SAND2016-4110PE

Used Fuel Disposition Campaign

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

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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

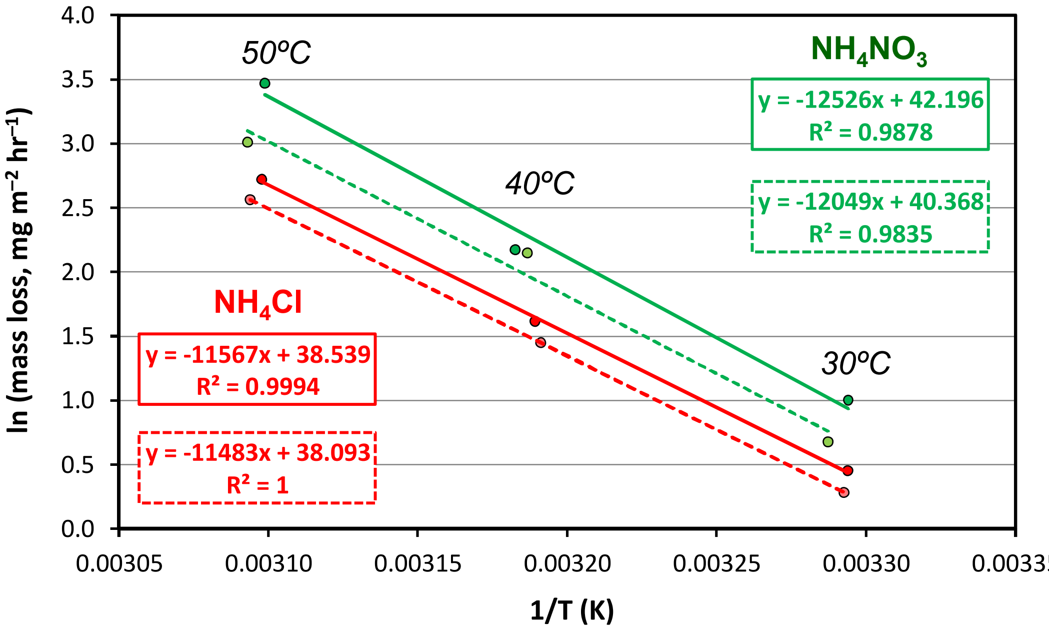
NH_4Cl

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**

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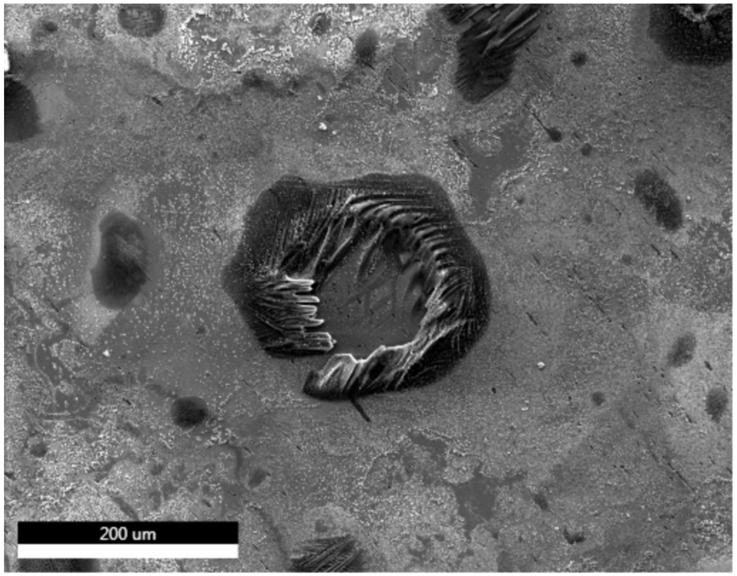
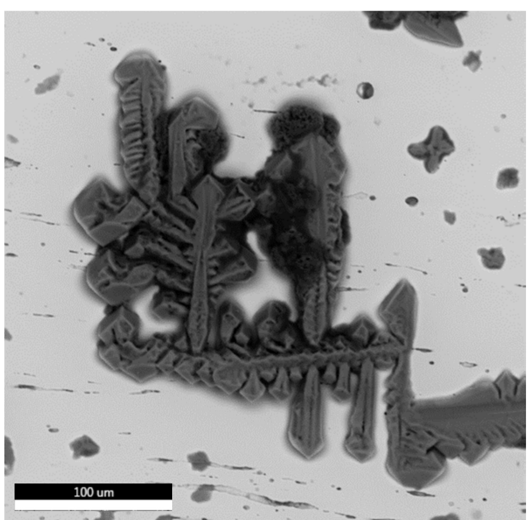
Inland sites

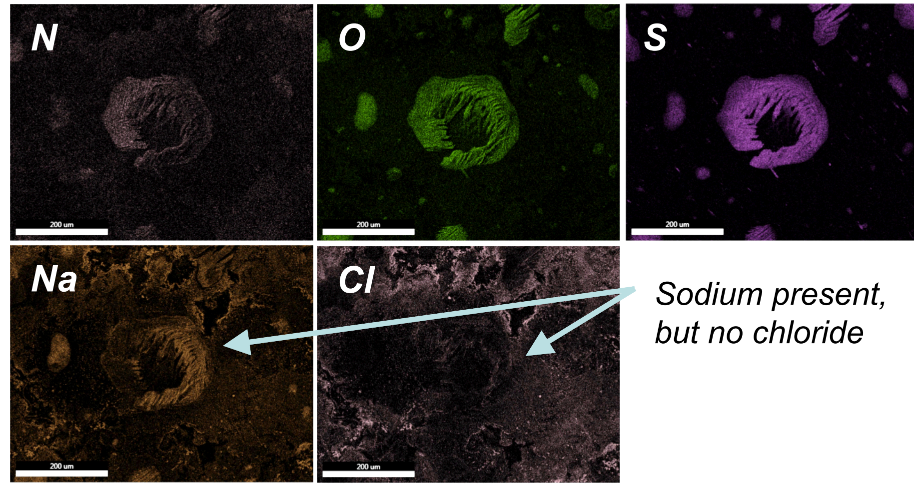
Brine Stability Experiments: $(NH_4)_2SO_4$ and NaCl Salt Mixture



