

# 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 6<sup>th</sup>, 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?)*

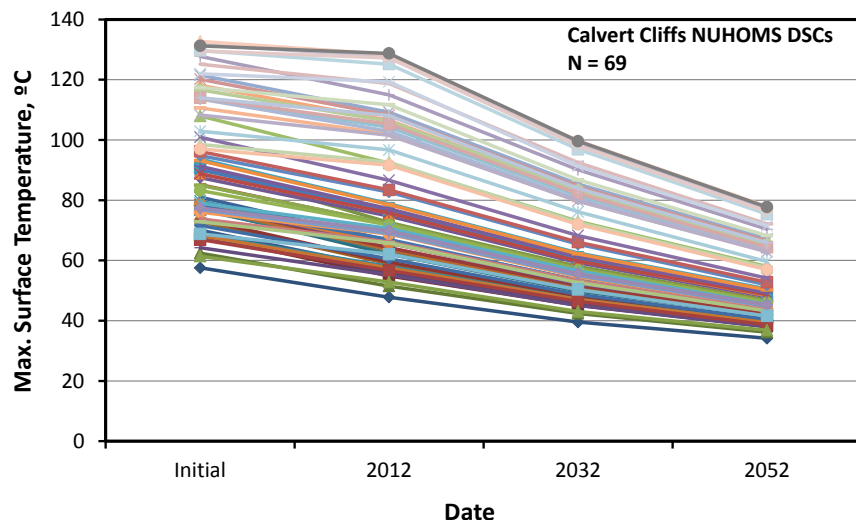
### ■ Deliquescence/condensation: salts are deposited on the storage container surface with dust or aerosols (for example, fog). Will deliquesce if conditions at the waste package surface permit:

- 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 <sup>(1)</sup>	40.8	0	186	B
			100	235	
			117	237	
	24PTH-L	31.2	117	203	
NUHOMS HSM-HD	24PTH-S-LC	24.0	117	176	C
	32PTH <sup>(2)</sup>	34.8	115	208	
	32PTH <sup>(3)</sup>	32.0	115	201	
	32PTH <sup>(4)</sup>	26.1	115	187	
HI-STORM	MPC-68	38.0	80	233	D
	MPC-32	38.0	80	242	

<sup>(1)</sup>Flat stainless steel heat shields

<sup>(2)</sup>Finned Al side shields

<sup>(3)</sup>Unfined Al side shields

<sup>(4)</sup>galvanized steel side shields

<sup>A</sup>NAC-UMS FSAR, Revision 5 (2005)

<sup>B</sup>NUHOMS FSAR, Revision 10 (2008)

<sup>C</sup>NUHOMS-HD FSAR, Revision 0 (2007)

<sup>D</sup>HI-STORM FSAR, Revision 8 (2010)

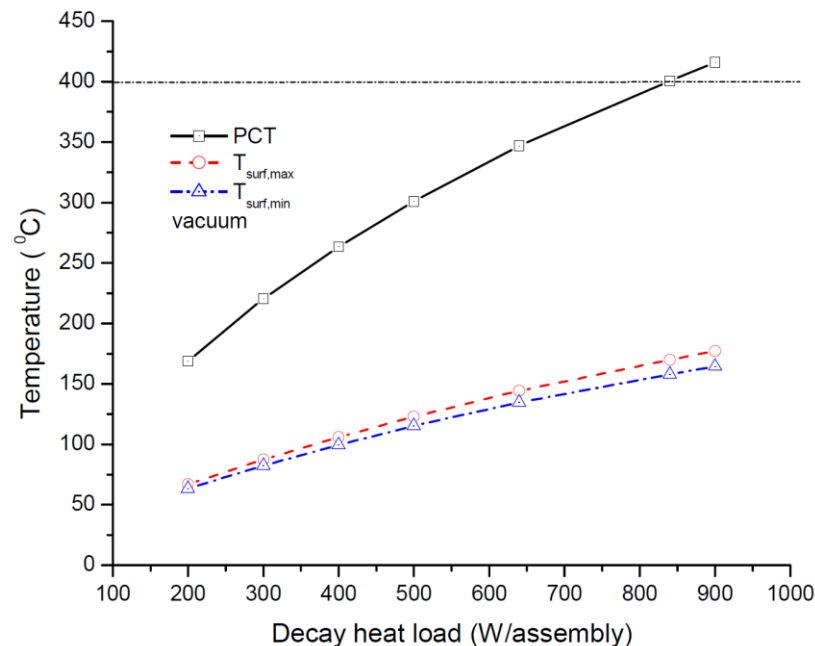
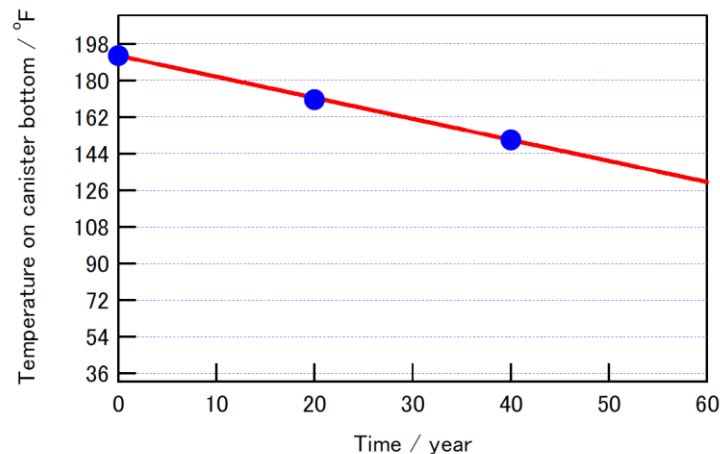
### Literature data—very sparse

