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SNF STORAGE CANISTER PITTING & SCC: CURRENT DOE:NE RESEARCH

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SANDIA NATIONAL LABORATORIES

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SPRING 2019

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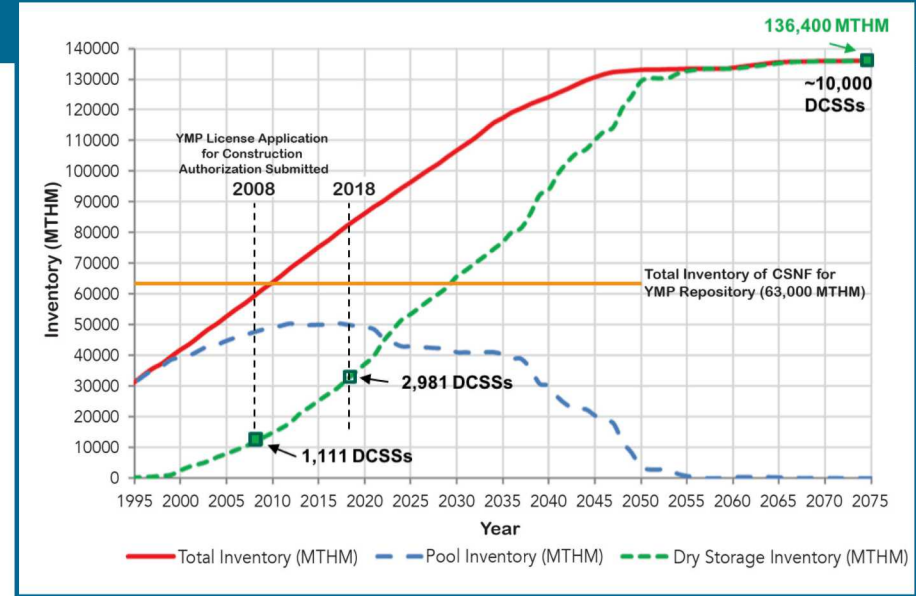
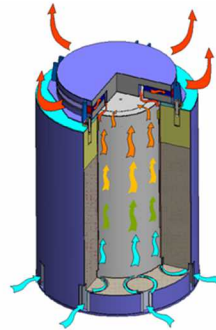


May 7-9, 2019

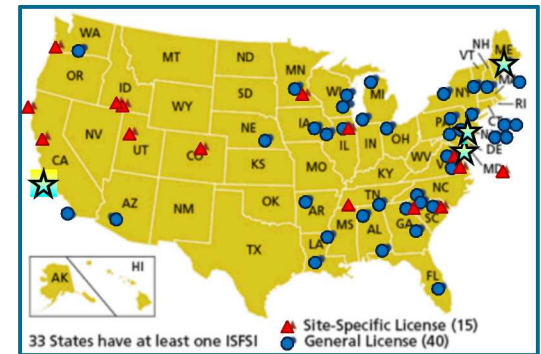
Background

- United States currently has over 80,000 metric tons of Spent Nuclear Fuel (SNF), about 30% in dry storage systems. The dry storage systems are interim storage until a permanent disposal site is developed, which is likely to be many decades.
- Most dry storage systems utilize stainless steel (304 SS) canisters stored in passively-ventilated overpacks. Canisters accumulate surface dust over time. If corrosive salts are present, SCC could occur.

How do we quantify risk?



LOCATIONS OF U.S. SPENT NUCLEAR FUEL INDEPENDENT STORAGE INSTALLATIONS (ISFSIs)



★ ISFSI locations sampled.

DOE Program Research Objectives

OVERALL OBJECTIVE

Improve ability to predict timing and location of potential canister penetration by SCC cracks

- What ISFSI locations are at greatest risk?
- Where on the canister surface is cracking likely to occur?
- When will cracking initiate and at what rate will cracks grow?
- How do we quantify risk of canister penetration by SCC?

GOALS OF EXPERIMENTAL WORK

- Improve understanding of electrolyte (*deliquescent brine*) physical and chemical characteristics and evolution with time, both before and after corrosion initiates
- Understand the relationship between surface environment (*T, RH, salt load and distribution*) and damage (*pitting/SCC*) distributions and rates
- Understand of the effects of material properties (*microstructure*) and mechanical environment (*residual stress intensity and depth profile*) on corrosion distributions and rates

Develop and parameterize a mechanistically-based probabilistic SCC model for improved prediction of canister performance.

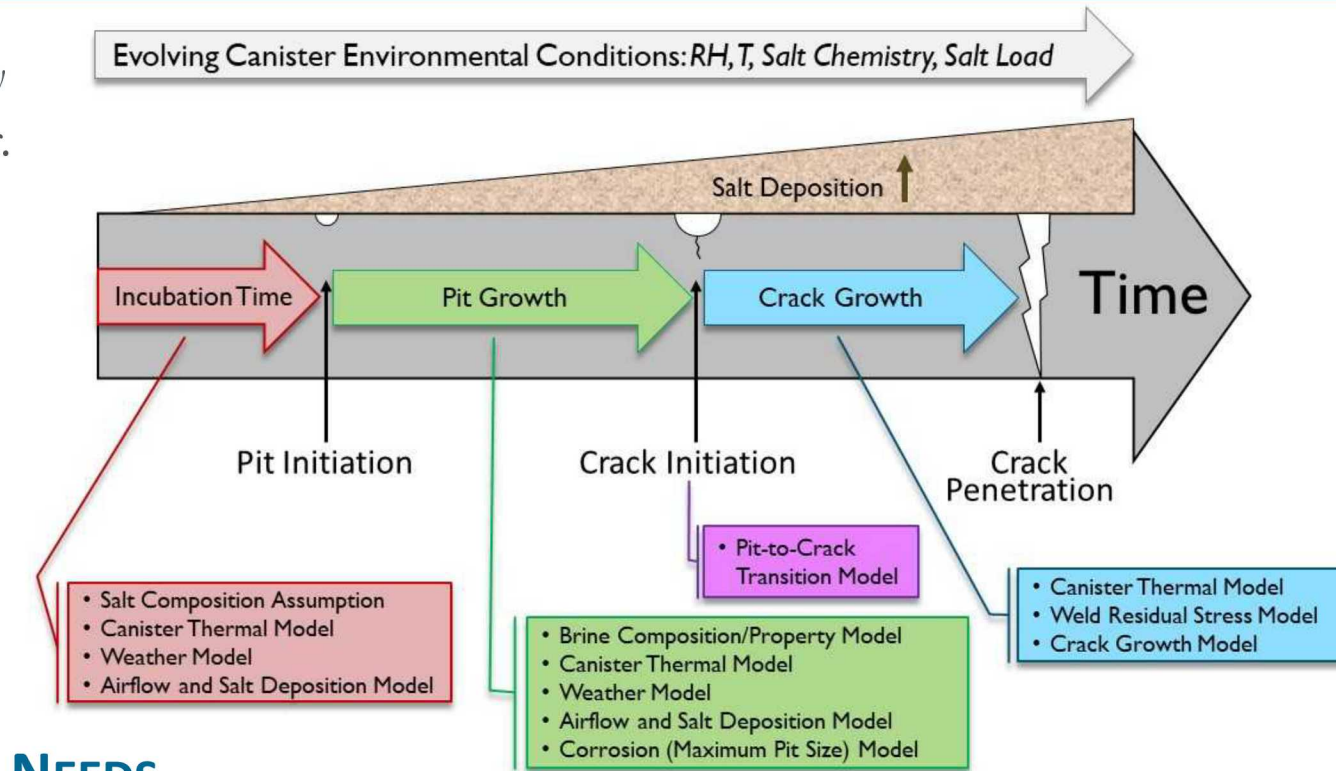
Integrated Mechanistic/Probabilistic Model for Canister SCC

