

# Spent Fuel and Waste Science and Technology

SAND2017-5541PE

## Session: Corrosion of Spent Nuclear Fuel Canisters

**SFWST Working Group Meeting**  
**May 24, 2017**

- **Charles Bryan (SNL): Status Update, SCC Experimental Work at SNL**
- **Scott Gordon (CSM): Field Test at Maine Yankee ISFSI**
- **Dave Olson (CSM): Stress Analysis – Modeling vs. Mockup Data**
- **Robert Sindelar (SRNL): SCC Testing at SRNL**
- **Glenn Grant (PNNL): Friction Stir Welding**
- **Discussion: Opportunities for Collaboration (as time allows!)**

# Spent Fuel and Waste Science and Technology

## Status Update, SCC Experimental Work at SNL

**Eric Schindelholz and Charles Bryan**  
Sandia National Laboratories

**Zhenzhen Yu and Xin Wu**  
Colorado School of Mines

**Jenifer Locke and Timothy Weirich**  
Ohio State University

**SFWST Working Group Meeting**  
**May 24, 2017**

- **Time line for SCC of spent nuclear fuel canisters**
- **Major events, collaborators and roles**
  - Incubation period
  - Pitting initiation and growth
  - Pit-to-crack transition
  - Crack growth
- **FY17 Experiments**
  - Stability of sea-salt brines
  - Evaluating pitting initiation and growth
  - Evaluating controls on pit-to-crack transition
  - Evaluating crack growth rates
- **Planned work for FY18**

# Canister SCC: Important Processes

**SNL** — *Surface Environment, Brine Stability*

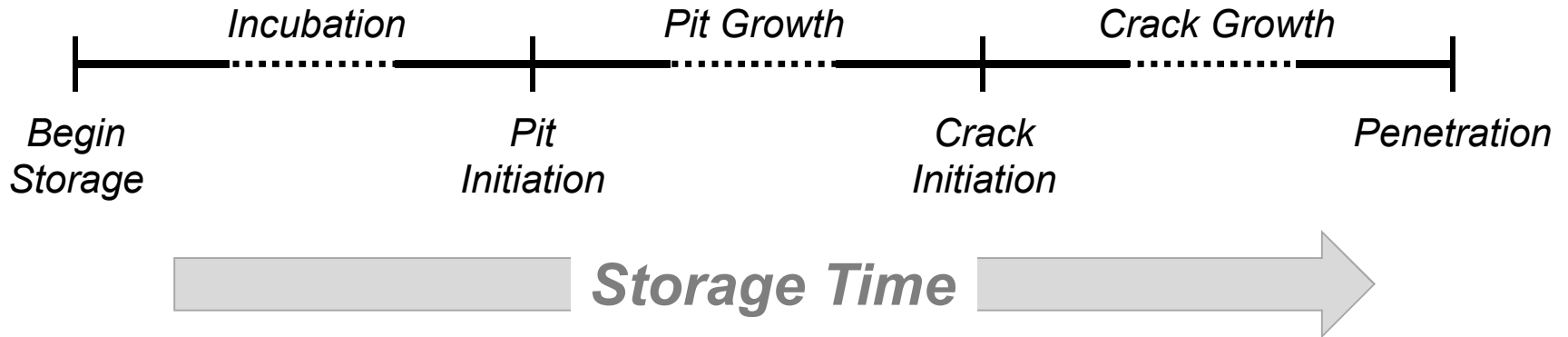
**SNL/OSU** — *Pitting initiation and growth,  
Pit-to crack transition (experimental)*

