SAND2012-10127C

SAND2012-10127C

Used Fuel Disposition Campaign

Interim Storage Container Corrosion Testing at SNL

David Enos, Charles Bryan

Sandia National Laboratories

EPRI/ESCP International Subcommittee Meeting

November 30th, 2012

Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

Goal of test program

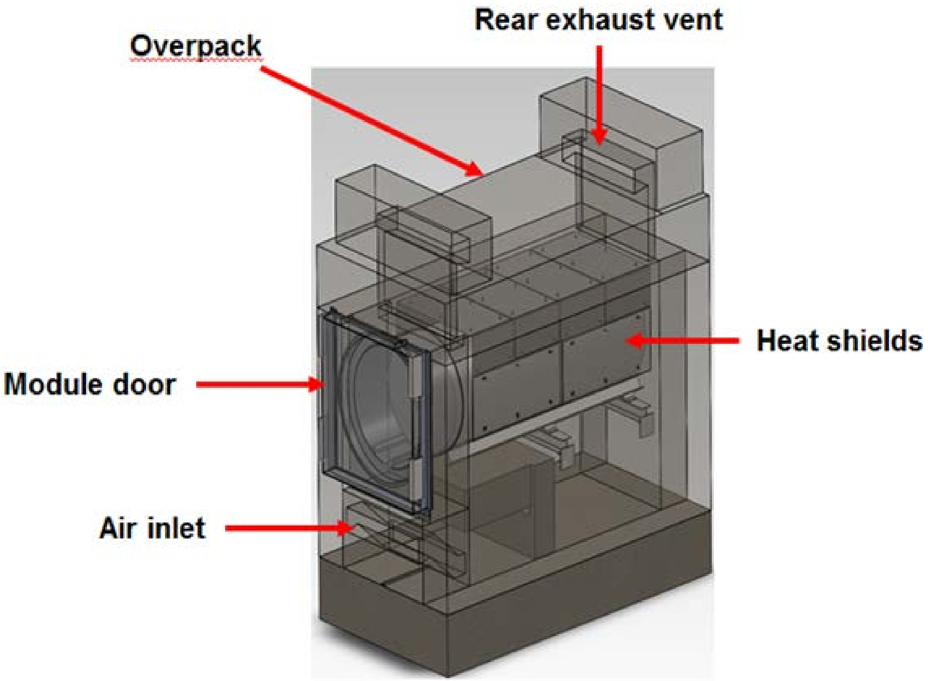
- **Understand nature of the deposit chemistries which may exist on the container surface, as well as pertinent environmental conditions**
  - Composition
  - Quantity
  - Temperature
  - Dewpoint

- **Understand the relevant corrosion degradation mechanisms which may result in the a potential breach of the container**
  - Localized attack
  - Stress corrosion cracking

Used
Fuel
Disposition

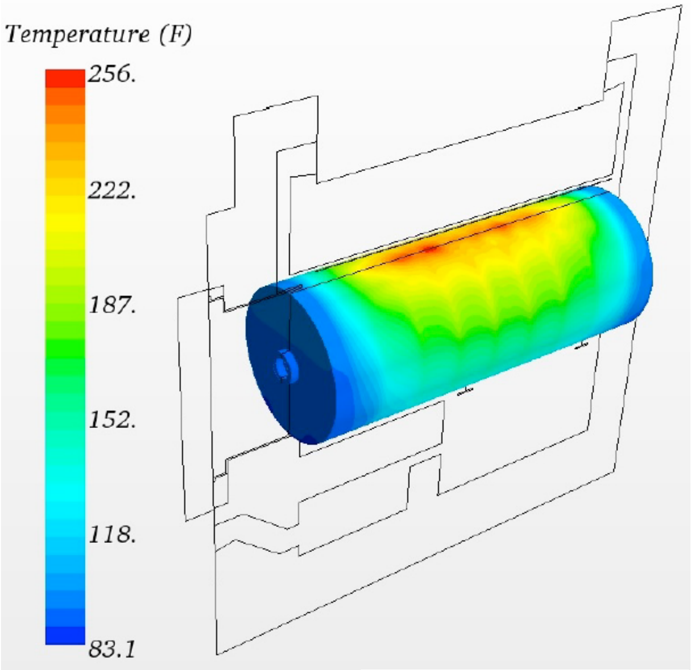
Characterization of the Conditions on the Surface of a Storage Container

- NRC inspection of the Calvert Cliffs ISFSI performed in June, 2012
- Imaging of two containers, coupled with temperature measurement and surface deposit sampling

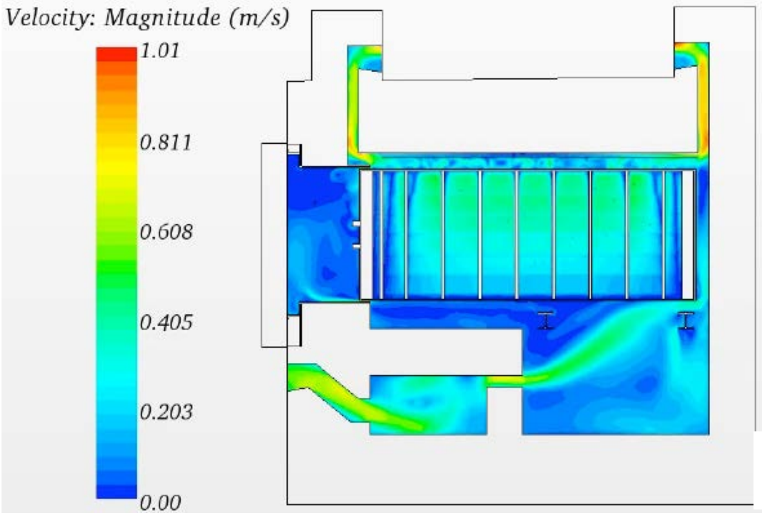


Parameters Controlling Deliquescence: Temperature

- **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)



FCRD-UFD-2012-000344
Figure 7.3

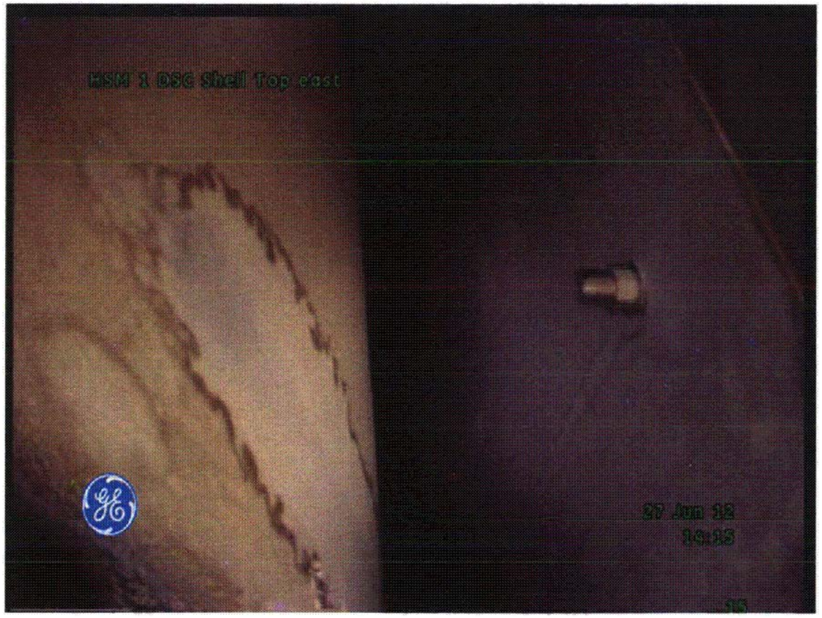


FCRD-UFD-2012-000344
Figure 7.1

- *However:*
  - *Provides snapshots, but does not model full temperature evolution through time.*
  - *Currently, for only one waste profile (thermal load)*