#### ■ Li et al. (2007):

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

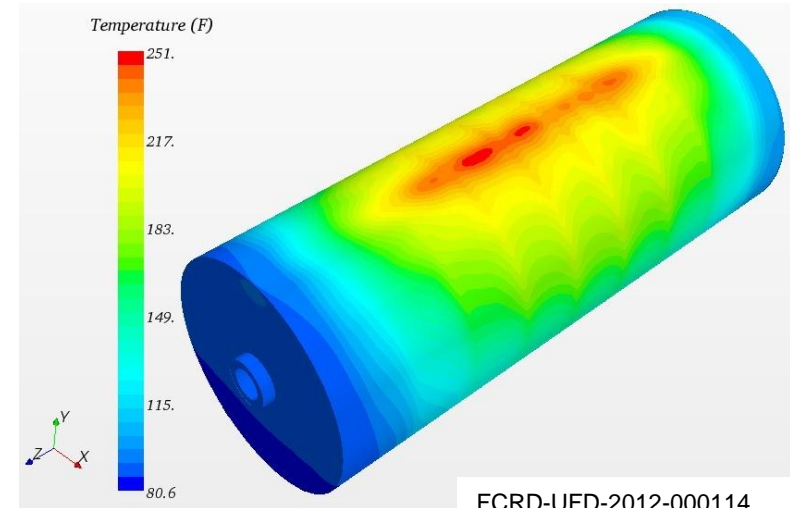
#### ■ Shirai et al. (2011):

