SAND2016-7967PE

Used Fuel Disposition Campaign

Environmental Considerations for SCC Testing

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Used
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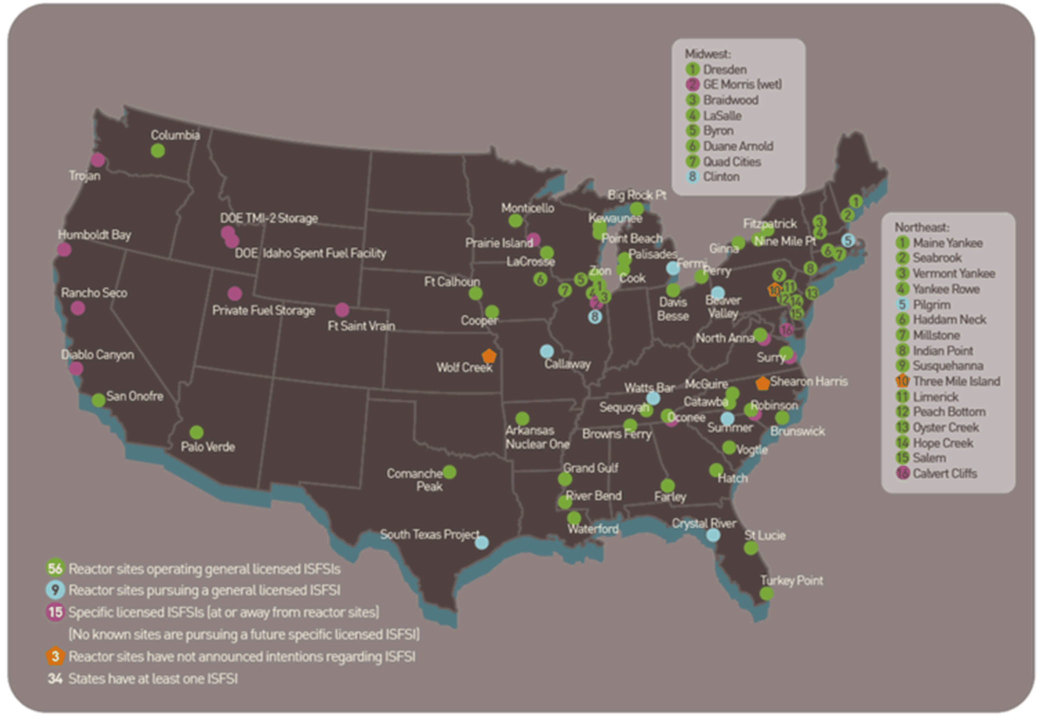
ISFSI locations

Different settings

- **Varying salt assemblages**
  - *Coastal (marine salt aerosols)*
  - *Inland (ammonium, sulfate, and nitrate-rich aerosols; possible road salts, cooling tower emissions)*
  - *Salt assemblages control DRH and RH_L (limiting RH for corrosion)*
- **Range of weather conditions**
  - *Dewpoints (absolute humidity (AH) values)*
  - *Ambient temperatures*
- **Temperature range of interest**
  - *Determined by RH_L and AH*

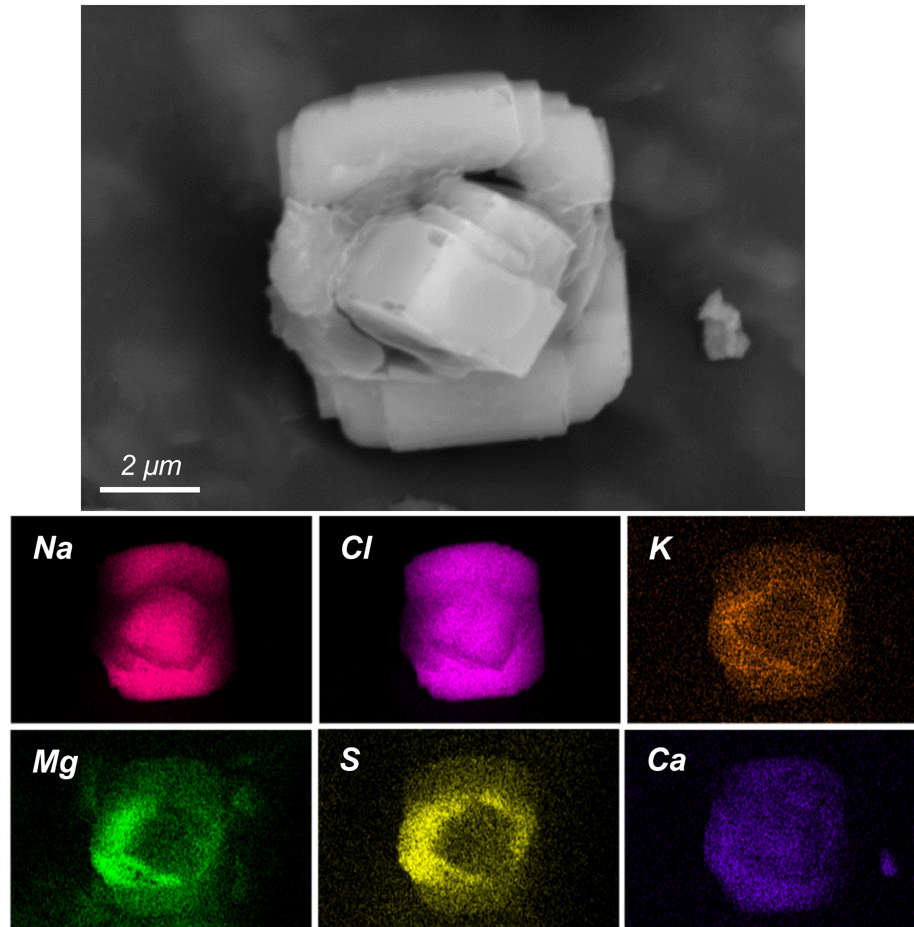


Marine aerosols—observed

Sea salt/spray — generally simulated with synthetic ocean water (ASTM D1141-98)

	Conc., mg/L	
Species	**ASTM D1141-98**	**McCaffrey et al. (1987)**
Na^+	11031	11731
K^+	398	436
Mg^{2+}	1328	1323
Ca^{2+}	419	405
Cl^-	19835	21176
Br^-	68	74
F^-	1	—
SO_4^{2-}	2766	2942
BO_3^{3-}	26	—
HCO_3^-	146	—
pH	8.2	8.2

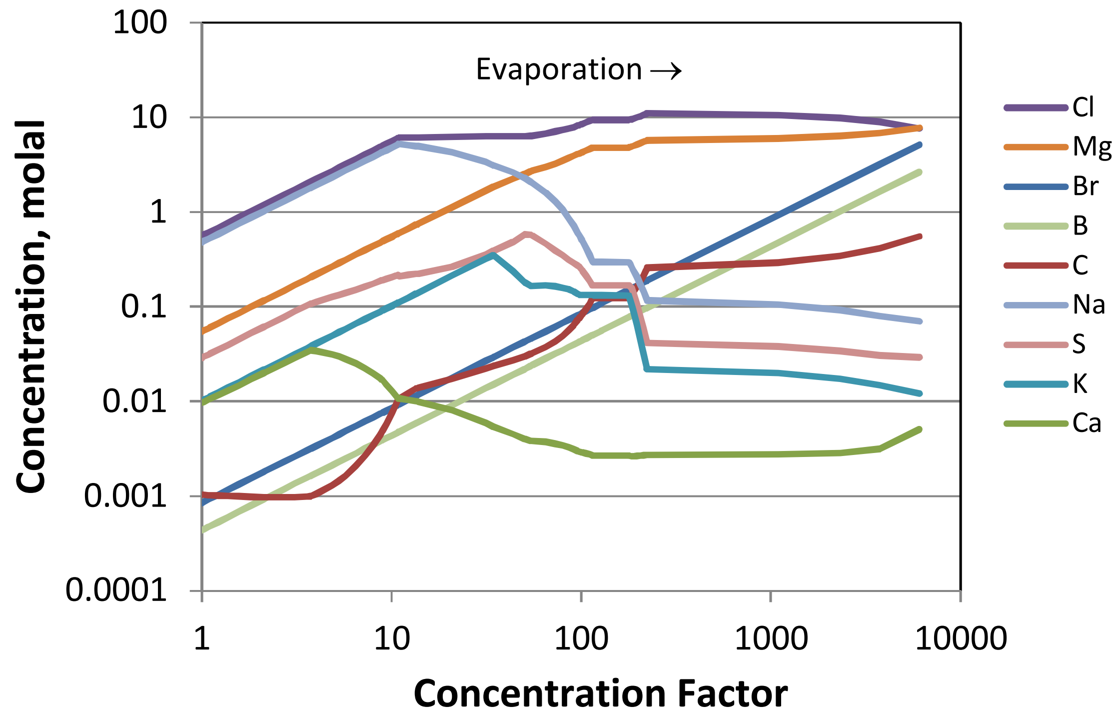
Sea-salt aggregate on Diablo Canyon ISFSI storage canister