Quantifying the Composition and Quantity of Surface deposits

- **Calvert Cliffs inspection**
  - SaltSmart device used to acquire surface chloride levels
  - Single measurement made at the 0900 location
  - 543 mg/m^2 (54.3 µg/cm^2) for container which was in service for 19 years
  - Significant particulate visible on the surface of the container

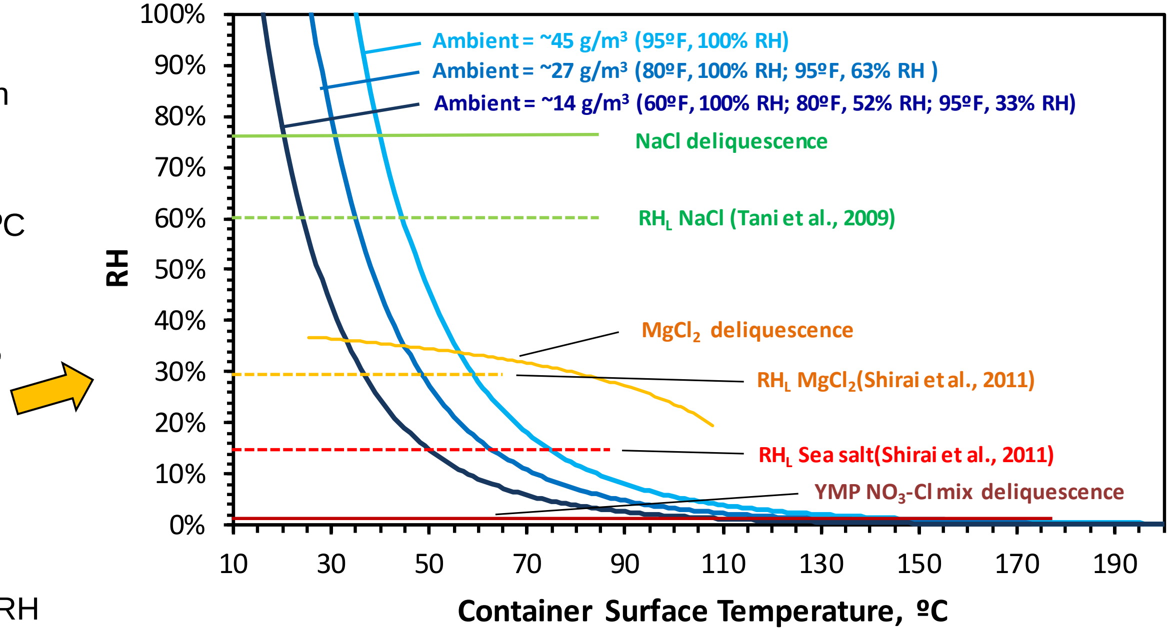


Images from July 27, 2012 supplemental information letter submitted from CENG to the NRC (Adams document no. ML12212A216)

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, 80.6ºF on PNNL HMS-15 model)
  - Maximum temperatures: >200ºC for largest containers (for example, 243ºC 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.

Is Localized Corrosion Possible Under Atmospheric Conditions?

- **For corrosion resistant materials such as Ni-Cr-Mo-W alloys or many stainless steels, theoretical limitations imply crevice corrosion is unlikely under these conditions**

- **Available active surface area outside of a potential crevice limits the ability for crevice corrosion to initiate and/or propagate.**

  - Relocation of cathode inside crevice does not allow maintenance of the critical crevice solution
    - *Turnbull (NPL), Kelly et al. (UVA)*

  - Limitation of cathodic capacity outside of the crevice
    - *Payer, et al. (CWRU), Kelly et al. (UVA)*

Work Described in this Presentation

- **Experiments began during previous repository work in order to assess if multi-salt assemblages on the waste package surface could initiate and sustain localized corrosion.**

- **Secondary goal is to strengthen the corrosion stifling argument**

  – Significant support in the form of modeling results which indicate that cathodic limitations will likely dominate

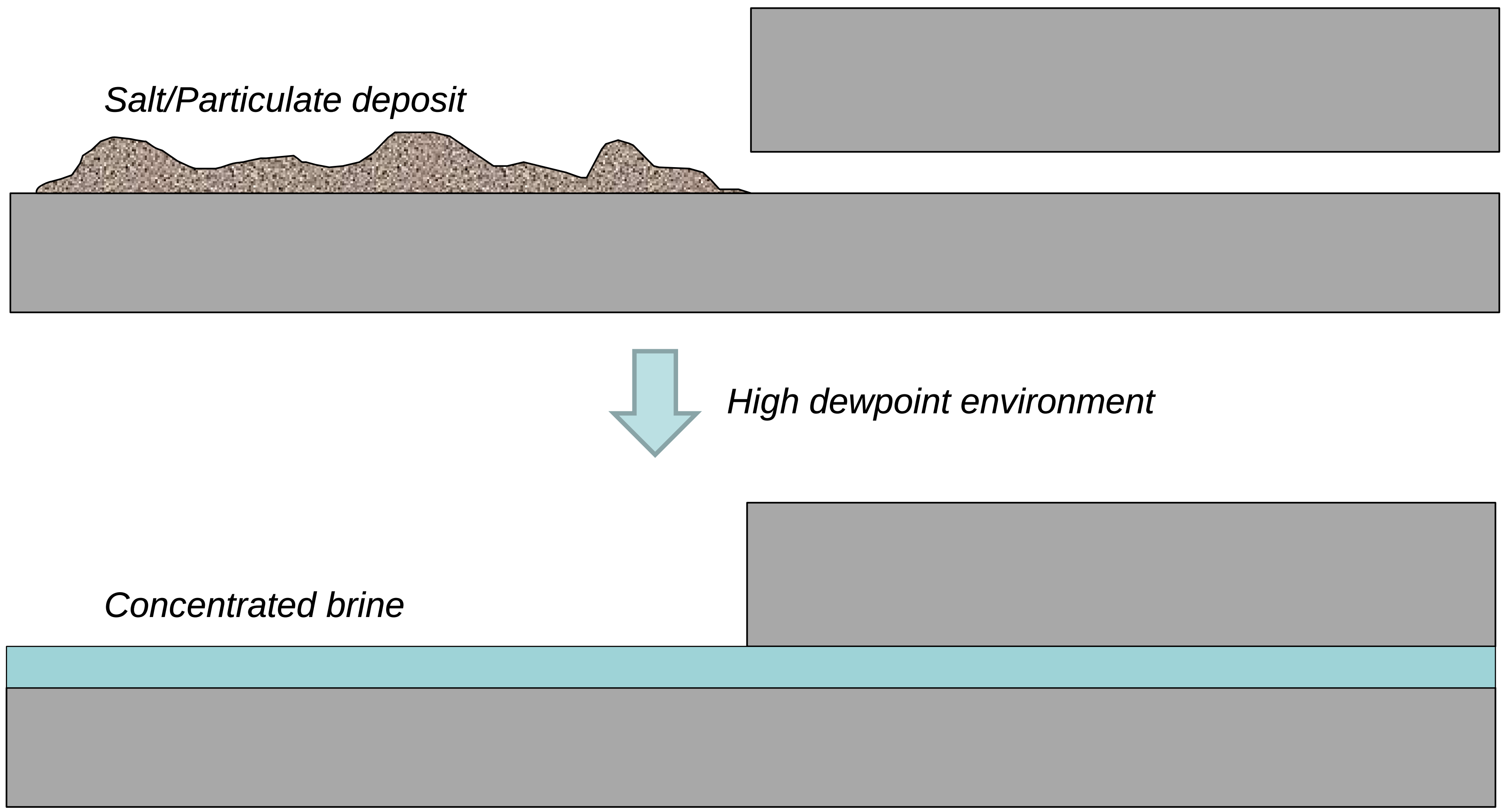
  – Critical need for a dataset which could provide direct support to the stifling argument

