U.S. DEPARTMENT OF ENERGY | Office of NUCLEAR ENERGY

Spent Fuel and Waste Science and Technology (SFWST)

Sandia National Laboratories

Clear SAND2020-11833C

DOE Stress Corrosion Cracking Research at Sandia National Labs

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ESCP Fall Workshop

Virtual Meeting

November 9, 2020

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Overview Slide: CISCC Program

DOE CISCC Program

PNNL
- Dust Deposition Analysis: Modeling
- Parametric crack growth studies as f(materials properties and environment)
- Crack Consequence
- Cold Spray Development

SNL
- Canister Environment: Sampling and Measurement
- Brine stability and thermodynamic modeling
- Corrosion as f(environment and material)
- Pitting model for parameterization
- Single effect CGR studies
- Crack Consequence
- Cold Spray Evaluation

SRNL
- CGR Validation: Big plate test

ORNL
- Crack Consequence

DOE Collaborations

NEUP

Cold Spray/Welding
- Purdue
- The Ohio State
- Univ. of Cincinnati
- Univ. of Idaho
- Univ. of Wisconsin

CGR
- Univ. of Virginia

Coatings and Mitigation
- N. Carolina State
- Univ. of Nebraska
- Univ. of Nevada Reno
- Univ. of S Carolina
- Univ. of Wisconsin Madison
- Virginia Tech

Other Collaborations

CGR and Pitting
- Univ. of Virginia
- The Ohio State
- Univ. of New Mexico
- DNV-GL

- EPRI
- EPRI
- EPRI

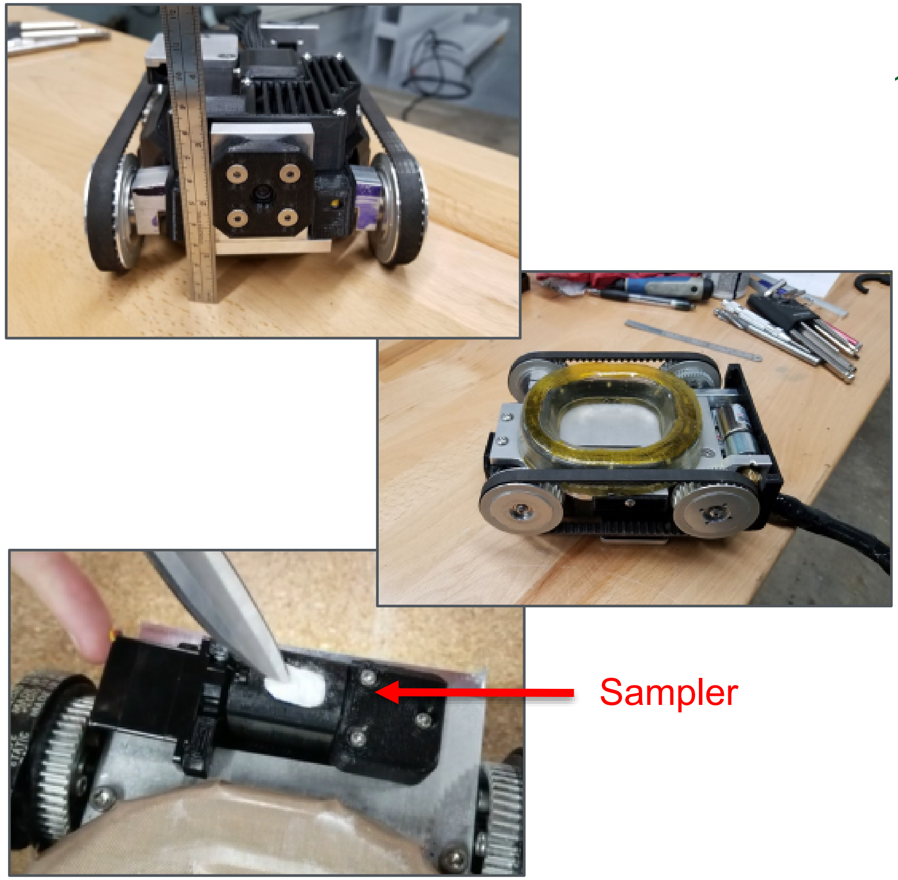
ISFSI Site Sampling – Orano Site "A"

First dust and salt data available from an inland site.

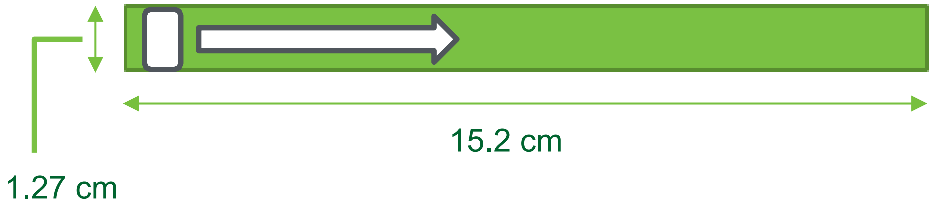
Horizontal Storage System Sampled 12, 2, and 4 o'clock, and above the rail.

Sample #	
Block A	2 o'clock
	Above HSM rail
Block B	4 o'clock (missing filter)
	None
Block C	10 o'clock
	HSM rail - left
Block D	12 o'clock - front third
	12 o'clock - back third
Block A	
Block B	
Block C	
Block D	
Scotchbrite	Average of 3
Filter blank #1	
Filter blank #2	

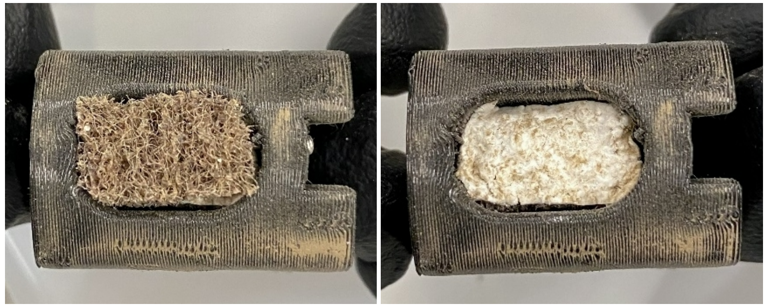
Samples were collected using the RTT vacuum crawler.



Sample was collected by moving crawler 6". Sampled area = 19.35 cm²



12 o'clock position – front third

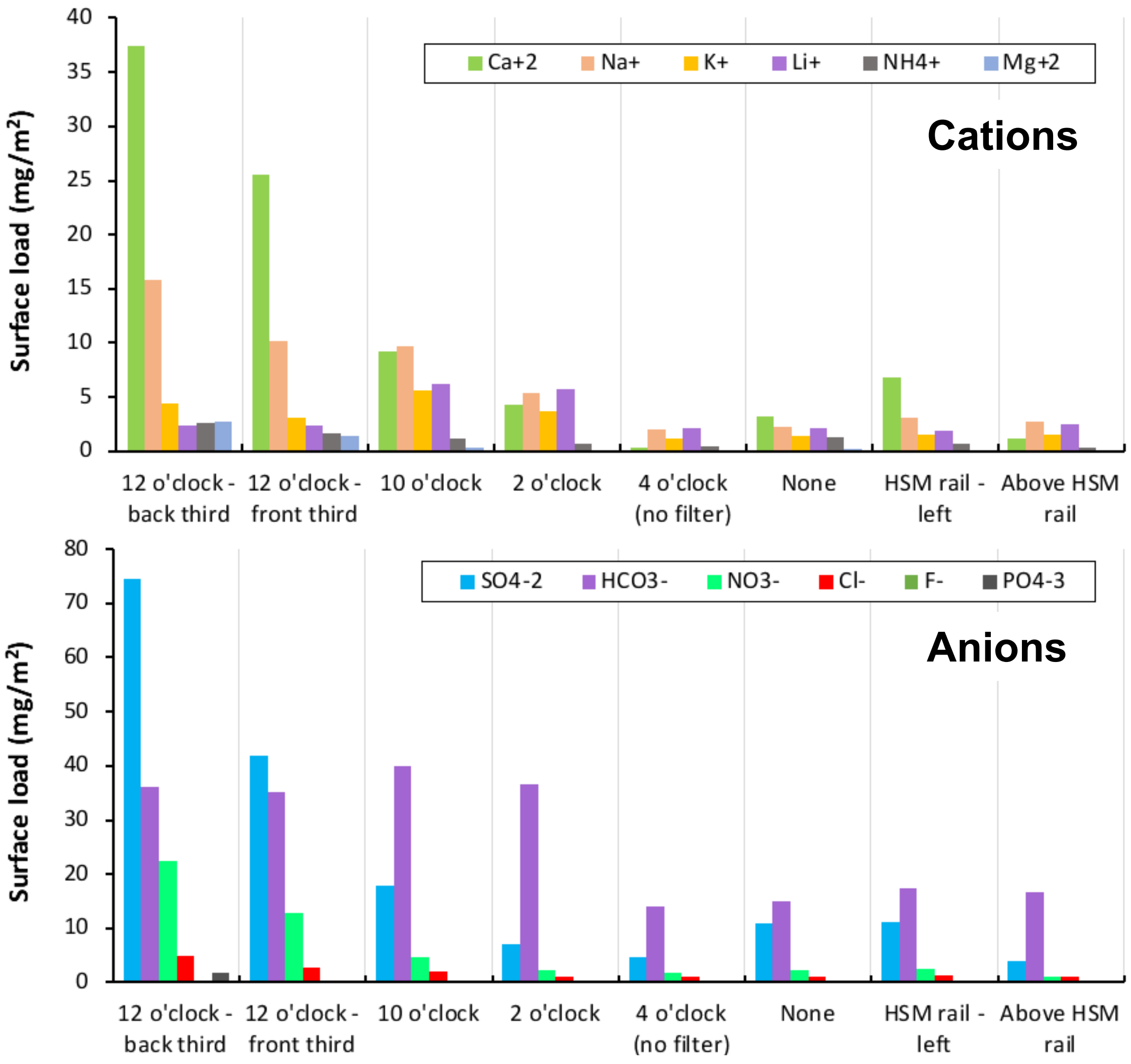


2 o'clock position

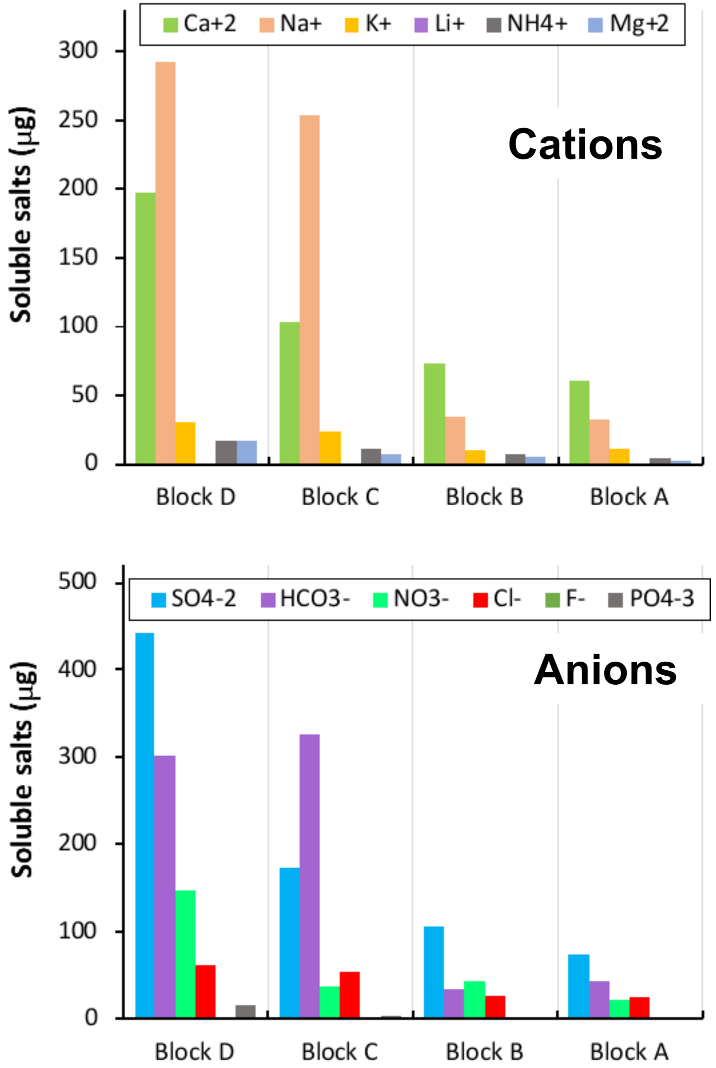
ISFSI Site Sampling – Orano Site "A"

Chemistry:

- Li leached from the Scotchbrite® pads. Not present in dust!
- Cations:
  Ca^{+2} >> Na^{+} > K^{+} > NH_4^{+} > Mg^{+2}
- Anions:
  SO_4^{-2} > HCO_3^{-} >> NO_3^{-} > Cl^{-}
- Chloride concentrations all
  < 5 mg/m^2



Samples



Blocks

Definition of Canister-Relevant Testing Environments

Testing to date:

- Sea-salts or individual sea-salt components
- Isolated or coalesced droplets on metal surface (corrosion tests) *or* immersed conditions (SCC testing)
- Constant T and RH

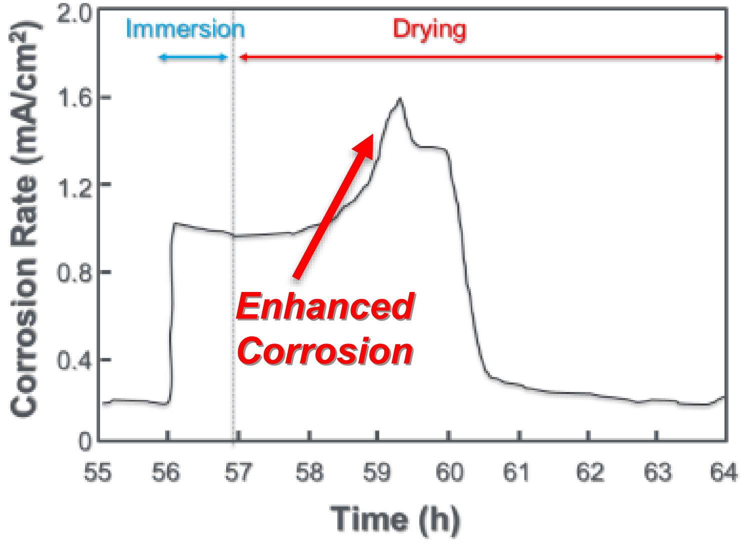
Canister-relevant testing environments:

- Diurnal cycles in T and RH
- More complex salt chemistry, even at near-marine sites (e.g., presence of nitrate)
- Presence of inert mineral grains (most abundant grains in dust, even at near-marine sites)

Definition of Canister-Relevant Testing Environments

Why significant? → Potential Influence on Corrosion:

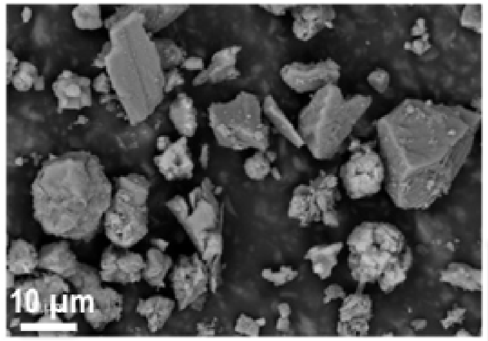
Diurnal Cycles



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

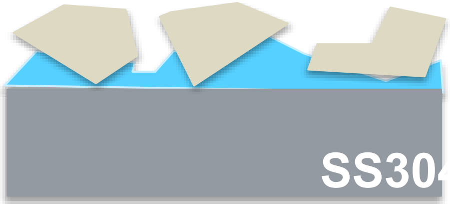
Corrosion rate increases upon initial drying (highly concentrated brine)

Dust/Precipitates



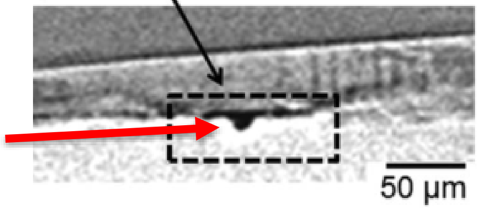
Dust at Diablo Canyon

Dust may act to spread water layer/ enhance corrosion



Crevice-like attack containing a pit

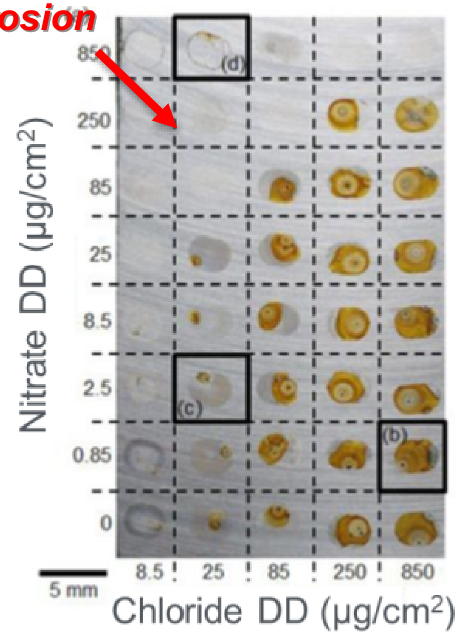
Enhanced Corrosion



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

Chemistry

Inhibited Corrosion



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

Other chemistries may mitigate corrosion

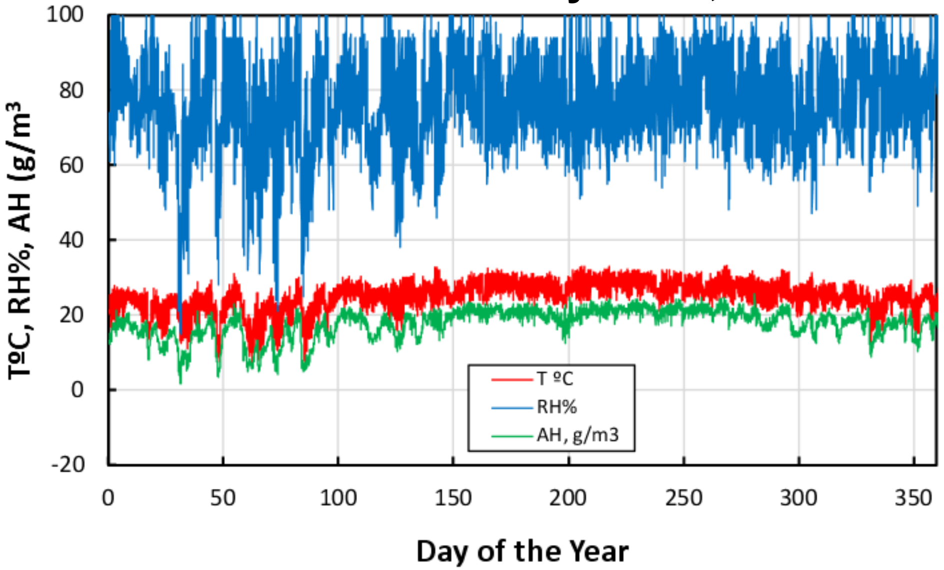
[1] Nishikata, A., Yamashita, Y., Katayama, H., Tsuru, T., Tanabe, K., & Mabuchi, H. (1995). *Corrosion science*, *37*(12), 2059-2069.
[2] Guo, L., Mi, N., Mohammed-Ali, H., Ghahari, M., Du Plessis, A., Cook, A., ... & Davenport, A. J. (2019).
[3] Cook, A. J., Padovani, C., & Davenport, A. J. (2017).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

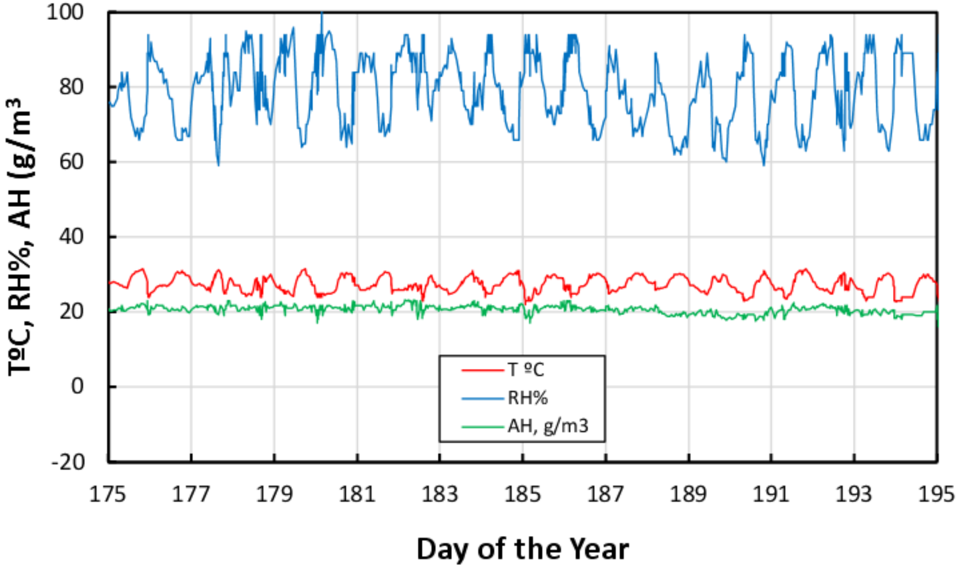
Diurnal Cycles in Temperature and RH

Evaluated ambient weather data representing several ISFSI sites. Daily cycles in T and RH vary with location, but show great similarities:

- Diurnal cycles are very regular, especially during summer months.
- T and RH strongly correlate, with ↑T = ↓RH.
- Absolute humidity (AH) varies significantly over seasonal cycles, but little over a day-night period

Weather at Turkey Point, FL

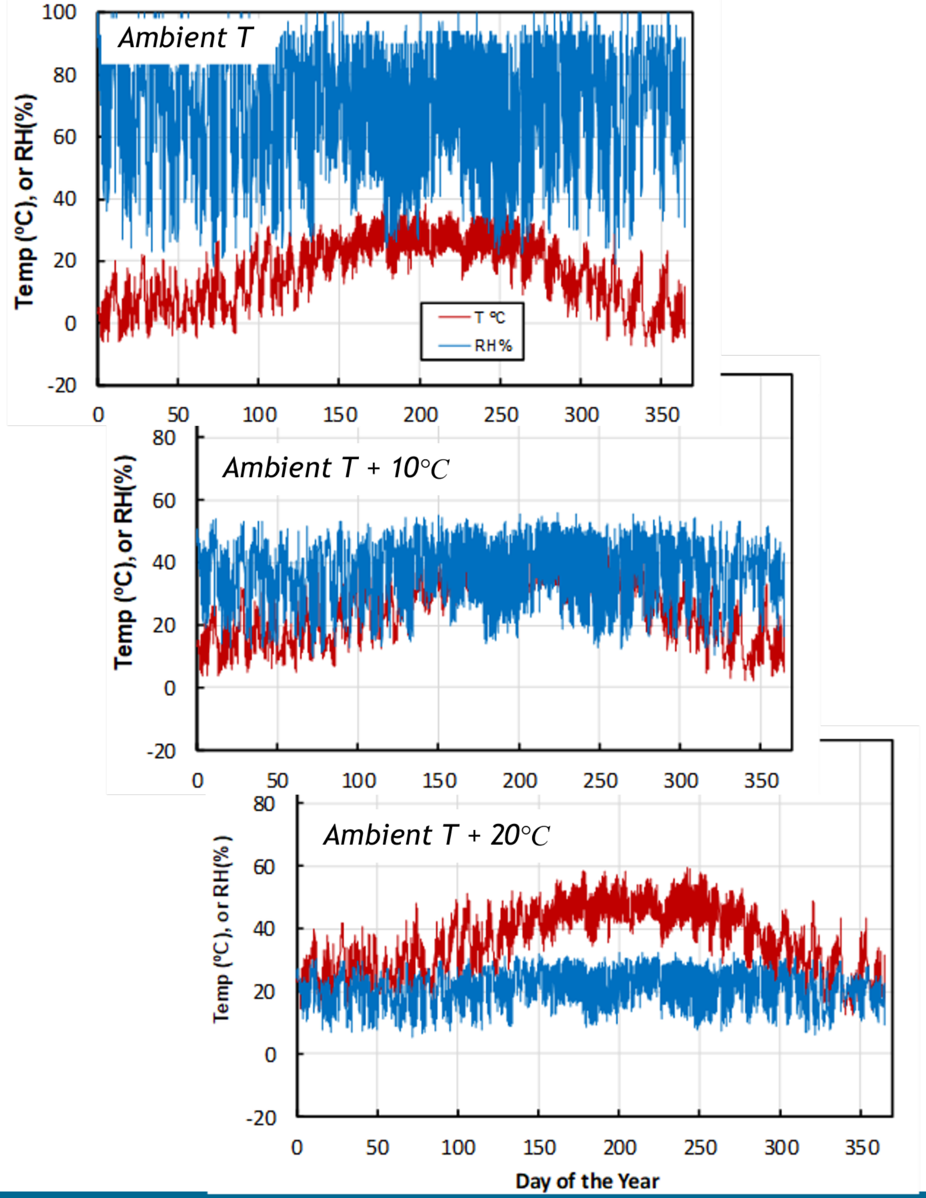




Diurnal Cycles in Temperature and RH

Daily cycles in T and RH are reflected on the canister surface, but offset due to heat load from the fuel.

