Used Fuel Disposition Campaign

Stress Corrosion Cracking of SNF Interim Storage Canisters:
SNL Research Status

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Sandia National Laboratories

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Overview

- **Environment**
  - Brine stability experiments, inland sites (new data on mixed salt assemblages)
  - Data gaps
- **Localized Corrosion Modeling**
  - General model (Chen and Kelly 2010 approach)
  - Data gaps
- **Experiment Plan for Localized Corrosion**
  - Localized corrosion initiation/propagation
  - Cathodic kinetics
- **Mockup Residual Stress Measurements**
- **Status of Expert Panel Review**
- ***Sample Materials Available***

ENVIRONMENT

Inland sites

Brine Stability Experiments: NH_4NO_3 and NH_4Cl degassing rates

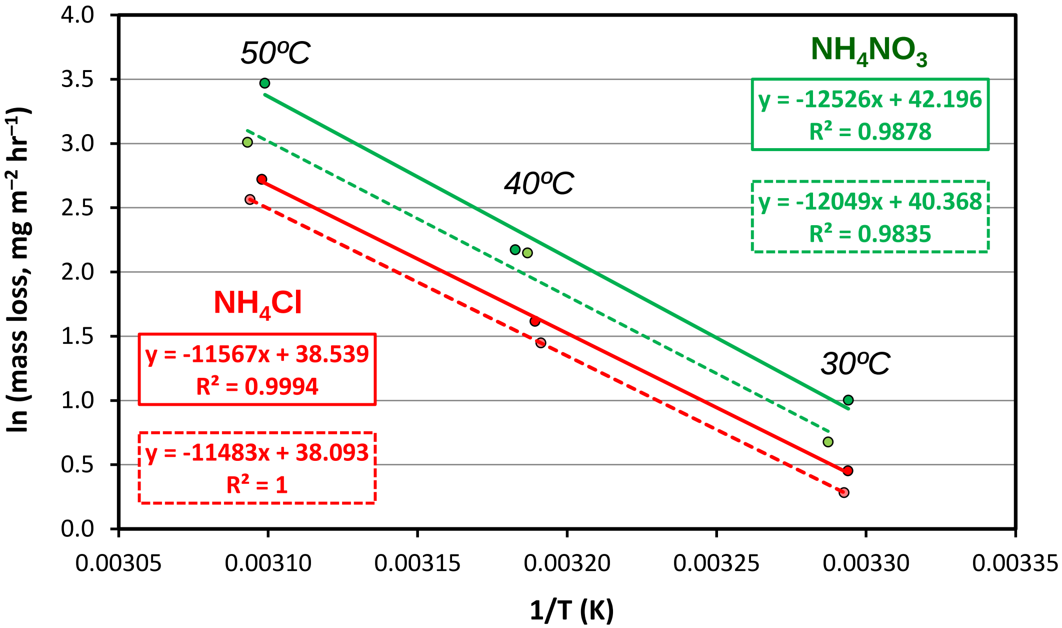
NH_4Cl

T, ºC	RH	Rate, mg/m^{-2} hr^{-1}	Days to degas 1 g/m^{-2}
	Dry		
49.8	12.6	-15.20	2.7
40.6	12.5	-5.03	8.3
30.6	13.0	-1.57	26.5
	Deliquesced		
50.2	63.9	-12.98	3.2
40.4	62.1	-4.26	9.8
30.7	72.9	-1.33	31.4

NH_4NO_3

T, ºC	RH	Rate, mg/m^{-2} hr^{-1}	Days to degas 1 g/m^{-2}
	Dry		
49.7	13.2	-32.10	1.3
41.2	13.2	-8.78	4.7
30.6	13.0	-2.72	15.3
	Deliquesced		
50.3	41.2	-20.28	2.1
40.8	41.0	-8.56	4.9
31.2	50.3	-1.97	21.2

$(NH_4)_2SO_4$ salt and brine are stable, and do not degas significantly



Salt	E_a, kJ/mol
NH_4NO_3, dry	104.1
NH_4NO_3, deliquesced	100.2
NH_4Cl, dry	96.2
NH_4Cl, deliquesced	95.5

Real dust aerosols are much smaller, and will degas even more rapidly.

Inland sites

Brine Stability Experiments: Mixed Salt Assemblages

- In the solid state, salts such as NaCl and $(NH_4)_2SO_4$ are known to be thermally stable, and could accumulate on a canister

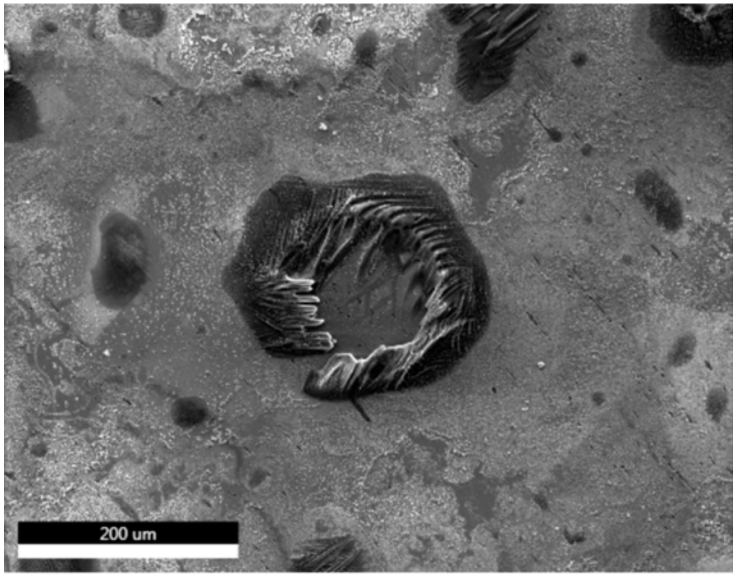
- However, once mixed salts deliquesce, then coupled ammonium/acid degassing can occur:

$$2NaCl(s) + (NH_4)_2SO_4(s) \leftrightarrow Na_2SO_4(s) + 2HCl(g) + 2NH_3(g)$$

- If these if the salts deliquesce and form a brine, chloride *should* be removed as well as ammonium