- Three-point curve for canister bottom

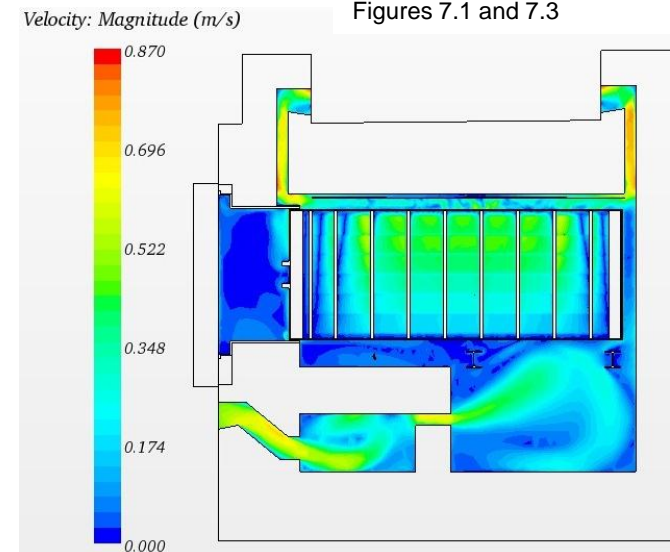


### ■ PNNL modeling

- 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

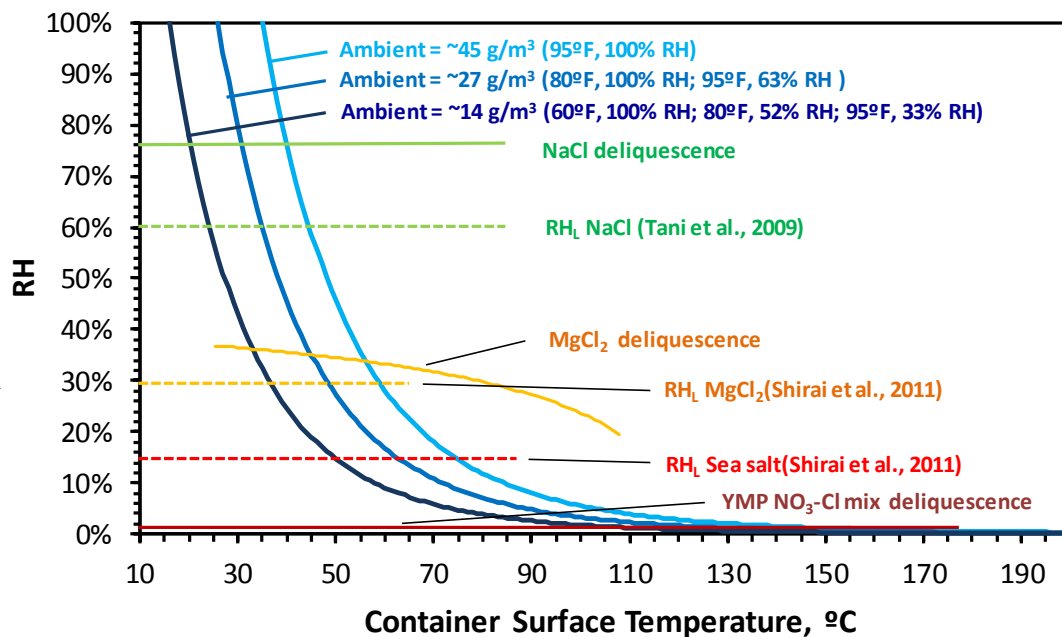


## Parameters Controlling Deliquescence: Temperature, RH

### ■ 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

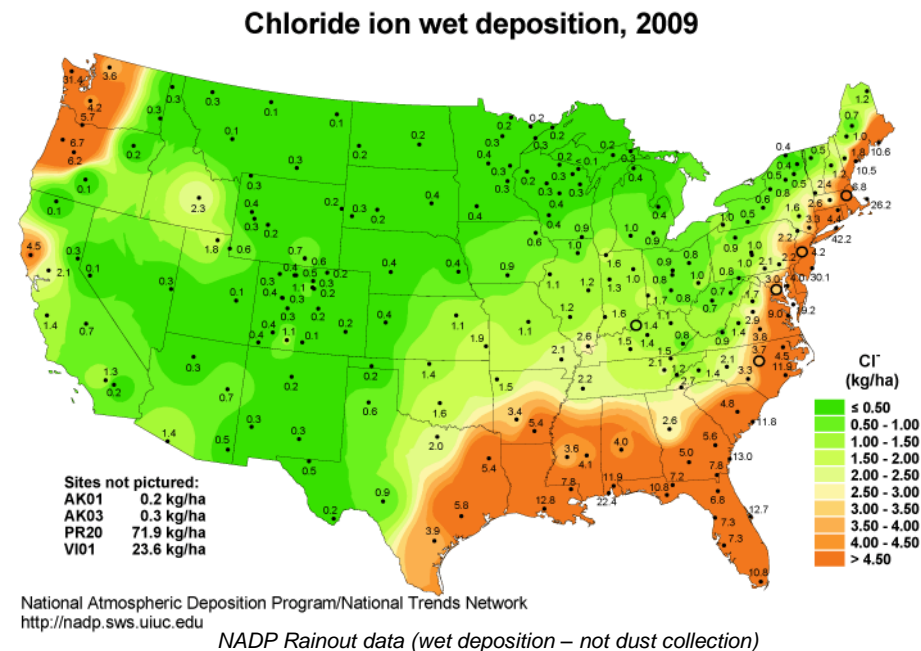
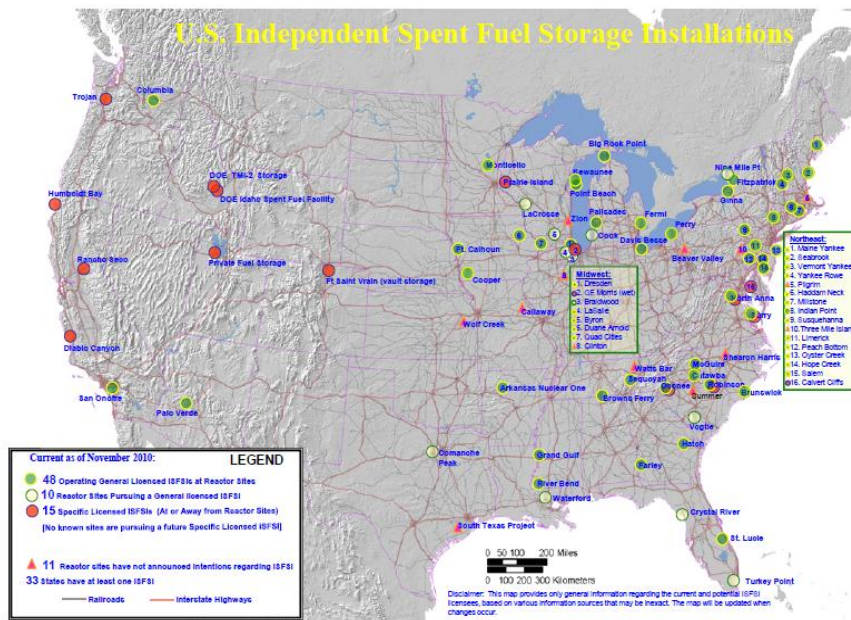
- Can be calculated from the ambient RH and air temperature (monitored) and the container surface temperature at a specific location. Will vary with daily/seasonal variations air RH/T and waste package T.



