

Used Fuel Disposition Campaign

Task 4: Dry Storage Material Degradation and Stress Corrosion Testing

US POC: David Enos

Collaborators: Charles Bryan (SNL), Neil Brown (LANL)

JFCS FCAWG Meeting

June 6th, 2012

Engineered Materials Experimental

- *Empirical: Evaluate corrosion initiation and rates over an envelope of environments encompassing field conditions*
- *Mechanistic: Evaluate processes that could inhibit corrosion initiation or stifle corrosion*



Field testing program

- *Assess site-specific environments*
- *Through sampling and data collection, define relevant envelope of conditions for corrosion experimental work*
- *Through sampling and testing, validate assumptions and predictions of experimental program and corrosion PA modeling*

Storage Container PA

To assess corrosion on a container-specific level, combine:

- *Site-specific data from the field testing program*
- *Experimental data from the corrosion experimental program*
- *Other data (thermal loads, ambient temperature and RH data)*

- **General corrosion: non-localized, results in even thinning of the storage container**
 - Dry oxidation—extremely slow, not a concern
 - *An aqueous solution is required*
- **Stress Corrosion Cracking: could result in rapid penetration, loss of structural integrity**
 - Residual stress from welding, thermal cycling, (impacts during transport?)
 - Mechanical stress due to static load?
 - *An aqueous solution is required*
- **Localized corrosion: could result in rapid penetration**
 - Crevice corrosion
 - Pitting
 - *An aqueous solution is required*
- **Under what conditions will an aqueous solution be present?**

Aqueous conditions

■ Immersed conditions: can they occur?

- Bolted casks
 - *No overpack*
 - *Weather cover can be insufficient to keep out rain*
 - *Observations of corrosion of bolts and seals*
- Welded casks
 - *Steel or cement overpack—protected from the weather*
 - *Overpack flooding due to clogged air intakes has been observed (assume transient?)*

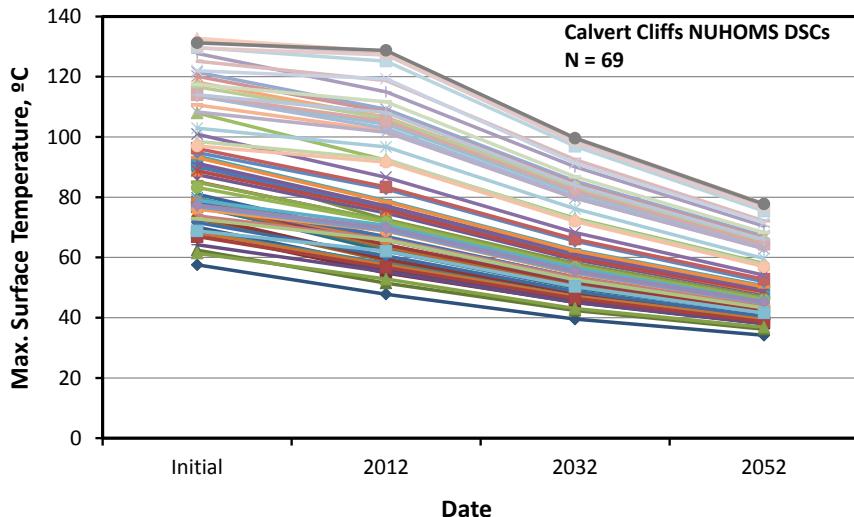
■ Deliquescence/condensation: salts are deposited on the storage container surface with dust or aerosols (for example, fog). Will deliquesce if conditions at the waste package surface permit:

- Temperature at the container surface
- Relative humidity at the container surface
- Composition of salts deposited

Parameters Controlling Deliquescence: Temperature

■ Storage System Safety Analysis Reports:

- Calculate only the maximum storage container surface temperatures
- Commonly use bounding, not representative, thermal loads
- *Generally*, do not provide temperature histories



Storage System	DSC Container type	Heat load (kW)	Ambient temp., °F	Max. shell temp., °C	Source
NAC UMS	24 PWR	23.0	76	177	A
			106	194	
	56 BWR	23.0	76	191	
			106	207	
NUHOMS HSM-H	24PTH-S ⁽¹⁾	40.8	0	186	B
			100	235	
			117	237	
	24PTH-L	31.2	117	203	
	24PTH-S-LC	24.0	117	176	
NUHOMS HSM-HD	32PTH ⁽²⁾	34.8	115	208	C
	32PTH ⁽³⁾	32.0	115	201	
	32PTH ⁽⁴⁾	26.1	115	187	
	HI-STORM	38.0	80	233	
			80	242	

⁽¹⁾Flat stainless steel heat shields

⁽²⁾Finned Al side shields

⁽³⁾Unfinned Al side shields

⁽⁴⁾galvanized steel side shields

^ANAC-UMS FSAR, Revision 5 (2005)

^BNUHOMS FSAR, Revision 10 (2008)

^CNUHOMS-HD FSAR, Revision 0 (2007)

^DHI-STORM FSAR, Revision 8 (2010)

