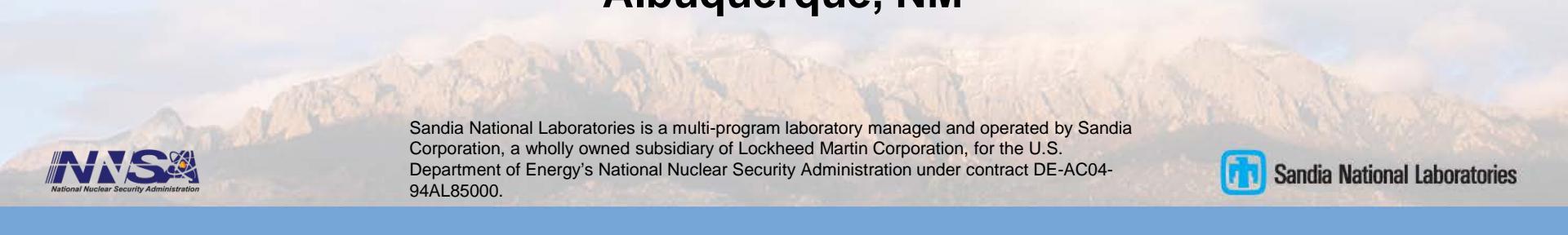


Impact of Atmospherically Deposited Solid Contaminants on Materials of Interest for the Interim and Long Term Storage of High Level Nuclear Waste

NACE International Corrosion 2012
Salt Lake City, UT

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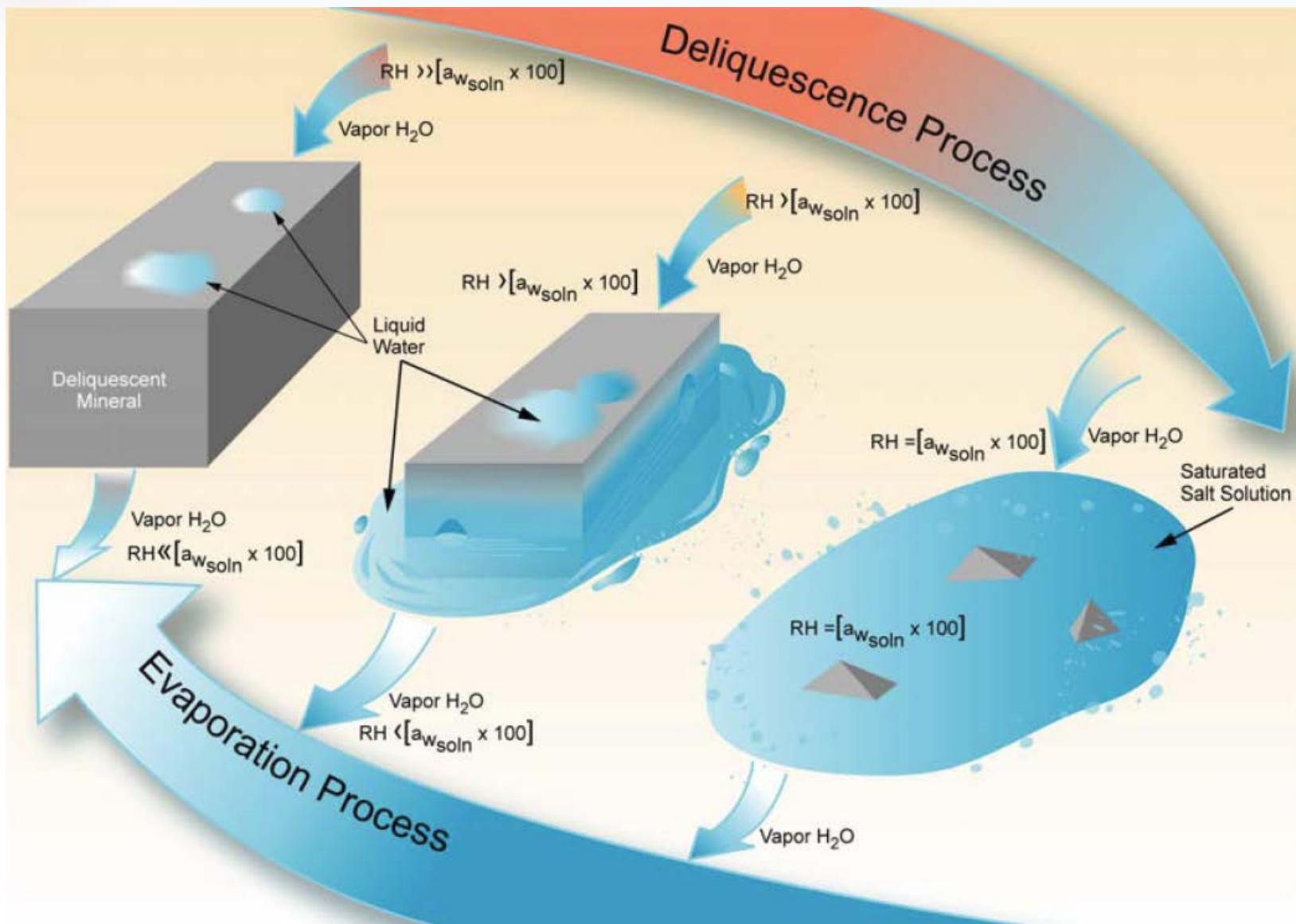
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Motivation for This Work