Seawater evaporation

Brine composition:

- *Upon evaporation, salts precipitate and redissolve. Removed salts dictate the composition of remaining brine*
- *Seawater evolves towards concentrated Mg-Cl brine as NaCl precipitates*
- *Br and B conserved (but YMP Pitzer database is not qualified for B, and may not be accurate)*
- *Ca, K, S are mostly removed by minerals, and are very low in the remaining brine.*



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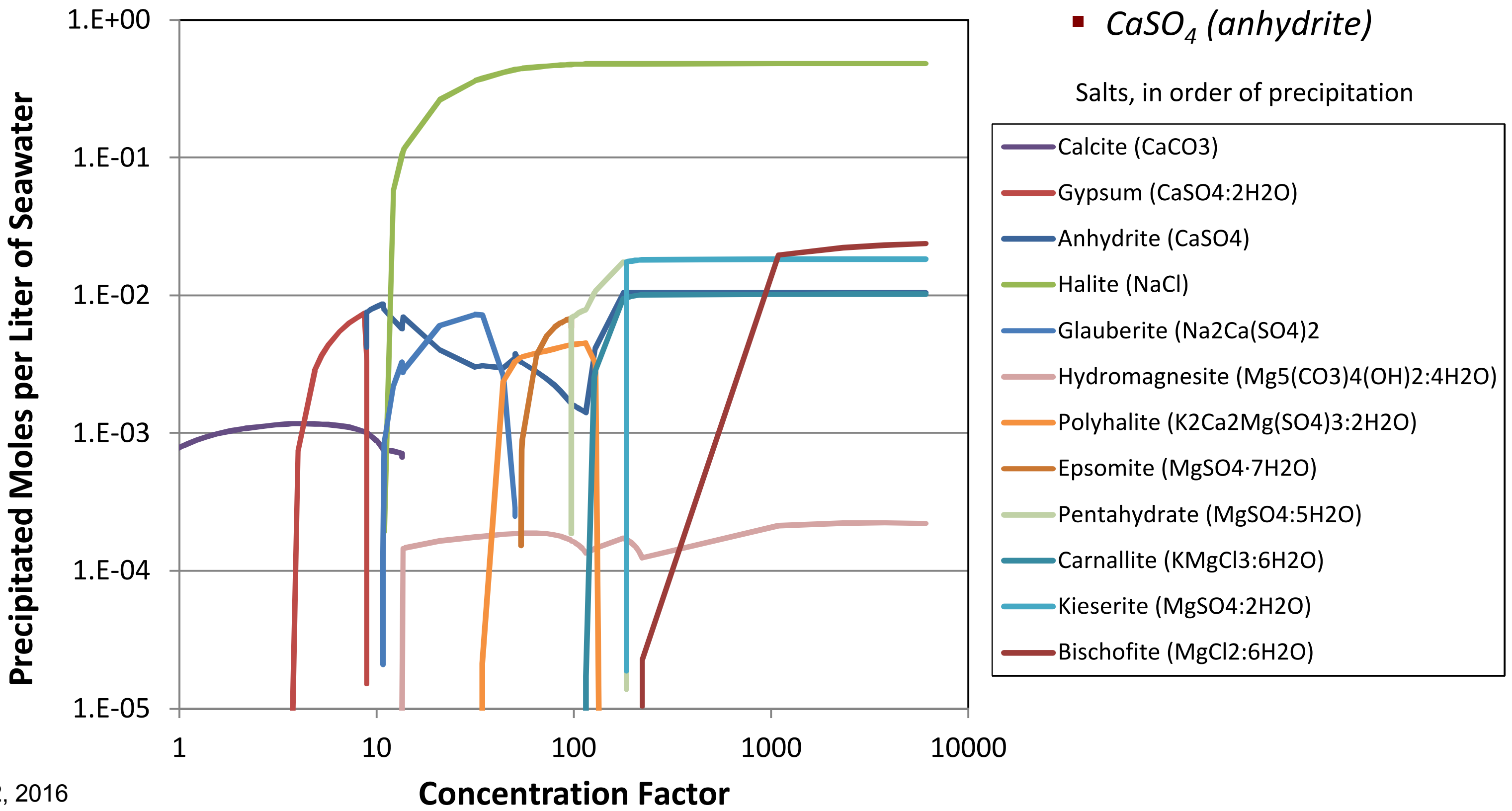
Seawater evaporation

Precipitated salts:

Upon evaporation, several salts precipitate and re-dissolve (order given below)

Final assemblage determines deliquescence RH (DRH)

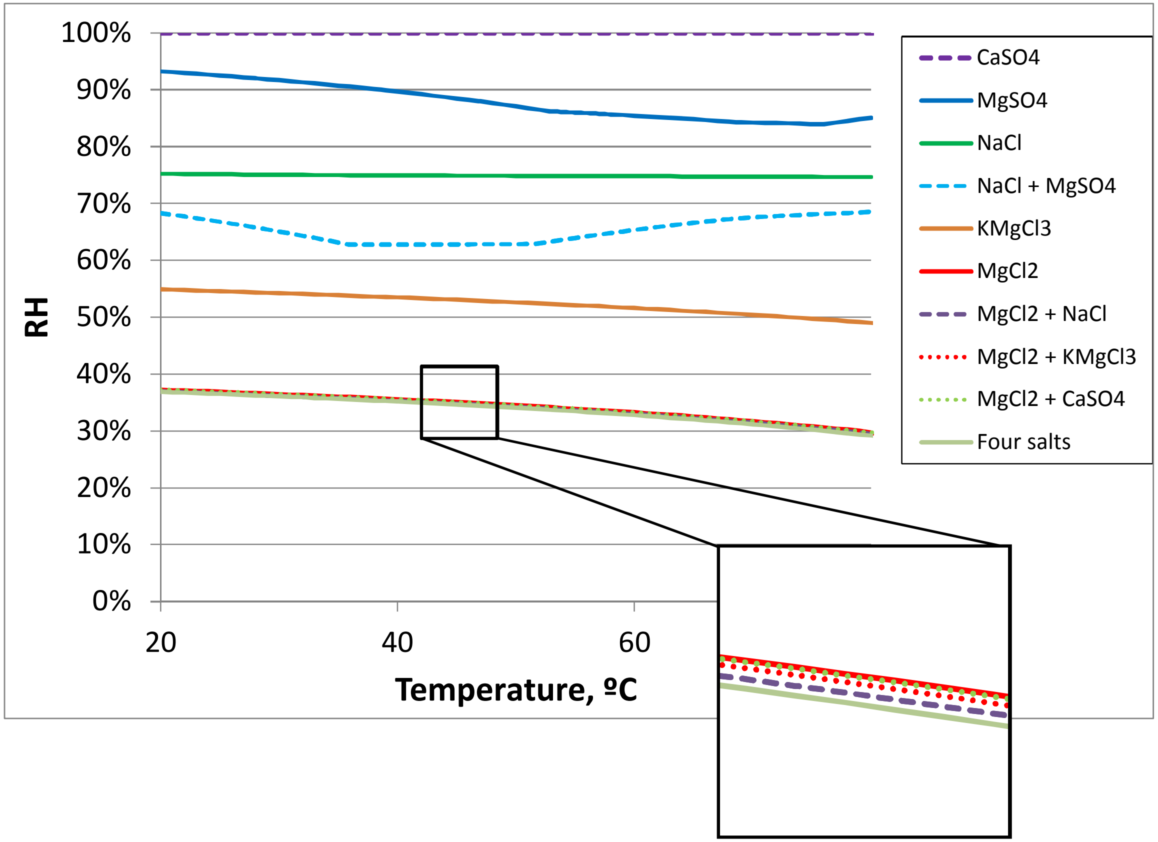
- *NaCl (halite)*
- *$MgCl_2$:6H_2O (bischofite)*
- *$MgSO_4$:2H_2O (kieserite)*
- *$KMgCl_3$:6H_2O (carnallite)*
- *$CaSO_4$ (anhydrite)*