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 has been evaluated**
  - Stainless steels used in interim storage applications
  - 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**

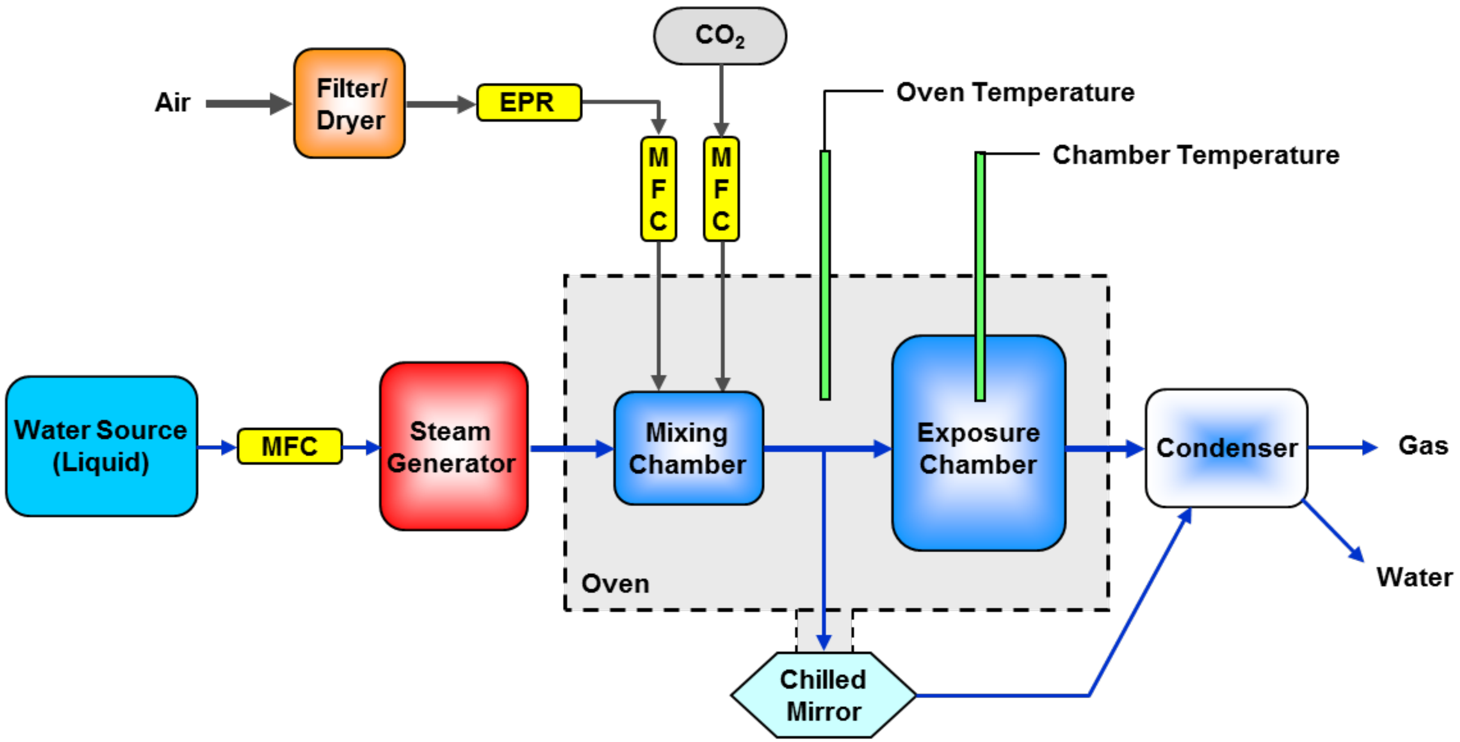
Schematic of a Crevice



Environmental conditions under consideration and why

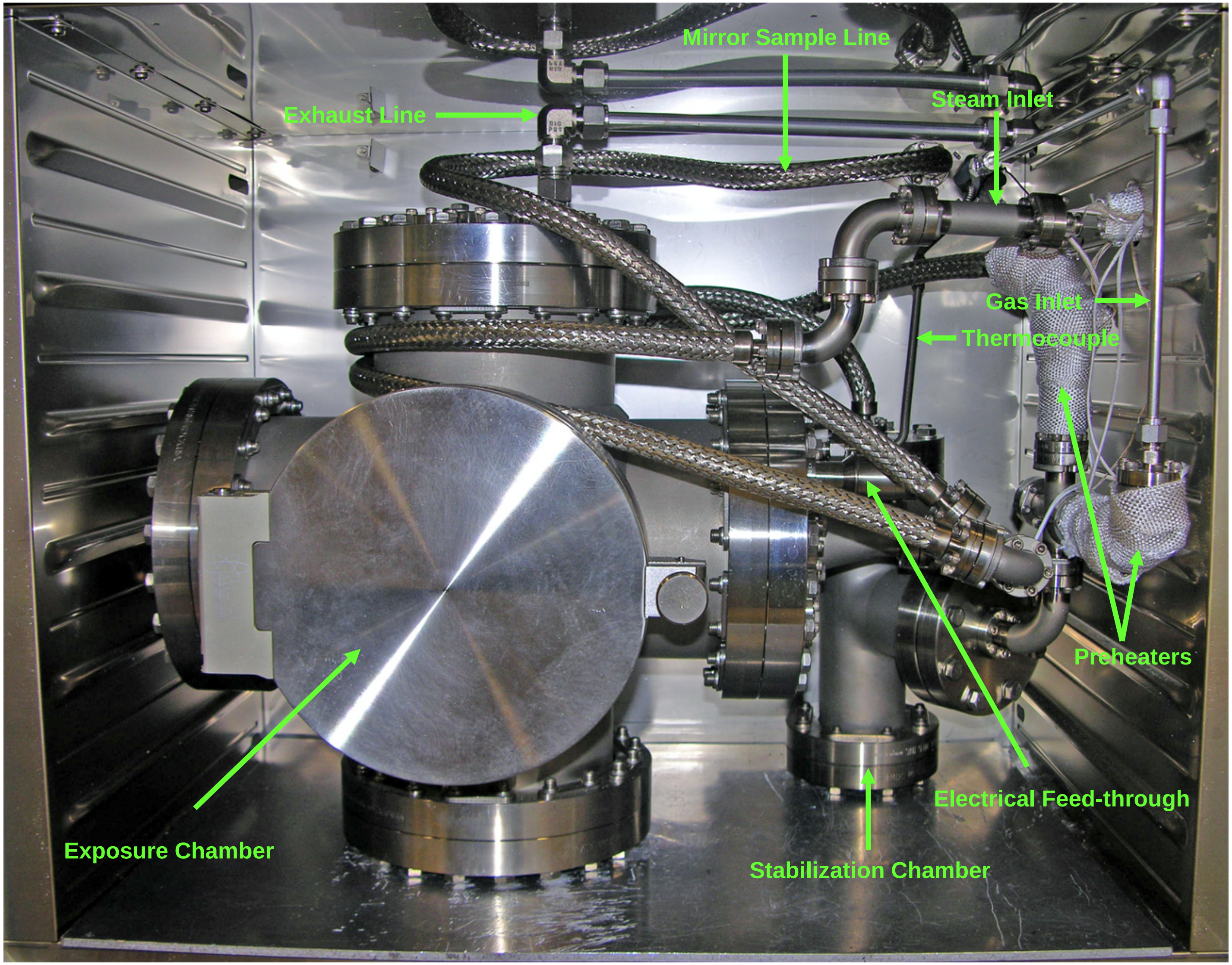
- **Temperature profiles identified via modeling and measurement**
  - Temperatures will begin well above the boiling point of water, then gradually decay over time
- **Heavy surface deposits observed on containers, containing potentially high concentrations of chloride bearing salts**
- **Considerable ongoing work evaluating the composition/nature of deposits anticipated at various storage sites**
- **Clear evidence of moisture intrusion in Calvert Cliffs ISFSI (conditions were dry on inspection, though) – observations at other sites (e.g., North Anna) have revealed considerable water present within the overpack**
- **Variety of conditions possible, ranging from warm and dry to hot with a very high water content in the air**

