Overview of NUREG/CR-7170, "Assessment of Stress Corrosion Cracking Susceptibility for Austenitic Stainless Steels Exposed to Atmospheric Chloride and Non-Chloride Salts"

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Outline

- Background
- NUREG/CR-7170 Contents
  - Testing with chloride-rich salts
  - Testing with non-chloride-rich species
- Conclusions

BACKGROUND

Motivation for Research Activity

- Stress corrosion cracking (SCC) has the potential to affect the safety function of spent nuclear fuel dry storage canisters.

- Research is needed to:
  - Evaluate technical bases for current NRC regulatory guidance,
  - Support NRC safety evaluations,
  - Determine whether further actions by industry are needed to manage potential degradation.

NRC Research Projects

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- NUREG/CR-7030, “Atmospheric Stress Corrosion Cracking Susceptibility of Welded and Unwelded 304, 304L, and 316L Austenitic Stainless Steels Commonly Used for Dry Cask Storage Containers Exposed to Marine Environments” – 2010

- NUREG/CR-7170, “Assessment of Stress Corrosion Cracking Susceptibility for Austenitic Stainless Steels Exposed to Atmospheric Chloride and Non-Chloride Salts” – 2013

Previous NRC-Sponsored Work – NUREG/CR-7030

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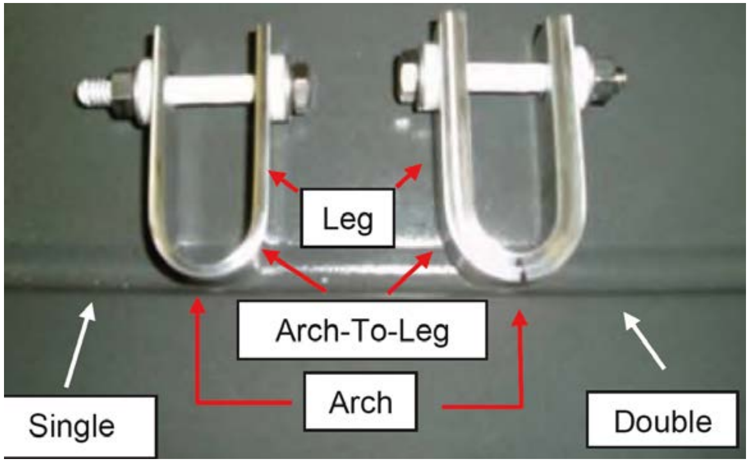
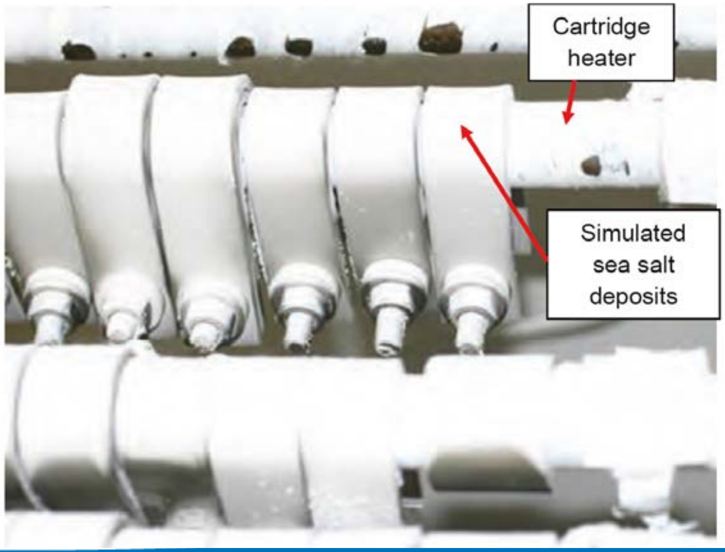


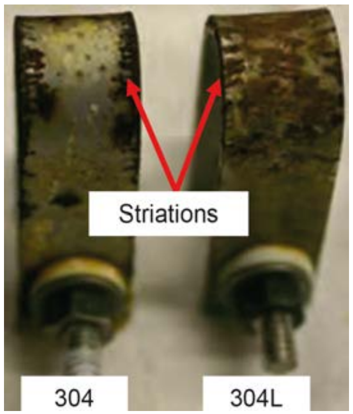
Cycle Number	Chamber Cycle	Cycle Time, min	Cycle Description
1	Salt fog	5	Deposit salt on the specimens
2	Ambient	60	
3	Salt fog	5	
4	Ambient	60	
5	Salt fog	5	
6	Ambient	60	
7	Salt fog	5	
8	Ambient	60	
9	Dry	100	Low relative humidity
10	Increase humidity	125	Increase relative humidity in chamber
11	High humidity	55	Highest relative humidity
12	Dry	180	Low relative humidity



Exposed stainless steel U-bend specimens to salt fog conditions at 43, 85, and 120^{o}C to evaluate susceptibility for cracking. Specimens had high surface salt concentration.

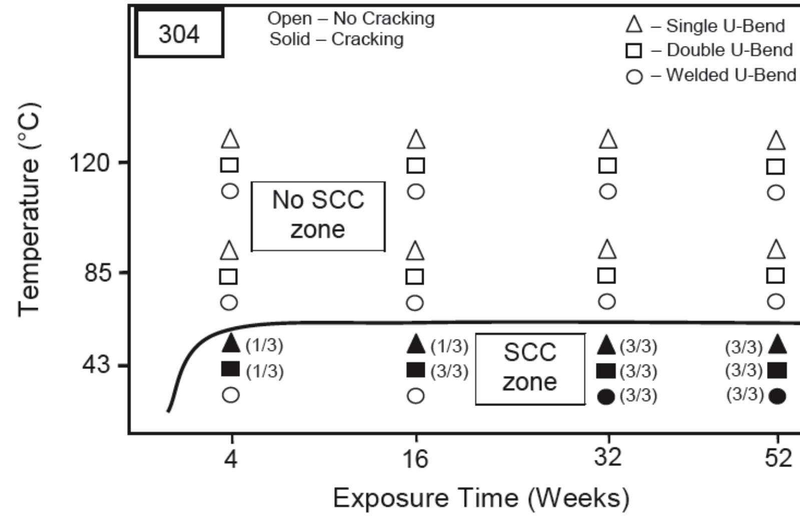
Previous NRC-Sponsored Work – NUREG/CR-7030

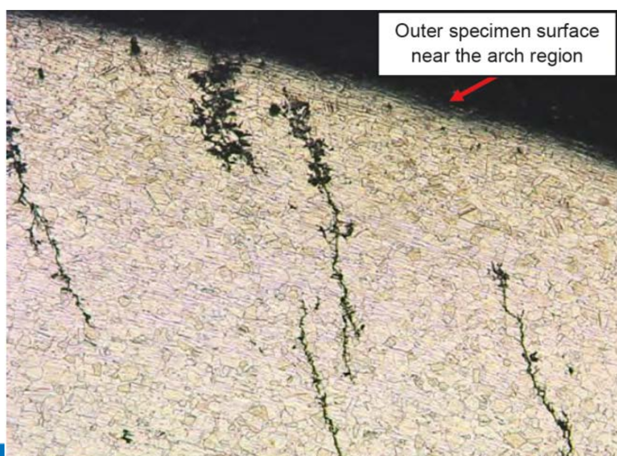
Specimens examined after 4, 16, 32, and 52 weeks exposure. Only specimens tested at 43°C showed cracking.

