SAND2012-3989C

Used Fuel Disposition Campaign

Corrosion Related Experimental Work

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Summary of Work in Progress

- **Two experimental programs are currently underway, with two very different goals**
  - Legacy experiments
  - Localized corrosion experiments under deliquescent conditions
- **Both experiments are applicable to a wide variety of potential interim and long-term repository solutions**

Long Term Immersion Tests

- **Initiated in 2010**
  - Opportunity cost associated with halting experiments was high – an alternative funding source was located to maintain the experiments at a maintenance level (i.e., no sample pulls or analyses)
  - Experiments being performed on Hastelloy C22 (i.e., “Alloy 22”) in two environments from previous studies (simulated acidified water (SAW) and simulated concentrated water (SCW)) and one generic environment (0.5M NaCl) at three temperatures
  - Goal: establish a general corrosion rate and temperature dependence which is free from the significant experimental uncertainties of previously generated data..
- **Details**
  - Samples polished to a mirror finish and pickled/passivated prior to exposure
  - Exposure flasks are inert (glass) and care has been taken to avoid contamination with organics or other materials
- **Current Status**
  - Specimens pulled at 3, 9, 18, and 24 months.
  - Weight change and surface condition being assessed
  - Experimental program will be concluded with a final report to be issued at the end of 3Q12

Used Fuel Disposition

Pourbaix Diagram for Cr in Chloride Containing Solutions

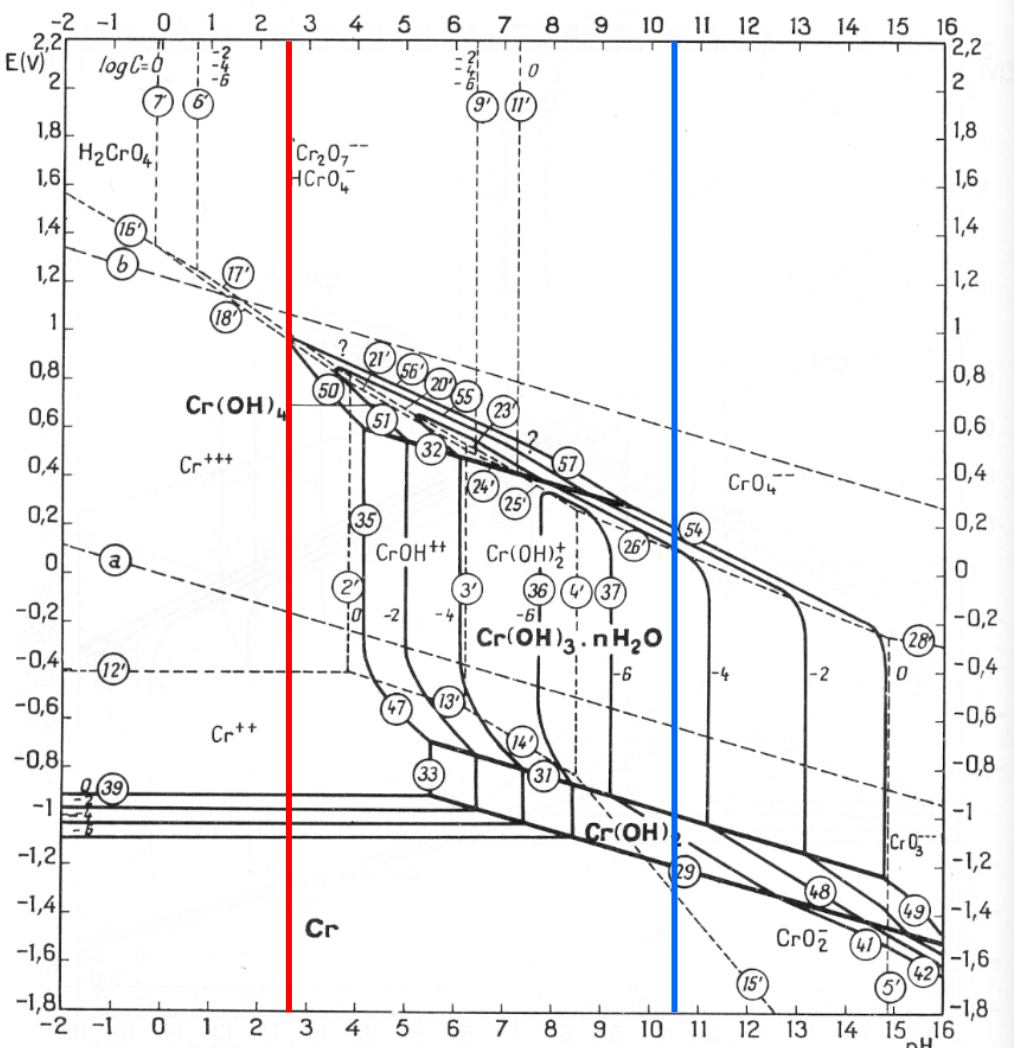
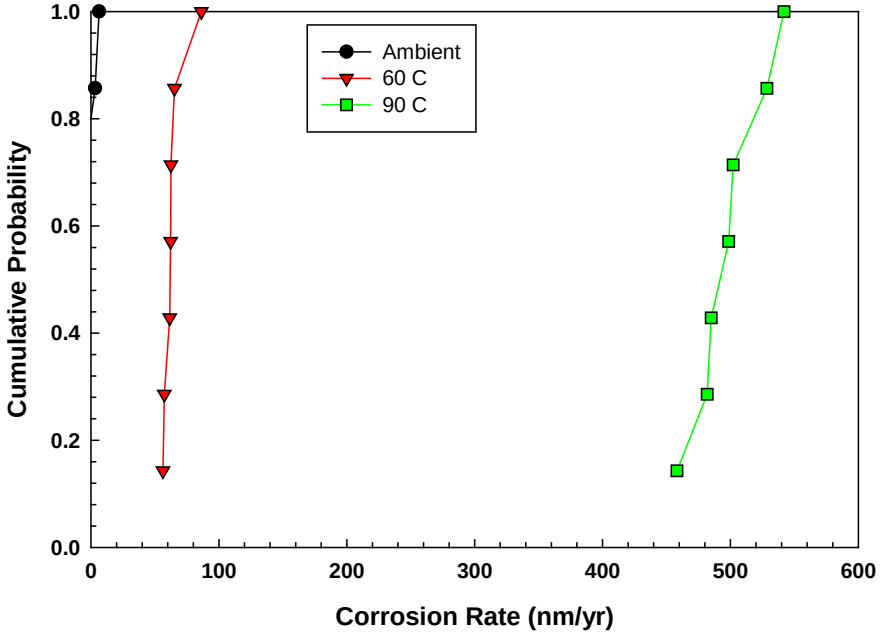


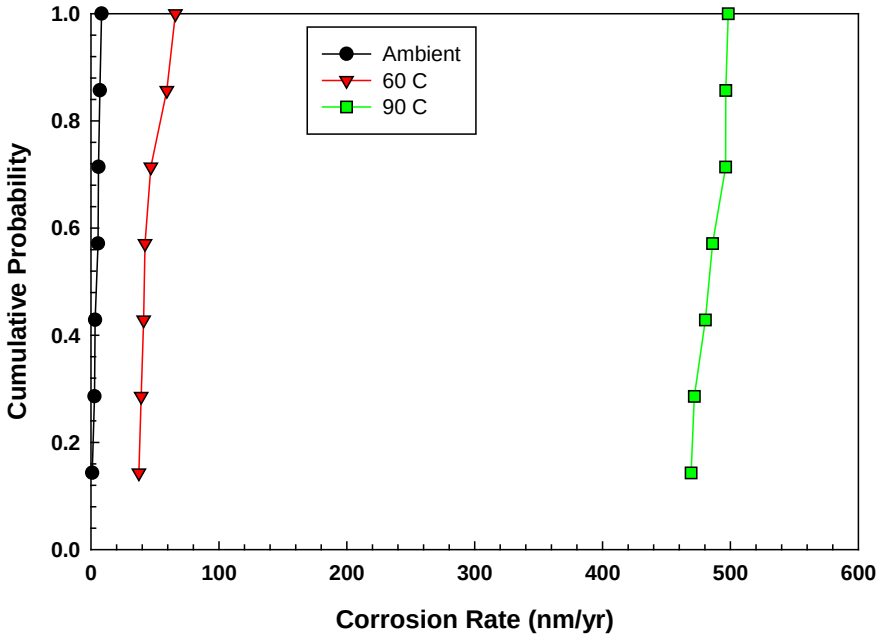
FIG. 4. Potential–pH equilibrium diagram for the system chromium–water, at 25°C.
In solutions containing chloride.
[Approximate representation made by considering $Cr(OH)_3.nH_2O$.]