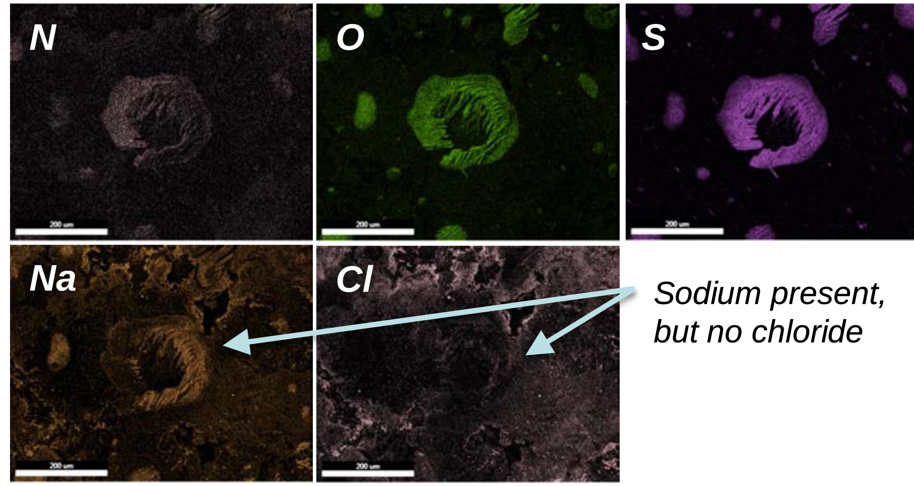
Inland sites

Brine Stability Experiments: *$(NH_4)_2SO_4$ and NaCl Salt Mixture*



Initial

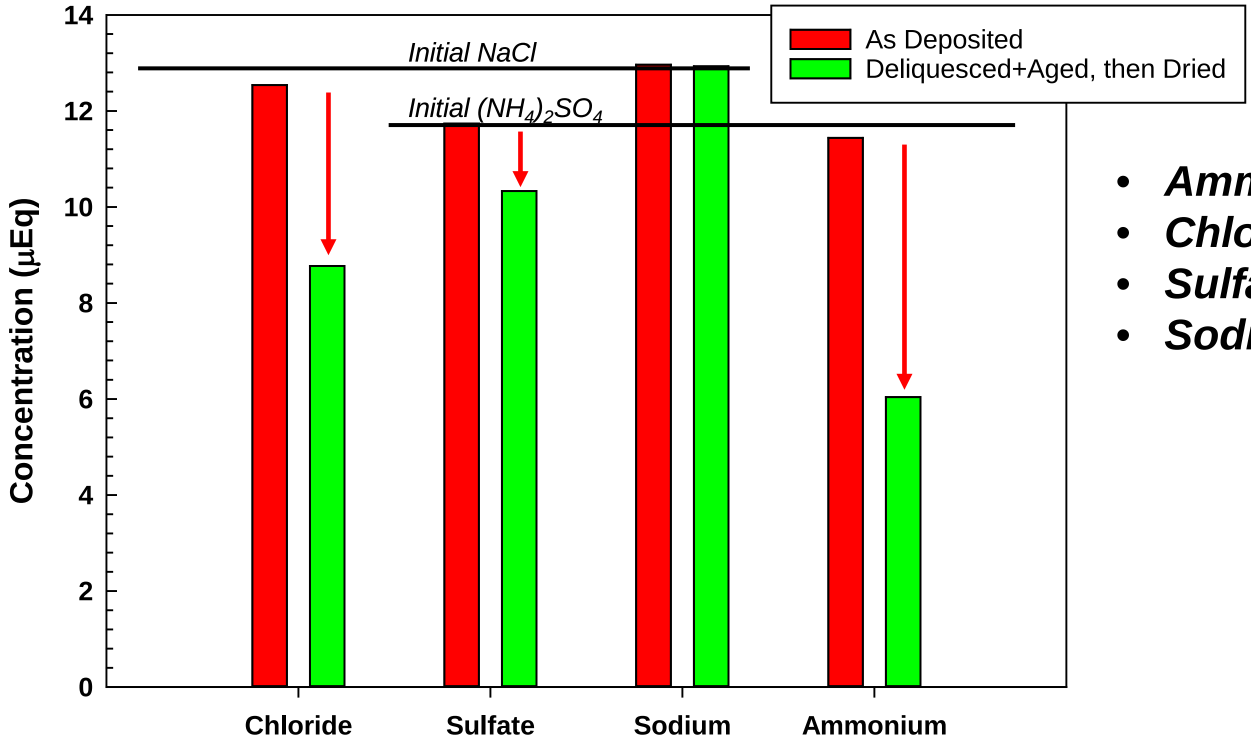
Final



- **Salts deposited on 303SS surface using an airbrush**
  - Ammonium sulfate deposited as an aqueous solution
  - Sodium chloride deposited using a methanol carrier (to prevent dissolution and mixing with ammonium sulfate)
- **Some reaction in the as-deposited state**
- **Salt mixture dried at 50ºC, 10% RH for 4 days, deliquesced at 50ºC, 75% RH 24 hours, and re-dried at 10% RH**
- **Salts recrystallized as large grains.**
- **Partial conversion to Na_2SO_4 (insufficient time for complete reaction)**

Environment: Inland sites

Brine Stability Experiments: *$(NH_4)_2SO_4$ and NaCl Salt Mixture*



- ***Ammonium loss***
- ***Chloride loss***
- ***Sulfate loss***
- ***Sodium unchanged***

- **Salts extracted from surface of control sample and deliquesced sample**
- **Degassing took place, as evidenced by reduction in chloride and ammonium (ammonium loss = chloride loss plus sulfate loss)**
- **Incidentally deposited chloride salts (e.g. road salts or cooling tower salts) will only form persistent chloride-rich brines *if the chloride deposition rate is greater than the ammonium deposition rate*.**

Environment: Data Gaps

- **Inland sites:**
  - Data on aerosol deposition rates (chlorides vs ammonium minerals)
  - Composition of canister surface deposits.
- **Marine sites:**
  - Stability of marine brines
  - Salt deposition rates and surface loads as a function of time, canister surface location.
  - Effect of insoluble particles in dust?