# 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



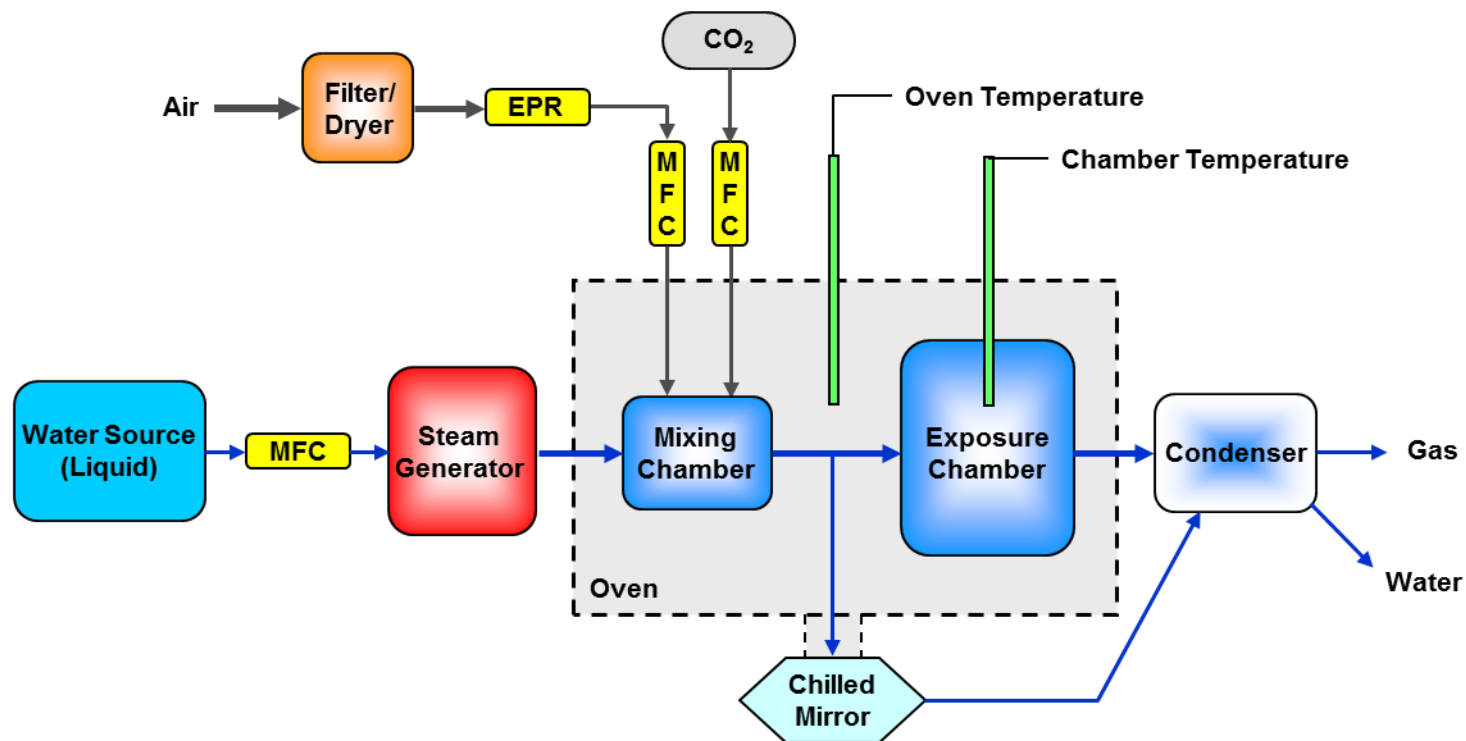
# **Assessment of Localized Corrosion Initiation for Relevant Alloys**