Used Fuel Disposition

SAW 3 and 9 month



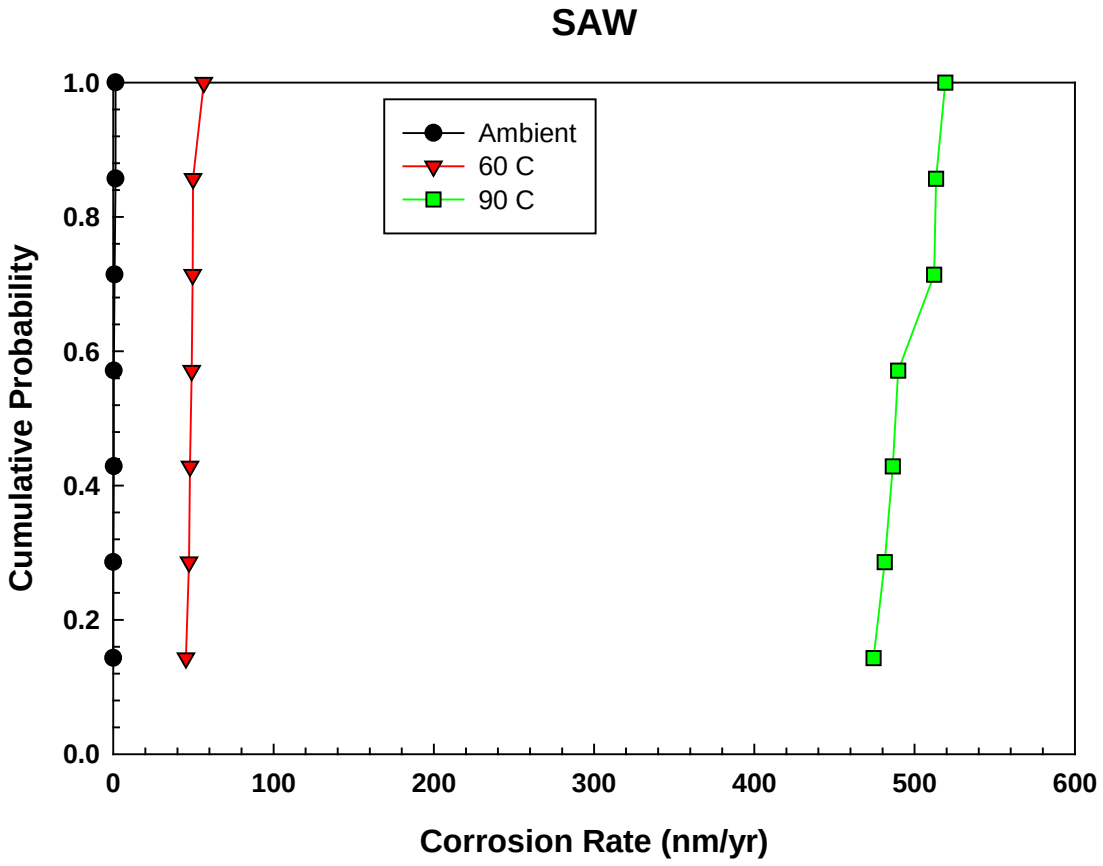
3 month

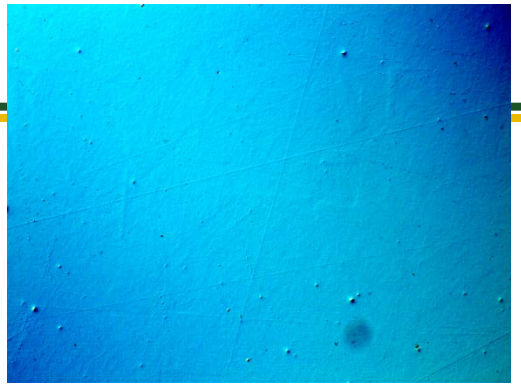


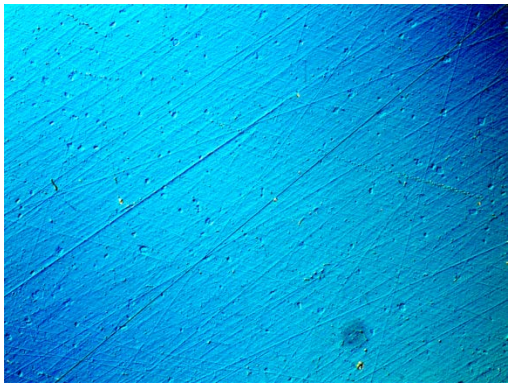
9 month

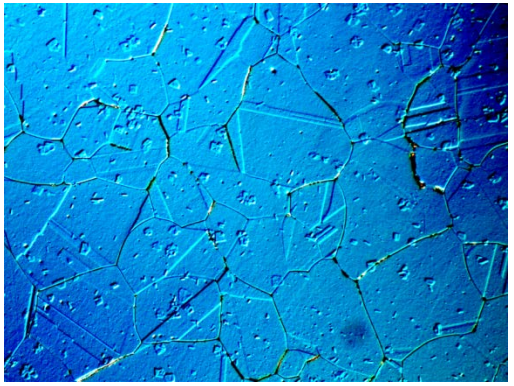
Used Fuel Disposition

SAW 18 month