LOCALIZED CORROSION MODELING

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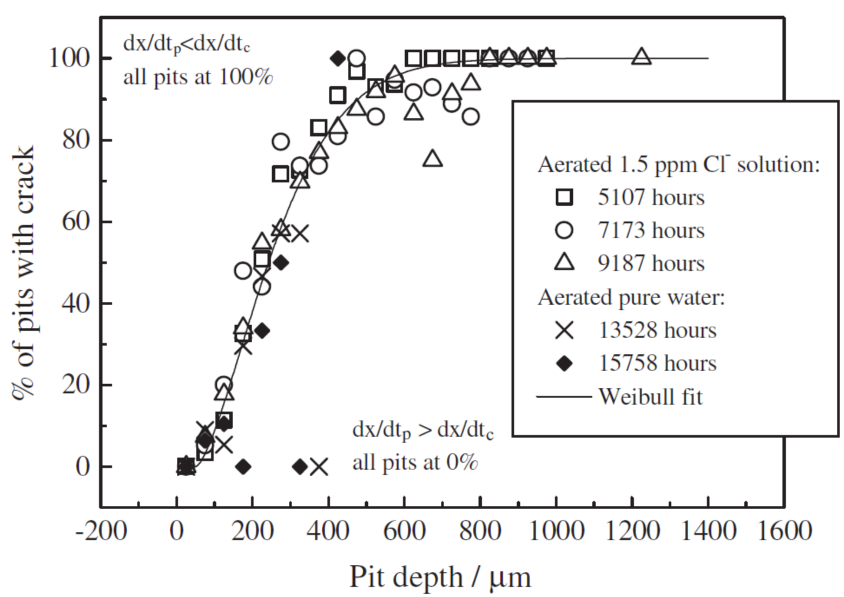
SNL SCC Modeling

Implementation of a Maximum Pit Size Model



Turnbull et al. (2009)

- **Localized corrosion (pitting) is a precursor for SCC**
- **A SCC crack will initiate from a pit once a threshold pit size is reached (Kondo criteria)** ***(more of a suggestion than a rule…)***

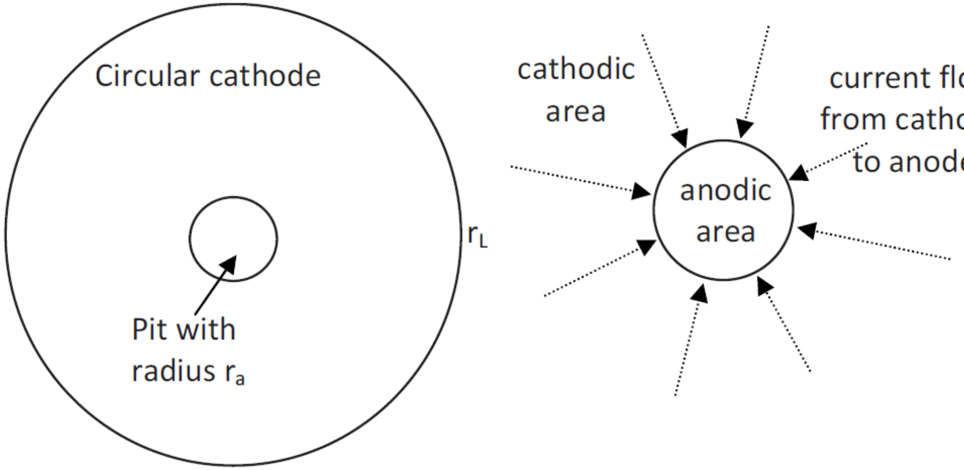
Estimation of the maximum pit size as a function of environmental conditions may potentially be used to estimate crack incubation times

Environmental Parameters for a Maximum Pit Size Model

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…



Max. cathode current

Brine conductivity

Brine layer thickness

Electrochemical term (from cathodic polarization curve)

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

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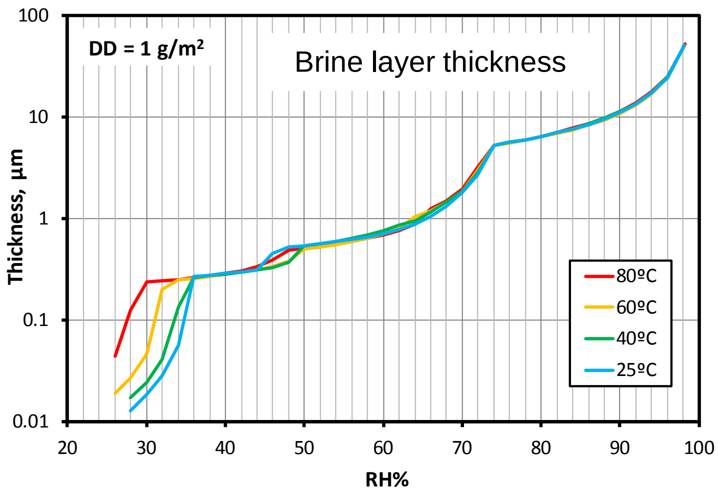
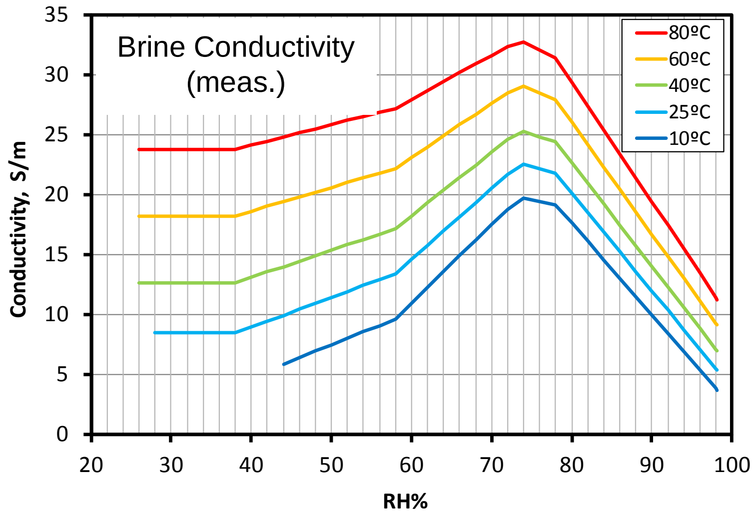
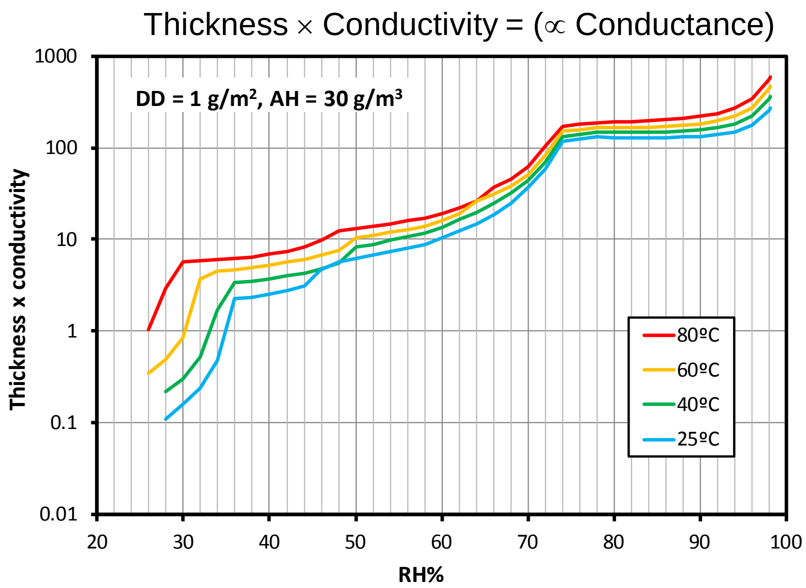
Evaporated Seawater Brine Properties







