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SNF Storage Canister Pitting and SCC: Current Research at Sandia National Labs

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Sandia National Laboratories

Spent Fuel and Waste Science & Technology Program

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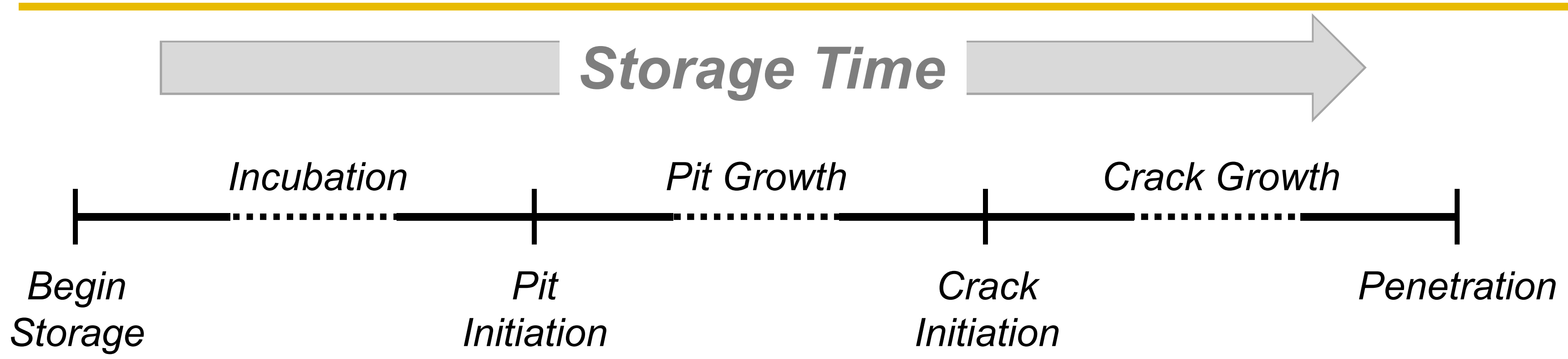
SNL Objectives

- *Advance definition of physical and chemical electrolyte characteristics – inform modeling and laboratory studies*
- *Understand relationship between surface environment and damage distributions and rates*
- *Quantify impact of material and mechanical environment variability on corrosion and SCC processes*

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)

NCSU (SNL) — SCC growth rates

OSU (SNL) — SCC growth rates

SNL/LANL — mockup pitting/cracking

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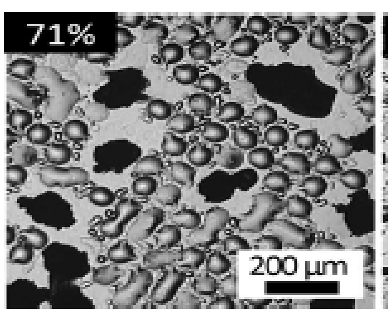
Linking Surface Environment and Material with Damage

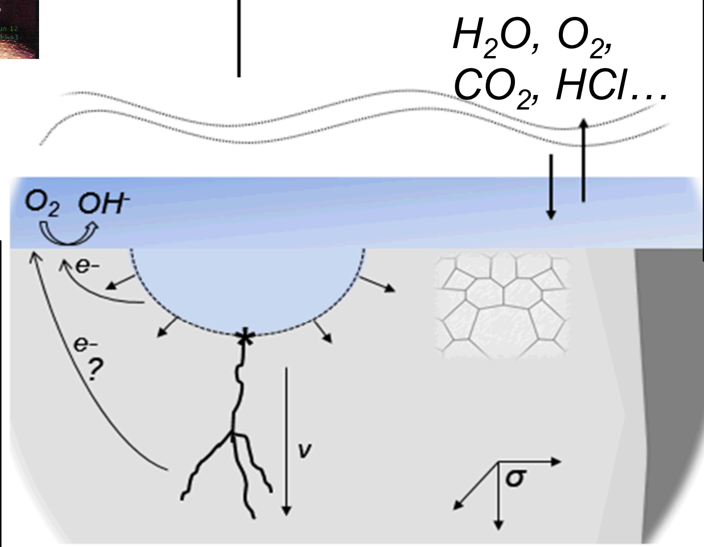
How representative are lab conditions?

Surface/atmospheric chemistry, RH variation

Environmental control of damage distribution and rates?



Salt loads and distributions, temperature, RH



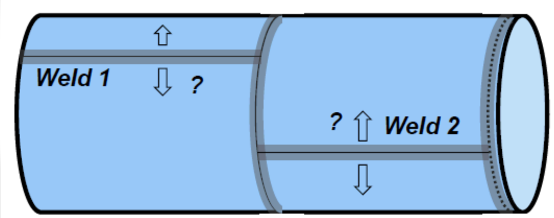
What are limits of model accuracy?

$$\frac{da}{dt} = \begin{cases} \alpha \exp\left[-\frac{Q_g}{R}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right] & \text{for } RH \geq DRH \text{ and } K_I > 0 \\ 0 & \text{for } RH < DRH \text{ or } K_I \leq 0 \end{cases}$$

EPRI, 2017

Benchmarking datasets, bounding limits, test assumptions, model confidence

Where to focus inspection?

