Stress Corrosion Cracking Research at Sandia National Labs

U.S. Nuclear Waste Technical Review Board
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Sandia National Laboratories

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Background—Program Goals

- United States currently has over 86,000 metric tons of Spent Nuclear Fuel (SNF); about 50,000 metric tons in dry storage systems.

- The dry storage systems are intended as interim storage until a permanent disposal site is developed. However, lack of a repository pathway means that some SNF will remain in storage for decades beyond the original storage system specifications.

- In most systems, SNF is stored in stainless steel (304 SS) canisters. Canisters are stored in passively-ventilated overpacks, and accumulate surface dust over time. Deliquescence of chloride-rich salts could potentially lead to Stress Corrosion Cracking (SCC).

- Understanding SCC of interim storage containers has been determined to be a high priority data gap (EPRI 2011; DOE 2012; NRC 2012).
  - Timing and conditions of occurrence
  - Risk of canister penetration
Canistered SNF Dry Storage Systems
Two Standard Designs, with passive cooling

**Vertical**—In vertical systems, the welded stainless steel canister sits upright within a steel-lined concrete overpack.

**Horizontal**—In horizontal systems, the welded canister rests on its side upon rails within a concrete vault.
Criteria for Stress Corrosion Cracking

To evaluate the potential for canister SCC, each must be considered

- Weld zone, Ranor 304 SS plate
- Dust on canister surface at Calvert Cliffs (EPRI 2014)

Chloride salts present at some sites. As canisters cool, corrosive brines may eventually form.

Goal: Evaluating the risk
- What sites are at risk?
- When will corrosion initiate?
- Evolution of corrosion damage?
- Timing of crack initiation?
- Rates of crack growth and timing of potential penetration?

Measured weld residual stresses (SNL 2016)
Overview Slide: CISCC Program

**DOE CISCC Program**

- **PNNL**
  - Dust Deposition Analysis: Modeling
  - Parametric crack growth studies as a function of material properties and environment
  - Crack Consequence
  - Cold Spray Development

- **SNL**
  - Canister Environment: Sampling and Measurement
  - Brine stability and thermodynamic modeling
  - Corrosion as a function of environment and material
  - Pitting model for parameterization
  - Single effect CGR studies
  - Crack Consequence
  - Cold Spray Evaluation

- **SRNL**
  - CGR Validation: Large Plate Test

- **ORNL**
  - Crack Consequence

**DOE Collaborations**

- **NEUP**
  - Purdue
  - The Ohio State
  - Univ. of Cincinnati
  - Univ. of Idaho
  - Univ. of Wisconsin
  - Univ. of Virginia
  - N. Carolina State
  - Univ. of Nebraska
  - Univ. of Nevada Reno
  - Univ. of S Carolina
  - Univ. of Wisconsin Madison
  - Virginia Tech

- **Other Collaborations**
  - Univ. of Virginia
  - The Ohio State
  - Univ. of New Mexico
  - DNV-GL
  - EPRI
  - EPRI
  - EPRI

*CGR = crack growth rate*
Timeline, Stress Corrosion Cracking of SNF Dry Storage Canisters

Sandia’s role:

- Defining the canister surface environment
- Importance of canister environment for pitting/SCC
  - Dust, diurnal cycles, salt and brine chemistry/composition
  - Environmental influences on pit morphology and implications
    - Pit-to-crack transition
  - Pitting kinetics
    - Brine composition and cathodic limitations – predicting maximum pit size
- Crack growth rate studies
- Mitigation and Repair—cold spray and coatings

Evolving Canister Environmental Conditions: RH, T, Salt Chemistry, Salt Load
Probabilistic Model for Canister SCC
Provides the Framework for Experimental Studies

Evaluating timing of canister SCC initiation and penetration

- Incorporates many submodels for different features, events, and processes
- Used to evaluate model sensitivities, to focus research on reducing uncertainties for highest-impact parameters
Dry Storage Canister SCC: Current work

Current focuses:
1. Deposited salt characteristics/compositions
2. Mg-chloride brine evolution
3. Canister Deposition Field Demonstration
4. Corrosion in more realistic environments
   - Diurnal cycles in T/RH
   - Inert dust
   - Additional anions (e.g., NO₃, SO₄)
5. Pit-to-crack transition—environmental and material dependencies
6. CGR—moving towards atmospheric testing
7. Cold spray/coatings
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Evolving Canister Environmental Conditions: RH, T, Salt Chemistry, Salt Load

2 yr exposure underway
Sample preparation for 2 yr exposure
Electrochemical evaluation