**CSM/SNL** — *Pitting initiation and growth (effect of stress)*

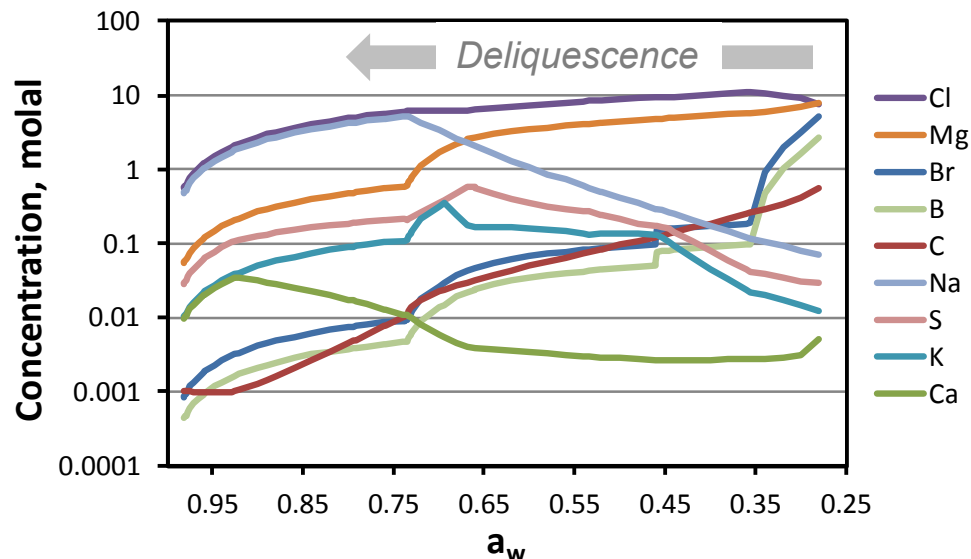
**CSM** — *Pit-to-Crack Transition (Modeling)*

**CSM/NCSU (SNL)** — *SCC growth rates*

**OSU (SNL)** — *SCC growth rates*



- Previous work: Demonstrated ammonium chloride or nitrate salts cannot persist at elevated temperatures in the solid state, nor can a brine containing  $\text{NH}_4^+$  and  $\text{Cl}^-$  or  $\text{NO}_3^-$ .
- Current efforts evaluate the stability of brines formed by sea-salt deliquescence.
- Sea-salt brines assumed to be those predicted by thermodynamic modeling of brine evaporation (deliquescence is the reverse process): initial deliquesced brines are Mg-Cl-rich, evolving to Na-Cl-rich brines with increasing RH.



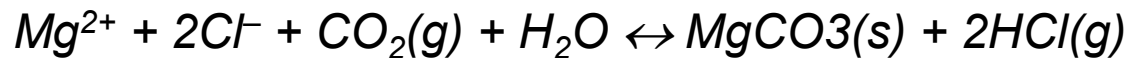
■ ***However***— equilibrium modeling fails to consider

- Effects of atmospheric exchange reactions occurring prior to corrosion
  - CO<sub>2</sub> and acid gas (H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>) absorption, HCl degassing
- Once corrosion initiates, effects of cathodic reactions on surface brine compositions (hydroxide generation, carbonation)