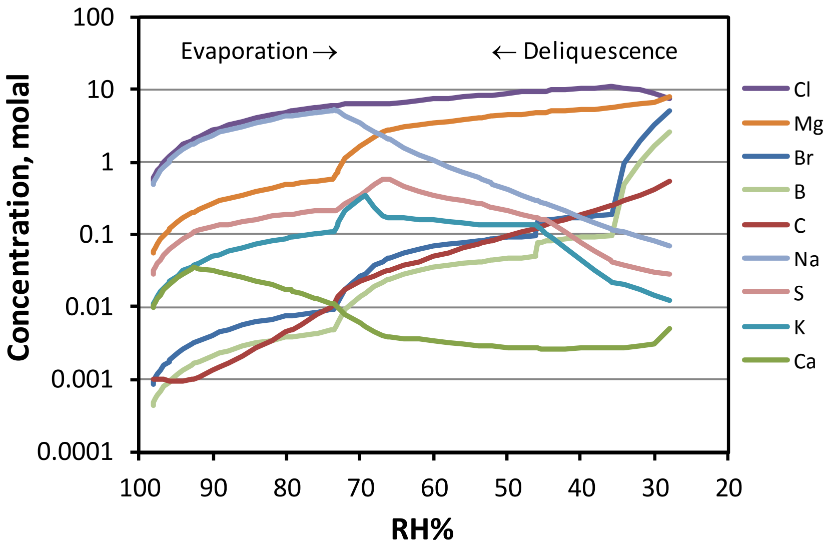


Variations in canister surface environment, material properties, and stress

Salt Compositions and RH_d:
Geochemical modeling of seawater evaporation

Brine composition:

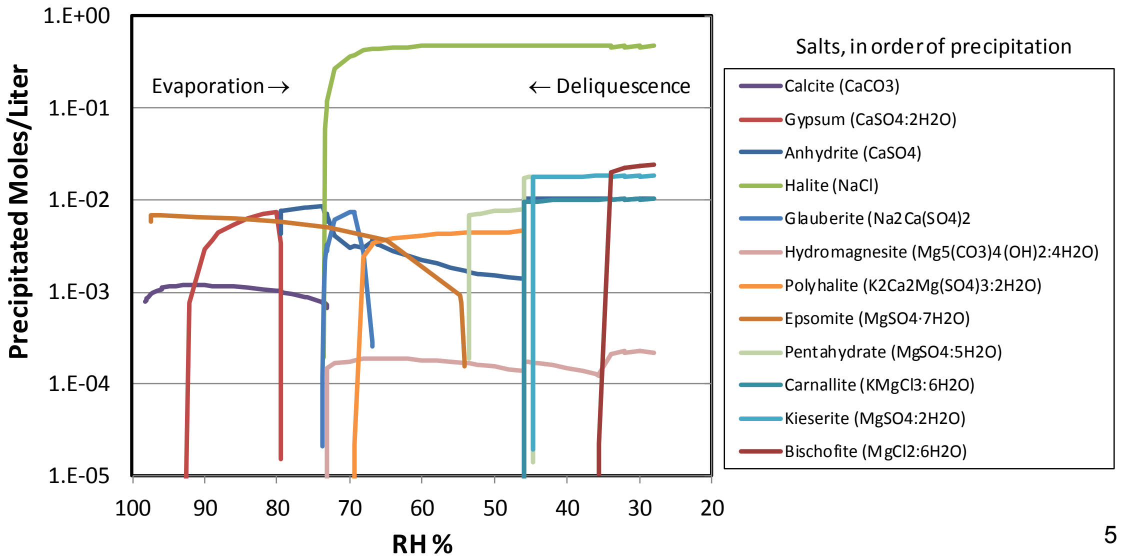
- Upon evaporation, salts precipitate and redissolve.
- Seawater evolves towards concentrated Mg-Cl brine as NaCl precipitates
- Br and B conserved (but may be model artifact)
- Ca, K, S are mostly removed by minerals, and are very low in the remaining brine.
- *Deliquescence is the reverse of evaporation.*



Precipitated salts:

- Upon evaporation, several salts precipitate and re-dissolve.

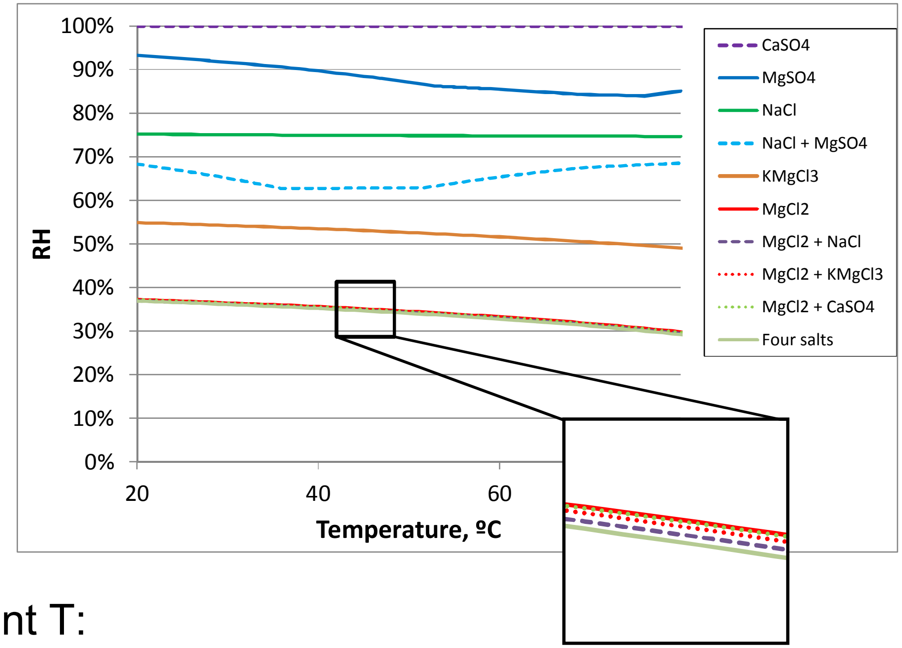
> *Final assemblage determines deliquescence RH (RH_d)*
> - *NaCl (halite)*
> - *$MgCl_2$:$6H_2O$ (bischofite)*
> - *$MgSO_4$:$2H_2O$ (kieserite)*
> - *$KMgCl_3$:$6H_2O$ (carnallite)*
> - *$CaSO_4$ (anhydrite)*



Predicted Deliquescence of Individual Sea-Salt Minerals and of Assemblage

Deliquescence points:

Salt composition	Mineral	DRH
Ca-SO_4	gypsum, anhydrite	>99%
Mg-SO_4	four different hydrates	93-84%
NaCl	halite	77%
$KMgCl_3$:$6H_2O$	carnallite (±sylvite)	55-49%
$MgCl_2$:$6H_2O$	bischofite	36-29%
$MgCl_2$:$6H_2O$ + other salts:	bischofite + other salts	~Same as $MgCl_2$:$6H_2O$



However, experimental data indicate that corrosion occurs at lower RH values…

- **Schindelholz et al. (2014)**: mild steel, ambient T:
  - $MgCl_2$—corrosion as low as 11% RH
  - Sea-salts—corrosion as low as 23% RH
- **NRC (2014)**: 304SS, variable T: Sea-salts—corrosion between 20% and 30% RH
- **Shirai et al. (2011)**: 304SS, 80ºC: Sea-salts—corrosion as low as 15% RH
- **Fairweather et al. (2008)**: 304SS: Sea-salts—corrosion at 15% RH, 45º and 60ºC.