Temperature at the waste package surface

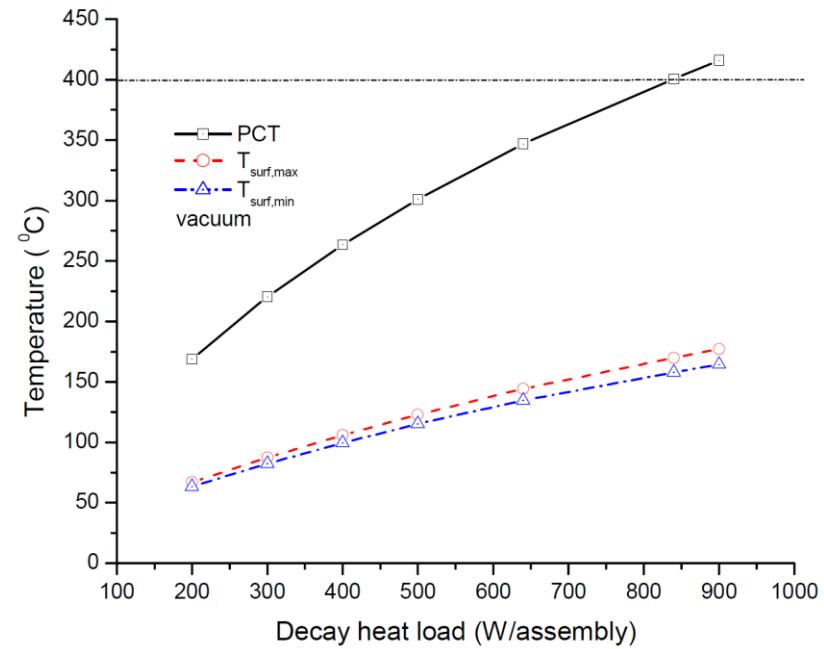
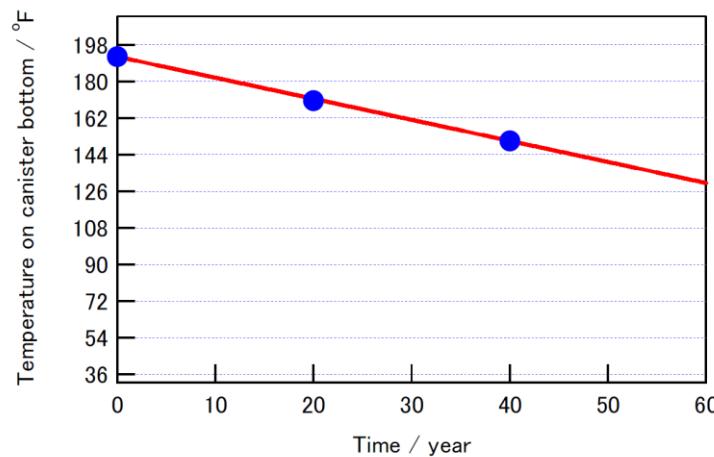
Literature data—very sparse

■ Li et al. (2007):

- 21 PWR cask (~ YMP TAD)
- $T_{max} = \sim 70^\circ\text{C}$ (200 W/assembly)— 170°C (900 W/assembly)

■ Shirai et al. (2011):

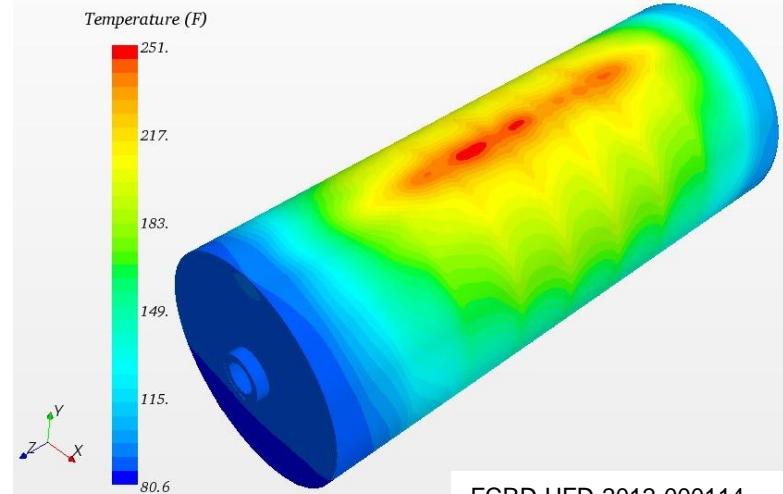
- Three-point curve for canister bottom



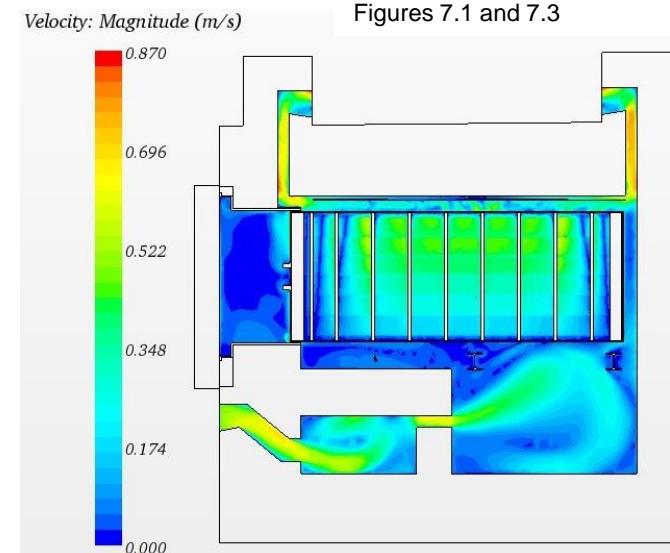
Parameters Controlling Deliquescence: Temperature

■ PNNL modeling

- Calvert Cliffs NUHOMS HSM-15 canister and storage module
- Temperature map of full canister surface, internals (huge temperature range on the surface, corresponding to a huge range in relative humidity)
- Provides ventilation velocities (useful for determining potential salt load)
- Seasonal temperature fluctuations evaluated (correspond to similar-magnitude temperature fluctuations on the container surface)
- However:
 - *Provides snapshots, but does not model full temperature evolution through time.*
 - *Currently, for only one waste profile (thermal load)*



