SAND2017-11835PE

Spent Fuel and Waste Science and Technology

Factors controlling SCC Initiation and Growth: Current Research at Sandia National Labs

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Spent Fuel and Waste Science & Technology Program

ASME Subcommittee Meeting
October 30, 2017

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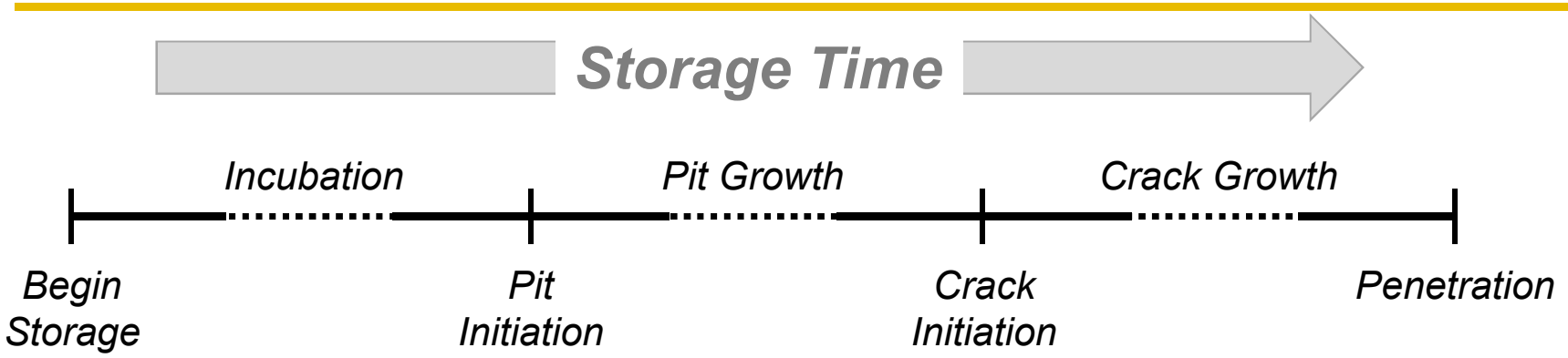
Session Schedule

General timeline for SCC of SNF storage canisters

- Incubation period
- Corrosion initiation (pitting)
- Pit growth
- Pit-to-crack transition (crack initiation)
- Crack growth and penetration

Canister SCC: Important Processes



SNL — Surface Environment, Brine Stability

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

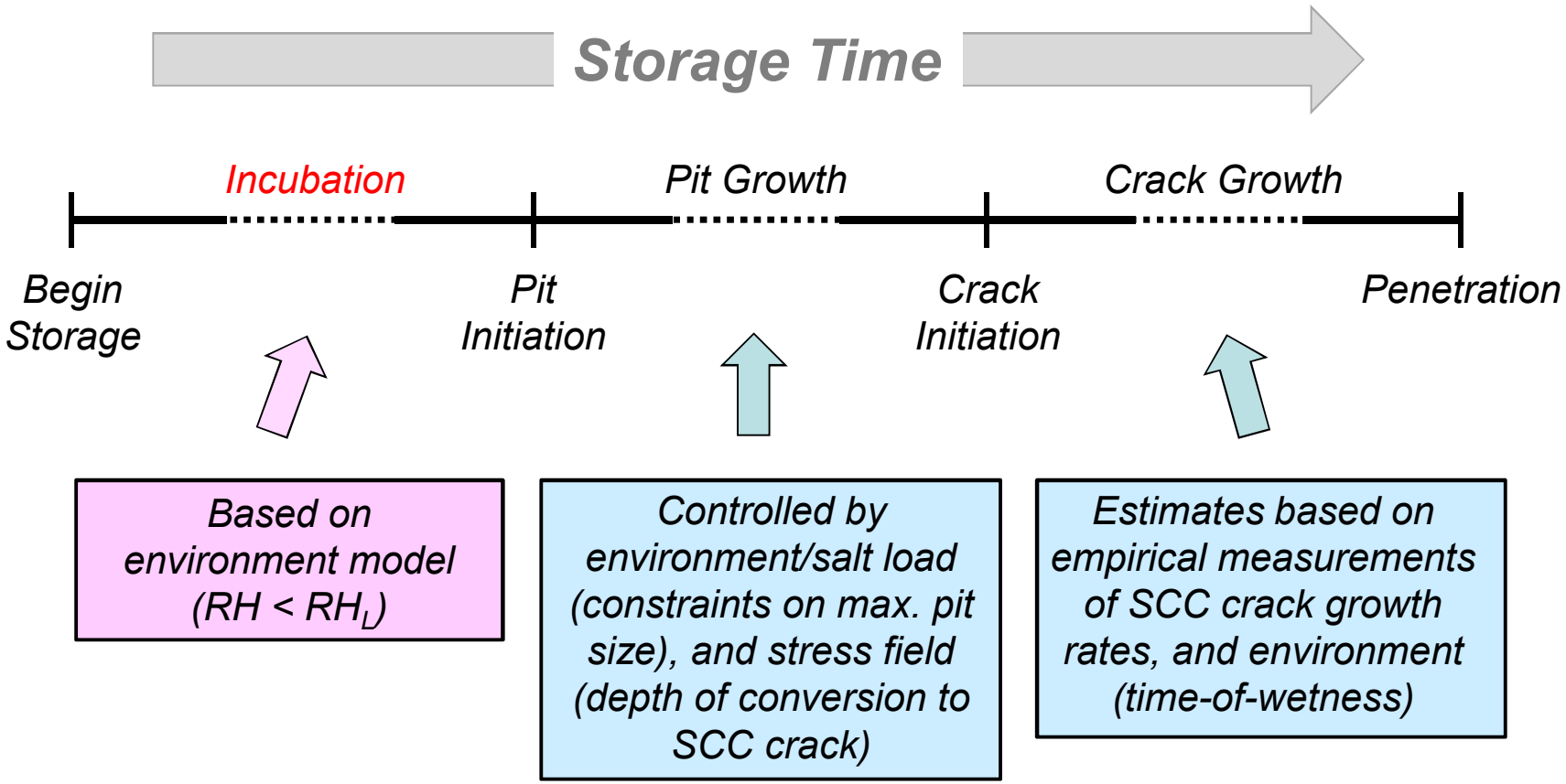
CSM/SNL — Pitting initiation and growth (effect of stress)

CSM — Pit-to-Crack Transition (Modeling)

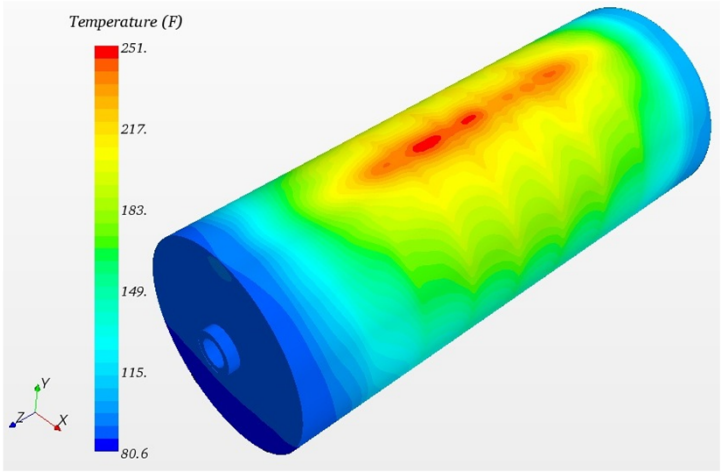
CSM/NCSU (SNL) — SCC growth rates

OSU (SNL) — SCC growth rates

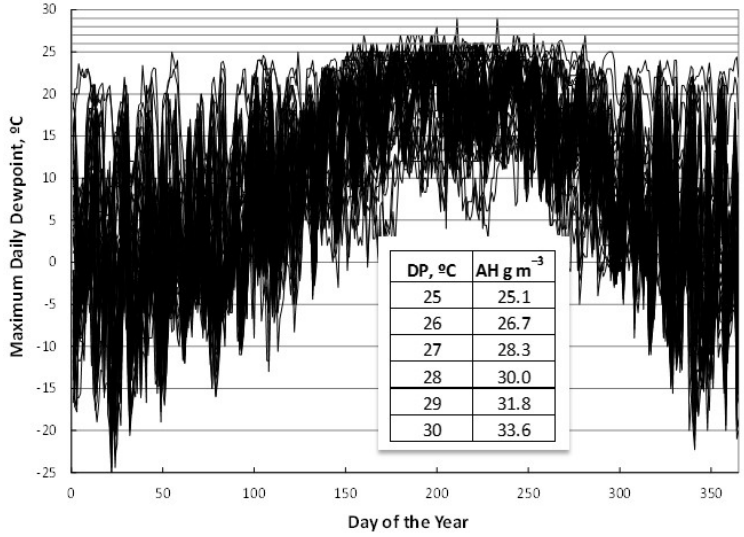
SRNL — SCC growth rates


Storage Time
Incubation
Pit Growth
Crack Growth
Begin Storage
Pit Initiation
Crack Initiation
Penetration
Based on environment model (RH < RH$_I$)
Controlled by environment/salt load (constraints on max. pit size), and stress field (depth of conversion to SCC crack)
Estimates based on empirical measurements of SCC crack growth rates, and environment (time-of-wetness)

Incubation Period



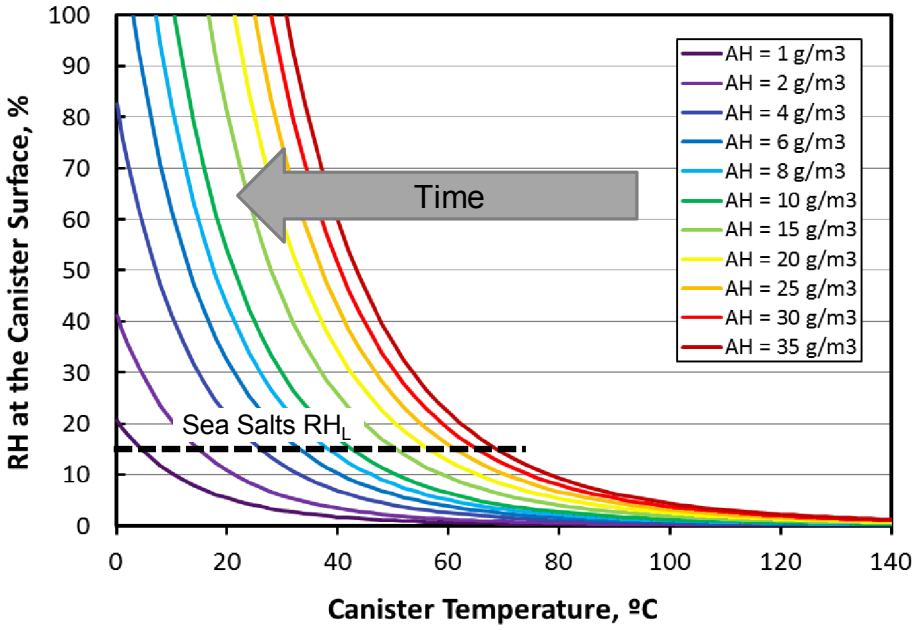
Surface temperature estimates



Site-specific National Weather Service data: daily and seasonal variations in AH

Canister surface RH = *f*(Ambient AH, canister surface T)

Use weather data and predicted canister surface temperature to predict RH at any location and time.