Schematic of High Temperature System



EPR = Electronic Pressure Regulator and MFC = Mass flow controller

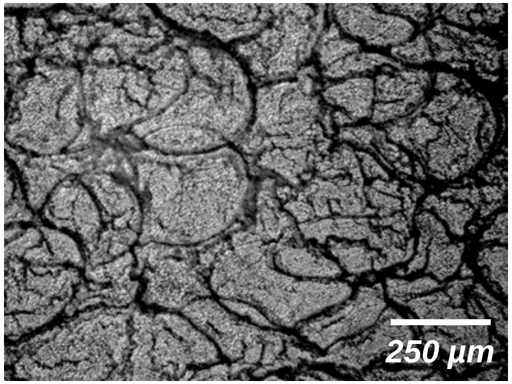
High Temperature, Controlled Dewpoint System



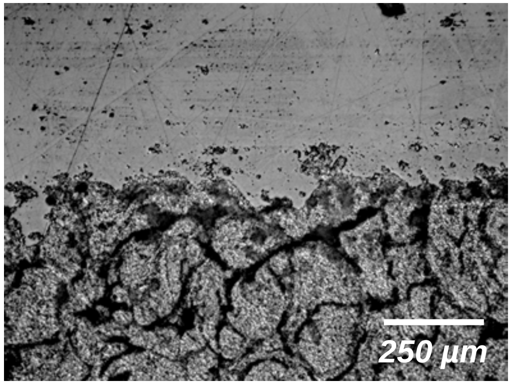
Used
Fuel
Disposition

Experiments in Chloride-Rich Brines

- *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 µg/cm² of a NaCl-KCl mixture (approx. 1 µm thick)*
- *T=105°C, T_d=~94.5°C (pure steam) for test intervals of 100 days*



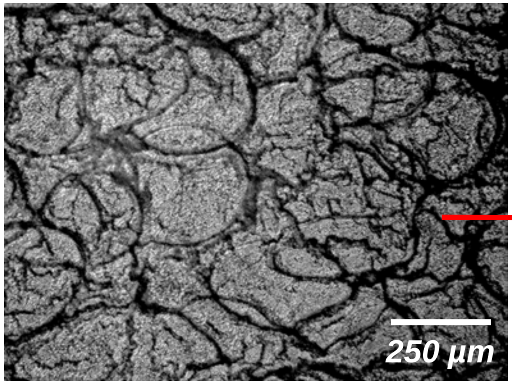
120 µg/cm²



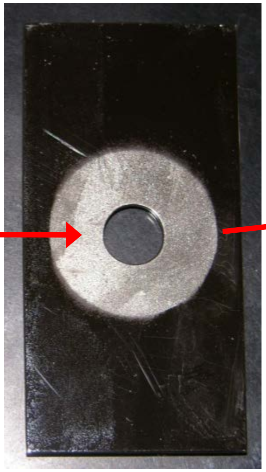
Wiped region

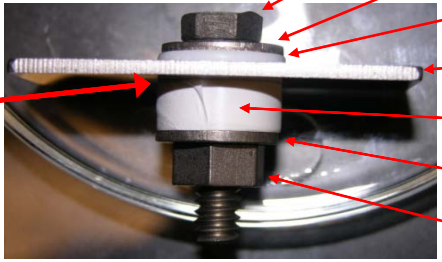
Dust Deliquescence Testing: Initiation Studies

- *Crevice former and salt on one side of coupon which was polished to a mirror finish*