---

**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**

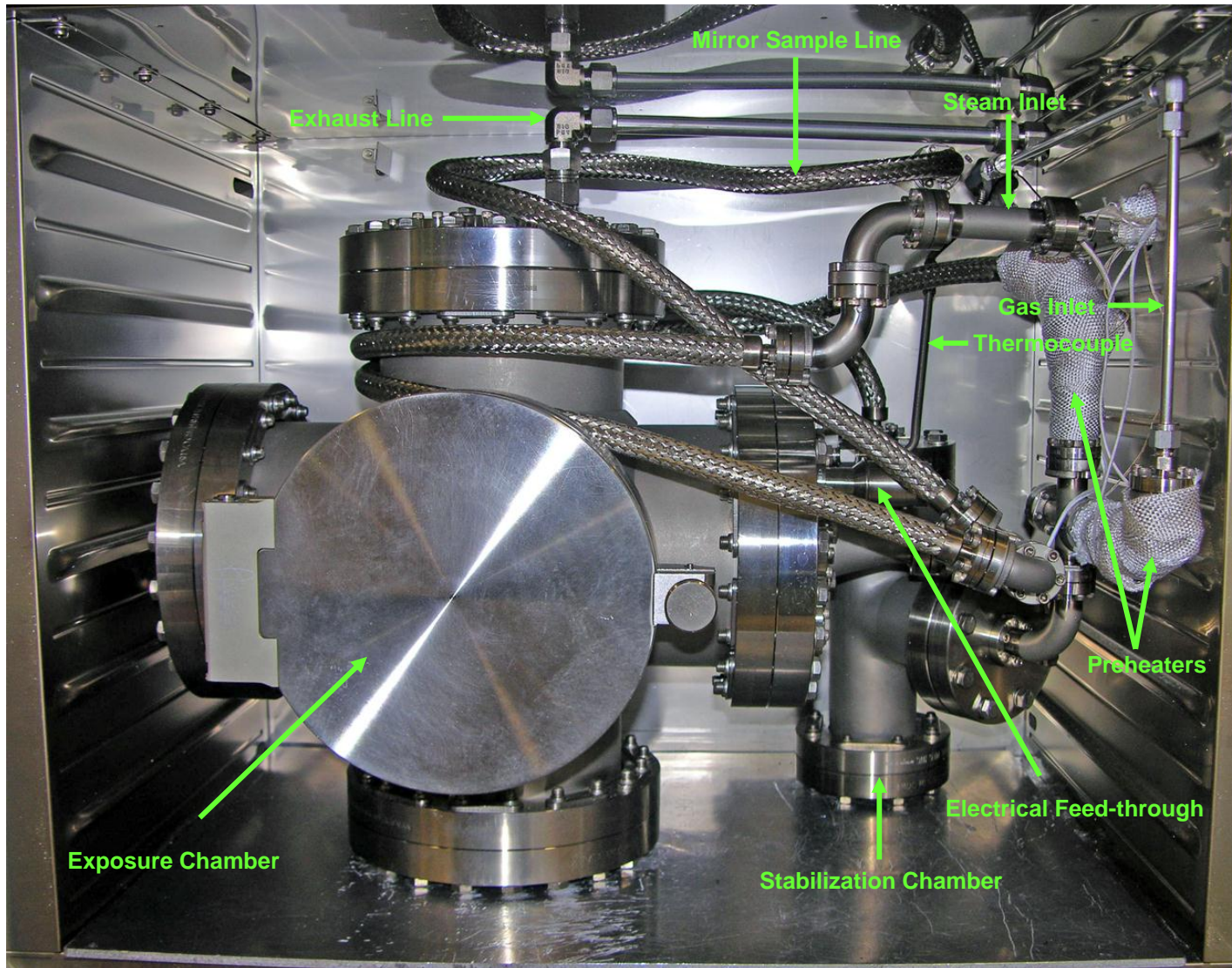
## Schematic of High Temperature System



EPR = Electronic Pressure Regulator and MFC = Mass flow controller

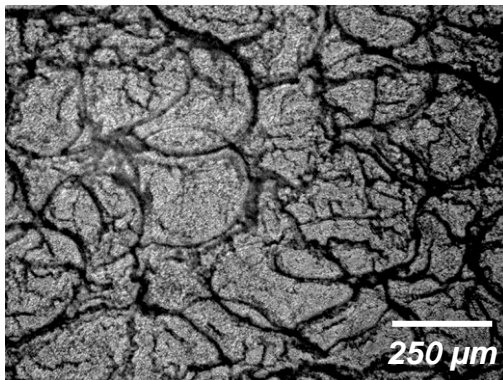
# Used Fuel Disposition

## High Temperature, Controlled Dewpoint System

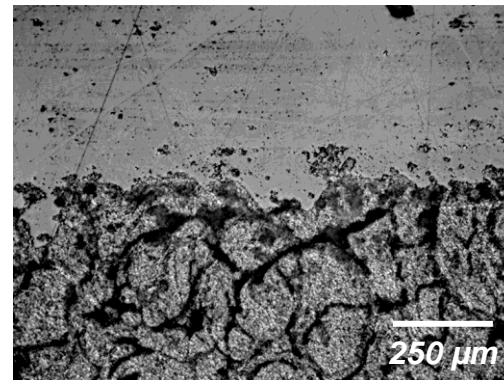




- Alloy 22, Inconel 625, Hastelloy C276, 80:20 Ni:Cr, 304SS, and 303SS evaluated
- PTFE coated ceramic crevice former torqued to 70 in-lbs, Mirror finish on coupon surface
- Range of salt loadings from 50 to 250  $\mu\text{g}/\text{cm}^2$  of a NaCl-KCl mixture
- $T=105^\circ\text{C}$ ,  $T_d\sim 94.5^\circ\text{C}$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



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

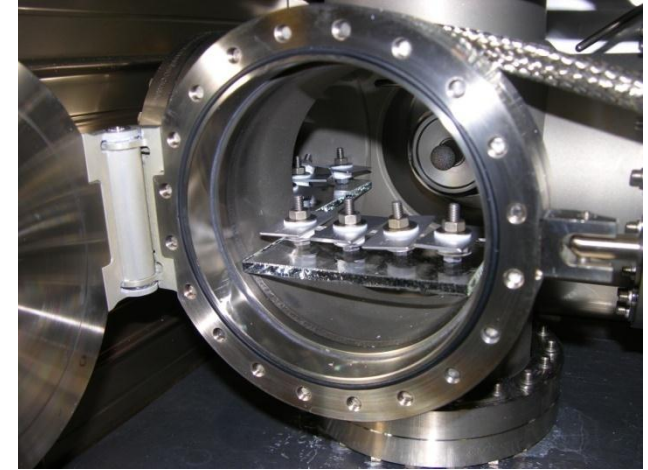


**Wiped region**

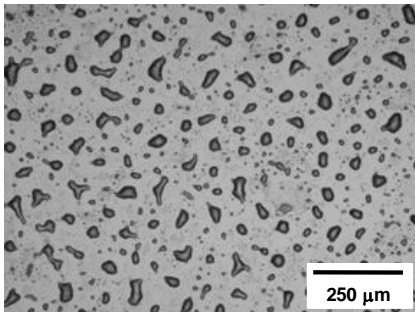
# Used Fuel Disposition

## Dust Deliquescence Testing: Initiation Studies

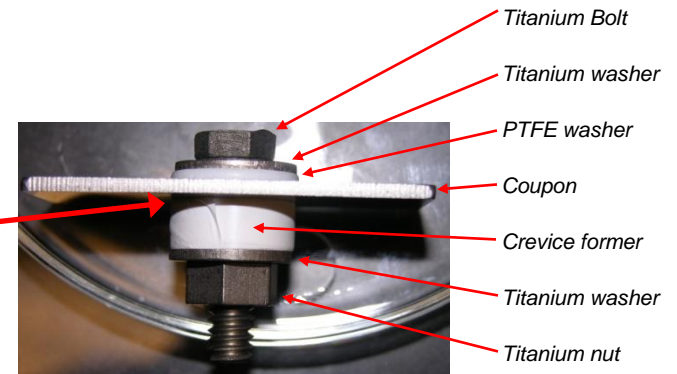
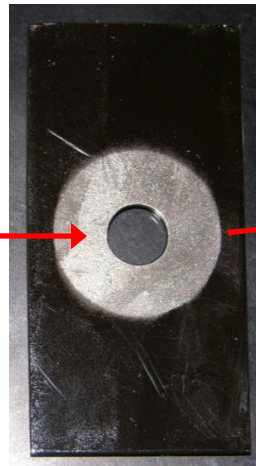
- Alloy 22, Inconel 625, Hastelloy C276, and 80:20 Ni:Cr evaluated
- PTFE coated ceramic crevice former torqued to 70 in-lbs
- Approximately  $400 \mu\text{g}/\text{cm}^2$  of 4 salt mixture  
Mole fraction:  $0.126 \text{ NaCl}$   $0.228 \text{ NaNO}_3$   
 $0.268 \text{ KNO}_3$   $0.378 \text{ Ca}(\text{NO}_3)_2$
- $T=180^\circ\text{C}$ ,  $T_d \sim 94.5^\circ\text{C}$  (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



