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Sandia National Laboratories
yucca mountain project
OCRWM Lead Laboratory for Repository Systems

Generating and Performing Experiments Within the In-Drift Environments Anticipated in the Proposed Yucca Mountain Repository

New Orleans, Louisiana

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Not LSN Relevant

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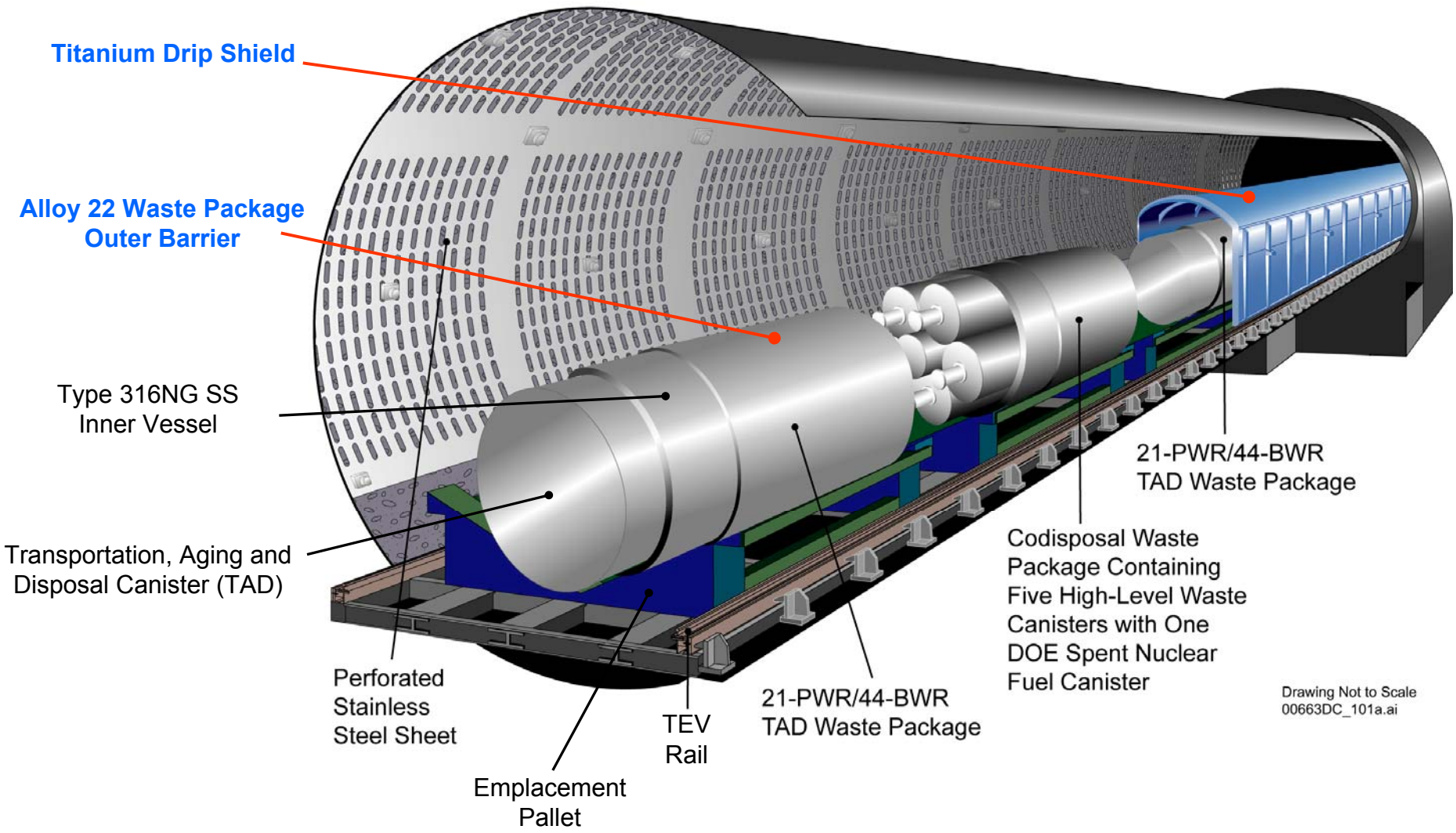
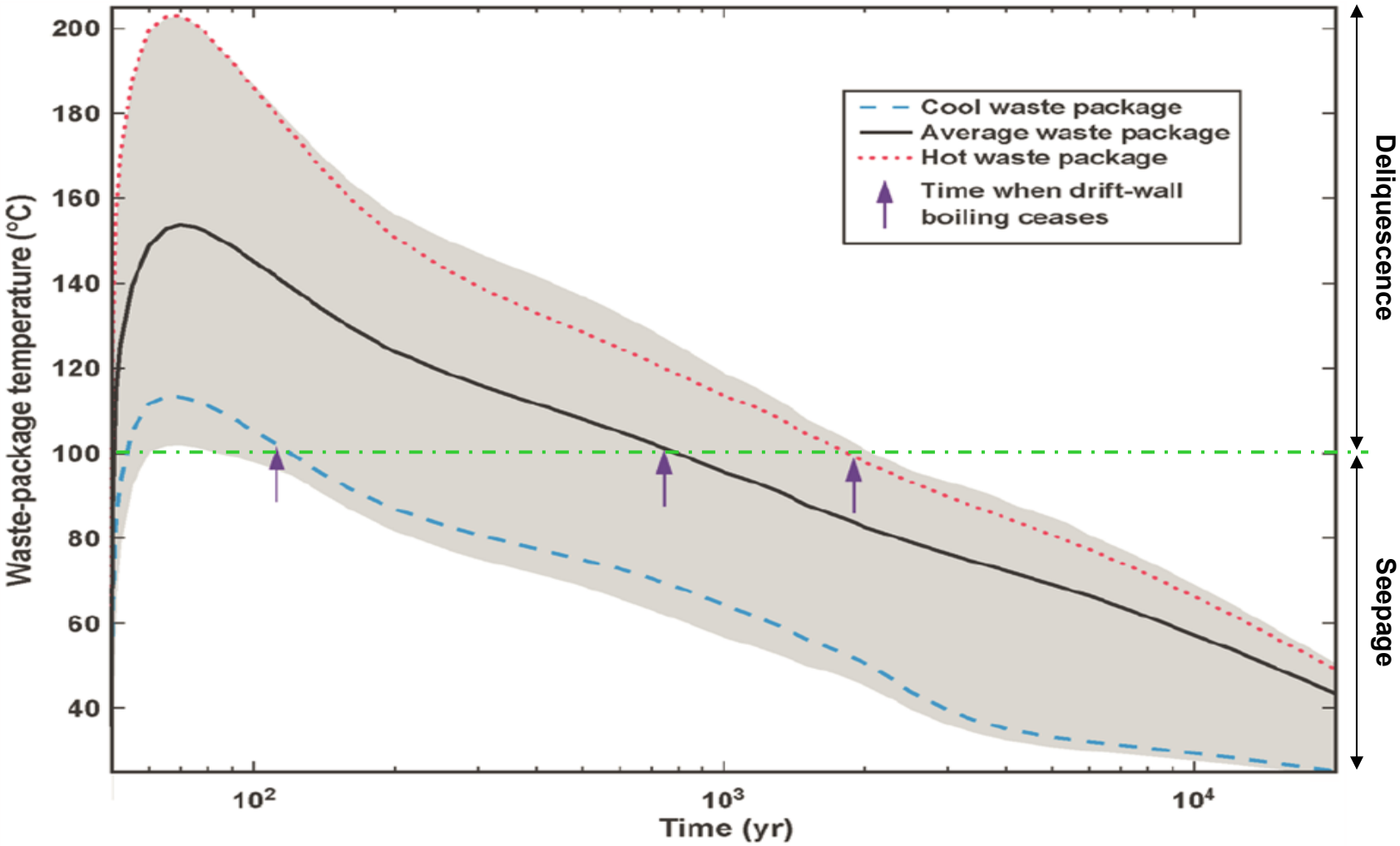
The Engineered Barrier System