FCRD-UFD-2012-000114
Figures 7.1 and 7.3



Parameters Controlling Deliquescence: Temperature, RH

Observed temperature range

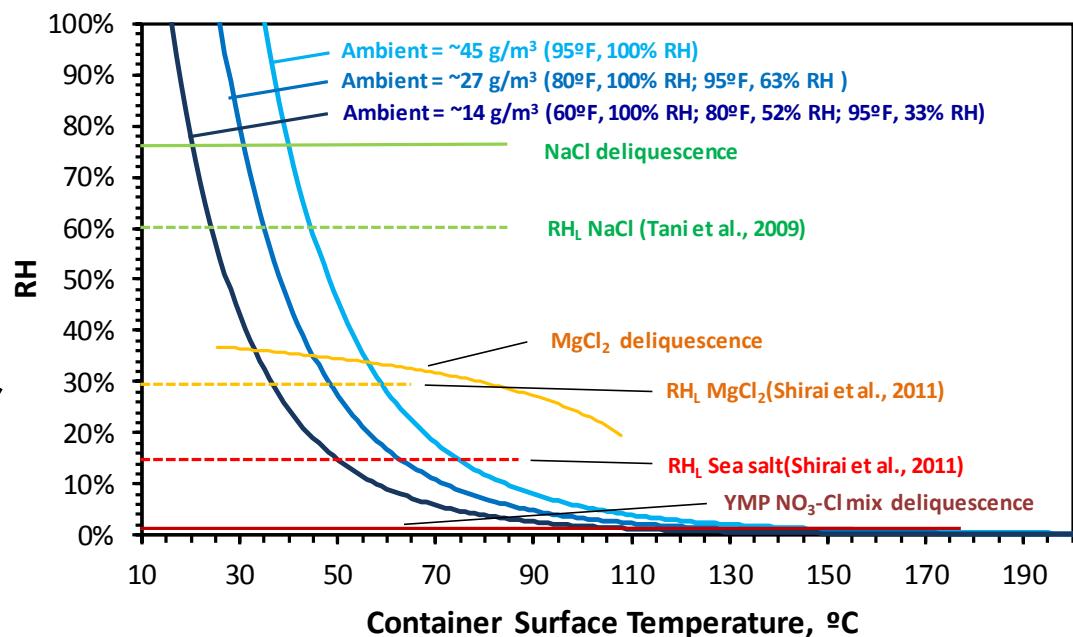
- Temperature range on even a single waste package surface is large.
- Minimum temperatures: ambient or near ambient (for example, 80.6°F on PNNL HMS-15 model)
- Maximum temperatures: >200°C for largest containers (for example, 243°C for HI-STORM 32 PWR container)

But we don't need to consider the entire temperature range, as depending on the salt compositions and RH, aqueous conditions will only exist over a limited range of temperatures



RH at the container surface

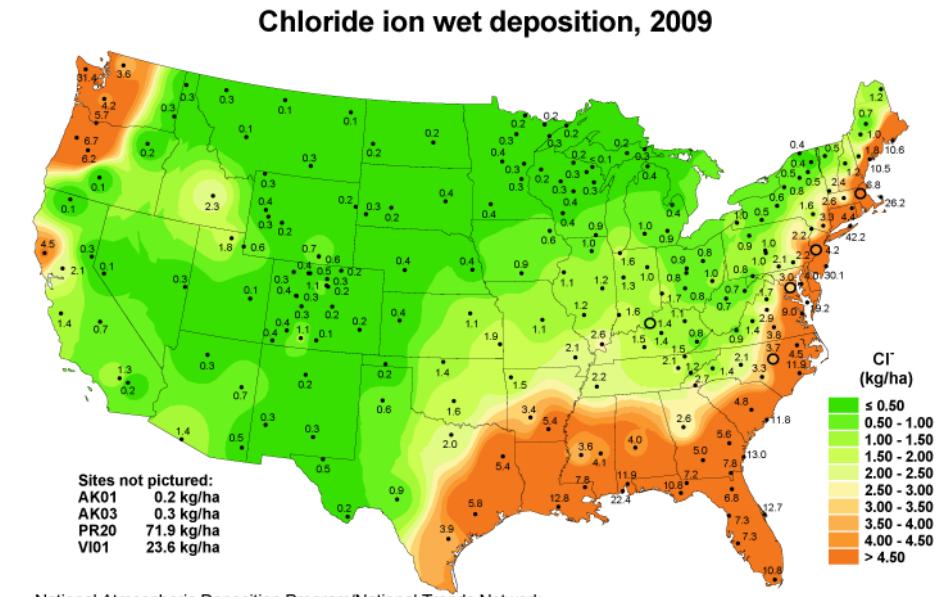
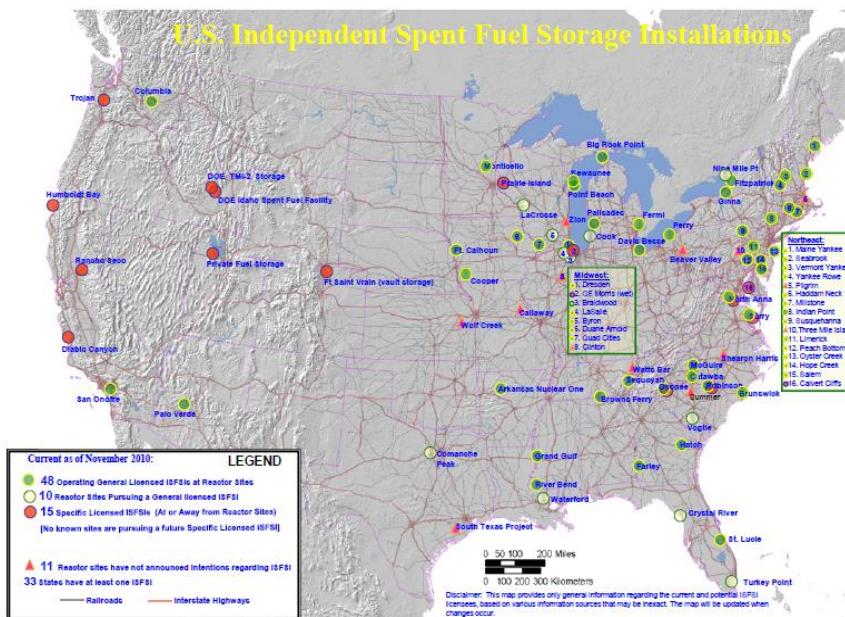
- Can be calculated from the ambient RH and air temperature (monitored) and the container surface temperature at a specific location. Will vary with daily/seasonal variations air RH/T and waste package T.