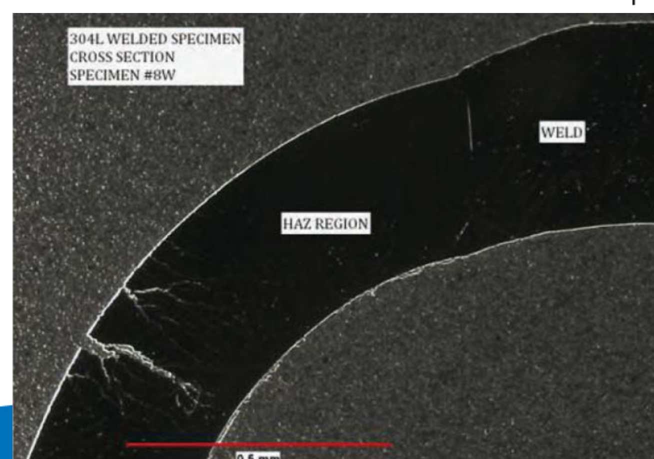


Exposed 52 weeks, 43°C

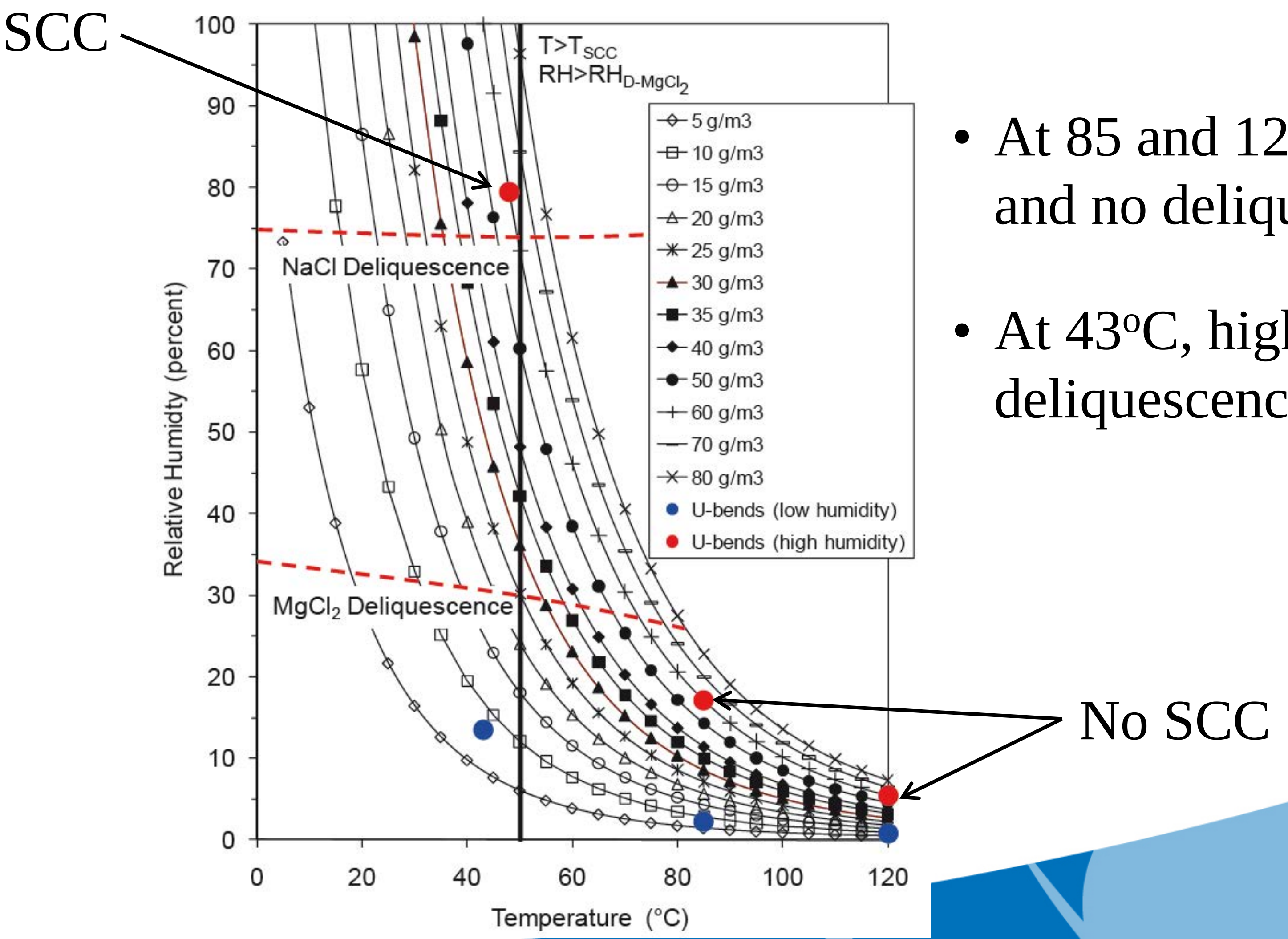
Exposed 52 weeks, 120°C







Previous NRC-Sponsored Work – NUREG/CR-7030



- At 85 and 120^{o}C, low RH and no deliquescence.
- At 43^{o}C, high RH and deliquescence of salt.

Need for Further Research

- Understand differences between results in NUREG/CR-7030 and other studies that have reported chloride-induced SCC at:
  - Lower salt concentration,
  - Lower humidity,
  - Higher temperature,
  - Lower stress/strain.

- Evaluate species other than chloride salts

- Work performed under contract at Center for Nuclear Waste Regulatory Analyses between October 2011 and October 2013.

NUREG/CR-7170 CONTENTS

Report Layout

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- Chapter 1 – Introduction
- Chapter 2 – Experimental approaches
- Chapter 3 – Tests with chloride salts
  - Section 3.1 – Deliquescence testing
  - Section 3.2 – Cyclic humidity SCC testing
  - Section 3.3 – Elevated temperature SCC testing
  - Section 3.4 – High humidity SCC testing
  - Section 3.5 – SCC testing at different specimen strain levels
- Chapter 4 – Tests with non-chloride-rich species
  - Section 4.1 – Literature survey of atmospheric species
  - Section 4.2 – Deliquescence testing
  - Section 4.3 – SCC testing with non-chloride-rich species
  - Section 4.4 – SCC testing with chloride and non-chloride species mixtures
- Chapter 5 – Conclusions

TESTS WITH CHLORIDE SALTS

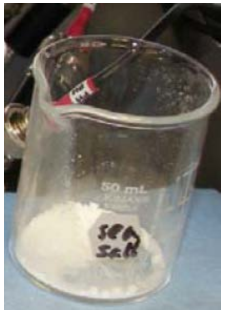
Chloride Salts Deliquescence Testing

- Test objective: Confirm humidity above which sea salt and constituents will deliquesce (DRH) and compare to calculated values.