Deliquescence RH Values for Sea Salts

Deliquescence points:

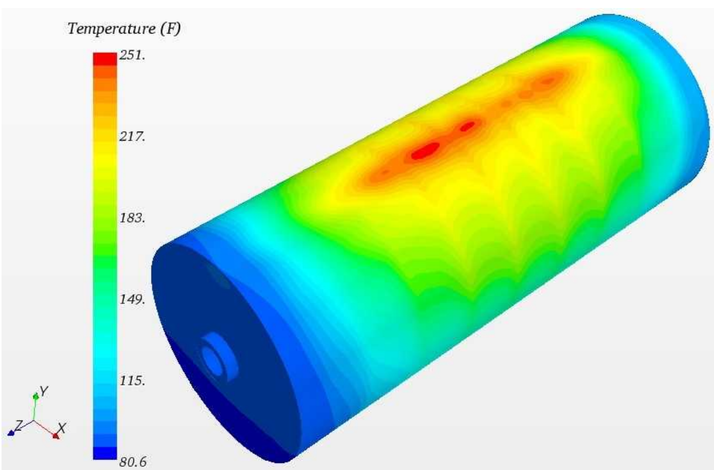
- $CaSO_4$ (gypsum or anhydrite): DRH >99%
- $MgSO_4$ (four different hydrates): DRH = 93-84%
- NaCl: DRH = ~77% at all temperatures
- $KMgCl_3{:}6H_2O$ (±sylvite): DRH = 55-49%
- $MgCl_2{:}6H_2O$: DRH = 36-29%
- $MgCl_2{:}6H_2O$ plus any or all other salts: DRH = ~Same as $MgCl_2{:}6H_2O$



But there is ample experimental evidence of corrosion, and even SCC, for seasalts and Mg-chloride at RH values below the DRH for Mg-chloride. Possible reasons: Metastable Mg-chloride brines persist to lower RH, thin adsorbed water films on salt surfaces can support corrosion.

Waste Package Surface Temperatures

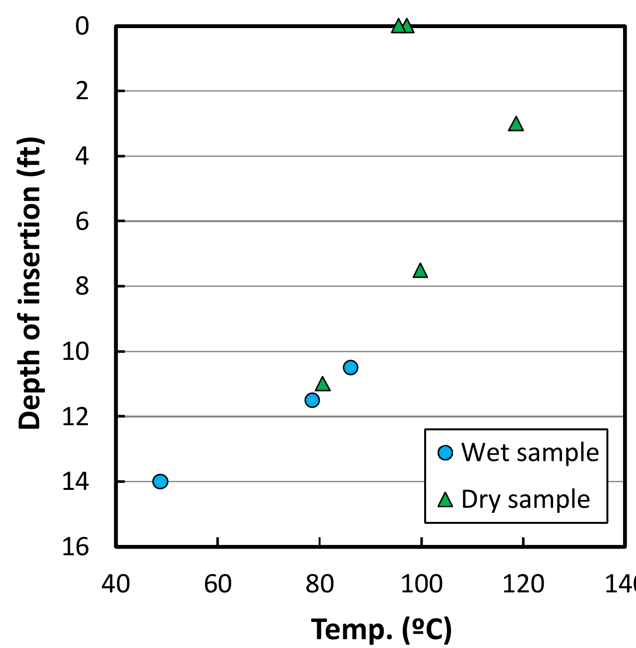
Efficient passive cooling means that there is a *large thermal variation* on the canister surface; some part of the canister rapidly reaches temperatures low enough to allow deliquescence.



Horizontal canister: *Modeled canister surface temperatures, NUHOMS 21PWR canister within its overpack. Fuel ~19 years in dry storage (heat load ~7.61 kW) PNNL (2012)*

Vertical canister:

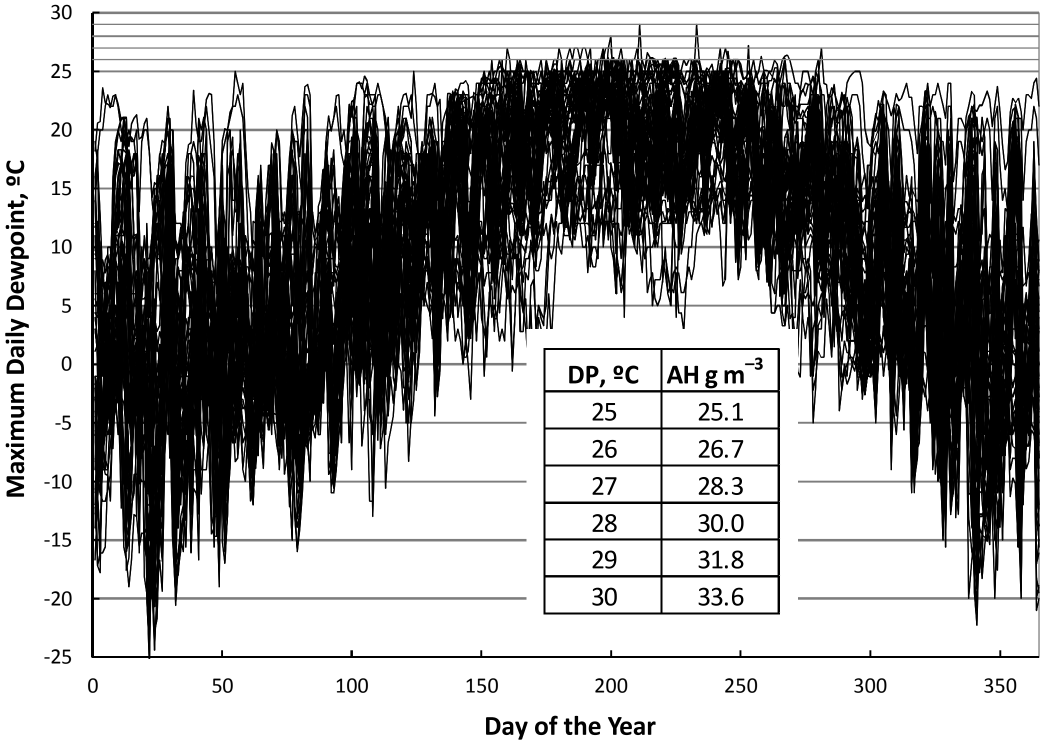
Measured canister surface temperatures, HOLTEC Hi-STORM 100 within its overpack. Fuel ~2 years in dry storage (heat load ~17 kW).