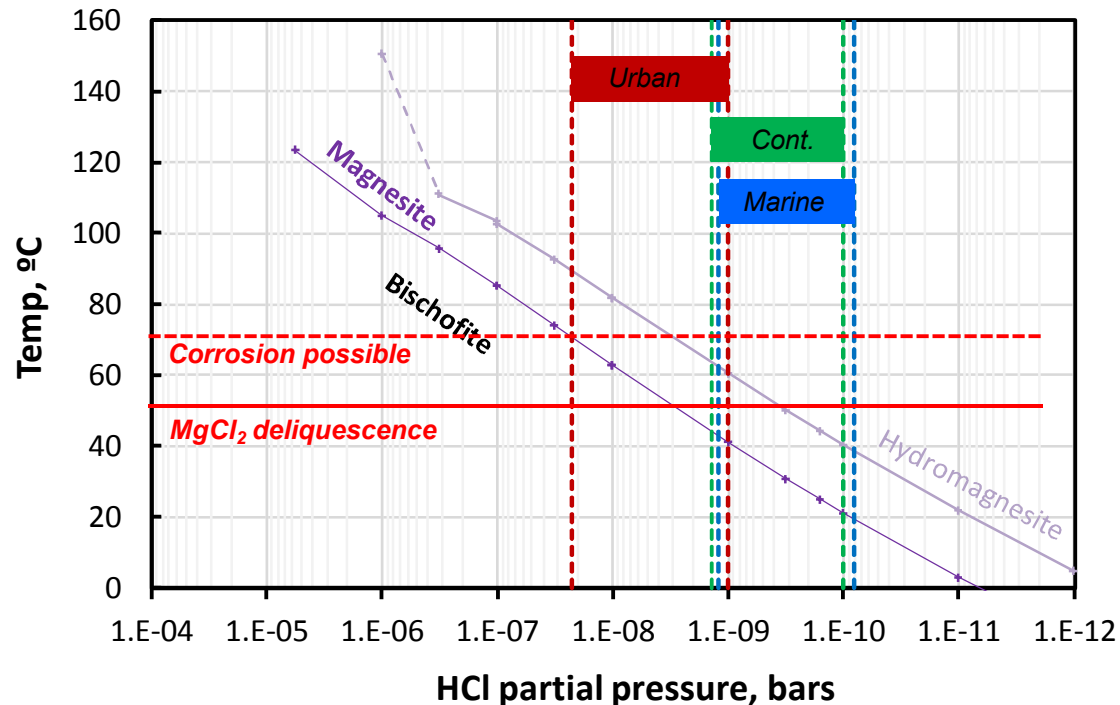
■ **FY 17 Experimental efforts**

- Effects of CO<sub>2</sub> absorption/carbonate precipitation on MgCl<sub>2</sub> brine stability
- Effects of cathodic reactions on surface brine films (composition and distribution)

- Brines may degas, or absorb HCl, depending on background acid gas concentrations.
- Current experiment (FY17) focuses on the effects of CO<sub>2</sub> exchange on Mg-chloride brines