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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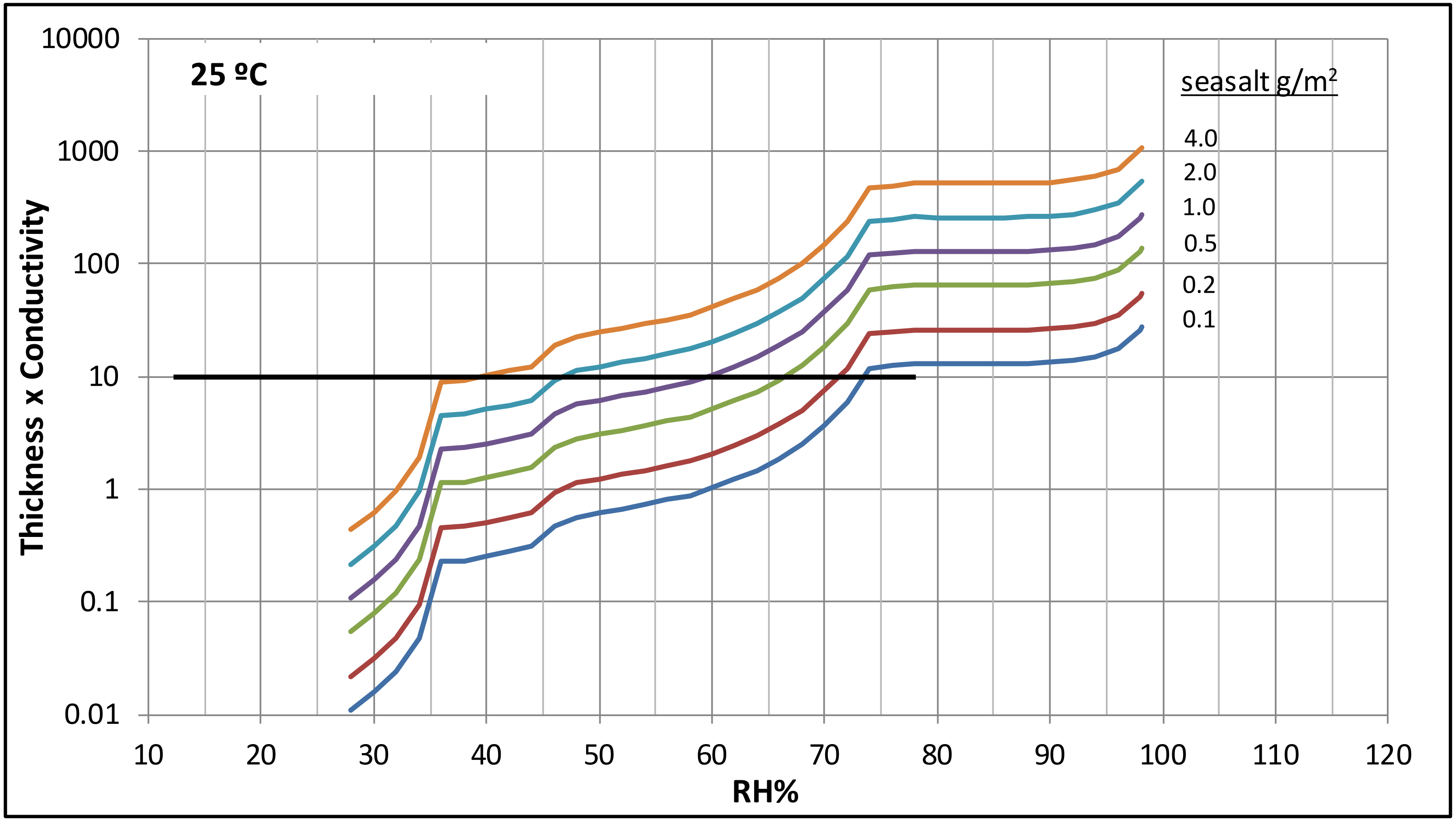
Evaporated Seawater Brine Properties

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



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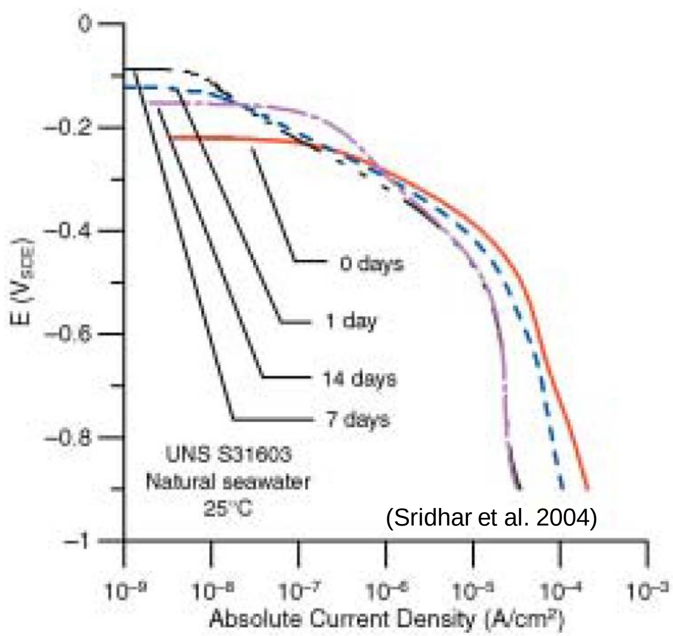
Measuring cathodic polarization data?