Current model developed by SNL is a work in progress.

Current and planned experimental work is intended to parameterize this model.

ISSUES

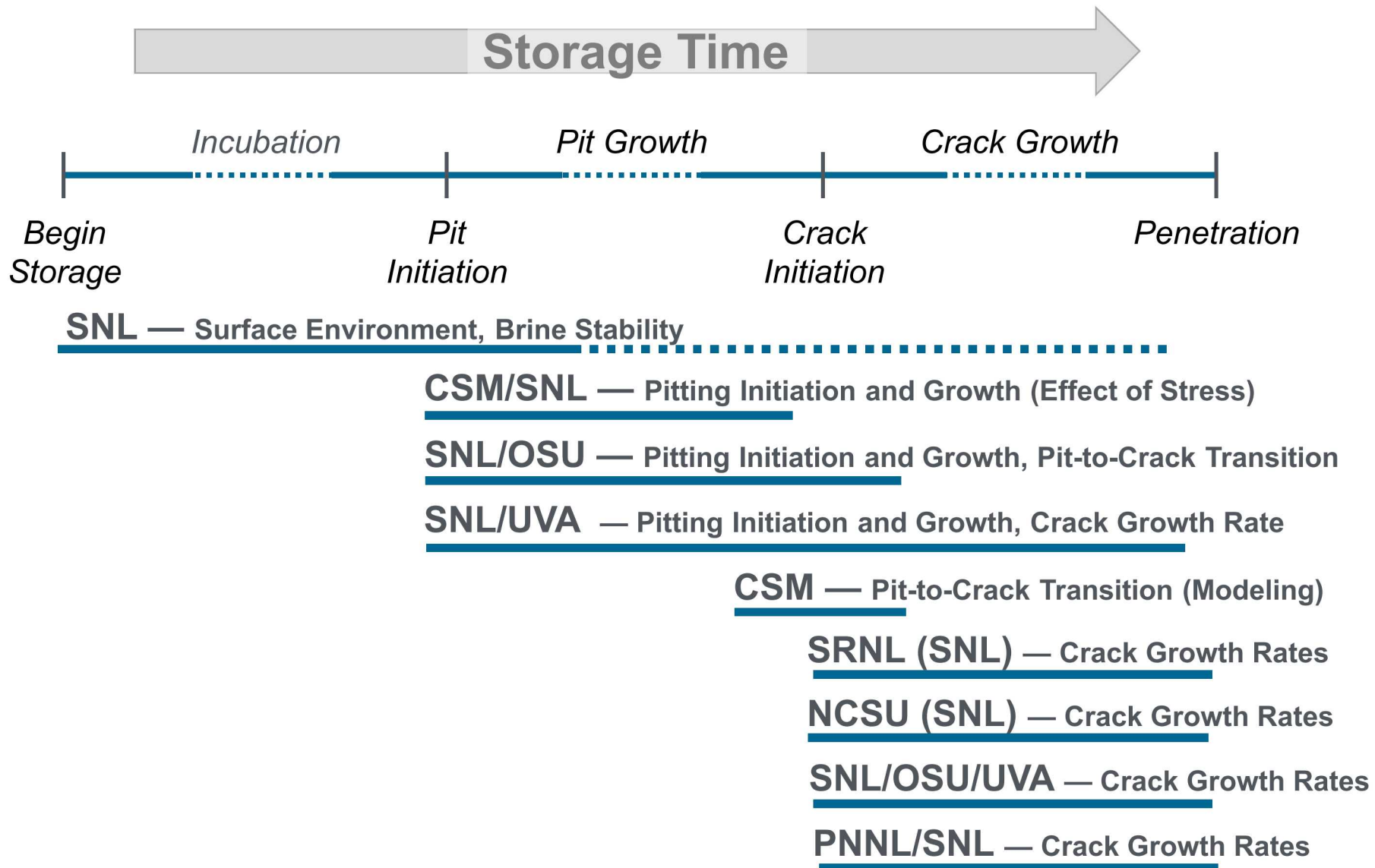
- Models and framework contains numerous assumptions and oversimplifications based on lack of data or mechanistic basis
- Sub-models have not been adequately validated



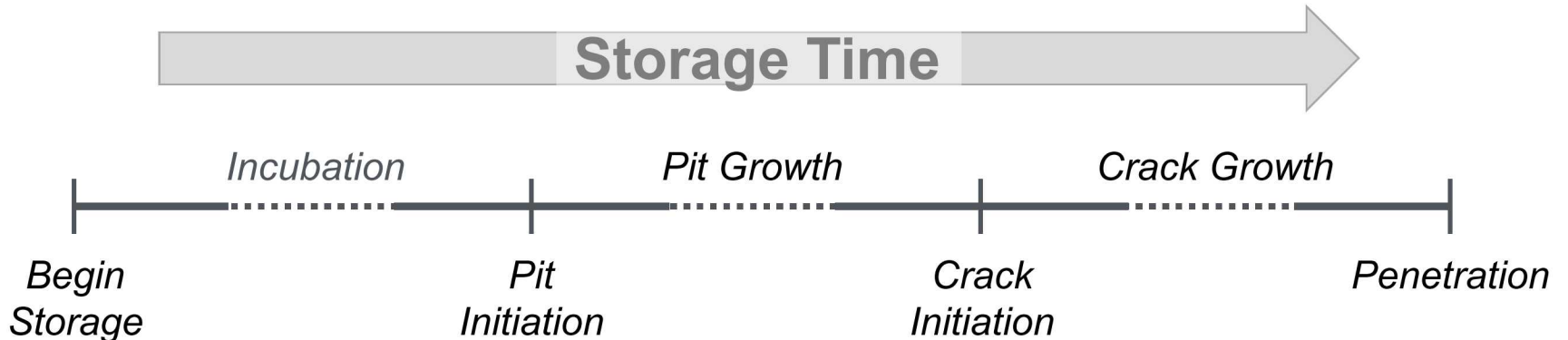
NEEDS

- Data for improved sub-model development and validation
 - *Improved data on salt compositions/deposition rates at ISFSI sites*
 - *Statistical pitting and SCC data for canister-relevant conditions*
- Improved scientific understanding of underlying mechanisms governing brine evolution, corrosion (pitting/SCC)

Canister SCC: Current DOE Efforts



Canister SCC: Surface Environment R&D



SNL — Surface Environment, Brine Stability



Expected salt/brine compositions

Determines corrosiveness, deliquescence properties of salts

Stability of salts and brines both before...