Used Fuel Disposition

Localized Corrosion under Deliquescent Conditions

- Experiments began during the YMP in order to assess if multisalt assemblages on the waste package surface could initiate and sustain localized corrosion.
- Secondary goal became clear while responding to contentions – the experimental data utilized to support the corrosion stifling argument was weak
 - Technical basis is very sound, but the argument in the SAR and contention responses depended heavily on modeling work conducted in academia (UVA, CWRU)
 - Critical need for a dataset which could provide direct support to the stifling argument



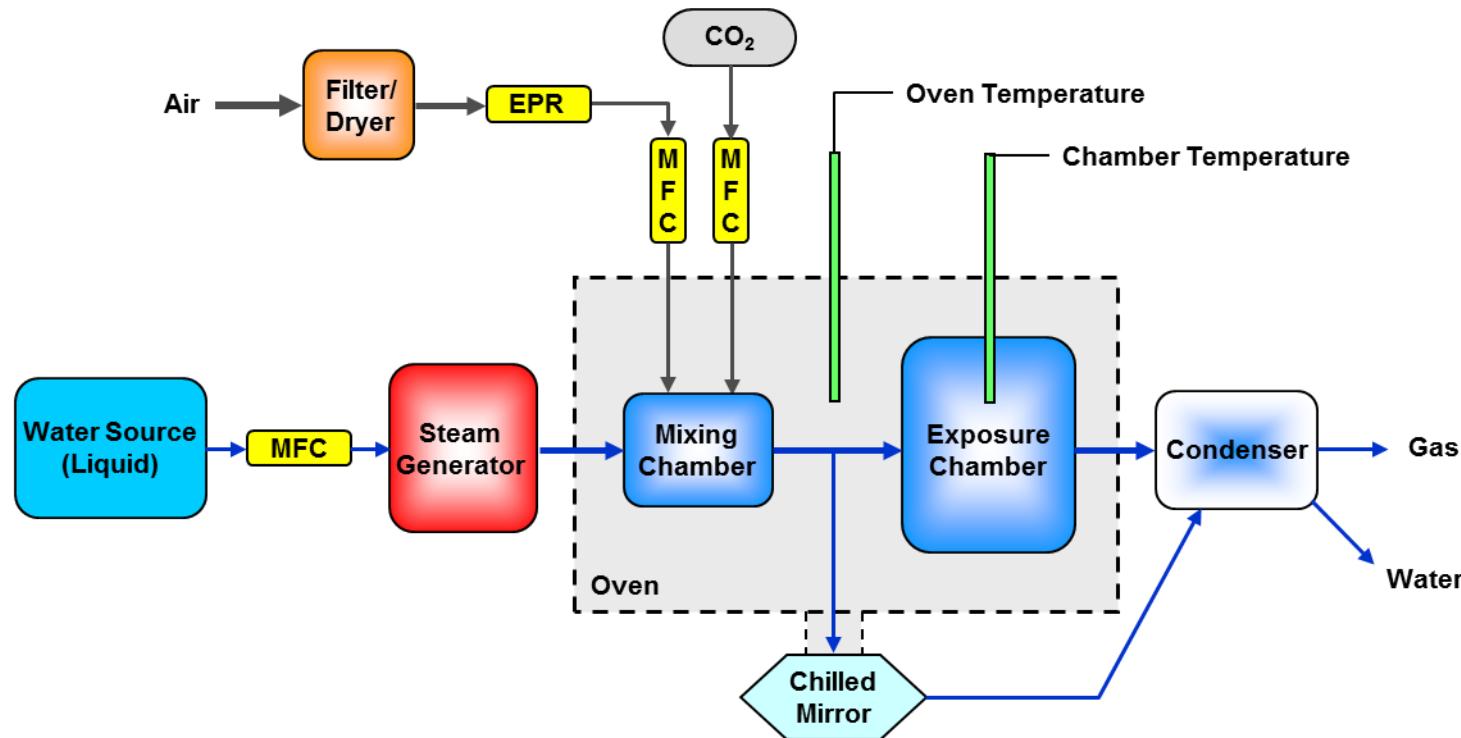
National Atmospheric Deposition Program/National Trends Network
<http://nadp.sws.uiuc.edu>

NADP Rainout data (wet deposition – not dust collection)

Goal: Establish if localized corrosion (crevice corrosion) can initiate under deliquescent conditions

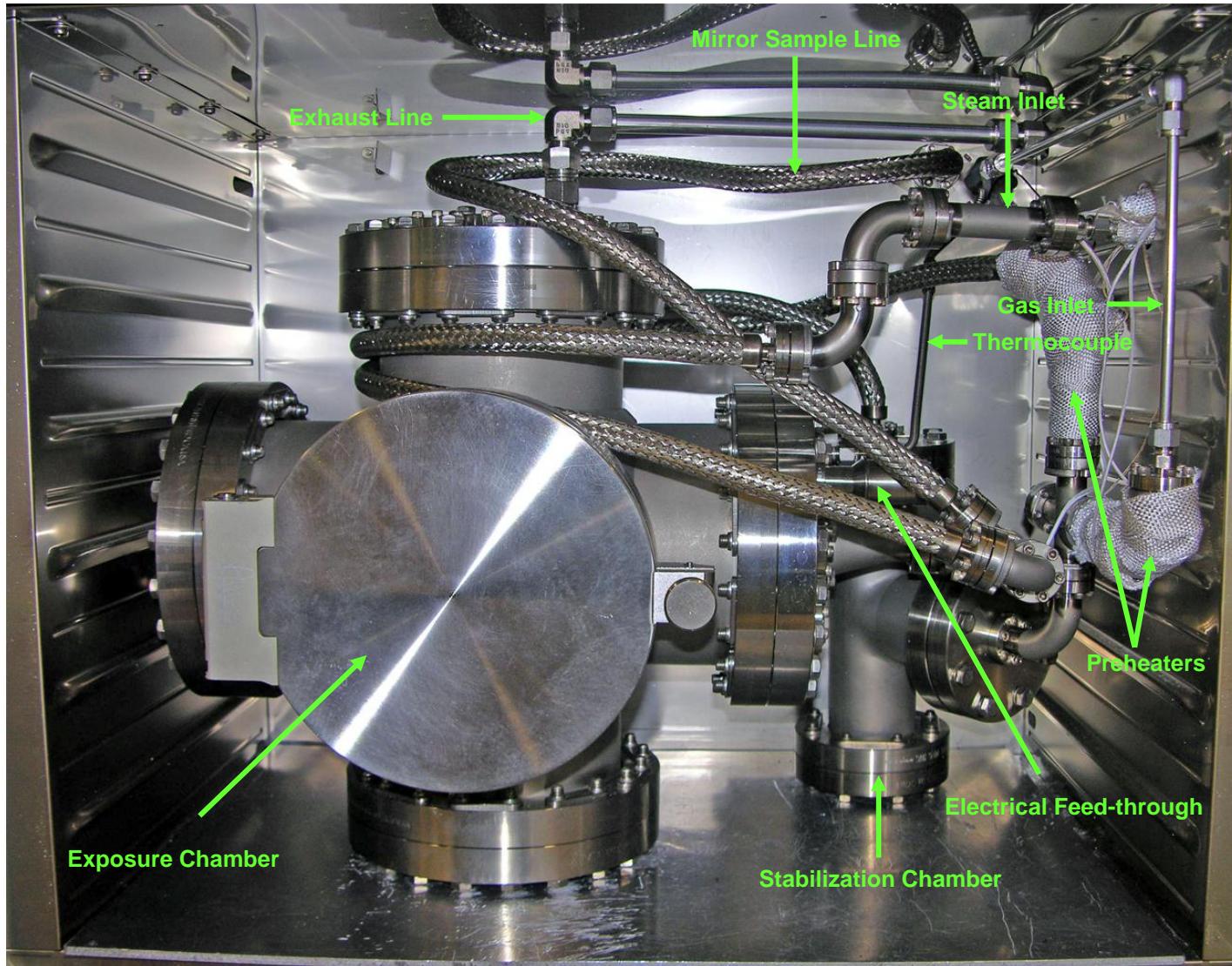
- A series of relevant materials are being evaluated
 - Alloy 22
 - Inconel 625
 - Hastelloy C276
 - 80:20 Ni:Cr
- Thin film of salt (with known mass loading) deposited on surface, followed by the use of a traditional PTFE coated ceramic crevice former