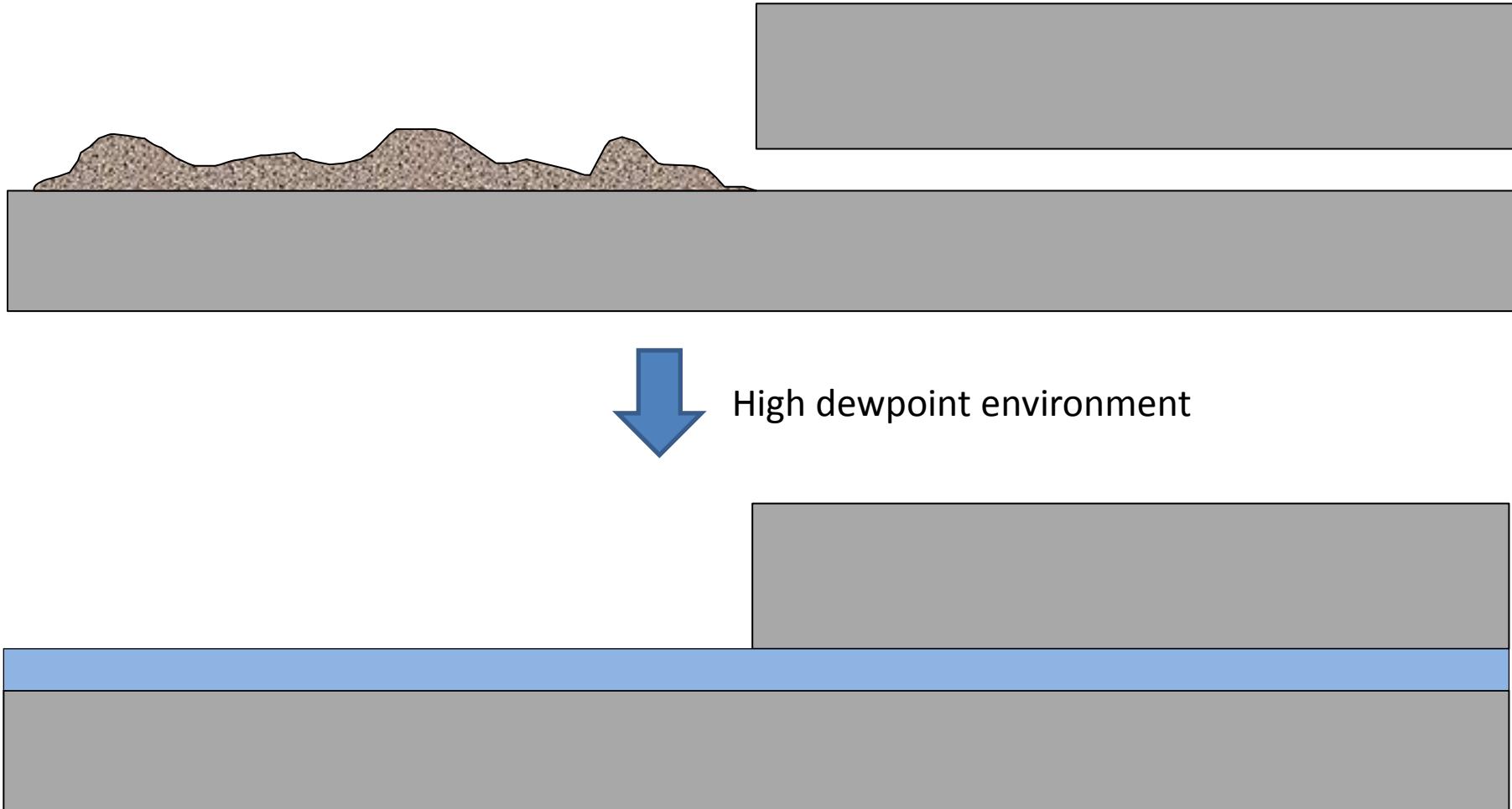
- Long Term Disposal: Numerous groups suggested that salts in dust could deliquesce and create a corrosive environment.
- Interim Storage: Analyses of the gaps in the storage of used nuclear fuel by DOE, EPRI, NRC, and the NWTRB have all identified environmental degradation of the storage system in one form or another as a key research area
 - Corrosion of metallic seals high priority in most analyses
 - SCC of weldments consistently a high priority (literature supports this as an issue)