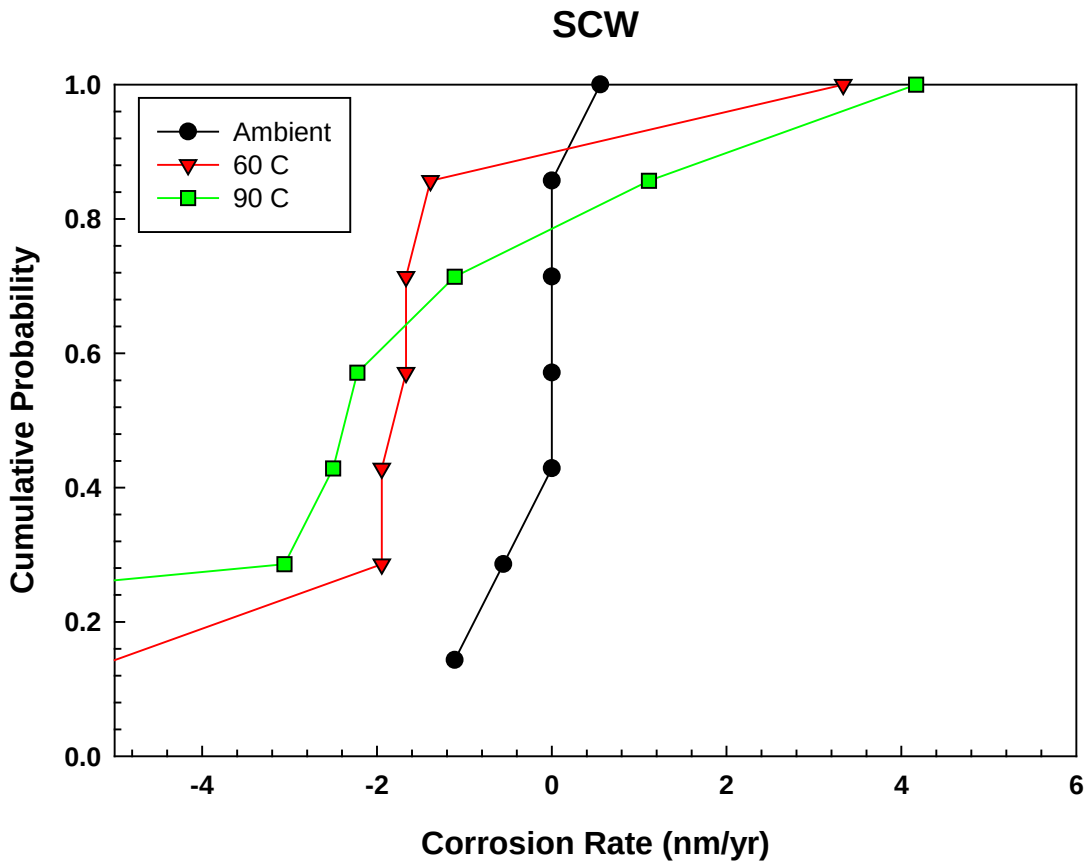






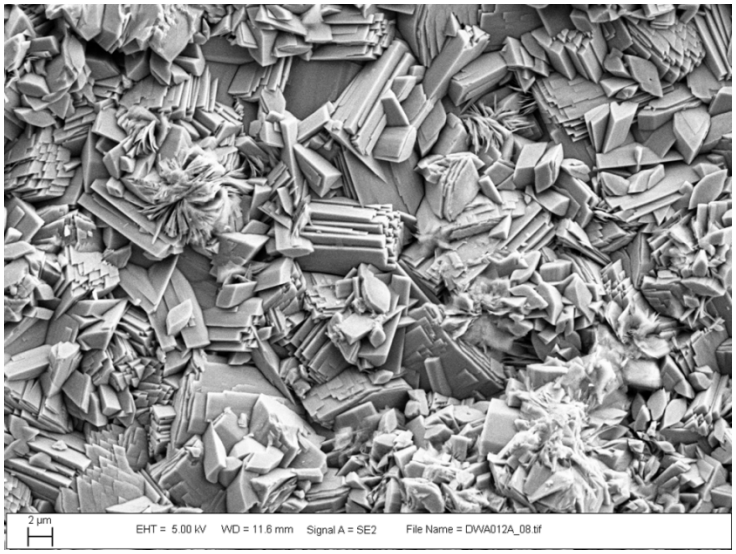
Used Fuel Disposition

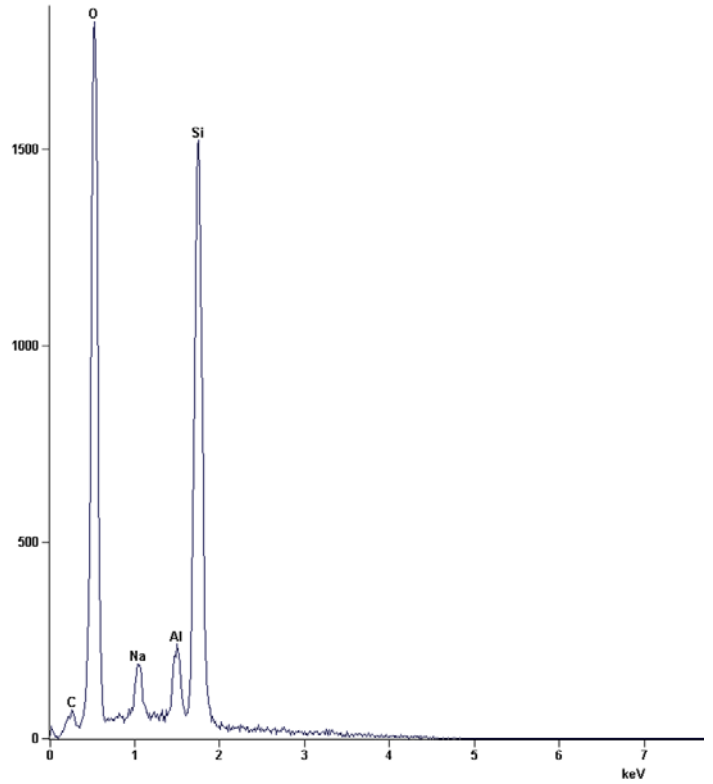
SCW 18 month

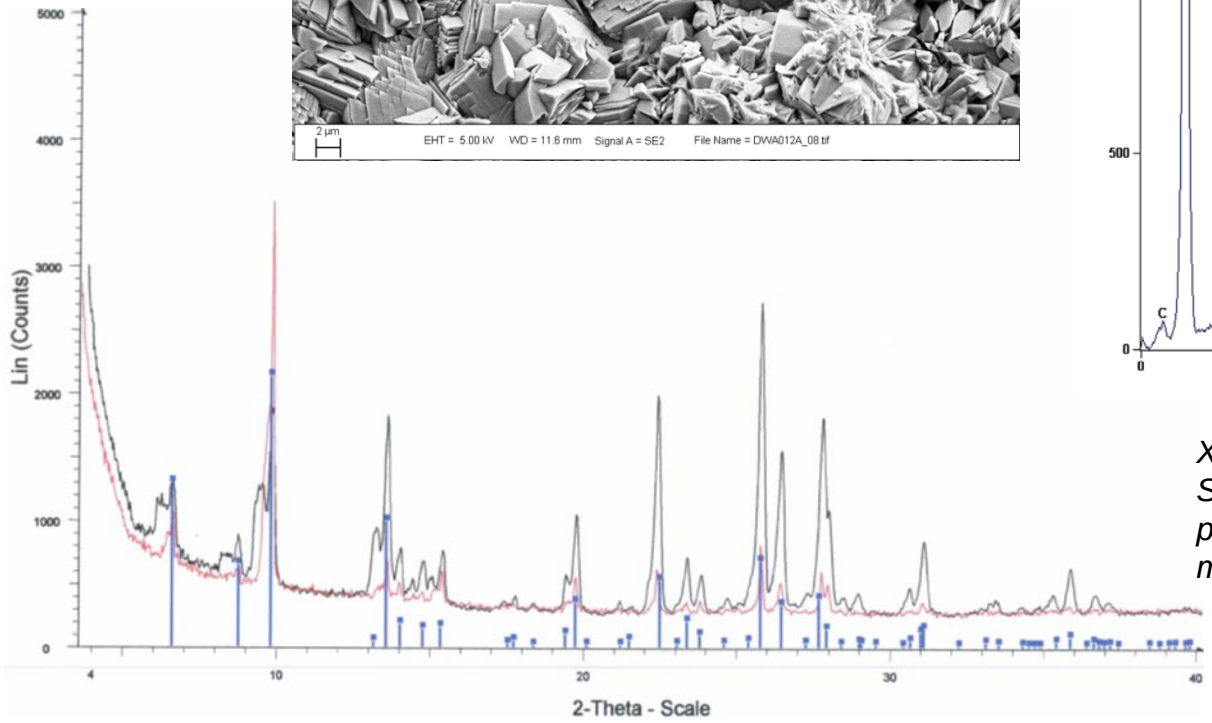


Used Fuel Disposition

Precipitate on 90°C SCW coupons