Initial

Final



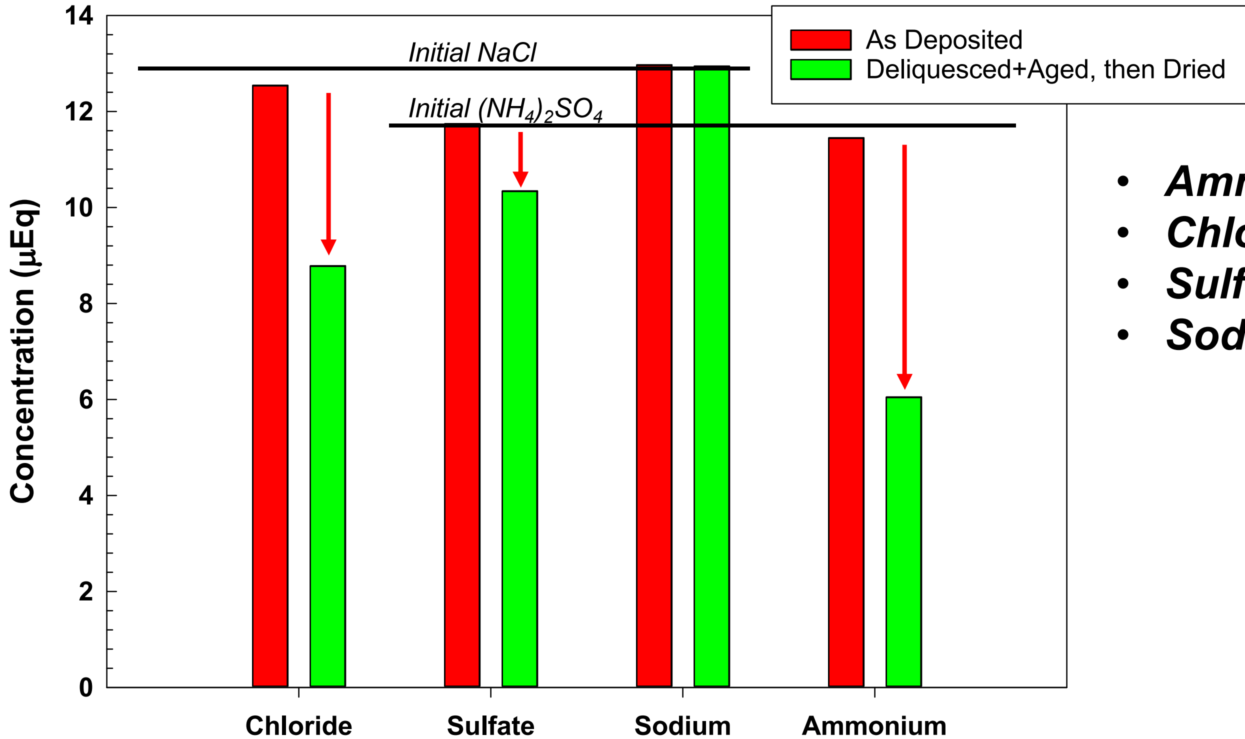


Sodium present, but no chloride

- **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 50°C, 10% RH for 4 days, deliquesced at 50°C, 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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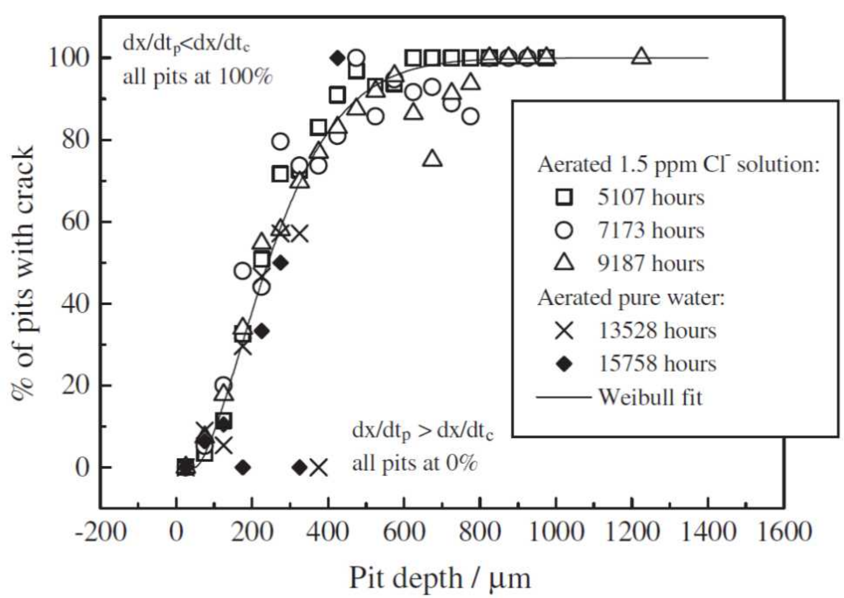
SNL SCC Modeling

Implementation of a Maximum Pit Size Model



Turnbull et al. (2009)