Evolution of Temperature/RH on the Waste Package Surface



Two Types of Chemical Environments

Deliquescence

- Soluble salts deposited on the WP during pre-closure
- Drip shields control post-closure dust accumulation
- Multi-salt assemblages control deliquescence at higher temperatures
- Brine compositions become dilute as T decreases RH increases
- Amount of brine contacting metal surfaces is limited
- Chemistry is moderated by contact with rock-forming minerals in dust
- Brines change with time due to degassing, deliquescence

Seepage

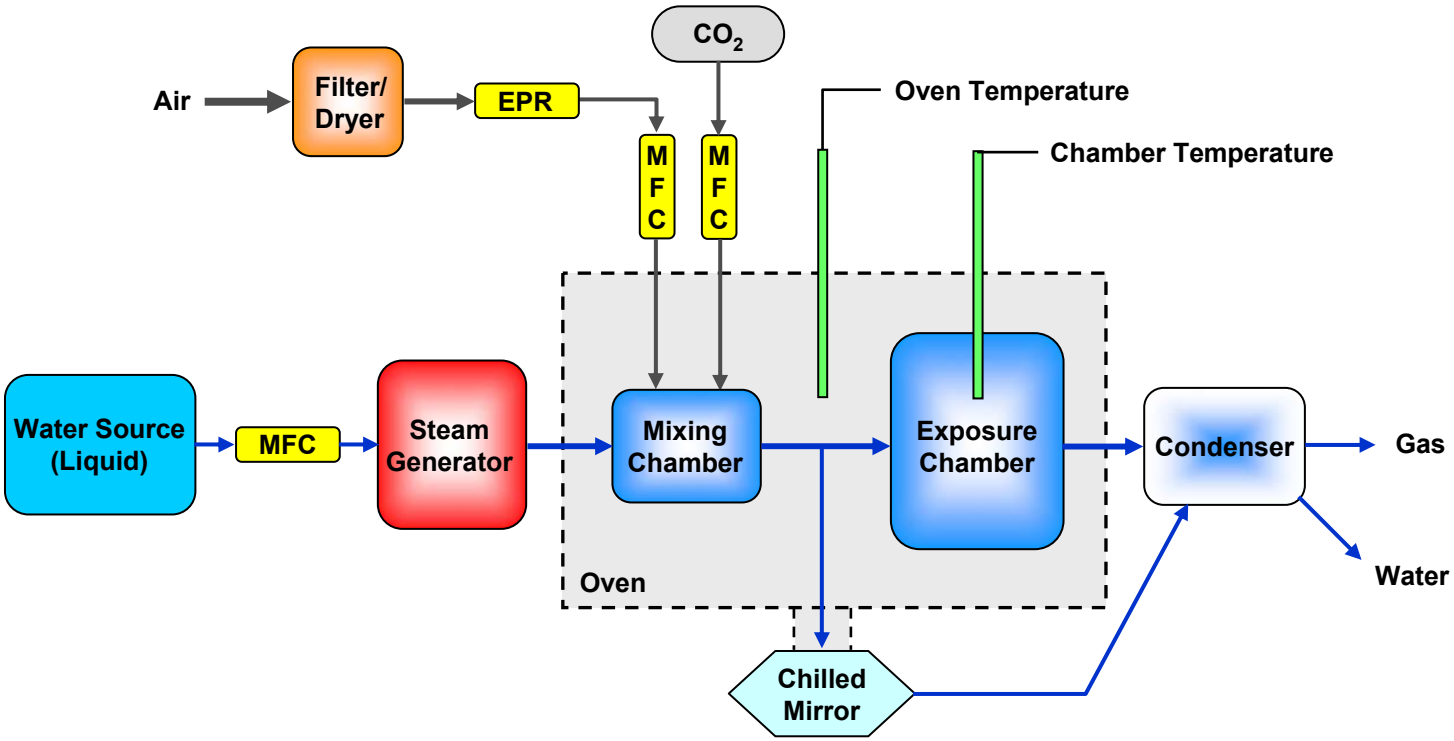
- Seepage may occur after cooldown (T_{WP} < 105°C)
- WP outer barrier is protected by the drip shields
- Residence time (equilibrium with T, RH at WP surface) controls the corrosion environment
- Chemical conditions (pH, Cl^-, NO_3^-, NO_3^-/Cl^-) are potentially corrosive early during cooldown
- Chemical fractionation may occur during transport