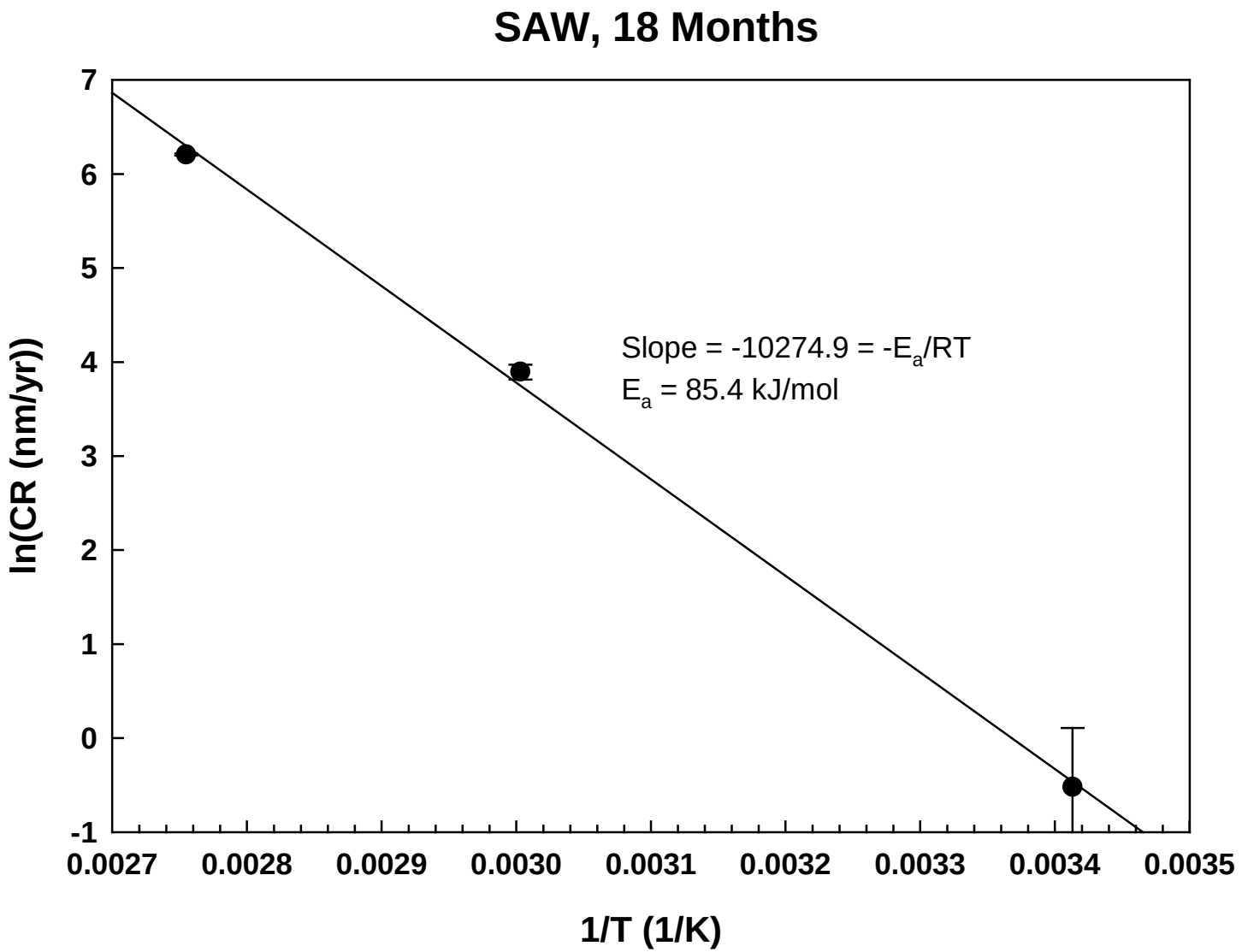






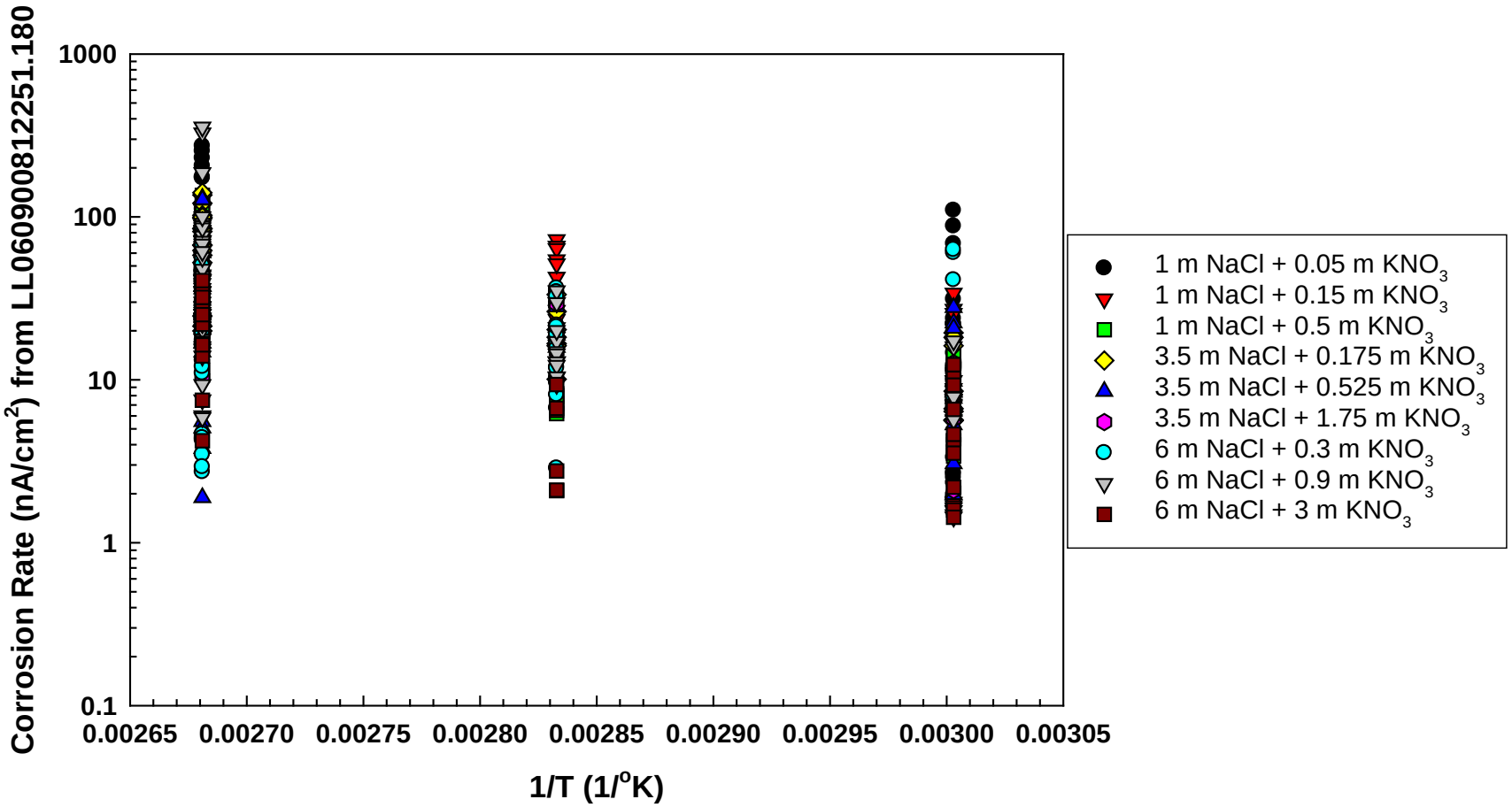
XRD patterns for the 3-month and 24-month SCW test coupons, along with matching phase patterns. The blue lines represent mordenite ($Na_{0.31}Al_{3.55}Si_{42.72}$, O_{96}•$2.76H_2O$)