Impacts temperature and timing of deliquescence

...and after initiation of corrosion

Impacts brine layer properties (composition, thickness), potentially causes brine dry-out

Sampling/analysis of salts collected from in-service SNF dry storage canisters

Focus of coastal sites, with high chloride aerosols

Prior to deliquescence

Experimental evaluation of ammonium salt stability

After deliquescence

Experimental evaluation of sea-salt ($MgCl_2$) brine stability

Effect of cathodic reactions:

Hydroxide production at the cathode can affect brine composition, stability

Incorporation of brine components into corrosion products

Chloride sequestration by iron oxyhydroxides

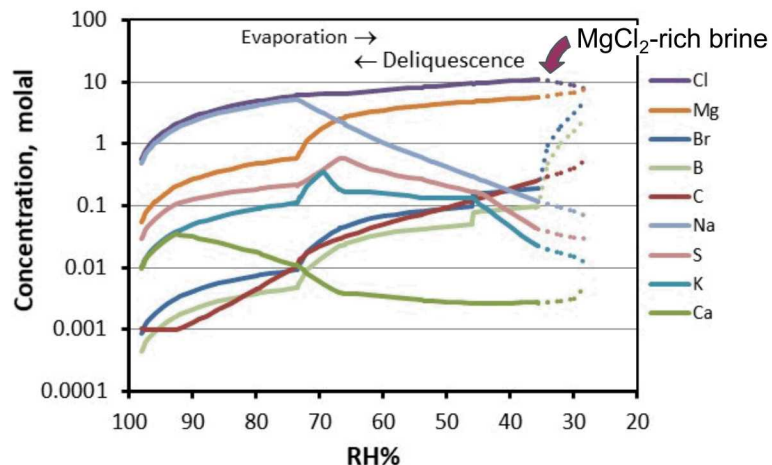
Deliquescent brine compositions

Sea-salt aerosols

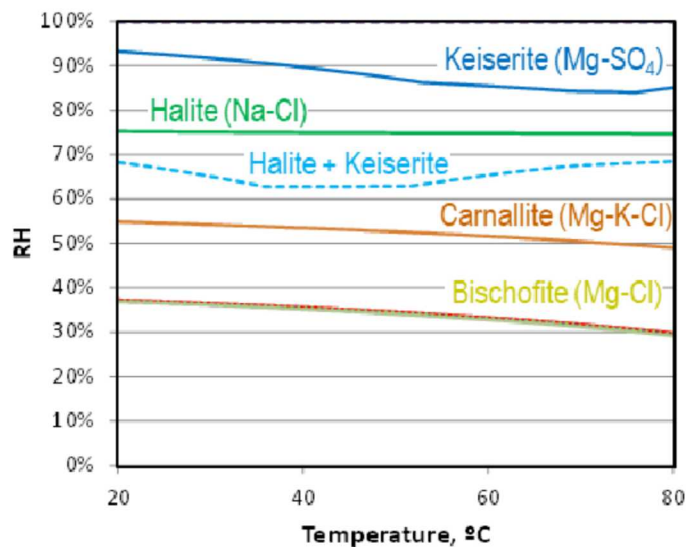
Aerosols are initially deposited dry (*hot canisters*). As temperatures drop, sea-salts deliquesce.

- Deliquescent brine compositions determined by thermodynamic modeling
- MgCl_2 brines form first—lowest deliquescence RH
- As canisters cool, brines volumes increase, and become more NaCl -rich

Brine compositions as a function of relative humidity (RH)



Deliquescence RH values for precipitated sea-salts



MgCl_2 brine stability on heated canister surfaces is important because:

- If MgCl_2 brine is not present, brine will not be present until much higher RH values are achieved
- Higher deliquescence RH corresponds to lower canister temperatures, delaying canister corrosion.

Mg-Cl Brine Stability Prior to Initiation of Corrosion

Experimental evaluation of Mg-Cl brine stability

DEGASSING EXPERIMENTS

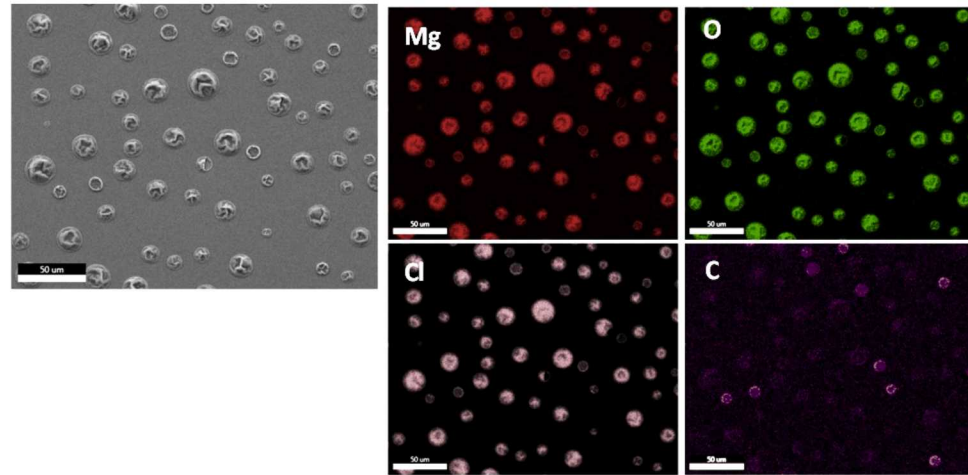
- MgCl₂ brine deposited as droplets on inert substrate, aged for 8 weeks in RH chamber
- Test environments
 - 48°C, 40% RH – near-maximum temperature for bischofite (MgCl₂·6H₂O) deliquescence under field conditions
 - 80°C, 35% RH – “accelerated” testing conditions used at Sandia and elsewhere; interpreting experiments requires understanding brine stability at this condition