Current Area of Interest

- Bulk of work conducted to date focused on seepage environments
- Deliquescent conditions have been addressed to a limited extent
  - Project data – Thin film experiments, Autoclave experiment
  - CNWRA – corrosion performance in bulk brines
- Focus of this work – behavior of engineered barrier materials under deliquescent conditions
  - Environmental conditions
  - Corrosion performance

Generation of a High Dewpoint Environment (95°C+) at Atmospheric Pressure

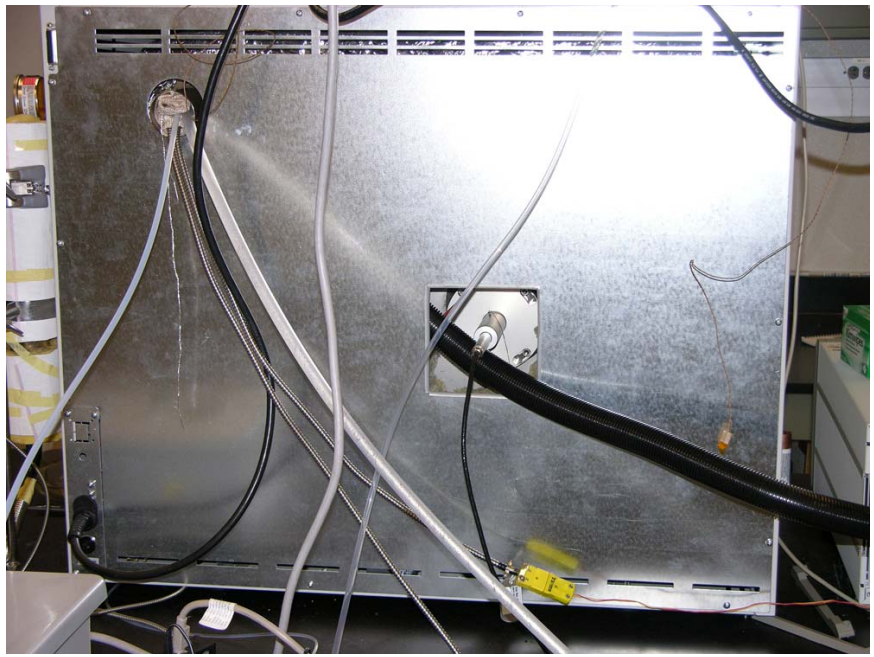
- Schematic of High-T, controlled moisture content system



EPR = Electronic Pressure Regulator and MFC = Mass flow controller

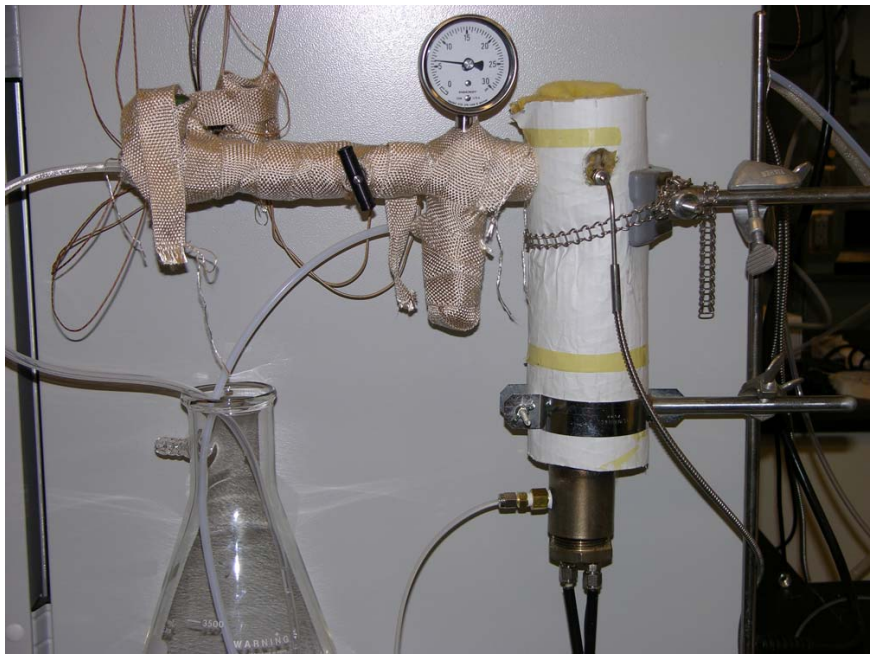
High Temperature, Controlled Dewpoint System