Activation Energy – Alloy 22 in SAW



Temperature Dependence of the General Corrosion Rate

Data used in AMR for T Dependence



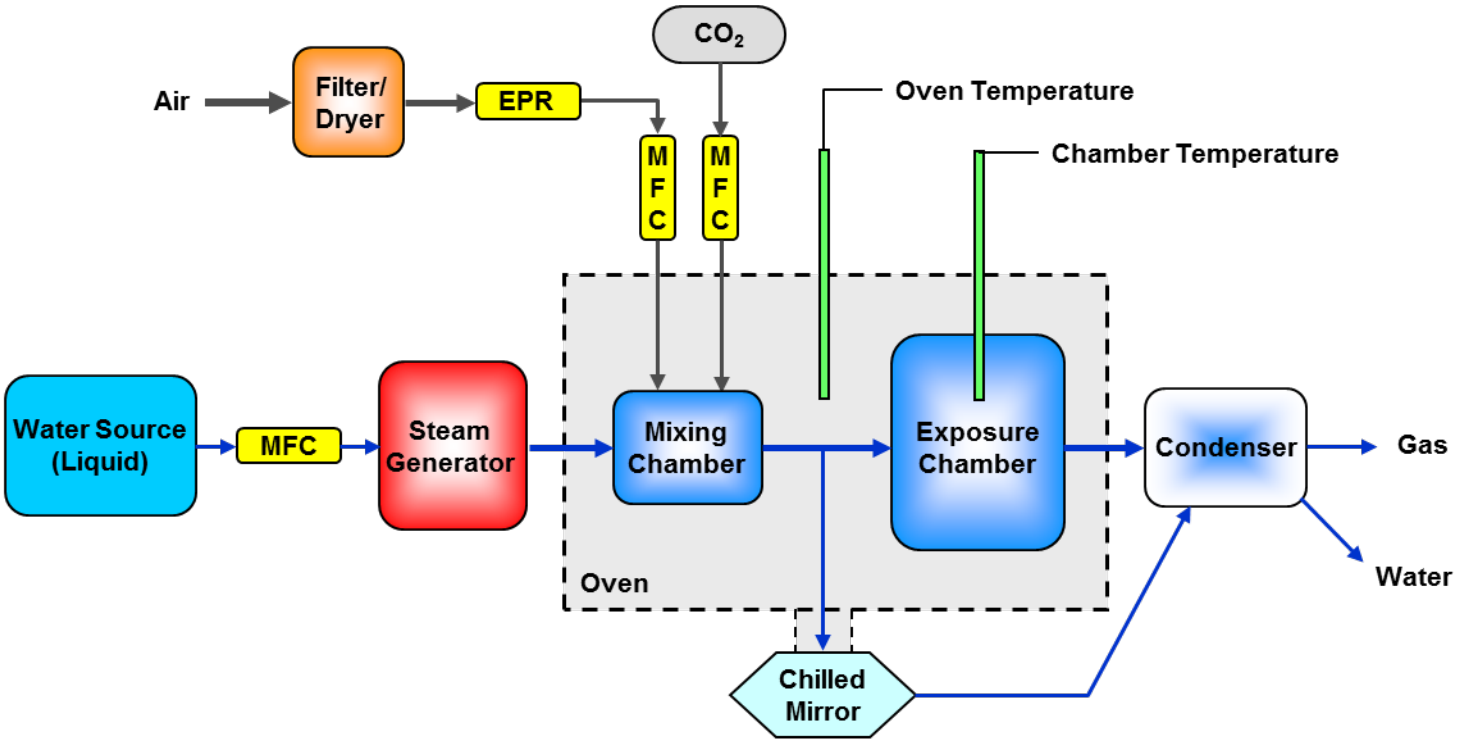
With uncertainty incorporated, the calculated activation energy ranged from 3.37 kJ/mol to 60.05 kJ/mol

Assessment of Localized Corrosion Initiation for Relevant Alloys

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

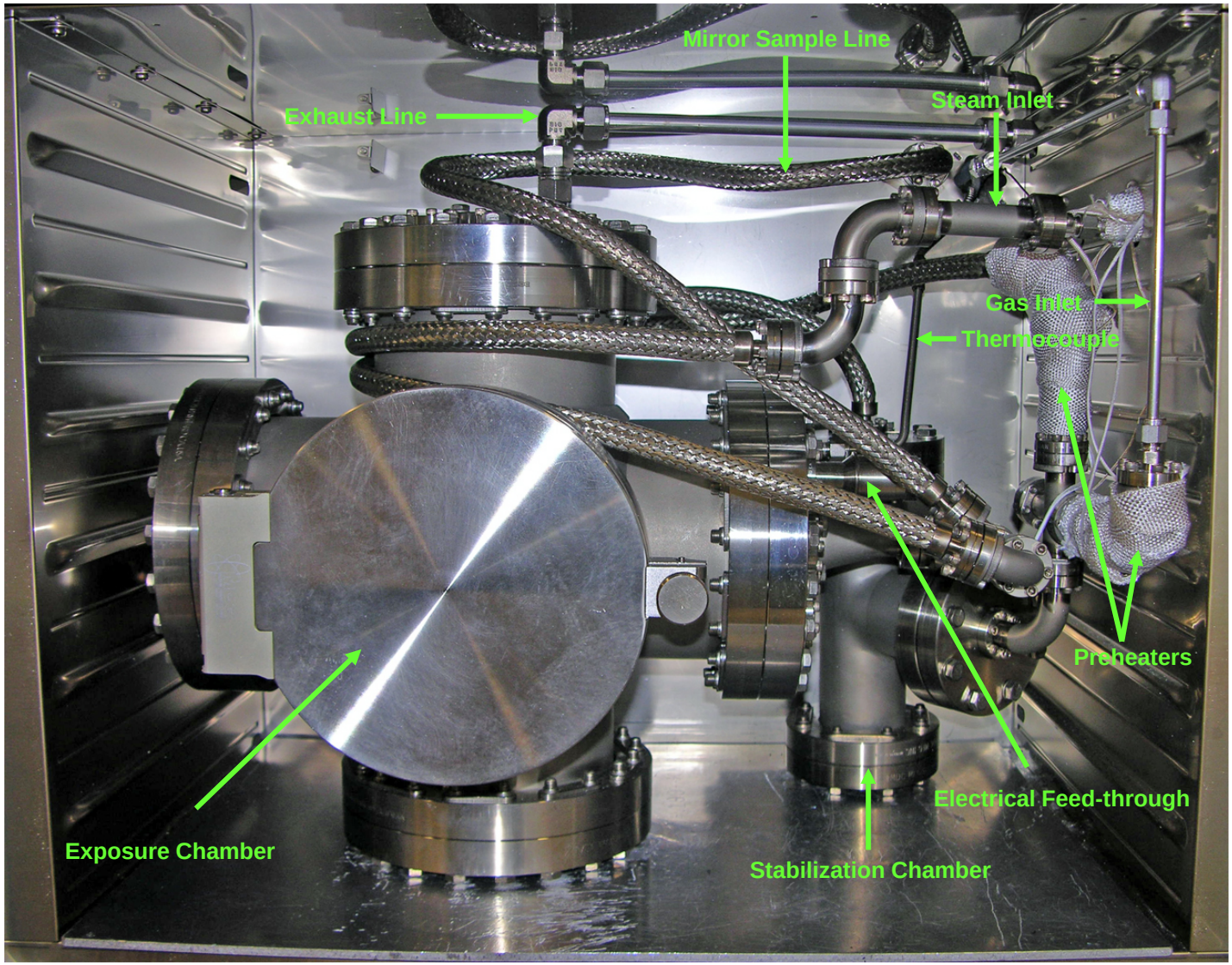
- **A series of relevant materials are being evaluated**
  - Alloy 22
  - Inconel 625
  - Hastelloy C276
  - 80:20 Ni:Cr
- **Thin film of salt (with known mass loading) deposited on surface, followed by the use of a traditional PTFE coated ceramic crevice former**

Schematic of High Temperature System



EPR = Electronic Pressure Regulator and MFC = Mass flow controller

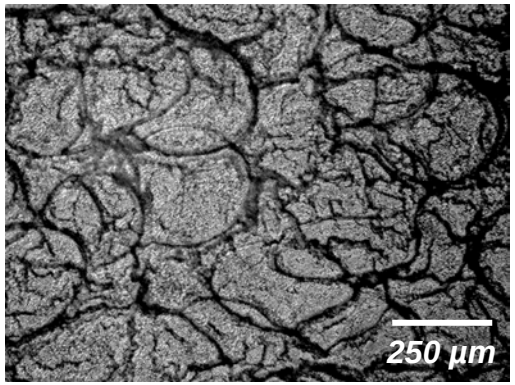
High Temperature, Controlled Dewpoint System