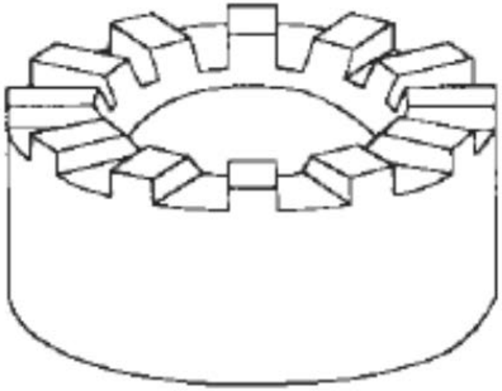


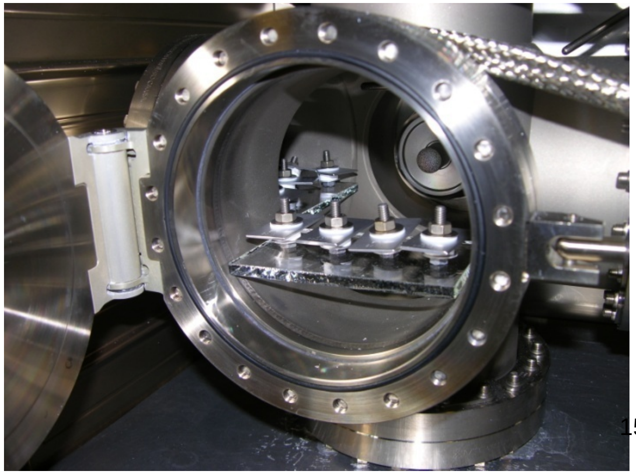
120 µg/cm^2



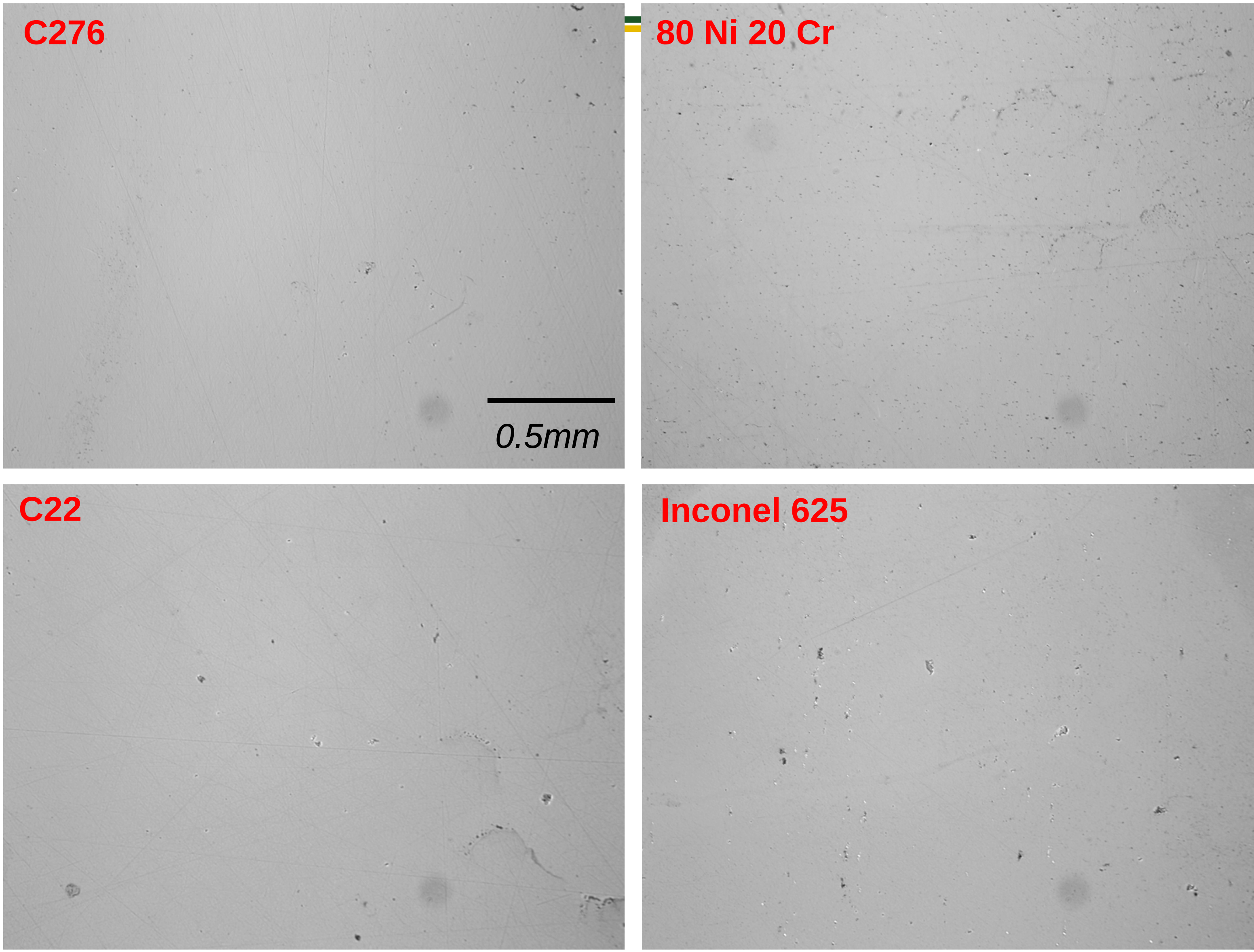


(All titanium hardware electrically isolated from the sample)





Nickel Alloys in Chloride Brines



No crevice corrosion initiation

Concerns brought up by observations on Ni-Cr-Mo alloys

- **Critical need to validate the capability of the technique to support the initiation and propagation of crevice corrosion in susceptible materials. (NWTRB, 2010)**

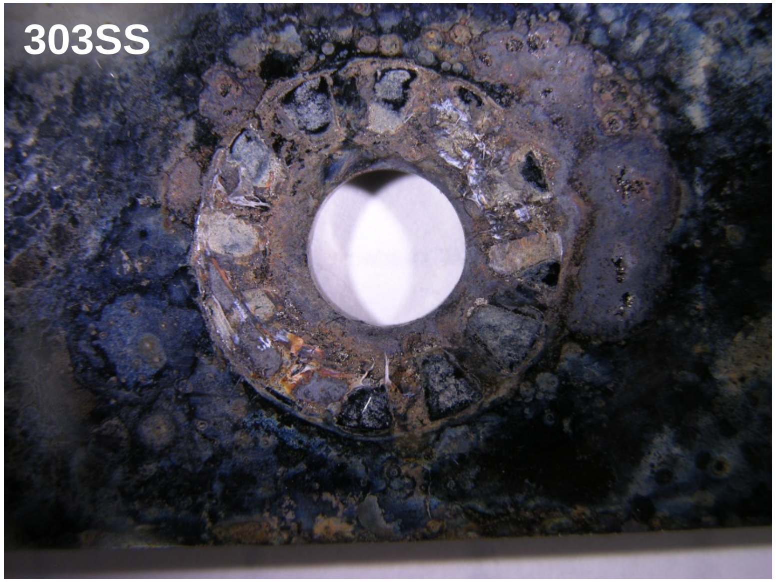
- **At the time work was focused on the behavior of Ni-Cr-Mo alloys – it was suggested that the incorporation of a very susceptible material be explored to see if attack was possible for a known problem material**

- **Experiments initiated on 303SS**
  - Free machining stainless steel with elevated sulfur content
  - Material is extremely susceptible to localized attack (pitting and crevice corrosion)

Used Fuel Disposition

Significant Attack observed on 303SS – effectively all crevice regions initiated and underwent extensive propagation

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

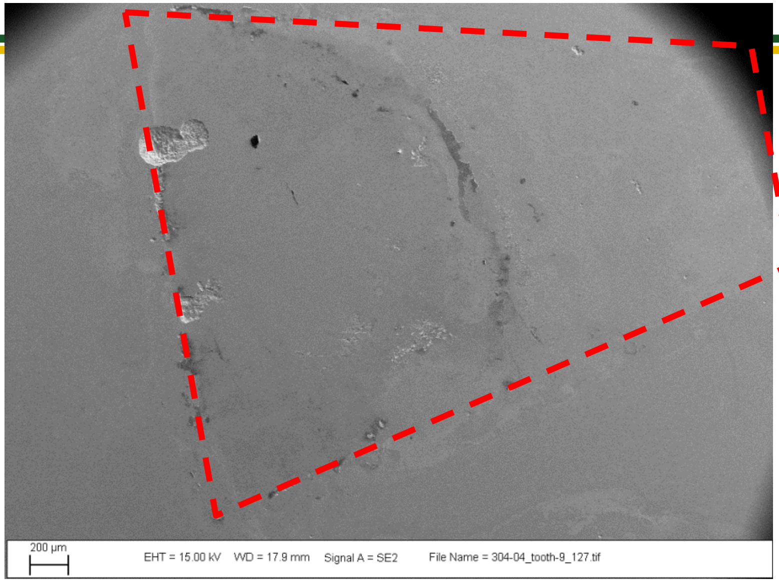
Stainless Steels in Chloride Rich Brines

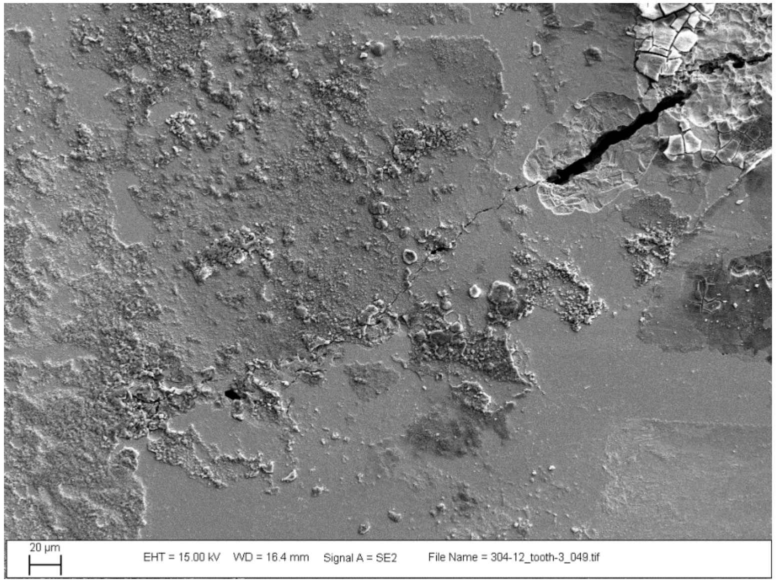
- 303SS too susceptible – significant attack wherever salt mixture was present
- Three different mass loadings evaluated (50, 100, and 200 µg/cm^2)
- Initial experiments performed for a period of 100 days
  - Initiation observed at all mass loadings
  - Extent of attack correlated with mass loading
- Samples exhibited SCC in a number of cases, but did not correlate with mass loading