RESULTS

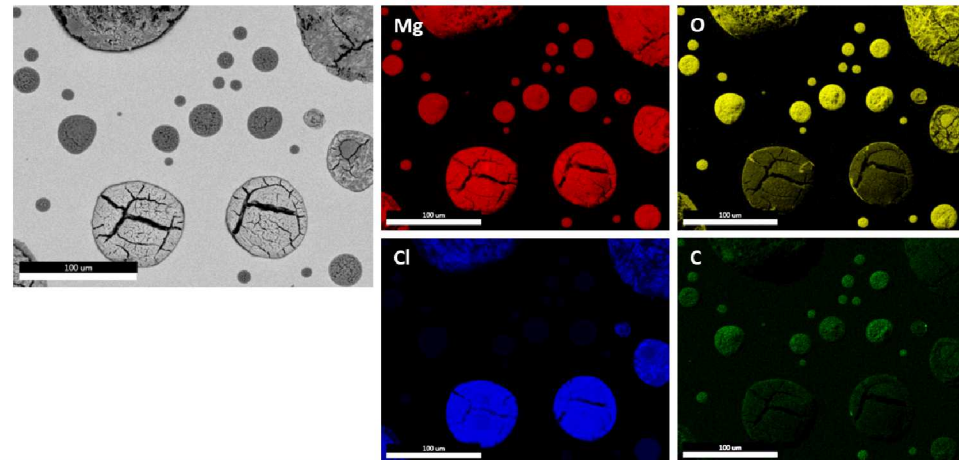
- In both cases, elevated temperatures drove degassing of HCl, and conversion of brine to less deliquescent phases
- 48°C, 40% RH – Mg-carbonate
- 80°C, 35% RH – Mg-carbonate and Mg-oxyhydroxide (Mg(OH)₂·MgCl₂·4H₂O)
- Low air flow rates in experimental system limited extent of conversion

Conclusion: Mg-Cl brines will degas and potentially dry out at elevated temperatures. Finding may limit conditions for brine formation on SNF storage canisters, delaying corrosion.

48°C, 40% RH (8 WEEKS): SEM IMAGE AND EDS ELEMENT MAPS, SHOWING PARTIAL CONVERSION OF MgCl₂ DROPLETS TO CARBONATE (DEPLETION OF CL AND ENRICHMENT IN C)



80°C, 35%RH (8 WEEKS): SEM IMAGE AND /EDS ELEMENT MAPS, SHOWING CONVERSION OF DROPLETS TO HYDROXYCHLORIDE AND CARBONATE (DEPLETION OF CL AND ENRICHMENT IN O AND C)

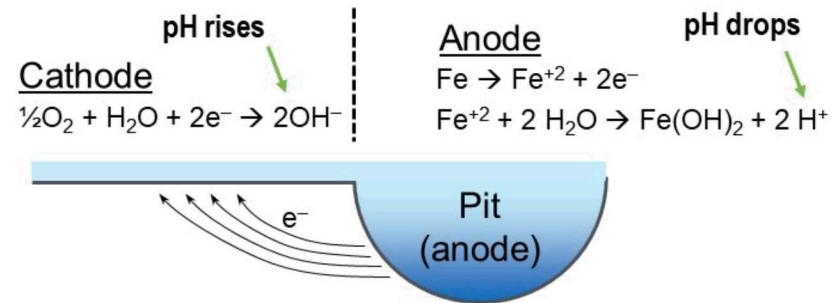


MgCl Brine Stability After to Initiation of Corrosion

CORROSION REACTIONS

- Cathode: hydroxide production via oxygen reduction will affect brine composition
 - *May affect cathode kinetics (and pit sizes) by changing brine composition and volume*
 - *May result in hydroxyl or carbonate precipitation, and eventually brine-dry-out.*

Corrosion cell



EXPERIMENTAL CONFIRMATION OF BRINE DRY-OUT

4-POINT BEND TEST

- 304 SS, MgCl₂ brine
- 80°C and 35% RH
- Results: white precipitate forms around corroding areas
 - *Mg-hydroxychloride (same phase as previously seen)*
 - *Not deliquescent under testing conditions; if reaction goes to completion, brine will dry out.*



Effects of Corrosion Reactions on Brine Stability:

Brine dry-out on the “big plate” test

BIG PLATE TEST

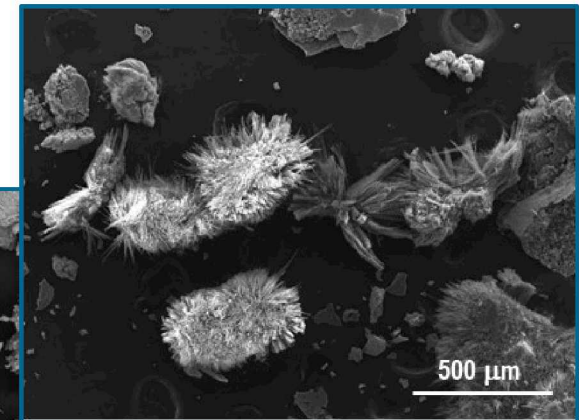
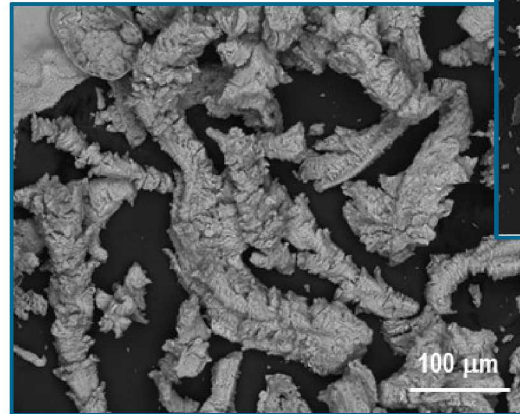
- Large weld samples from Sandia canister mockup
- 80°C, 35% RH, salt load 8 g/m² MgCl₂ deposited as salt fog
- Samples examined after 2 and 8 months
- By 8 months, surface and corrosion products were dry
- What happened to the brine?



ANALYSIS OF CORROSION RESIDUES

- Mg-hydroxychloride identified by SEM and XRD
- SEM/EDS: metal corrosion products enriched in chloride; phase identified by XRD as akageneite: Fe³⁺_{7.6}Ni_{0.4}O_{6.4}(OH)_{9.7}Cl_{1.3} (about 6 wt% Cl)

Mg-hydroxychloride, identified by XRD as $2\text{Mg}(\text{OH})_2 \cdot \text{MgCl}_2 \cdot 4\text{H}_2\text{O}$



Chloride-bearing metal corrosion products; akageneite identified by XRD.