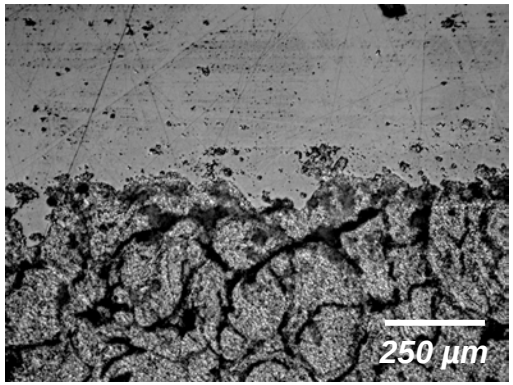
Used Fuel Disposition

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/cm^2 of a NaCl-KCl mixture*
- *T=105°C, T_d=~94.5°C (pure steam) for test intervals of 100 days*



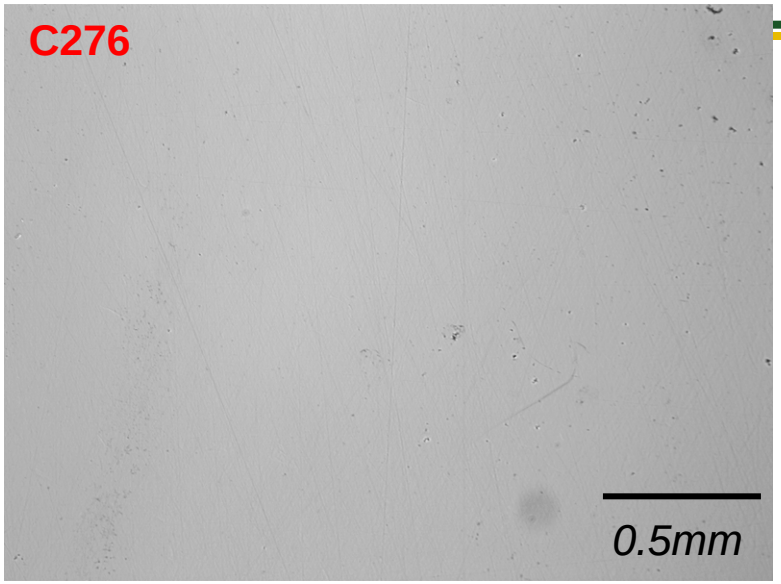
120 µg/cm^2

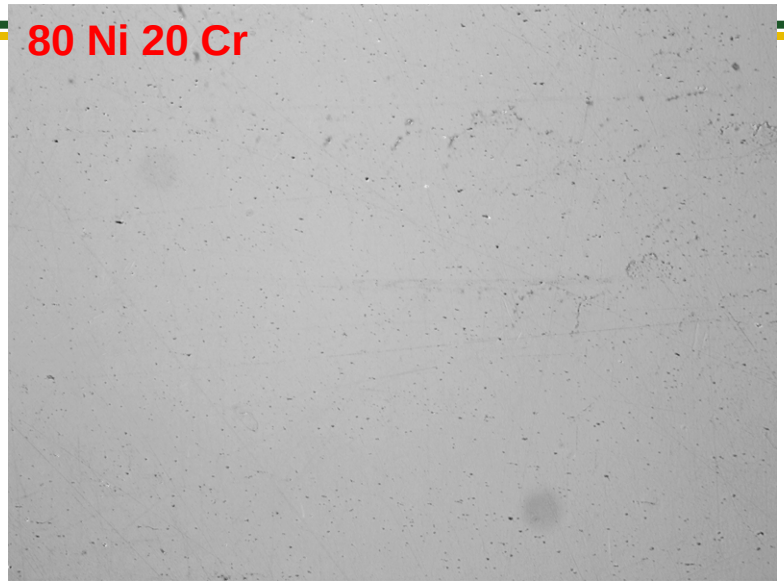


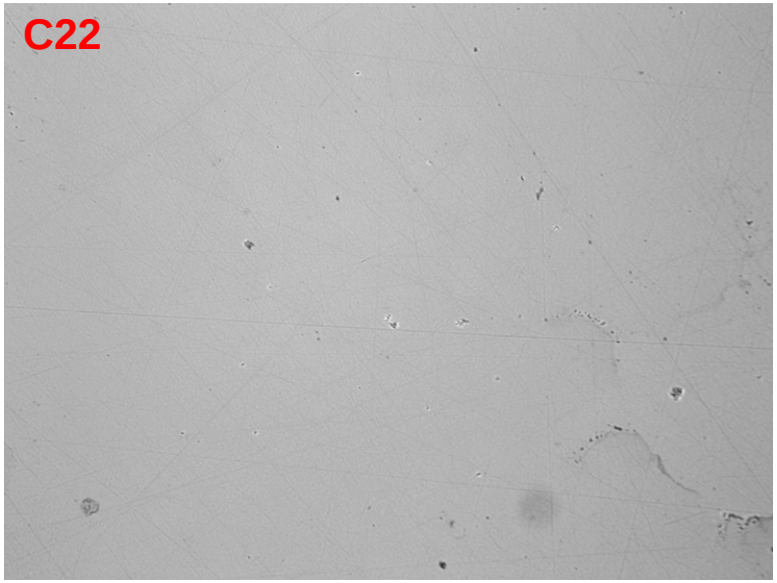
Wiped region

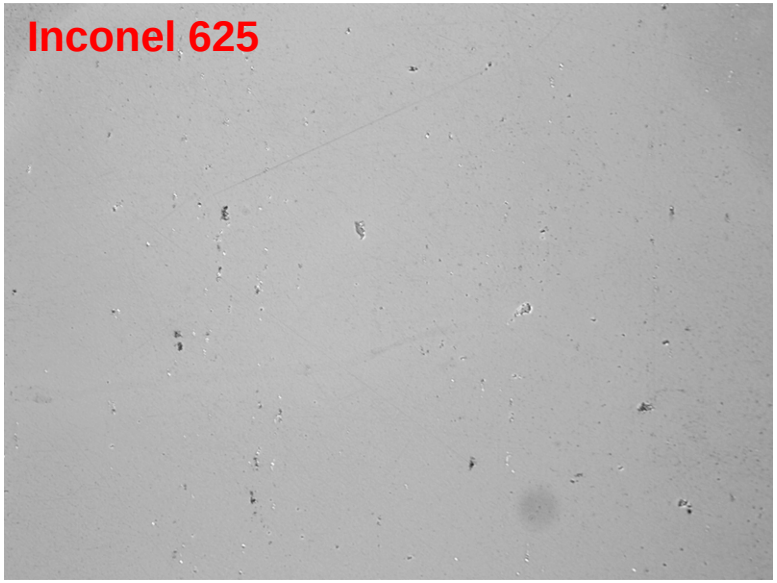
Used Fuel Disposition

Nickel Alloys in Chloride Brines





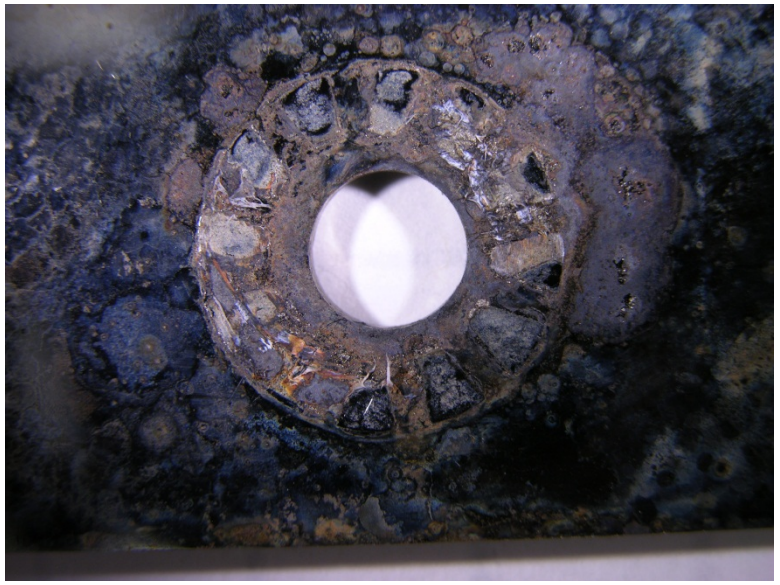




No crevice corrosion initiation

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

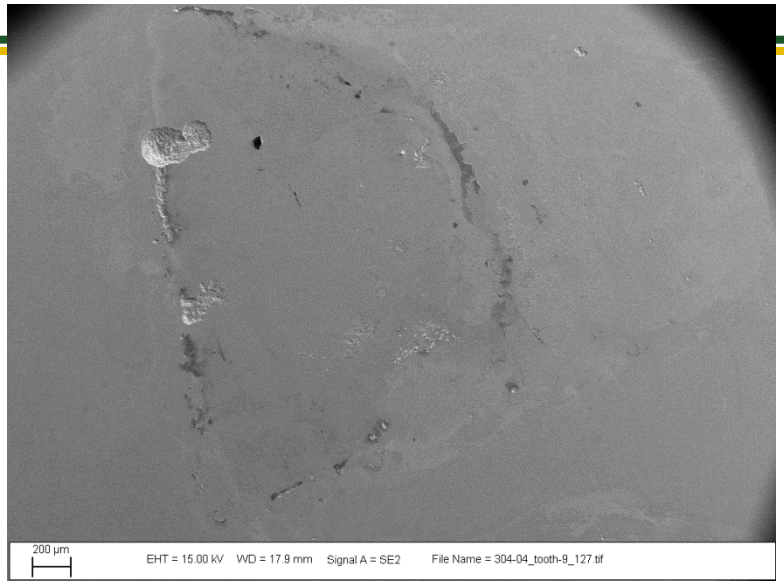
Stainless Steels in Chloride Rich Brines

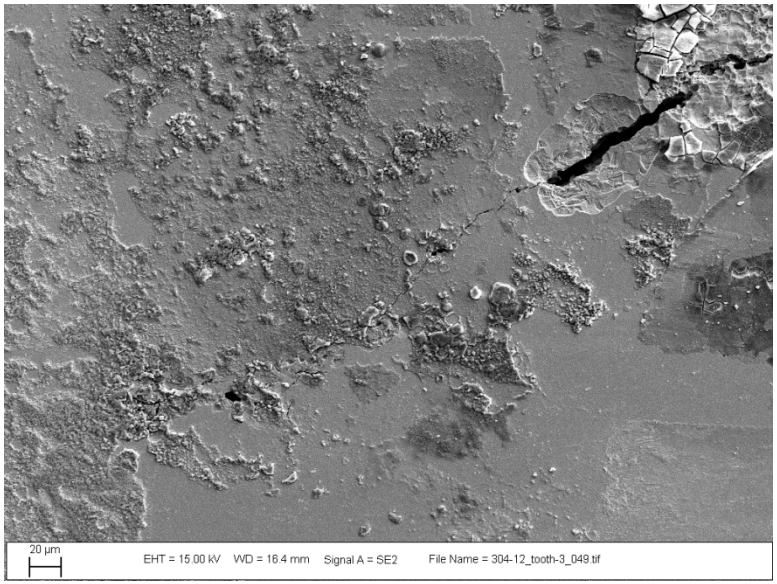
- Three different mass loadings evaluated (50, 100, and 200 μg/cm^2
- Initiation observed at all mass loadings, but extent of attack correlated with mass loading
- Samples exhibited SCC in a number of cases, but did not correlate with mass loading
- 303SS too susceptible – significant attack wherever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