- Calculate canister surface RH using ambient AH and canister surface T, using the water equation of state of Wagner and Pruß (2002)*
- Overall results—Small increases in canister temperature correlate with:
  - Lowering of canister surface RH relative to ambient RH
  - Narrowing of the RH band



* Wagner W. and Pruß A. (2002). "The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use." *Journal of Physical and Chemical Reference Data* 31(2): 387-535.

Diurnal Cycles in Temperature and RH

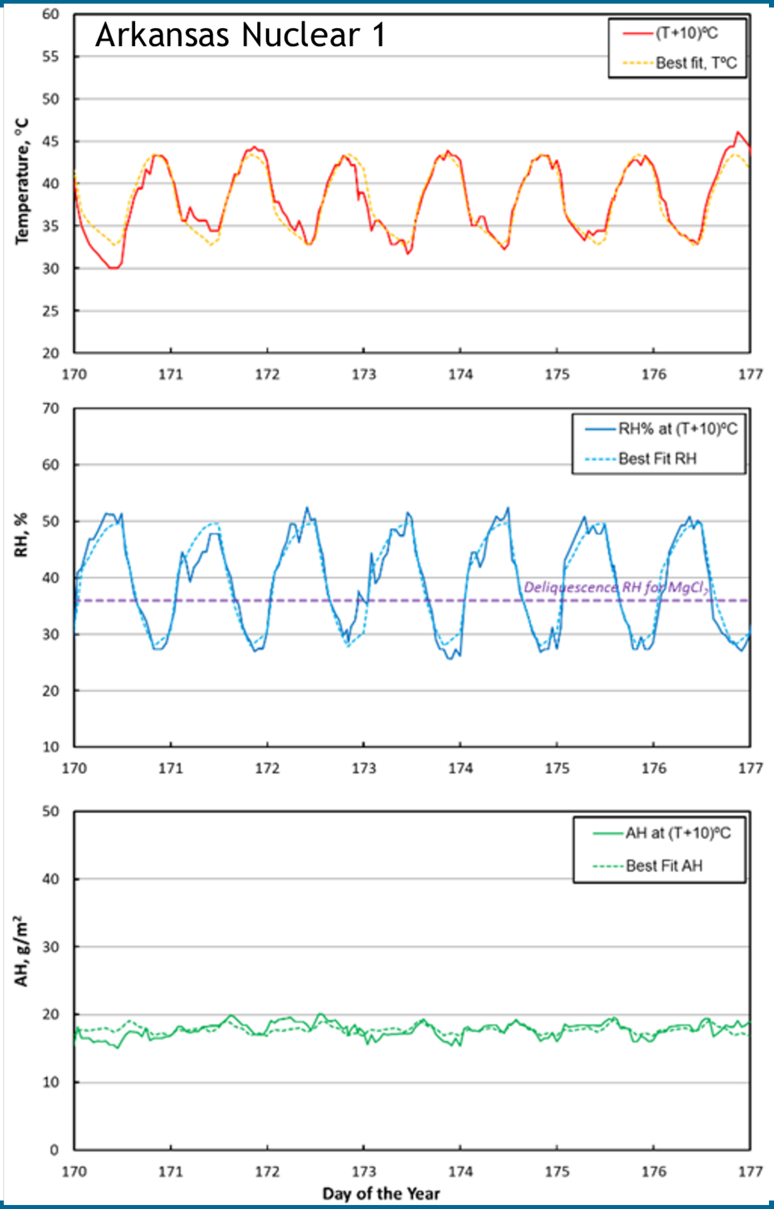
<u>RH value of interest</u>: 35% RH, the DRH for bischofite

- Selected AR-1 data as showing the largest diurnal variation in RH.
- Selected a ΔT of 10ºC to best bound the bischofite DRH
- Derived a best-fit 12-step T/RH cycle that best fits calculated T, RH data
- Tested cycle to ensure it could be implemented: large simultaneous changes in T and RH could result in transients. No transients.

Best-fit diurnal cycle that crosses the bischofite DRH

Hour	Temp. ºC	RH, %
2	41.68	30.33
4	36.45	41.68
6	35.27	43.92
8	34.35	46.69
10	33.69	48.68
12	32.74	49.54
14	33.44	49.57
16	38.24	40.98
18	40.55	34.62
20	42.69	30.62
22	43.51	27.82
24	42.97	29.15

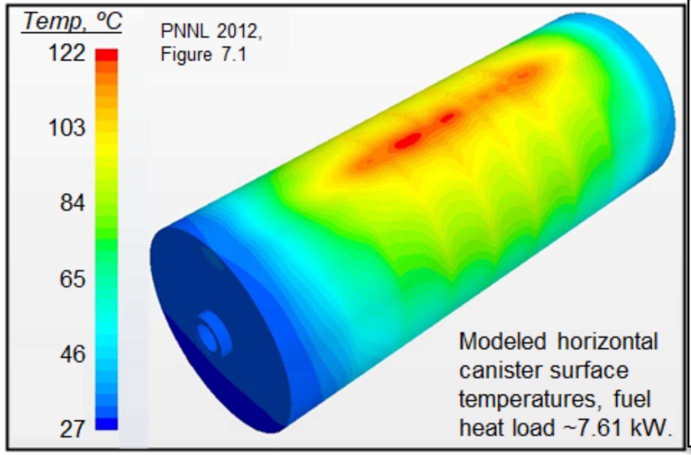
These are relevant testing conditions, that will eventually apply to all canisters. ***The same calculation was carried out for the conditions of NaCl deliquescence, but they are not relevant for testing, because…***

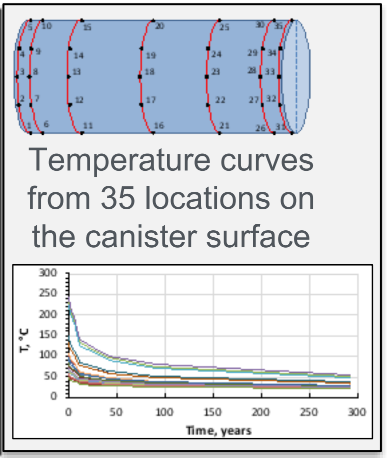


Diurnal Cycles in Temperature and RH

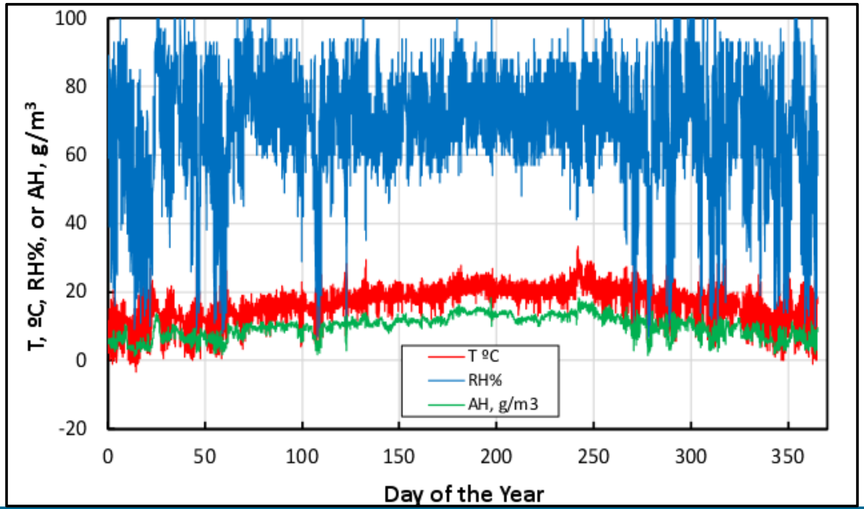
…the deliquescence RH for bischofite is reached in 10-20 years at some locations on the canister surface, but the DRH for NaCl is not reached for hundreds of years at any location

Canister thermal data



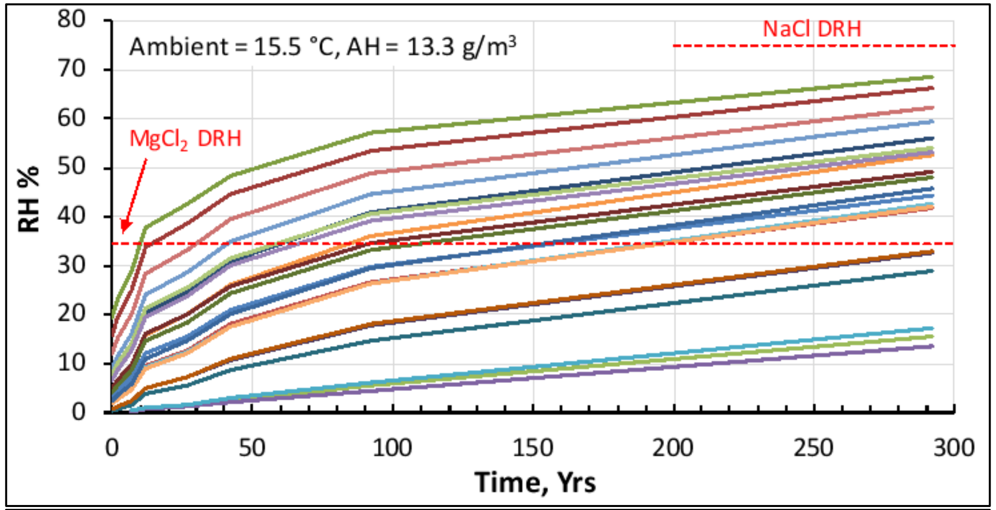


Weather data



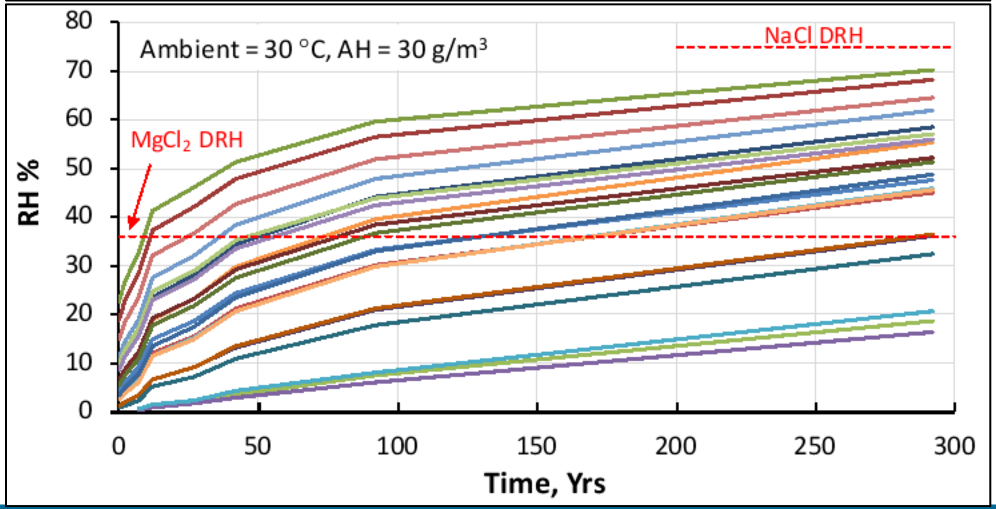
Base-case thermal model

- Ambient air T = 60°F (15.5°C)
- Max. AH = 13.3 g/m^3



Base-case model +14.5°C to match observed field AH

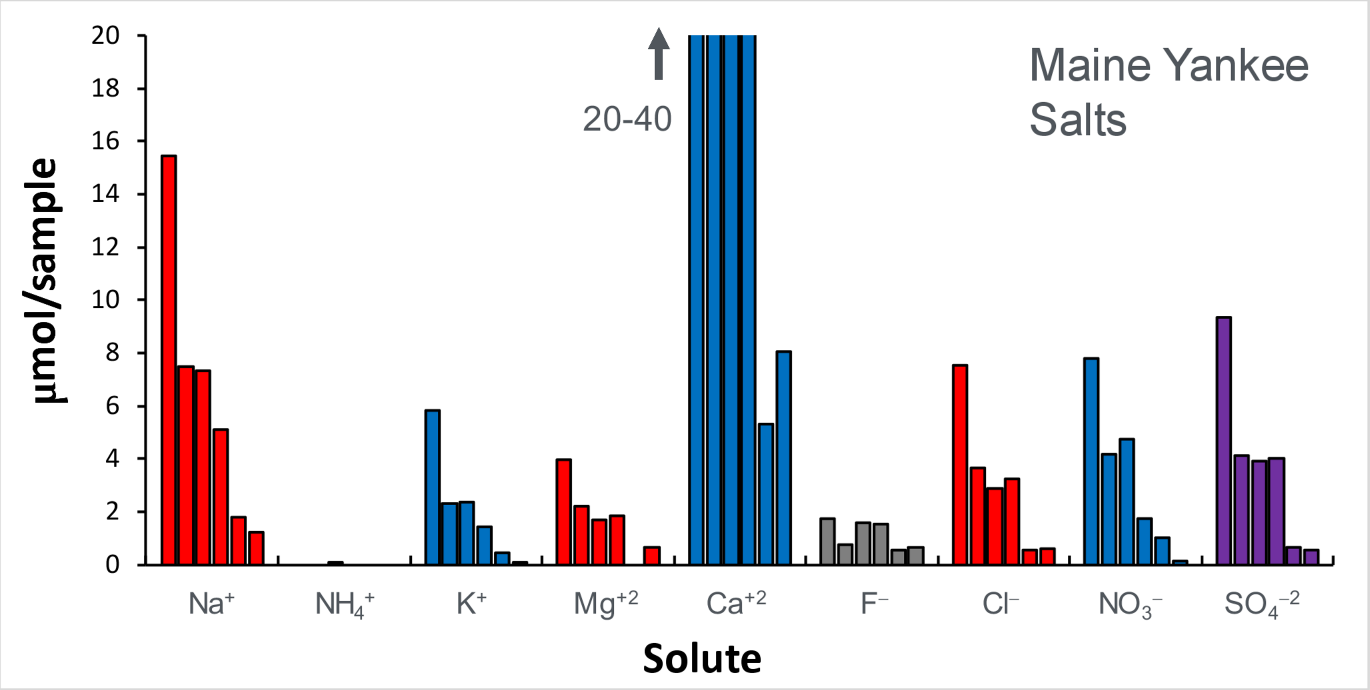
- Ambient air T = 86°F (30°C)
- Max. AH = 30 g/m^3