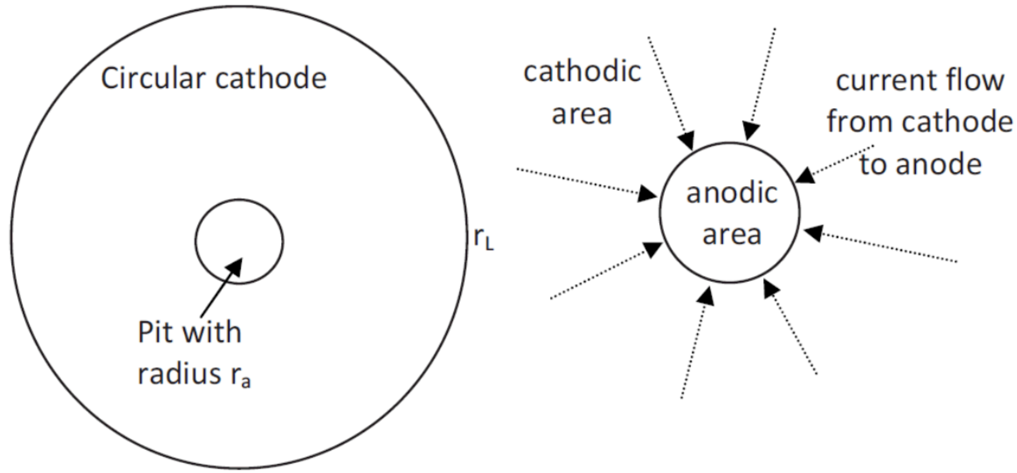
- **Localized corrosion (pitting) is a precursor for SCC**
- **A SCC crack will initiate from a pit once a threshold pit size is reached (Kondo criteria)** ***(more of a suggestion than a rule…)***

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.



Max. cathode current

Brine conductivity

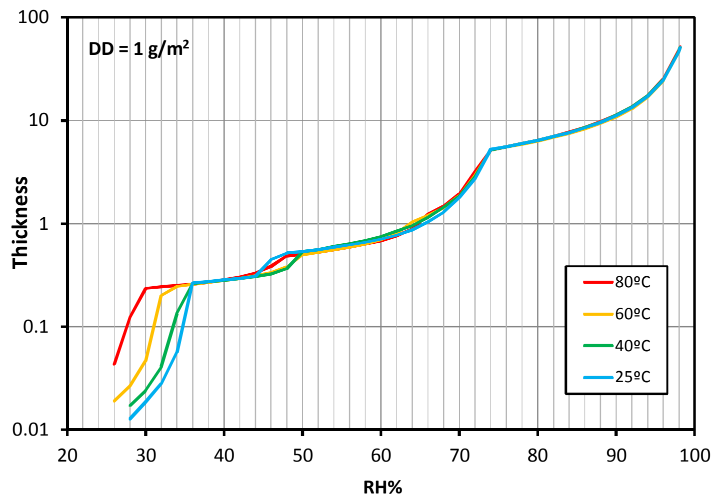
Brine layer thickness

Electrochemical term (from cathodic polarization curve)

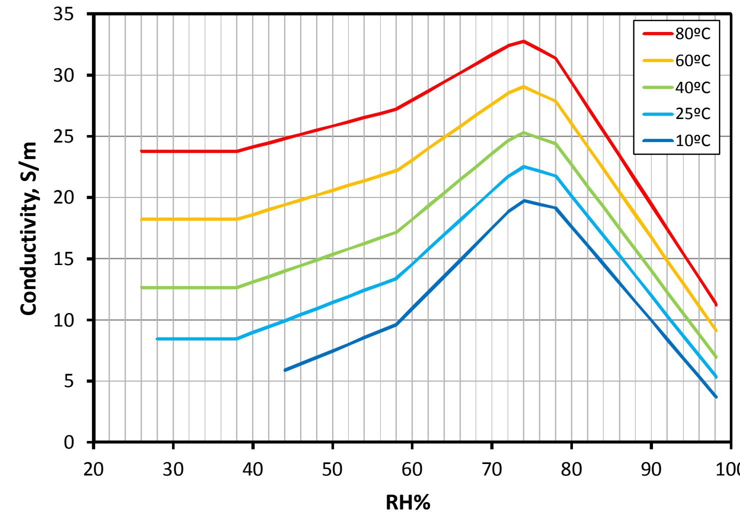
$$\ln I_{c,max} = \frac{4\pi k W_L \Delta E_{max}}{I_{c,max}} + ln\left[\frac{\pi e r_a^2 \int_{E_{corr}}^{E_{rp}} (I_c - I_p) dE}{\Delta E_{max}}\right]$$

Evaporated Seawater Brine Properties

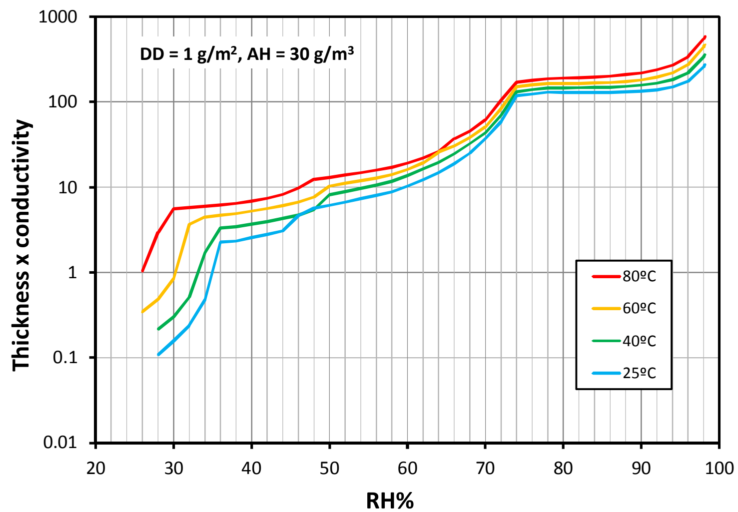
Brine layer thickness



Brine Conductivity



Thickness × Conductivity = (∝ Conductance)



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

<u>Electrochemical data</u>? Cathodic polarization curve measurements will be carried out.

