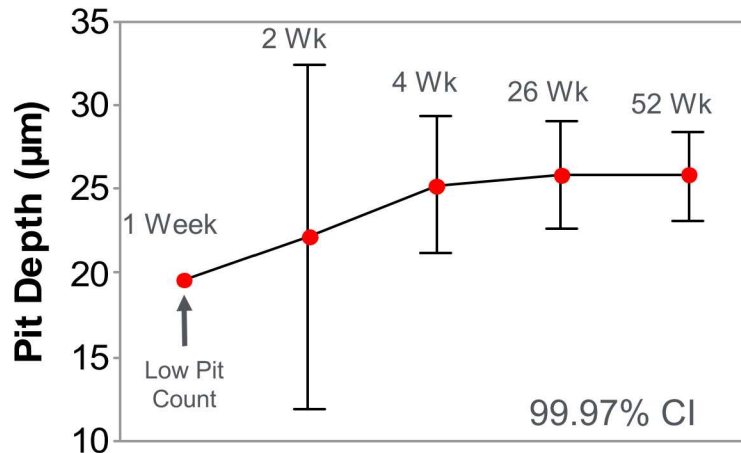


# Pit Growth Kinetics Appear to be Strong Function of RH

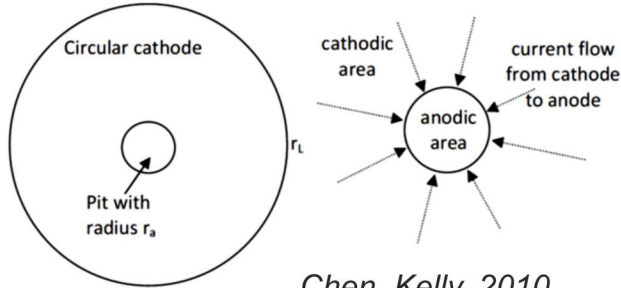
Average Pit Depth 40%RH, 300 $\mu\text{g}/\text{cm}^2$



Average Pit Depth 75%RH, 300 $\mu\text{g}/\text{cm}^2$



# Prediction of Maximum Pit Size from Brine Characteristics and Electrochemical Kinetics



Chen, Kelly, 2010

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

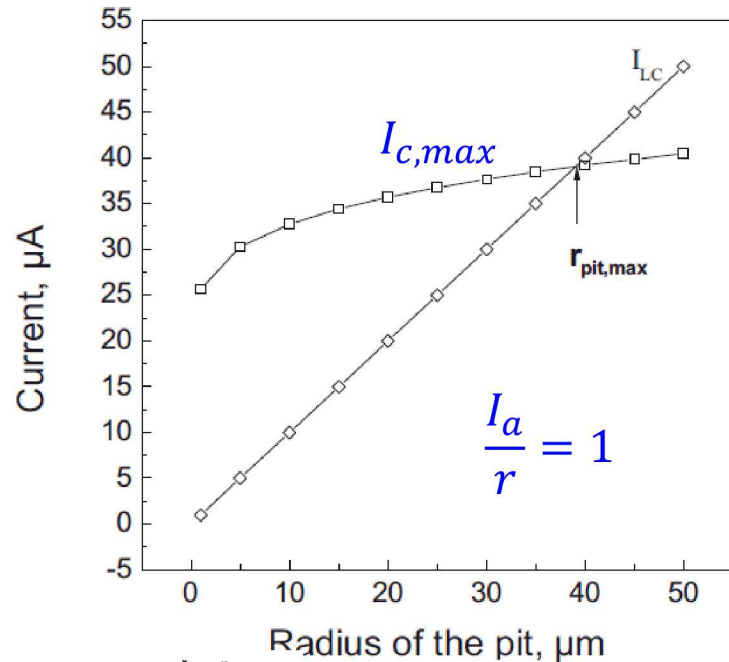
Max. cathode current  
Brine conductivity  
Brine layer thickness  
Cathodic Kinetics

## Challenge:

Information on electrochemical parameters lacking for expected canister brine conditions (electrolyte thickness and chemistry)