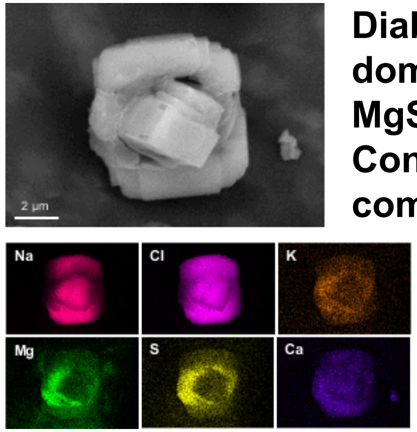
Soluble Salt Chemistry

While salts in dust collected from Diablo Canyon ISFSI appear to be dominantly sea salts, soluble salt compositions at East Coast sites differ significantly from sea-salts

- Significant contribution from continental salts (relatively enriched in Ca, K, SO_4, NO_3, sometimes NH_4).
- Effect of sea salt particle-gas conversion reactions (reactions with SO_2, NO_x convert chlorides to nitrates, sulfates)



Sea-salt aerosols from Diablo Canyon ISFSI



Diablo Canyon salt aggregates: dominantly NaCl with interstitial $MgSO_4$ and trace K, Ca phases. Consistent with seawater ion compositions.

Use Maine Yankee data to produce a normalized salt composition

Normalized salt composition

Species	Normalized molar conc.
Na^+	1.0000
K^+	0.3516
Ca^{+2}	4.8576
Mg^{+2}	0.2655
Cl^-	0.4838
NO_3^-	0.5223
SO_4^{-2}	0.5985
HCO_3^-	*9.3947

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* Based on charge balance

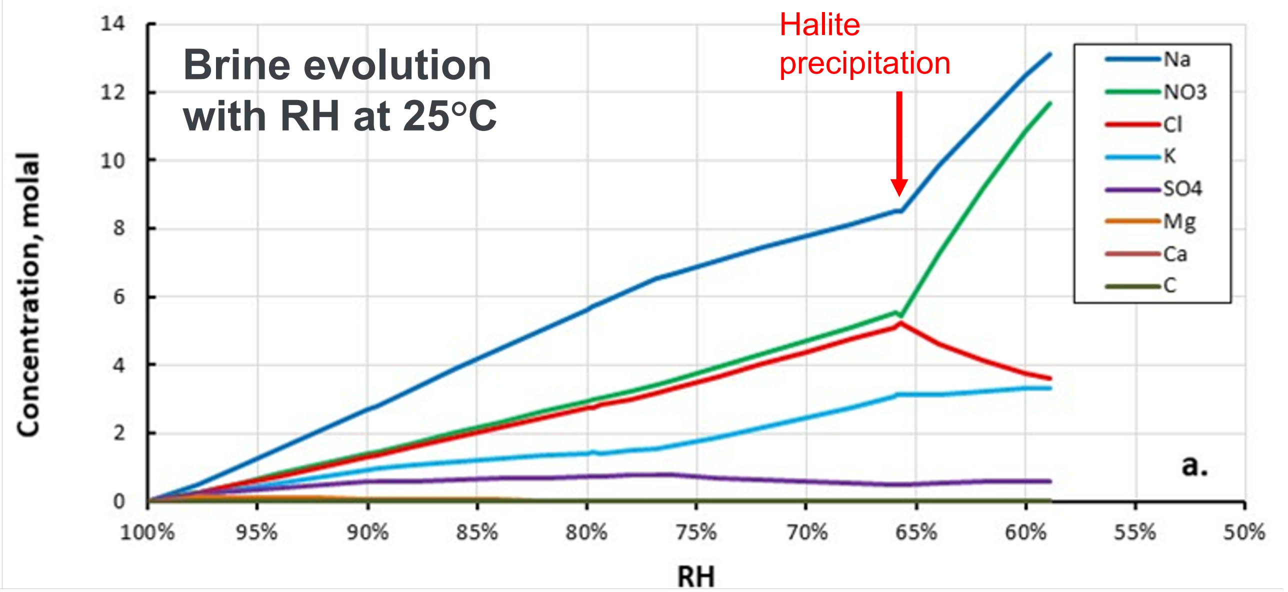
* Based on charge balance

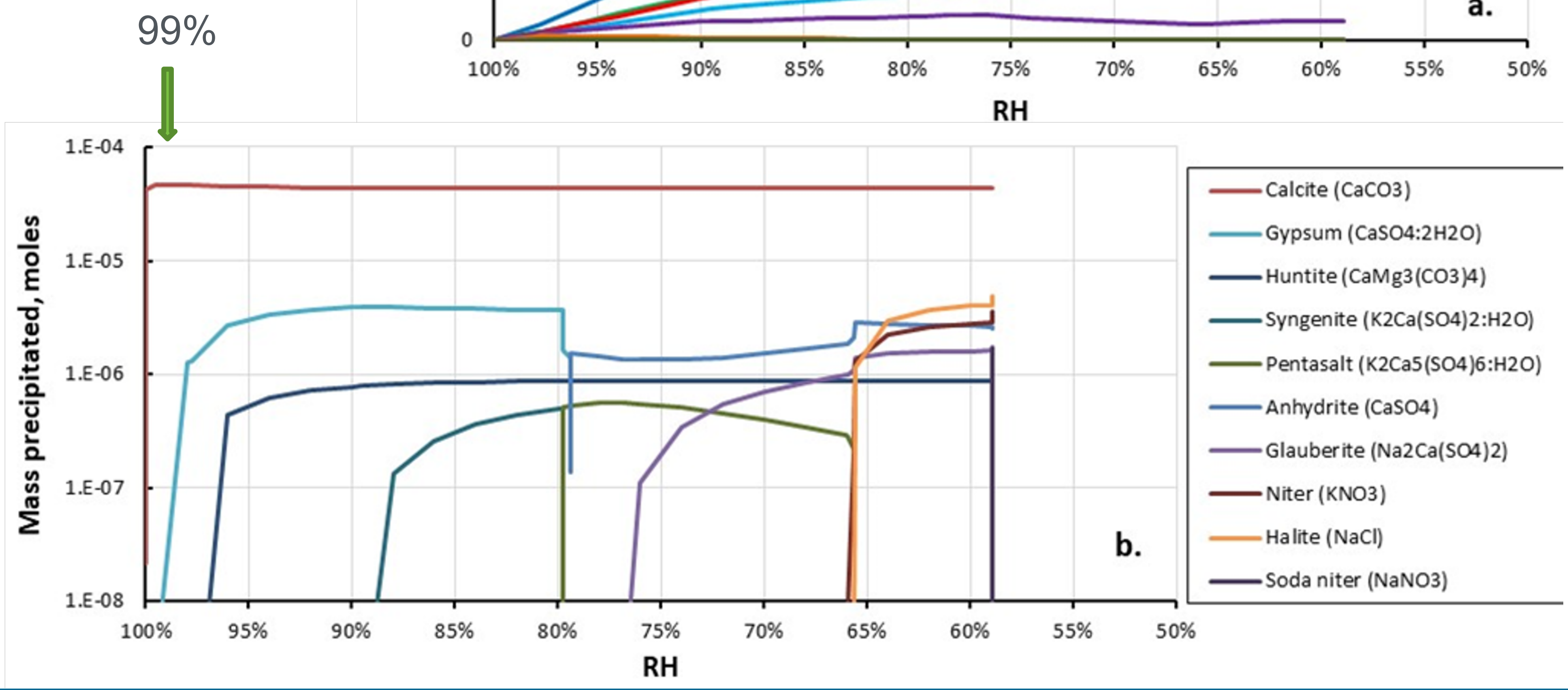
Soluble Salt Chemistry

<u>Goal</u>—identify a brine composition that can be deposited as aerosols on samples for atmospheric corrosion testing.

<u>Method</u>—use EQ3/6 and Pitzer database to simulate evaporation of the identified salt composition. Target composition—0.2-0.4 molal (≈99% RH). Brine must be stable as a liquid *(no precipitates!)*

<u>Problem:</u> Using normalized salt composition, salts precipitate at low degrees of evaporation (0.003 molal)





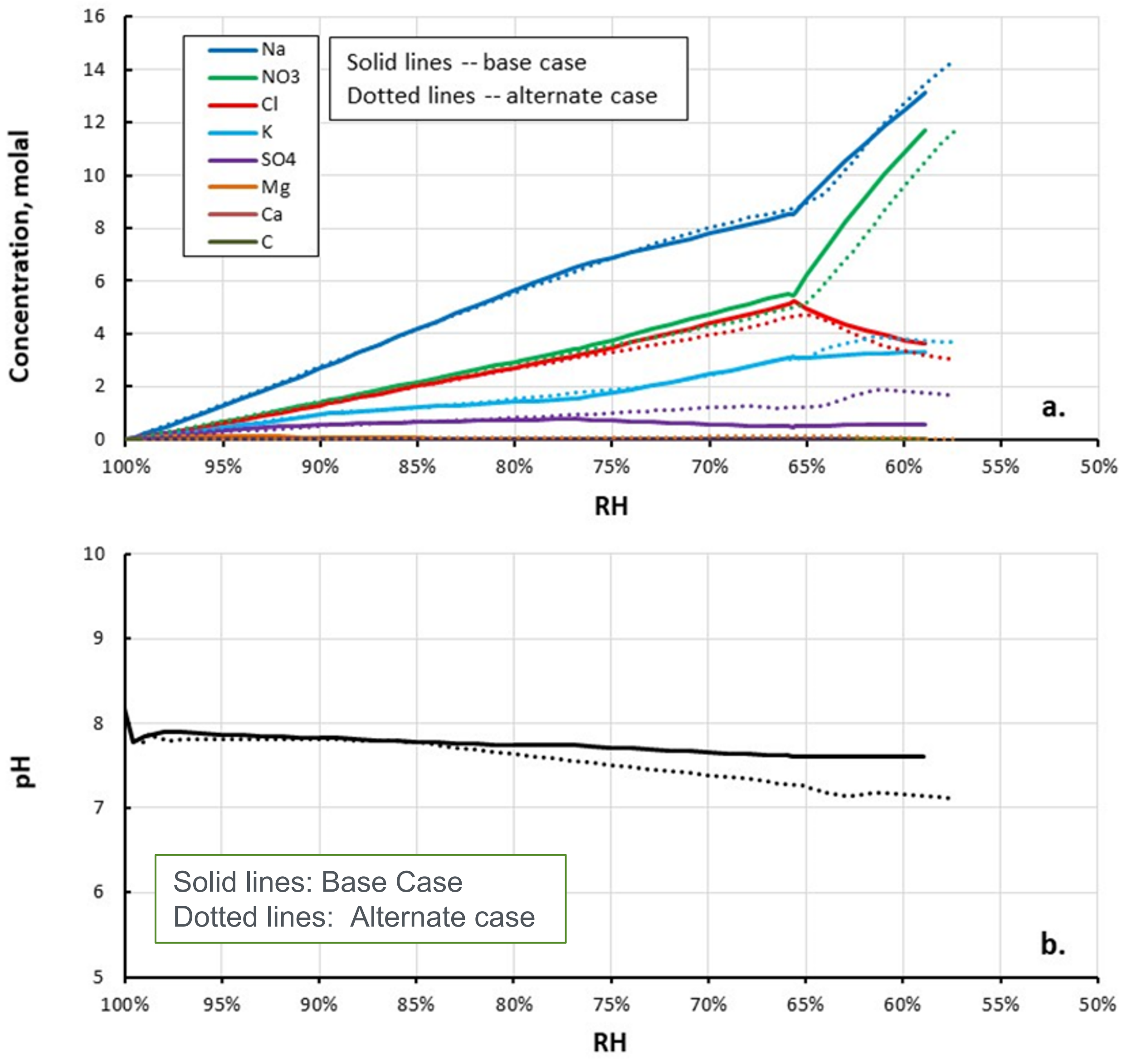
Soluble Salt Chemistry

Goal—identify a brine composition that can be deposited as aerosols on samples for atmospheric corrosion testing.