Corroding plate dried out.

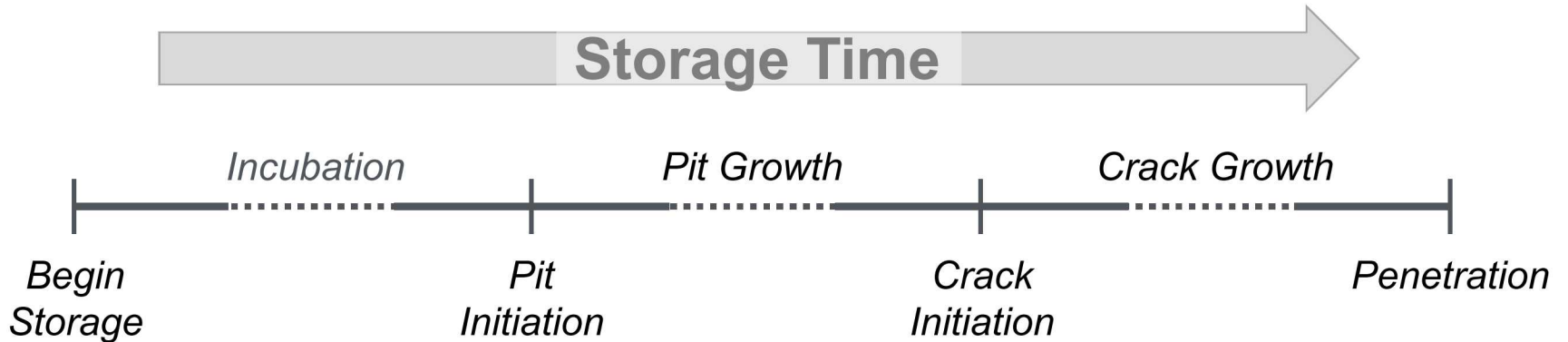
- 1) MgCl₂ converted to hydroxychloride (cathodic reactions/degassing?)
- 2) Chloride was sequestered in corrosion products (removal of brine component)

Summary: Characterization of the Environment

- As canister surface temperatures drop, deposited sea-salt aerosols will deliquesce, initially forming magnesium chloride-rich brines.
- Concentrated Mg-Cl brines are unstable at elevated temperatures, degassing HCl.
 - *Concomitant precipitation of a carbonate- or hydroxide-containing phase buffers the pH, allowing continued degassing.*
- Once corrosion initiates:
 - *The oxygen reduction reaction (ORR) produces hydroxides, and may promote precipitation of hydroxide-containing phases.*
 - *Corrosion products may sequester significant amounts of Cl from the brine.*
- In both cases, precipitation removes brine components, reducing brine volume at a given RH and eventually leading to dry-out.

Understanding brine stability is critical to predicting corrosion behavior under field conditions, and to interpreting laboratory test results.

Canister SCC: Corrosion Testing



SNL — Surface Environment, Brine Stability

CSM/SNL — Pitting Initiation and Growth (Effect of Stress)

SNL/OSU — Pitting Initiation and Growth, Pit-to-Crack Transition

SNL/UVA — Pitting Initiation and Growth

CSM — Pit-to-Crack Transition (Modeling)

SRNL (SNL) — Crack Growth Rates

NCSU (SNL) — Crack Growth Rates

SNL/OSU/UVA — Crack Growth Rates

PNNL/SNL — Crack Growth Rates

How do Surface Environment and Material Condition Affect Pitting and SCC?

How do Surface Environment and Material Condition Affect Pitting and SCC Onset?

IN THE SNL MODEL, CRACKING INITIATES ONCE A CRITICAL PIT SIZE OCCURS. FIRST WE EVALUATE PIT GROWTH AS A FUNCTION OF ENVIRONMENT.

ENVIRONMENT, $f(t)$

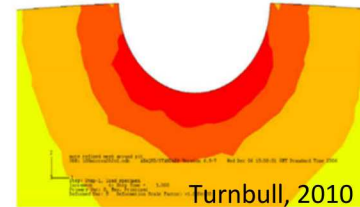
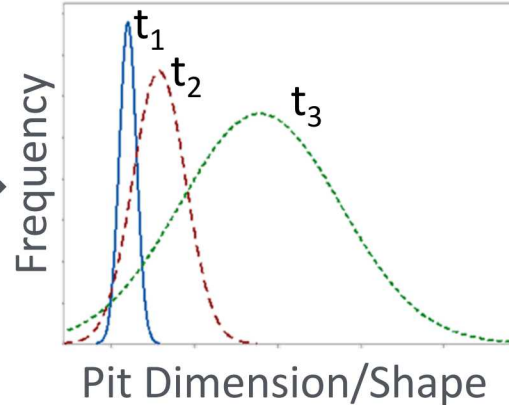
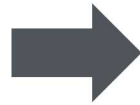
RH, T, Salt Chemistry, Salt Load

MATERIAL

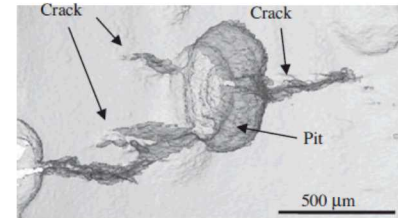
304H, 304L, 316L

MATERIAL CONDITION

Nominal stress/strain,
microstructure, surface finish



Stress intensity
threshold (K_{SCC})?
weakest link features?