Diurnal Cycles
Dust/Precipitates
Chemistry

- Observation of crevice-like on a SS304 sample with surface deposits$^2$
- Dust at Diablo Canyon
- Inhibited Corrosion
- Nitrate DD (µg/cm$^2$)
- Chloride DD (µg/cm$^2$)

304L plate with mixed droplets of MgCl$_2$ + Mg(NO$_3$)$_2$
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No significant difference in corrosion between masked/blended CS
Defining the Canister Surface Environment
Site sampling and thermodynamic modeling

**Why significant?** Influence on Corrosion:

**Dust/Precipitates**

- Dust may act to spread water layer and enhance corrosion.
- Observation of crevice-like attack containing a pit on a SS304 sample with surface deposits.

**Chemistry**

- 304L plate with mixed droplets of MgCl₂ + Mg(NO₃)₂
- Enhanced corrosion.
- Corrosion rate increases upon initial drying (highly concentrated brine).

**Diurnal Cycles**

- Changes in the corrosion rate, $i_{corr}$, and potential during a wet/dry cycle of carbon steel.

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Canister Surface Environment
ISFSI Site Sampling – Orano Sites “A” and “B”

First dust and salt data available from inland sites.

Samples were collected using the RTT vacuum crawler.

Sample was collected by moving crawler 6”. Sampled area = 19.35 cm²

Chemical analysis by IC and TIC analyzer/SEM analysis

12 o’clock position – front third

15.2 cm

1.27 cm

2 o’clock position

Sampler
Site “A”

Chemistry:

- Li leached from the Scotchbrite® pads. Not present in dust!
- Cations: $Ca^{+2} > Na^+ > K^+ > NH_4^+ > Mg^{+2}$
- Anions: $SO_4^{−2} > HCO_3^- > NO_3^- > Cl^−$
- Chloride concentrations all < 5 mg/m²
Site “B”

Chemistry:

- Li leached from the Scotchbrite® pads. Not present in dust!
- Cations:
  \[ \text{Ca}^{+2} \approx \text{Na}^{+} > \text{K}^{+} > \text{Mg}^{+2} > \text{NH}_4^{+} \]
- Anions:
  \[ \text{SO}_4^{-2} > \text{NO}_3^{-} >> \text{Cl}^{-} > \text{HCO}_3^{-} \]
- Chloride concentrations all < 30 mg/m²
Canister Surface Environment
ISFSI Site Sampling – Orano Sites “A” and “B”

Salt Loads by Canister Surface Location

### Site “A”
- **12 o’clock (front third)**: 134.7 mg/m²
- **12 o’clock (rear third)**: 202.6 mg/m²
- **10 o’clock**: 90.3 mg/m²
- **Blank (no filter)**: 37.4 mg/m²
- **Above HSM Rail (left)**: 44.8 mg/m²
- **Above HSM Rail (right)**: 28.3 mg/m²

### Site “B”
- **12 o’clock**: 613.7 mg/m²
- **10 o’clock**: 644.3 mg/m²
- **2 o’clock**: 408.0 mg/m²
- **4 o’clock**: 49.7 mg/m²
- **Long. Weld**: 165.2 mg/m²
- **8 o’clock**: 165.2 mg/m²
- **Above HSM Rail (left)**: 173.0 mg/m²
- **Above HSM Rail (right)**: 321.7 mg/m²

Approximate location of the HSM Rails.
Thermodynamic model for Mg-Cl-(OH)-H₂O system: Consistent thermodynamic data is necessary to model MgCl₂ brine stability in at different T, RH, P_HCl

Draft of journal article is in development
**MgCl$_2$ brine degassing experiment**

- Exposed at 48°C, 40% RH (near upper T for deliquescence on a canister)
- Very small dispersed droplets (high surface area to increase extent of reaction)
- High air flow (9 L/min)
- Exposed for 2, 4, 8, 16 weeks

**Formation of “shells” over droplets (hydroxychlorides?)**

**Why important?**

Mg-chloride brine stability may impact:

- Timing of corrosion initiation on canisters
- Brine volumes and corrosion extent/evolution
- Corrosion morphology
- Interpretation of experimental results and extrapolation to field conditions
Evaluate deliquescence of multi-component nitrate-containing salt assemblages

- **Deliquescence RH (DRH) for nitrate-containing salt assemblages is poorly predicted by thermodynamic models**
- We will measure deliquescence RH (DRH) of typical salt mixtures.
- **Why?** Accurate DRH provides improved prediction of temperature and timing of brine formation/potential corrosion initiation.
  - Define range of conditions for laboratory testing
  - Assess timing of brine formation at individual sites.
- Measure deliquescence of salts in dusts collected from actual sites?
  - Methodology: quartz crystal microbalance (QCM) and/or other instruments