Solution—Subtract solution components to achieve necessary concentrations without precipitation, while affecting brine evolution as little as possible. *Brine composition evolves similarly to original solution; no precipitation at 99% RH (0.4 molal).*

Brine composition to use:

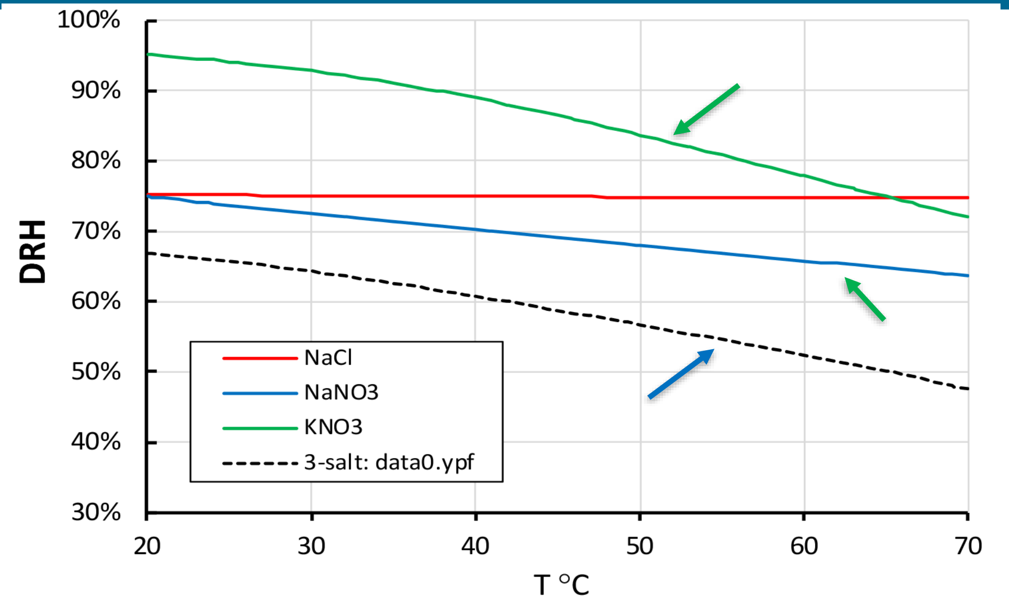
Species	Conc., molal	To mix:	
		Salt	Wt, grams
Na^{+}	2.417E-01	NaCl	5.3590
K^{+}	8.499E-02	$NaNO_3$	3.5070
Ca^{+2}	9.416E-03	KNO_3	8.5929
Mg^{+2}	3.209E-03	$CaCl_2$	1.0450
Cl^{-}	1.169E-01	$MgCl_2{:}6H_2O$	0.6524
NO_3^{-}	1.263E-01	Na_2SO_4	7.6789
SO_4^{-2}	5.406E-02	$NaHCO_3$	0.0543
HCO_3^{-}	6.467E-04	**SUM**	26.8896

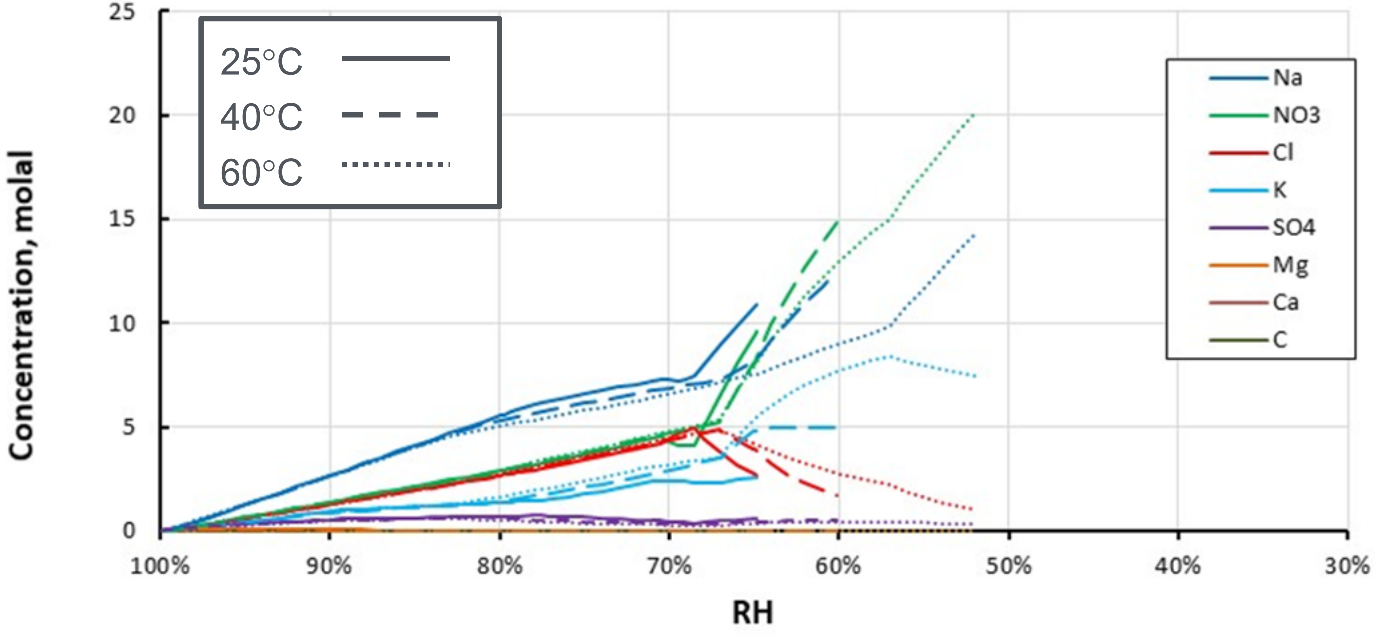


Soluble Salt Chemistry

<u>Deliquescence properties of the identified salt assemblage:</u> ***Necessary to determine range of relevant testing conditions***

- Solubility of nitrate salts increases significantly with temperature, so the DRH drops.
- DRH of the predicted salt assemblage decreases with increasing temperature
- Concentration of deliquescent brine increases as temperatures increase





Conclusions

- Identified a brine composition for use in atmospheric testing.
- Duplicating field conditions requires not only matching Cl/NO_3 ratios of the starting salts, but also incorporation of minor species that play a large role in buffering the brine pH.
- Presence of nitrate can greatly affect the deliquescence RH and possible range of testing conditions (T, RH).

Inert Dust Effects

Diagenetic mineral fragments (quartz, aluminosilicates, carbonates) are the most abundant dust particles on canister surfaces; plant matter (e.g., pollen) can also be common. Salts are a minor component.

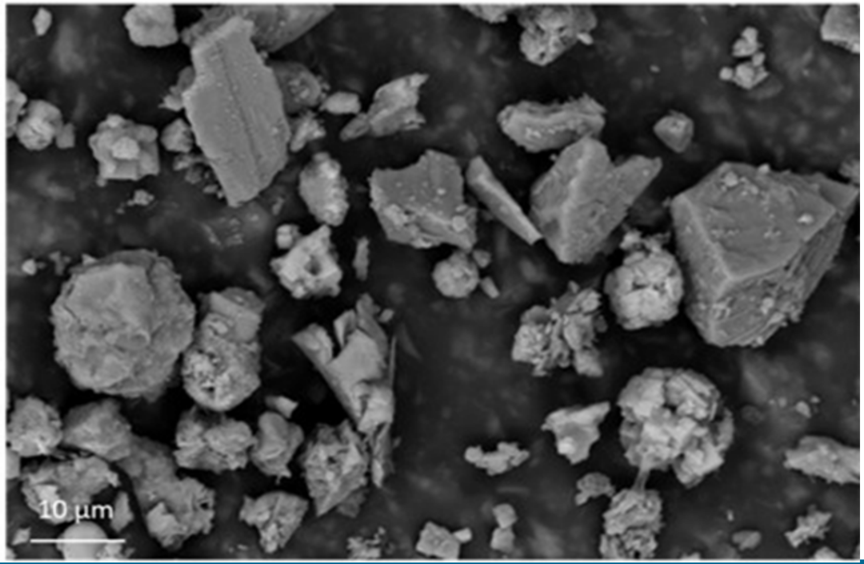
Possible effects of inert minerals:

- Brine spreading via capillary processes—development of a larger cathode
- Crevice corrosion, in occluded regions under larger grains

To evaluate the potential *physical* effects of inert dust minerals, we characterized dust particle sizes, and will perform corrosion tests using sea-salts and inert mineral particles of representative sizes.

Hope Creek

Diablo Canyon



Inert Dust Effects

Procedure: Determine dust size distributions from SEM images of dust collected from in-service canisters (sampling bias towards smaller particles). Evaluated dust from four sites:

Hope Creek ISFSI (New Jersey)

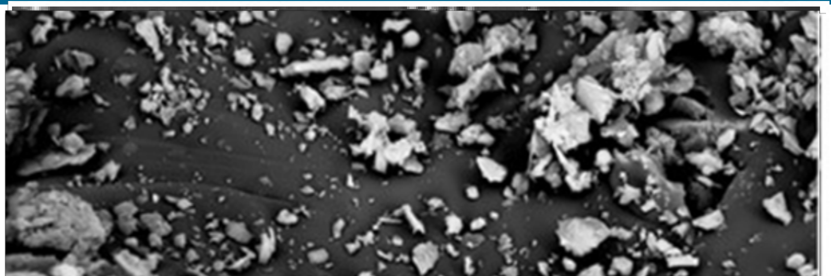
Calvert Cliffs ISFSI (Maryland)

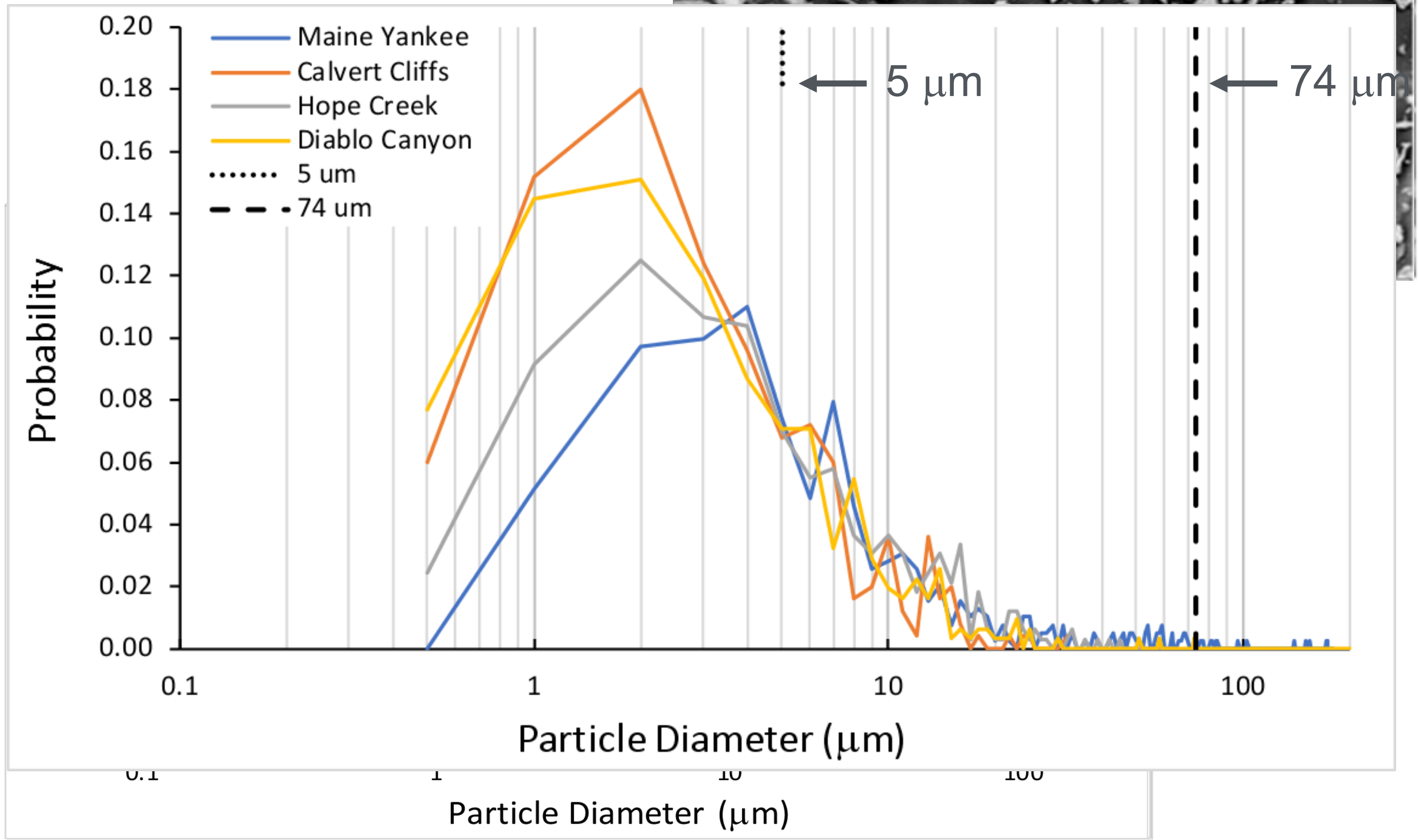
Diablo Canyon ISFSI (California)