Possible Range of AH at ISFSI Sites

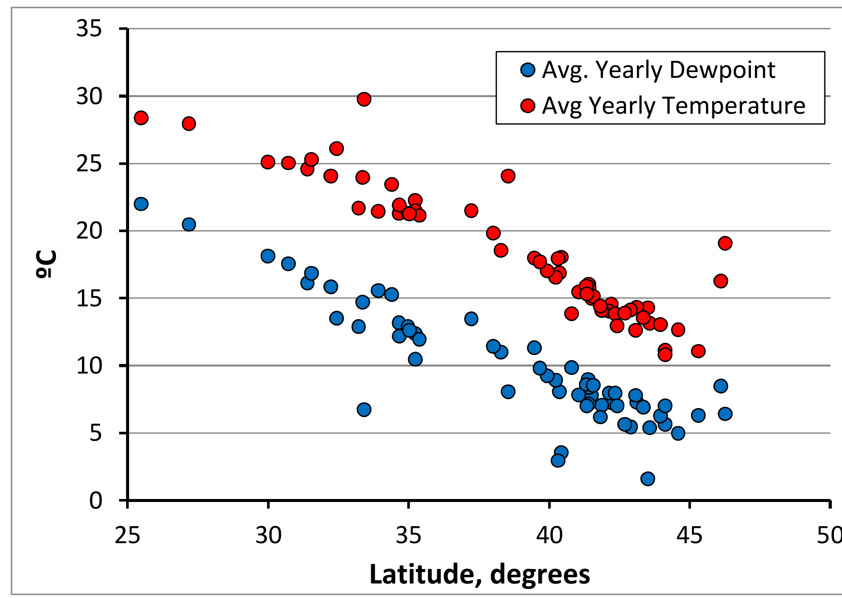
NRC/CNWRA (2014) suggested 30 g/m^3 was an upper limit for AH, "based on meteorological monitoring data"

Weather data from 65 ISFSI sites, collected for the probabilistic SCC model, confirm this is true.



DP, ºC	AH g m^{-3}
25	25.1
26	26.7
27	28.3
28	30.0
29	31.8
30	33.6

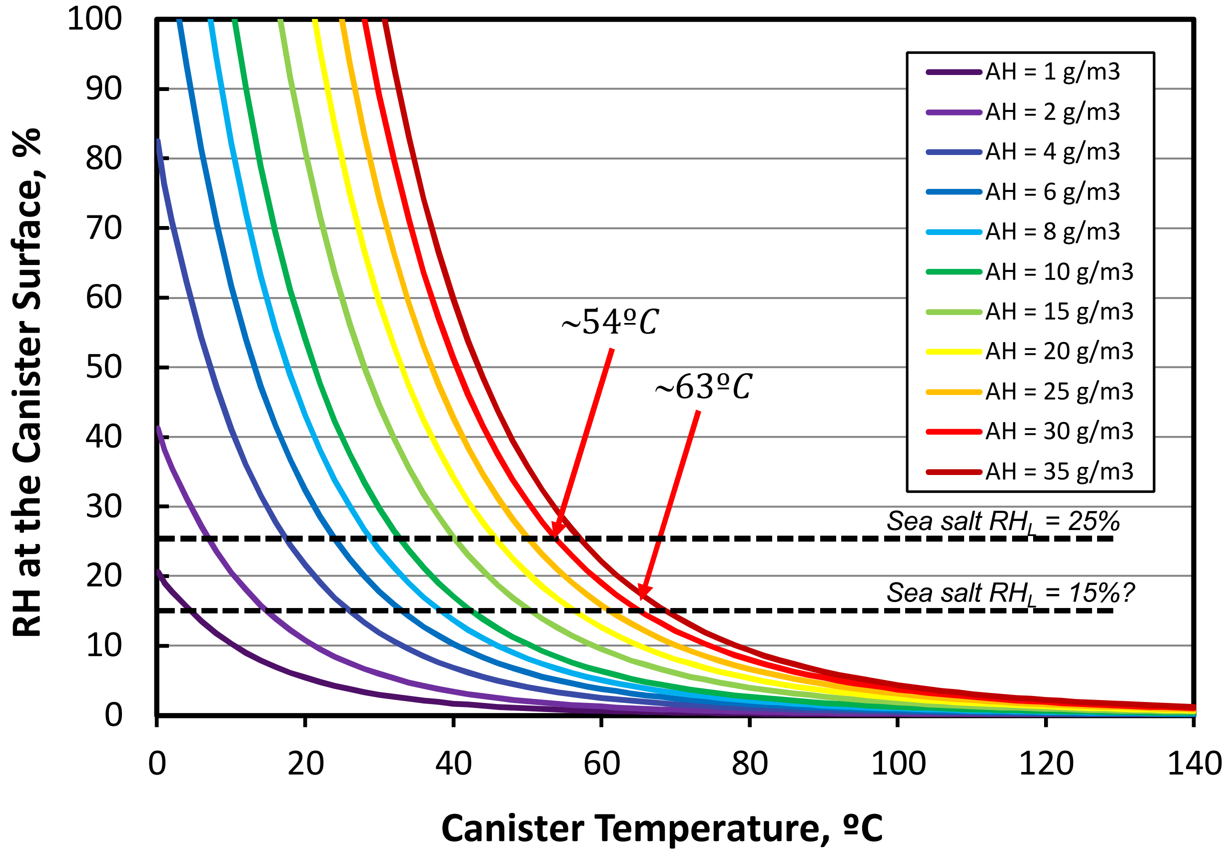
Average yearly dewpoint may be a better indicator of time of wetness. Dominant control on average AH? Latitude.



Used Fuel Disposition

Temperature Range of Interest

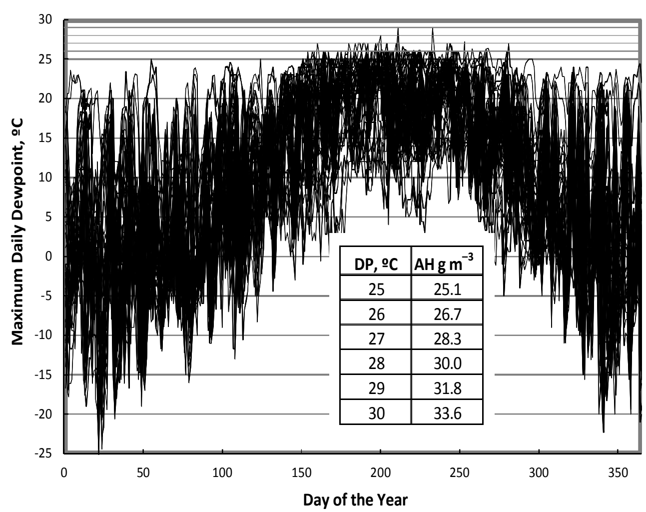
The temperature range of interest for corrosion experimental work is a function of AH and the assumed RH_L for sea-salts.



Possible Environmental Conditions for Testing

- **Absolute humidity – 30g/m^3 maximum**
- **Temperature – reasonable values – relevant to sites**
- **Constant RH, Variable T**
- **Constant T, Variable RH**

% RH	Temperature				
75	**35**				
70	35				
65	35		Inaccessible		
60	35				
55	**35**	40			
50	35	40			
45	35	40	45		
40	**35**	40	**45**		**55**
35	35	40	45	50	
30	35	40	45	50	



High-lighted values will be used for pitting tests at SNL.

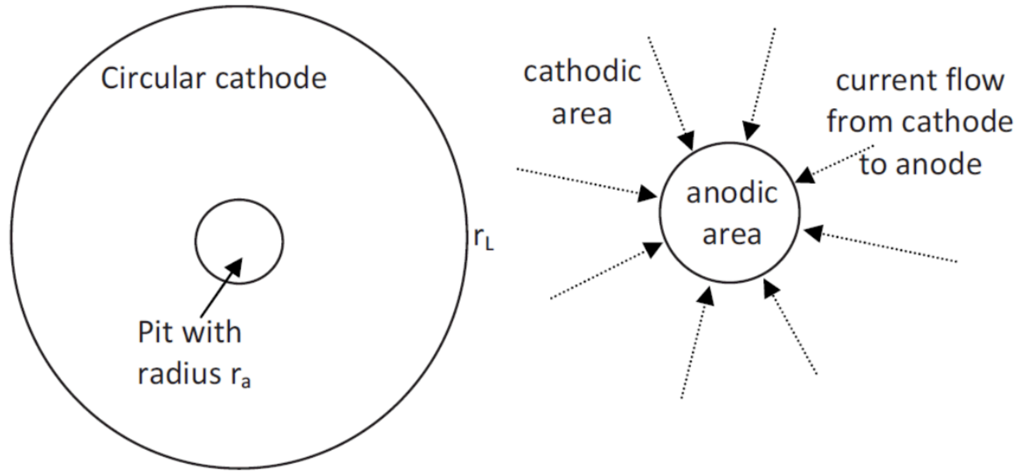
PIT INITIATION AND GROWTH: PROPOSED TESTING CONDITIONS

Environmental controls on maximum pit size

Chen and Kelly (2010): Max pit size is a function of the maximum cathode current.