Atmospheric Corrosion Processes

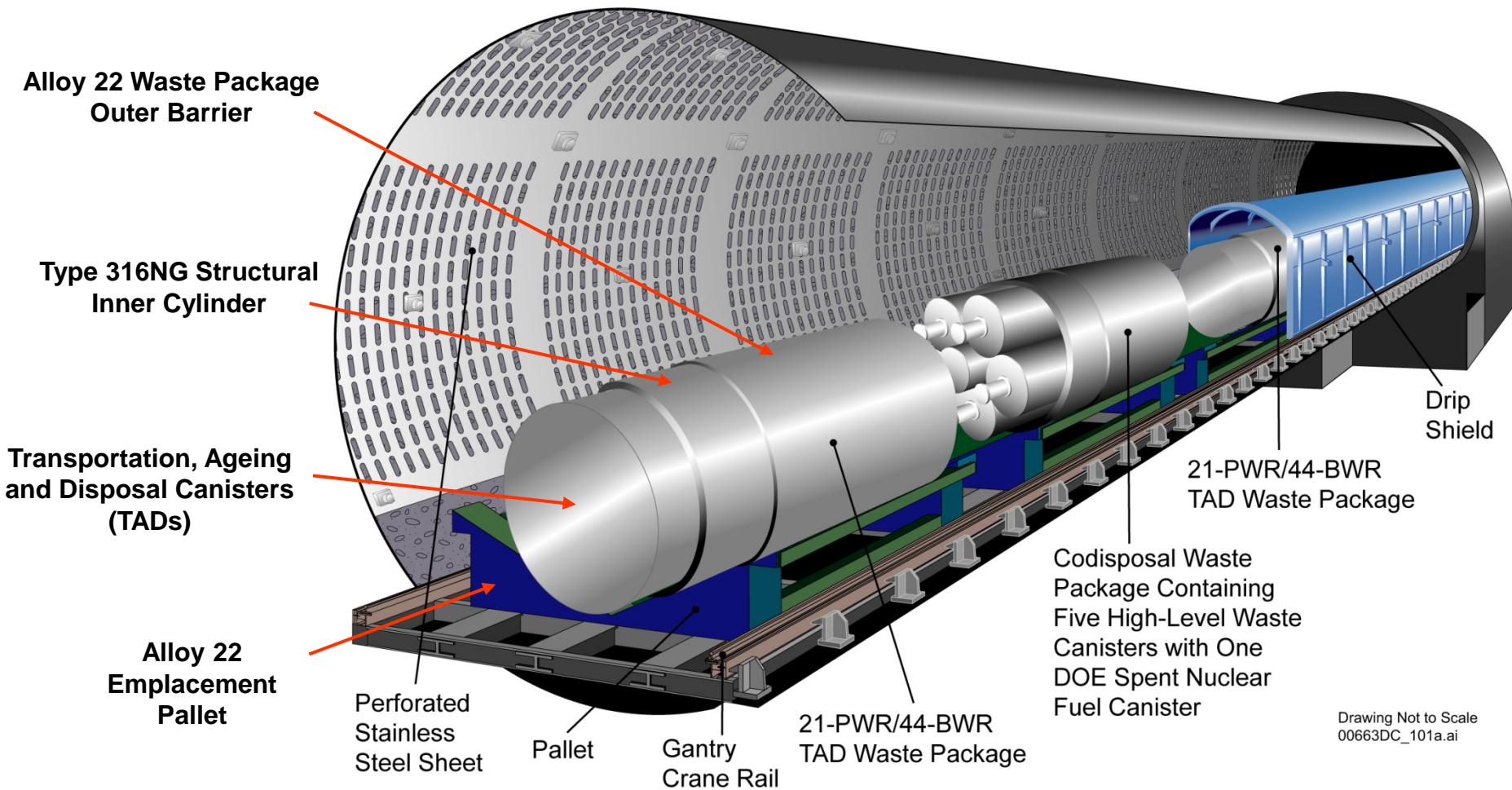




Schematic of Crevice



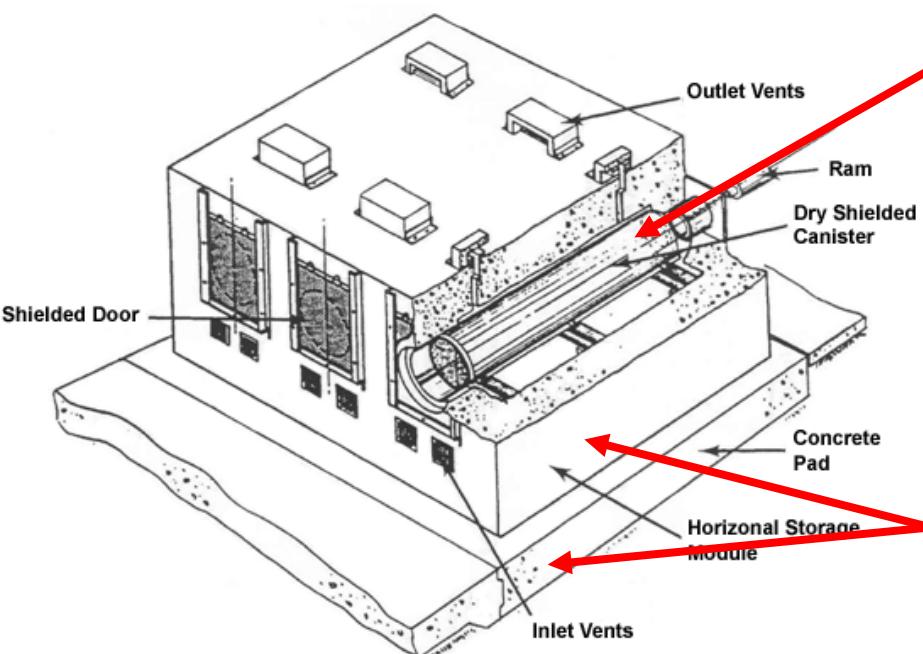
Long Term Disposal



Drawing Not to Scale
00663DC_101a.ai

Interim Storage Systems

Welded (e.g., NUHOMS)



Stainless Steel

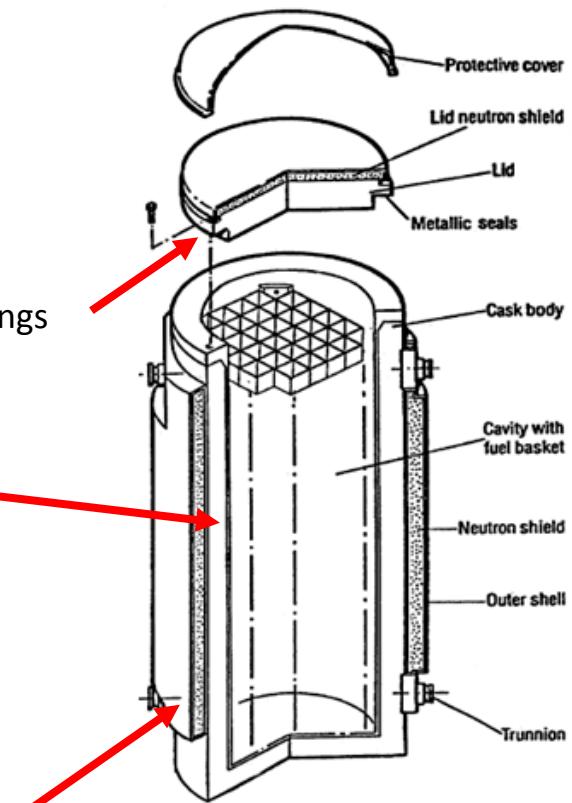
Metal and Polymer O-rings

Carbon Steel

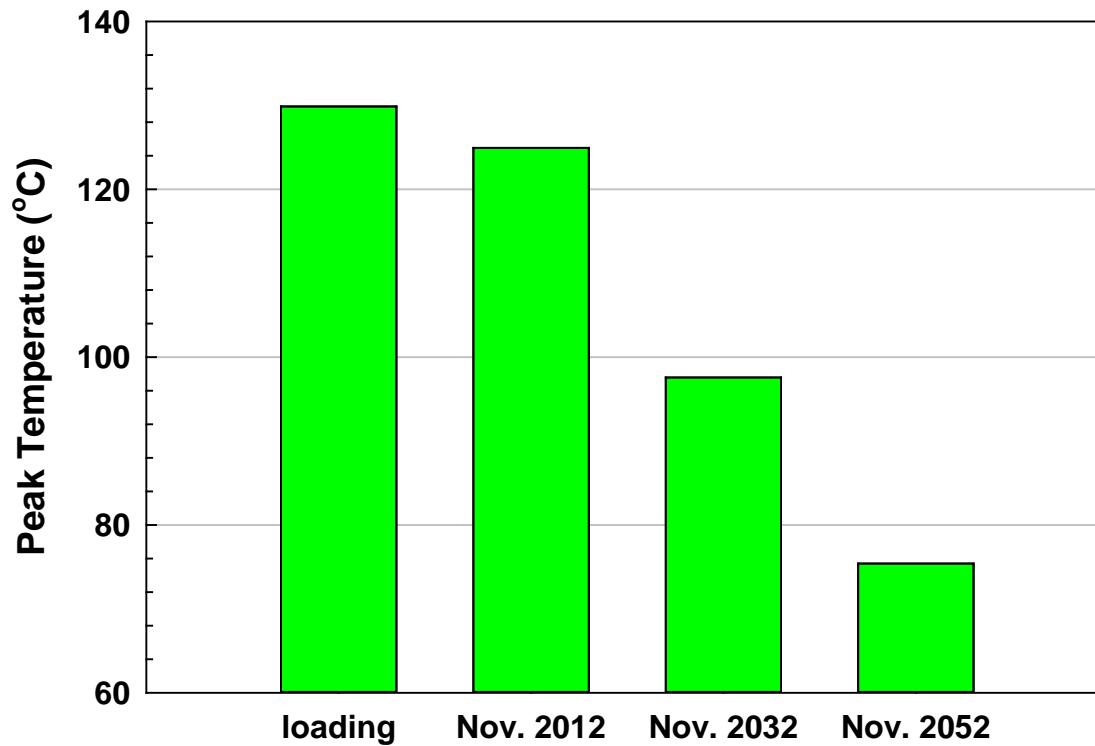
Reinforced Concrete

Polymeric Material

Bolted (e.g., TN-32)