Used Fuel Disposition

Impact of Salt Loading on 304SS 50 µg/cm²

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

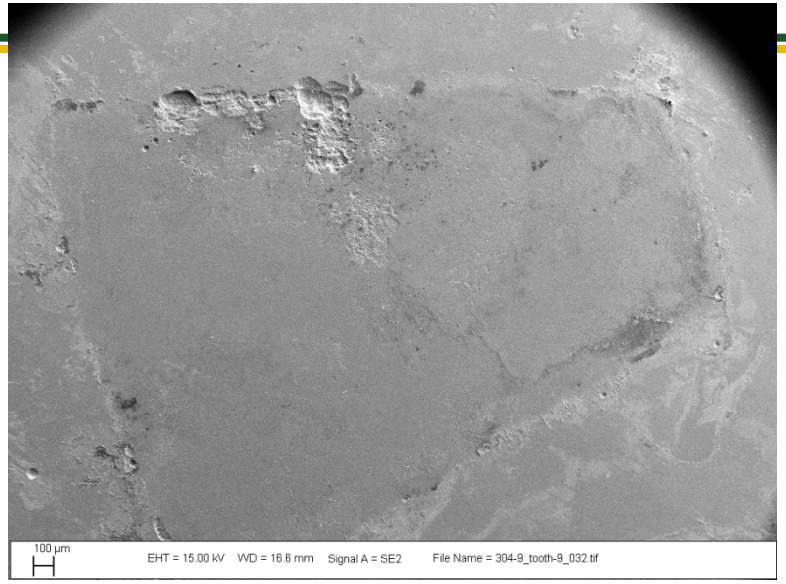


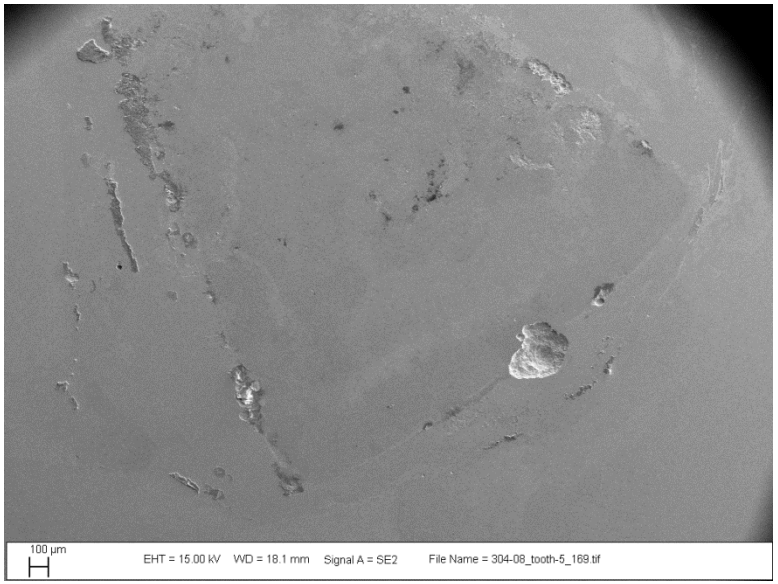


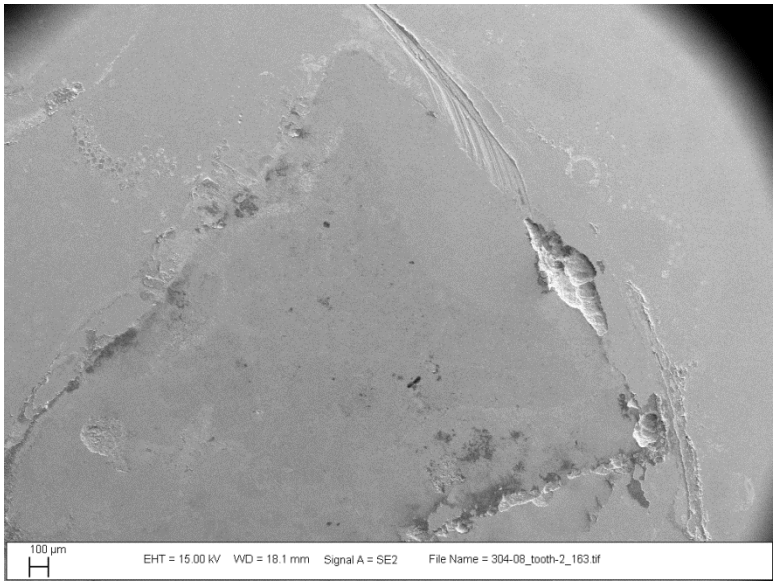
Used Fuel Disposition

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)*



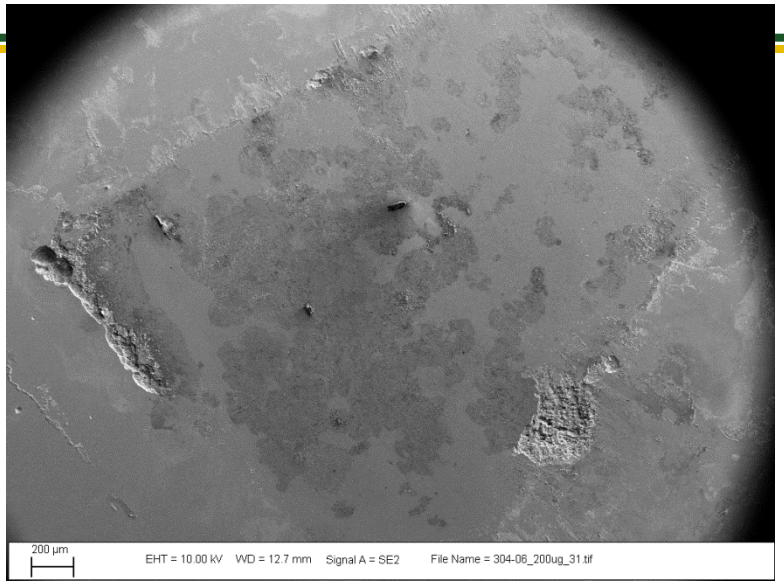


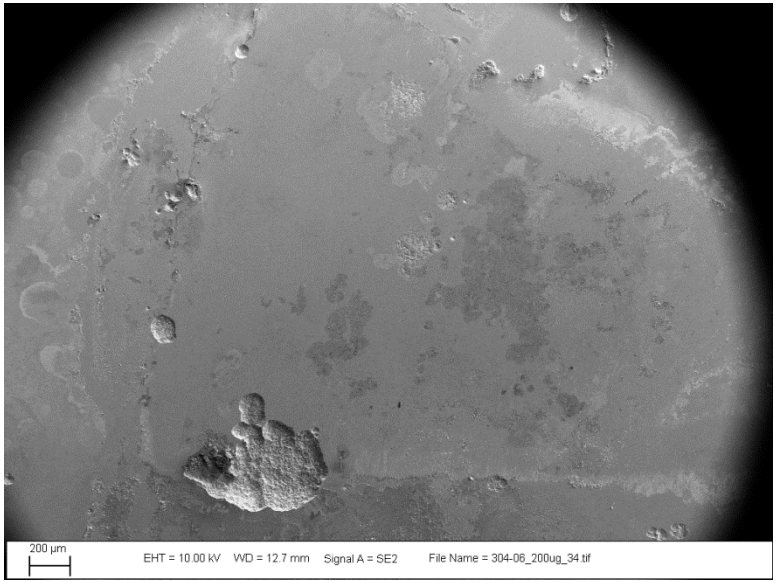


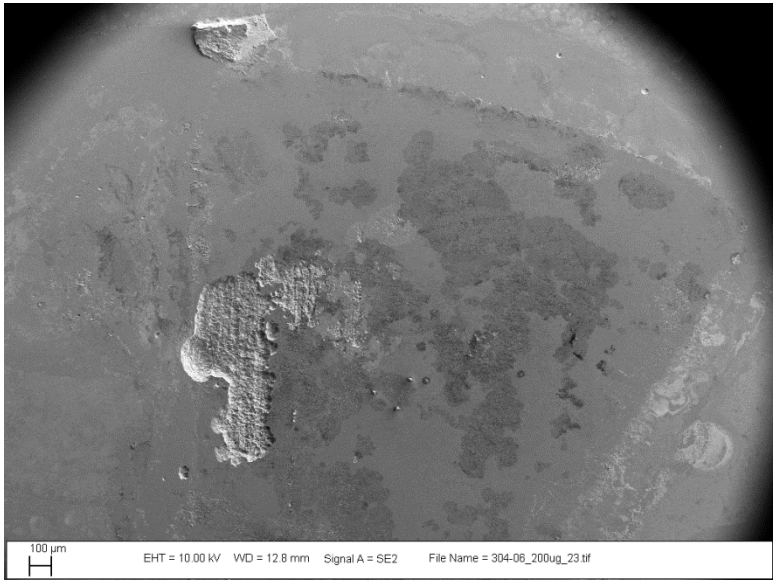
Used Fuel Disposition

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)*







Ongoing work

- **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

New Work: Immersion Testing

- **Goal is to establish accurate general corrosion rates for interim storage casks under relevant conditions**
  - Stainless steels in welded and unwelded condition
  - Metallic seal (o-ring) materials
- **Need information**
  - Are general corrosion rates really needed?
  - Technical basis for relevant environments?

New Work: Deliquescence Testing

- **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

New Work: Copper in Anoxic Water