Schematic of High Temperature System

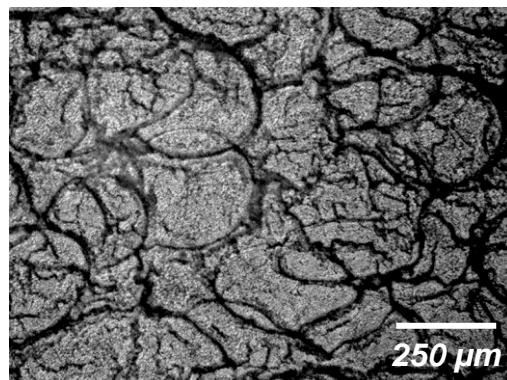


EPR = Electronic Pressure Regulator and MFC = Mass flow controller

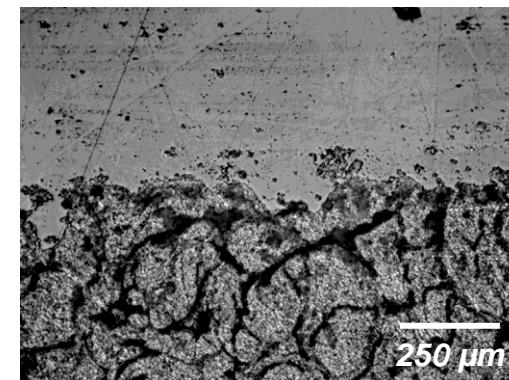
High Temperature, Controlled Dewpoint System



- Alloy 22, Inconel 625, Hastelloy C276, 80:20 Ni:Cr, 304SS, and 303SS evaluated
- PTFE coated ceramic crevice former torqued to 70 in-lbs, Mirror finish on coupon surface
- Range of salt loadings from 50 to 250 $\mu\text{g}/\text{cm}^2$ of a NaCl-KCl mixture
- $T=105^\circ\text{C}$, $T_d=\sim 94.5^\circ\text{C}$ (pure steam) for test intervals of 100 days



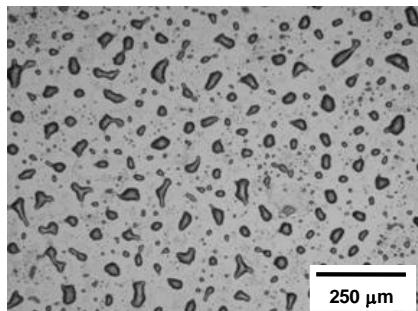
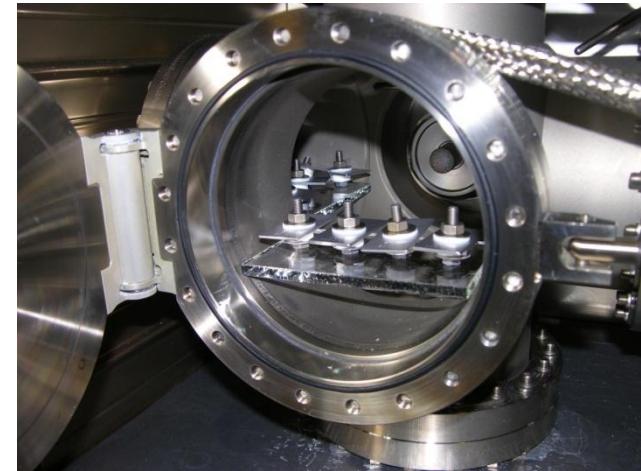
120 $\mu\text{g}/\text{cm}^2$