Are these modeling and experimental results relevant to field conditions?

Effects of Atmospheric Exchange Reactions

- **Equilibrium modeling fails to consider the effects of atmospheric exchange reactions occurring prior to corrosion —CO_2 and acid gas (H_2SO_4, HNO_3) absorption, HCl degassing:**

$$NaCl(s, aq) + HNO_3(g) \leftrightarrow NaNO_3(s, aq) + HCl(g)$$

$$2NaCl(s, aq) + H_2O + \tfrac{1}{2}O_2 + SO_2(g) \leftrightarrow Na_2SO_4(s) + 2HCl(g)$$

And similar reactions that occur with Ca, Mg. For instance:

$$Mg^{+2}(aq) + 2Cl^{-}(aq) + H_2O + CO_2(g) \rightarrow MgCO_3(s) + 2HCl(g)$$

- **Laboratory testing minimizes atmospheric exchange and the effect of these reactions, as well.**

We are currently evaluating the Mg-carbonation, which is strongly temperature-dependent.

Once corrosion initiates, cathodic reactions (hydroxide generation, carbonation) can also modify surface brine compositions and distributions, and promote atmospheric exchange. We are also evaluating these reactions.

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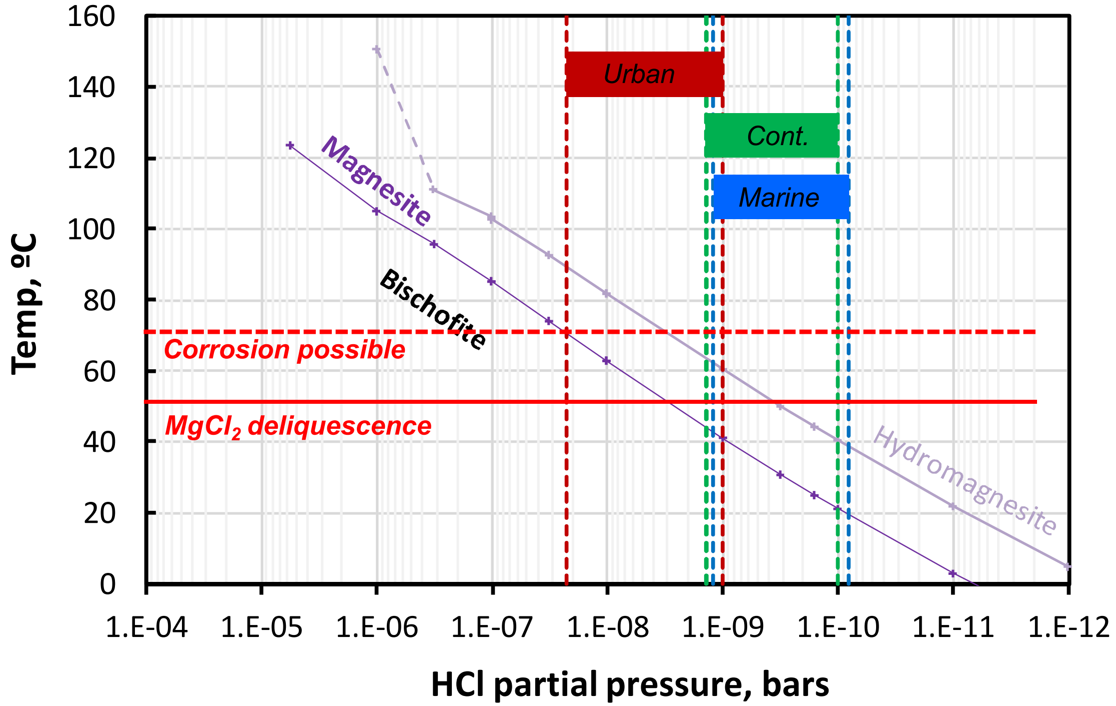
$MgCl_2$ Brine Stability at Elevated Temperatures

$$Mg^{2+} + 2Cl^{-} + CO_2(g) + H_2O \leftrightarrow MgCO_3(s) + 2HCl(g)$$

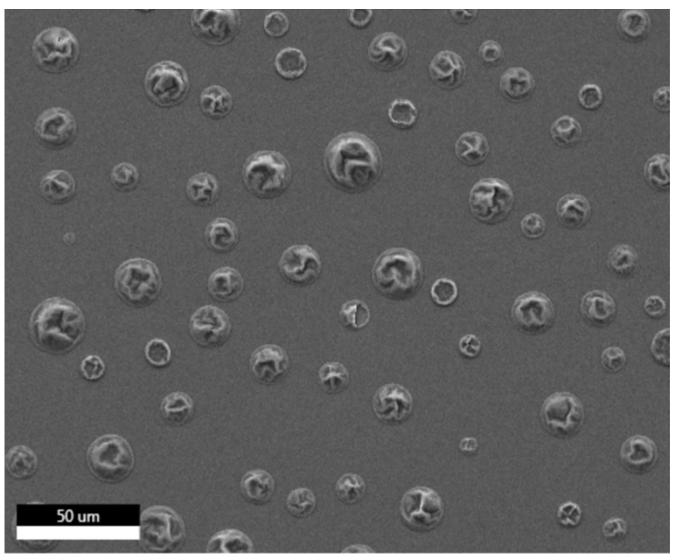
- **Brines may degas or absorb HCl, depending on background acid gas concentrations**
- **$MgCl_2$ brine stability is a function of temperature and atmospheric HCl concentration; brine may absorb CO_2 and convert to Mg-carbonate**
- **$MgCl_2$ brine stability experiments in progress**
  Difficult to run—carbonation is minimized in laboratory settings by low gas exchange rates