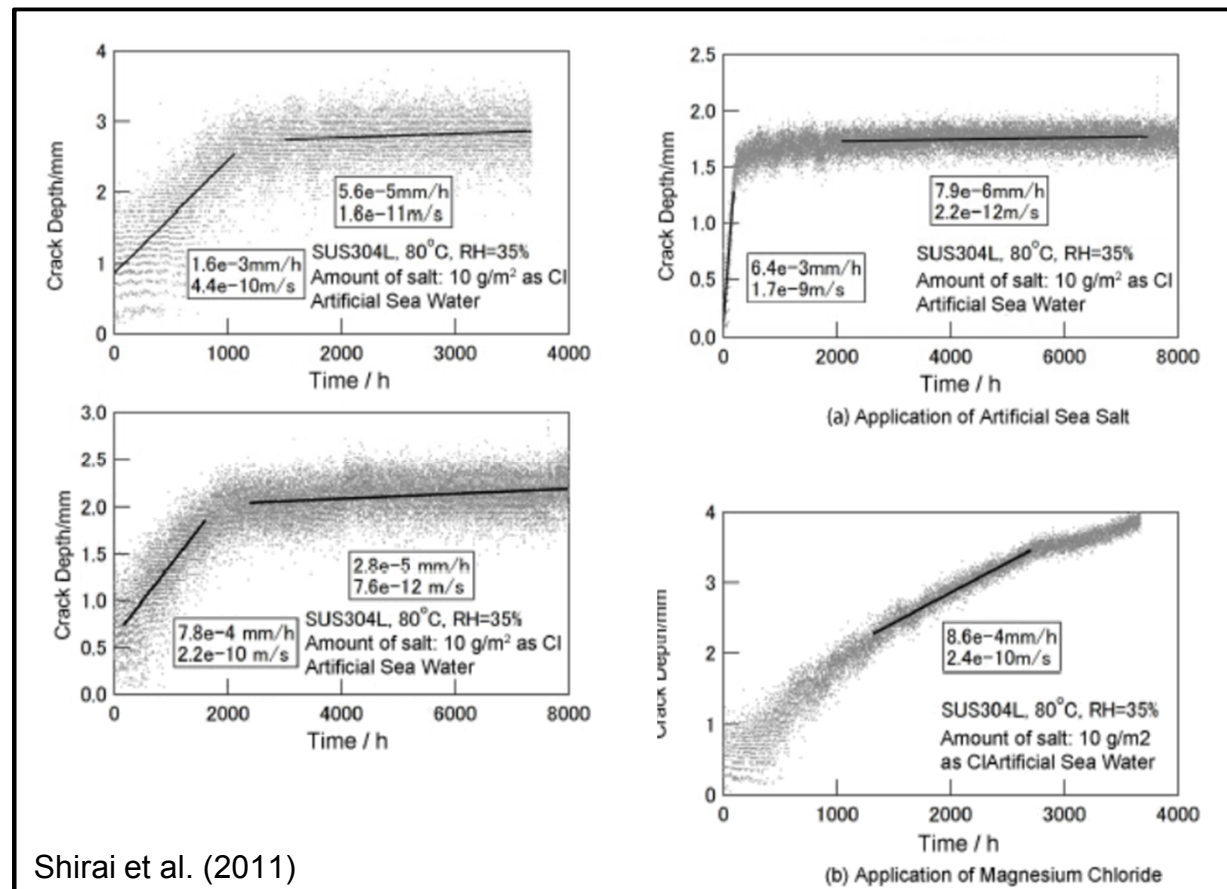


- MgCl<sub>2</sub> brine stability is a function of temperature and atmospheric HCl concentration; brine may absorb CO<sub>2</sub> and convert to Mg-carbonate
- Other acid gas reactions (e.g., H<sub>2</sub>SO<sub>4</sub>) may be more important under field conditions.
- However, carbonation may be VERY important for laboratory experiments (e.g. CRIEPI).
- MgCl<sub>2</sub> brine stability experiments in progress (one-month sampling showed little reaction (low gas flow rates?))



CO<sub>2</sub> absorption/carbonation may be VERY important for some laboratory experiments. For instance, CRIEPI.

*At 80°C, 35% RH, air exchange of only a few cubic meters would be necessary to convert the small amount of MgCl<sub>2</sub> present in the sea-salts to carbonate, drying out the brine.*



Shirai et al. (2011)

**Knowledge Gaps:**

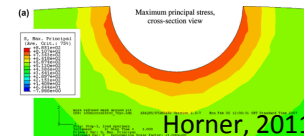
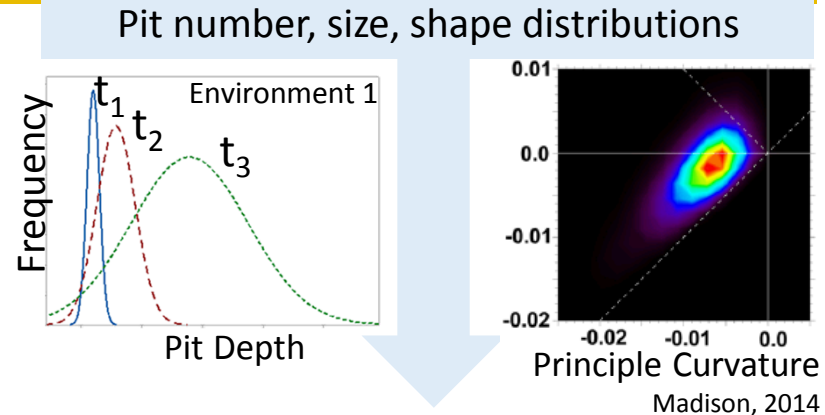
- Pitting kinetics, damage distributions (max pit size?) under ISFSI-relevant environmental conditions (T, RH, salt load)
- Pit-crack transition controlling factors

**Goals:**

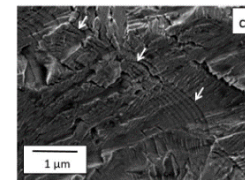
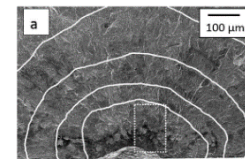
- 1) Quantify relationship between environment and pitting damage distributions and rates
- 2) Identify hierarchical weakest links for pit corrosion feature to SCC crack transition

**Approach:**

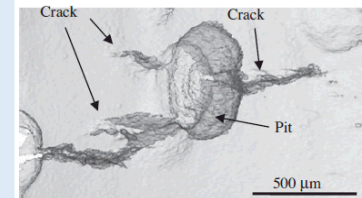
- Parametric coupon-level pitting experiments in ISFSI-relevant environments
- Constant load marker band SCC tests in same environments to determine corrosion features that act as crack initiation sites



??  $K \geq K_{th}$



Donahue, 2016



Horner, 2011

Micromorphological characterization of  
pit-crack initiation sites

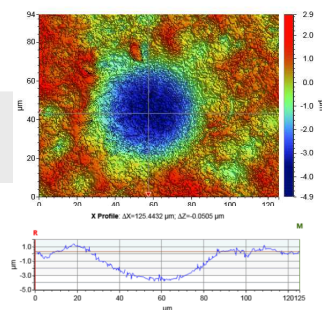
High-throughput Approach for Building Parametric Datasets