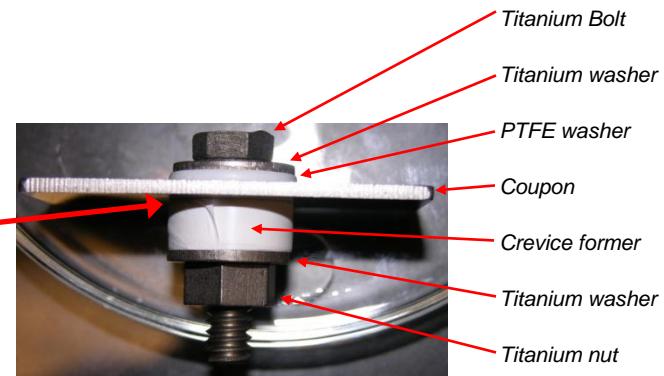
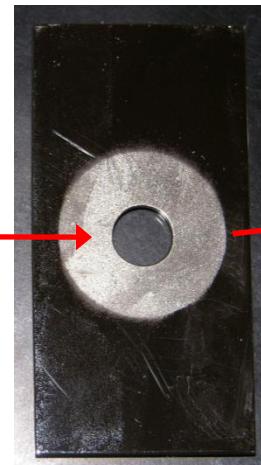
Wiped region

Dust Deliquescence Testing: Initiation Studies

- Alloy 22, Inconel 625, Hastelloy C276, and 80:20 Ni:Cr evaluated
- PTFE coated ceramic crevice former torqued to 70 in-lbs
- Approximately 400 $\mu\text{g}/\text{cm}^2$ of 4 salt mixture
Mole fraction: 0.126 NaCl 0.228 NaNO_3
 0.268 KNO_3 $0.378 \text{ Ca}(\text{NO}_3)_2$
- $T=180^\circ\text{C}$, $T_d=\sim 94.5^\circ\text{C}$ (pure steam) or $\sim 92^\circ\text{C}$ for 25 days
- Crevice former and salt on one side of coupon which was polished to a mirror finish



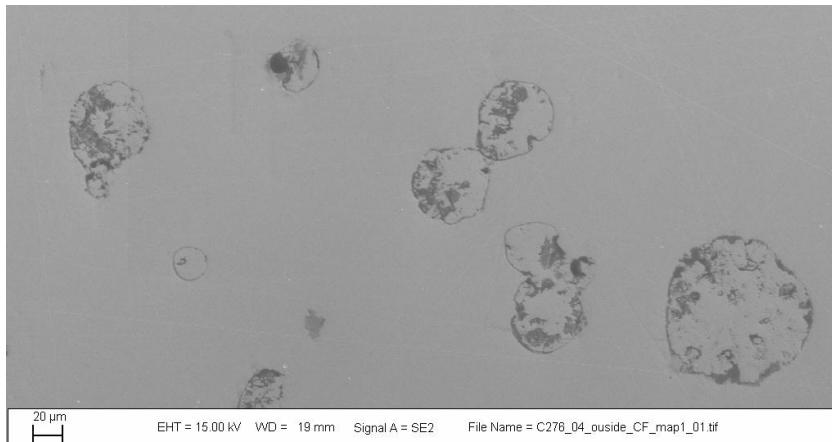
Salt mixture on an Alloy 22 Coupon



(All titanium hardware electrically isolated from the sample)

Dust Deliquescence Testing: Initiation Studies

- Once removed from system, coupons were subjected to a single cycle of the weight loss coupon cleaning procedure to remove salt deposits
- No visible signs of crevice corrosion on any of the materials exposed to pure steam, or at a dewpoint of 92°C.*
- Visible deposits left by salt mixture (inside and outside creviced regions) for both exposure conditions, indicating degassing has taken place

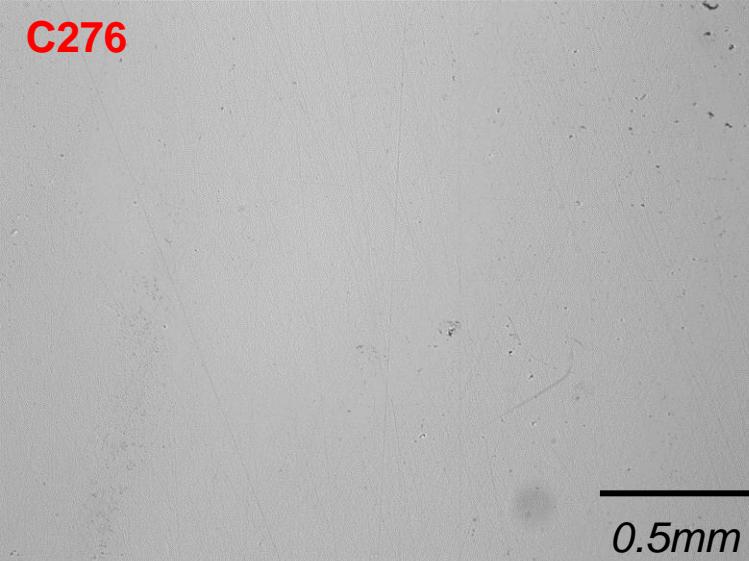


*Deposits remain on surface
despite HCl based cleaning
process (region shown is outside
the crevice former)*