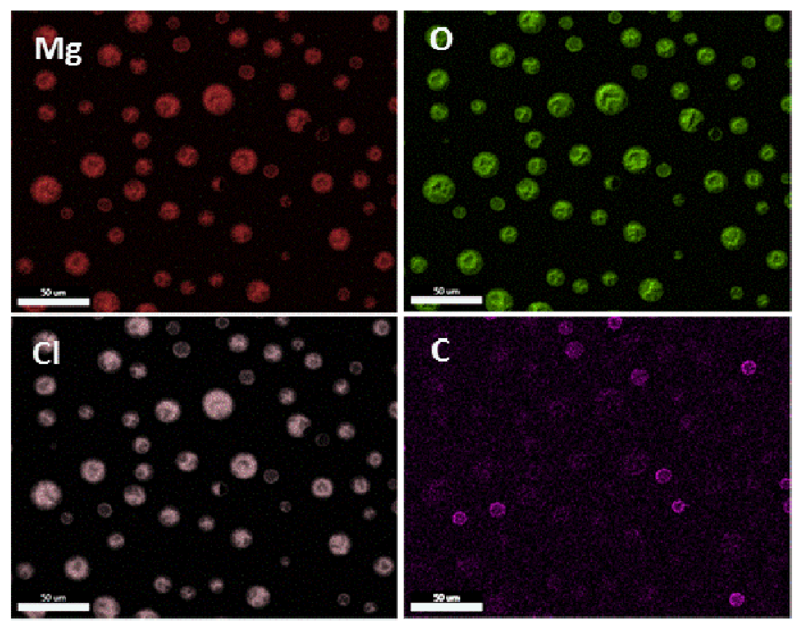


Preliminary Experimental Results:

$MgCl_2$ brine at 48ºC, 40%RH, $P_{HCl} = 0$

- ***$MgCl_2$ brine, 48ºC, 40% RH, for two months in an RH chamber with 2 L/minute air flow.***
- ***Partial conversion to carbonate observed; later chemical analysis suggests <10% chloride lost.***
- ***Airflow too low to support complete conversion. At 48ºC, one m^3 of air can only remove 1.3 ug (hydromagnesite) to 13 ug (magnesite) chloride.***





Significance of Experimental Results

Other acid gas reactions (e.g., H_2SO_4) may be more important under field conditions. However, considering carbonation may be VERY important for planning and interpreting laboratory experiments.

- **Limited airflow in experiments, will minimize effect of atmospheric exchange reactions relative to field conditions.**
- **Experiment design may strongly affect results. E.g.,**
  - *RH chamber, high air flow → HCl degassing and brine dryout*
  - *RH controlled by saturated salt solution → no air flow, no HCl degassing, no dryout*
  - *Results may be affected by total amount of chloride or number of samples present.*
- **Background acid gas concentrations in lab (HCl, H_2SO_4 or SO_2, HNO_3) may have a large effect.**
- **Accelerated (high temperature) tests may be especially affected, as HCl degassing is favored at elevated temperatures.**
  - *Running additional experiment at accelerated conditions (80°C and 35% RH) to evaluate potential for degassing and dry-out*

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Pitting Damage Quantification Experiments:

Inform Probabilistic Models and Pit-Crack Transition

<u>Knowledge Gaps:</u>

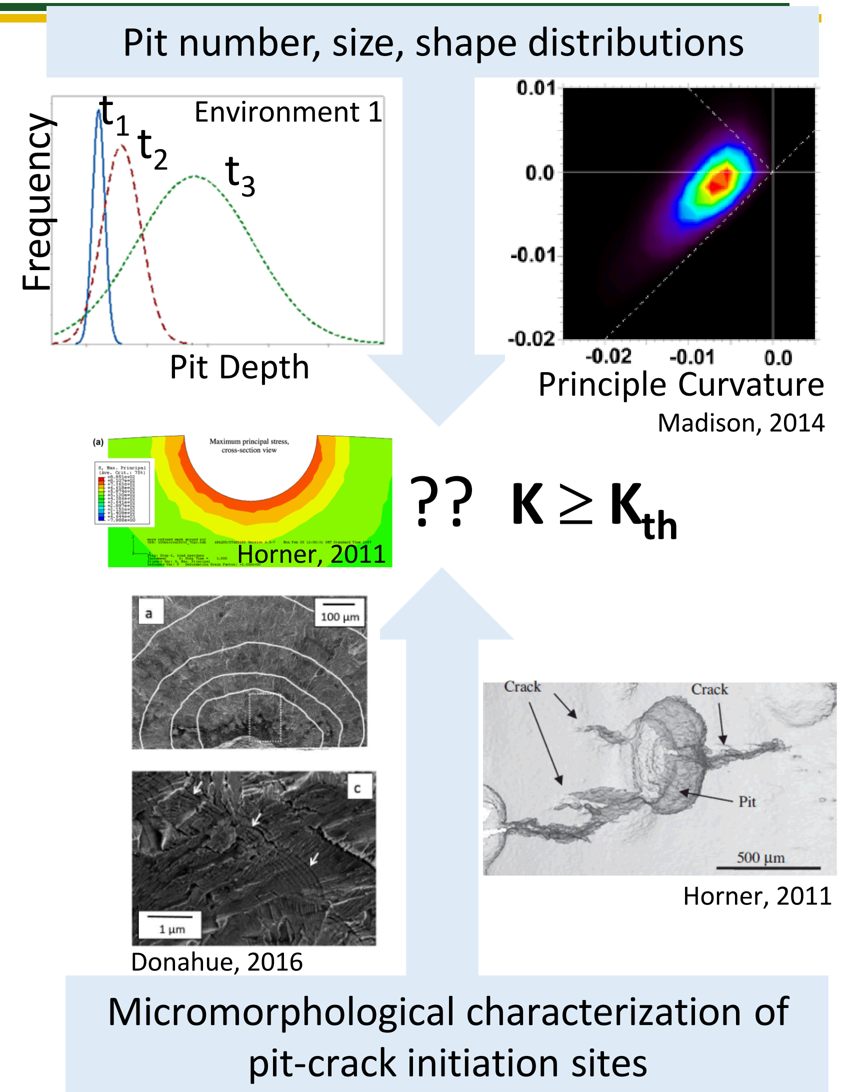
- Pitting kinetics, damage distributions (max pit size?) under ISFSI-relevant environmental conditions (T, RH, salt load)
- Pit-crack transition controlling factors