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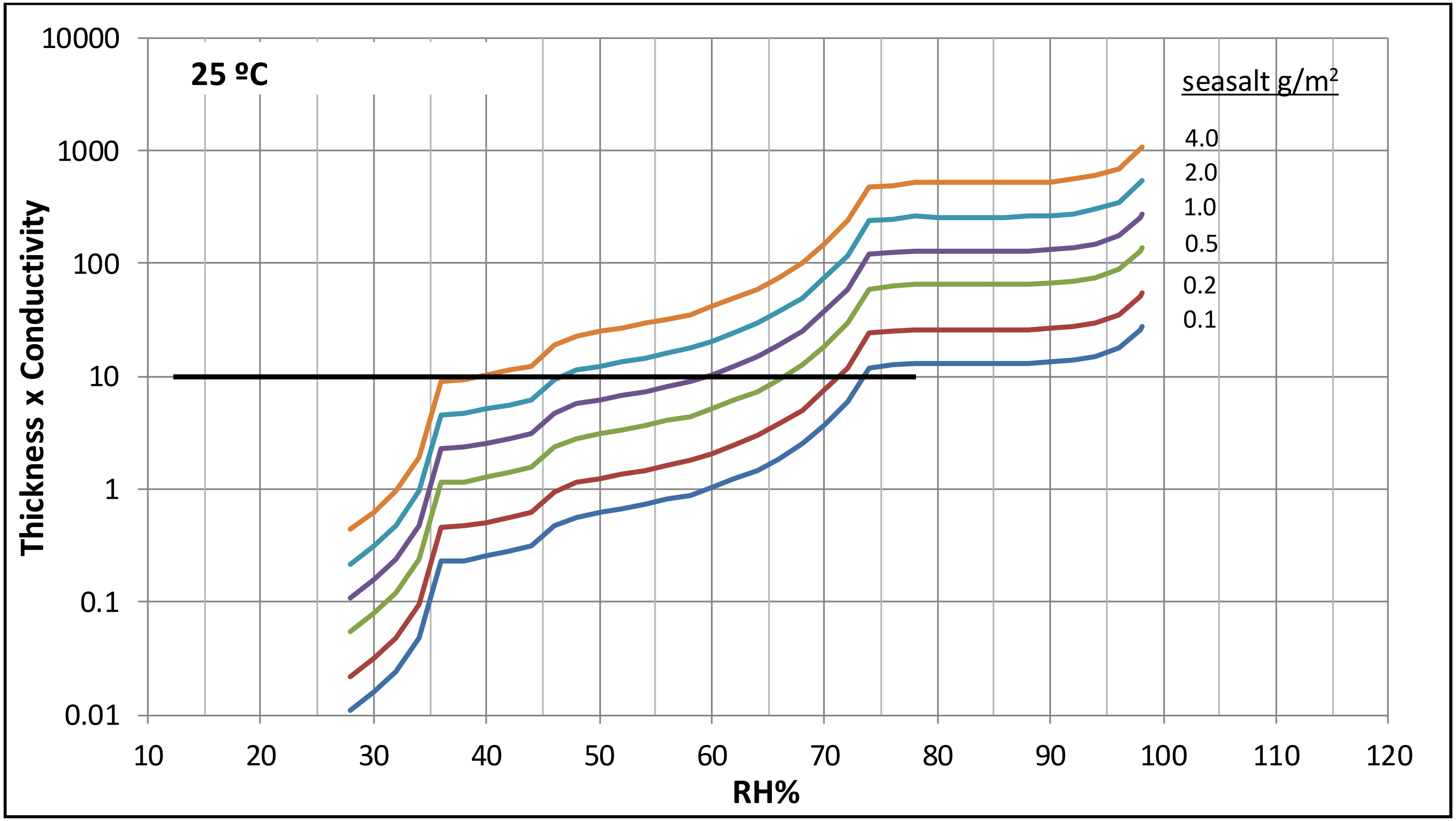
Evaporated Seawater Brine Properties

Effect of Salt Load



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

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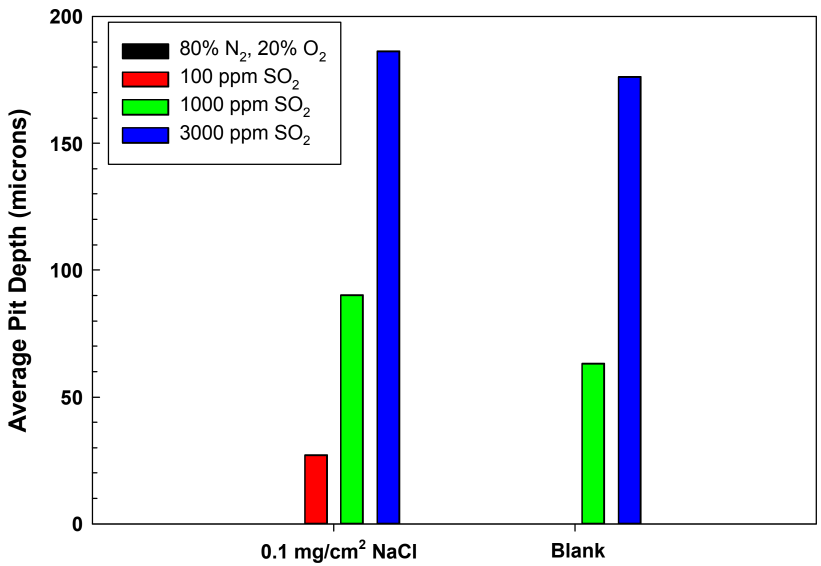
Characterization of Localized Corrosion under Atmospheric Conditions

- **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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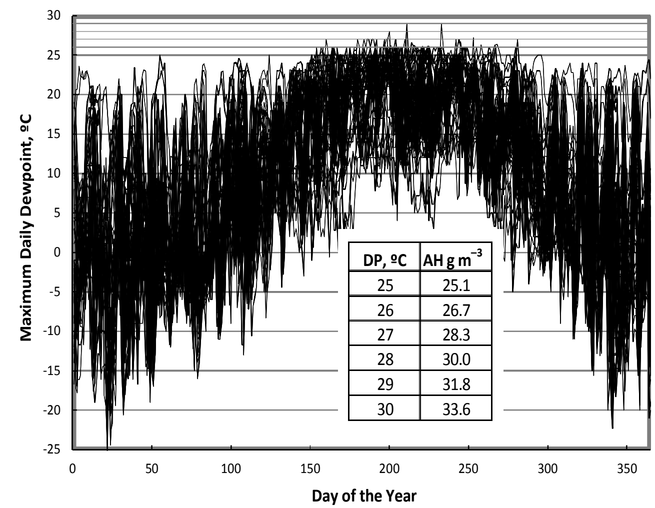
Environmental Conditions for Testing