Large uncertainties in thermodynamic predictions of DRH
Canister Surface Environment
Canister Deposition Field Demonstration (CDFD)

Principal goal: Evaluate dust/salt deposition on canister surfaces under realistic storage conditions, in part to parameterize and validate PNNL dust deposition model

- Canisters: 32PTH2 NUHOMS (Orano/TN)
- Vaults: horizontal storage modules (HSMs)
- Heater rods used to simulate fuel heat loads. Heat loads:
  - 0 kW
  - 10 kW
  - 40 kW
- Duration: up to 10 years

Proposed sampling locations on the canister surface
Canister-Relevant Environments for Laboratory Corrosion Testing

- **Dust Exposures**
  - Atmospheric Exposure – 3 conditions

- **Chemistry**
  - Immersed scoping measurements

- **Cyclic Exposures**
  - Atmospheric Exposure – diurnal cycle
## Canister-Relevant Environments for Laboratory Corrosion Testing

### Dust Exposures
- Atmospheric Exposure – 3 conditions

### Chemistry
- Immersed scoping measurements

### Cyclic Exposures
- Atmospheric Exposure – diurnal cycle

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74 µm dust deposited with seawater

1 month exposure – 304 coupons with seawater & dust

- Static low RH
- Diurnal Cycle
- Static high RH
Dust Exposures
- Atmospheric Exposure – 3 conditions

Chemistry
- Immersed scoping measurements

Cyclic Exposures
- Atmospheric Exposure – diurnal cycle

74 µm dust deposited with seawater

1 month exposure – 304 coupons with seawater & dust

Passivating effects of Nitrates: Concentration Dependent

Nitrate at Field Sites

Lab Exposures

4.3 M NaCl with:
- 1.1 NaNO₃
- 2:1 NaNO₃
- 4:1 NaNO₃
- 9:1 NaNO₃
- 24:1 NaNO₃
- 0 NaNO₃

E (V vs. Ag/AgCl) vs. log(I) (A/cm²)
Canister-Relevant Environments for Laboratory Corrosion Testing

**Dust Exposures**
- Atmospheric Exposure – 3 conditions

- 74 µm dust deposited with seawater

1 month exposure – 304 coupons with seawater & dust

**Chemistry**
- Immersed scoping measurements

**Cyclic Exposures**
- Atmospheric Exposure – diurnal cycle

- Stochastic and variable dependent

### Nitrate at Field Sites

- 4.3 molal NaCl (4:1 NaNO₃)
Canister-Relevant Environments for Laboratory Corrosion Testing

Dust Exposures
- Atmospheric Exposure – 3 conditions

74 µm dust deposited with seawater

1 month exposure – 304 coupons with seawater & dust

Chemistry
- Immersed scoping measurements

Nitrate at Field Sites

Cyclic Exposures
- Atmospheric Exposure – diurnal cycle

Diurnal profile for lab exposures

Post Exposure Corrosion Damage

Stochastic and variable dependent

Effects of increased temperature: de-passivates
Prediction of Maximum Pit Sizes

- Pit (anode) must be supported by cathodic reduction reaction forming an inherent galvanic couple.
- In finite water layers, cathode limited by ohmic drop.
- Finite cathode → Finite anode → Finite pit.

**Conservative estimates of the maximum pit**

Roughly 1.5 x larger estimate

76 % Max Pit ~ 230 µm
40 % Max Pit ~ 110 µm

**Prediction of Maximum Pit Sizes**

**Comparison to long-term pitting exposures**

**Conservative estimates of the maximum pit**

Roughly 1.5 x larger estimate

- 76 % Max Pit ~ 230 µm
- 40 % Max Pit ~ 110 µm

**Potential influences on cathode**

\[ \text{pH} > \text{pH}_{\text{crit}} \]

\[ \text{Mg(OH)}_2 \]

\[ \text{OH}^- \]

\[ R_{\text{cath w/ precip.,WL}} \]

\[ \text{pH} > \text{pH}_{\text{crit}} \]

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**Prediction of Maximum Pit Sizes**

**Comparison to long-term pitting exposures**

**Conservative estimates of the maximum pit**

Roughly 1.5 x larger estimate

- 76 % Max Pit ~ 230 µm
- 40 % Max Pit ~ 110 µm

When comparing to exposures, prediction of maximum pit sizes with precipitation is **directly inline for 40% RH**

- 76 % Max Pit ~ 190 µm
- 40 % Max Pit ~ 70 µm


Prediction of Maximum Pit Sizes
Parameterization of the model

Environmental influences on corrosion damage (maximum pit size)

- Decreasing RH increases maximum pit sizes to a maximum at ~ 75% RH
- Increasing temperature slightly decreases maximum pit sizes
- Increasing salt deposition increases maximum pit size
Environment and material influence on pit shape – why significant?