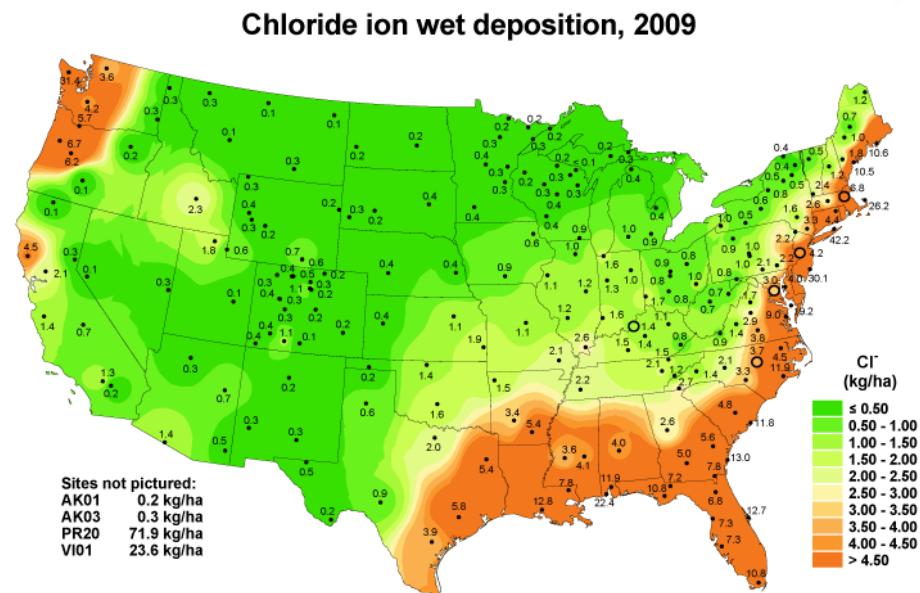
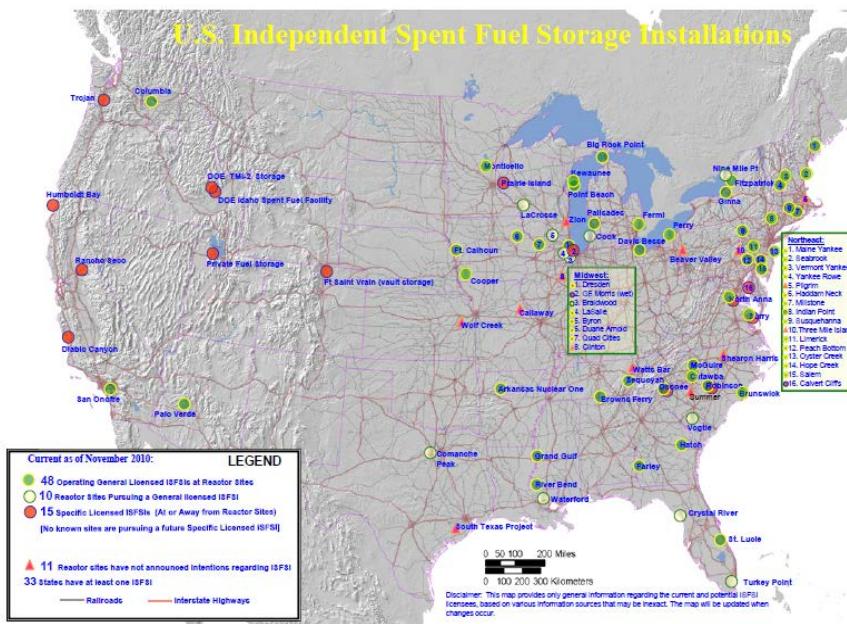
Peak Interim Storage Container Temperatures (Example: Calvert Cliffs ISFI)



From Calvert Cliff's response to NRC RAI Question O-6 (Figure 1, Container 65)

Environmental Conditions

- Many interim storage sites are located in marine environments where significant deposition of marine aerosols is anticipated



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



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 the YMP 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

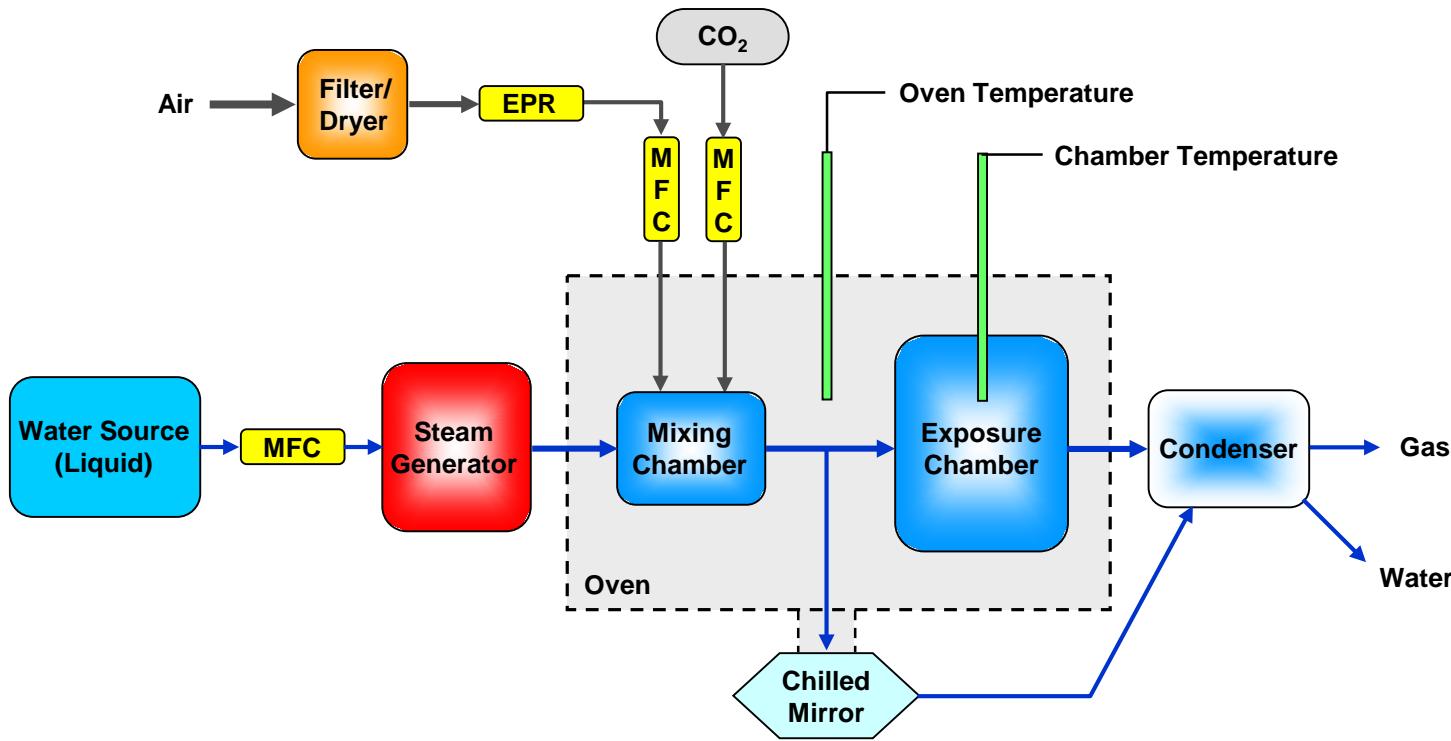


Experimental Approach

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

- A series of relevant materials is being evaluated
 - *Long term disposal:* Alloy 22 and less corrosion resistant analogs
 - *Interim storage:* 304 and 303SS
- Thin film of salt (with known mass loading) deposited on surface, followed by the use of a traditional PTFE coated ceramic crevice former
- Exposure to elevated temperature and dewpoint environment for periods of up to 100 days