- Test methodologies:

<u>Salts in beakers</u>

– Place dry salts in beakers
– Gradually increase, then decrease humidity
– Observe beakers for moisture absorption and dry out

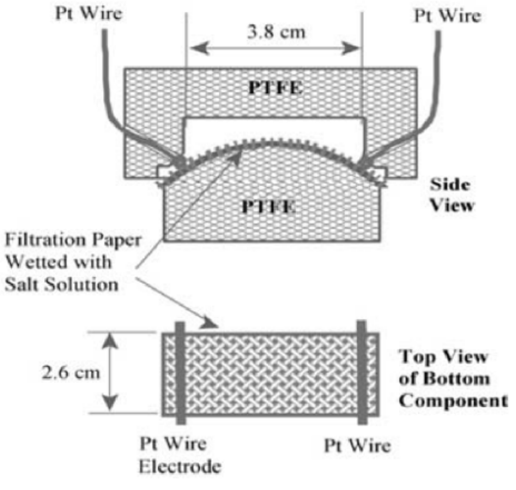


Low RH: Salt is dry

High RH: Salt has deliquesced

<u>Conductivity cell impedance measurement</u>

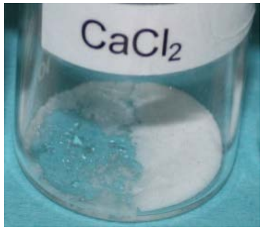
– Place on filter paper attached to electrodes
– Gradually increase, then decrease humidity
– Measured impedance drop when salt deliquesces



Example Test Results at 45^{o}C

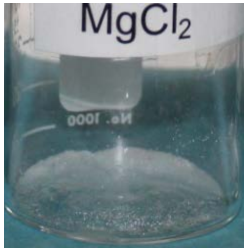
RH = 16%

RH = 19%



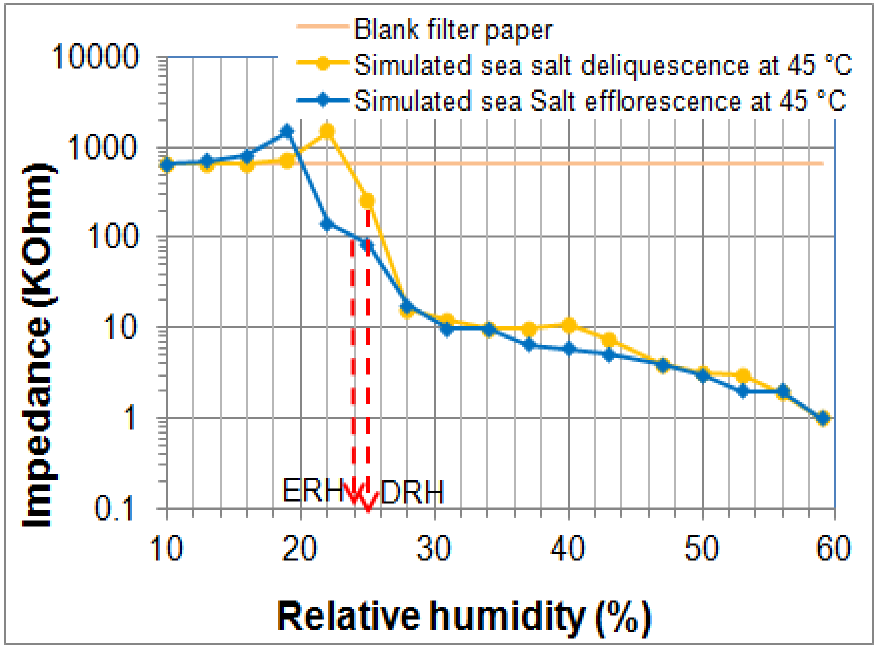
RH = 31%

RH = 34%



RH = 25%

RH = 31%



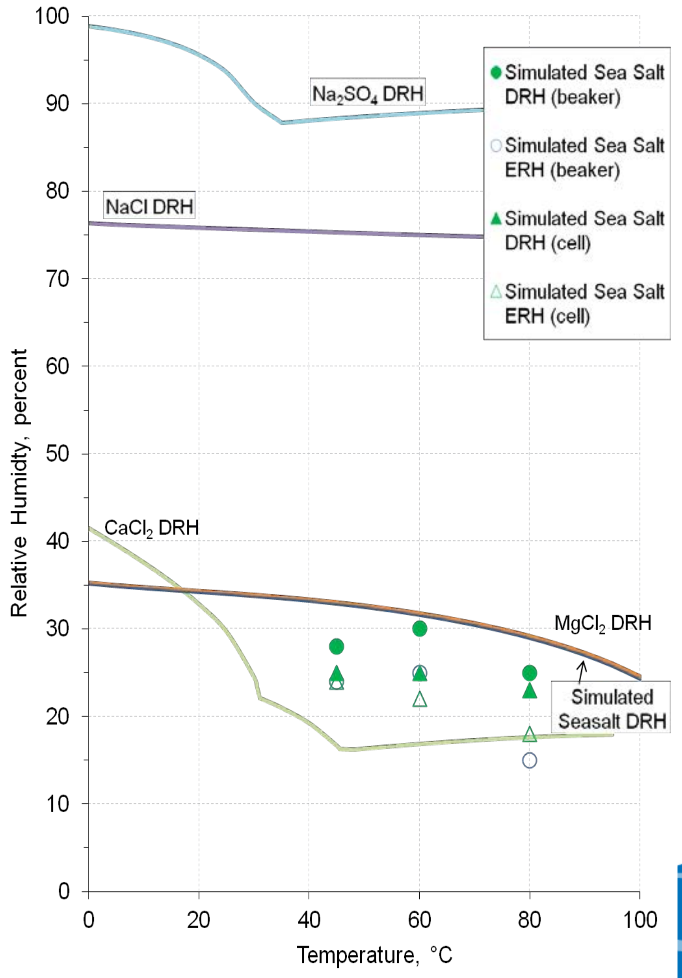
Sea Salt Composition									
NaCl	$MgCl_2 \cdot 6H_2O$	Na_2SO_4	$CaCl_2$	KCl	$NaHCO_3$	KBr	H_3BO_3	$SrCl_2 \cdot 6H_2O$	NaF
58.490	26.460	9.750	2.765	1.645	0.477	0.238	0.071	0.095	0.007

Test Results

- For $CaCl_2$, $MgCl_2$, NaCl, and Na_2SO_4, the measured DRH was close to values calculated by thermodynamic software (OLI Analyzer), indicated by solid lines on figure.