**Why is pit shape significant?**

Pit-to-crack transition based on Kondo Criteria


Canister-Relevant Testing Environments: Pit to Crack

**Large Scale Exposure Testing: U-bend coupons to examine pit to crack transition**

**Initial Exposures:**

- #4 Machine Finish (60 grit) 304L
- 300 \( \mu g/cm^2 \) artificial seawater
- or 500 \( \mu g/cm^2 \) \( MgCl_2 \)
- Exposure: diurnal cycle and static 40% RH

Initial Optical Observations

Salt Deposition

Example stress modeling
Crack Growth Rate – Lab setup and Calibration

• Final CGR lab setup complete
• DCPD testing in air underway

Example: DCPD testing in air

Crack length vs time
Crack Growth Rate in Relevant Brine Environments

- **Final CGR lab setup complete**
- **DCPD testing in air underway**

**Example: Saturated MgCl₂ Tests Compared to NaCl**

Developing an understanding of DCPD and fractography in saturated salt solutions
Mitigation and Repair: Canister Coatings Evaluation

1. Collaborative effort with industrial partners
   • Based on FY20 coatings report

2. Collaboration with PNNL to evaluate cold spray as a potential mitigation and repair strategy
SNL-Industrial Collaboration– Initial coatings for evaluation

**Coating types:**
4 collaborating companies, 11 variants

1. Gentoo - 1 + Zn-rich Primer
2. Gentoo - 2 + Zn-rich Primer
3. Zn-rich Primer
4. CRACKSTOP GAMMABLOCK PLUS
5. 5- variants of Gentoo with and without Zn-rich primer

- Durable ceramic hybrid inorganic/polymer coating with/without galvanic protection

1. OXPEKK Resin
2. OXPEK- Sulfonated

- 2- variants of Polyetherketoneketone (OXPEKK). High temperature thermoplastic with high radiation resistance

1. CRACKSTOP GAMMABLOCK
2. GAMMABLOCK
3. 3- variants of modified polyimide, polyurea, phenolic resins. Durable, chemically inert and can include additives to increase corrosion resistance

1. Single component hybrid inorganic/modified polyurethane coating resulting in a quasi-ceramic structure.
SNL – PNNL collaboration:
Cold Spray – Accelerated Corrosion Testing

Accelerated Corrosion Testing for Cold Spray Optimization:

ASTM G-5: potentiodynamic polarization in 0.6 M NaCl

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Cold Spray Samples with Edge Processing

- Blended edge
- Masked edge

Metastable pitting reduced by polishing/grinding cold spray surface
SNL – PNNL collaboration:  
**Cold Spray – Accelerated Corrosion Testing**

### Cold Spray Matrix

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**Accelerated Corrosion Testing for Cold Spray Optimization:**

**ASTM G48: full immersion pitting 6% by weight FeCl₃**

**Post ASTM G-48 Exposure**

- Majority of attack at interface and influenced by edge type
SNL – PNNL collaboration:
Cold Spray – Accelerated Corrosion Testing

Accelerated Corrosion Testing for Cold Spray Optimization:

ASTM G48: full immersion pitting 6% by weight FeCl₃,
Post ASTM G-48 Exposure

• Attack influenced by material type and process gas/porosity of cold spray.

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PNNL M3 Report 2021
Summary: Primary Goals of Current and Future Work

- **Environmental Studies:**
  - Analysis of dust from in-service canisters—characterization of canister surface environments for corrosion testing
  - Mg-chloride brine stability (timing/temperature of corrosion, extent and morphology of corrosion, etc.)
  - Brine DRH as a function of salt composition (timing/temperature of brine development)
  - Dust/salt deposition (CDFD)

- **Corrosion testing and modeling in canister relevant environments**
  - Examining influence of canister-relevant environments on corrosion (pitting and pit to crack)
  - Expanding modeling efforts to account for non-static brine/corrosion conditions to better predict pitting and SCC initiation

- **Crack growth rate**
  - Installed, calibrating, and reviewing initial tests in varied brine environments to explore potential effects on CGR

- **Coatings**
  - Developed MOU with industry partners, received initial coatings for evaluation at SNL
  - Collaborated with PNNL for accelerated corrosion evaluation of CS coatings
Acknowledgements

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Questions?