## Assumptions:

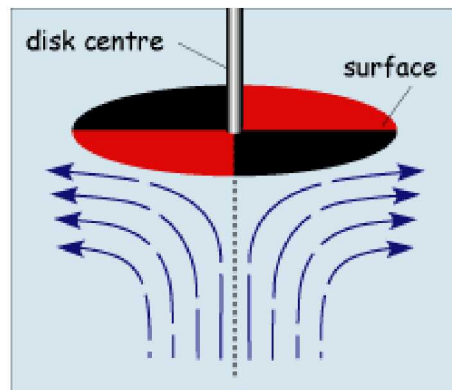
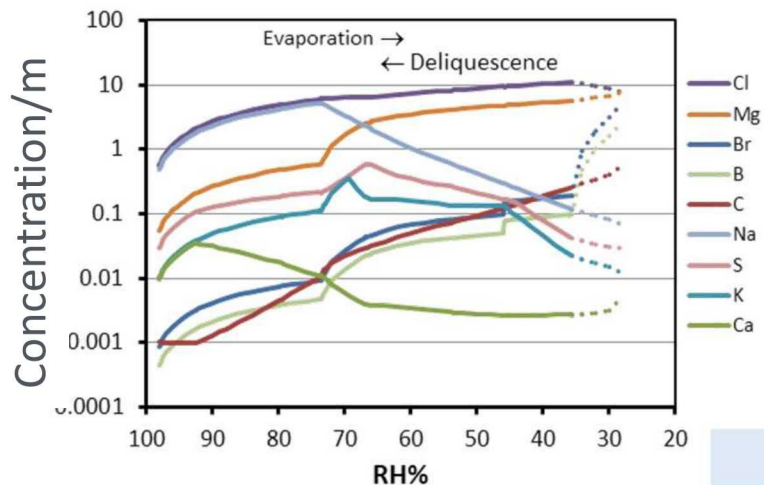
1. Continuous brine layer
2. Hemispherical pit
3. Cathodic and anodic kinetics independent of time (fixed electrolyte conditions)



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



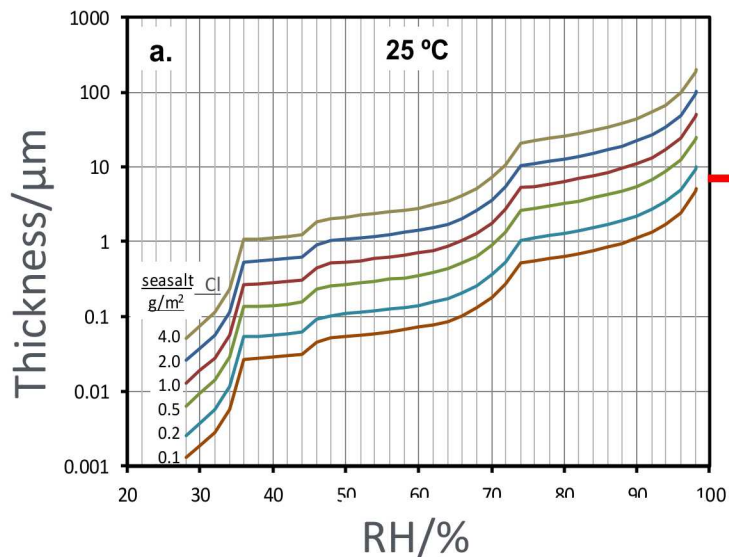
# Measurement of Electrochemical Parameters in Analog Electrolyte Brines as f(T RH, salt load)