Used
Fuel
Disposition

Impact of Salt Loading on 304SS 50 µg/cm²

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

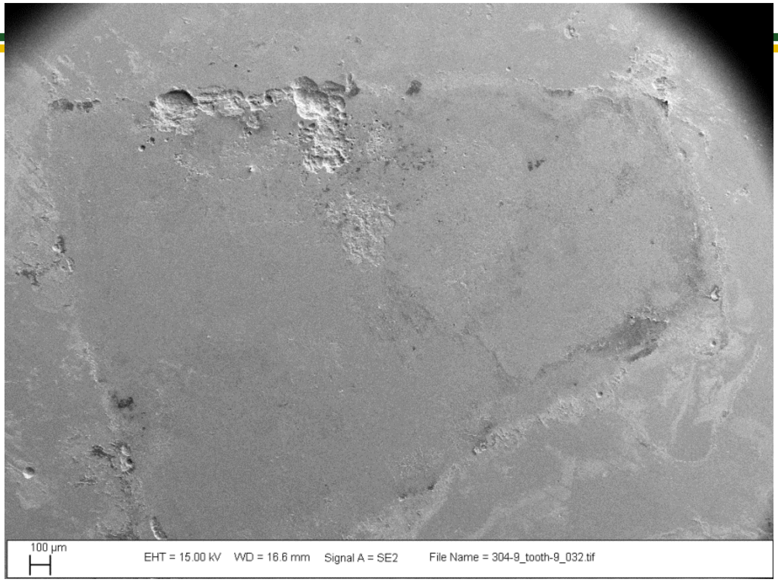


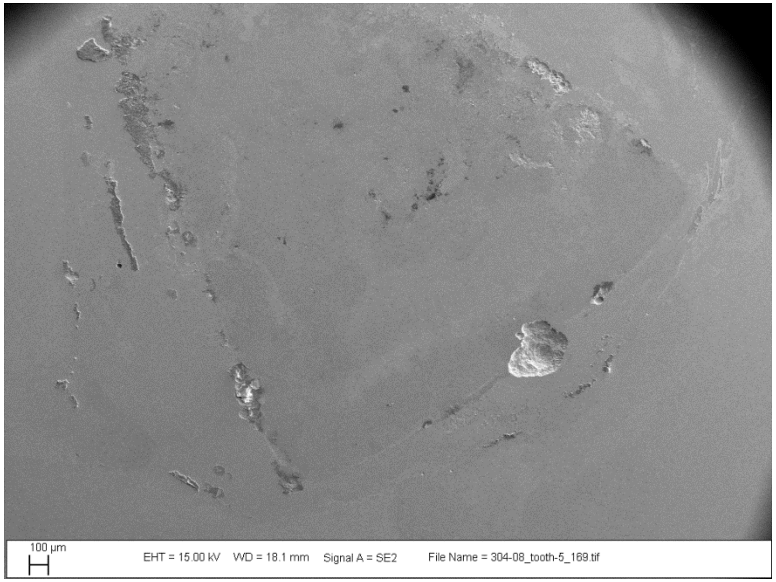


Used
Fuel
Disposition

Impact of Salt Loading on 304SS 100 µg/cm^2

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

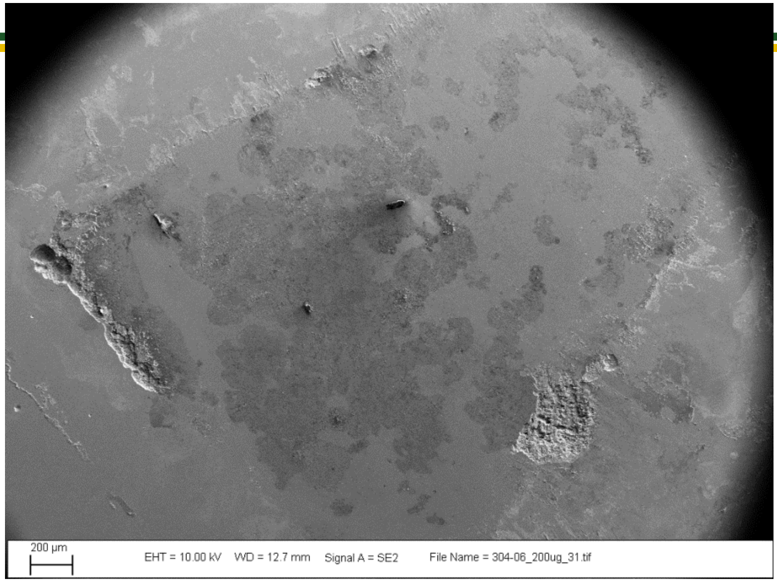


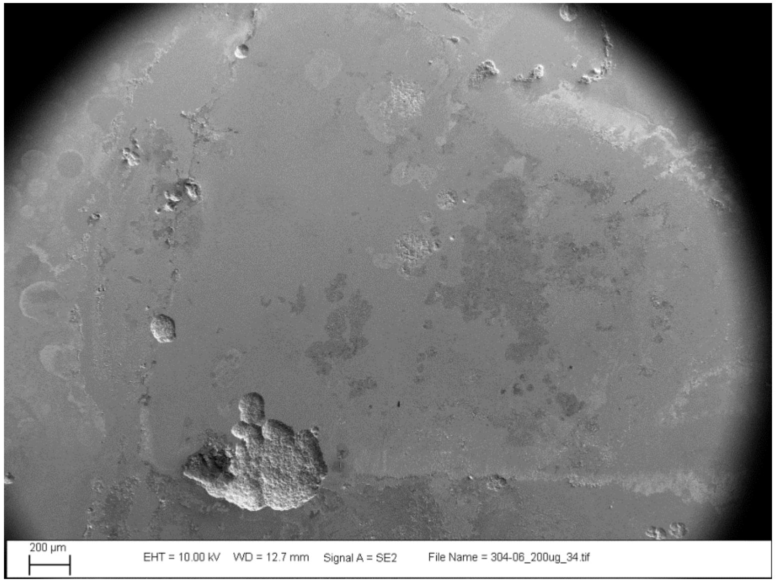


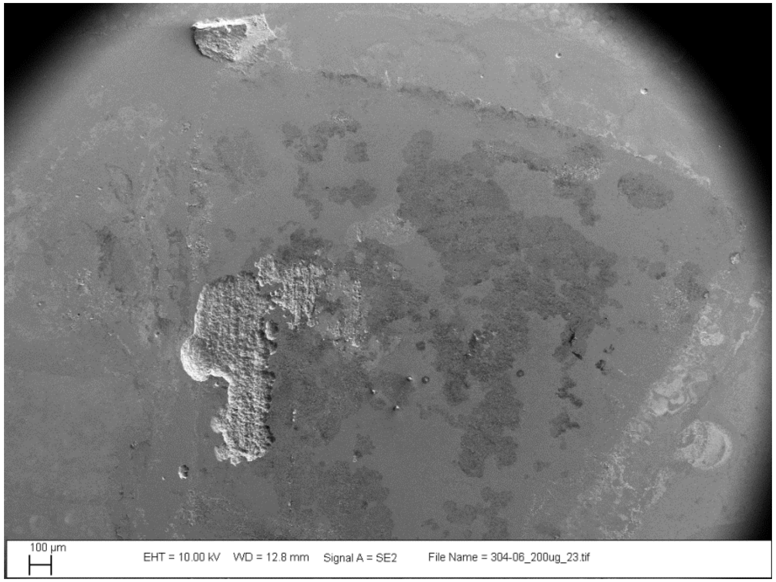
Used
Fuel
Disposition

Impact of Salt Loading on 304SS 200 µg/cm²

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







Is There a Time Dependence for Crevice Corrosion Under Deliquescent Conditions?