Timing of corrosion initiation—point in time at which RH_L is first reached.

Summing time when $RH > RH_L$ provides "time of wetness"; time when corrosion can actually occur.

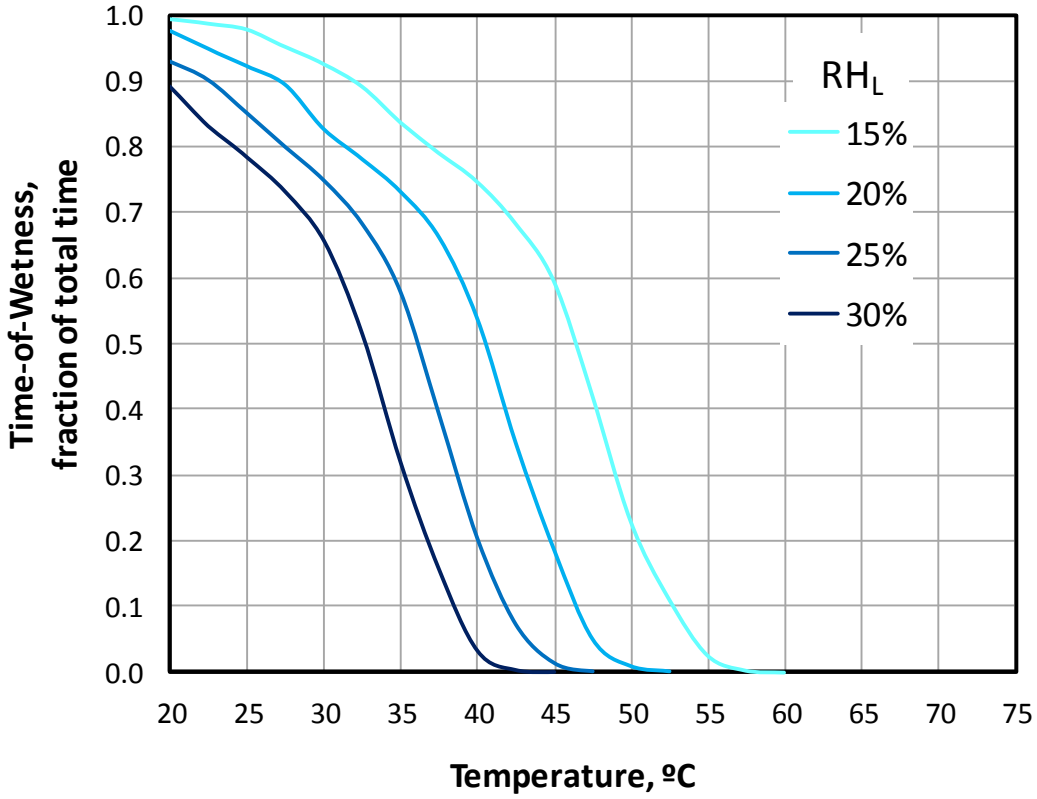
Both vary with canister surface location.

Concept of Time-of-Wetness

Time-of-wetness:

- *Corrosion only occurs when a threshold RH (RH_L) is exceeded.*
- *Corrosion can start-stop on a daily or seasonal basis, as a function of changing T, AH*
- *Total integrated time when aqueous conditions exist is time-of-wetness*
- *Rationale: External cathode, required to support corrosion at the anode, is only present when aqueous conditions exist on the metal surface.*
- *Widely accepted approach (ASTM procedure G84-89). However, many reasons to challenge time of wetness on a conceptual basis. (e.g., Schindelholz et al., 2013)*

Calculated time-of-wetness as a function of canister surface temperature and RH_L. Based on one year of weather data from the Oceanside Municipal Airport near the San Onofre ISFSI.



Salt Compositions and RH_d:
Geochemical modeling of seawater evaporation

Brine composition:

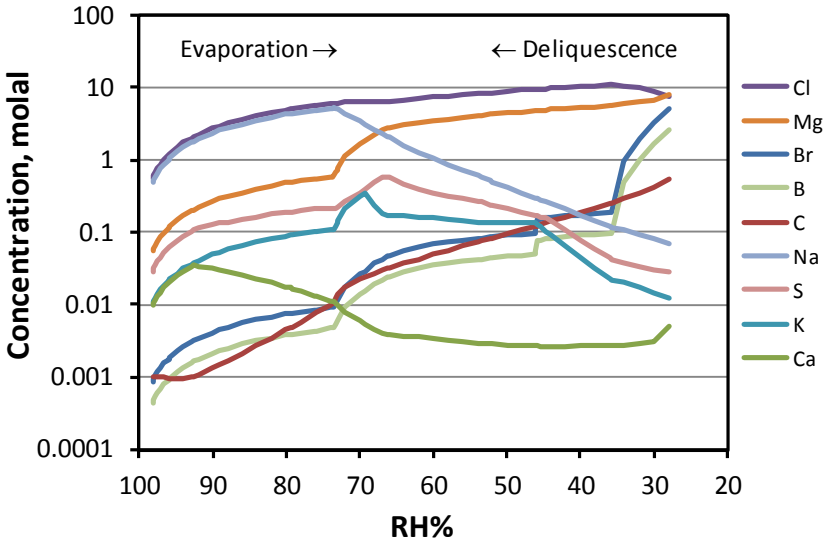
- Upon evaporation, salts precipitate and redissolve. Removed salts dictate the composition of remaining brine
- Seawater evolves towards concentrated Mg-Cl brine as NaCl precipitates
- Br and B conserved (but Pitzer database used for these calculations is not qualified for B, and may not be accurate)
- Ca, K, S are mostly removed by minerals, and are very low in the remaining brine.
- *Deliquescence is the reverse of evaporation.*

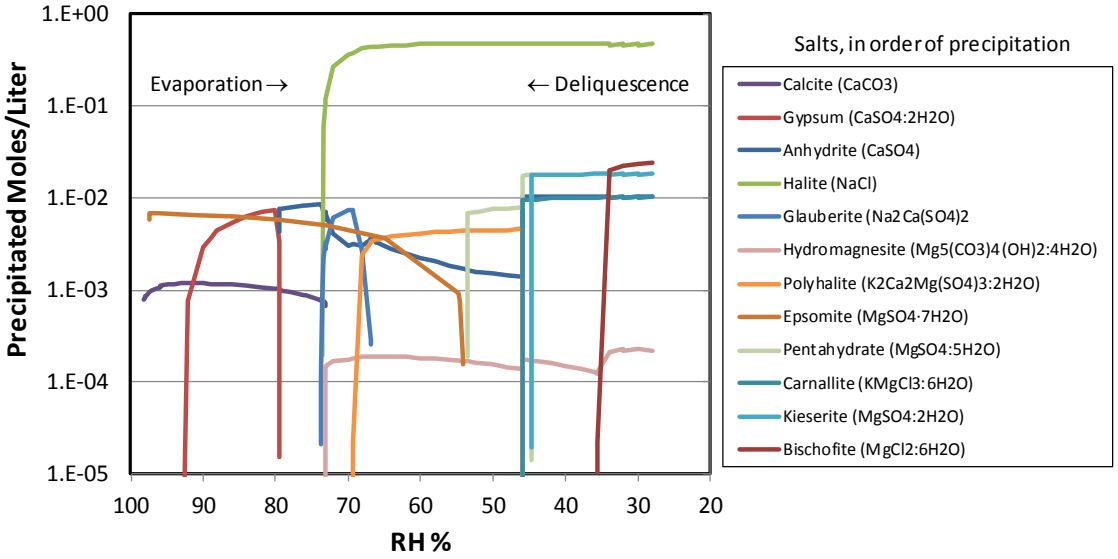
Precipitated salts:

- *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)*

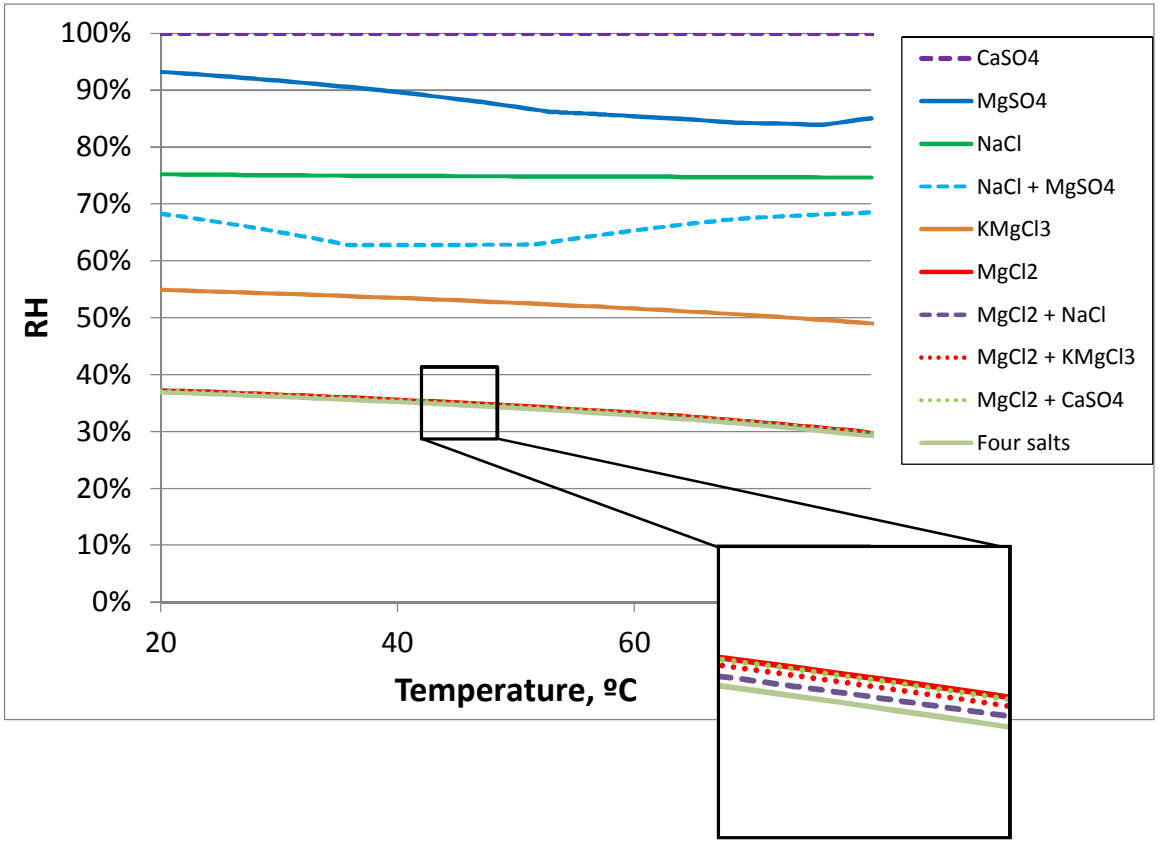




Predicted Deliquescence of Individual Sea-Salt Minerals and of Assemblage

Deliquescence points:

- Ca-SO_4 (gypsum or anhydrite): DRH >99%
- Mg-SO_4 (four different hydrates): DRH = 93-84%
- NaCl: DRH = ~77% at all temperatures
- $KMgCl_3:6H_2O$ (±sylvite): DRH = 55-49%
- $MgCl_2:6H_2O$: DRH = 36-29%
- $MgCl_2:6H_2O$ plus any or all other salts: DRH = ~Same as $MgCl_2:6H_2O$

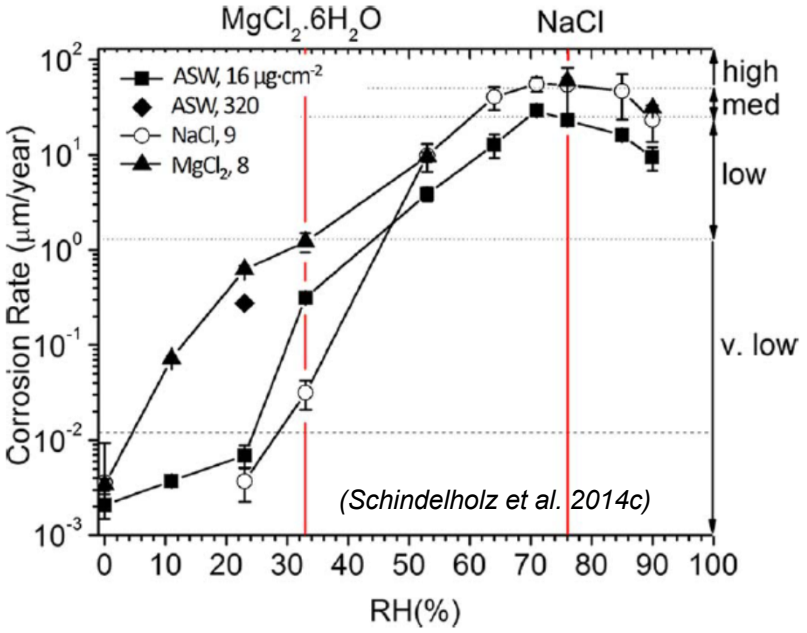


But is deliquescence RH = RH_L? Experimental data indicate that corrosion occurs at lower RH values...

RH_d vs RH_L (RH Threshold for Corrosion)

Corrosion Below the Deliquescence RH

- *NaCl (DRH 77%)*
  - *Schindelholz et al. (2014b) summarizes several studies--corrosion of mild steel at RH values of 50-58% RH. Their own study showed corrosion as low as 33% RH.*
  - *Once corrosion starts, it can persist to lower RH (at least 27% RH) due to highly deliquescent iron chloride salts.*
- *$MgCl_2$ (DRH ~33%) (Schindelholz et al. 2014c)*
  - *Observed corrosion (mild steel) as low as 11% RH (21ºC), at a loading of 8 µg/cm².*
- *Sea-salts (Schindelholz et al. 2014c)*
  - *Corrosion (mild steel) observed as low as 33% RH (21ºC), at a loading of 16 µg/cm².*
  - *Corrosion observed as low as 23% RH (21ºC), at a loading of 160 mg/m².*
  - *Inferred that at higher sea-salts loadings, results would match $MgCl_2$*
- *Observations of SCC*
  - *NRC (2014)—SCC (304SS) observed as between 20% and 30% RH (variable temperatures), using sea-salts.*
  - *Shirai et al. (2011)—SCC (304SS) observed at 15% RH and 80ºC, using sea-salts.*
  - *Fairweather et al. (2008)—SCC (304SS) observed at 15% RH and 45ºC and 60ºC, using $MgCl_2$.*



Sea-salt RH_L for SCC of 304 SS poorly constrained, and may be a function of salt load. Could be as low at 15%.

However, those experimental results assume that sea-salts are unmodified by reactions with atmospheric gases

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

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

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

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

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

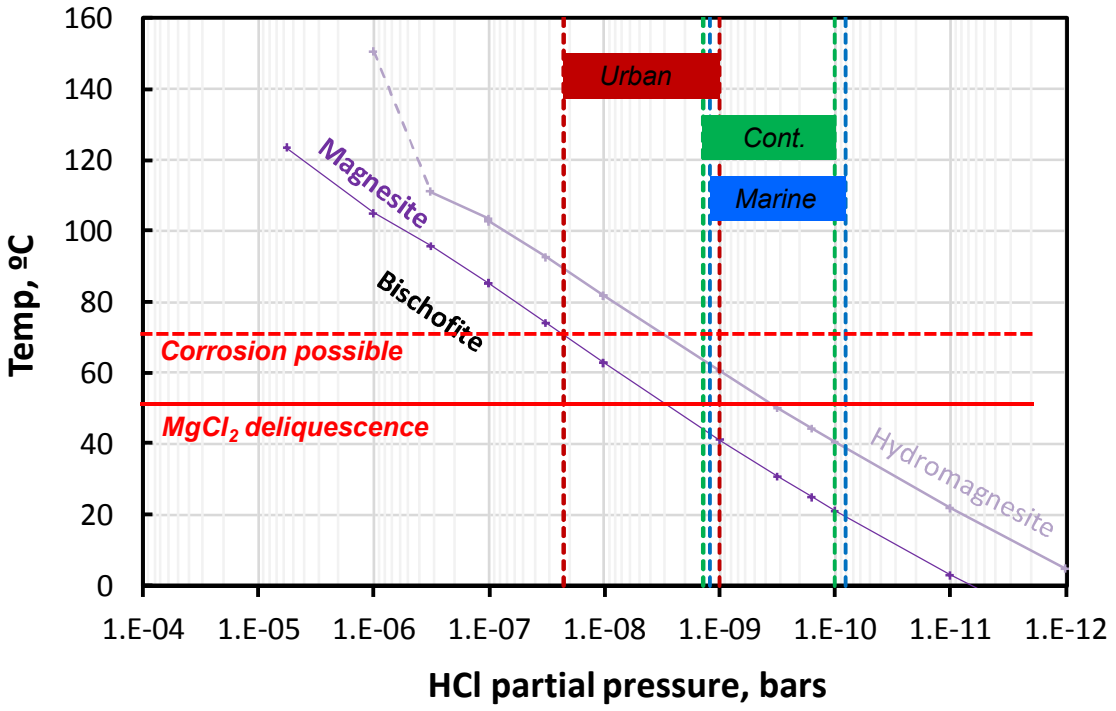
    We are currently evaluating the last reaction, which is strongly temperature-dependent.

  - Once corrosion initiates, effects of cathodic reactions on surface brine compositions (hydroxide generation, carbonation). We are also evaluating these reactions.