Rotating disc electrode to simulate brine layer thickness > 1 μm

SNL/UVA

Cathodic polarization curves



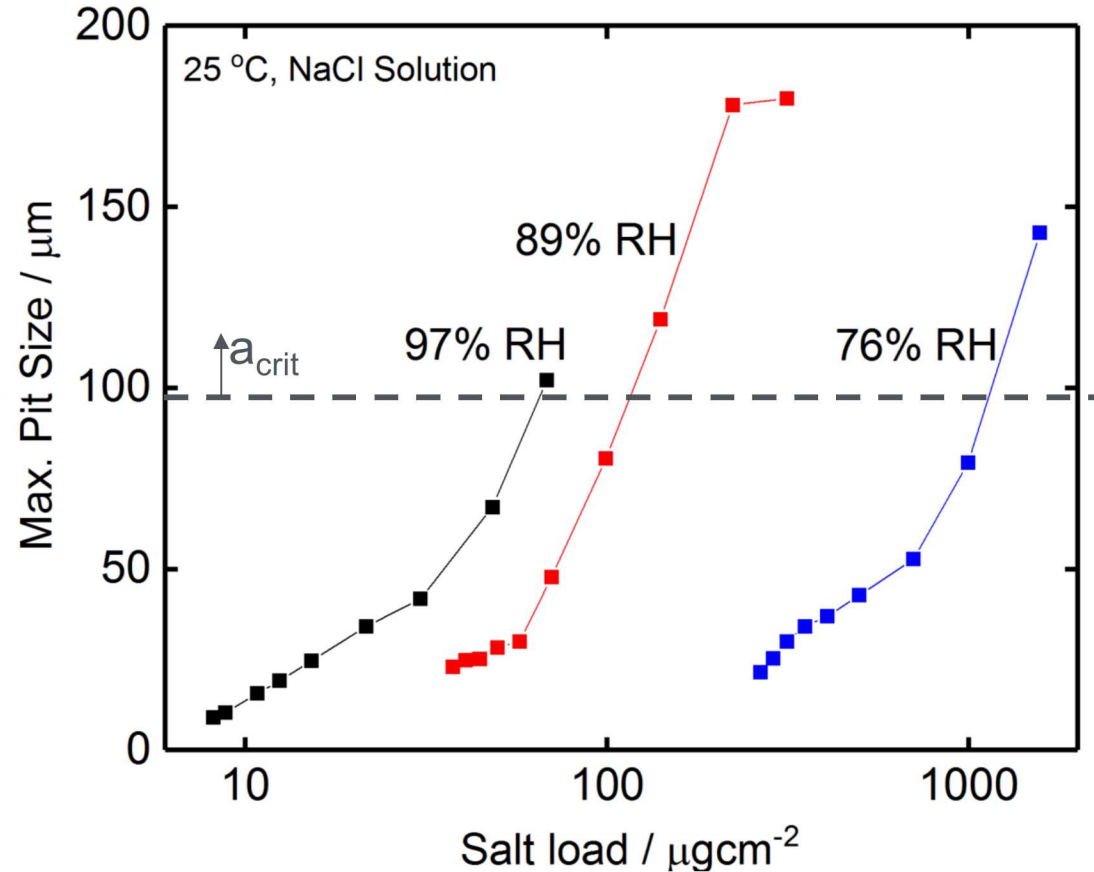
$$\ln I_{c,max} = \frac{4\pi kW_L \Delta E_{max}}{I_{c,max}} + \ln \left[ \frac{\pi e r_a^2 \int_{E_{corr}}^{E_{rp}} (I_c - I_p) dE}{\Delta E_{max}} \right]$$

# Cracking Susceptibility Based on Maximum Pit Size Predictions

Conceptual calculations of **hemispherical** maximum pit size derived from cathodic kinetics measured in NaCl brines