- 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	



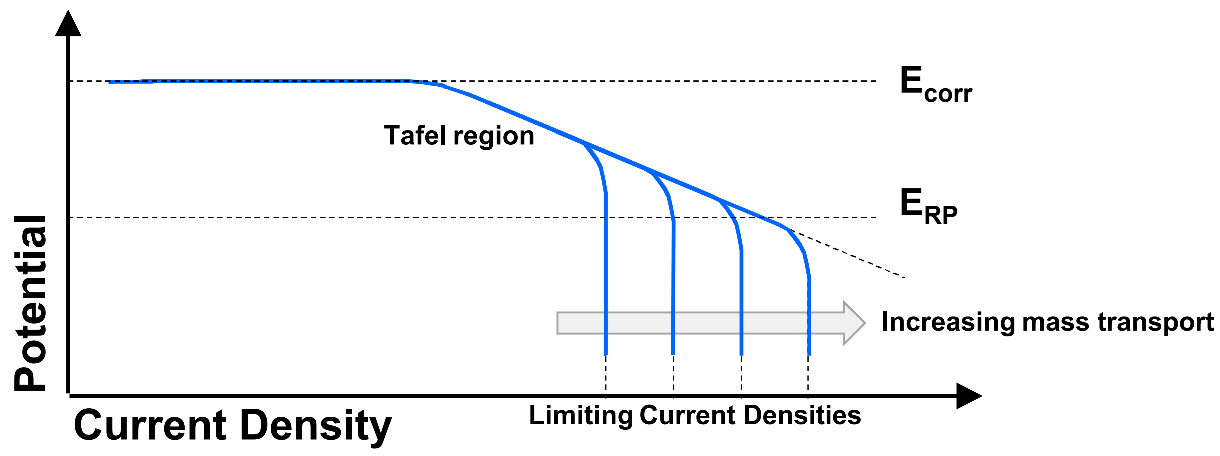
Test Matrix: Localized Corrosion

- **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)**

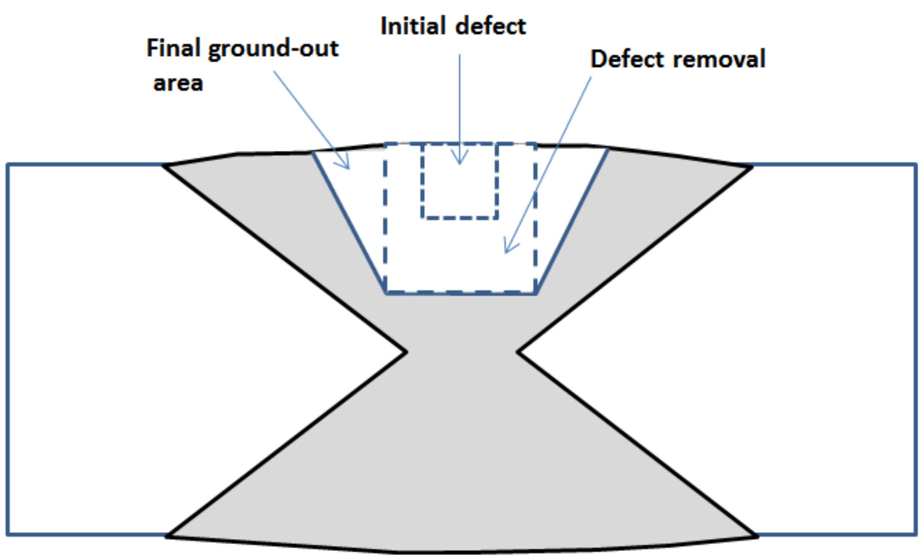
Cathodic Kinetics: Test Matrix

- **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)*
    - *RDE or RCE (flowing) – if necessary*

MOCKUP RESIDUAL STRESS MEASUREMENTS

Weld Repair on Circumferential Weld

- Welds were fabricated via submerged arc welding using a well defined protocol/schedule – very low defect density
- Manufacturer (Ranor) created a repair typical for this type of weld (simulating a local defect due to entrained slag at a weld stop/start point, etc.)
- mock defect into the container by drilling a 1/8” diameter hole partially into the center of the weld root. They then went back and “removed” that defect, by drilling out additional material using a ¼” drill, after which they ground the edges of the site such that the opening of the hole was approximately 0.5” wide. Repair completed via TIG.