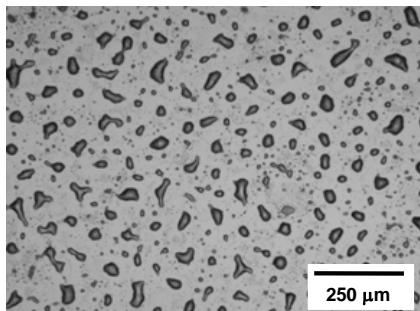
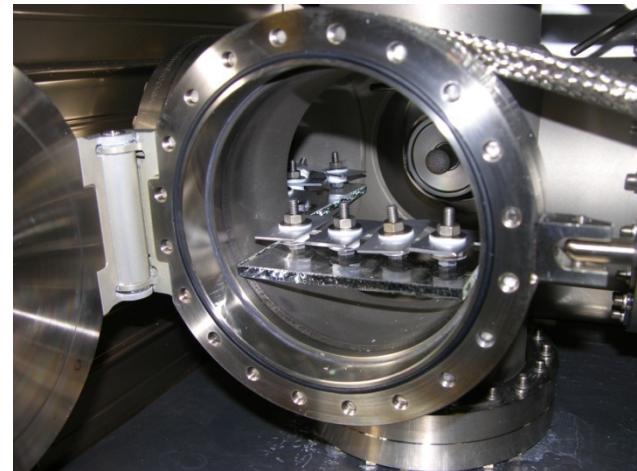
Elevated Temperature, High Dewpoint Exposure System



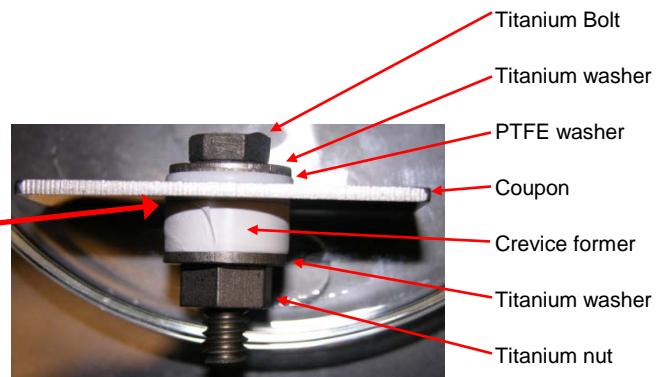
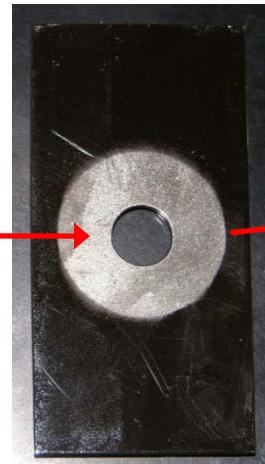
EPR = Electronic Pressure Regulator and MFC = Mass flow controller

Experiments in Nitrate-Rich Brines

- 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



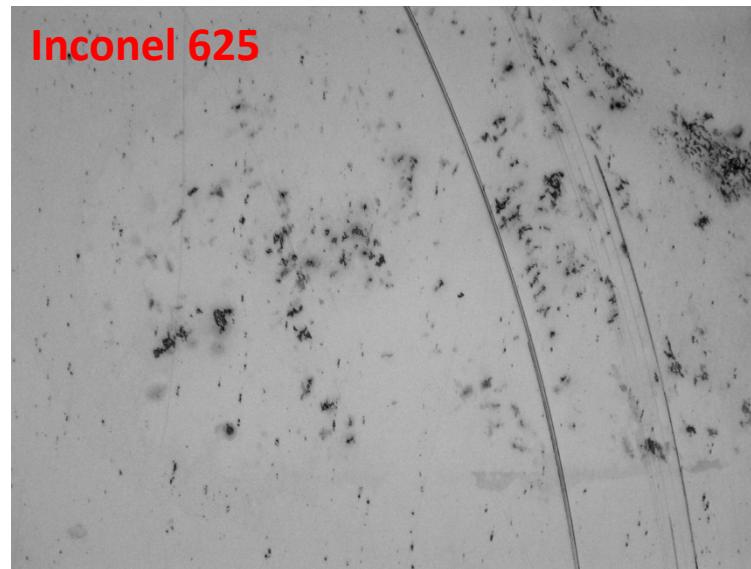
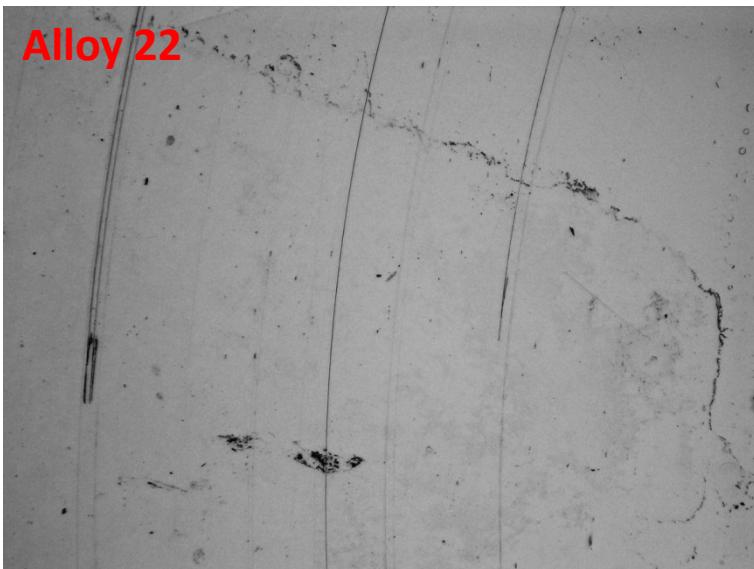
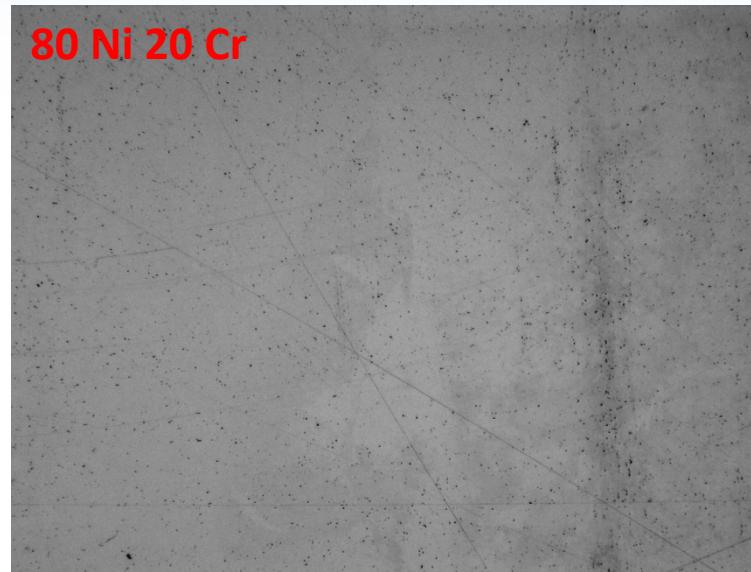
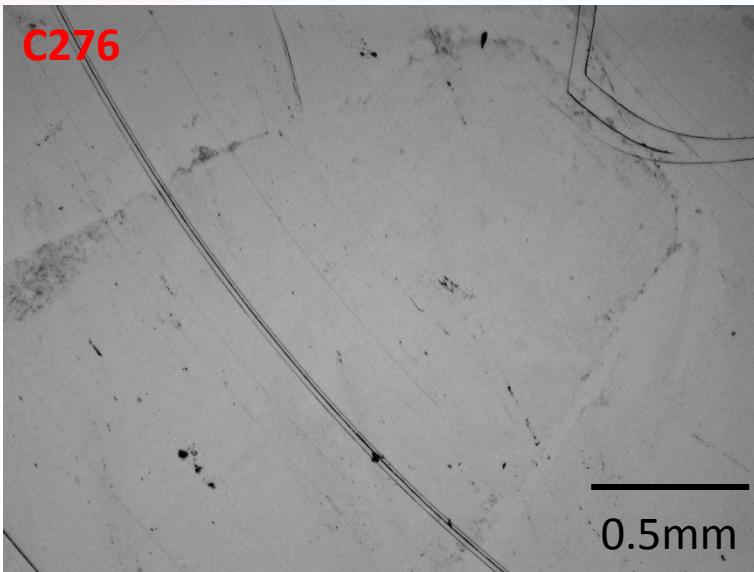
Salt mixture on an Alloy 22 Coupon