Used Fuel Disposition

Nickel Alloys in Chloride Brines

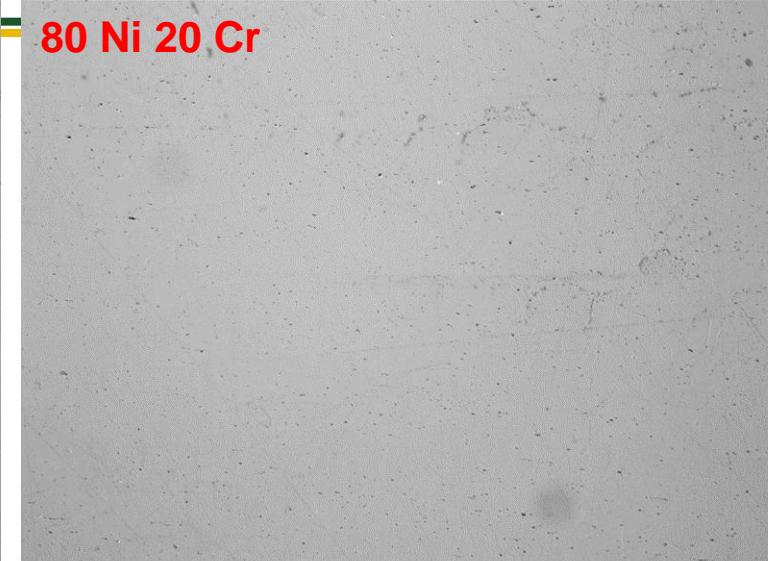
C276



0.5mm

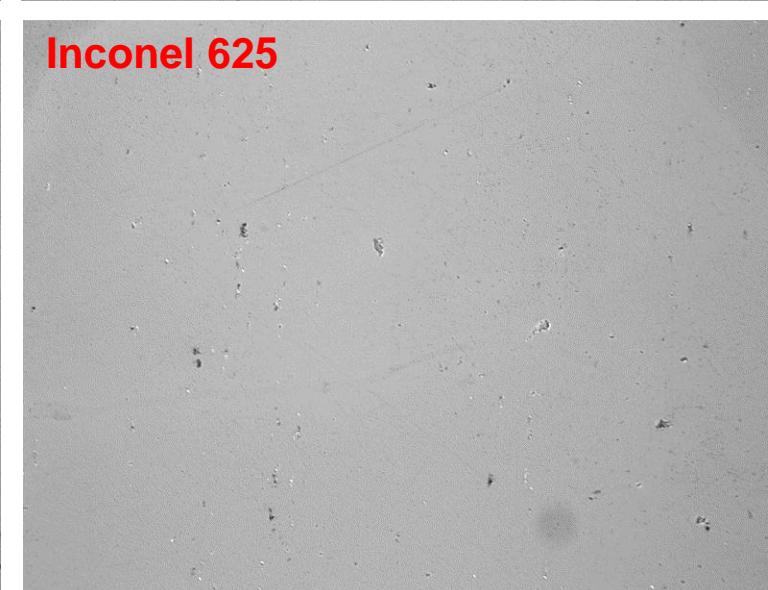
C22

80 Ni 20 Cr



0.5mm

Inconel 625



0.5mm

*No crevice
corrosion
initiation*

Significant Attack on 303SS

To alleviate concern that technique was not capable of supporting crevice corrosion even on highly susceptible materials, 303SS was introduced into the test matrix

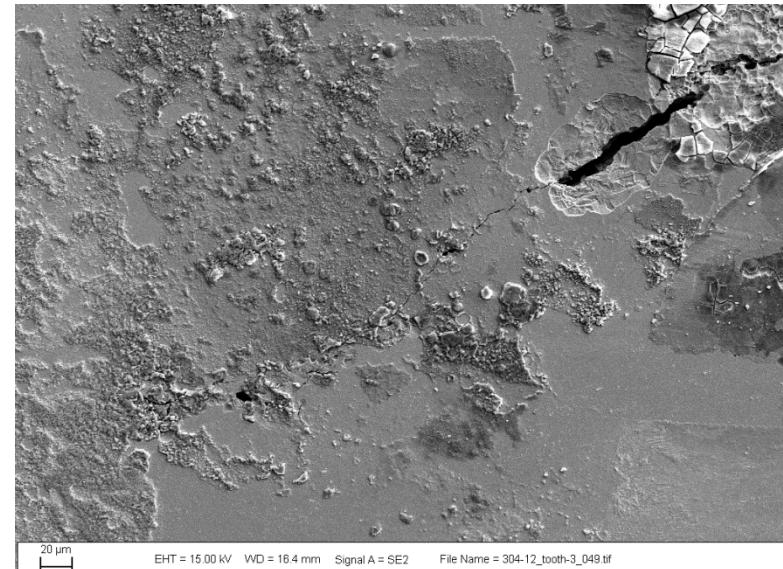


Evaluation of the impact of salt loading was pursued for 304SS (difficult to interpret 303SS results as material was too active) to explore stifling argument

- Three different mass loadings evaluated (50, 100, and 200 $\mu\text{g}/\text{cm}^2$)
- Initiation observed at all mass loadings, but extent of attack correlated with mass loading
- Samples exhibited SCC in a number of cases, but did not correlate with mass loading
- 303SS too susceptible – significant attack wherever salt mixture was present

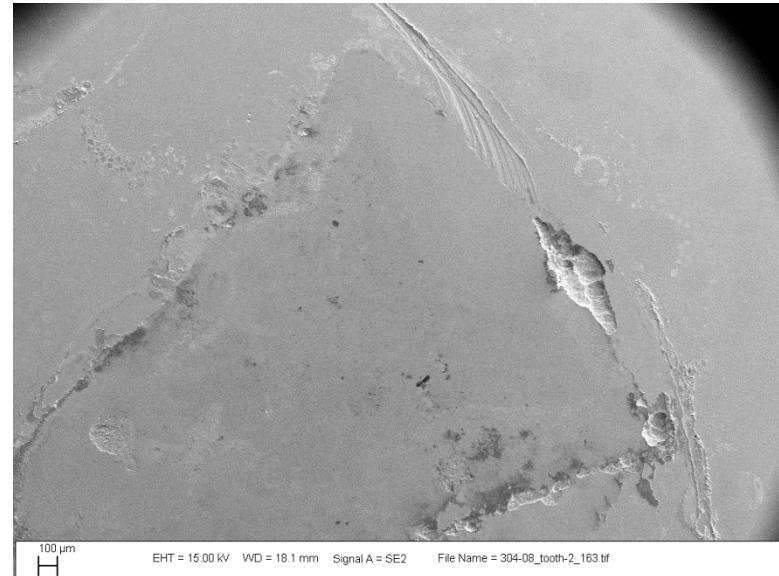
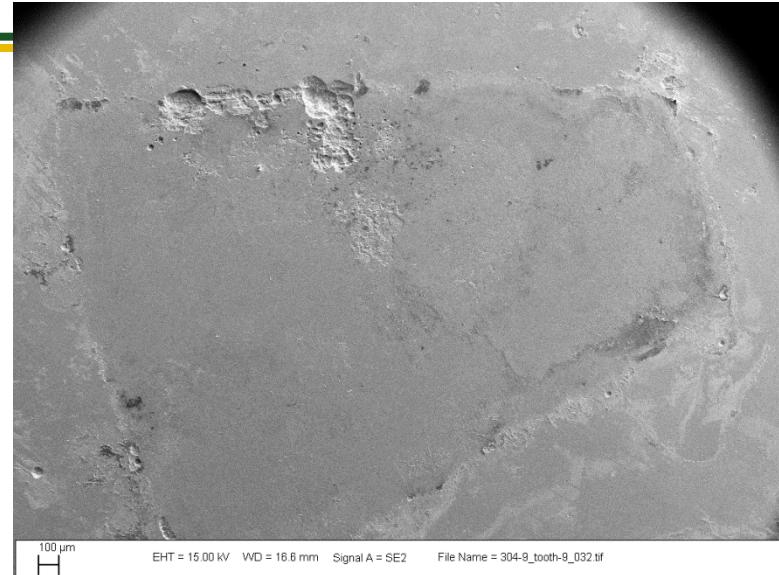
Impact of Salt Loading on 304SS 50 $\mu\text{g}/\text{cm}^2$