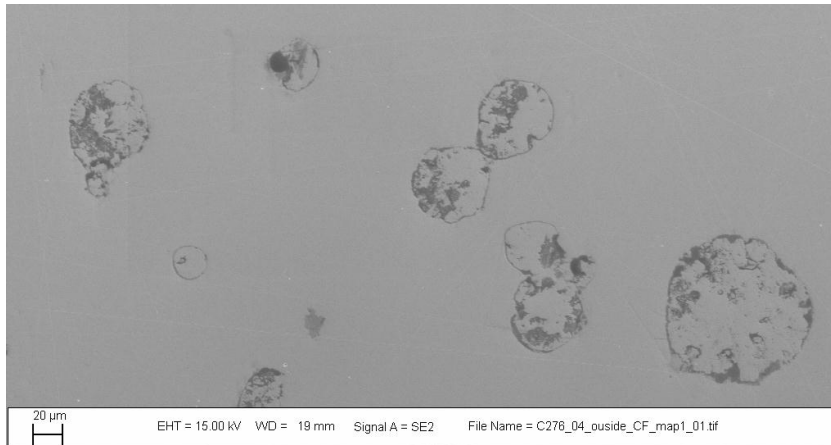
Salt mixture on an Alloy 22 Coupon



(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

80 Ni 20 Cr

C22

Inconel 625

*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*



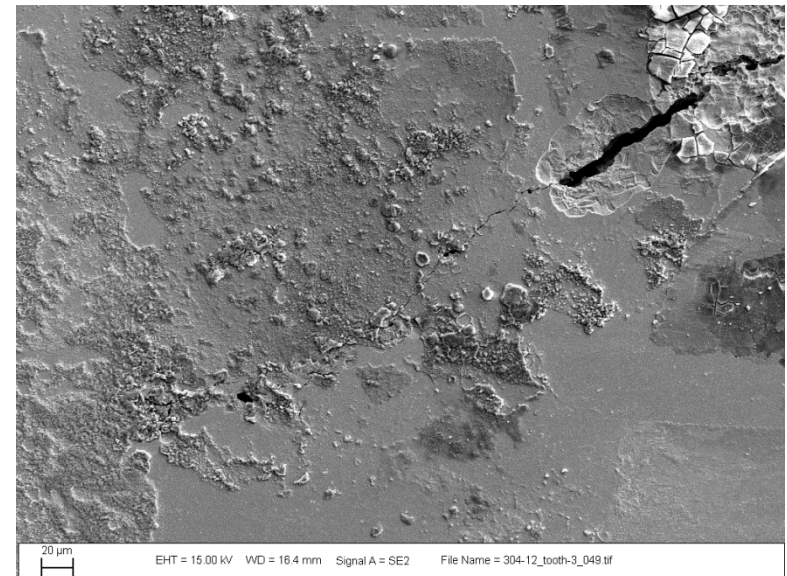
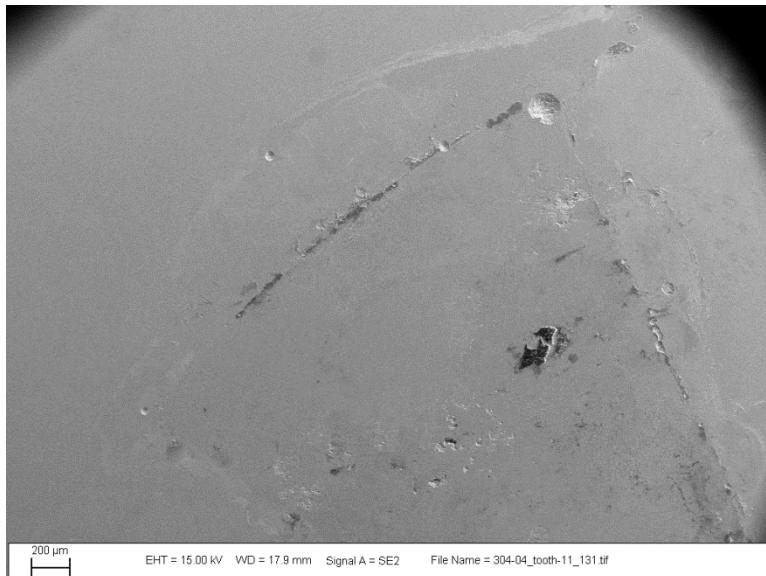
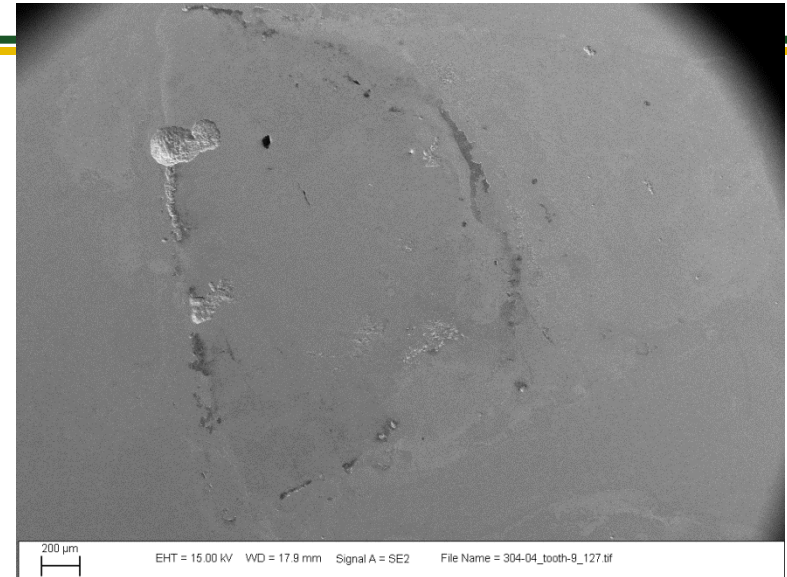
*Evaluation of the impact of salt loading was pursued for 304SS (difficult to interpret 303SS results as material was too active) to explore stifling argument*