Pits modeled as being hemispherical, stifle once the pit becomes so large that the anodic current requirement exceeds the available cathode current.

Weakness: assumes a uniform brine layer…



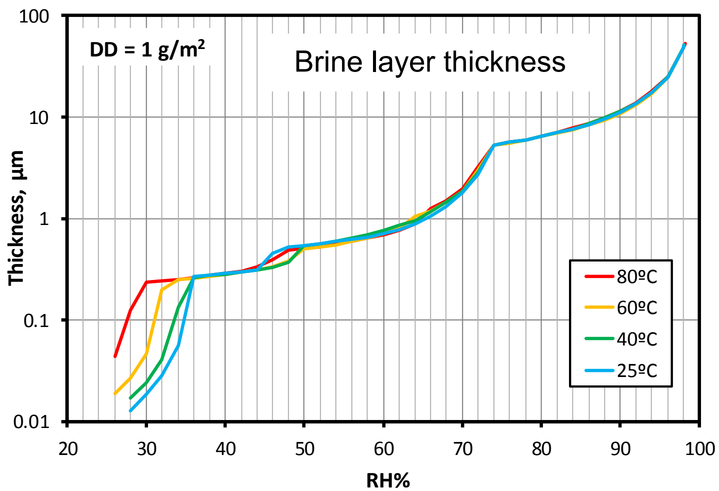
Electrochemical term (from cathodic polarization curve)

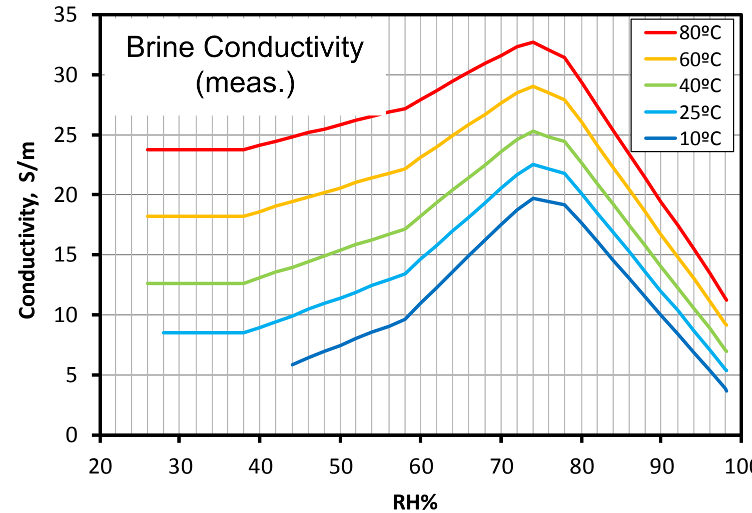
Max. cathode current · ***Brine conductivity*** · ***Brine layer thickness***

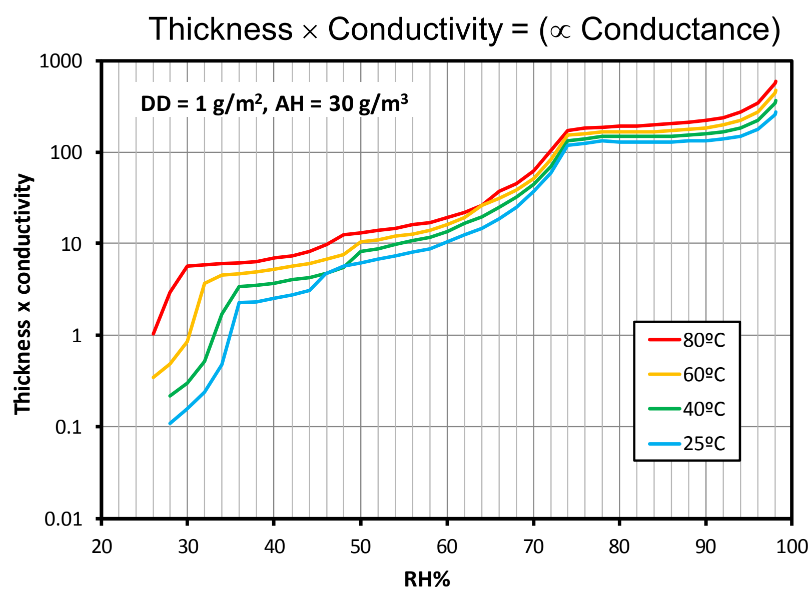
$$\ln I_{c,max} = \frac{4\pi k W_L \Delta E_{max}}{I_{c,max}} + ln\left[\frac{\pi e r_a^2 \int_{E_{corr}}^{E_{rp}} (I_c - I_p)\, dE}{\Delta E_{max}}\right]$$

Used Fuel Disposition

Evaporated Seawater Brine Properties







Values based on geochemical modeling, literature data, and measured data for brine densities and conductivities (4 brines, from 98-38% RH)

Changes in RH have a much greater effect on brine layer thickness (brine volume) than on brine conductivity.