$MgCl_2$ Brine Stability

$$Mg^{2+} + 2Cl^- + CO_2(g) + H_2O \leftrightarrow MgCO3(s) + 2HCl(g)$$

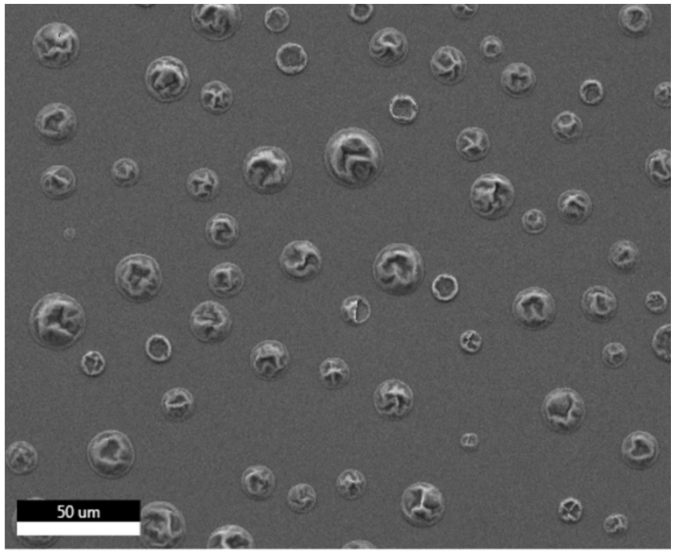
- Brines may degas, or absorb HCl, depending on background acid gas concentrations.
- $MgCl_2$ brine stability is a function of temperature and atmospheric HCl concentration; brine may absorb CO_2 and convert to Mg-carbonate
- $MgCl_2$ brine stability experiments in progress **(difficult to run—air capacity for HCl is low)**

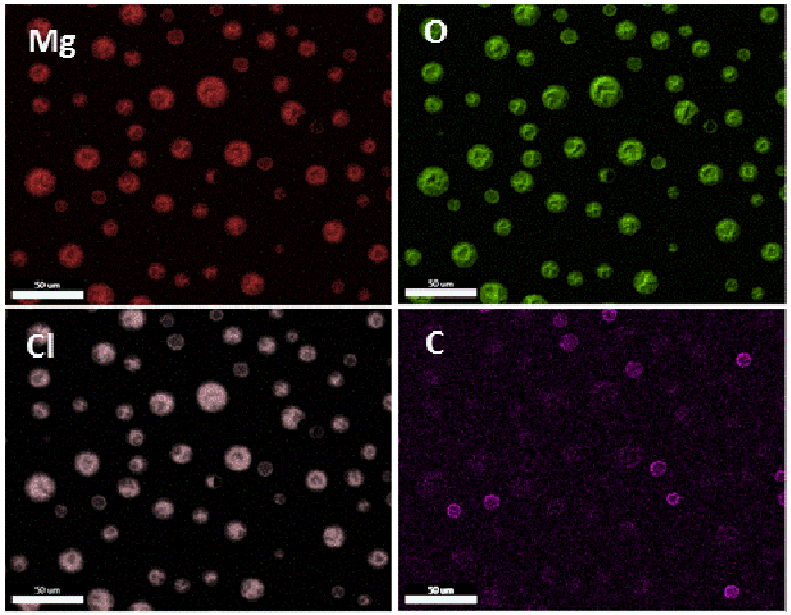


Experimental results:

$MgCl_2$ 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 (some smaller droplets converted); later chemical analysis suggests 20% chloride lost. (But results erratic).***
- ***Only partial conversion expected; airflow too low to support complete conversion. At 48ºC, can only remove 1.3 ug (hydromagnesite) to 13 ug (magnesite) chloride per cubic meter of air.***



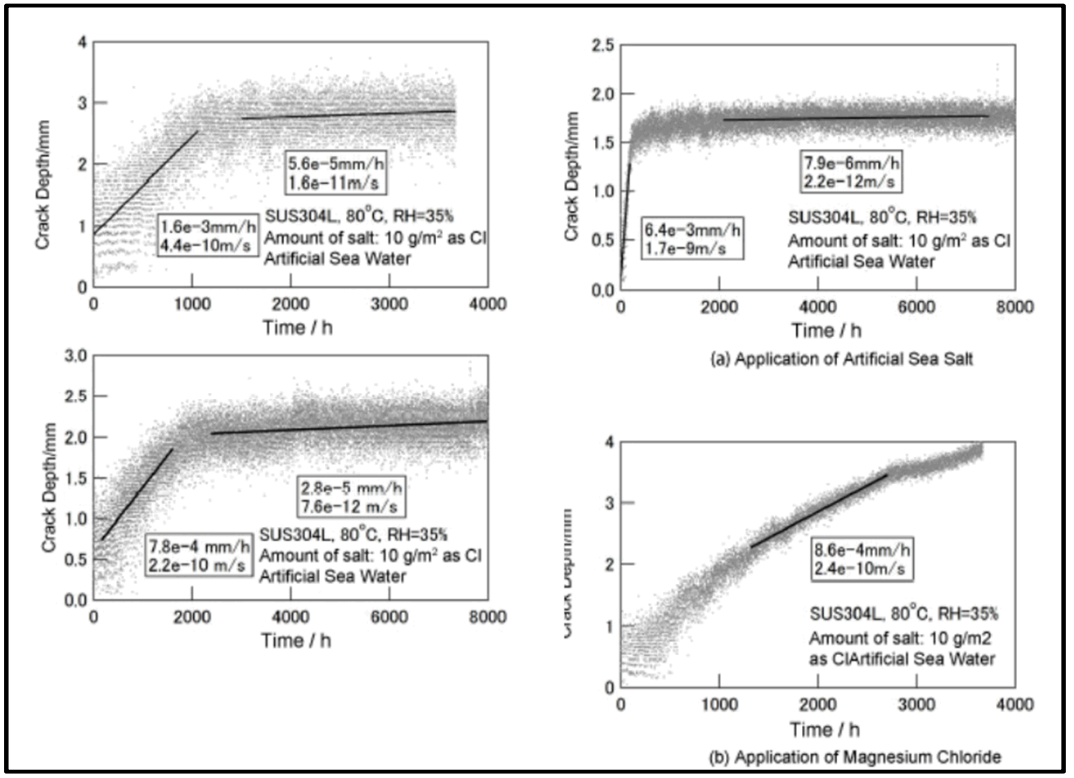


$MgCl_2$ Brine Stability

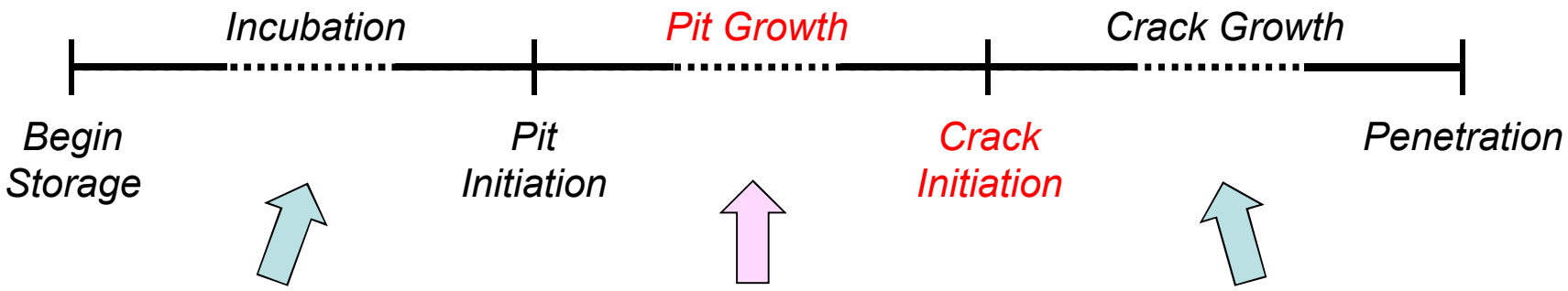
Other acid gas reactions (e.g., H_2SO_4) may be more important under field conditions. However, considering carbonation may be VERY important for interpreting laboratory experiments.

- *CRIEPI experiments: At 80ºC, 35% RH, air exchange of only a cubic meter is necessary to convert the small amount of $MgCl_2$ present in the sea-salts to carbonate, drying out the brine.*
- *Difficulties in initiating SCC in some tests?*

We are running $MgCl_2$ stability experiments under identical conditions to CRIEPI right now.



Pit Growth and SCC Crack Initiation



Based on environment model ($RH < RH_I$)

Controlled by environment/salt load (constraints on max. pit size), and stress field (depth of conversion to SCC crack)

Estimates based on empirical measurements of SCC crack growth rates, and environment (time-of-wetness)

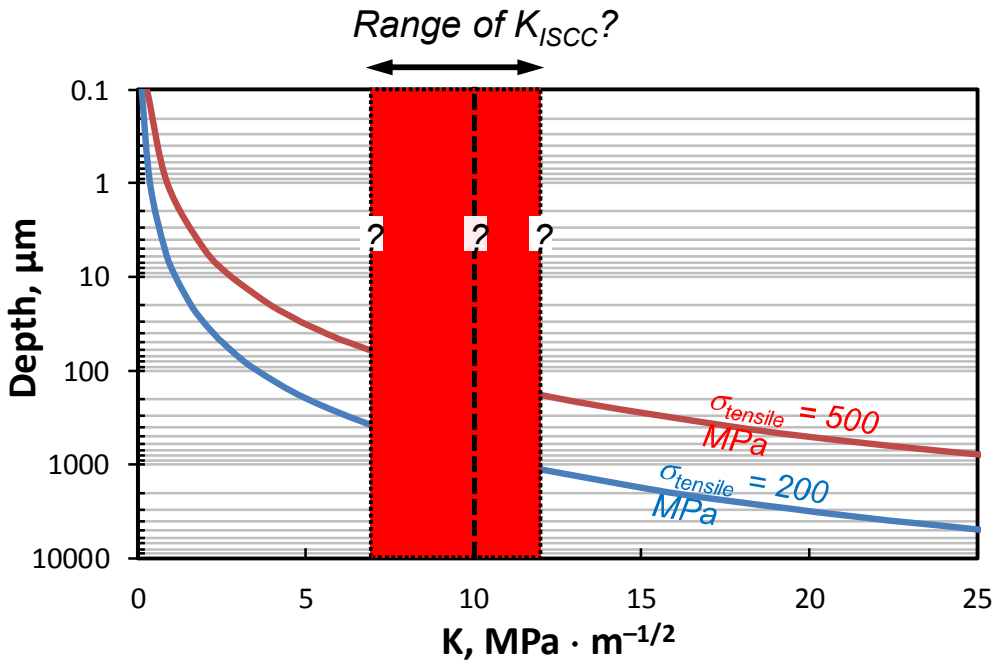
Pitting and SCC Crack Initiation

Pitting and SCC crack initiation

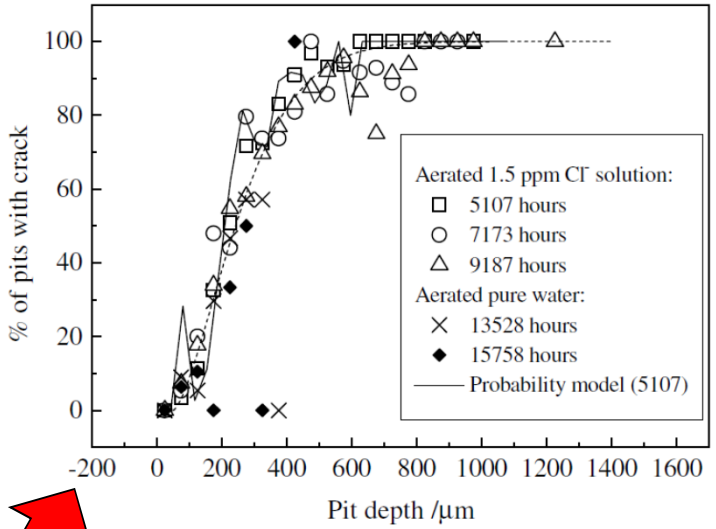
- Corrosion starts (pits form) once the RH_L is exceeded.
- *Pits grow over time, but for any given set of environmental conditions (T, RH, salt load), pit depths reach a limiting value.*
- *M*aximum pit depth model (Chen and Kelly 2010) can be used to calculate the maximum possible pit depth over time as a function of environmental parameters (temperature, RH, and deposited salt density).
- Pits generate aggressive chemistry and act as local stress focusers. SCC cracks initiate from corrosion pits on the metal surface.
- Depth of pit-to-crack transition can be *estimated* using the “Kondo criterion” (Kondo, 1985).