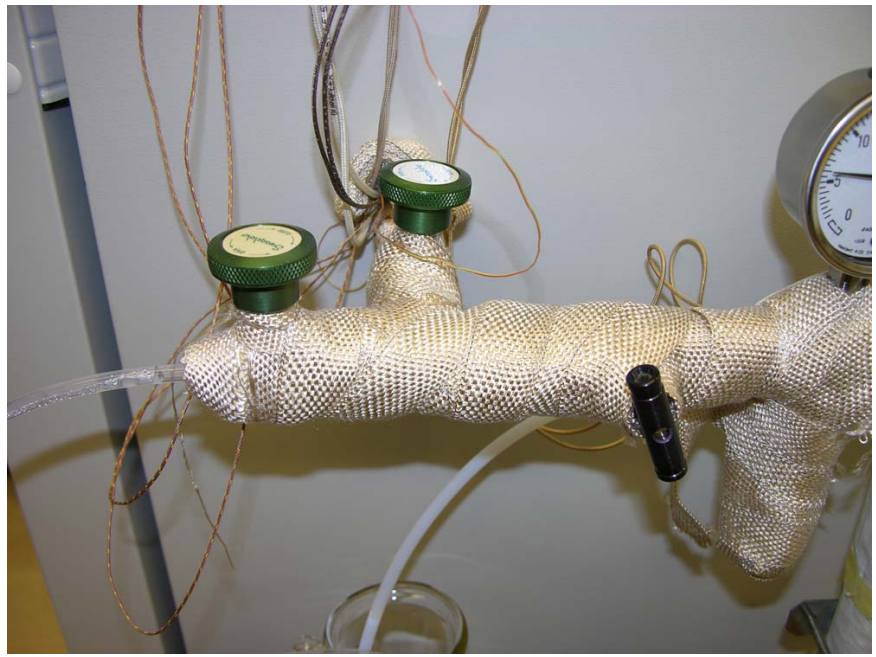
High Temperature, Controlled Dewpoint System



- **Preheaters within the oven as well as heated lines required to prevent condensation**

High Temperature, Controlled Dewpoint System





- **Steam delivery system allows precise mass control of water delivery to the exposure chamber**

Relevant Dust Sources and Composition

Current model is based on two sources of dust:

- **Yucca Mountain tunnel dusts**
  - **Dominantly rock powder, <1% highly soluble salts (Peterman et al., 2003, *IHLRWM Conf. Proceedings*)**
  - **Important deliquescent mineral assemblages:**
    - **$NaCl$-KNO_3**
    - **$NaCl$-KNO_3-$NaNO_3$**
    - **$NaCl$-KNO_3-$NaNO_3$-$Ca(NO_3)_2$**
- **Atmospheric dust**
  - **Site-specific data, 6 locations near YM (Reheis and Kihl, *JGR*, 1995)**
    - **Highly soluble salt load—10.5% (avg)**
    - **Carbonate content—9.5% (avg)**
  - **Solubles—National Atmospheric Deposition Program (NADP) regional precipitation (rain-out) data**

Sample #	Ca mg/L	Mg mg/L	K mg/L	Na mg/L	NH_4^+ mg/L	NO_3^- mg/L	Cl^- mg/L	SO_4^{2-} mg/L	NO_3^-/Cl^-
NV00-2002	0.48	0.044	0.013	0.059	0.26	1.14	0.09	0.46	7.3
NV00-2001	0.66	0.068	0.042	0.113	0.69	2.15	0.16	1.01	7.7
NV00-2000	1.21	0.137	0.055	0.263	1.01	3.24	0.36	1.35	5.2

NADP/NTN 2000, Part 2.; NADP/NTN 2001, Part 2.; NADP/NTN 2002, Part 2.

Brine Evolution in a Thin Dust Layer

- **Quantity of salts is low in the brine layer**
  - **1.8 µL/cm^2 (18 µm thick layer) at 120°C – decreasing with increasing temperature**

- **Numerous processes which may alter the composition of the brine**
  - **Acid degassing**
  - **Reaction with other material in the dust**
  - **Dilution due to changes in atmospheric dewpoint**

- **Relevant brine composition will be a function of the initial salt chemistry in the dust, but will not necessarily be identical to the initial chemistry.**