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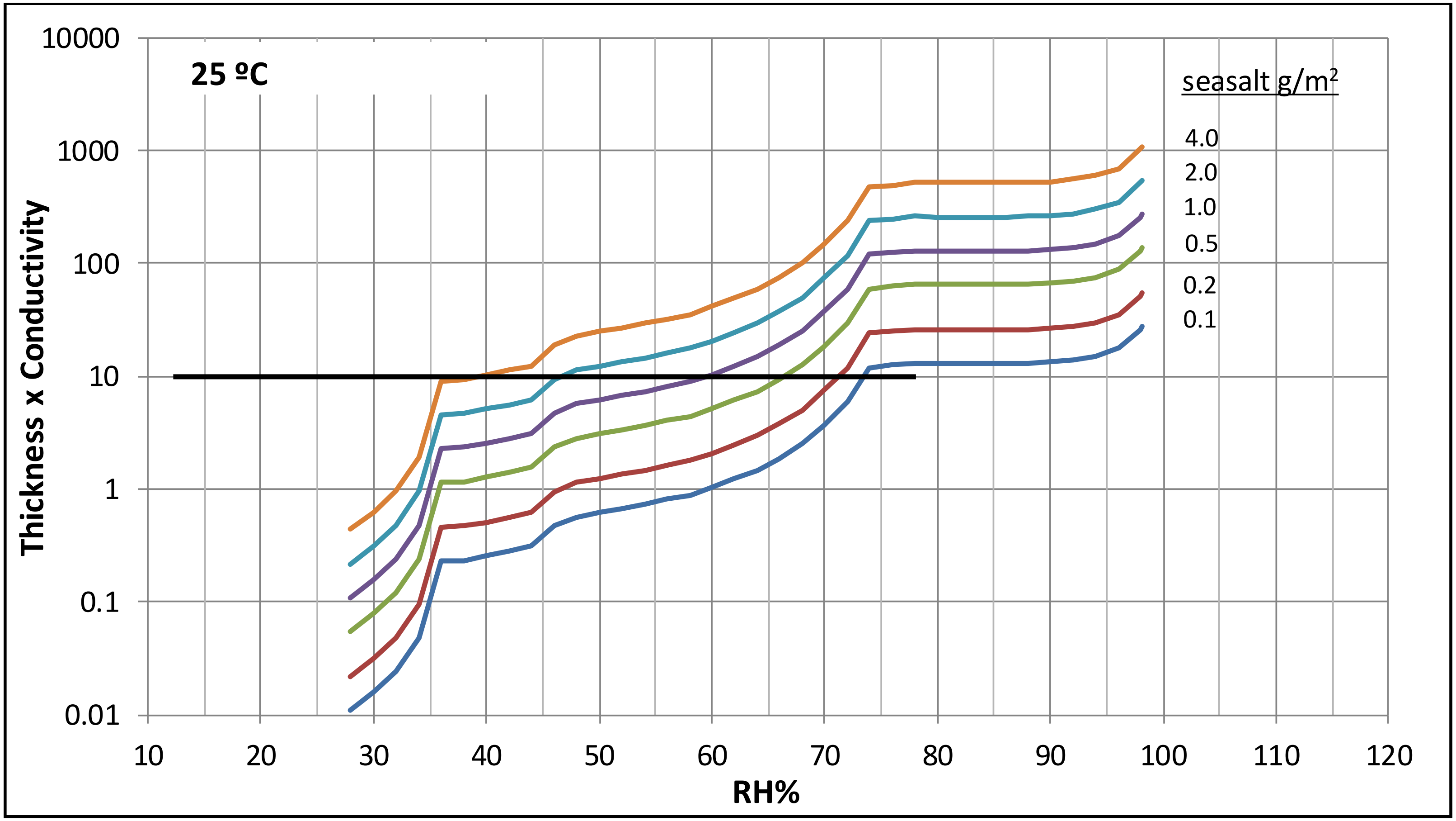
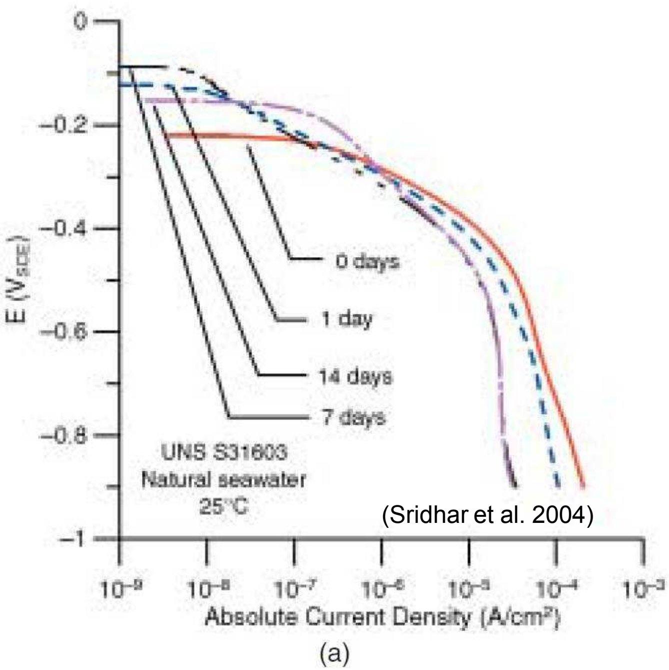
Evaporated Seawater Brine Properties

Effect of Salt Load—Is this why it is difficult to define a minimum salt load for SCC?



Measuring cathodic polarization data

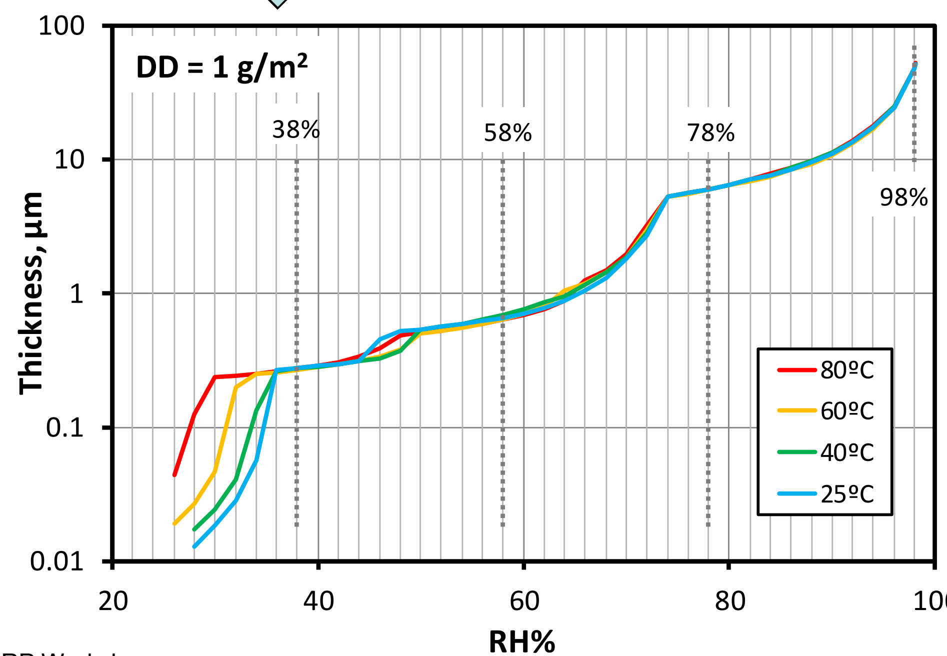
Limited available data: Cathodic polarization curve for seawater at 25ºC, 316 SS



To characterize variability in cathode kinetics with brine composition, measure polarization curves in four brines corresponding to:

- Unevaporated Seawater (98% RH)
- Evap. to 78% RH
- Evap. to 58% RH
- Evap. to 38% RH

- Temperatures: 3 (Ambient, 40ºC, 60ºC)
- Alloys: 1 (304)
- Test methodology: RDE (flowing)



Test Matrix: Localized Corrosion

- **Environmental conditions: 5**
- **Alloys: 304/304L, 304/304H**
- **Metallurgical conditions: annealed, sensitized (621°C, 24h)**
- **Surface conditions: 2**
- **Salt loading levels: 4 from 0.005 – 1 g/m^2 chloride**
- **Time intervals: 5 (1, 3, 6, 12, 24 months)**

- **Characterization of the localized corrosion process**
  - Maximum pit size as function of time
  - Pit geometry as function of time
  - Pit number density and size distribution as function of time

STRESS CORROSION CRACKING: PROPOSED TESTING CONDITIONS

Proposed Approach

- **Isolate and independently evaluate different parameters.**
  - Material properties
    - *Composition (304 / 304H / 316)*
    - *As-received and sensitized*
    - *We have purchased materials for use (304/304H)*
  - Brine Composition
    - *Variations with RH and temperature.*
  - Effect of cathodic limitation due to thin brine films
    - *Changes in crack growth rate (CGR)?*
    - *OR, changes in size of the active crack front (anode area)?*

Used
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Disposition

Sample Materials

- **SNL purchased two 4' x 8' x $^5/_8$" plates (cut into 4' x 1' strips) of 304 SS for production of testing samples:**

Material	C%	Co%	Cr%	Cu%	Mn%	Mo%	N%	Ni%	P%	S%	Si%
304/304L	0.0216	0.1980	18.3105	0.3915	1.8280	0.2855	0.0889	8.1125	0.3250	0.0010	0.2510
304/304H	0.0418	0.1345	18.1930	0.4005	1.7495	0.2985	0.0844	8.0725	0.0335	0.0010	0.2930

Currently being used by CSM IRP members and SwRI

- **Canister mockup materials: Canister leftovers now at SNL, will be cut into pieces for testing in October**

Material	C%	Co%	Cr%	Cu%	Mn%	Mo%	N%	Ni%	P%	S%	Si%
Plate (304/304L)	0.0223	0.1865	18.1	0.4225	1.7125	0.318	0.0787	8.027	0.0305	0.0023	0.255
Weld Filler (308L) (lot 1)	0.014	--	19.66	0.16	1.7	0.11	0.058	9.56	0.025	0.01	0.39
Weld Filler (308L) (lot 2)	0.012	--	19.71	0.192	1.73	0.071	0.053	9.75	0.024	0.012	0.368

Mockup weld characterization will determine degree of sensitization, and samples will be made to duplicate that.