Maine Yankee ISFSI (Maine)

<u>For testing purposes:</u>

- Inert mineral – **quartz**
- Fine particles to evaluate capillary brine spreading: **5 μm Min-U-Sil quartz**
- Coarse particles to evaluate crevicing: **74 μm (200 mesh) Sil-Co-Sil quartz**
- **Mixed 5 μm/74 μm to evaluate coupled effects**





Pitting Exposures in the Defined Environments

- Current Status:
  - Cyclic exposures in-progress
  - Dust exposures under calibration
  - Mixed chemistry exposures in development

- Objective:
  - Gain pitting statistics across more relevant environments
  - Inform better the potential influences on corrosion and SCC initiation

Cyclic Exposure Test Plan:

Sample	Seawater Deposition	Surface Finish	Cycle		Exposure Time (weeks)						Total Sam.
	µg/cm^2	Grit/polish	Site	0	1	2	4	26	52	78 / 104	
304H	300	120	Arkansas Nuclear 1	2	3	3	3	3	3	3	20
304H	300	1200	“	2	3	3	3	3	3	3	20
304L	300	120	“	2	3	3	3	3	3	3	20
304L	300	1200	“	2	3	3	3	3	3	3	20
316L	300	120	“	2	3	3	3	3	3	3	20
316L	300	1200	“	2	3	3	3	3	3	3	20
Total:				12	18	18	18	18	18	18	120

**In-progress, pulled exposure times to 4 weeks*

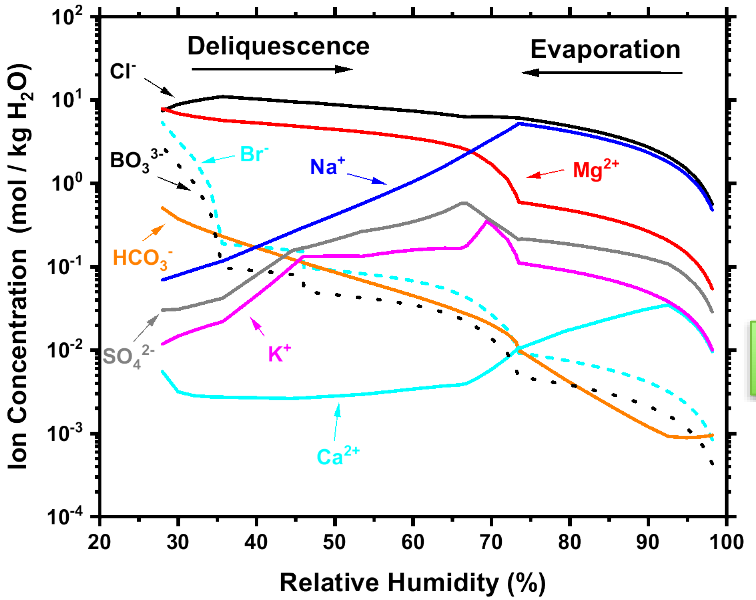
Dust Exposure Test Plan:

Coupon Size	Total	5.0 um	74 um	Mix	No Dust	1 month	6 month	12 month	24 month	Notes
8x8	6	2	2	1	1	0	0	1	1	* Pull no dust and mix at 24 months
4x4	18	5	5	5	3	0	2	2	2	*Pull no dust at final three sampling intervals
2x2	67	21	21	21	4	5	5	6	6	*Pull one no dust per time interval
2x1	38	11	11	11	5	3	3	3	3	*Pull one no dust per time interval and two at 24 months
2x1 (304L, 2017 exposures)	31	9	9	9	4	2	2	3	3	*Pull one no dust per time interval
Total	**160**	**48**	**48**	**47**	**17**	**10**	**11**	**12**	**15**	

**Dust deposition process under calibration, exposure to be started shortly*

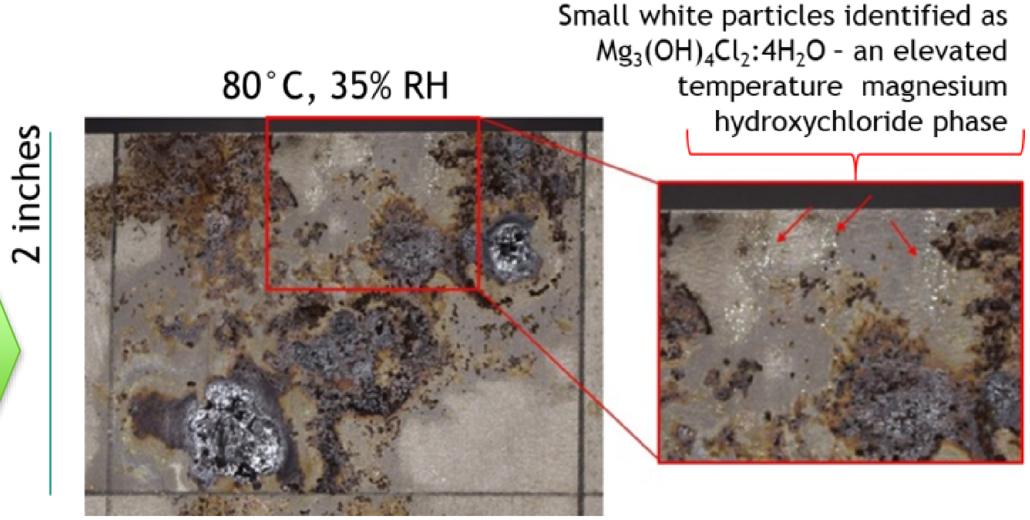
Importance of $MgCl_2$

What brines are likely to form on the surface?



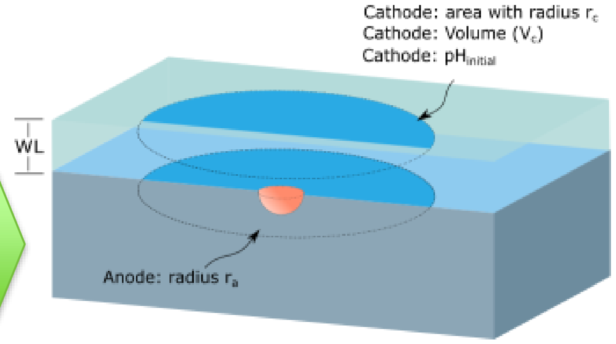
$MgCl_2$ Dominated Brine for > 300 years!

Why is $MgCl_2$ Significant?



Formation of precipitates can lead to brine dry-out

How do $MgCl_2$ brines impact corrosion?



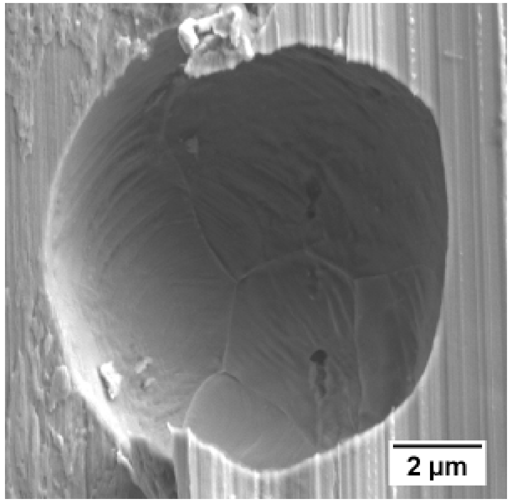
…and SCC initiation?

Pit Morphology

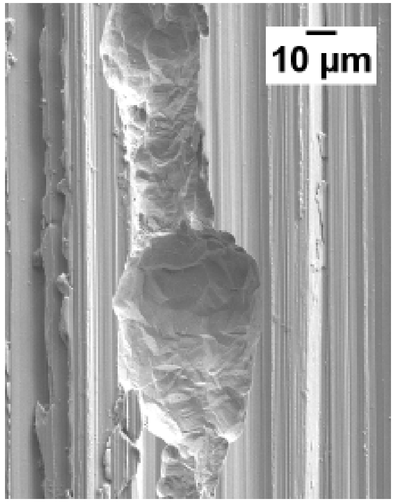
Brine composition greatly impacts resultant pit morphology…

NaCl Dominated Brines

76 %RH Seawater

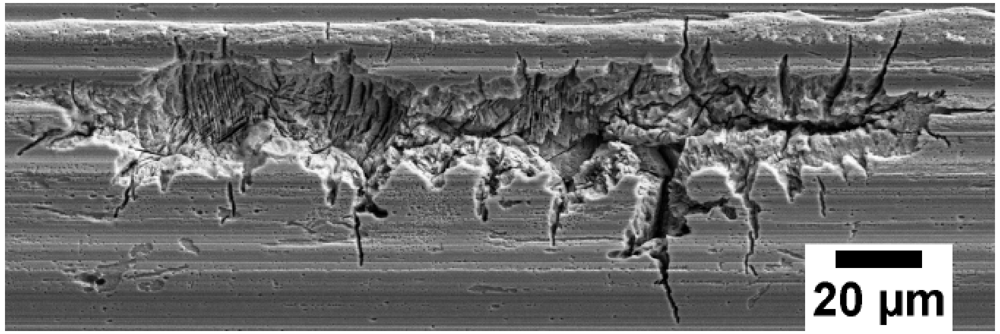


5.22 M NaCl

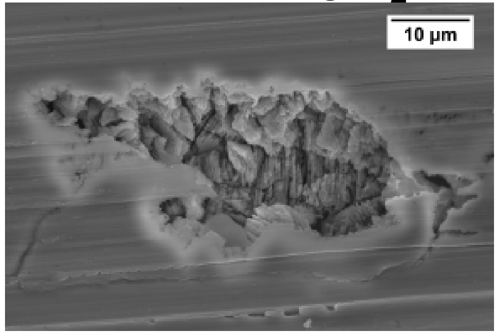


$MgCl_2$ Dominated Brines

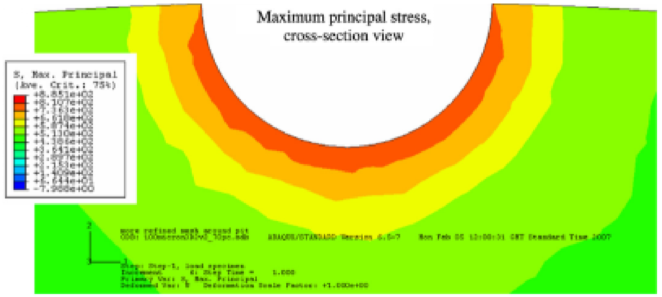
40 %RH Seawater

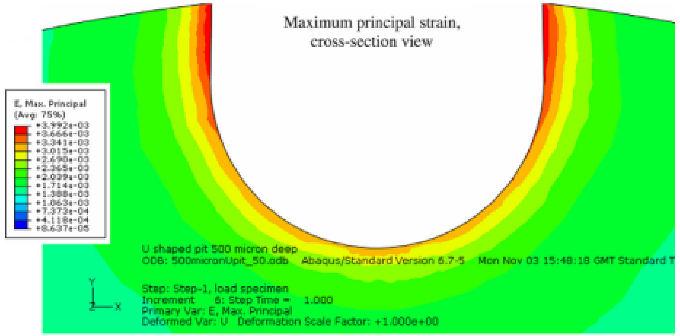


4.47 M $MgCl_2$



Pits formed in $MgCl_2$ brines are much larger and more irregular in shape…why would this be