- Measured DRH and efflorescence RH (ERH) for simulated sea salt were between DRH for $CaCl_2$ and $MgCl_2$

- Apparent trend of slight decreasing DRH with increasing temperature



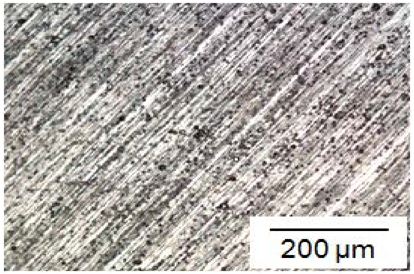
Cyclic Humidity SCC Testing

- Test objectives:
  - Identify whether SCC can initiate at AH limited to about 30 g/m^3, which is reference point for limit in natural conditions (not assumed as limit for canister in the field).
  - Investigate effects of surface salt concentration and material condition on SCC susceptibility

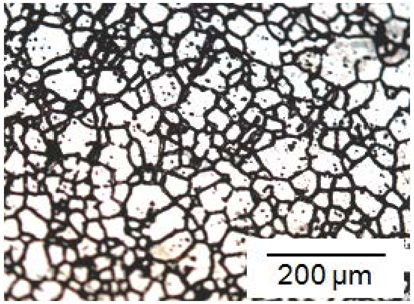
- Test methodology:
  - Deposited 0.1, 1, or 10 g/m^2 of sea salt on ASTM G30 U-bend specimens
    - Expose to salt fog for various times
    - Quantity determined by control specimen weight gain
  - Specimens were Type 304 in as-received or furnace sensitized (2 hours at 650^{o}C) conditions
  - Specimens were exposed in air to cyclic AH between about 15 and 30 g/m^3 at various temperatures
  - Specimens were not contacted by liquid water during exposure so SCC would only occur by salt deliquescence.

Test Specimens

As-received

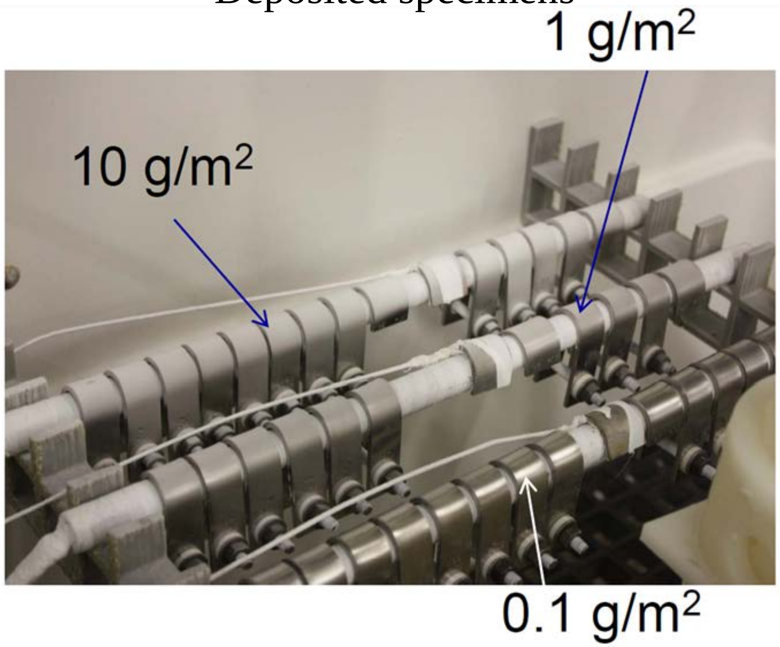


Sensitized



U-bend specimen

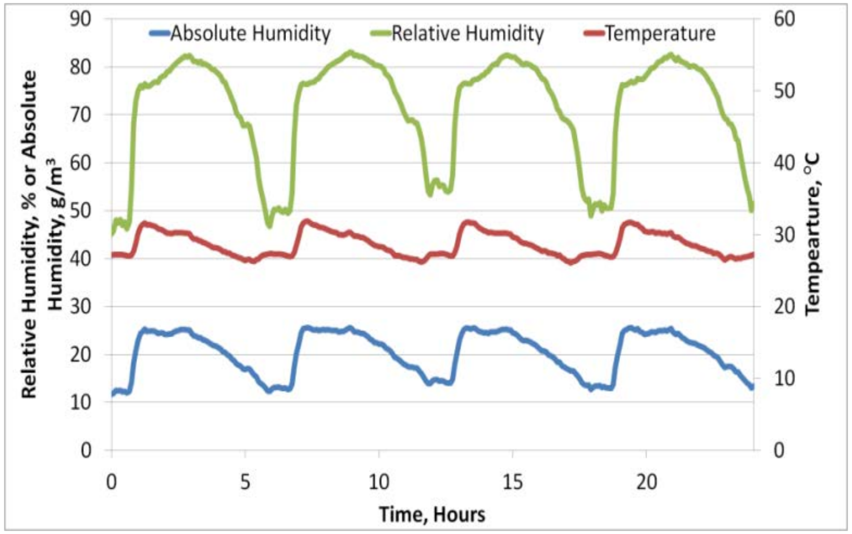
Deposited specimens



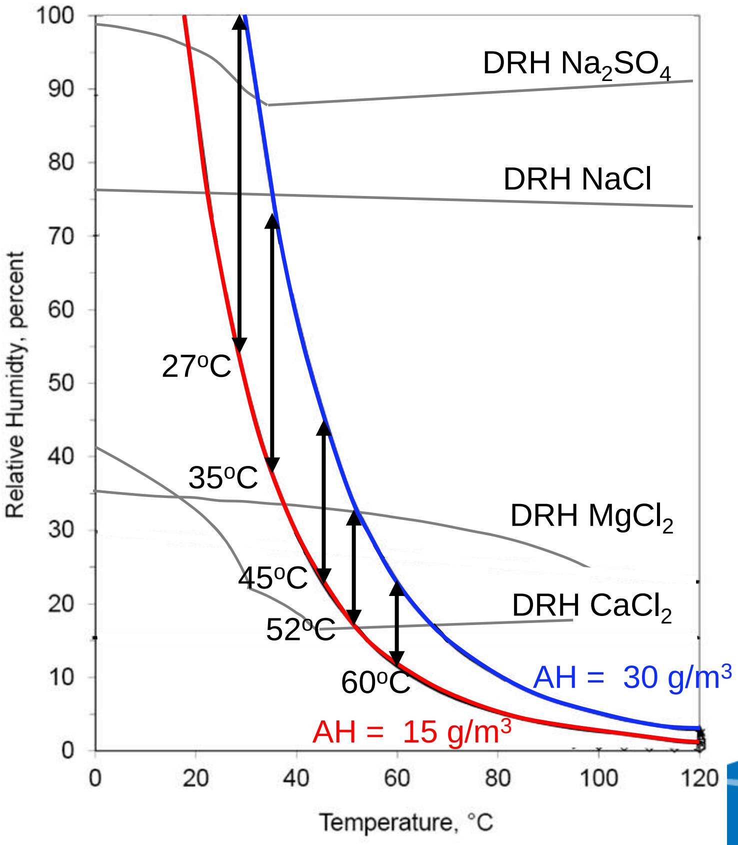
Chemical Composition of Type 304 Stainless Steels											
Material	**C**	**S**	**Mn**	**P**	**Si**	**Cr**	**Mo**	**Ni**	**Cu**	**N**	**Fe**
Type 304 Heat 2N739	0.039	0.002	1.21	0.026	0.55	18.19	N/A	8.07	N/A	0.042	Bal
Type 304 Heat 257524	0.046	0.003	1.06	0.021	0.50	18.41	0.01	8.23	0.04	0.050	Bal