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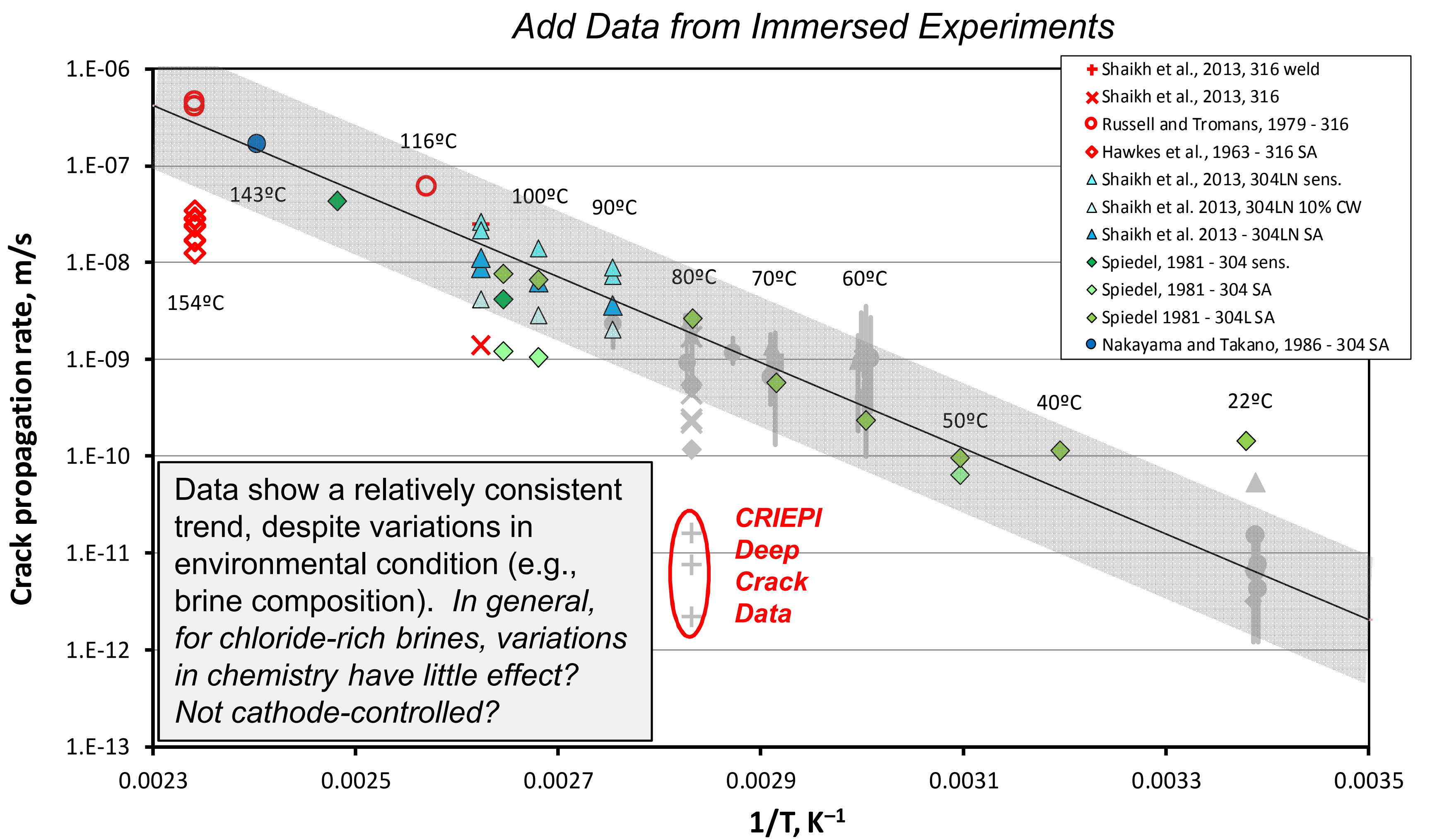
Available data



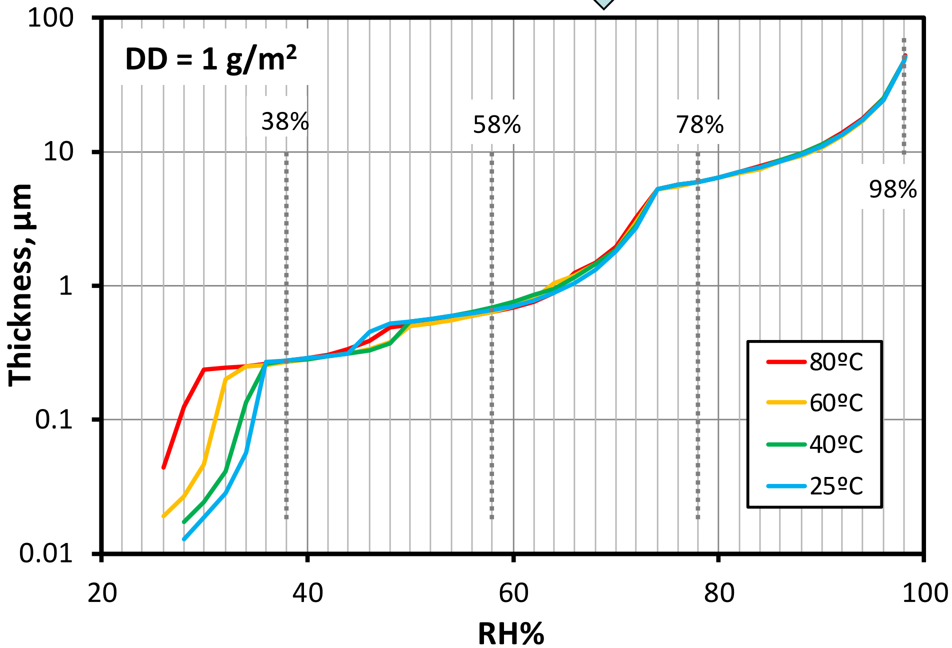
Test Matrix: Effects of Brine Composition

- ***Sample geometry*:** Compact tension
- ***Material:*** As received, sensitized 304, 304H
- ***Crack growth rate measurement technique*:** DCPD
- ***Environments:***
  - ASTM Artificial ocean water
  - Concentrated to 78% RH (factor of 9.4)
  - Concentrated to 58% RH (factor of 68)
  - Concentrated to 38% RH (factor of 100)
- ***Temperatures:* 25ºC, 40ºC, 60ºC**
- ***Loading conditions:***
  - Fatigue pre-crack in air
  - Constant K if possible, or slowing declining K

Brine Compositions

Use same brines as used for measuring cathodic kinetics:

- Unevaporated Seawater (98% RH)
- Evap. to 78% RH
- Evap. to 58% RH
- Evap. to 38% RH



Brine compositions

- based on EQ3/6 calculations of evaporated seawater evolution at 25ºC
- Predicted compositions at a given RH do not vary greatly with temperature

Component (molality)	ASTM seawater	78% brine	58% brine	38% brine
Na^+	0.498	4.507	0.719	0.145
K^+	0.011	0.096	0.144	0.032
Mg^{2+}	0.057	0.513	3.907	5.500
Ca^{2+}	0.011	0.015	0.003	0.003
Cl^-	0.580	5.250	7.941	10.610
Br^-	0.001	0.008	0.077	0.181
F^-	0.0001	—	—	—
SO_4^{2-}	0.030	0.196	0.289	0.059
BO_3^{3-}	0.0005	0.004	0.040	0.093
HCO_3^-	0.002	0.006	0.064	0.215