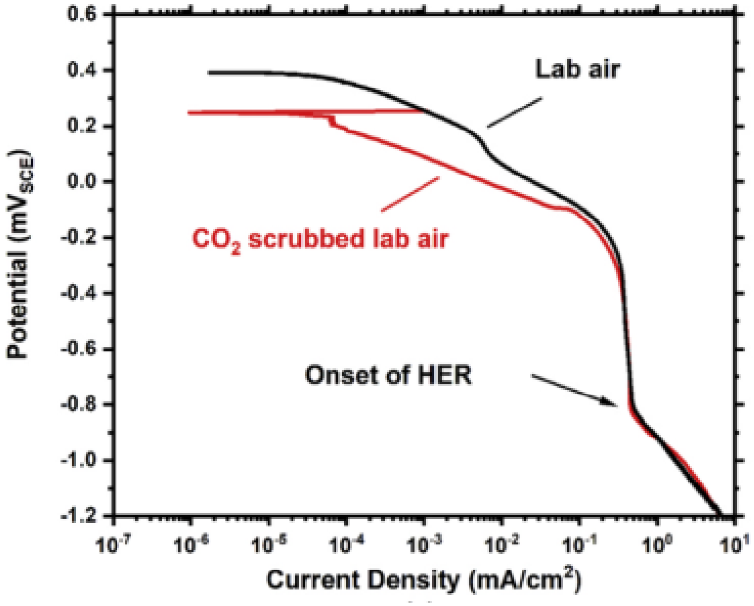


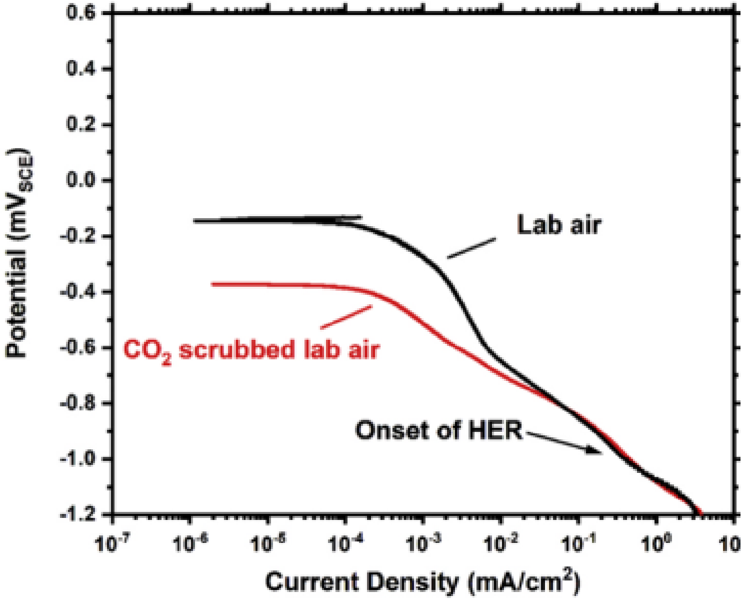
Pit geometry influences stress distribution → influences susceptibility for SCC initiation.

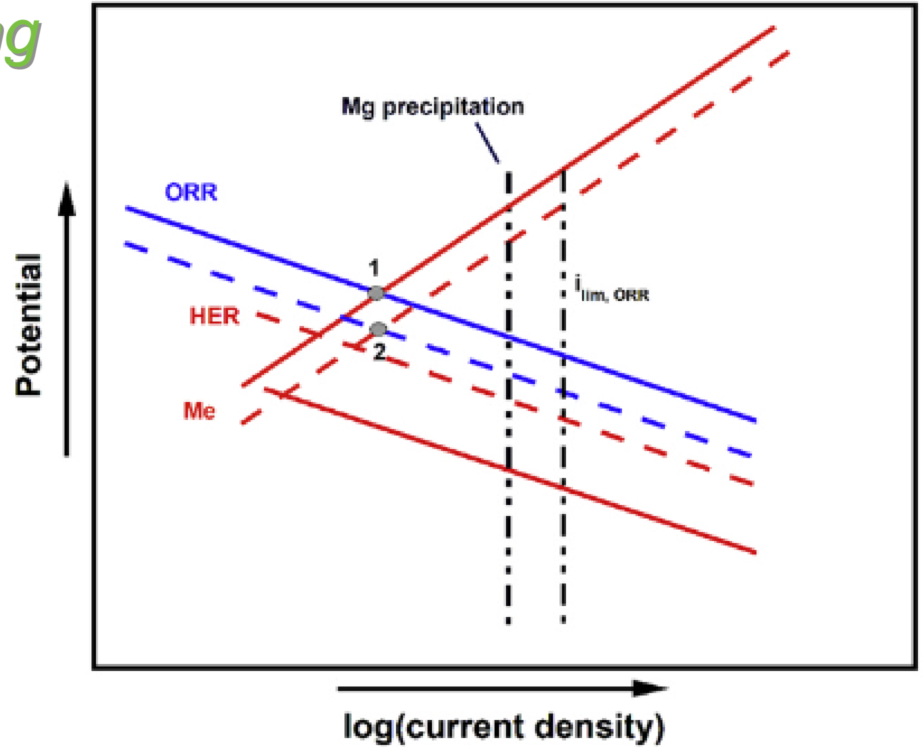
Cathodic Reactions

- To further understand the influence of brine composition on pit morphology we have to determine the influence on governing corrosion kinetics…
  - ***What is the influence of brine composition on resultant cathodic kinetics?*** *…dominated by HER over ORR*

Implications: H may influence near surface cracking





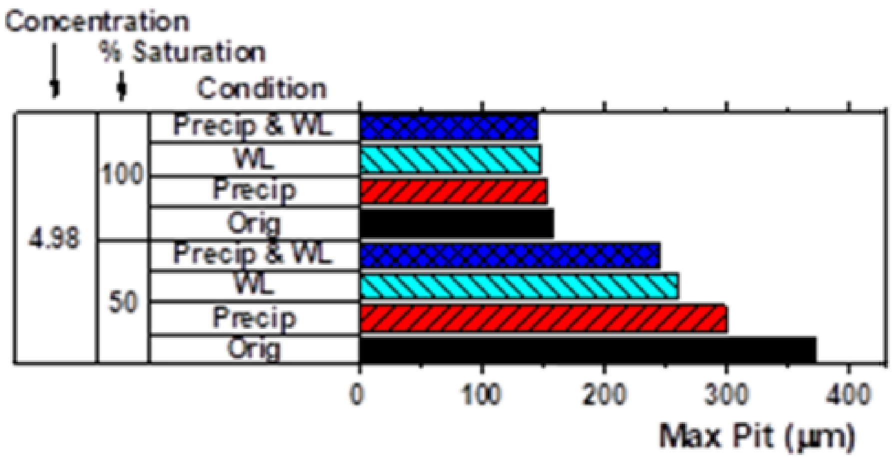


Results published in:

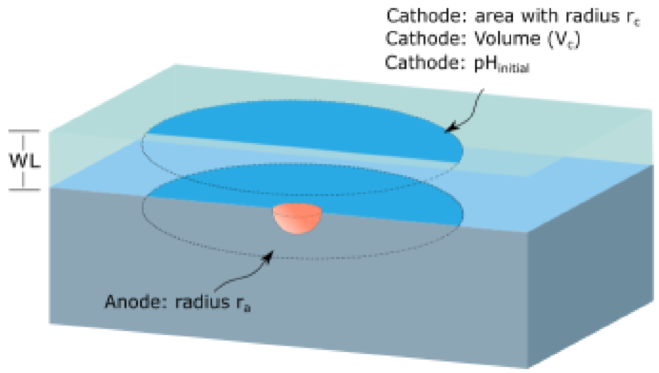
Katona, R. M., Carpenter, J. C., Knight, A. W., Bryan, C. R., Schaller, R. F., Kelly, R. G., & Schindelholz, E. J. (2020). Importance of the hydrogen evolution reaction in magnesium chloride solutions on stainless steel. Corrosion Science, 177, 108935.

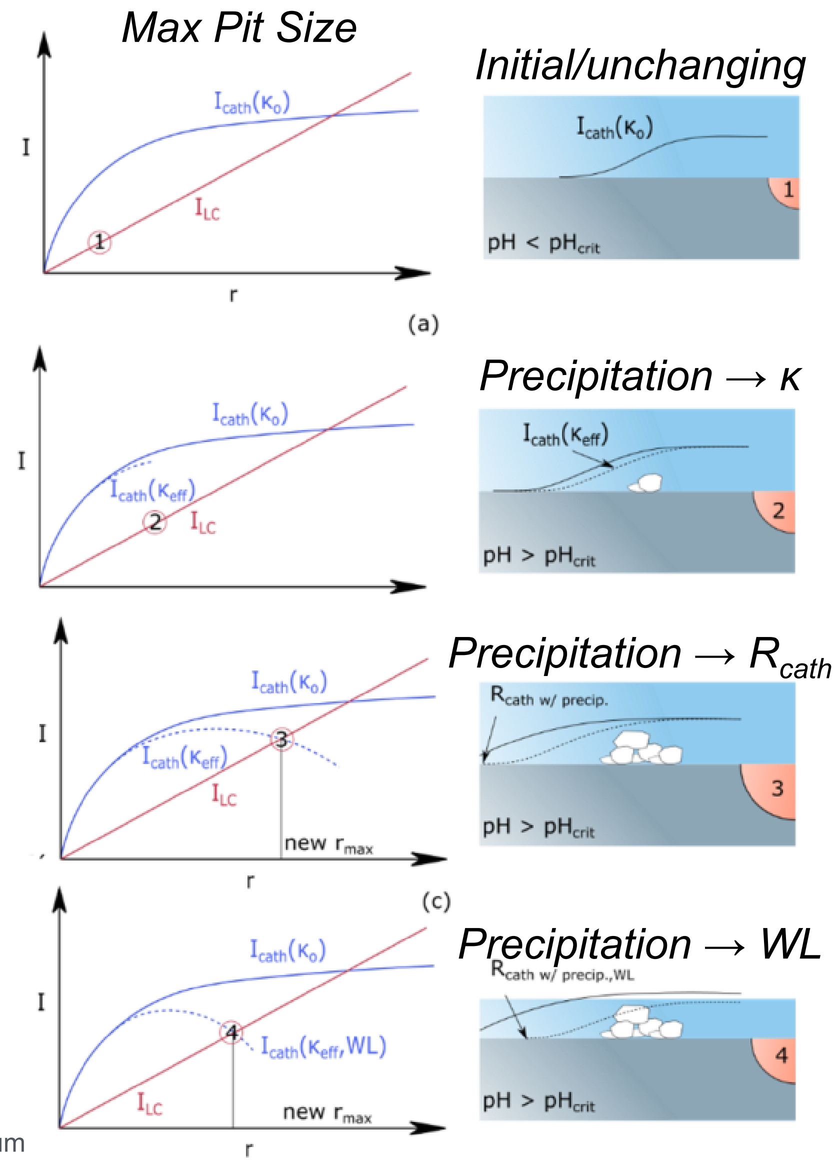
Evolution of Cathodic Brines

- Considering cathodic precipitation in prediction calculation decreases predicted maximum pit sizes significantly



Pit Schematic





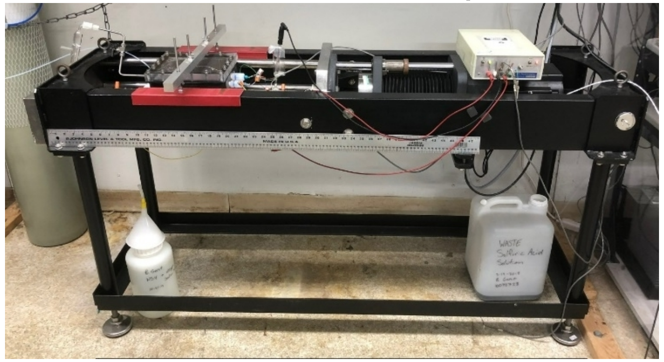
Results submitted to:

R. M. Katona, A. W. Knight, C. R. Bryan, R. F. Schaller, R. G. Kelly. Quantitative Assessment of Environmental Phenomena on Maximum Pit Size Predictions in Marine Environments. Submitted to Electrochimica Acta. 2020