Test Conditions

Chamber humidity cycle



Test temperatures



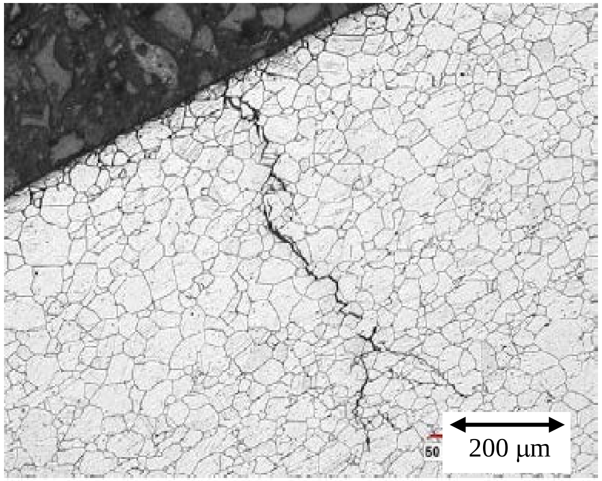
- Four humidity cycles per day
- Temperature above refers to ambient test chamber temperature
- Individual specimen temperatures controlled by cartridge heaters

Test Results

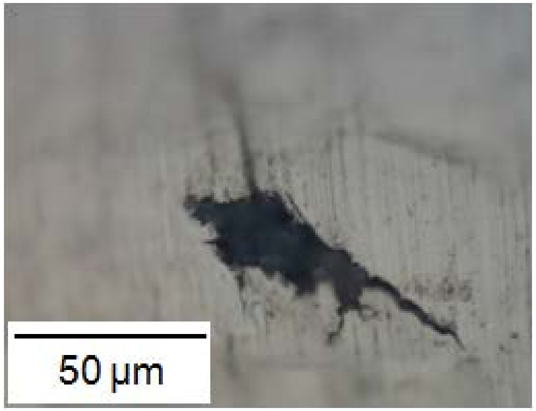
Temperature (°C)	Exposure Time	SCC Observed?	Lowest salt concentration at which SCC was observed
27	8 months	No	N/A
35	4 – 12 months	Yes	0.1
45	4 – 12 months	Yes	0.1
52	2.5 – 8 months	Yes	1
60	6.5 months	Yes	10

Salt deliquesced and drained off of specimens

Pitting on specimens at 10 g/m^2 (top), 1 g/m^2 (middle), and 0.1 g/m^2 (bottom)



Cross section of sensitized, 0.1 g/m^2 specimen at 45°C after 4 months



Top view of sensitized, 10 g/m^2 specimen at 60°C for 6.5 months

Elevated Temperature SCC Testing

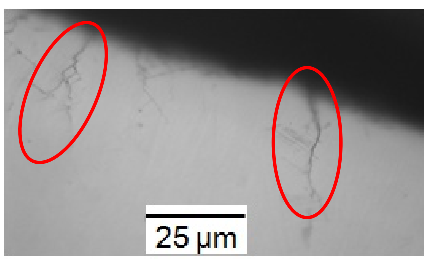
- Test objective: Evaluate SCC susceptibility in the temperature range of 60 to 80^{o}C
- Test methodology:
  - Deposited 10 g/m^2 of sea salt on ASTM G30 U-bend specimens
  - Exposed specimens in air at different humidity levels

Test Conditions			
Temperature (°C)	Relative Humidity (%)	Absolute Humidity (g/m^3)	Maximum Test Duration (Months)
60	22	29	1
	25	33	2.75
	30	39	5.75
	35	46	1
	40	52	1.5
80	28	82	2.5
	35	102	2.25
	40	117	1

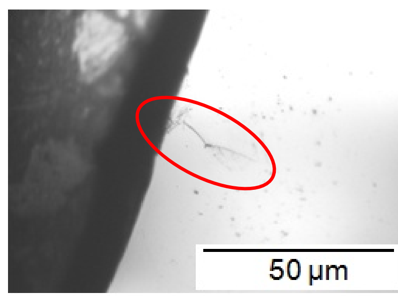
Test Results

- SCC initiation observed at RH as low as 25% at 60°C and 28% at 80°C
- Sensitized specimens showed greater extent of cracking

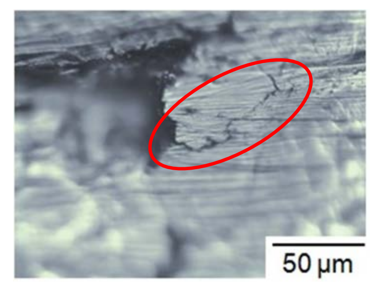
Sensitized, 60°C, 30% RH



As-received, 80°C, 35% RH



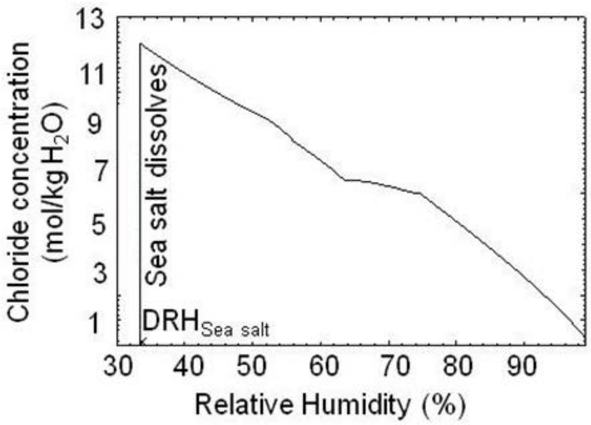
Sensitized, 80°C, 28% RH



High Humidity SCC Testing

- Test objective: Equilibrium chloride concentration in saturated solution decreases with increasing RH. Dilution of chlorides at high RH could reduce SCC susceptibility. Tests were performed at high RH to determine whether SCC could initiate.