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

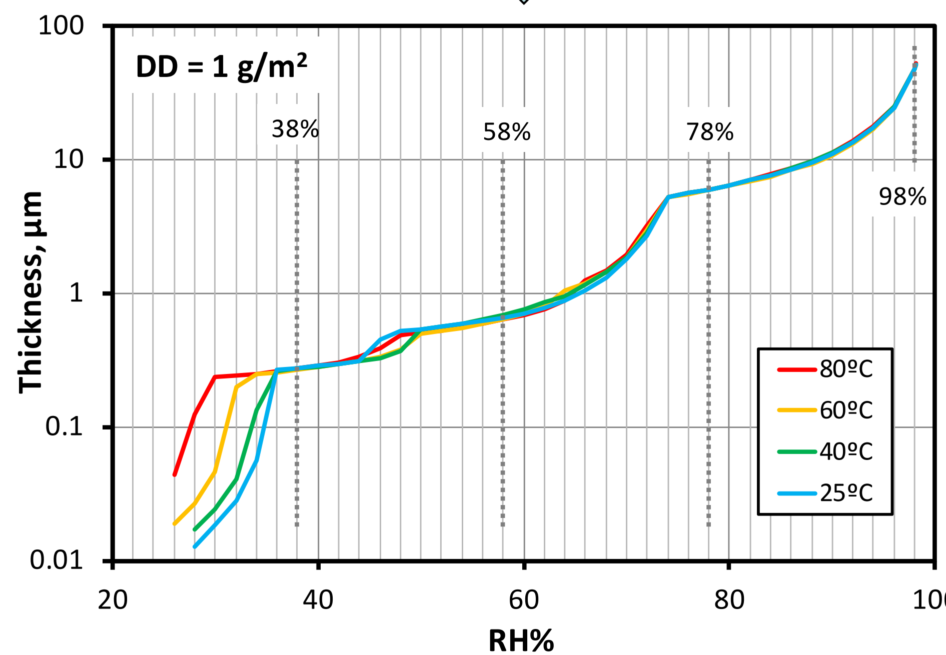


(Sridhar et al. 2004)

(a)

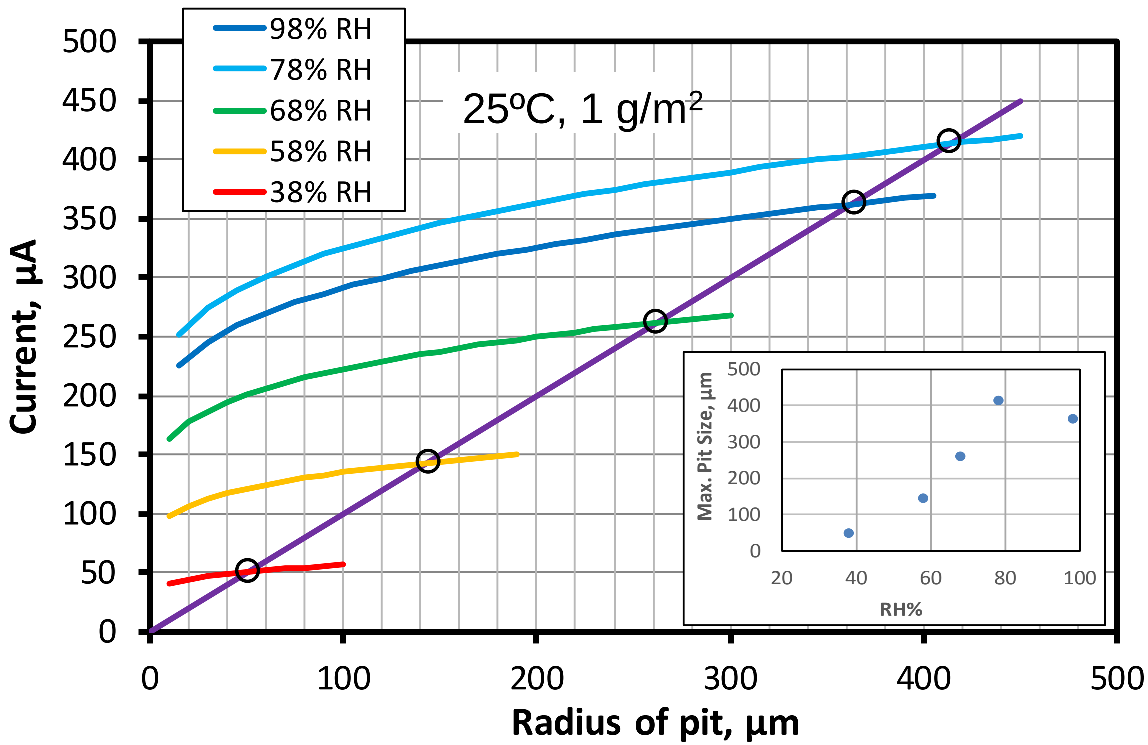
To characterize variability in cathode kinetics with brine composition, measure polarization curves in four brines corresponding to:

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



Example: Calculated Maximum Pit Sizes

Example of Chen and Kelly maximum pit size model results



Caveat: only seawater (98% RH) cathodic polarization data available at this time

Localized Corrosion Modeling: Data Gaps

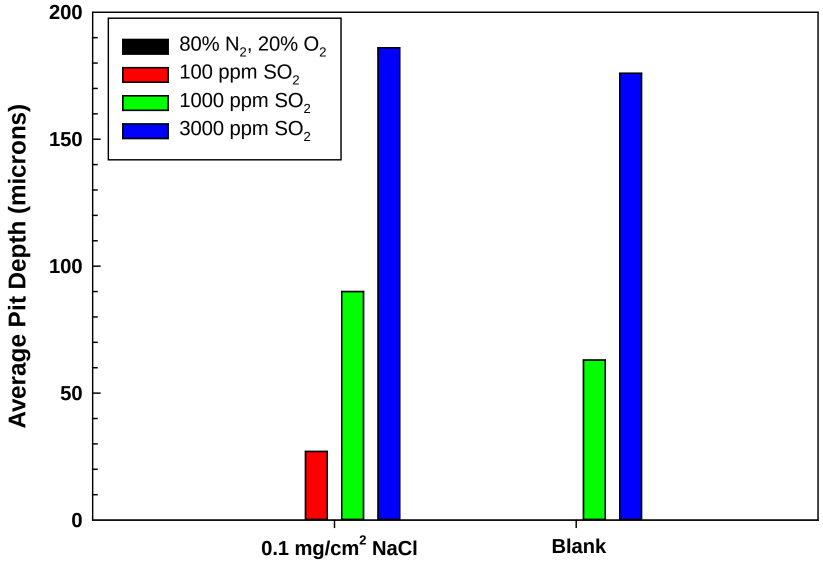
- **Need better calibration and validation data**
  - Existing validation data are only for poorly-constrained field conditions
  - Salt loads, RH conditions poorly defined.
- **Lack of data for cathodic kinetics in concentrated brines formed by evaporated seawater**
  - SNL will measure cathodic polarization curves in concentrated brines.
- **Pit-to-crack transition criteria defined, but applicability may be limited.**
  - Effects of surface roughness, surface preparation, etc.
  - Good data sets required to evaluate model applicability

Experimental work to assess localized corrosion processes will provide necessary data to calibrate and validate the maximum pit size model.