- 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

# Used Fuel Disposition

## 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*

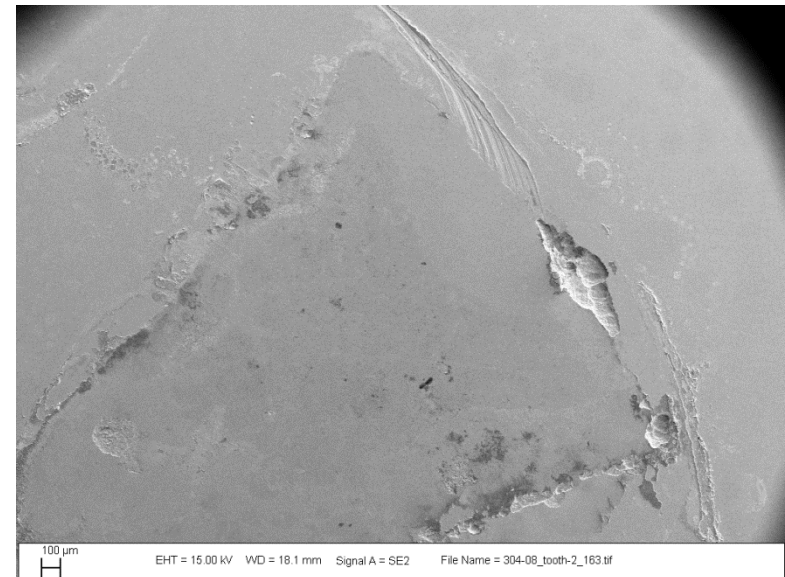
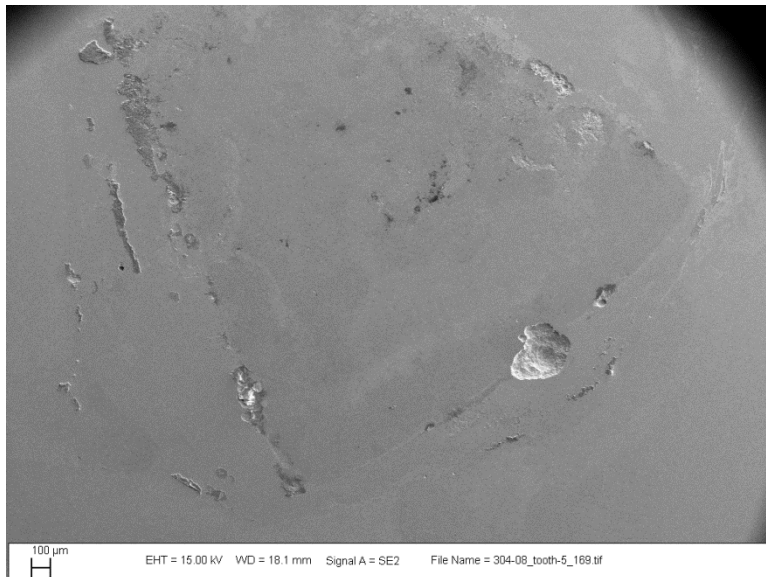
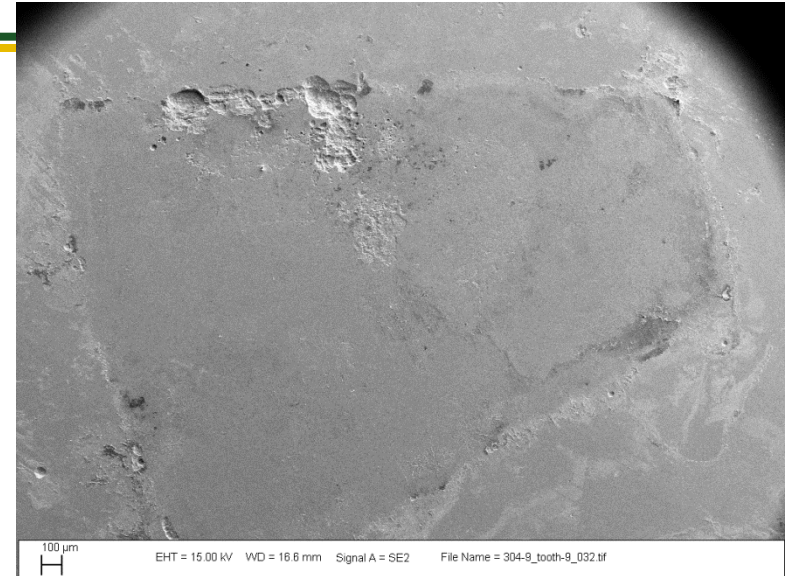