- **While the experiments at 100 days do illustrate that localized attack is possible for a variety of relevant chloride surface concentrations, they do not answer our initial question/concern**
  - Does initiation time correlate with mass loading?
  - Is the likelihood of initiating localized corrosion at a given site a function of the quantity of brine present on the surface?
  - Is it that the extent of damage is a result of the mass loading (i.e., attack advances and stifles) or is it that the rate of attack is a function of the mass loading?

Time dependence of localized attack

- **Same mass loadings and material as in longer time period experiments**
  - 304SS, polished to a mirror surface to simplify surface inspection
  - PTFE coated ceramic crevice former, torqued to 70 in-lbs
  - 50, 100, and 200 µg/cm^2 of a NaCl/KCl mixture
  - Material deposited using airbrush technique using a methanol carrier

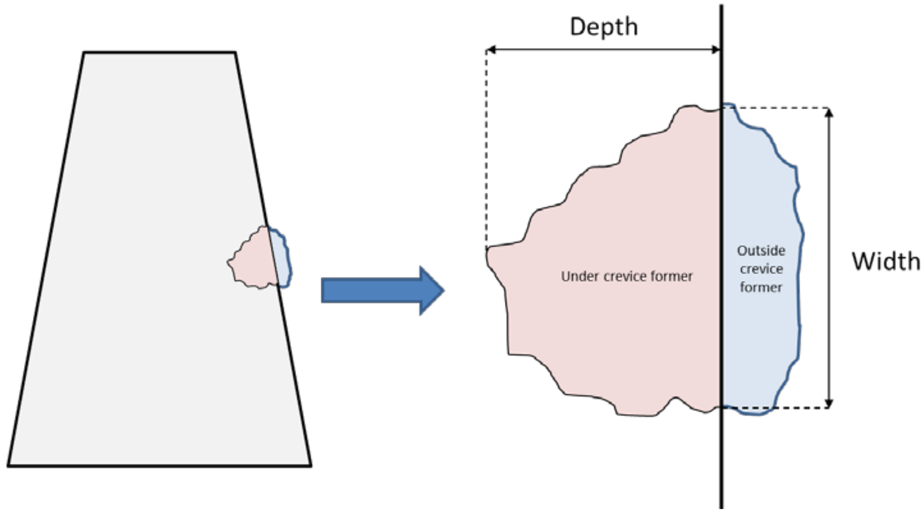
- **Environmental conditions**
  - Temperature of 100-102°C
  - Pure steam environment (dewpoint equal to boiling point of water)

- **Multiple time intervals to build on 100 day experiments**
  - 7, 14, 25, and 50 days

- **Data analysis is proving to be problematic**
  - Large number of areas to quantify
  - Difficult to assess size/shape/depth of sites

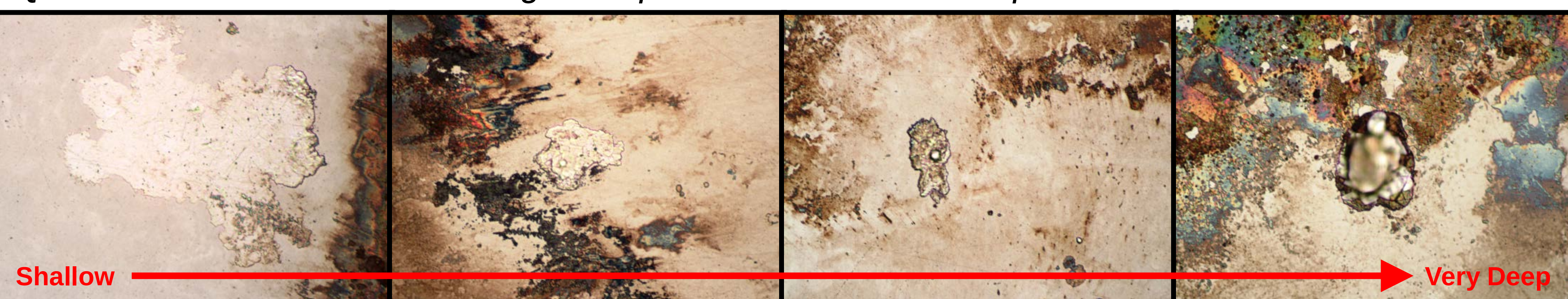
Optical Characterization of Sites

- **Quantify the number, size, and shape of all crevice sites initiated on 4 representative teeth from each sample**



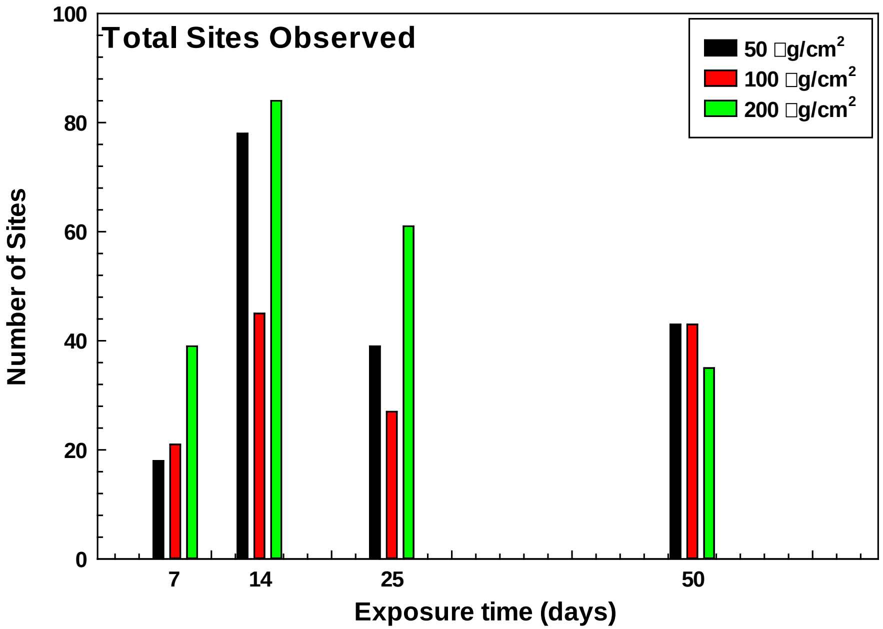
Quantitative measurement of the width and depth beneath crevice former for each site