- Test methodologies:
  - Immersed U-bend specimens in prepared saturated solutions at 30°C and 90% RH
  - Deposited 10 g/m^2 of sea salt on U-bend specimens for exposure at 30°C and 90% RH



Calculated chloride concentration in saturated sea salt solution as function of RH at 30°C

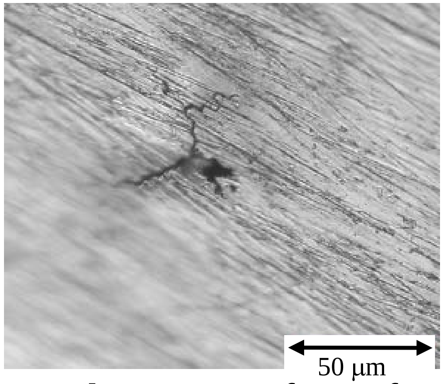
U-bend specimens immersed in solution

Test Results

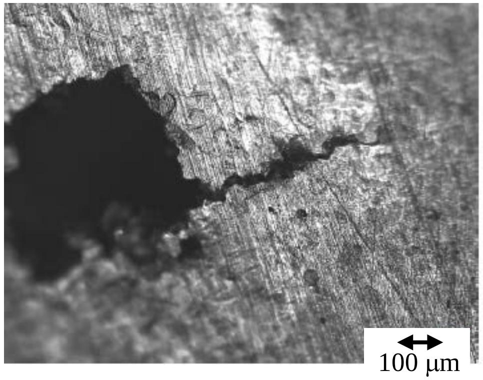
- For specimens with deposited salt, salt quickly deliquesced and ran off sides of specimens with no SCC observed.
- For immersed specimens in sea salt, NaCl, $MgCl_2$ and $CaCl_2$, pitting and SCC were observed within 5 weeks.

Chloride and Salt Concentrations in Saturated Solutions at 30°C and 90% RH			
		Chloride Concentration (mol/kg H_2O)	**Salt Concentration (g/kg H_2O)**
Solution	Sea salt	2.71	203
	NaCl	2.79	163
	$MgCl_2$	3.01	306
	$CaCl_2$	3.16	232

Specimens immersed in sea salt after 5 weeks, as received (L); sensitized (R)



Cracking on surface of specimen immersed in sea salt



Cracking on surface of specimen immersed in $MgCl_2$

C-Ring SCC Testing

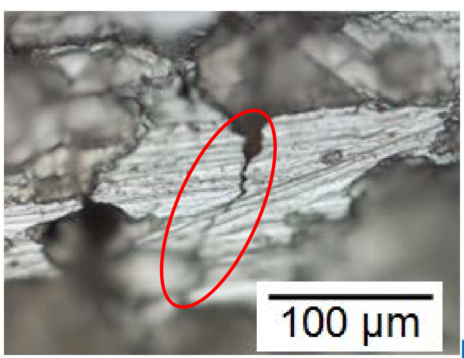
- Test objective: U-bend specimens represent a highly strained state, 13-14% at the apex. These may not be representative of canister conditions. SCC initiation at lower strain levels was evaluated using C-ring specimens.

- Test methodologies:
  - Specimens fabricated following ASTM G38-01 and deposited with 1 or 10 g/m^2 of salt
  - Specimens were strained to slightly above yield stress (~0.4% strain) or 1.5% strain, as measured by strain gage.
  - Specimens were exposed at conditions of 35^{o}C and 72% RH, 45^{o}C and 44% RH, and 52^{o}C and 32% RH (AH ~ 30 g/m^3 at each temperature)

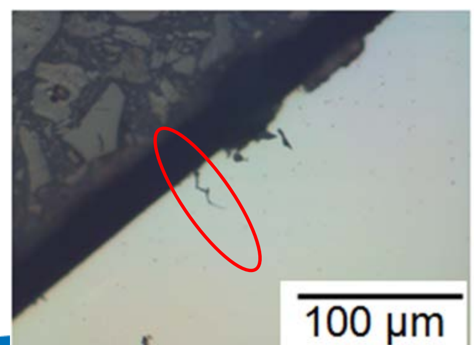
Test Results

Temperature (°C)	RH (%)	AH (g/m³)	Salt Concentration (g/m²)	Strain (%)	Exposure Time (months)	Crack Initiation
35	72	29	1	0.4	2	No
			10	0.4	3	Sensitized only
45	44	29	1	0.4	3	No
			10	0.4	3	No
				1.5	2	Sensitized and as-received
52	32	29	1	0.4	2	Sensitized and as-received
			10	0.4	3	Sensitized only
				1.5	2	Sensitized and as-received

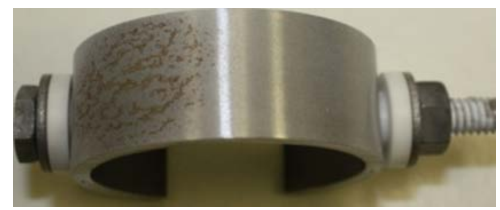
Sensitized, 35°C, 0.4% strain, 10 g/m² salt