**Need to understand relevant limits of numerous assumptions including:**

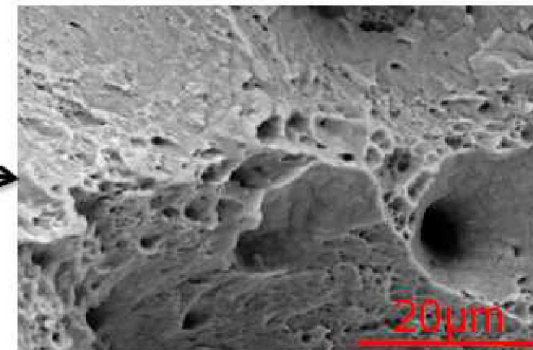
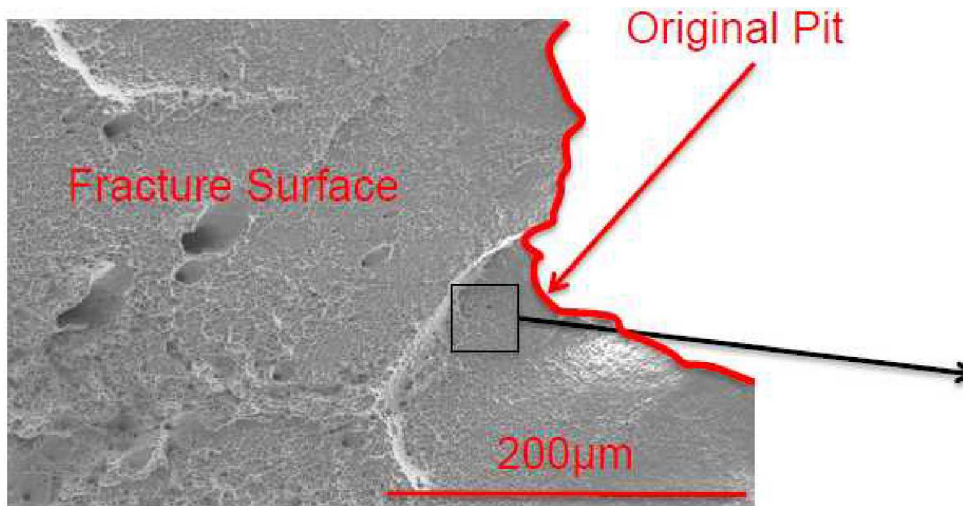
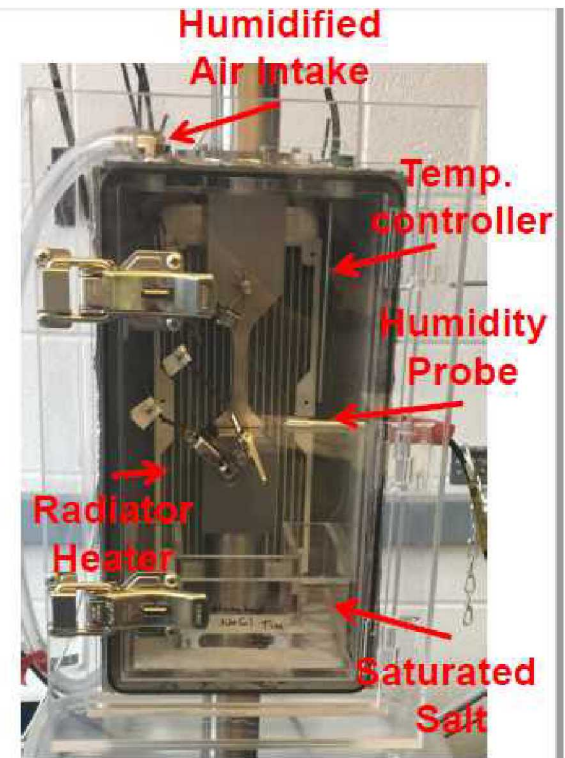
- lab = field  $E_{chem}$  parameters?
- Electrolyte and surface attributes are constant or changes due to corrosion or other processes are inconsequential
- Effects of Material features (microstructure) and stress/strain are negligible



Example:  $K_{ISCC} = 5 \text{ Mpa} \cdot \text{m}^{1/2}$ ,  $\sigma = 500 \text{ MPa}$

# Pit-to-Crack Transition Features Under Constant Load

- Tests up to 1.2X yield strength for 34 days @ 75%RH
  - Loading repeat sequence:
    - 6 Hours: Constant Load 1.2X Yield Strength
    - 20 min: .7 R-ratio, 1Hz
    - 20 min: .7 R-ratio, .1Hz
    - 20 min: .7 R-ratio, .01Hz
- Saturated ethanol/sea-salt applied to the gauge length of specimen to provide electrolyte for SCC.
- No Failure or visible crack after 34 days – sample pulled to failure.



# Summary

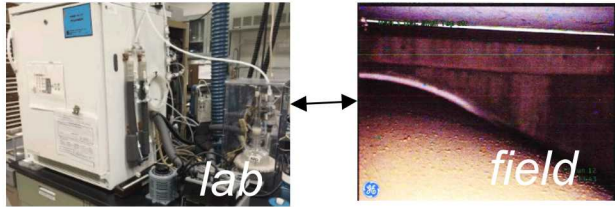
- RH, salt load and surface finish have strong affect on 304 corrosion damage distributions and rates.
- Damage datasets on baseline 304H are being generated to quantify the effect of RH, T, and salt load for SCC model development/validation.
- Experiments are underway to identify material and environmental conditions leading to damage with highest propensity for crack initiation.
- A deterministic/electrochemical maximum pit size model is being extended and validated under canister-relevant conditions.

## Impact

- Relevance and role of environment and material on crack initiation probability and rates → identify red flag conditions.
- Extend and validate maximum pit size model and shape/size factor initiation criterion as tool for risk-based ranking.