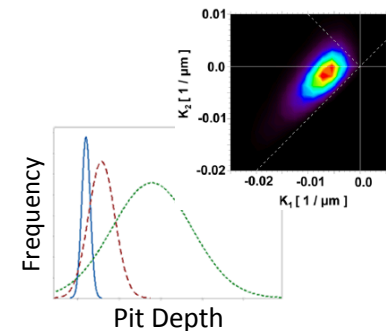
Inkjet printing for high-throughput salt loading

%RH	Temperature (°C)				
75	35				
70	35				
65	35				
60	35				
55	35	40			
50	35	40			
45	35	40	45		
40	35	40	45	50	55
35	35	40	45	50	
30	35	40	45	50	

ISFSI-Relevant Conditions



Optical profilometry and pit analysis (OSU)



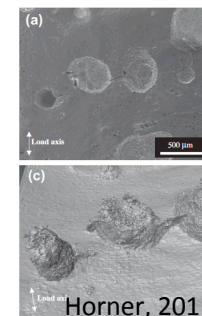
Pitting kinetics and shape distributions (SNL/OSU)

**Approach:**

- 304H coupon and tensile test bars loaded with artificial sea salt and exposed to fixed environmental conditions for up to 2 years
- Material details:
  - 304H, unsensitized and sensitized
  - Mirror, 120 grit “mill” finish
  - 10 and 300 ug/cm<sup>2</sup> seasalt



Serial Sectioning (SNL)



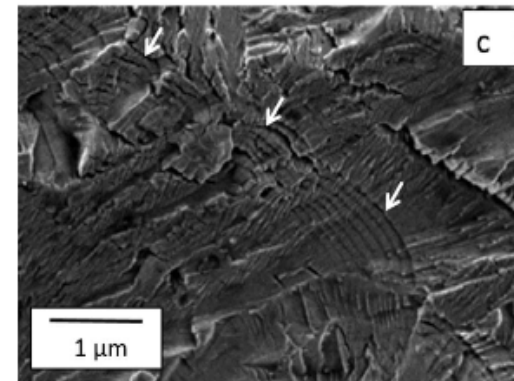
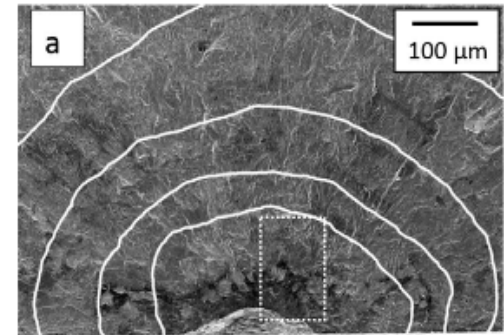
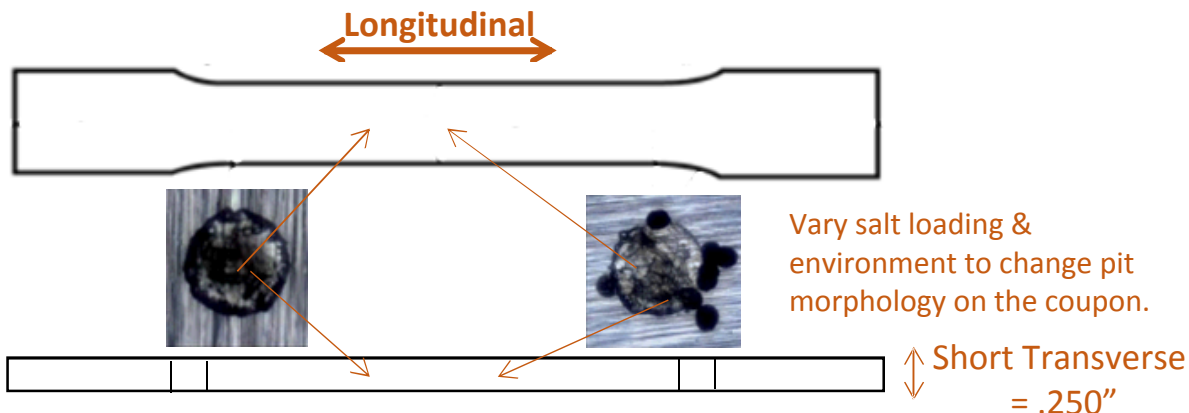
X-ray Microtomography (SNL)

Pit Micromorphology Characterization

# Spent Fuel and Waste Science and Technology Pit to Crack Transition Study

**Goal:** Quantify the hierarchical weakest link for corrosion feature to SCC crack transition

- Variables:
  - Pit features (ex. narrow vs. wide)
  - Corrosion morphology (Single vs. Satellite Pits)
  - Material type
- Method: SCC testing
  - Gauge length of longitudinal tensile bars will be loaded with salt and corroded in a humidity controlled chamber.
  - Constant load with intermittent high R ripple fatigue loads during SCC tests to determine corrosion features that act as crack initiation sites.