EXPERIMENT PLAN FOR LOCALIZED CORROSION

Characterization of Localized Corrosion under Atmospheric Conditions

- **Little data available on long term distribution of pits on atmospherically exposed 304SS**
  - Validation datasets from Chen and Kelly model over uncontrolled conditions
  - Focus on maximum pit size, rather than distribution
  - Times from 1-10 years to peak
  - Atmospheric contaminants matter, but aren't often considered



Atmospheric chemistry will be often more complex than just humidity

Example – Johnson, et. al, Corrosion Science, Vol. 22, no. 3, pp. 175-191 (1982)

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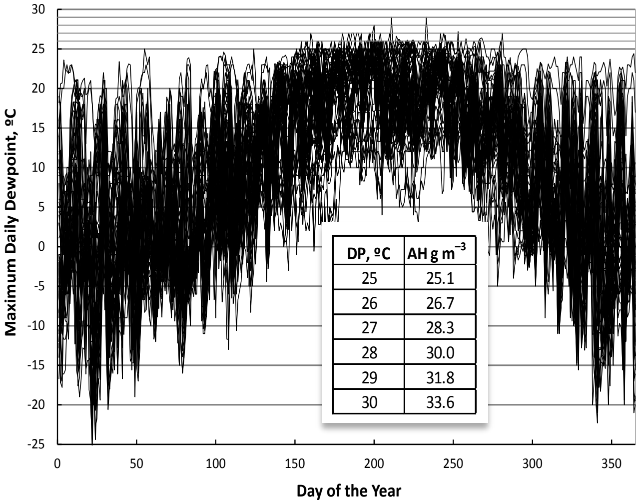
Environmental Conditions for Testing

- **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				
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	



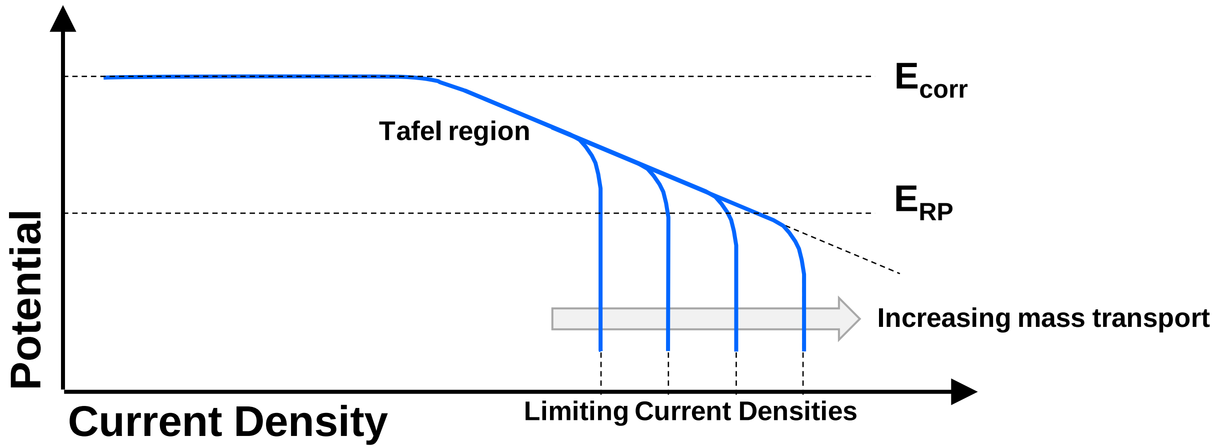
Test Matrix: Localized Corrosion

- **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

Cathodic Kinetics

- Schematic cathodic polarization curve: What do we need?



- Scaling difficulties – extending from a bulk measurement to a thin film (establish if limiting or assume Tafel over potential range)

Cathodic Kinetics: Test Matrix

- **Experiments**
  - Solution chemistries at 25ºC
    - *ASTM ocean water (98% RH)*
    - *Concentrated to 78% RH (factor of 9.4)*
    - *Concentrated to 58% RH (factor of 68)*
    - *Concentrated to 38% RH (factor of 100)*
  - Temperatures: 3 (Ambient, 40C, 60C)
  - Alloys: 3 (304, 304L, 316L)
  - Test methodologies
    - *Immersion (stagnant) (static tests did not work—moving on the flowing conditions)*
    - *RDE or RCE (flowing)*

STRESS CORROSION CRACKING: PRELIMINARY TEST PLAN

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)?*

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

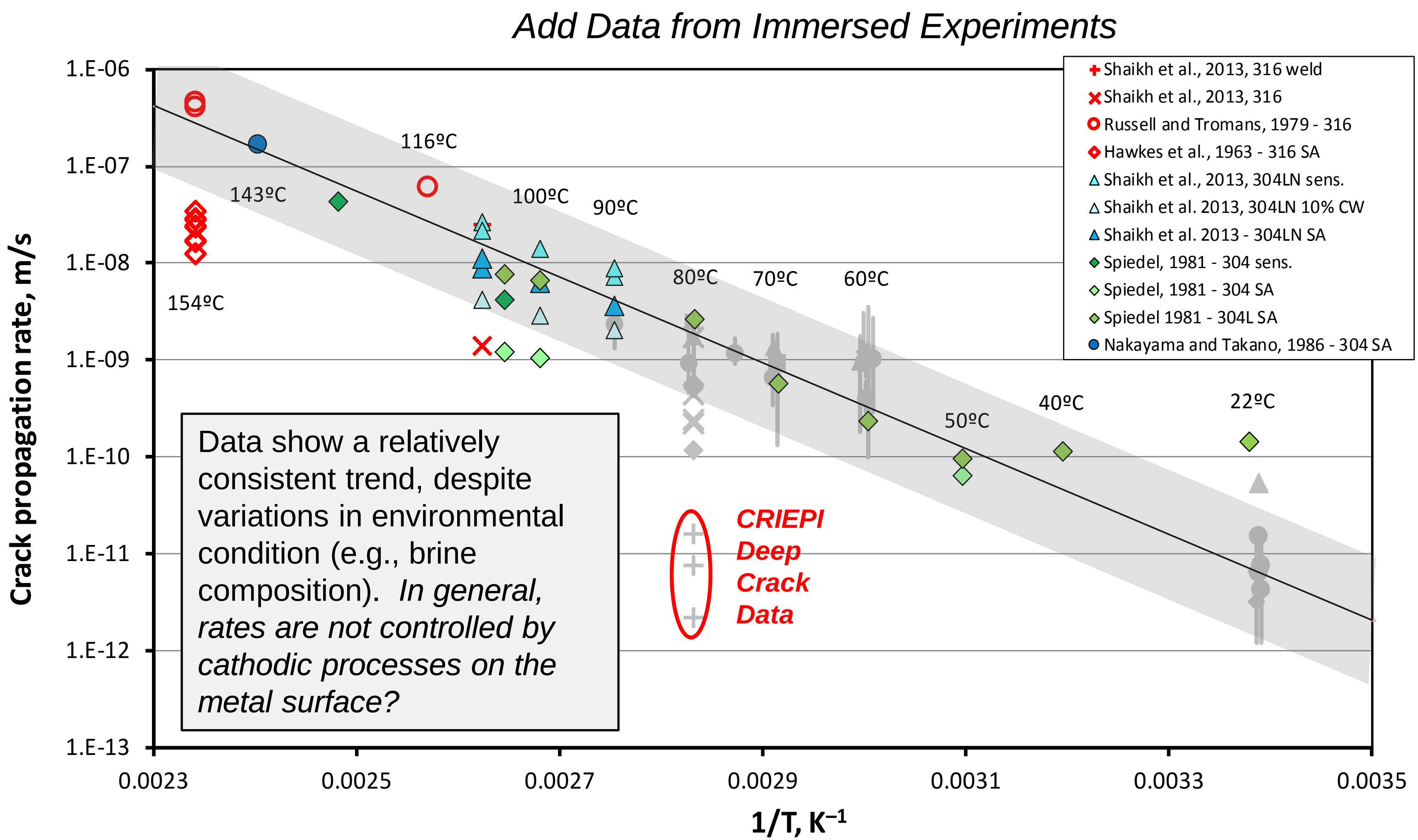
Currently being used by CSM IRP members and SwRI