Crack Initiation: the "Kondo Criterion"

*"Kondo criterion". **Pit-to-crack transition** occurs when the pit depth is equal to the depth at which an equivalent-depth SCC crack would have a crack-tip stress intensity factor (K) that exceeds K_{ISCC} for the metal.*



Experimental data from Turnbull et al. (2006)

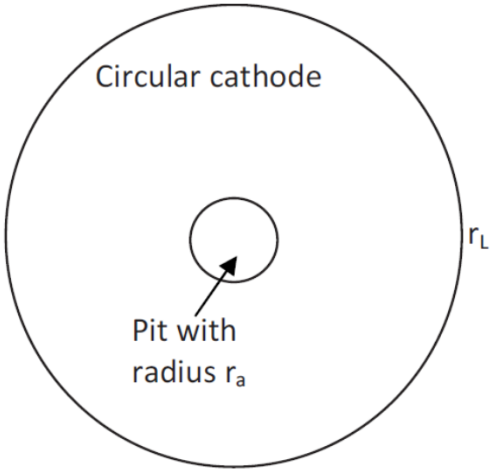


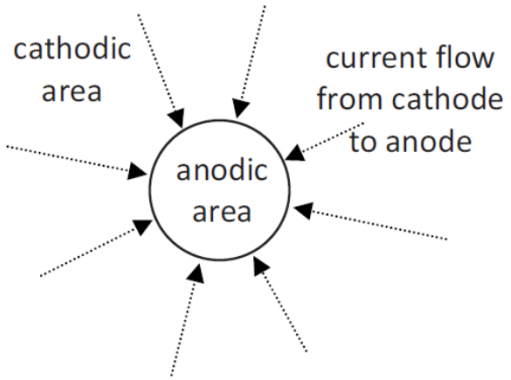
Stochastic process: As a pit deepens, the likelihood of a crack initiating increases.

Maximum Pit Size Model

Chen and Kelly (2010): Max pit size is a function of the maximum available cathode current.

Pits are modeled as being hemispherical, and stifle once the pit becomes so large that the anodic current requirement exceeds the available cathode current.





Max. cathode current

Brine conductivity

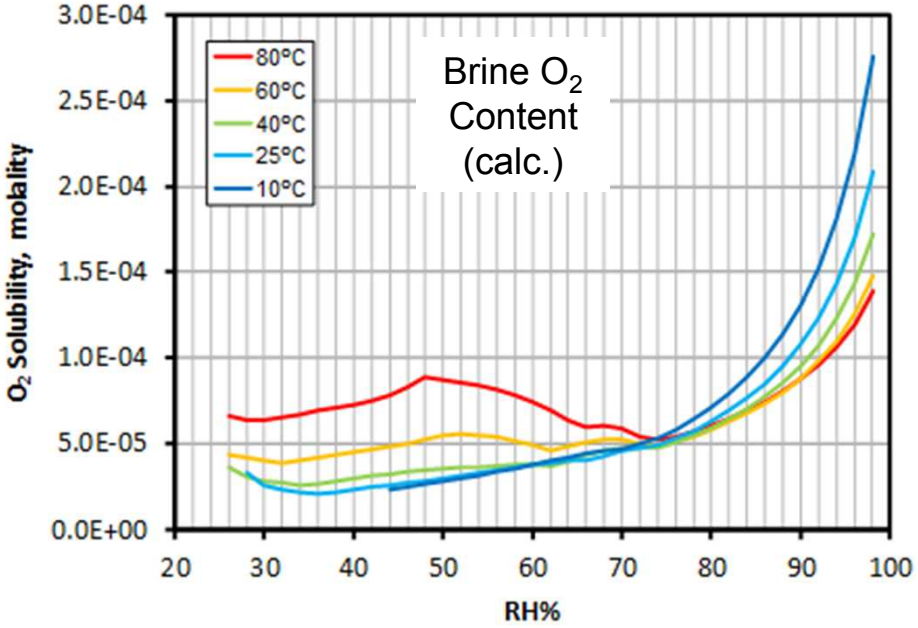
Brine layer thickness

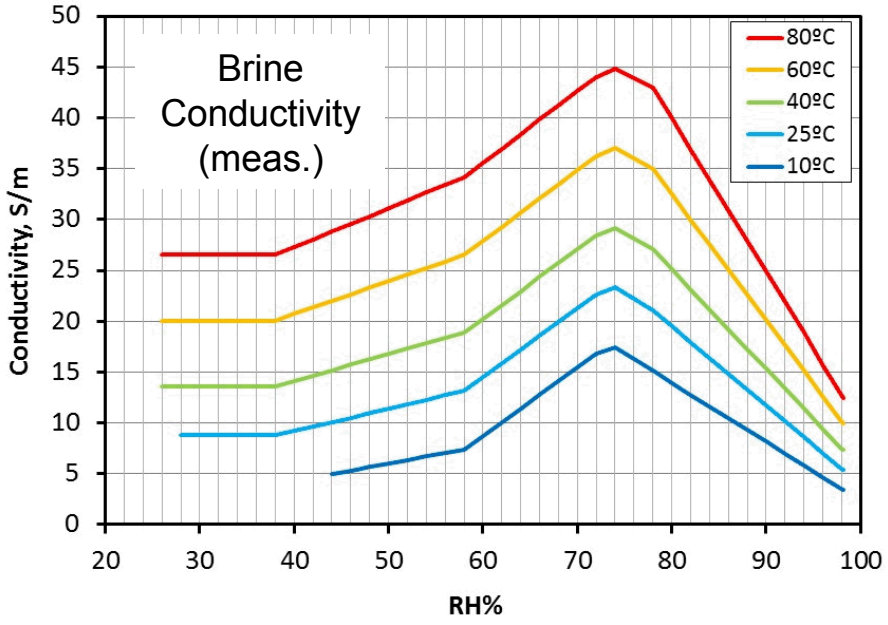
Electrochemical term (from cathodic polarization curve)

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

Parameterizing the Model for Sea-Salt Brines

Values are based on geochemical modeling, literature data, and measured data for brine densities and conductivities (4 brines, from 98-38% RH).





Original *Chen and Kelly* (2010) model: Based on NaCl brines (dry out at ~75% RH).

Parameterizing the Model for Sea-Salt Brines, conc.

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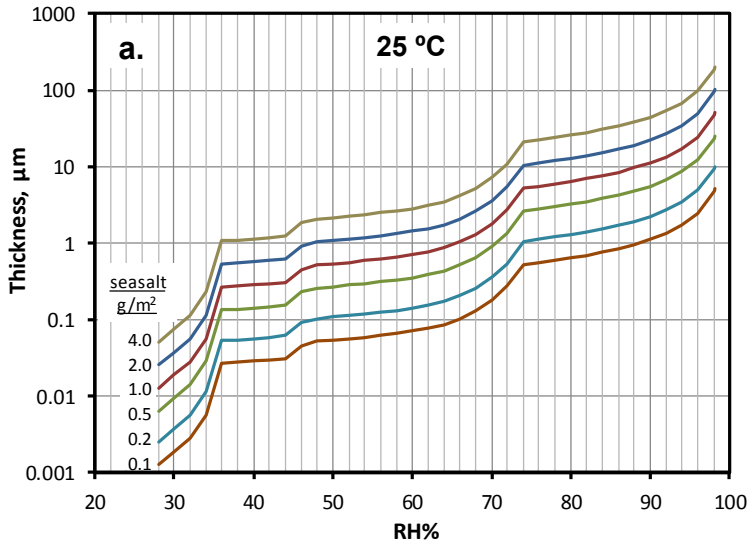
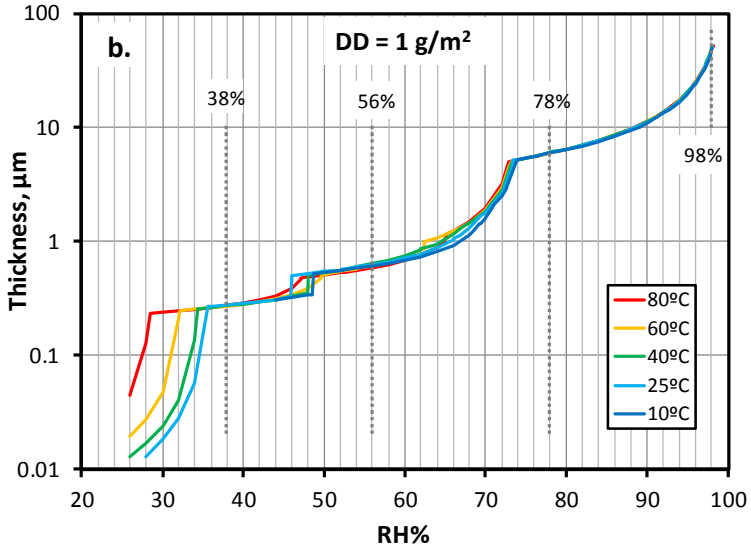




Original *Chen and Kelly* (2010) model: Based on NaCl brines (dry out at ~75% RH).