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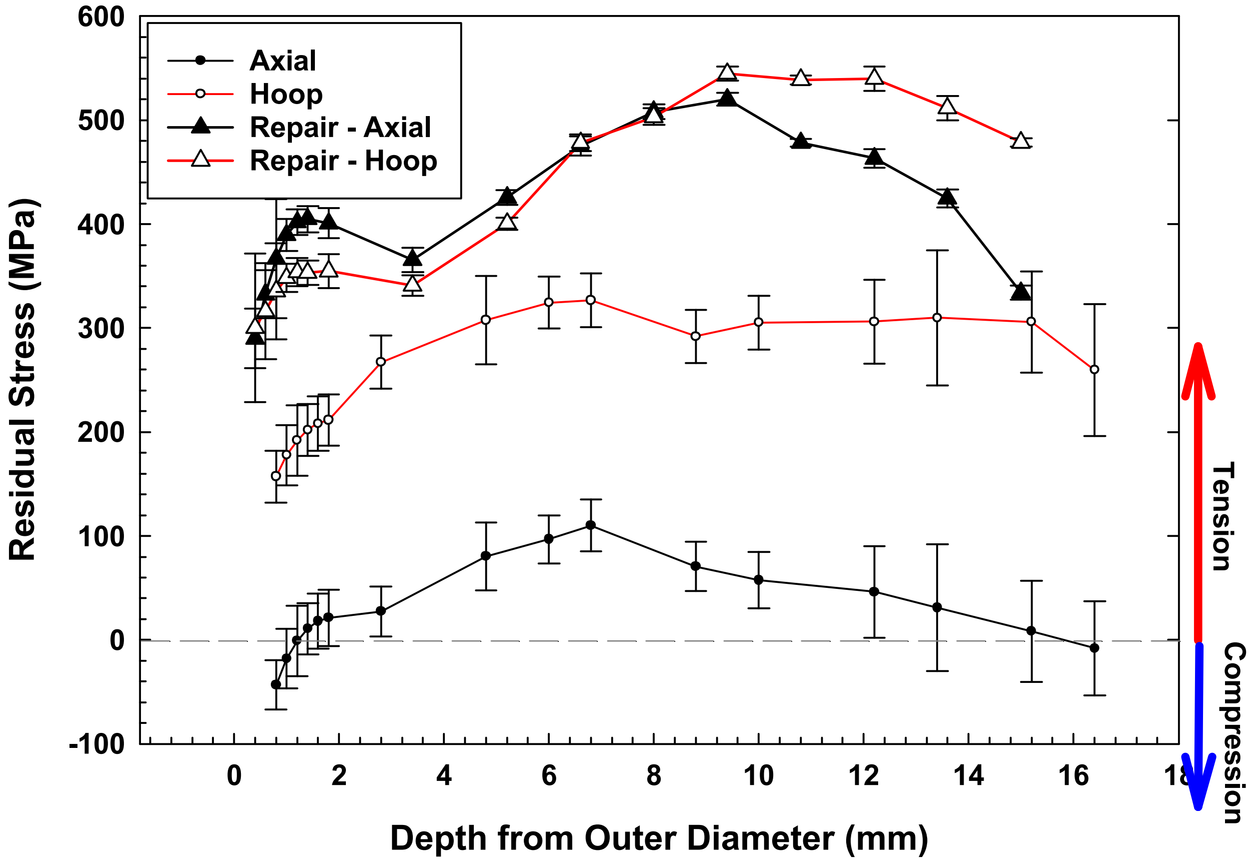
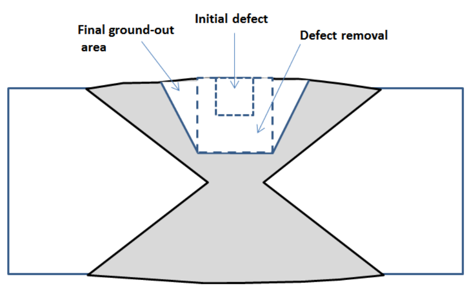
Residual Stresses in Repair: Circumferential Weld (Centerline)

- Dramatic increase in magnitude of stresses, particularly in the axial direction, when a repair is made



- *DHD near surface, iDHD in bulk*
- *Both axial and hoop stresses dramatically increased in weld repair*



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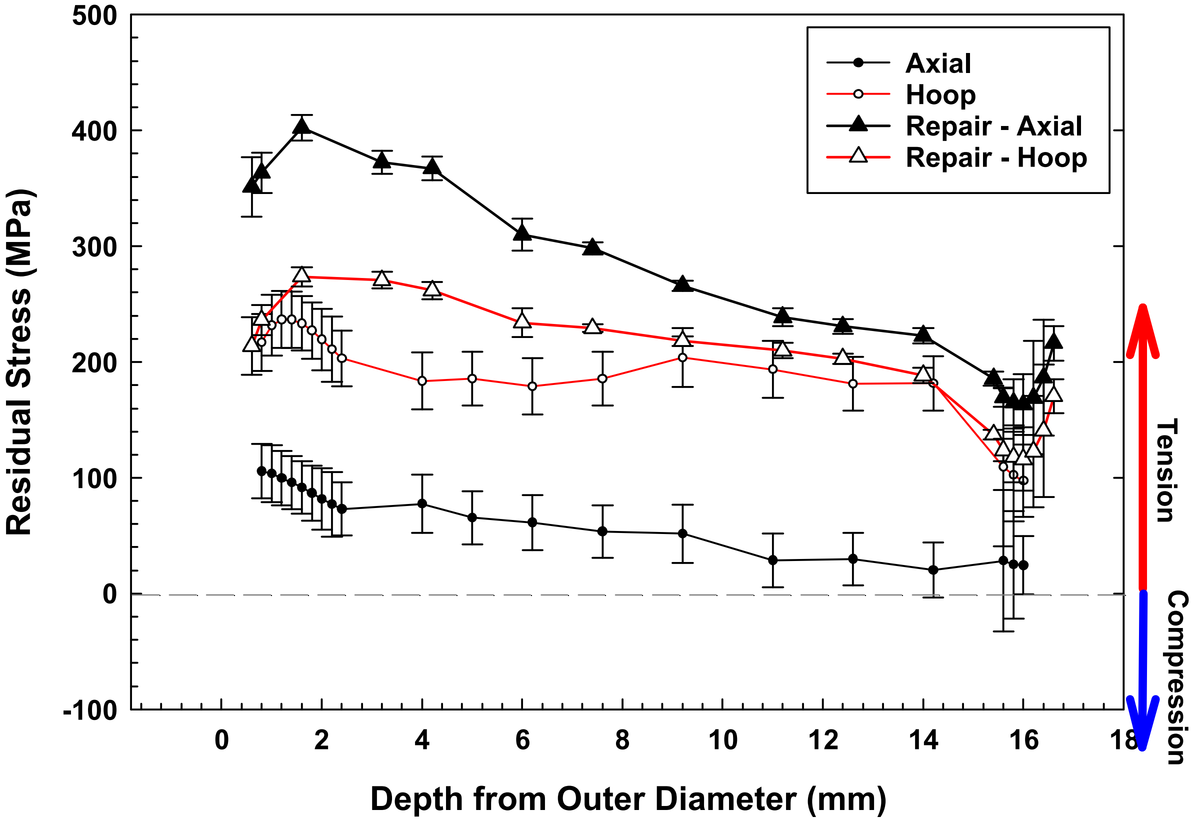
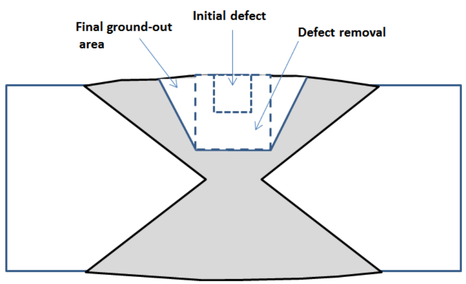
Residual Stresses in Repair: Circumferential Weld (HAZ)