# Used Fuel Disposition

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

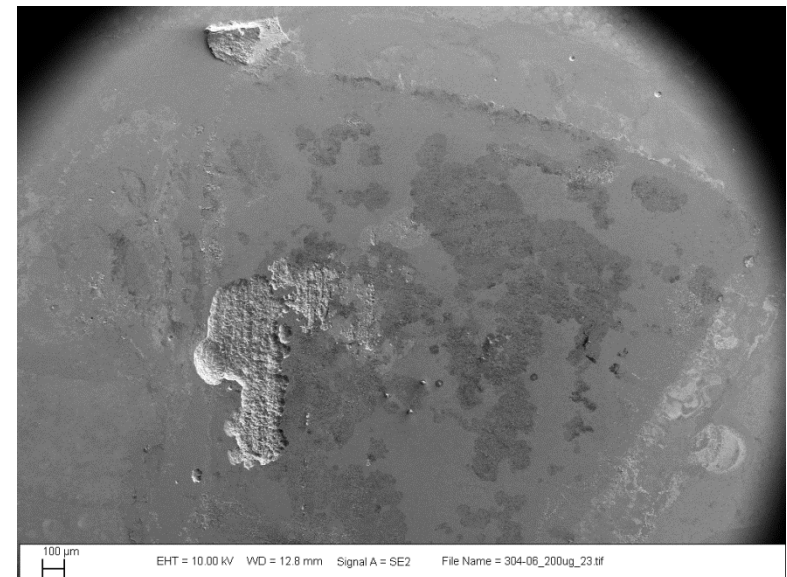
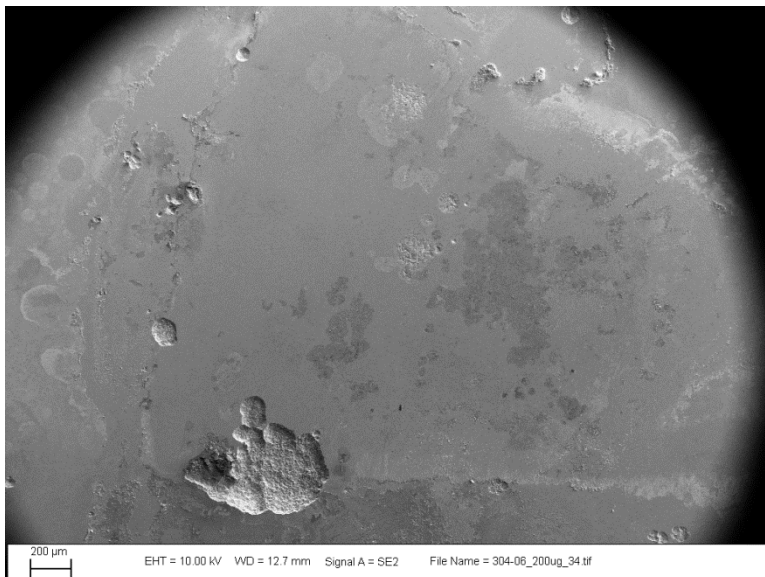
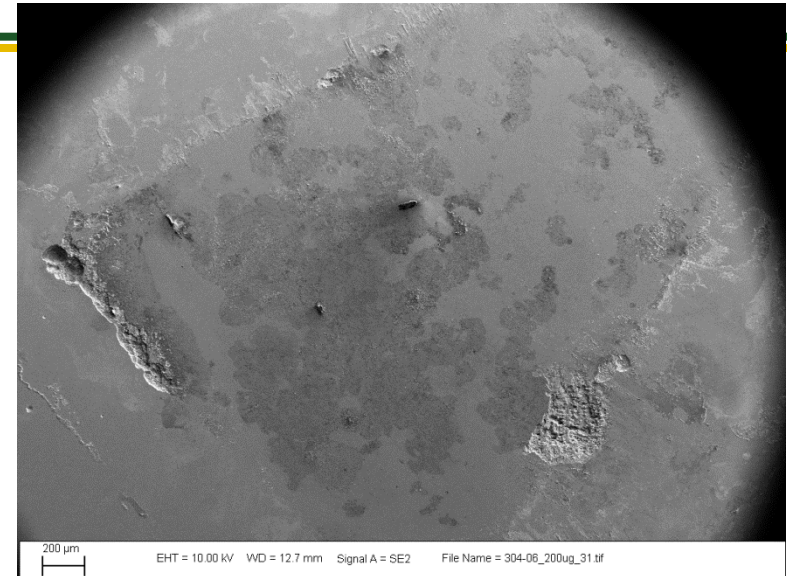
- *More teeth where crevice corrosion initiated*
- *Typically multiple sites on teeth where crevice corrosion initiated*
- *Propagation more extensive (further/deeper)*



# Used Fuel Disposition

## 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)*



# Stress Corrosion Cracking

---

- **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