Horner, 2011

Crack initiation

Effect of Humidity on Pitting and Cracking

TESTING RESULTS: AGED FOR ONE YEAR, SAMPLED PERIODICALLY, AND CHARACTERIZED THE PITS THAT FORMED

ENVIRONMENT, $f(T)$

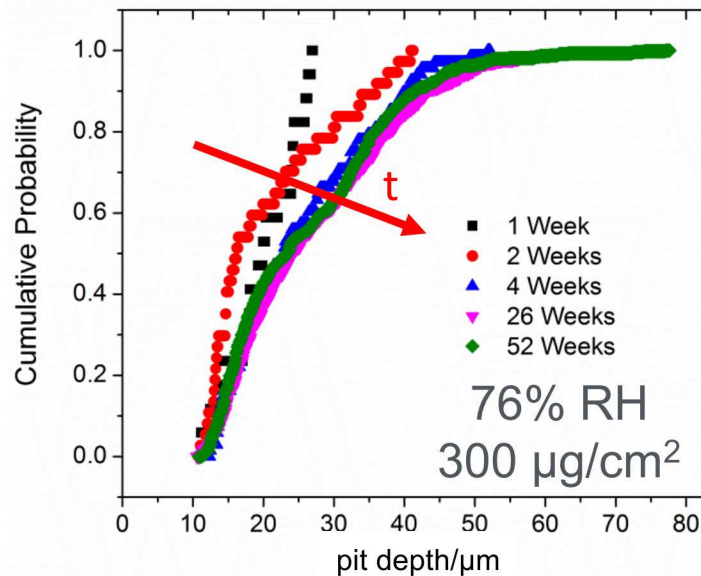
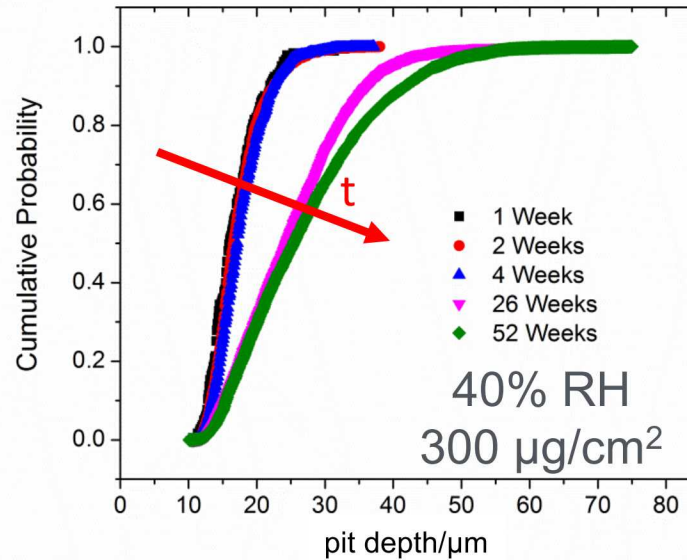
RH, T, seasalt, $10 \mu\text{g}/\text{cm}^2$ and $300 \mu\text{g}/\text{cm}^2$

MATERIAL

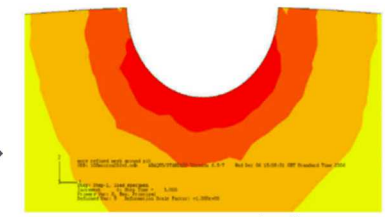
304H (unsensitized)

MATERIAL CONDITION

Ground to 120 grit size

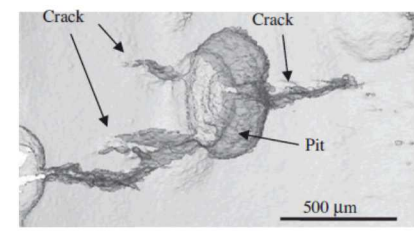


$K = f(\text{pit depth}, \sigma)$,
assuming hemispherical pits



Turnbull, 2010

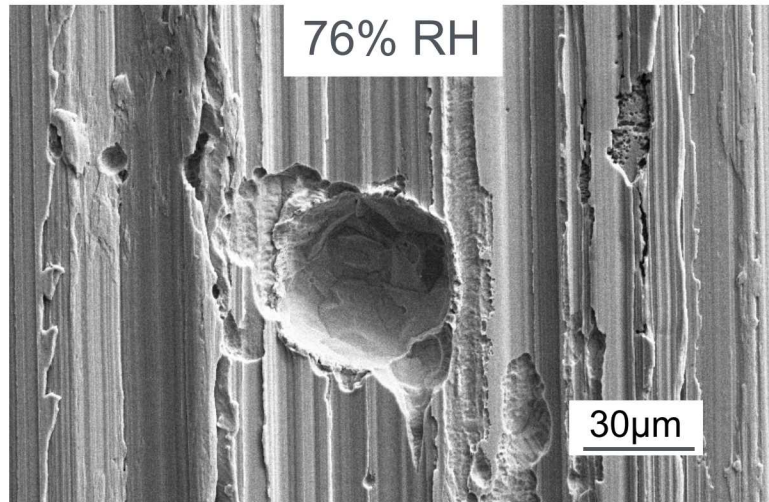
$K > K_{ISCC} ?$ Crack ?
initiation



Horner, 2011

Humidity Controls Pit Morphology and Cracking

HEMISPHERICAL PITS (NaCl RICH BRINE)

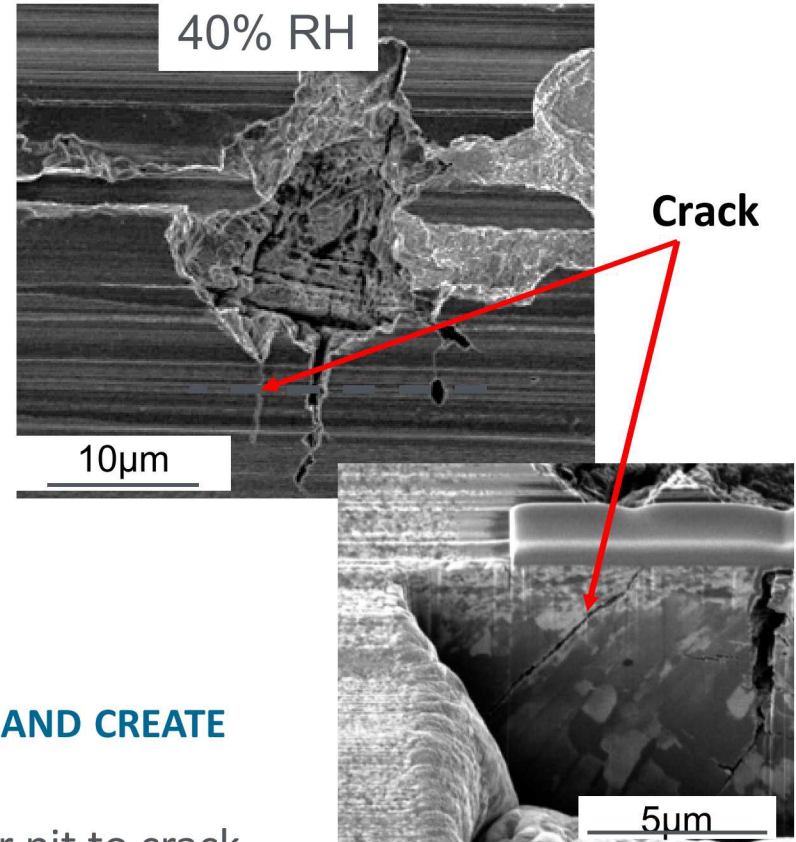


COMMONLY ASSUMED PIT MORPHOLOGY

BRINE CHARACTERISTICS CHANGE AT DIFFERENT RHs AND CREATE DIFFERENT PIT MORPHOLOGIES.