(All titanium hardware electrically isolated from the sample)



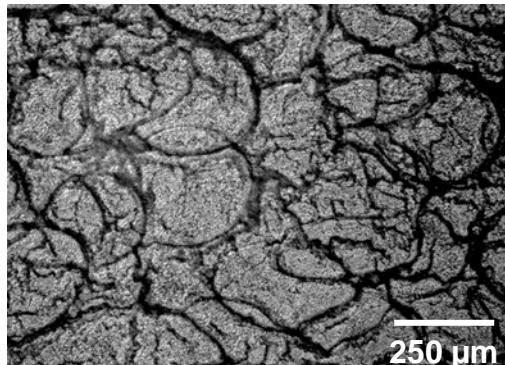
Nickel Alloys in Nitrate Rich Brines



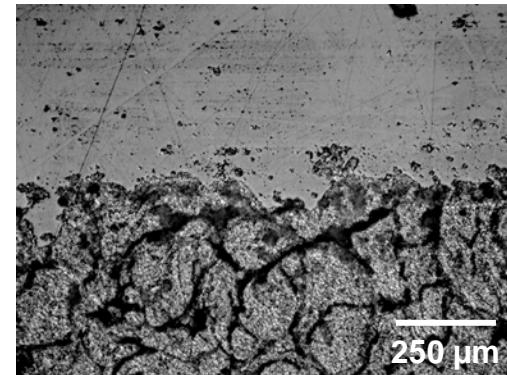
No crevice
corrosion
initiation

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

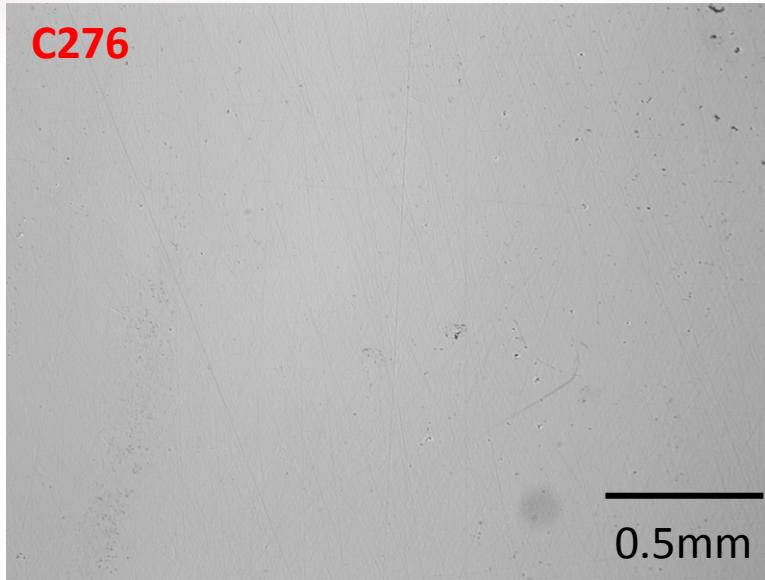


Wiped region

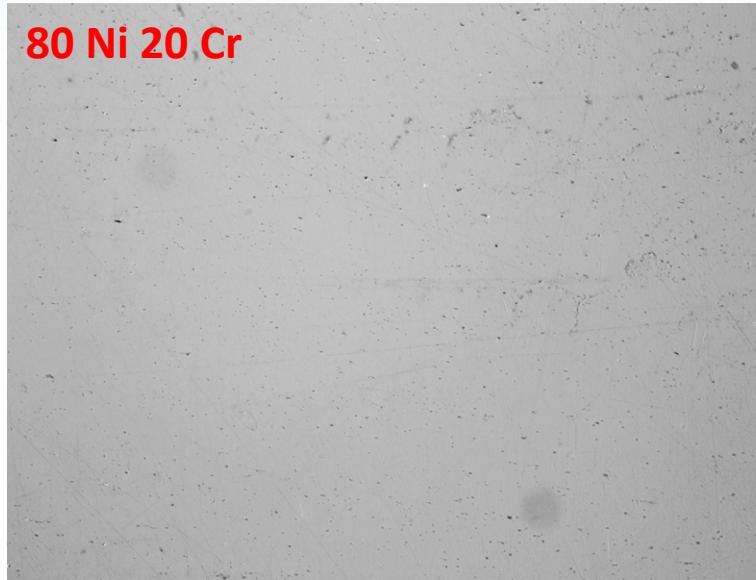


Nickel Alloys in Chloride Brines

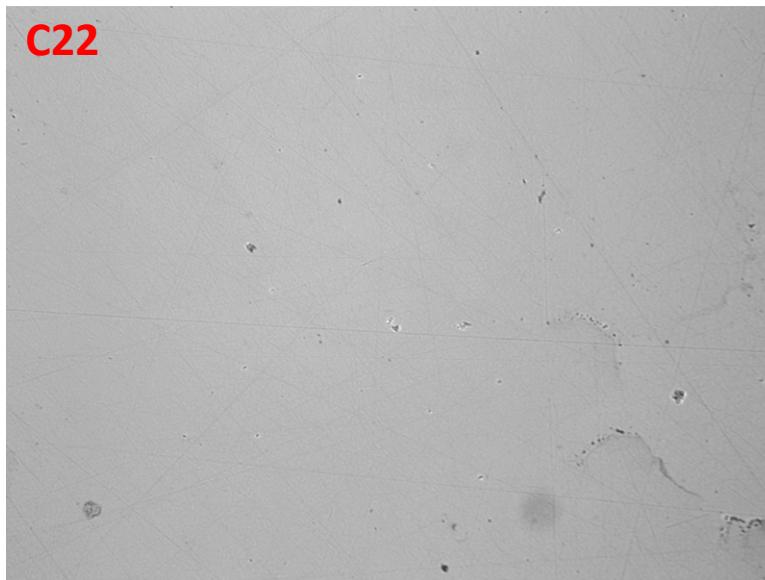
C276



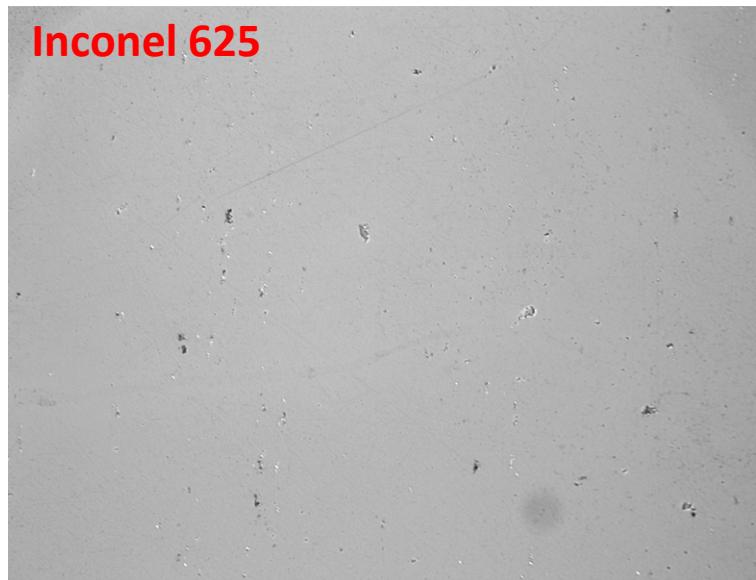
80 Ni 20 Cr



C22



Inconel 625