<u>Goals:</u>

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

<u>Approach:</u>

- 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



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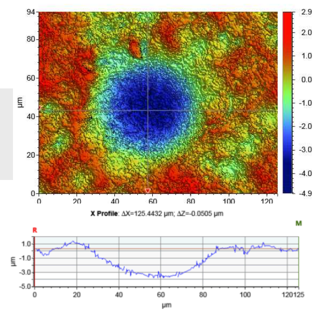
Pitting Kinetics and Damage Distributions:
Coupon-Level Studies

High-throughput Approach for Building Parametric Datasets

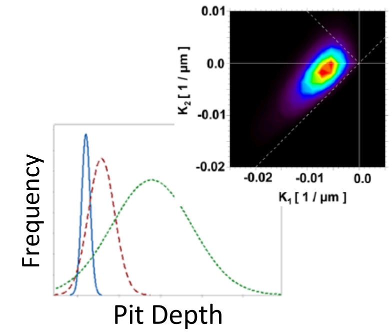
Inkjet printing for high-throughput salt loading

%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		55
35	35	40	45	50	
30	35	40	45	50	

ISFSI-Relevant Conditions



Optical profilometry and pit analysis (OSU)

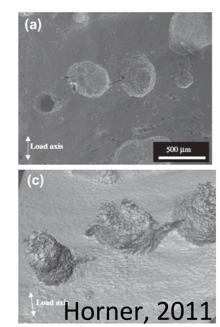


Pitting kinetics and shape distributions (SNL/OSU)

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^2 sea-salt

Serial Sectioning (SNL)



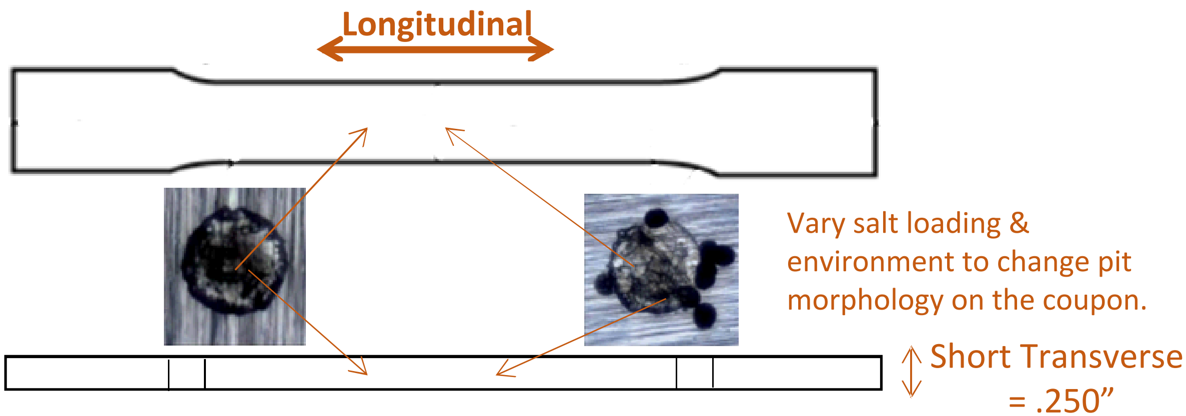
X-ray Microtomography (SNL)

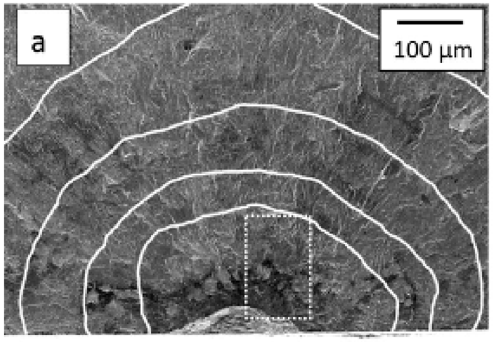
Pit Micromorphology Characterization

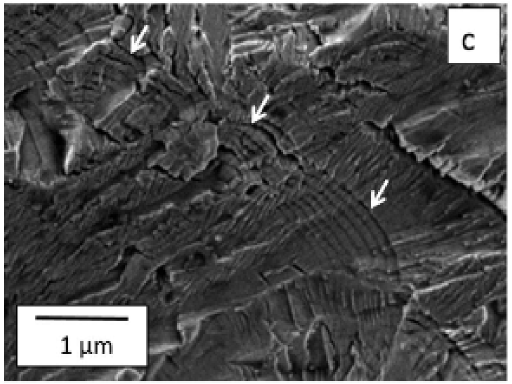
Pit-to-Crack Transition Study

Goal: Quantify the hierarchical weakest link for pit-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.*

Impact of Corrosion on Surface Environment, Damage Distributions, and Rates:

Inform Deterministic Models

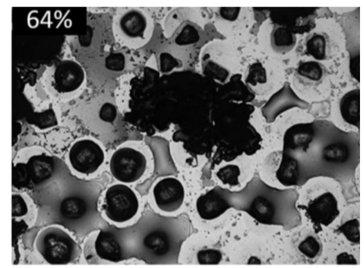
Knowledge Gaps:

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

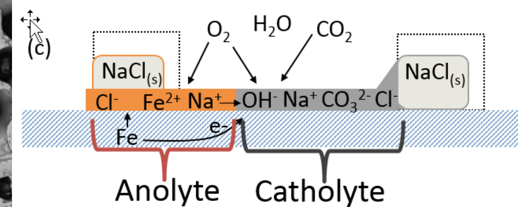
Goals:

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

NaCl on steel



Schindelholz, 2014

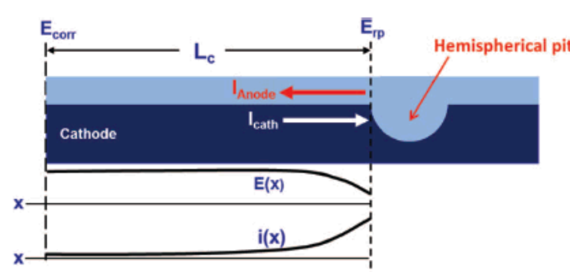


maximum pit size *crack growth rate (?)*

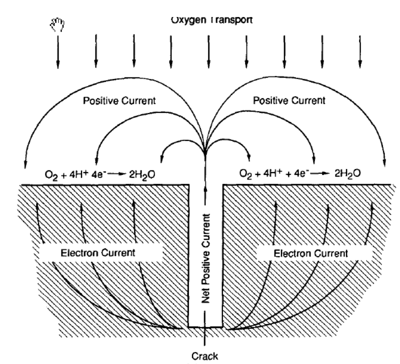
SNL: Eric Schindelholz, Charles Bryan, Chris Alexander

OSU/EFRC Jen Locke, Tim Weirich (PhD student)

CSM Zhenzhen Yu, Xin Wu



Chen et al. 2008



MacDonald, 1991

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

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40	35	40	45		55
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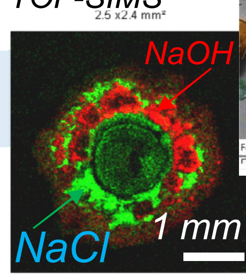
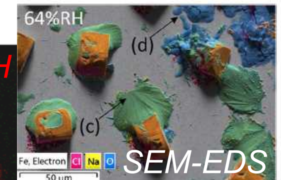
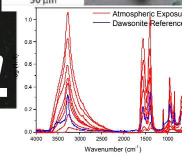
ISFSI-Relevant Conditions

TOF-SIMS

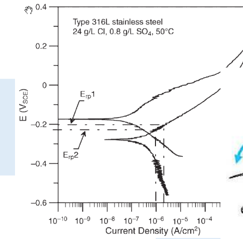


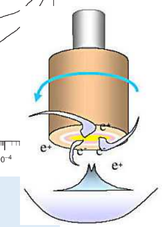




Raman

Extent of electrolyte coverage and chemistry distribution





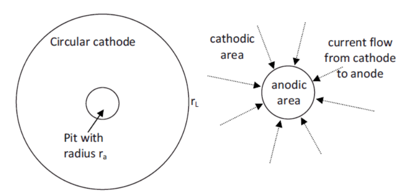
Cathodic and anodic kinetics in analog surface chemistries

Approach:

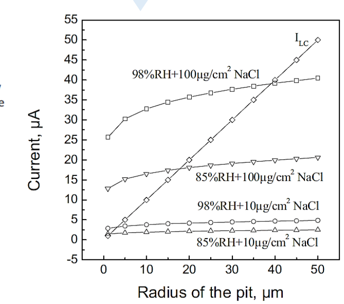
- *Post-exposure surface analyses of coupons from pitting experiments:*
- *TOF-SIMS, MicroRaman/FTIR, Auger Spectroscopy*
- *Cathodic kinetics of 304 in analog surface chemistries (sea-salt brines, carbonate brines)*
- *Establish variance in max pit size model predictions due to evolving electrolyte,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



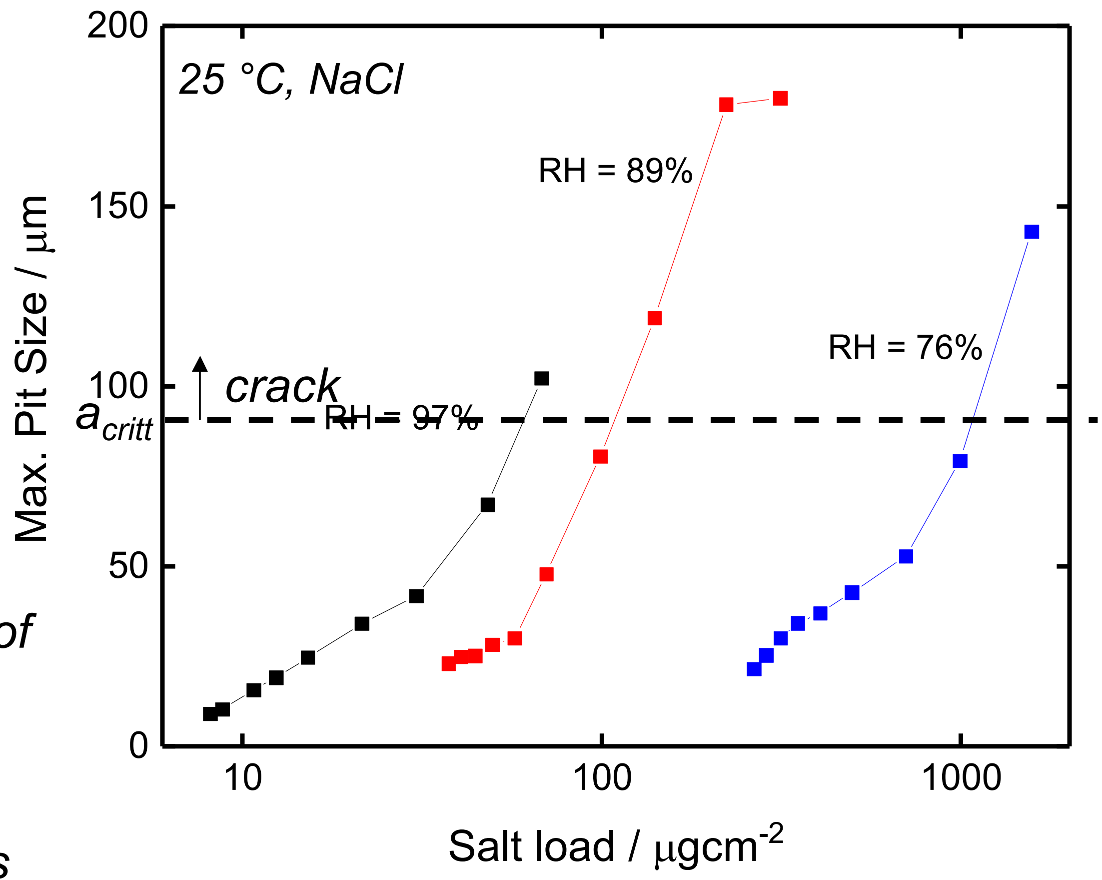
Maximum pit size as function of RH and salt loading