- **Copper corrosion in electrochemically reducing environments**
  - Traditional understanding is that copper (metal) is thermodynamically stable under such conditions, and as such corrosion will not take place.
  - Recent studies claim to demonstrate that corrosion of copper can take place at an appreciable rate under these conditions, But…
    - *Corrosion product has been theorized, but not observed/documented*
    - *Corrosion detection is based upon the observation of a hydrogen partial pressure which is claimed to be the result of water reduction (presumably supporting oxidation of the copper)*
  - Experimental work will explore several potential artifacts which may explain the literature results as well as explore the corrosion behavior of copper in relevant aqueous environments.

Used Fuel Disposition

Copper in Anoxic Water

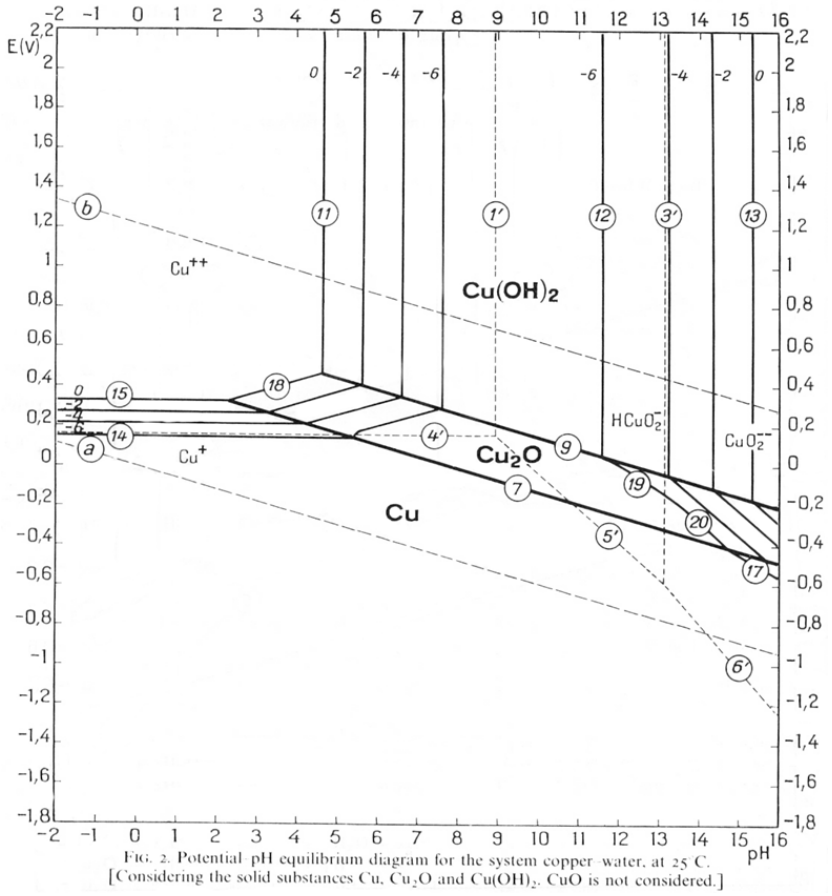


FIG. 2. Potential–pH equilibrium diagram for the system copper–water, at 25 C. [Considering the solid substances Cu, Cu_2O and $Cu(OH)_2$. CuO is not considered.]

Copper in Anoxic Water: Approach