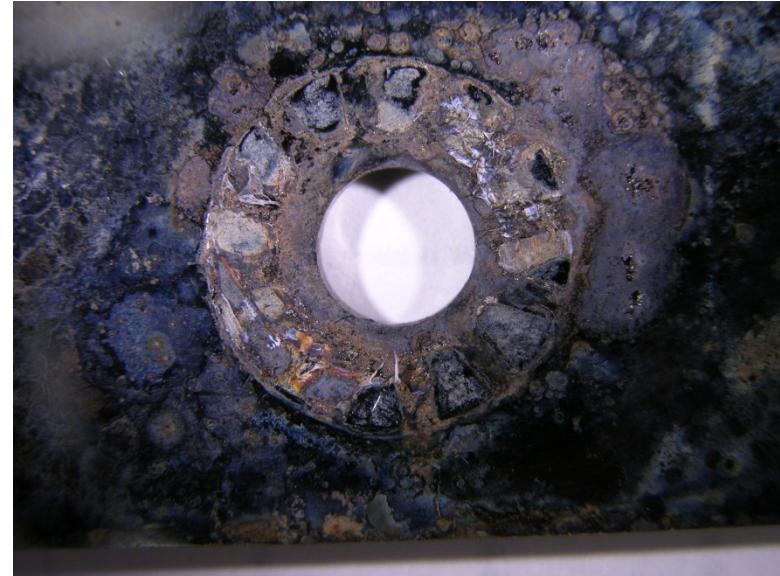


No crevice
corrosion
initiation



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



Stainless Steels in Chloride Rich Brines

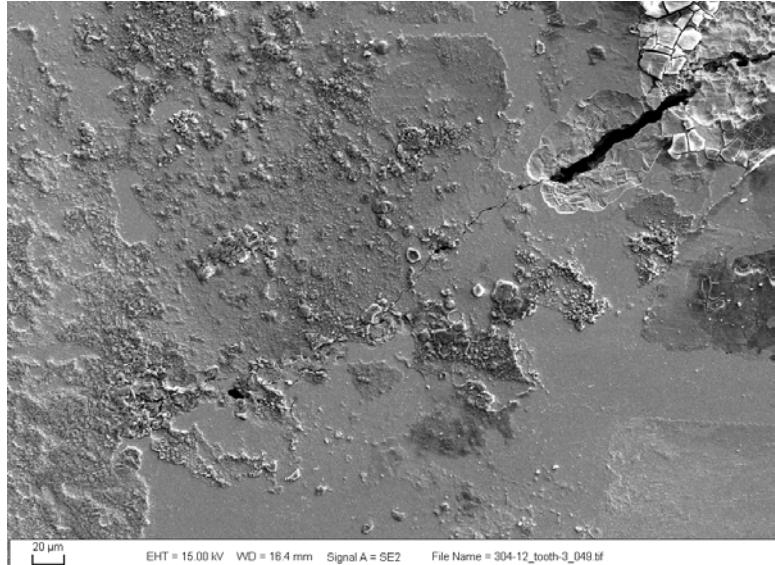
- Three different mass loadings evaluated (50, 100, and 200 $\mu\text{g}/\text{cm}^2$)
- Initiation observed at all mass loadings, but extent of attack correlated with mass loading
- Samples exhibited SCC in a number of cases, but did not correlate with mass loading
- 303SS too susceptible – significant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