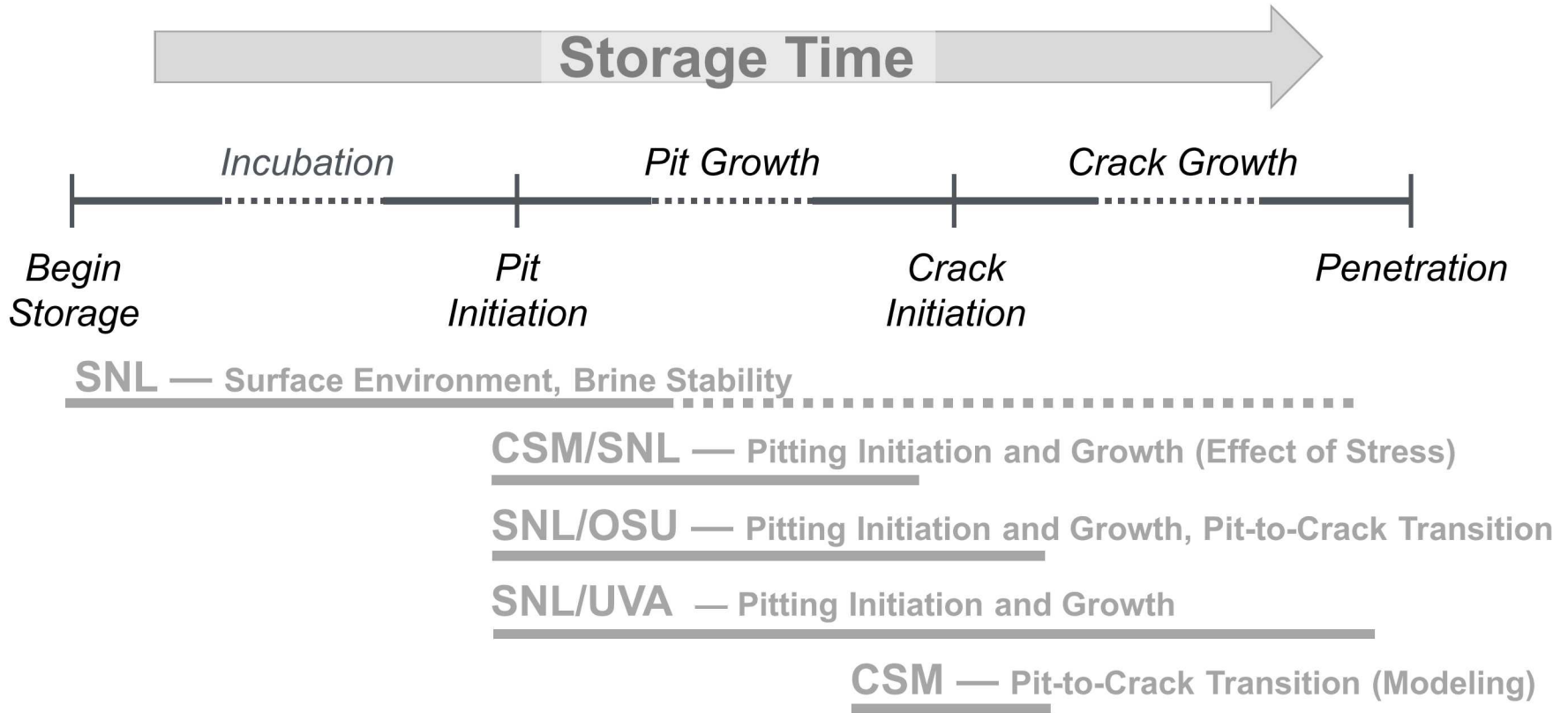
- Latest results challenge standard assumptions for pit to crack transition.
- Predicting cracking is more complicated.
- Current work focused on understanding factors for crack initiation

IRREGULAR PITS AND CRACKS (MgCl₂ RICH BRINE)



CROSS-SECTION THROUGH CRACKED REGION

Canister SCC: SCC Crack Growth Rates



What are crack growth rates as function of material and environment?



- SRNL (SNL)** — Crack Growth Rates
- NCSU (SNL)** — Crack Growth Rates
- SNL/OSU/UVA** — Crack Growth Rates
- PNNL/SNL** — Crack Growth Rates

Crack Growth Rates Under Canister Relevant Conditions (SRNL, PNNL, SNL)

KNOWLEDGE GAPS

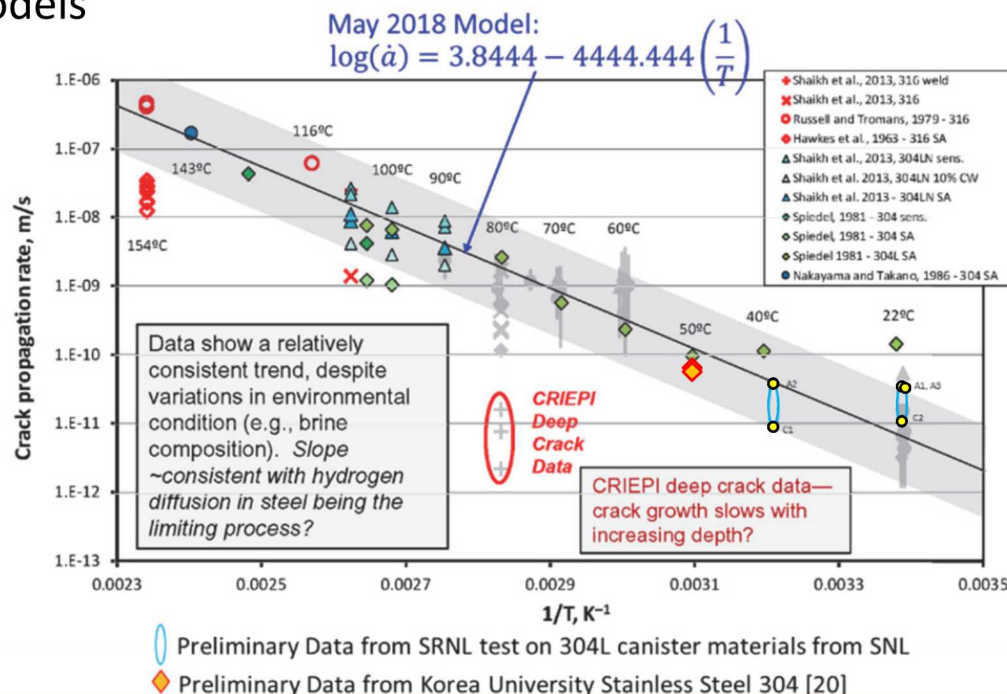
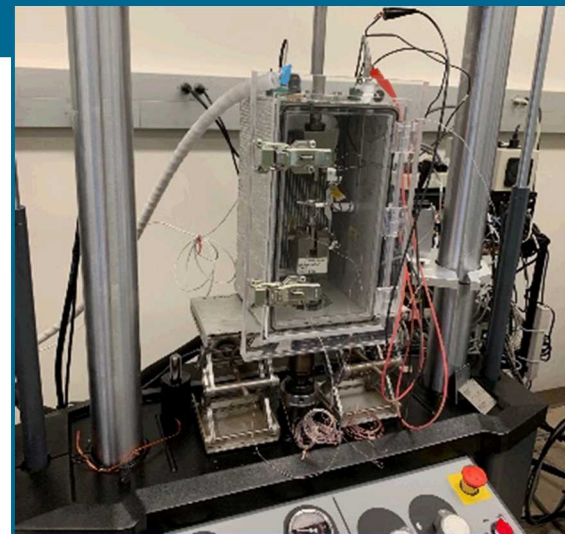
CGR data for austenitic SS in relevant atmospheric environments is lacking