- *At least small sites on most teeth*
- *Cracking observed on some teeth*
- *Propagation limited in extent*



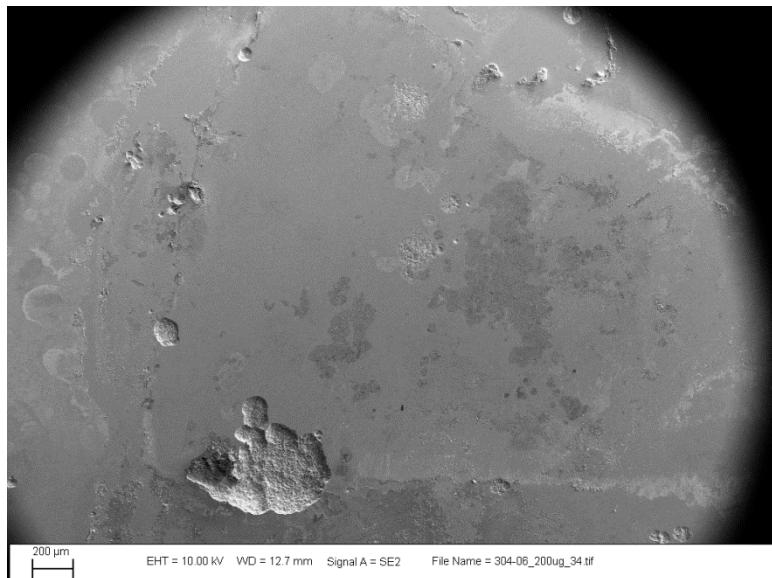
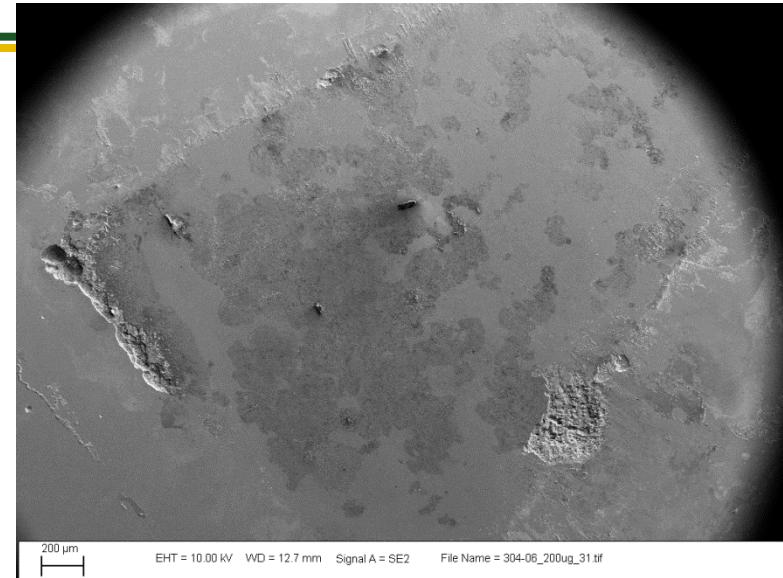
Impact of Salt Loading on 304SS 100 $\mu\text{g}/\text{cm}^2$

- *More teeth where crevice corrosion initiated*
- *Typically multiple sites on teeth where crevice corrosion initiated*
- *Propagation more extensive (further/deeper)*



Impact of Salt Loading on 304SS 200 $\mu\text{g}/\text{cm}^2$

- *Crevice corrosion initiated on most teeth*
- *Typically multiple sites on teeth where crevice corrosion initiated*
- *Propagation more extensive (sites tended to be larger/deeper)*



- Considerable literature clearly indicating that austenitic stainless steels have a significant risk of SCC due to weld residual stresses
 - Caseres and Mintz, 2010 (NUREG/CR-7030)
 - Prosek, et al., 2009 (Corrosion, Vol. 65, no. 2, pp. 105-117)
 - Shirai, et al. 2011 (IHLRWMC 2011, Albuquerque, NM, pp. 824-831)
 - Tani et al., 2009 (Corrosion, Vol. 65, no. 3, pp. 187-194)
 - Cook, et al., 2010 (ECS Transactions, Vol 25 (37), pp. 119-132.)
 - Others.
- Critical combination of stress and environment leads to SCC
 - If a liquid brine can be formed, cracking appears to be viable
 - No brine layer = no cracking.
- Mitigation strategies, such as low plasticity burnishing or laser/shot peening, have not been pursued by cask manufacturers.

- Experimental work defined in technical work plan FCRD-UFD-2012-000052
- Aqueous Immersion
 - Completion of Alloy 22 and issue final report
 - Initiate experiments on materials of interest to interim storage
- Dust Deliquescence
 - Time dependence of damage on 304SS
- Copper Corrosion in Anoxic Water
 - Hydrogen permeation measurements on Pd under humid, anoxic conditions

- **Experiments to date have been fixed, long term (100 day) tests**
 - No information on damage propagation
- **New experiments focus on gaining knowledge of the time dependence of corrosion propagation**
 - Similar sample geometry and salt loading
 - Test periods will vary
 - Extent of damage, time of initiation, etc. will be quantified