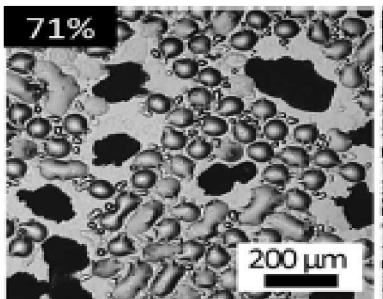
# Summary: Environment and Material Relations to SCC Damage Distributions and Rates

How representative are lab conditions?

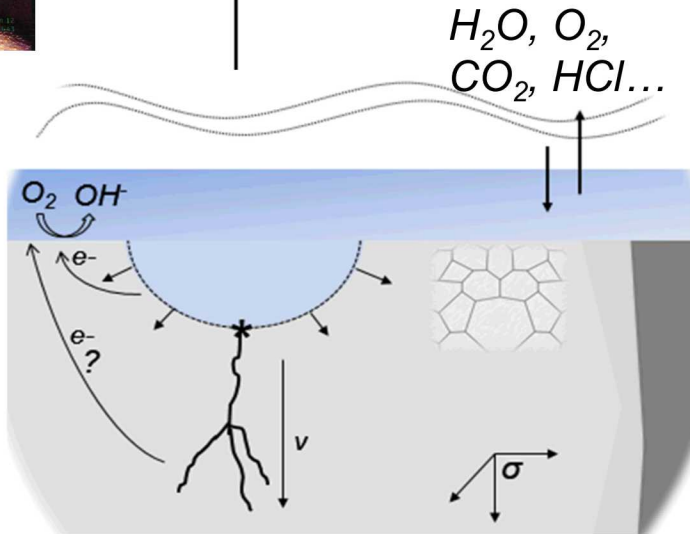


Surface/atmospheric chemistry, RH variation

Environmental control of damage distribution and rates?



Salt loads and distributions, T, RH



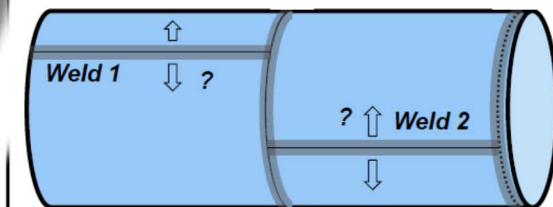
What are limits of model accuracy?

$$\frac{da}{dt} = \begin{cases} \alpha \exp\left[-\frac{Q_g}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] & \text{for } RH \geq DRH \text{ and } K_1 > 0 \\ 0 & \text{for } RH < DRH \text{ or } K_1 \leq 0 \end{cases}$$

EPRI, 2017

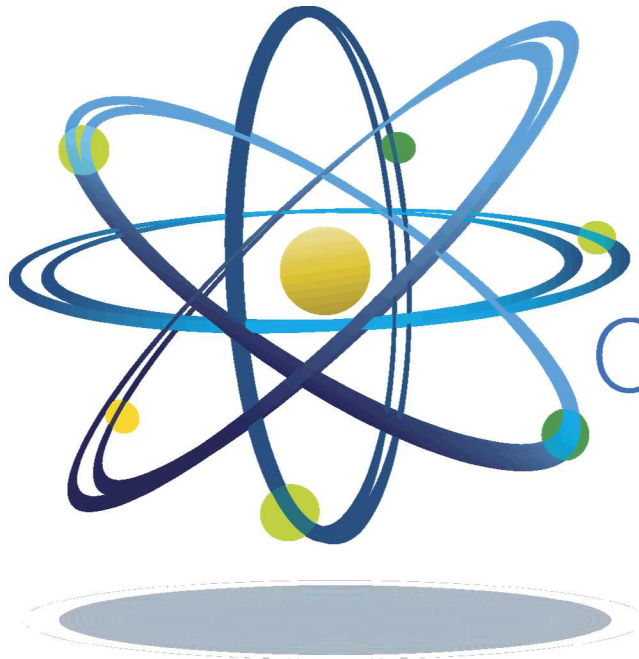
Benchmarking datasets, bounding limits, test assumptions, model confidence

Where to focus inspection?



Variations in canister surface environment, material properties, and stress

# Questions?



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