Processes Affecting Brine on the Waste Package Surface

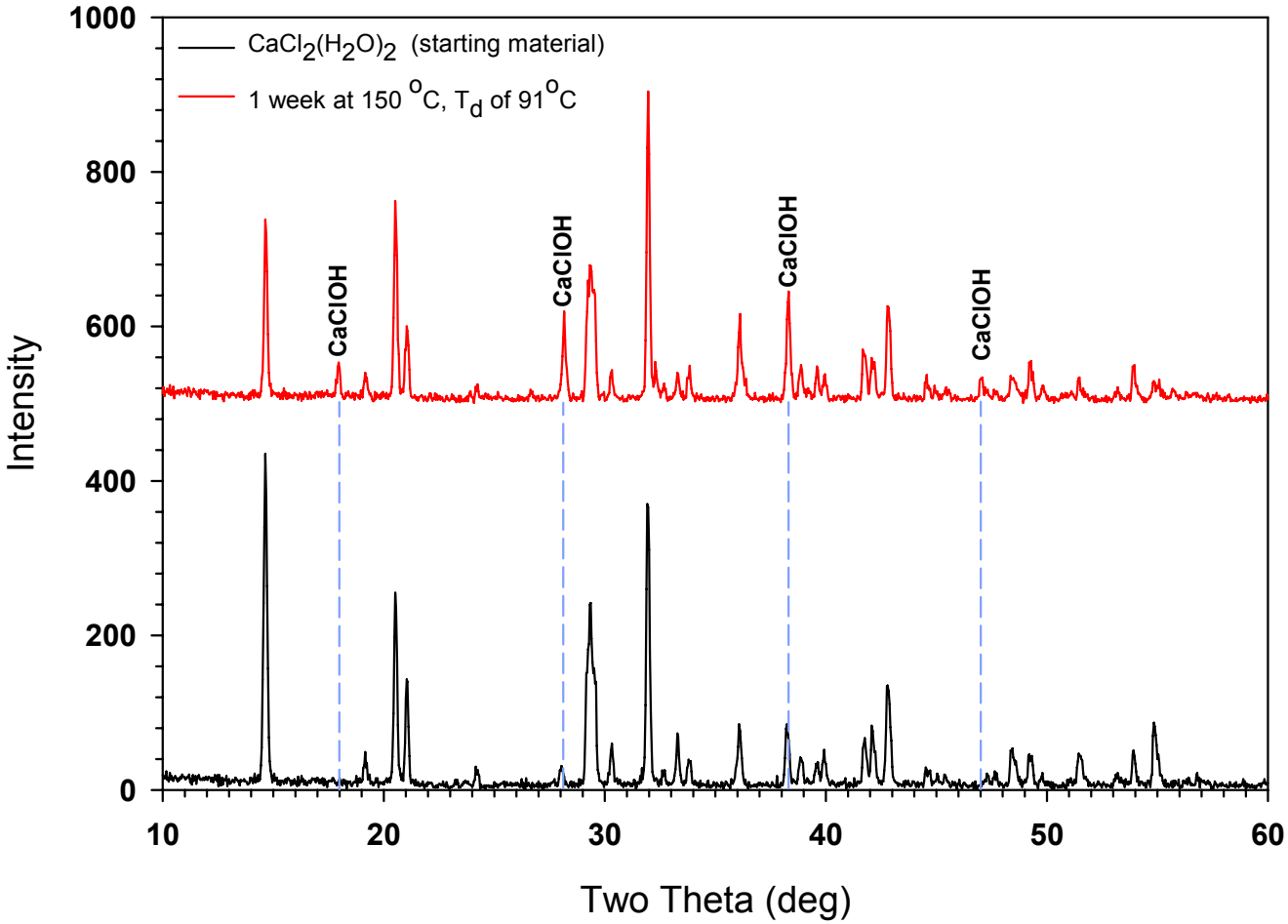
- Acid degassing — $H^+_{(aq)} + Cl^-_{(aq)} \leftrightarrow HCl_{(aq)} \leftrightarrow HCl_{(g)}$
  - Ca-chloride brines degas and dry out (TGA experiments)
  - Multiple-salt assemblages can deliquesce at higher temp:
    - Acid-degassing may occur initially, but less as pH increases
    - Brines may not degas sufficiently to dry out
    - NO_3/Cl minimum ratio is controlled by temperature
- Reactions with silicate minerals in dust
  - Silicate dissolution buffers pH
  - Ca, Mg removed from brine as silicate phases
  - Deliquescence RH generally increases (brines may dry out)
  - Possible consumption of chloride by silicates
    - Scapolite-, cancrinite-, sodalite-, prehnite-group minerals
    - Clays (exchange for hydroxides)
- Dilution with decreasing temperature, increasing humidity

Acid Degassing Example: Calcium Chloride

- 1 week exposure at 150°C with a T_d of 91°C

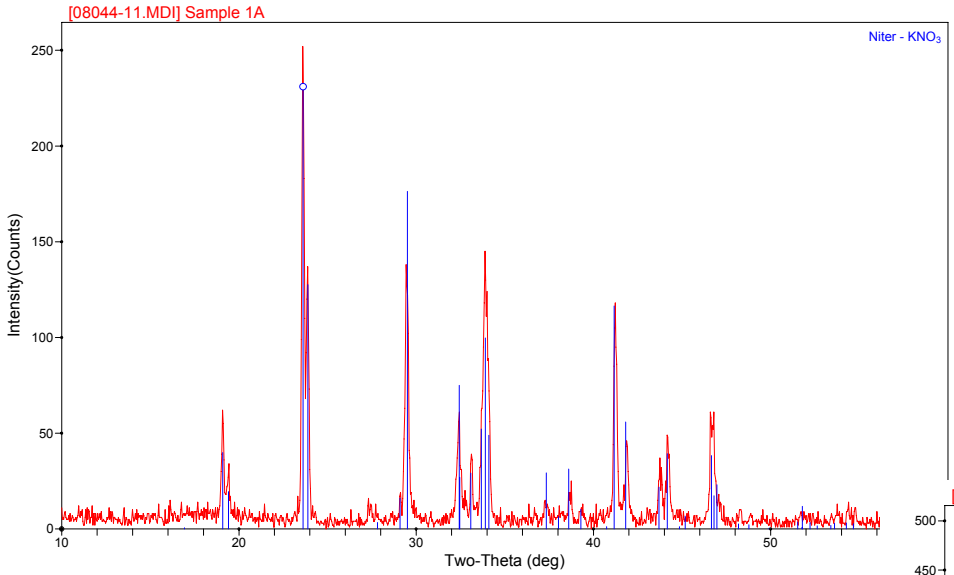
- **Salt deliquesced than dried out (at least macroscopically)**