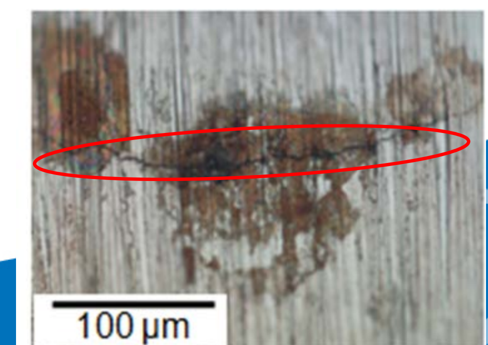


As-received, 45°C, 1.5% strain, 10 g/m² salt

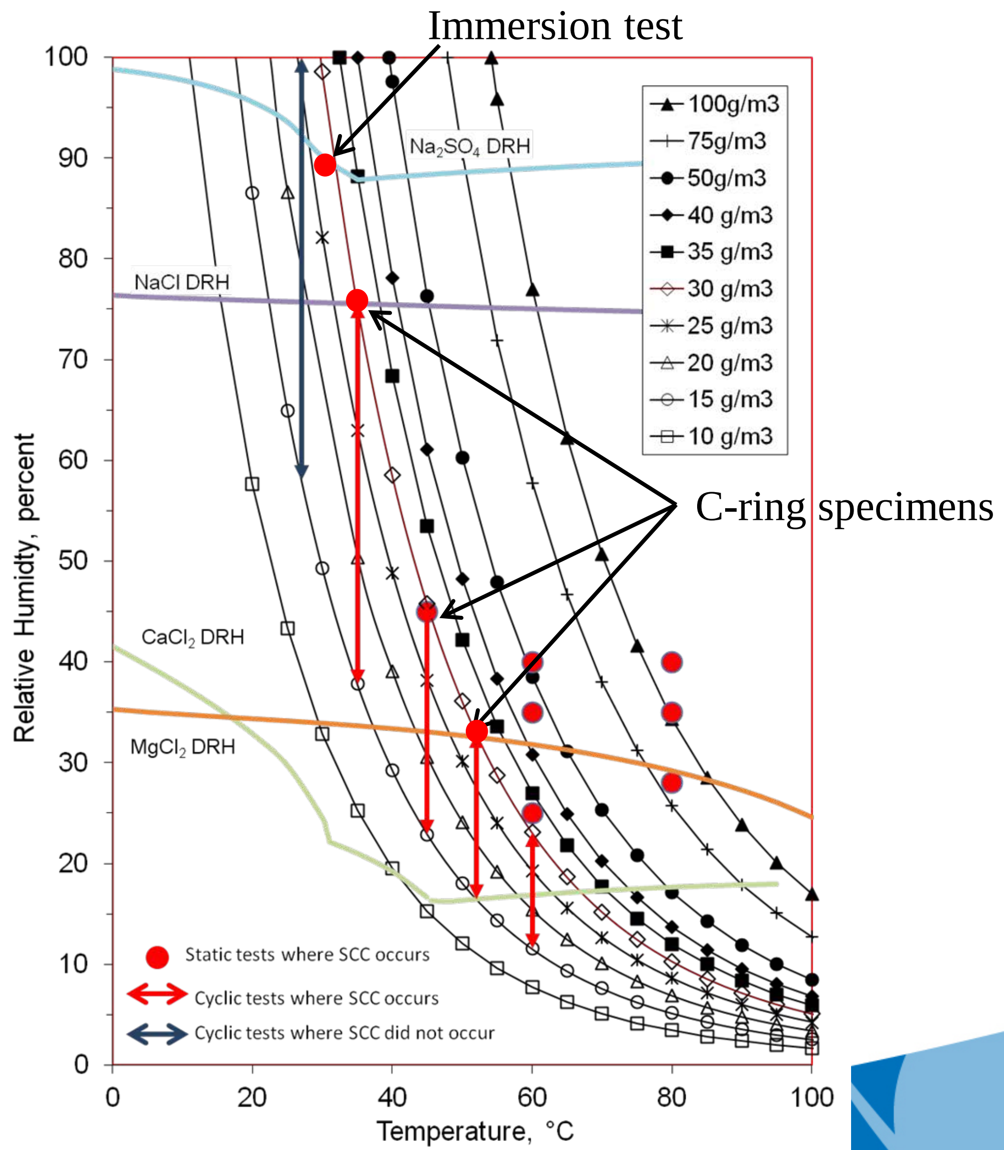


Sensitized, 52°C, 0.4% strain, 1 g/m² salt





Visualization of Test Results



TESTS WITH NON-CHLORIDE-RICH SPECIES

Literature Survey

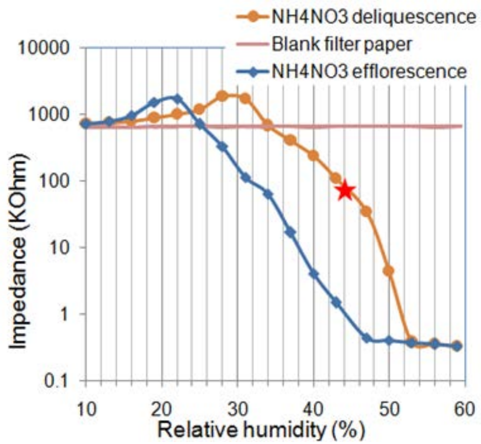
- Besides chloride salts, other atmospheric species could arise from industrial, agricultural, and commercial activities near ISFSI sites
- Survey of atmospheric monitoring data in U.S. identified common species containing ammonium, sulfate, and nitrate ions
- Representative set of species were selected for testing:
  - Ammonium sulfate – $(NH_4)_2SO_4$
  - Ammonium bisulfate – NH_4HSO_4
  - Ammonium nitrate – NH_4NO_3
  - Fly ash – class F, mostly alumina, silica, and iron, less than 20% lime
- Tests were also performed with chloride and non-chloride-rich salt mixtures: NH_4NO + NaCl

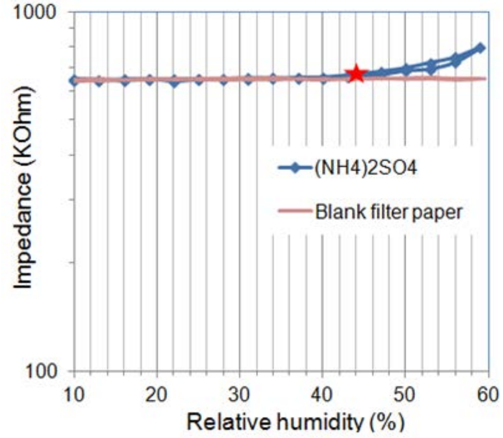
Deliquescence Testing

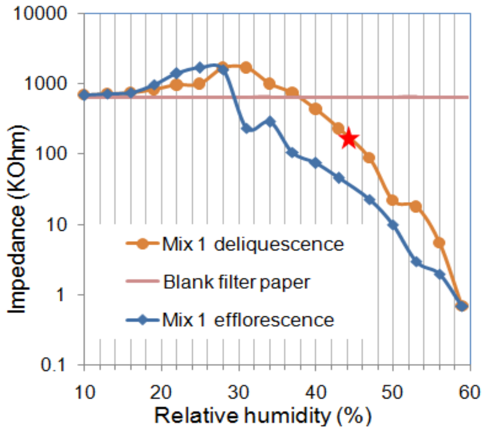
- Beaker and impedance cell methodologies, similar to chloride salt testing
- Tests performed between 35 and 60^{o}C
- Species tested
  - $(NH_4)_2SO_4$
  - NH_4HSO_4
  - NH_4NO_3
  - Mixtures of $(NH_4)_2SO_4$ + NH_4NO_3 with SO_4^{2-}:NO^{3-} mole ratios of 0.5, 1.0, and 3.0
  - Fly ash
  - Mixtures of NH_4NO_3 + NaCl with NO^{3-}:Cl^- mole ratios of 3.0 and 6.0

Example Test Results

Impedance tests at 45°C







NH_4NO_3 + NaCl at 45°C, 46% RH

NH_4NO_3 + NaCl at 45°C, 49% RH

Deliquescence Test Results

DRH in Temperature Range of 35 – 60°C (%)									
Pure Salts and Salt Mixture	**NH_4HSO_4**	**NH_4NO_3**	**$(NH_4)_2SO_4$**	**Fly Ash**	**$(NH_4)_2SO_4 + NH_4NO_3$ Mole Ratio**			**NH_4NO_3 + NaCl Mole Ratio**	
					0.5	**1.0**	**3.0**	**3.0**	**6.0**
Calculated DRH, percent	35-40	45-55	75-80	N/A	50-65	50-65	50-65	N/A	N/A
DRH by Conductivity Cell, percent	35-45	40-55	~80	No deliq.	50-60	50-60	50-60	N/A	N/A
DRH by Beaker, percent	30-45	40-60	~80	No deliq.	50-70	50-70	50-70	30-35	30-35

- Observations are consistent with calculations made by thermodynamic software
- $(NH_4)_2SO_4$ and fly ash have very high DRH. DRH for other species is lower but still somewhat higher than that of sea salt.
- DRH of mixture may be lower than that of pure constituents