- Dramatic increase in magnitude of stresses, particularly in the axial direction, when a repair is made



- *4mm from weld toe*
- *DHD near surface, iDHD in bulk*
- *Hoop stress increased in region of weld repair*
- *Axial stress dramatically increased in weld repair*
- *Less significant increase in hoop stress at ID, but axial stress is elevated*



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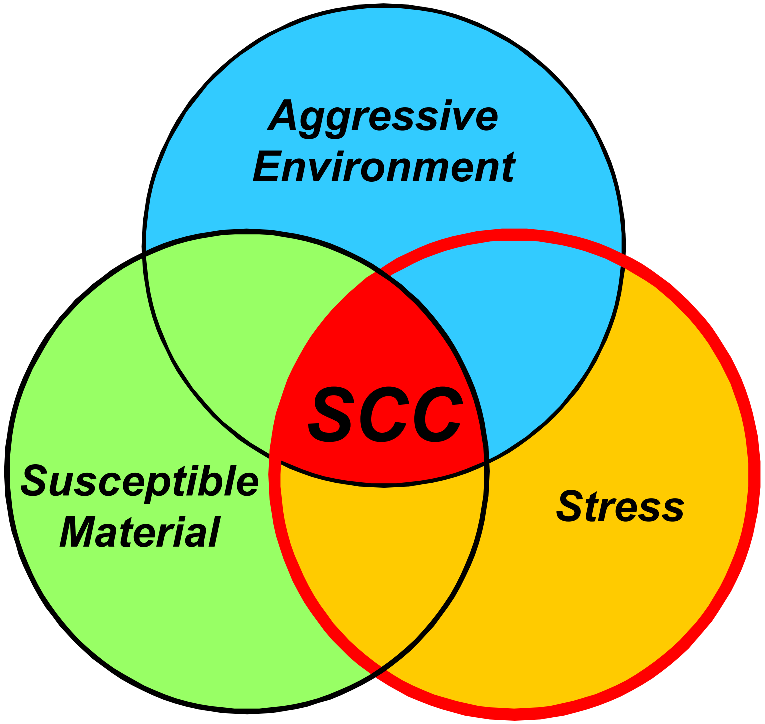
Path Forward for Residual Stress Measurement



- Tensile stress exists through-thickness at both longitudinal and circumferential welds
- Weld repairs exacerbate the stresses observed

- Contour measurements are in progress
- Evaluation of the magnitude of the plastic strain along the weld fusion zone
- Residual stress testing will be complete and the report will be finalized in June