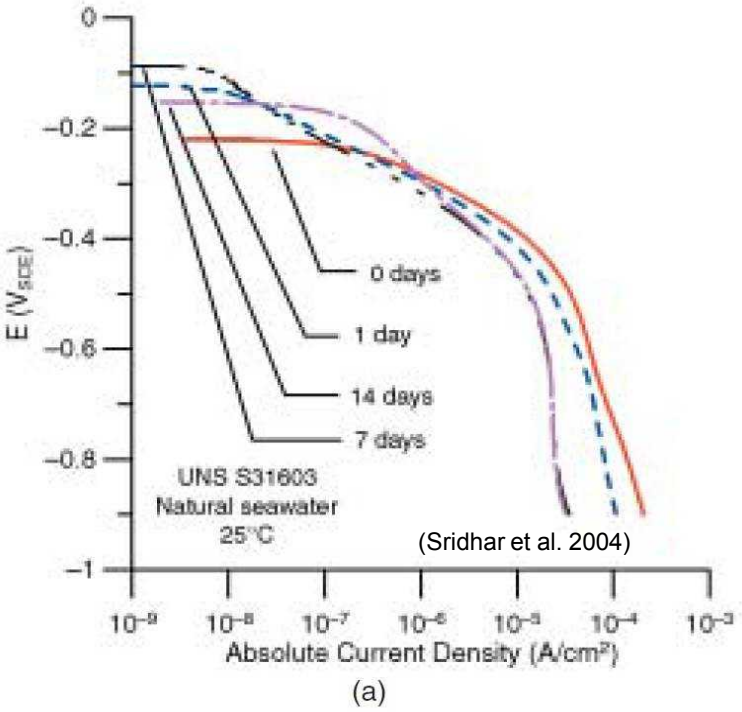
Assumption: *Brine forms a continuous brine layer.* This seems unlikely at *low salt loads or low RH values. However:*

- *Experimental data suggest that the cathode can extend well beyond the perimeter of salt grains (Schindelholz et al., 2013), and cathodic reactions can cause salt redistribution on the metal surface*
- *Insoluble dust particles will increase brine film continuity via capillary effects.*

Other Needed Data:

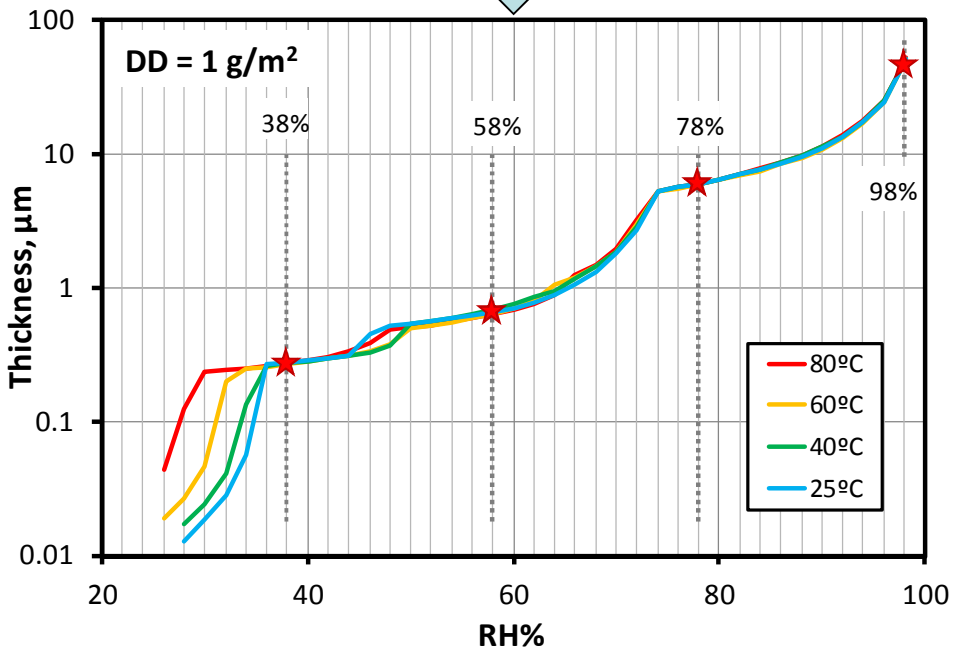
Cathodic Polarization Curves and electrochemical parameters for concentrated brines

Currently, limited available data:
Cathodic polarization curve for seawater at 25ºC, 316 SS (Sridhar et al. 2004)



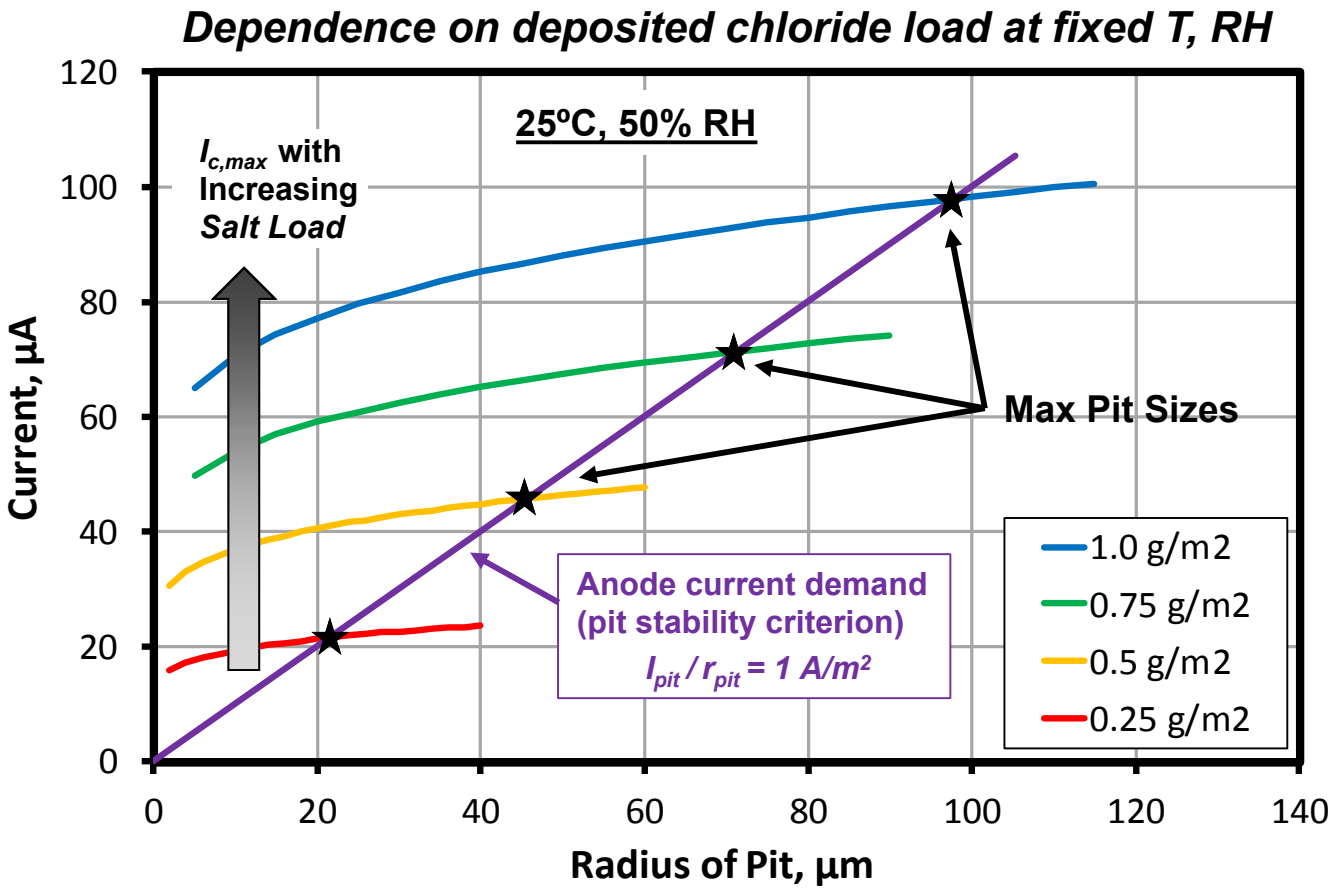
To characterize variability in cathode kinetics with brine composition, SNL is measuring polarization curves and other electrochemical parameters in four brines corresponding to:

- Unevaporated Seawater (98% RH)
- Evap. to 78% RH
- Evap. to 58% RH
- Evap. to 38% RH



Determining Maximum Pit Size

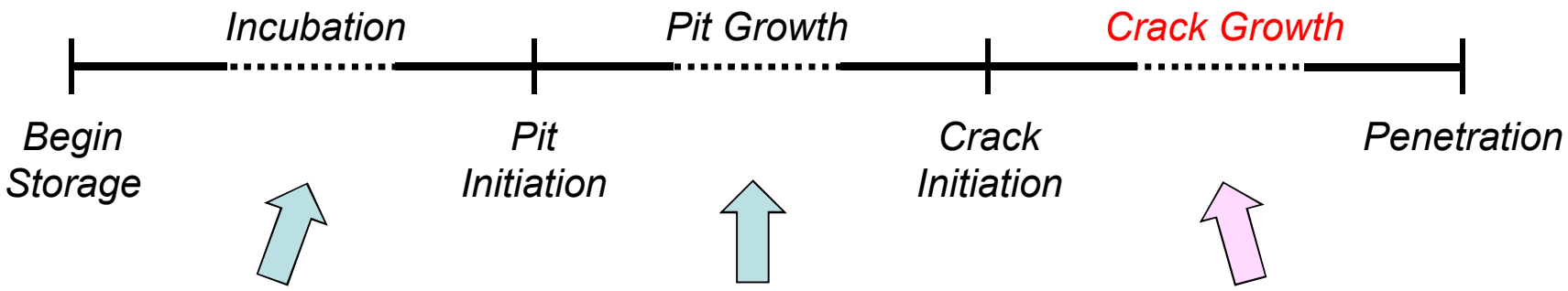
Maximum pit size is determined the intersection of the anode current demand and the available cathode current.