conceptual calculations of maximum pit size derived from cathodic kinetics measured in NaCl brines

Conditions supportive of critical hemispherical pit sizes exceeding a known K_{ISCC} can be predicted

Need to understand relevant limits of numerous assumptions including:

- *Echem parameters in lab = field*
- *Electrolyte and surface attributes are constant or changes due to corrosion or other processes are inconsequential*



K_{ISCC} = 6, σ= 500 MPa

Linkage of Material Variance to Electrochemical Corrosion/Cracking Processes for Prediction of Damage Initiation Sites

Knowledge Gap:

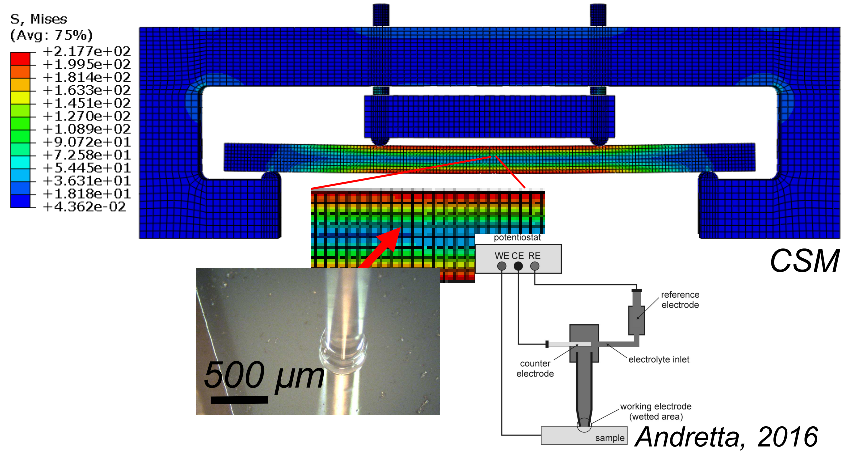
How material characteristics (microstructure, stress/strain) and environment (T, RH, salt load) impact electrochemical processes governing SCC

Goal:

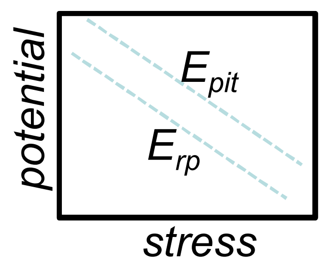
Prediction of pitting and repassivation characteristics of 304 under varied static stress loads

Approach:

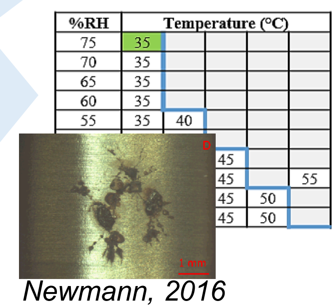
- Microelectrochemical mapping of CSM 4-point bend test specimens as a function of stress load
- Develop model to capture pitting characteristics as function of stress/strain with correlation to CSM 4-point bend atmospheric exposures



Microelectrochemical mapping (SNL)



Stress effect on localized corrosion susceptibility



Pit distribution on atmospherically exposed samples (CSM)