Calcium Chloride Degassing at 150°C with a T_d of 91°C

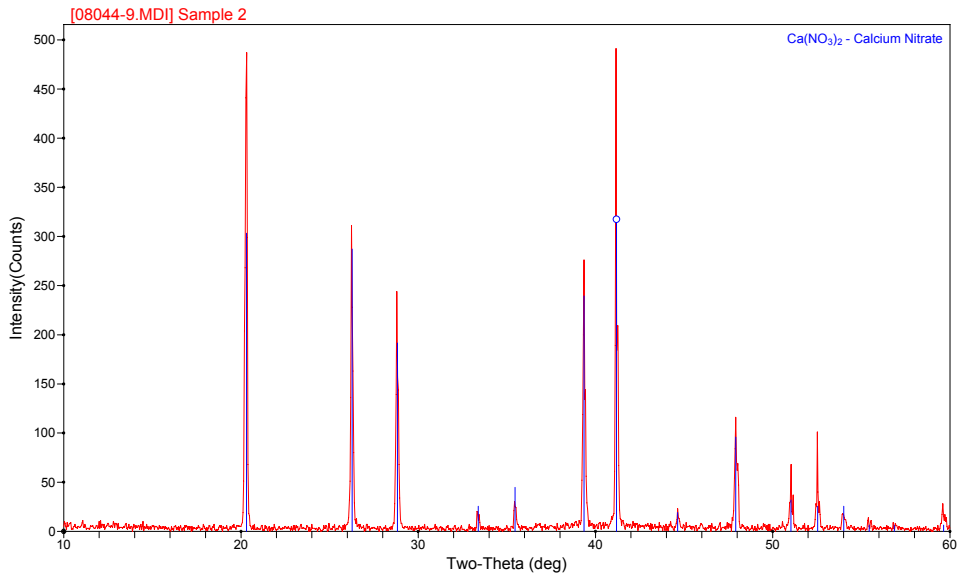


- **CaClOH formed, presumably accompanied by chloride loss as $HCl_{(g)}$**

Multi-Salt Assemblage Behavior



KNO3
1.5 wks at T=180C, Tdew=94.5C
No changes observed

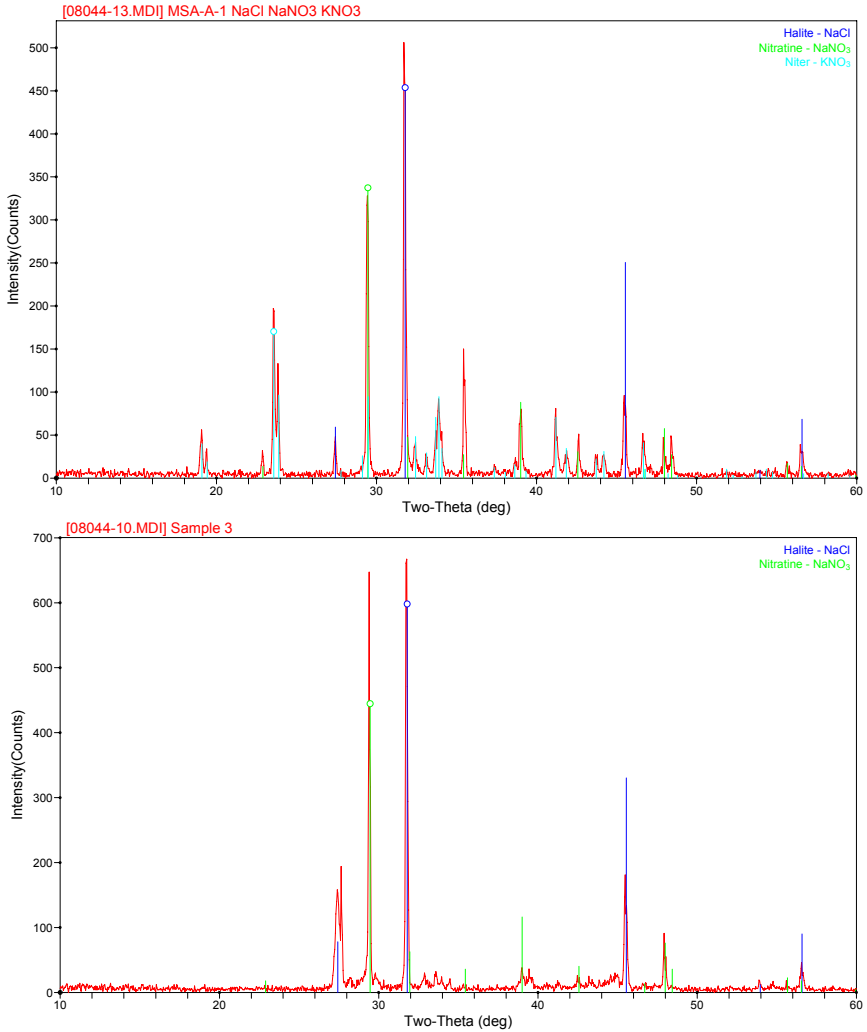


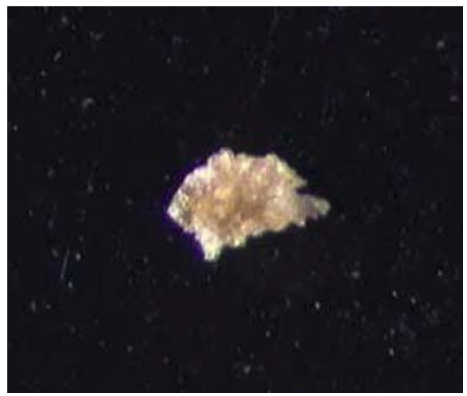
Ca(NO3)2 * 3H2O
1.5 wks at T=180C, Tdew=94.5C
Water removed, but material otherwise unchanged

Multi-Salt Assemblage Behavior

Three salt mixture ($NaCl+KNO_3+NaNO_3$)