Sandia Research on Pitting

- **Long-term (2-year) pitting experiments, varying T, RH, salt load**
  - Test maximum pit size model
  - Evaluate salt redistribution in response to corrosion reactions
  - *Collaboration with Ohio State University*
- **Measurements of cathodic polarization curves on relevant brines**
  - *Collaboration with University of Virginia*
- **Effects of stress on pitting, and pit-to-crack transition**
  - *Collaboration with Colorado School of Mines*
  - *Collaboration with Ohio State University*

SCC Crack Growth



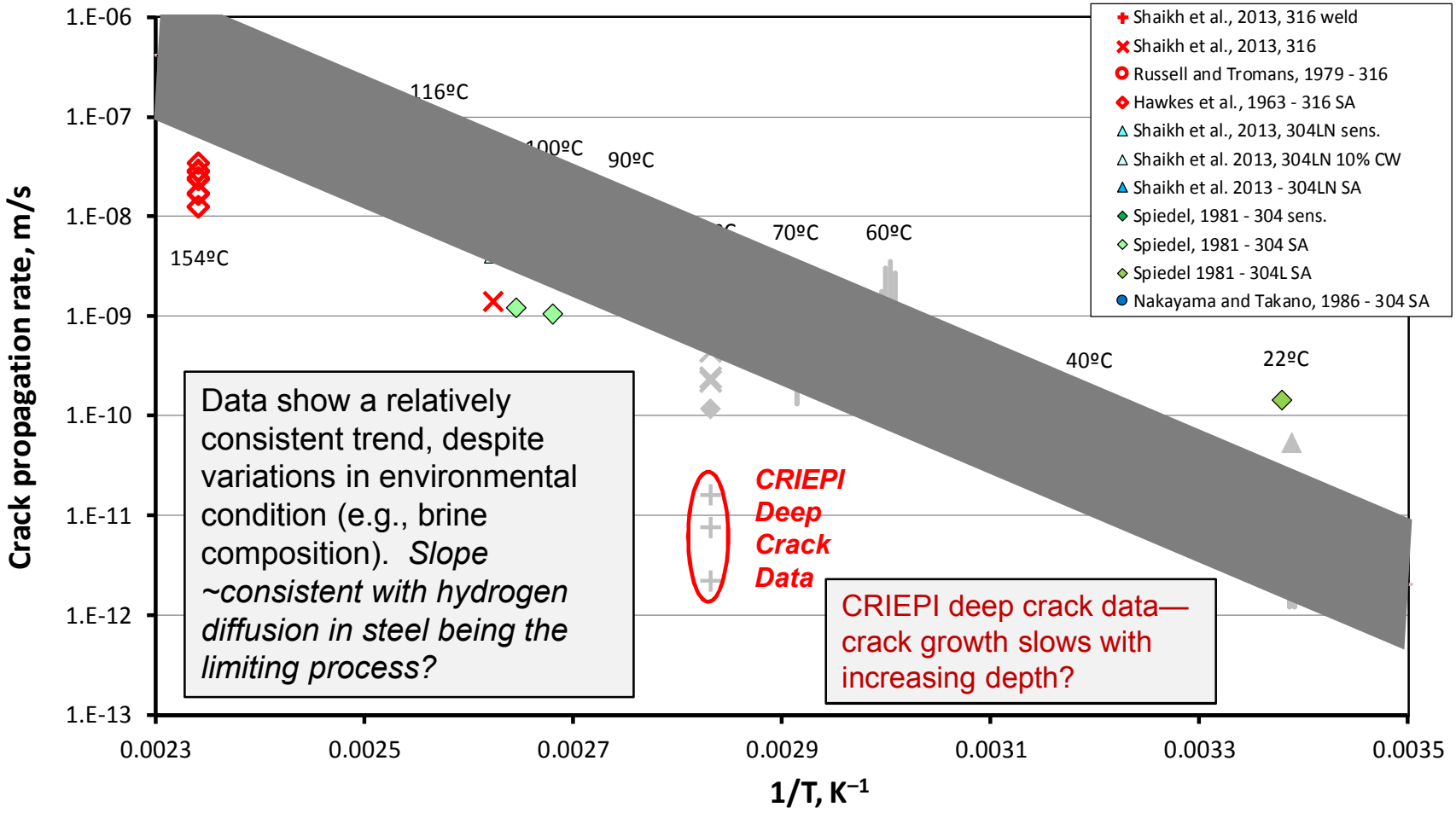
Based on environment model ($RH < RH_I$)

Controlled by environment/salt load (constraints on max. pit size), and stress field (depth of conversion to SCC crack)

Estimates based on empirical measurements of SCC crack growth rates, and environment (time-of-wetness)

Literature Crack Growth Rates

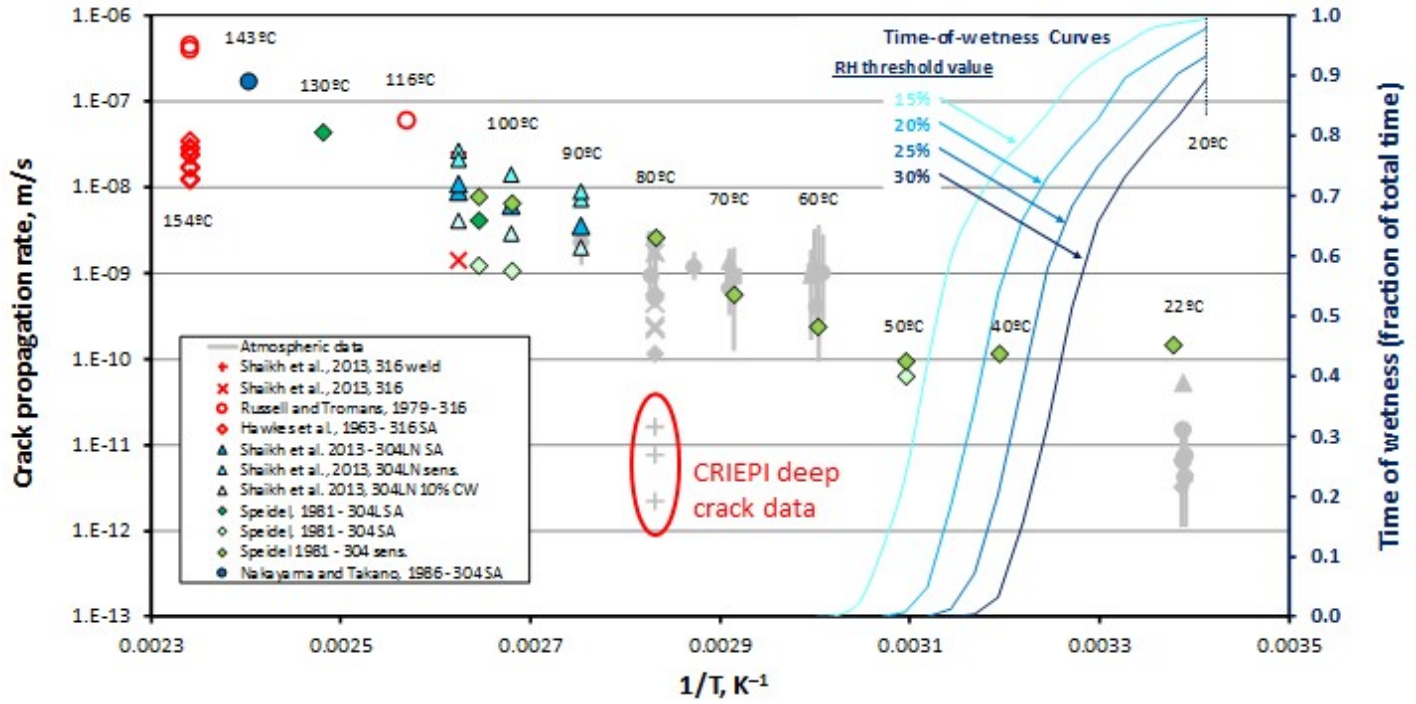
Data for 304 SS and 316 SS



Role of Time-of-Wetness

Model assumption: Crack Penetration Rate = CGR × Time-of-Wetness

Time of wetness decreases with increasing temperature, limiting crack growth

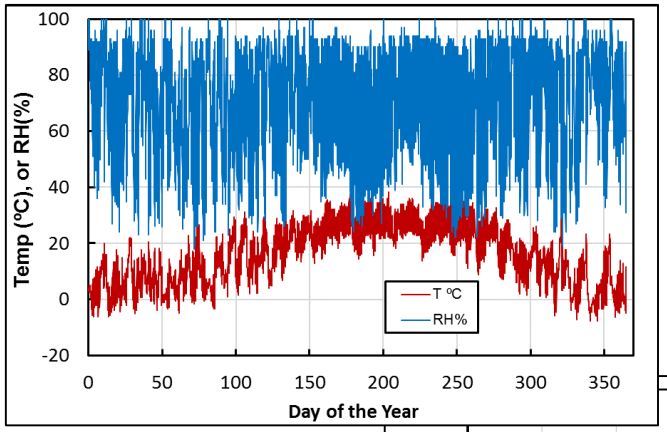


- ***Time-of-wetness concept based on removal of cathode during times of dry-out. Fairly well accepted for pitting, may not occur for stainless steel SCC:***
  - *Some data (Andresen and Morra 2008) indicate that an external cathode is not necessary for stainless steel SCC.*
  - *Cracks are not as subject to dry-out (high capillarity, presence of highly deliquescent metal salts)*

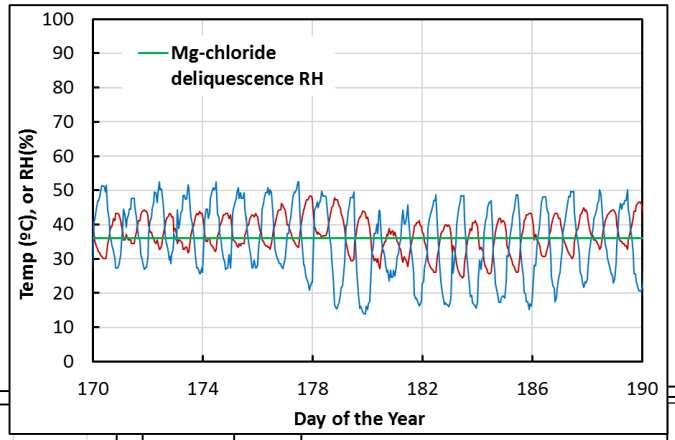
SNL Researchl: Crack Growth Rates

- **Effects of Brine Composition on CGR** (*Collaboration with North Carolina State University (CSM IRP)*)
- **Testing to evaluate time-of-wetness control on crack growth at SNL(?)**
  - *Use prototypical daily fluctuations in T and RH*