- **Canister mockup materials: Canister leftovers will be returned to SNL in June/July, and cut into pieces for testing**

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.

Available data



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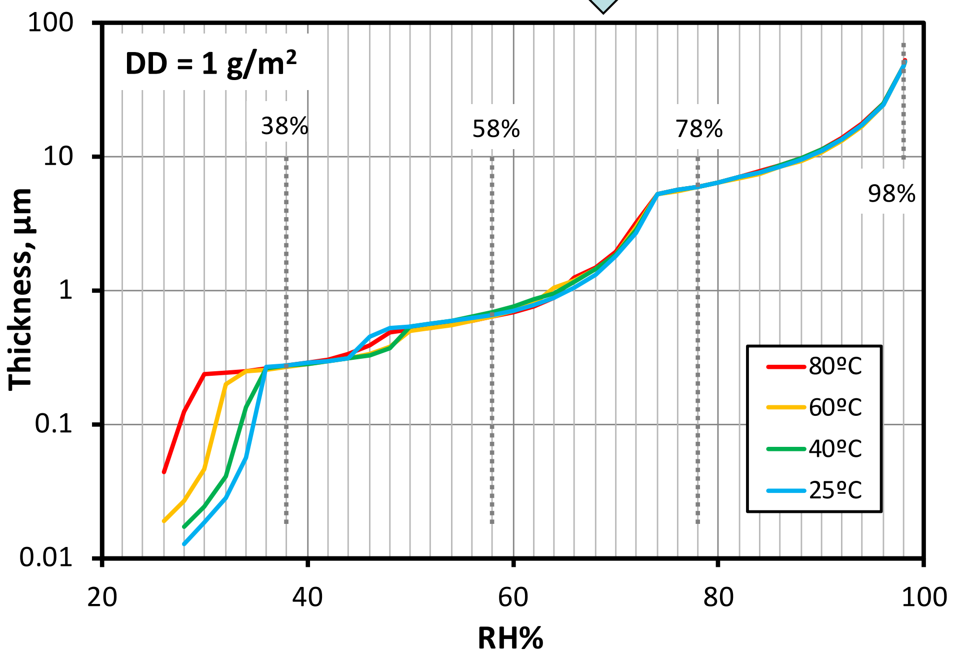
Brine Compositions

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

Test Matrix: Effects of Brine Composition

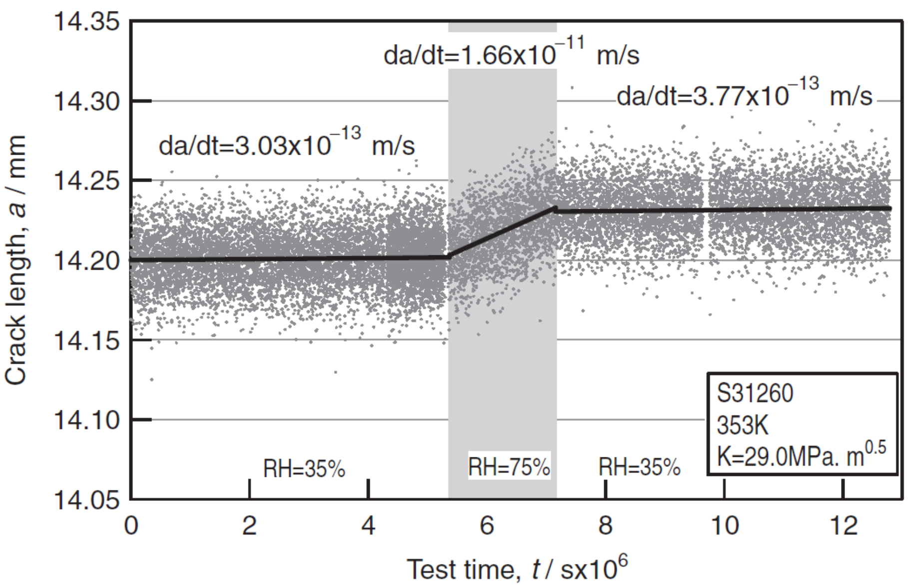
- ***Sample geometry*****:** Compact tension
- ***Material:*** As received, sensitized 304, 304H
- ***Crack growth rate measurement technique*****:** DCPD
- ***Environments:***
  - ASTM Artificial oceanwater
  - Concentrated to 78% RH (factor of 9.4)
  - Concentrated to 58% RH (factor of 68)
  - Concentrated 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