SCC Testing – Non-Chloride Species Only

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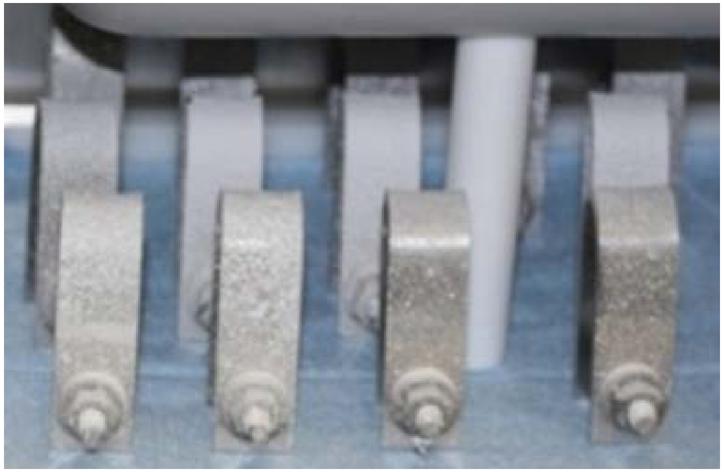
- Test objective: Determine if SCC could initiate for austenitic stainless steel exposed to the non-chloride-rich species

- Test methodology:
  – Deposited large quantities (>100 g/m^2) of species on ASTM G30 U-bend specimens by spray bottle. Other specimens were buried in bins of solid salt.
  – Exposed specimens in air at 45^{o}C and 44% RH for 6 weeks followed by 35^{o}C and 72% RH for 1 month (AH ~ 30 g/m^3 at both temperatures)



Test Results

- No cracking observed on specimens exposed to any species, even above measured DRH.
- Most specimens appeared near pristine after removing salt, except for extensive general corrosion on specimens exposed to NH_4HSO_4
  - Deliquescent solution pH for most species is in range of about 4 to 5
  - Deliquescent solution pH for NH_4HSO_4 is about -1 to -2

Specimens exposed to NH_4NO_3

Specimens exposed to $NH_4NO_3 + (NH_4)_2SO_4$ mixture

Specimens exposed to NH_4HSO_4

SCC Testing – Chloride and Non-Chloride Salt Mixtures

- Test objective: Determine if SCC could initiate for austenitic stainless steel exposed to chloride-rich and non-chloride-rich mixed salts

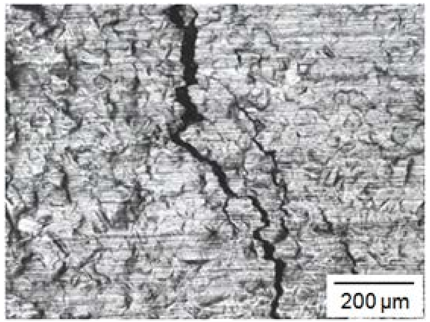
- Test methodology:
  - Deposited NH_4NO_3 + NaCl mixtures on ASTM G30 U-bend specimens by spray bottle. Solution pH was about 3.5 to 4.
  - Amount of chlorides on specimens were less than 10 g/m^2.
  - Exposed specimens in air at 45^{o}C and 44% RH for up to 4 months

Specimen Type	Molar Ratio of NH_4NO_3 to NaCl	Amount of NH_4NO_3 and NaCl Deposited (g/m^2)	Calculated Amount of NaCl Deposited (g/m^2)
As-Received	3	54	6.4
	6	74	4.9
Sensitized	3	62	7.4
	6	83	5.5

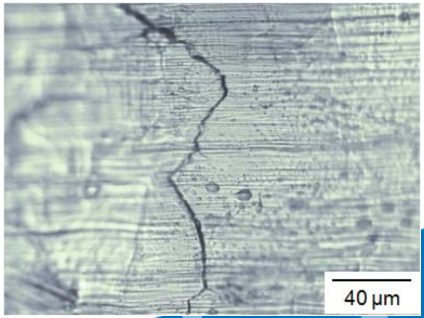
Test Results

- Extensive cracking on specimens, larger cracks than any other specimens in test program
- Presence of nitrate does not appear to inhibit cracking in these test conditions.

Specimens exposed to NH_4NO_3 + NaCl with NO^{3-}:Cl^- mole ratio of 3.0



Specimens exposed to NH_4NO_3 + NaCl with NO^{3-}:Cl^- mole ratio of 6.0



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CONCLUSIONS

Conclusions from Chloride Salt Tests

- Between 35 and 80°C, SCC initiated by deliquescence of sea salt is observed when RH is higher than about 20 to 30%, which is slightly above measured DRH for $CaCl_2$. At lower temperatures, this RH may be reached at AH well below 30 g/m^3.
- SCC initiation is observed at salt quantity as low as 0.1 g/m^2, but seems more extensive at higher amounts. The quantity of 0.1 g/m^2 is not considered to be a threshold, but only the lowest value tested.
- SCC initiation is observed at strain as low as 0.4, where the stress is thought to be close to the yield stress. The extent of cracking increases with increasing strain.
- Sensitized material seems more susceptible to SCC than material in as-received condition.

Conclusions from Non-Chloride Species Tests

- Austenitic stainless steel did not appear susceptible to SCC when exposed to the ammonium, sulfate, and nitrate bearing species or fly ash evaluated in this test program, even above the species' DRH.

- Crack initiation was observed for mixtures of the chloride and non-chloride species, even with the presence of a large quantity of nitrate.

Additional References

- L. Miller, T. Mintz, X. He, R. Pabalan, Y. Pan, G. Oberson, D. Dunn, “Effect of Stress Level on the Stress Corrosion Cracking Initiation of Type 304L Stainless Steel Exposed to Simulated Sea Salt,” 16th International Conference on Environmental Degradation of Materials in Nuclear Power Systems – Water Reactors, Asheville, NC, August 11-15, 2013, ADAMS Accession Number ML13220A332.

- T. Mintz, X. He, L. Miller, R. Pabalan, Y. Pan, L. Caseres, G. Oberson, D. Dunn, “Coastal Salt Effects on the Stress Corrosion Cracking of Type 304 Stainless Steel,” NACE Corrosion 2013, Orlando, FL, March 17-21, 2013, ADAMS Accession Number ML13016A127.

- X. He, R. Pabalan, T. Mintz, G. Oberson, D. Dunn, T. Ahn, “Scoping Study of Effect of Salts in Non-Coastal Particulate Matter on Stress Corrosion Cracking of Type 304 Stainless Steel,” NACE Corrosion 2013, Orlando, FL, March 17-21, 2013, ADAMS Accession Number ML13018A120.

- G. Oberson, D. Dunn, T. Mintz, X. He, R. Pabalan, L. Miller, “US NRC-Sponsored Research on Stress Corrosion Cracking Susceptibility of Dry Storage Canister Materials in Marine Environments,” Waste Management Conference 2013, February 24-28, 2013, Phoenix, AZ, ADAMS Accession Number ML13029A490.

- G. Oberson, “Handout – Status of Ongoing NRC Research on Stress Corrosion Cracking of Spent Nuclear Fuel Dry Storage Canisters,” Regulatory Issue Resolution Protocol Public Meeting, Rockville, MD, December 18, 2012, ADAMS Accession Number ML13022A314.