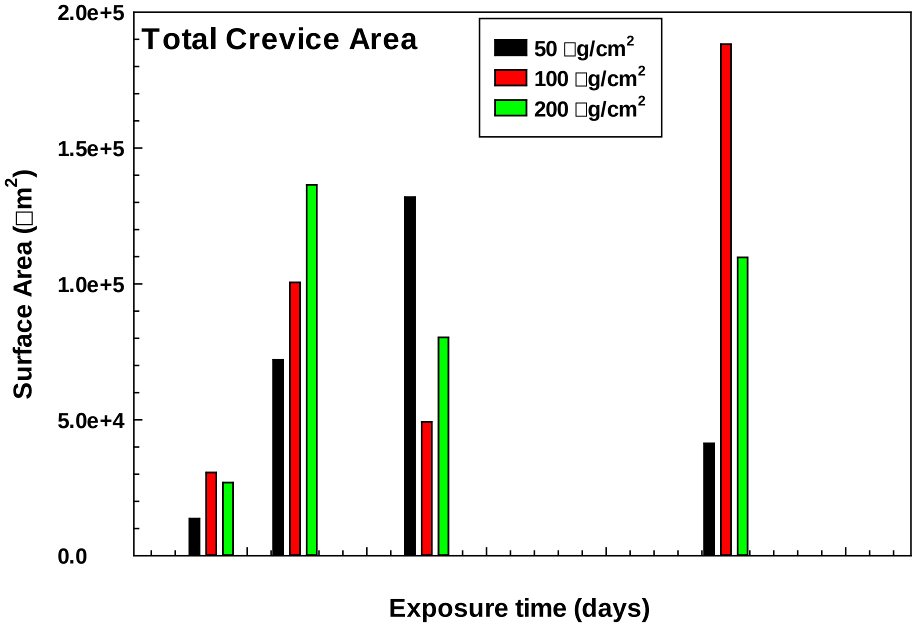
Qualitative assessment of the degree of penetration into the sample surface for each site



Used
Fuel
Disposition

Total Number and Surface Area of Sites (Summed Over 4 Crevice Teeth)

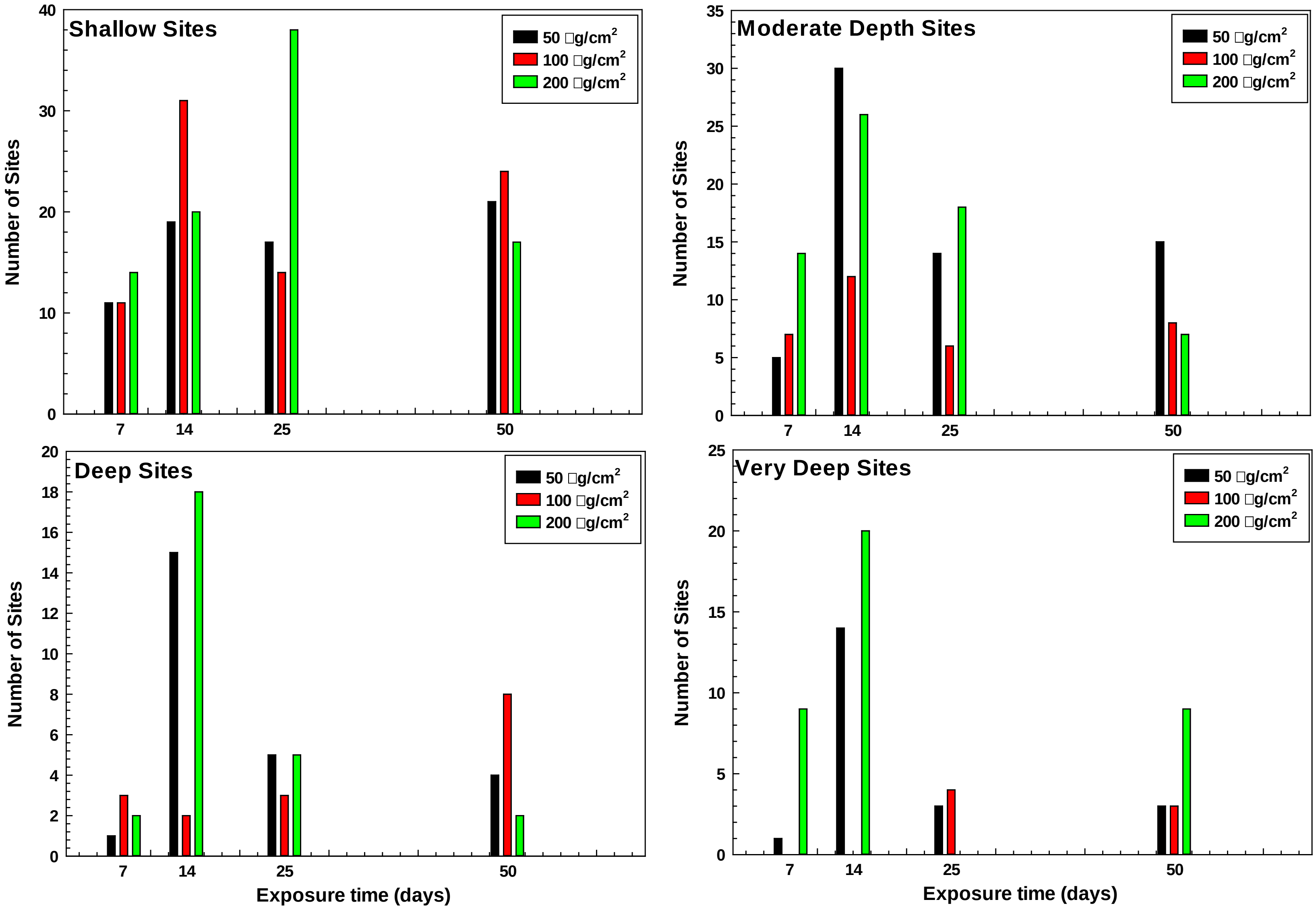




- **Number density and overall surface area of sites appears to increase and stabilize after 14-25 days (but data is too sparse to be conclusive)**

Used
Fuel
Disposition

Number of Sites of Each “Depth” as a Function of Time



Summary

- Containers for both interim storage and long term disposal will be under environmental conditions where salt particulates will be deposited that are capable of forming a brine at elevated temperature and humidity.
- Information from the literature suggests that localized corrosion under conditions where limited reactant is present should be difficult due to limitations in the cathodic capacity
- Tests at moderate temperature with a chloride rich brine did not result in crevice corrosion initiation for a variety of Ni-Cr-X alloys
- Crevice corrosion initiation was observed on both 303 and 304SS under moderate temperature, chloride rich brines
- The extent of attack was characterized for 304SS and was found to correlate with the quantity of salt deposited on the metal surface prior to the experiment.

Conclusions

- **Ni-Cr-X alloys are resistant to crevice corrosion initiation where limited reactant and a thin electrolyte layer is present, consistent with assertions in the literature**
- **304 and 303 SS were susceptible to crevice corrosion initiation**
- **The extent of damage on 304SS roughly correlated with the quantity of reactant present**
  - Number of sites seemed to be stable after a short time period
  - Surface area roughly correlated with mass loading
  - Need more data…
- **Results suggest that crevice corrosion will stifle under conditions where limited reactant is present, presumably due to cathodic limitations or consumption of the reactant**

Acknowledgements

At Sandia National Labs

- Sam Lucero – Salt deposition and experimental setup
- Alice Kilgo – Surface preparation
- Kirsten Norman – Assistance with data analysis
- Bonnie McKenzie – Electron microscopy

NWTRB

- David Duquette, Ron Latanison – Fruitful technical discussions