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

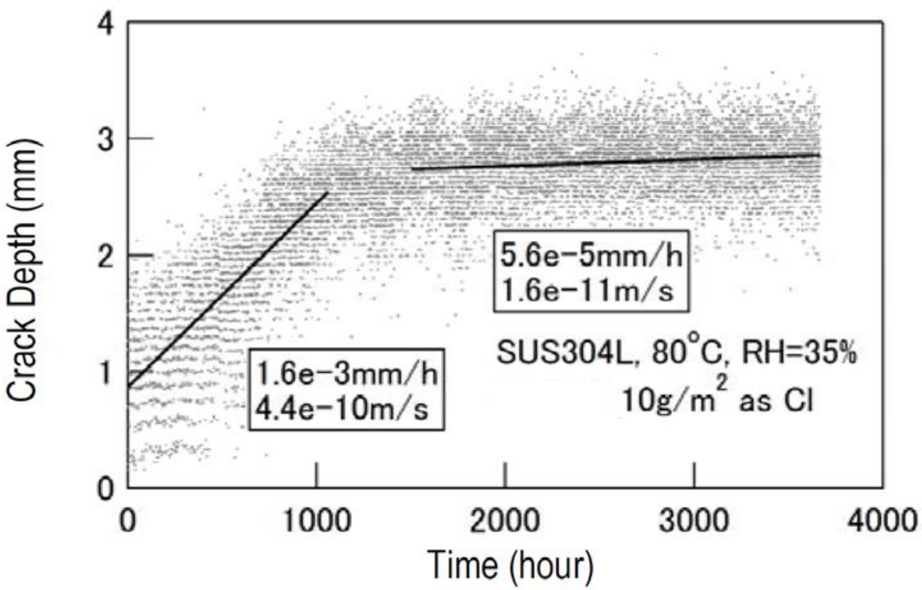
Observed (CRIEPI):

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) assumed to be constant.

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

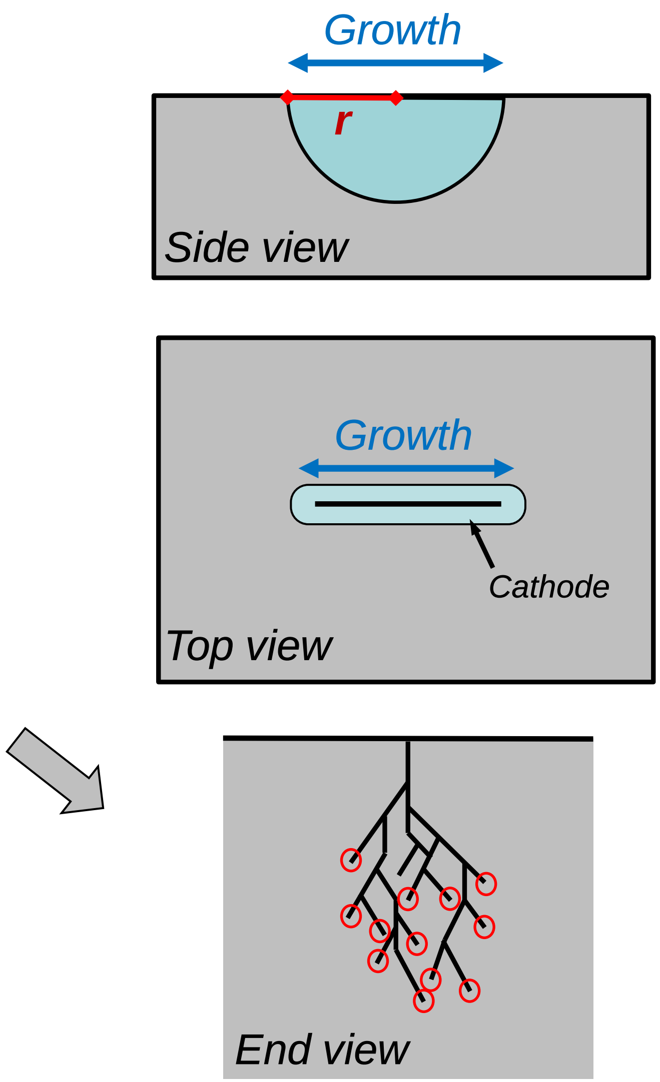


Shirai et al., (2011) 4-point bend specimen, 304 SS. Crack growth rate initially high, decreases as crack grows beyond ~ 3 mm.



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

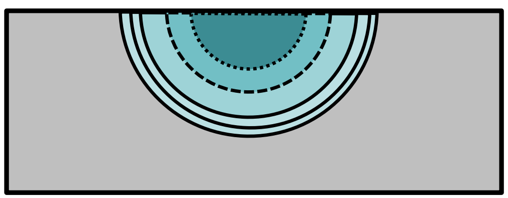
- **Possible explanations for CRIEPI data**
  - <u>CT specimens</u> Lower RH = thinner brine film = smaller cathode = cathodic limitations on crack growth
  - <u>4-point bend specimens</u> As elliptical crack grows, anode growth rate exceeds cathode growth rate = cathodic limitations on crack growth?
    - Cathode growth rate ∝ surface length of crack (2*r*)
    - Anode growth rate ∝ length of crack front (πr) ***plus branching***



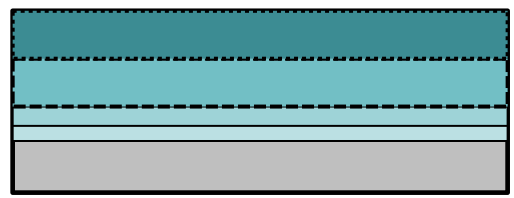
Potential Effects of Atmospheric Conditions (Thin Brine Films) on SCC Crack Growth Rates

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

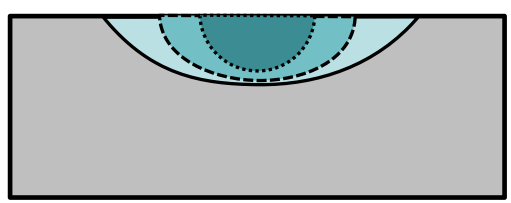
*Semicircular crack,
4-point bend specimen*



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*

Test Matrix: Effects of Cathode Limitations due to Thin Brine Layer

- ***Sample geometry*****:** 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.

STATUS OF
EXPERT PANEL REVIEW

Expert Panel Summary

- **Panel**
  - Peter Andresen
  - Alan Turnbull
  - John Scully
  - Rob Kelly
- **Topics Discussed**
  - Environment
  - Localized corrosion
  - Crack Initiation
  - Crack propagation
  - Experimental techniques
- **Report in draft, will be finalized and released shortly**

Summary

- **Environment**
  - Reactions with NH_4 phases may limit Cl-bearing brine formation at inland sites
  - Need more field data on canister surface deposits at inland and marine sites
- **Localized Corrosion Modeling**
  - Implemented maximum pit size model in SNL probabilistic model
  - Max pit sizes should be limited by environmental conditions (T, RH, salt load)
- **Experiment Plan for Localized Corrosion**
  - Development and growth of pits as a function of T, RH, salt load, material properties, and surface finish
  - Cathodic kinetics as a function of brine composition, temperature
- **Experiment Plan for Localized Corrosion**
  - Use CT specimens, immersed conditions to evaluate effects of brine composition on CGR
  - Use 4-point bend specimens, full-width EDM notch to evaluate effects of cathodic limitations due to thin brine layers
- **Status of Expert Panel Review**