GOALS

- 1) Quantify SCC behavior of SS via CGR vs. K in atmospheric conditions
- 2) Validation and development of SCC models

APPROACH

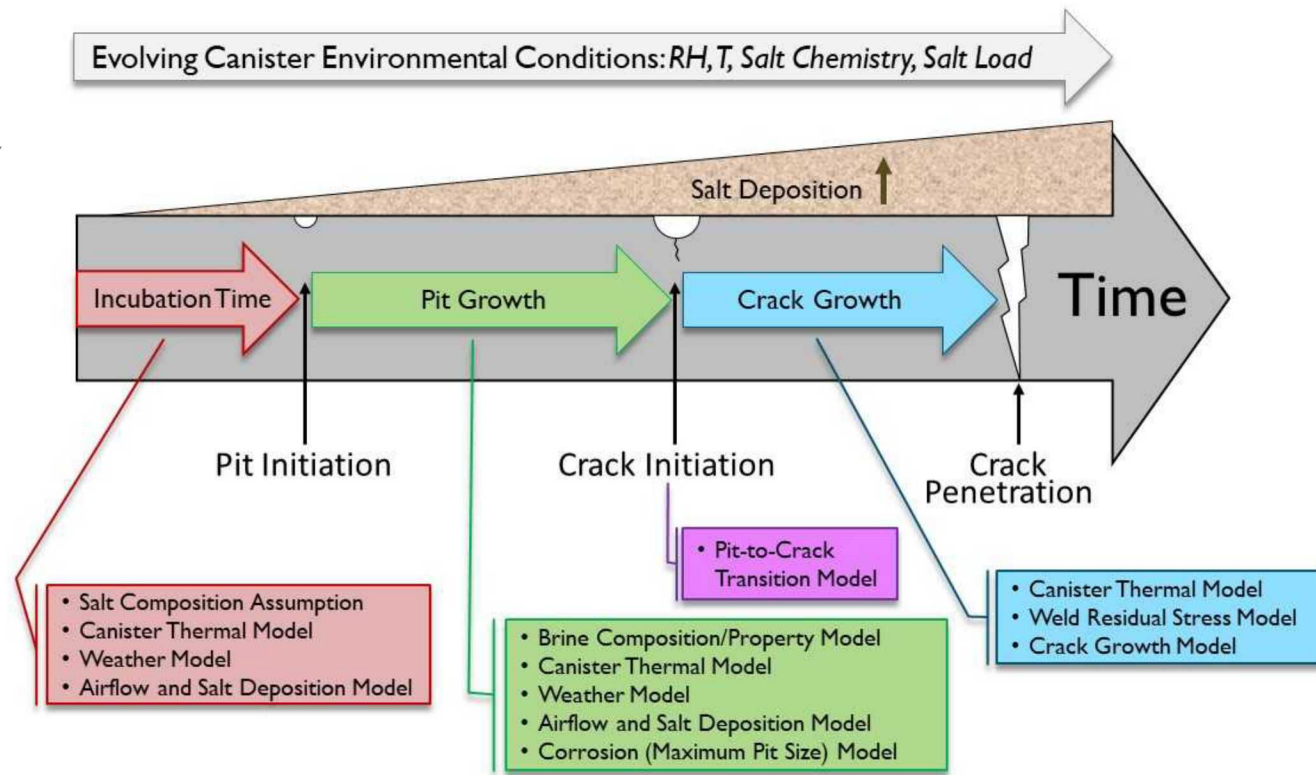
- High-fidelity fracture mechanics testing of crack growth rate as function of environment (*salt load, RH, T*) and material condition (*e.g., sensitized*)
- Develop probabilistic description of SCC growth and validate existing models



Integrated Mechanistic/Probabilistic Model for Canister SCC

CURRENT MODEL

developed by SNL is a work in progress. Current and planned experimental work is intended to parameterize this model.



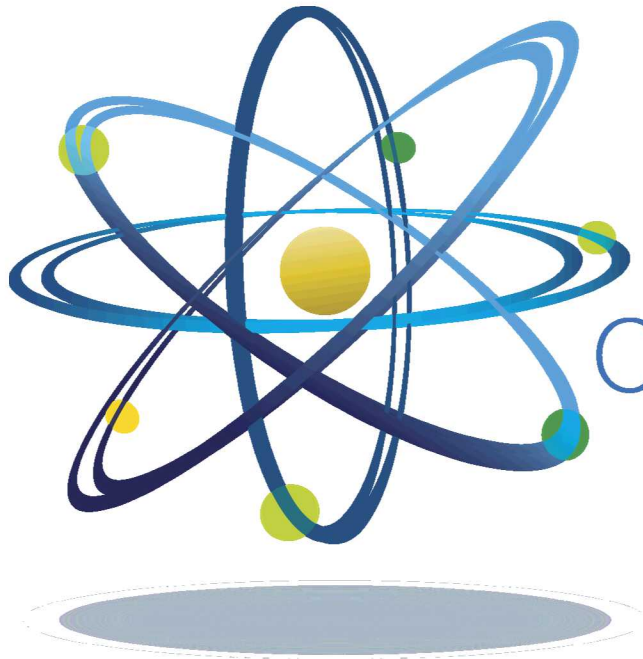
ISSUES

- Models and framework contains numerous assumptions and oversimplifications based on lack of data or mechanistic basis
- Sub-models have not been adequately validated

NEEDS

- Data for improved sub-model development and validation
 - Improved data on salt compositions/deposition rates at ISFSI sites
 - Statistical pitting and SCC data for canister-relevant conditions
- Improved scientific understanding of underlying mechanisms governing brine evolution, corrosion (pitting/SCC)

Questions?



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