J. R. Donahue and J. T. Burns, Effect of chloride concentration on the corrosion-fatigue crack behavior of an age-hardenable martensitic stainless steel, *International Journal of Fatigue* 91 (2016), 79-99.

# Spent Fuel and Waste Science and Technology Plans – (2) SCC Testing

- *How does corrosion morphology affect crack initiation?*
- *Use same environmental conditions as coupon corrosion tests for SCC testing.*
  - *Pitting characteristics fully characterized for corrosion coupons/sacrificial tensile bars. This data will help explain cracking results.*



- *Load salt and corrode side of coupons (red)*
- *Remove from humidity chamber and print salt on face of coupon (green)*
  - *Extra salt on face will contribute electrolyte to the crack tip during propagation*

## Sampling plan for corrosion coupons

Environment	Salt Load	1 wk	2 wk	1 mo.	6 mo.	12 mo.	18 mo.	24 mo.
35°C, 40%RH	300 µg/cm <sup>2</sup>	X	X	X	X	X	X	X
35°C, 75%RH	10 µg/cm <sup>2</sup>	X	X	X	X	X	X	X
35°C, 75%RH	300 µg/cm <sup>2</sup>	X	X	X	X	X	X	X

*\*Matrix same as coupon tests, but with low-humidity / low-salt-load samples removed*

## Knowledge Gaps:

- Relevance and accessible limits of existing deterministic damage models relative to canister conditions

## Goals:

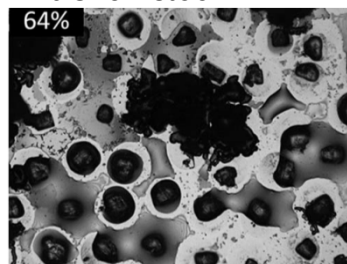
- 1) Characterize electrolyte coverage and chemistry distribution during exposure in ISFSI-relevant environment
- 2) Quantify impact on electrochemical processes driving pitting and SCC

SNL: Eric Schindelholz, Charles Bryan, Chris Alexander

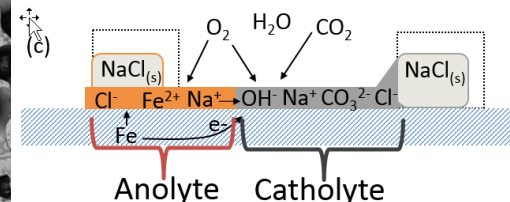
OSU/EFRC: Jen Locke, Tim Weirich

CSM: Zhenzhen Yu, Xin Wu

NaCl on steel

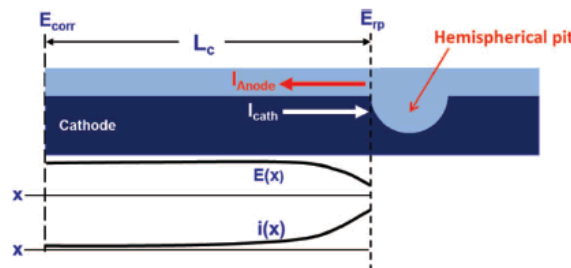


Schindelholz, 2014

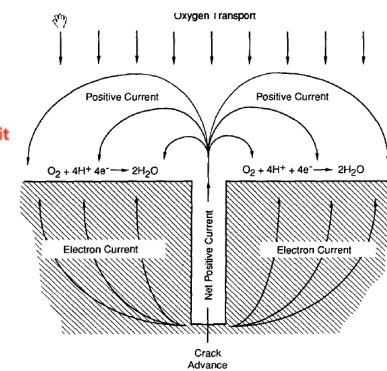


maximum pit size

crack growth rate (?)