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 this summer**

SAMPLE MATERIALS AVAILABLE

Sample Materials Available

- **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

- **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

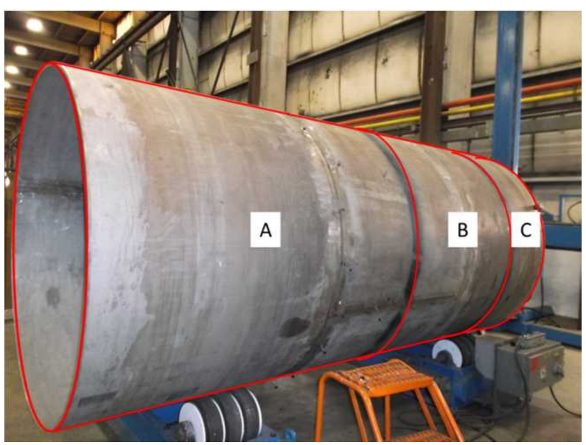
Summary

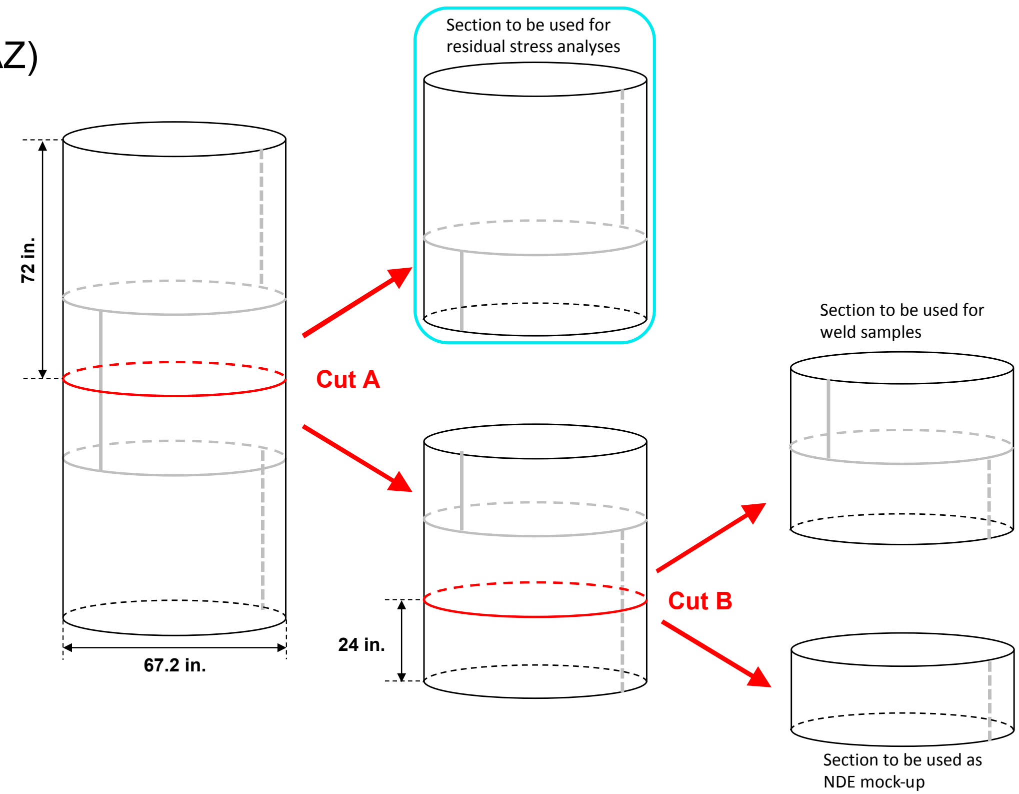
- **Environment**
  - Reactions with NH_4 phases may limit Cl-bearing brine formation at inland sites
  - Need more field data on canister surface deposits at inland and marine sites
- **Localized Corrosion Modeling**
  - Implemented maximum pit size model in SNL probabilistic model
  - Max pit sizes limited by brine layer properties (RH, salt surface load), may inhibit SCC initiation
- **Experiment Plan for Localized Corrosion**
  - Measuring development and growth of pits as a function of T, RH, salt load, material properties, and surface finish
- **Mockup Stress Measurements**
  - High through wall tensile stresses present in welds and HAZ, especially high at weld repairs
  - Final report due end of June
- **Status of Expert Panel Review**
- **Sample Materials Available**

BACKUP SLIDES

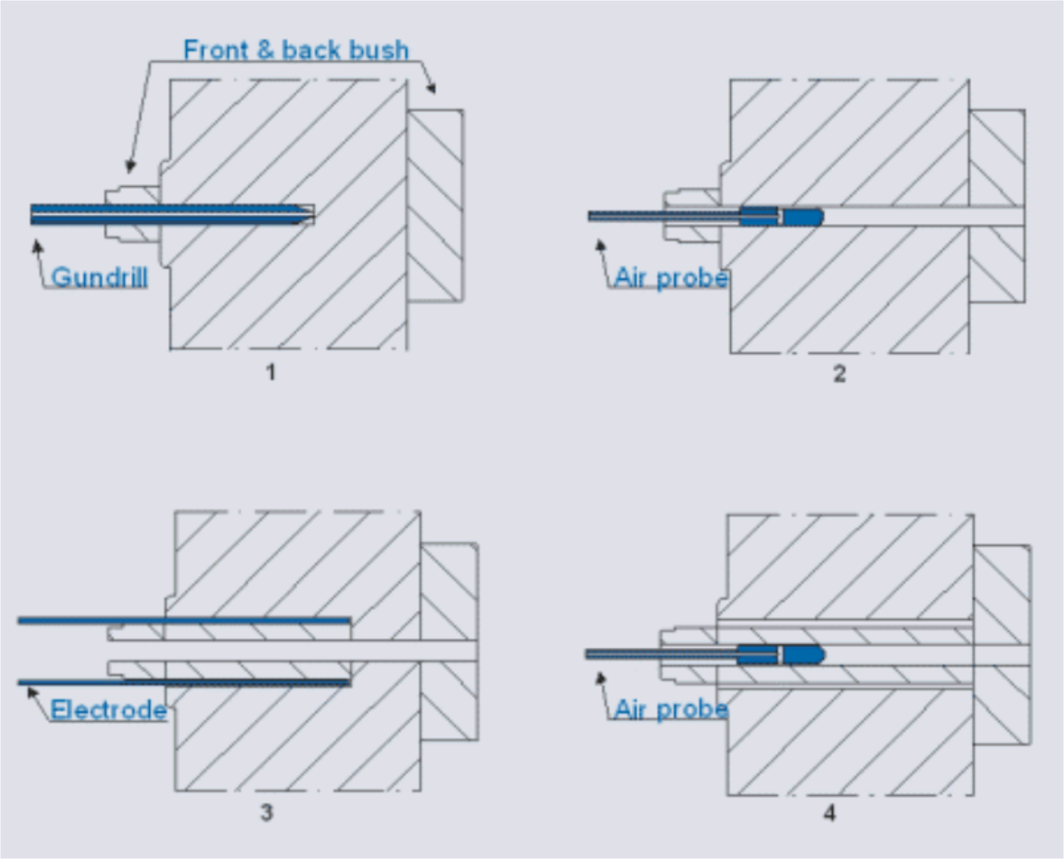
Residual Stress Measurement

- **<u>Goal:</u> Establish if there is sufficient through-wall tensile stresses to support SCC crack propagation**
- **Full-scale mockup container simulating a NUHOMS 24P container (produced at Ranor using procedures established for containers at Calvert Cliffs ISFSI)**
- **Series of key areas are being assessed**
  - Base metal (far from welds)
  - Circumferential Weld (Centerline and HAZ)
  - Longitudinal Weld (Centerline and HAZ)
  - Weld Repair





Deep Hole Drilling



Images from www.veqter.co.uk/residual-stress-measurement/deep-hole-drilling

- Hole precisely drilled through region to be characterized
- Air probe used to measure the inner diameter of the hole as a function of position
- EDM used to cut core around the hole, relaxing the constraint placed by the surrounding material
- Air probe used to measure the resulting distortion of the hole inner diameter
- Stress state calculated from displacements
- Complicated when stresses are high (requires modified technique)

- Get one dimensional map of initial stress state without cutting up structure
- Semi-destructive, labor intensive ($)