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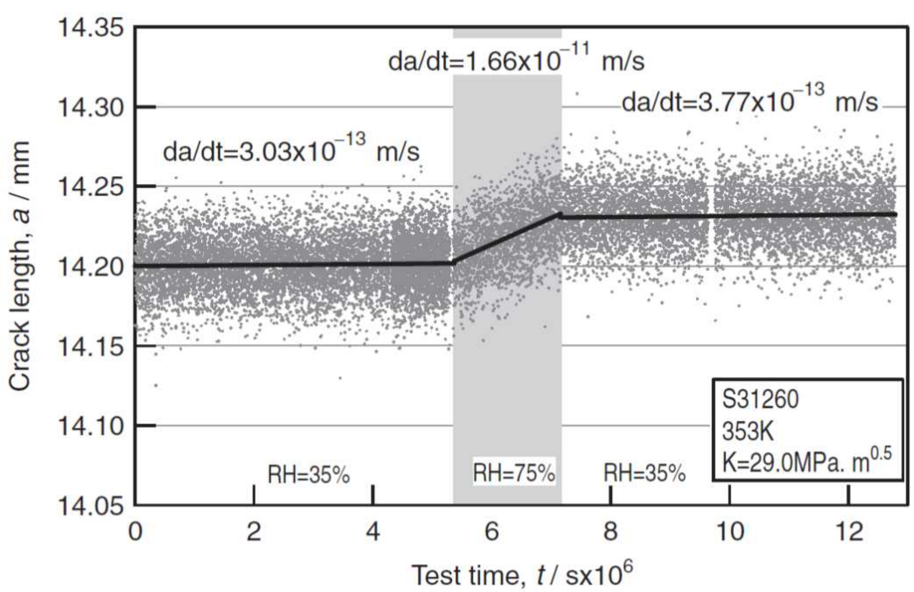
Potential Effects of Atmospheric Conditions (Thin Brine Films) on SCC Crack Growth Rates

Observed (CRIEPI):

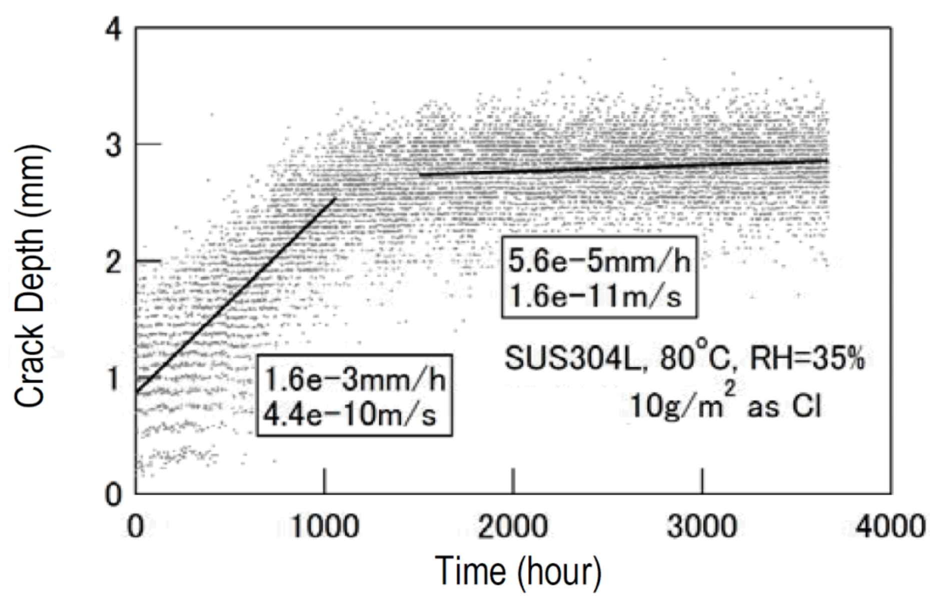
In both cases, CGR was measured by DCPD; CGR is not really a function of depth, but of crack area—to convert to depth, crack geometry (aspect ratio) was assumed to be constant.

Proposed explanation for CRIEPI data: Crack growth slows as crack deepens, due to cathodic limitations related to thin brine films.

Tani et al., (2007) CT specimen, 312 SS. Crack growth rate low or zero (35% RH), increase RH (75% RH) and CGR increases markedly



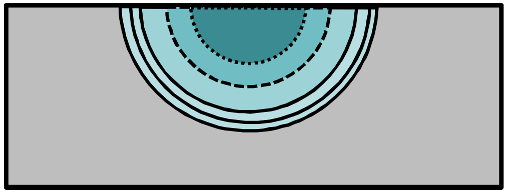
Shirai et al., (2011) 4-point bend specimen, 304 SS. Crack growth rate initially high, decreases as crack grows beyond ~ 3 mm.



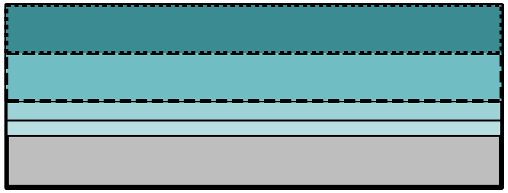
Potential Effects of Atmospheric Conditions (Thin Brine Films) on SCC Crack Growth Rates

- **Possible effects of cathodic limitation due to thin brine films**
  - Anode morphology does not change, but growth rate slows. Uniform growth rate along anode

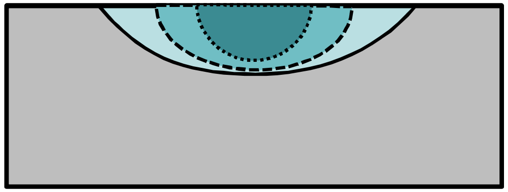
*Semicircular crack,
4-point bend specimen*



CT specimen

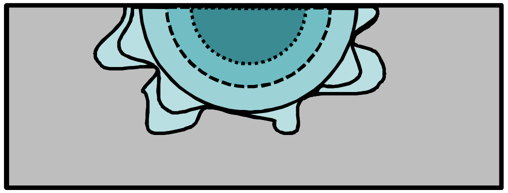


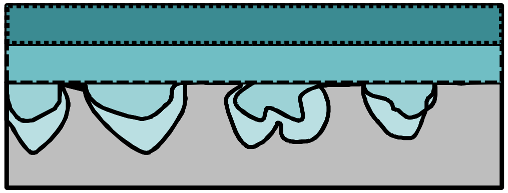
  - CGR varies along the anode and crack morphology changes? Preferential growth near the surface (shorter transport distances)?



Potential Effects of Atmospheric Conditions (Thin Brine Films) on SCC Crack Growth Rates

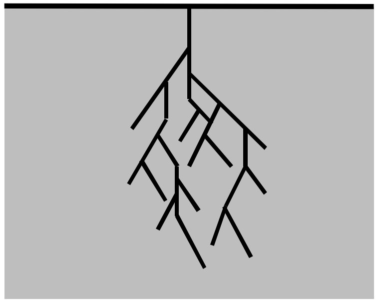
- **Possible effects, cont.**
  - Parts of anode stifle while other parts continue to grow. Crack front becomes non-uniform. (anode becomes smaller, but crack growth rate does not necessarily decrease in areas where growth is occurring)



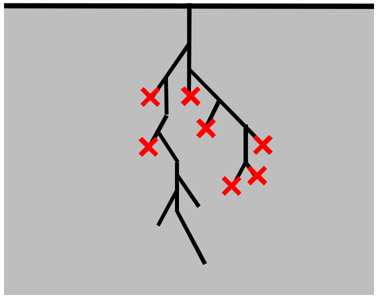


  - But cracks have a third dimension; anode area could shrink by having some branches stifle. Fewer active branches when cathode limited? *(Would this result in higher K and faster crack growth?)*

No cathodic limitation



Cathodic limitation



Proposed Testing Conditions: Effects of Cathode Limitations due to Thin Brine Layer

- ***Sample geometry***: *uniform tension of possible, or,* 4-point bend, full-width EDM notch
- ***Material:*** As received, sensitized, cold worked 304, 304H
- ***Crack growth rate measurement technique***: DCPD
- ***Environments:***
  - Proof of concept:
    - *Salt load 0.05 g Cl (as $MgCl_2$)*
    - *40ºC, 60% RH*
  - If initial try is successful:
    - *Salt loads from 0.01 to 5 g/m^2 as seawater*
    - *25ºC, 40ºC, 60ºC*
    - *38, 58, and 78% RH (use only T, RH combinations possible on canister surfaces?)*
  - Concentrated to 38% RH (factor of 100)
- **Sample evaluation:** Serial sectioning
- **Goals—evaluate:**
  - Crack front uniformity
  - Degree of branching
  - Effectiveness of DCPD at detecting initiation and growth
  - Evidence for changes in crack growth rate with depth, salt load, RH, due to cathodic limitations.