Chen et al. 2008



MacDonald, 1991

# Spent Fuel and Waste Science and Technology

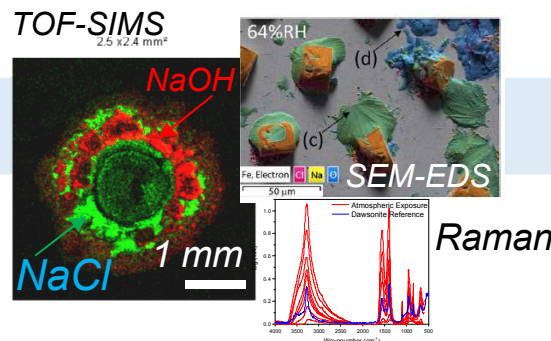
# Impact of Corrosion on Surface Environment, Damage Distributions, and Rates: Coupon-Level Studies



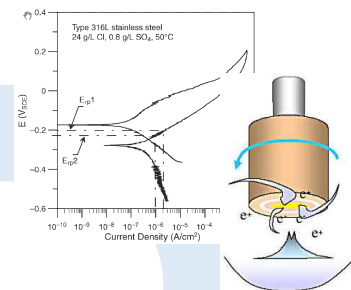
Inkjet printing for high-throughput salt loading

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ISFSI-Relevant Conditions



Extent of electrolyte coverage and chemistry distribution

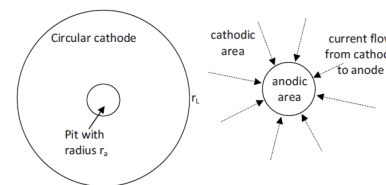


## Approach:

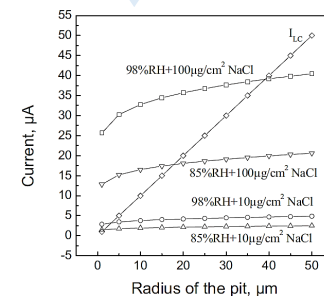
- Post-exposure surface analyses of coupons from pitting experiments:
- TOF-SIMS, MicroRaman/FTIR, Auger Spectroscopy
- Cathodic kinetics of 304 in analog surface chemistries (sea-salt brines, carbonate brines)
- Establish variance in max pit size model predictions due to evolving electrolyte, extend knowledge to CSM SCC electrochemical model

Max. cathode current, Brine conductivity, Brine layer thickness, Cathodic kinetics

$$\ln I_{c,max} = \frac{4\pi k W_L \Delta E_{max}}{I_{c,max}} + \ln \left[ \frac{\pi e r_a^2 \int_{E_{corr}}^{E_{rp}} (I_c - I_p) dE}{\Delta E_{max}} \right]$$



Chen and Kelly, 2010



**Knowledge Gap:**

How material characteristics (microstructure, stress/strain) and environment (T, RH, salt load) impact electrochemical processes governing SCC

**Goal:**

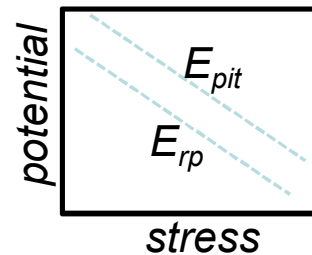
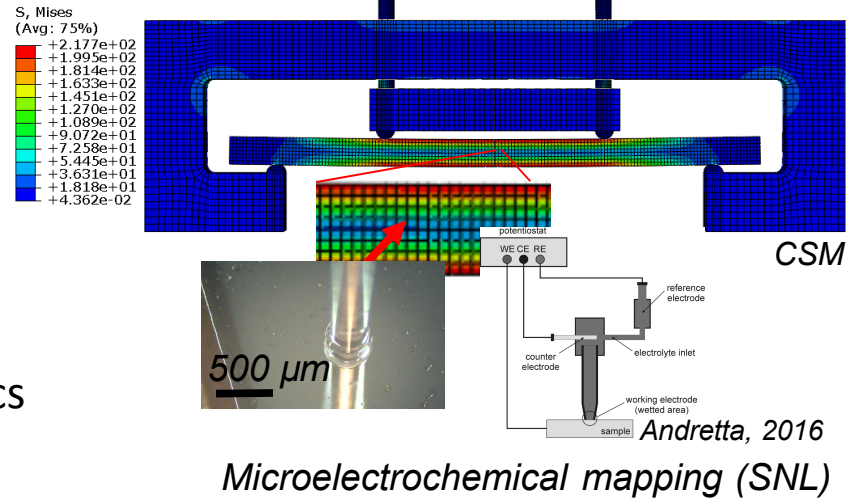
Prediction of pitting/repassivation characteristics of 304 under varied static stress loads