Crack Growth Rates

Vertical Setup

Horizontal Setup

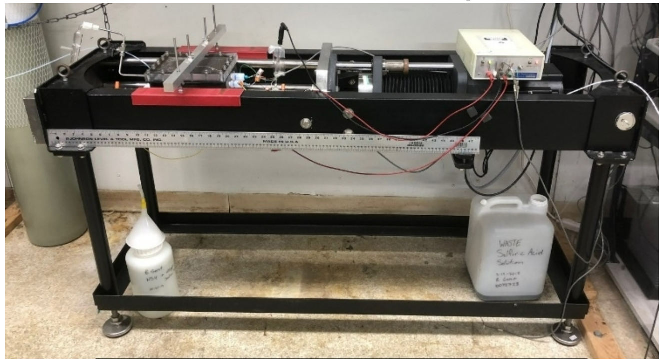


Four load frames acquired, installed, calibrated, and running initial tests

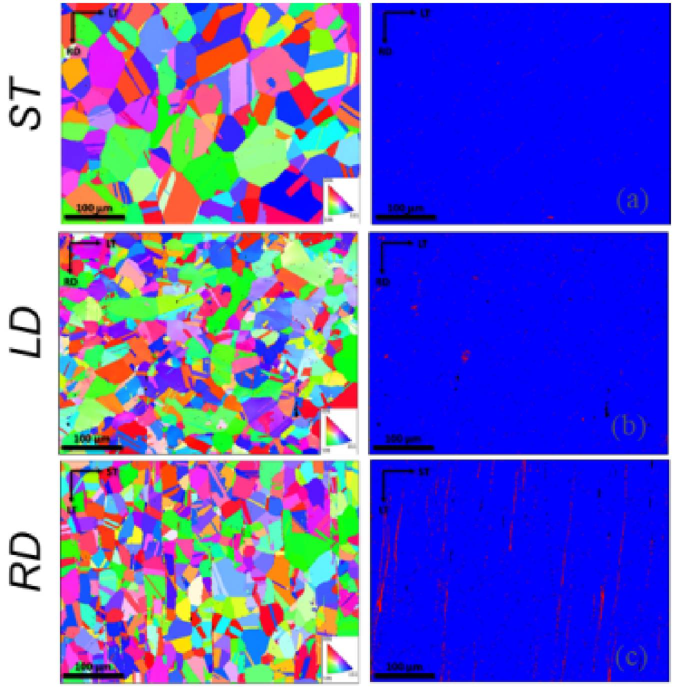
Crack Growth Rates

Vertical Setup

Horizontal Setup



Microstructural Characterization of 304L



Initial Full Immersion Environments for CGR Testing

Temperature (°C)	Frequency (Hz)	Environment Type
35	10^{-2}-10^{-9}	5.3M NaCl
45	10^{-2}-10^{-9}	5.3M NaCl
55	10^{-2}-10^{-9}	5.3M NaCl
35	10^{-2}-10^{-9}	4.98 M $MgCl_2$
55	10^{-2}-10^{-5}	4.98 M $MgCl_2$
35	10^{-2}-10^{-9}	40% RH Seawater
35	10^{-2}-10^{-5}	75% RH Seawater

304L material characterized

Initial full immersion environments selected for CGR testing:

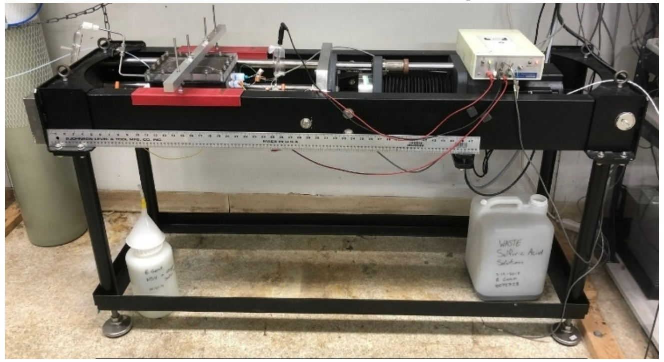
-Temperature

-Brine Composition

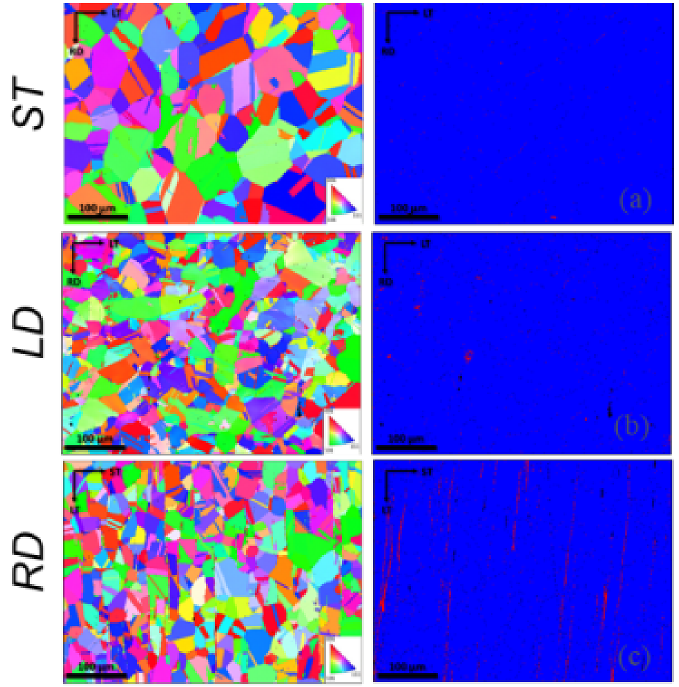
Crach Growth Rates

Vertical Setup

Horizontal Setup



Microstructural Characterization of 304L



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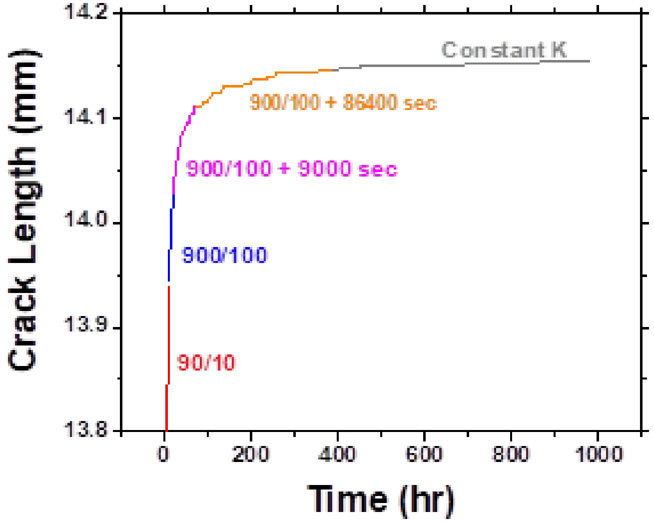
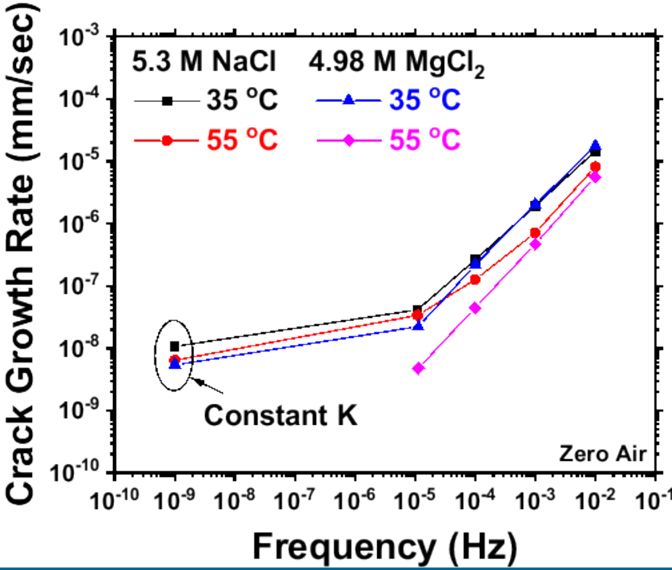
Tapered approach to constant K CGR



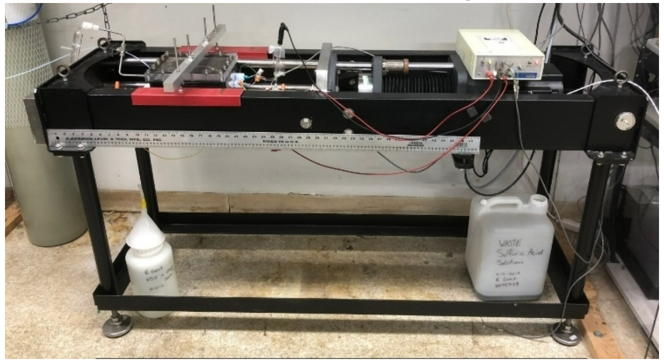
Initial CGR results



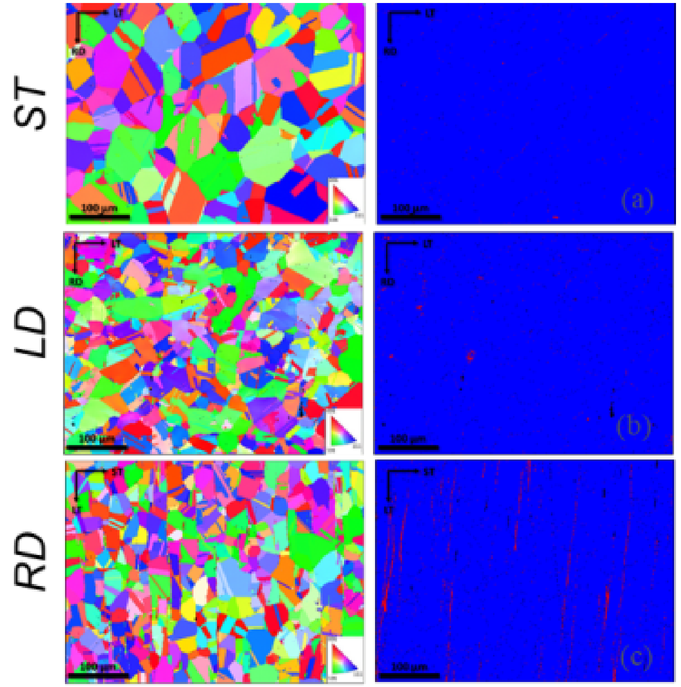
Crack Growth Rates

Vertical Setup

Horizontal Setup



Microstructural Characterization of 304L



Initial Full Immersion Environments for CGR Testing

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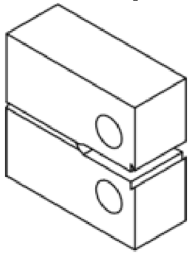
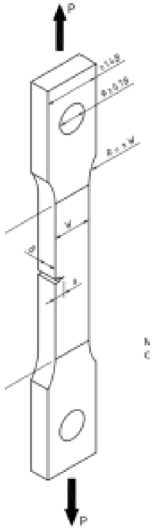
CT Sample

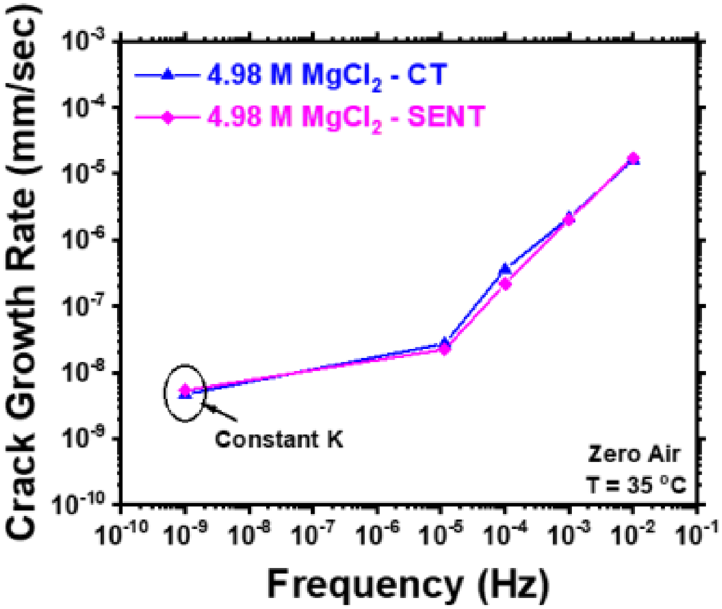




SENT Sample

Comparison of CT vs. SENT geometry

-SENT geometry may lend itself to atmospheric testing



Summary Slides

- **Determination of canister-relevant environments**
  - ISFSI site sampling and thermodynamic modeling enable better prediction of potential brines on canister surfaces.
  - Applying information gained about these brines to develop enhanced corrosion testing; including both potential corrosion accelerants (cycling and dust) and inhibitors (nitrates).
  - Additionally, have shown that $MgCl_2$-dominant brines will be present for long time periods (>300 years) on the canister surface
- **Corrosion testing and modeling in canister relevant environments**
  - Expanding testing to more relevant scenarios to better establish controlling factors for pitting and potential SCC initiation
  - Expanding modeling efforts to account for non-static brine/corrosion conditions to better predict pitting and SCC initiation
- **Crack growth rate**
  - Installed and started initial tests in varied brine environments to explore potential effects on CGR
  - Verified sample geometry to initiate atmospheric testing

Acknowledgements

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Questions?

Clean. **Reliable. Nuclear.**