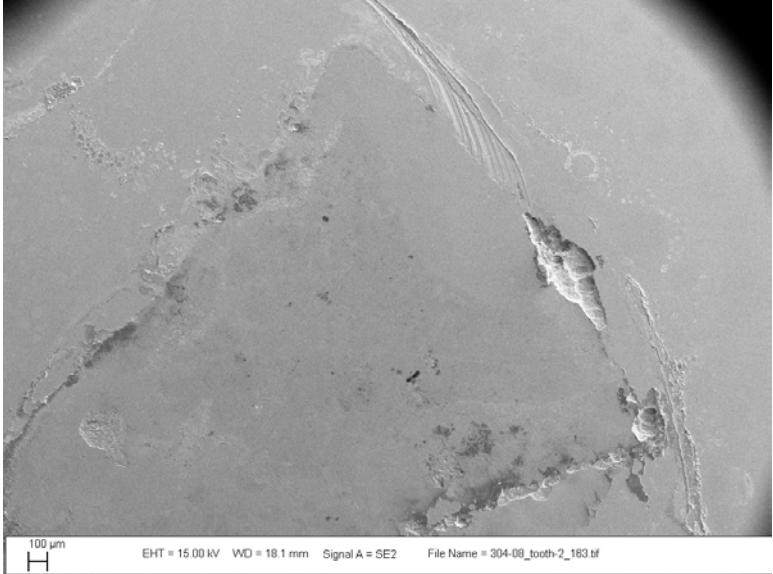
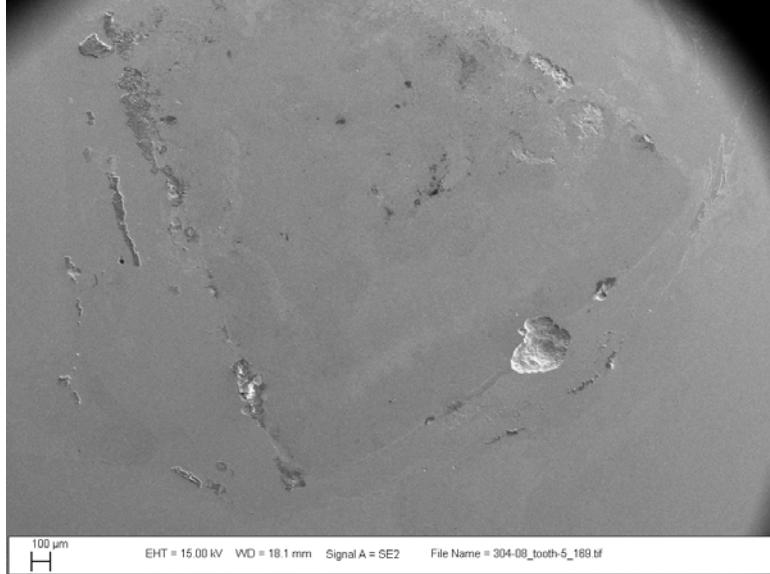
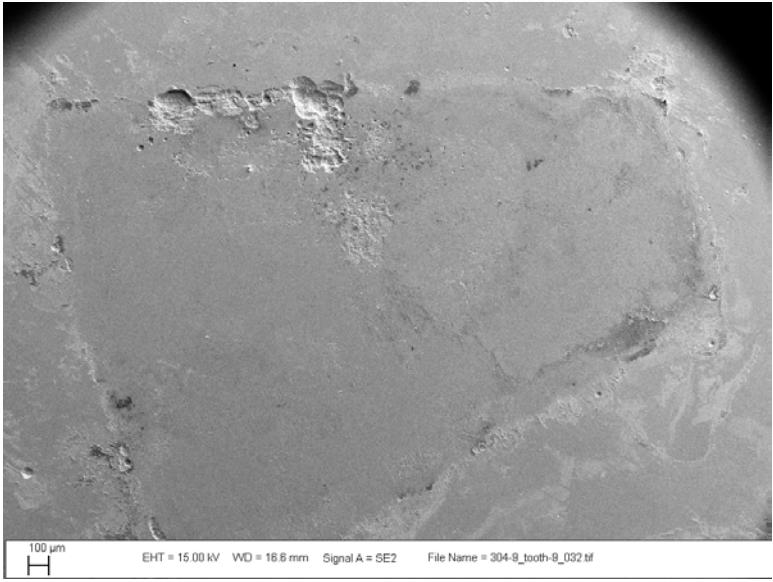




Impact of Salt Loading on 304SS

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)

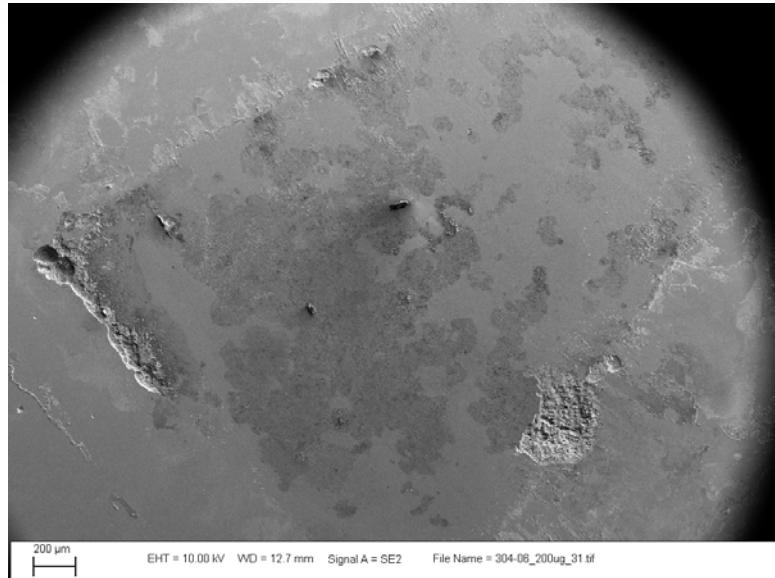
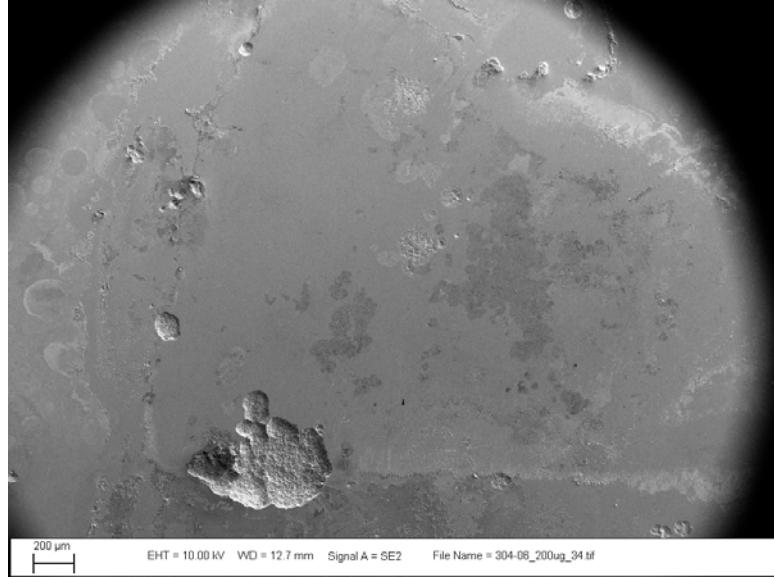




Impact of Salt Loading on 304SS

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)





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 high temperature with a nitrate rich brine did not result in crevice corrosion initiation for a variety of Ni-Cr-X alloys
- 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
- 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

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- Sam Lucero – Salt deposition and experimental setup
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