**Approach:**

- Microelectrochemical mapping of CSM 4-point bend specimens as a function of stress load
- Develop model to capture pitting characteristics as function of stress/strain with correlation to CSM 4-point bend exposures

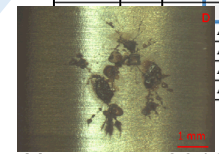
SNL: Eric Schindelholz, Charles Bryan, Chris Alexander

CSM: Zhenzhen Yu, Xin Wu



Stress effect on localized corrosion susceptibility

%RH	Temperature (°C)	
75	35	
70	35	
65	35	
60	35	
55	35	40
	45	
	45	55
	45	50
	45	50



Pit distribution on atmospherically exposed samples (CSM)

Newmann, 2016

■ **Stability of Deliquescent Sea-salt Brines**

- Thermodynamic calculations suggest Mg-Cl brines are not stable at elevated temperatures
- Significant implications for timing of deliquescence, conditions of corrosion
- Long-term experiments underway (after one month, little or no effect)

■ **Pitting Damage Quantification and Pit-Crack Transition**

- 2 year coupon test initiated
- OSU tensile specimens and will be added to test, Q3
- Post analysis of first coupon pulls (1 wk, 2wk, 1 month) planned for Q3, 4

■ **Surface Chemistry/Electrochemistry Characteristics**

- Demonstrated ability to map cathodic chemistry using TOF-SIMS
- Chemistry mapping of first coupon pulls (above), Q4
- Cathodic kinetics in concentrated seawater and catholyte brines, Q3,4
- Variance in max pit size predictions using Chen-Kelly model with above inputs, Q4

■ **Electrochemical Pitting-Stress Linkage**

- Coordination with CSM for experimental design and sample acquisition, Q1
- Adapt microcapillary platform and demonstrate mapping of 4-point bend specimen, Q4

- **SNL Full-Diameter Cylindrical Canister Mockup**
  - Stress measurements completed and final report issued in late 2016
  - Weld and base metal samples cut from the canister for dissemination to interested parties
- **Additional Corrosion Test Materials purchased by SNL (4' x 8' x 5/8" plates)**
  - 304L
  - 304H (almost all distributed)
- **Samples shared with the following entities**
  - Colorado School of Mines (IRP) – materials characterization/corrosion testing
  - EPRI – NDE development and testing
  - NAC International – NDE testing
  - North Carolina State University(CSM IRP) – corrosion testing
  - Ohio State University (EFRC) – corrosion testing
  - ORNL – mechanical properties testing
  - SRNL – materials characterization/corrosion testing
  - SwRI – corrosion testing
- **One-half of the canister left—will be sectioned into samples in FY18**

- **Once pit characterization techniques are demonstrated, increase pitting corrosion test matrix (additional T, RH, salt loads)**
- **Impact of salt morphology/configuration (salt particle size and distribution)**
- **Electrochemical mapping of canister mockup weld/HAZ**
  - Potential Galvanic effects
  - Degree of sensitization
- **Coupon Size Effect**
  - Chen and Kelly (2010) model predicts cathodes larger than our current coupon size
- **Corrosion testing of large mockup specimen**
  - Link between lab tests on homogeneous specimens and corrosion in real weld zones
  - Possible weld/HAZ/base metal galvanic effects (potentially affect pit sizes, locations, morphology)
  - Locations of SCC initiation in weld zones
  - SCC crack orientations/morphologies

# Summary: Current Efforts

**SNL** — *Surface Environment, Brine Stability*

Timing of  
corrosion and  
extent of damage

Environmental  
controls on pit size  
and crack initiation, pit  
size/shape controls on  
crack initiation

**SNL/OSU** — *Pitting initiation and growth,  
Pit-to crack transition (experimental)*

**CSM/SNL** — *Pitting initiation and growth (effect of stress)*

**CSM** — *Pit-to-Crack Transition (Modeling)*

SCC crack growth  
rates: effect of  
environment

**CSM/NCSU (SNL)** — *SCC growth rates*

**OSU (SNL)** — *SCC growth rates*



**IMPACT:** Improved prediction of timing of corrosion initiation, SCC initiation and growth, and potential canister penetrations times. Will provide critical information for development of ASME standard for canister inspections, and system Aging Management Plans.