- 1.5 wks at T=180°C, T_{dew}=94.5°C

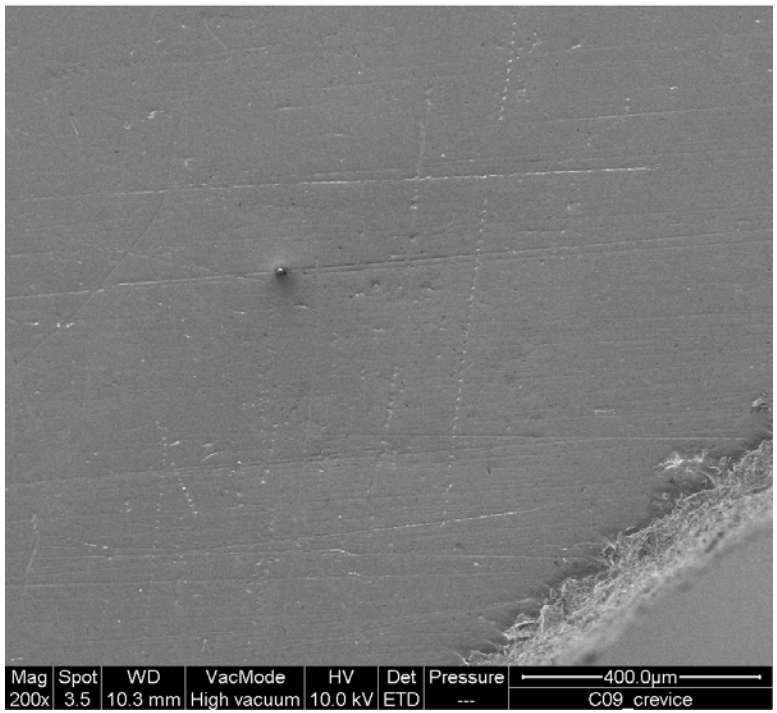


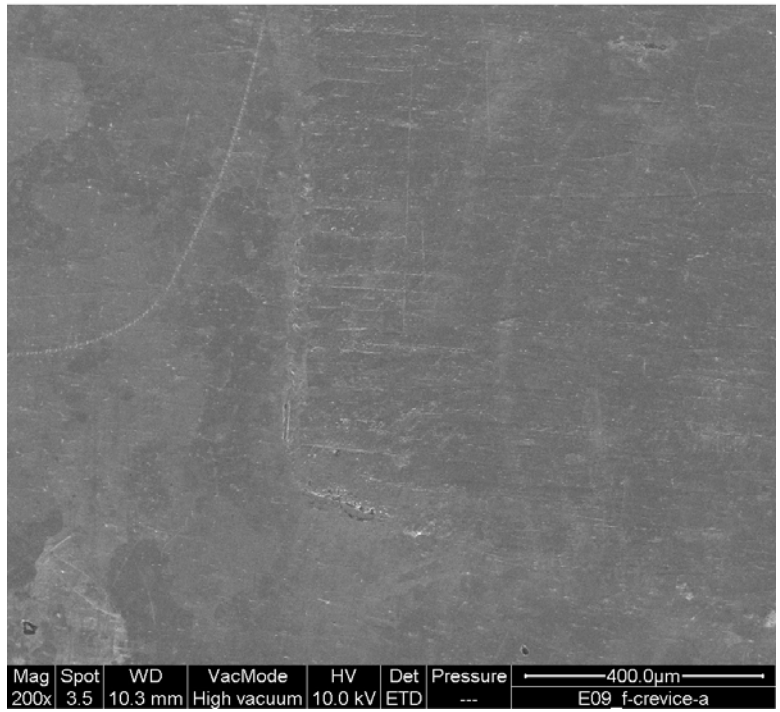


Transformation evident in long term thin film experiments - Insoluble particle formed from 4-salt mixture after 50 days at 180°C, pure steam

Alloys 22 and 825 under Deliquescent Conditions

- Samples exposed to 180°C, T_d=~100°C for 50 days
- Samples had a $NaCl+NaNO_3+KNO_3$ or $NaCl+NaNO_3+KNO_3+Ca(NO_3)_2$ thin salt film





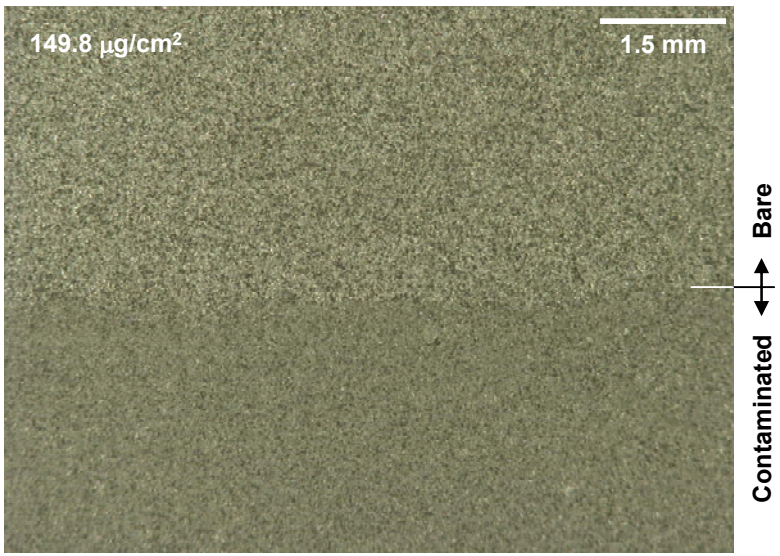
- Neither the Alloy 22 nor the 825 Samples exhibited crevice corrosion
- Note that the 825 sample pictured has not been cleaned – deposits from the salt film are still present