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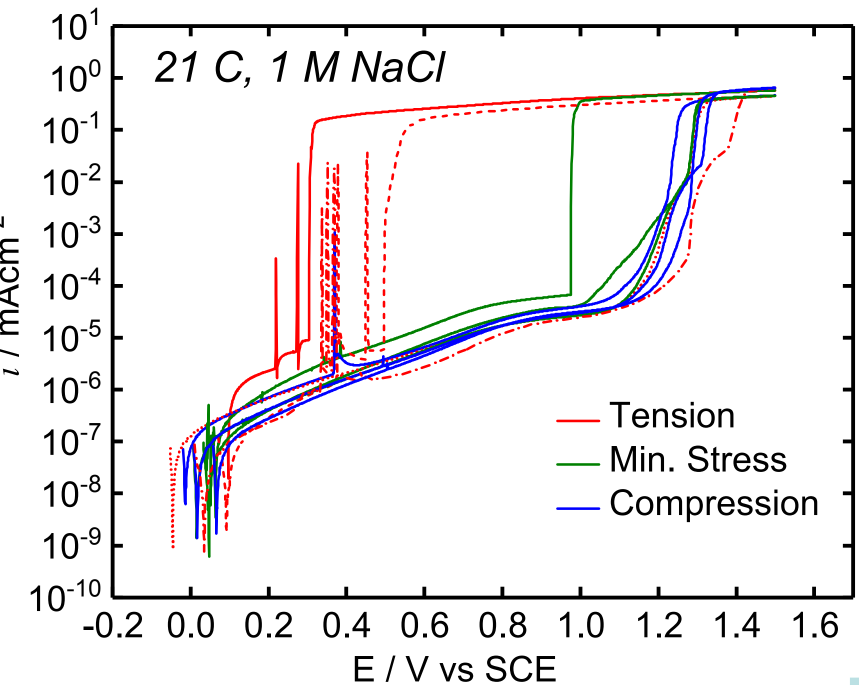
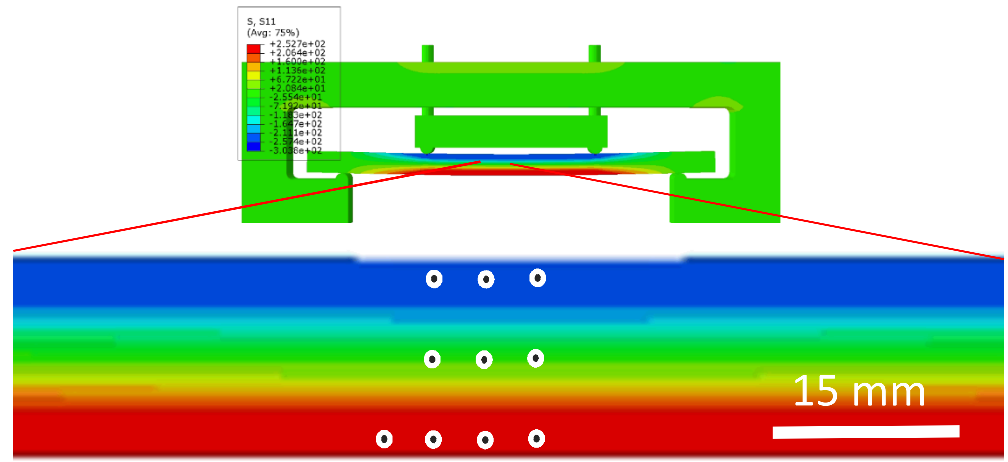
Tensile Stress Decreases Pitting Potential in 304L Material





σ (MPa)	E_{OCP} (mV)	$E_{breakdown}$ (mV)
253	-47 to 96	302 to 1379
-2	16 to 64	975 to 1279
-303	-14 to 66	1227 to 1315

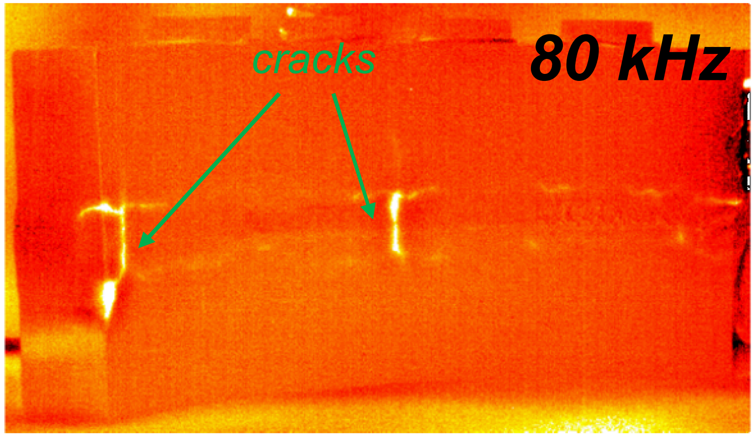
Will send this to CSM-would make more sense for Zhenzhen to include this in her presentation if she is talking about 4point bend

Linkage of Material Variance to Electrochemical Corrosion/Cracking Processes for Prediction of Damage Initiation Sites

Knowledge Gap:
Relationship between canister-relevant material characteristics (microstructure, stress/strain) and relative pit/crack susceptiblity

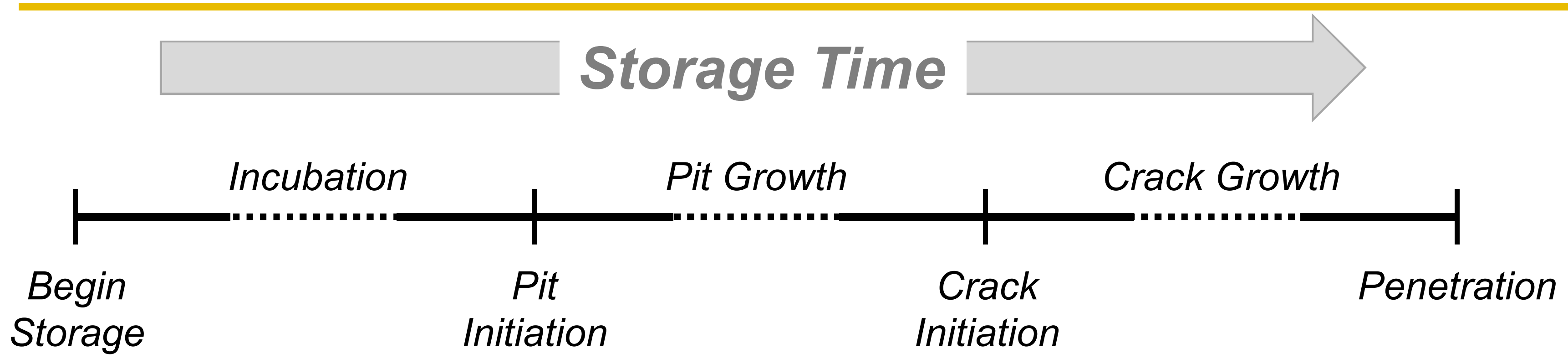
Goal:
Identify preferential pitting and crack initiation sites for material conditions representative of canister

Approach:
- Expose mockup plate to corrosive lab conditions
- Document pit and crack distribution over course of exposure
- Postmortem characterization of pit and crack geometry in relation to stress and material



Vibrothermography crack detection method -courtesy M. Remillieux

Summary:
Canister SCC: Important Processes



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SNL/LANL — mockup pitting/cracking