Work performed by R.Rebak, T.Lian, J.Rard, and K.Evans at LLNL

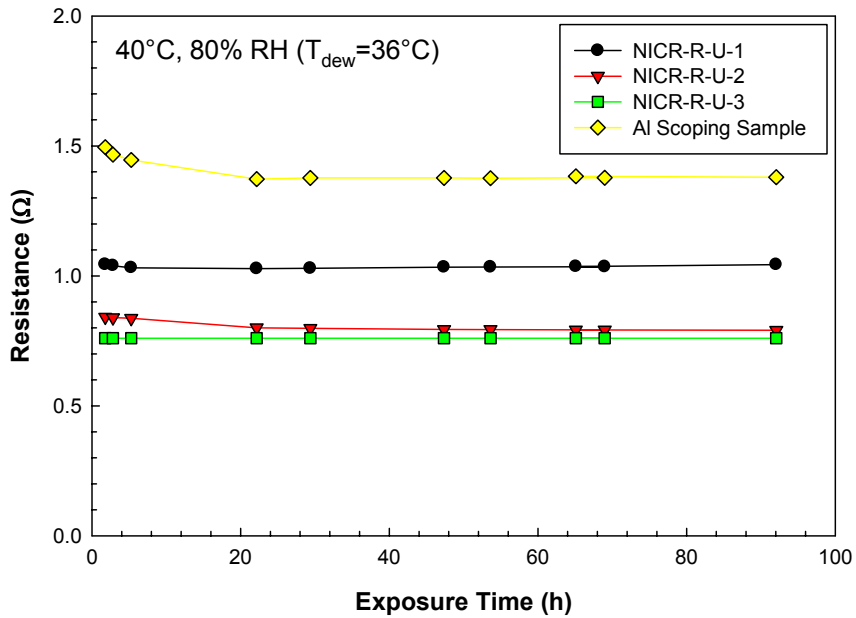
Monitoring Corrosion Under Thin Dust Layer

Proof of concept experimentation

- **Fixture capable of operating in low and high temperature chambers**
- **Samples decorated with ~150µg/cm^2 of 4 salt mixture ($NaCl+NaNO_3+KNO_3+Ca(NO_3)_2$)**



(Alloy 22 coupon shown – rougher surface finish than ribbons)



Summary

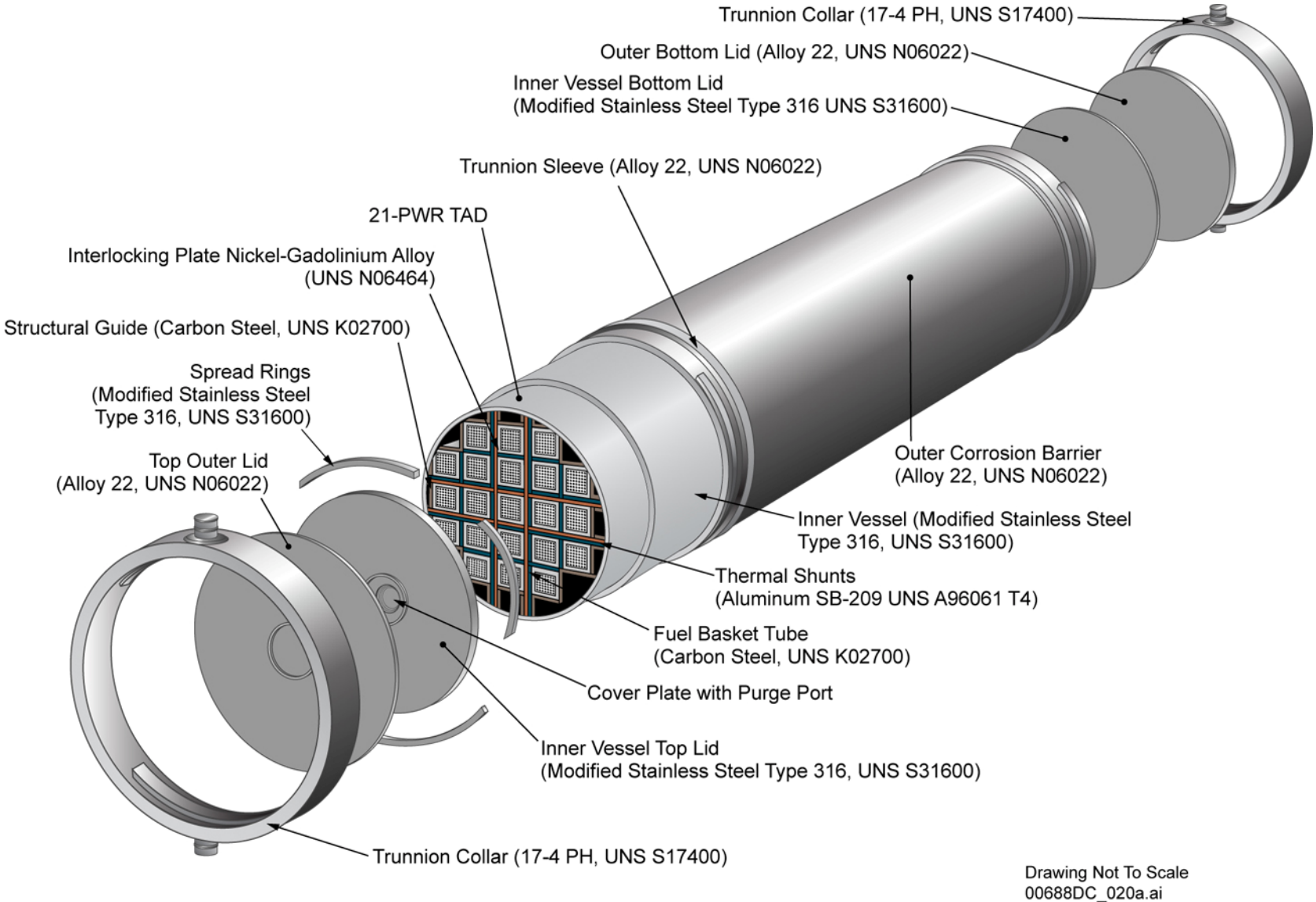
- Environmental chamber has been designed and assembled which allows precise control of the dewpoint at elevated temperatures
  - T_{dew} up to $T_{boiling}$ and $T_{chamber}$ in excess of 250°C.
  - Access to all anticipated in-drift conditions during the thermal pulse.

- Brine evolution is a key aspect to assessing corrosion performance during the deliquescent period.

- Electrical techniques aimed at observing corrosion under aggressive conditions are under development.

Backup Material

Schematic of a Waste Package



The Natural and Engineered Barrier System