Weather near Arkansas Nuclear One

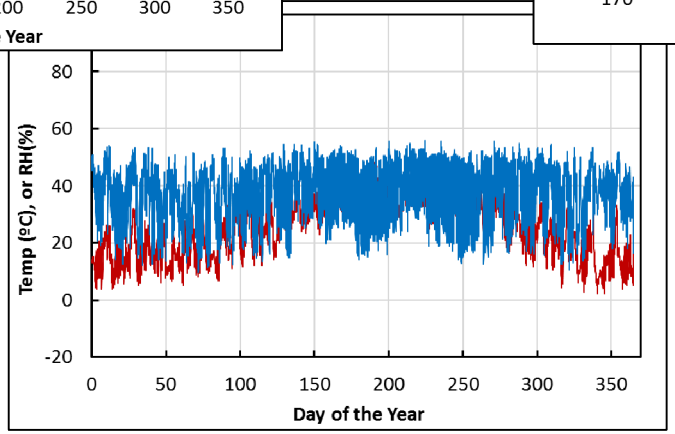


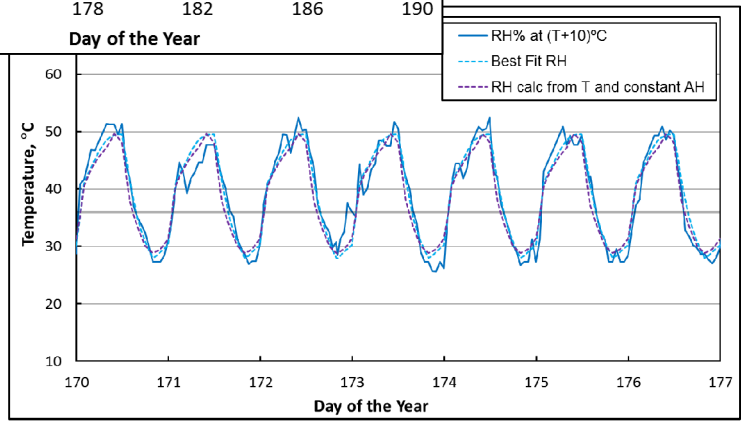
Focus on region crossing DRH



Fit with simple algorithm for lab implementation

Add temperature delta of 10ºC





Conclusions

- **Initiation of corrosion controlled by deliquescence behavior of salts**
  - Assumption of sea-salts ($MgCl_2$ controls RH_D/RH_L) may be highly conservative
  - Elevated temperatures may be more protective for corrosion initiation and growth than we assumed (*especially in laboratory tests at accelerated conditions*).
- **Over time, cooling (increasing RH) and increasing salt loads result in:**
  - Thicker and more conductive brine films (potentially larger pits)
  - Larger pits → greater risk of SCC initiation (stochastic)

Conclusions, cont.

- **Crack growth rates are difficult to predict**
  - Probably a strong temperature dependence
  - *May* be a cathodic limitation effect for atmospheric corrosion (thin brine films)
    - Crack growth *may* slow with increasing crack depth
    - Limited time-of-wetness with increasing temperature *may* limit penetration
    - Laboratory testing under realistic conditions very difficult

Backup slides

Pitting Damage Quantification Experiments:
Inform Probabilistic Models and Pit-Crack Transition

Knowledge Gaps:

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

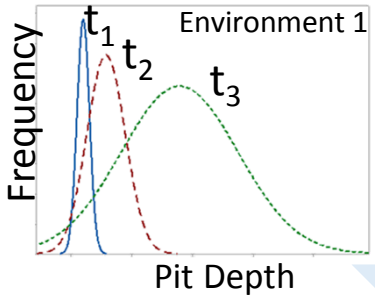
Goals:

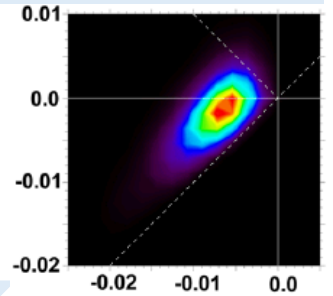
1) Quantify relationship between environment and pitting damage distributions and rates
2) Identify hierarchical weakest links for pit corrosion feature to SCC crack transition

Approach:

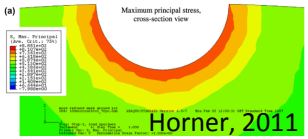
- Parametric coupon-level pitting experiments in ISFSI-relevant environments
- Constant load marker band SCC tests in same environments to determine corrosion features that act as crack initiation sites

Pit number, size, shape distributions



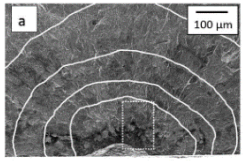


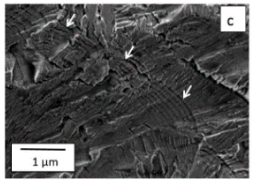
Madison, 2014



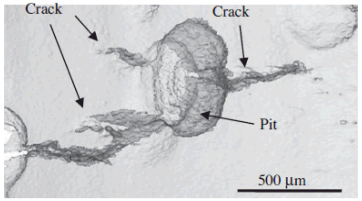
Horner, 2011

?? $K \geq K_{th}$





Donahue, 2016



Horner, 2011

Micromorphological characterization of pit-crack initiation sites

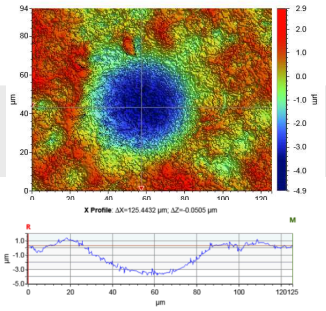
Pitting Kinetics and Damage Distributions:
Coupon-Level Studies

High-throughput Approach for Building Parametric Datasets

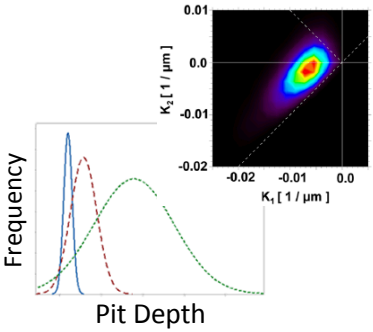
Inkjet printing for high-throughput salt loading

%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)

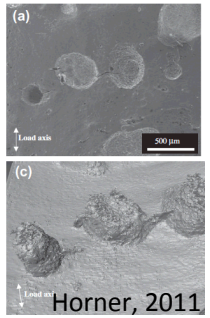


Pitting kinetics and shape distributions (SNL/OSU)

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 seasalt

Serial Sectioning (SNL)



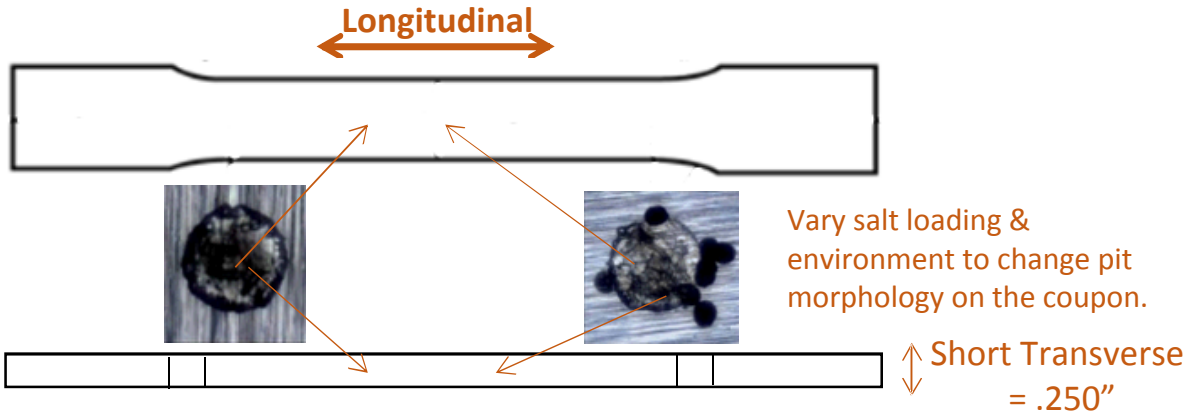
X-ray Microtomography (SNL)

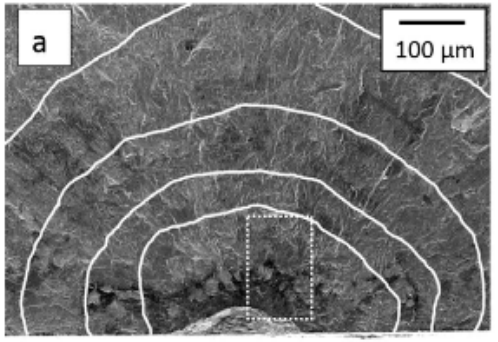
Pit Micromorphology Characterization

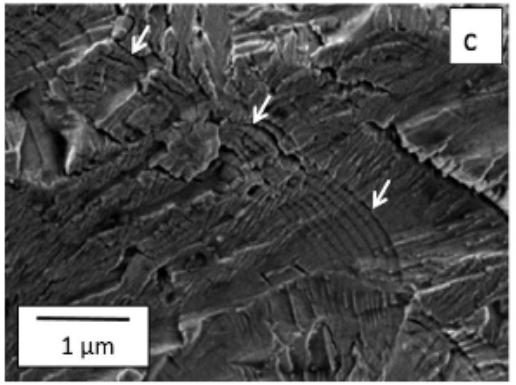
Pit to Crack Transition Study

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.*

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^2	X	X	X	X	X	X	X
35°C, 75%RH	10 µg/cm^2	X	X	X	X	X	X	X
35°C, 75%RH	300 µg/cm^2	X	X	X	X	X	X	X

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

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:

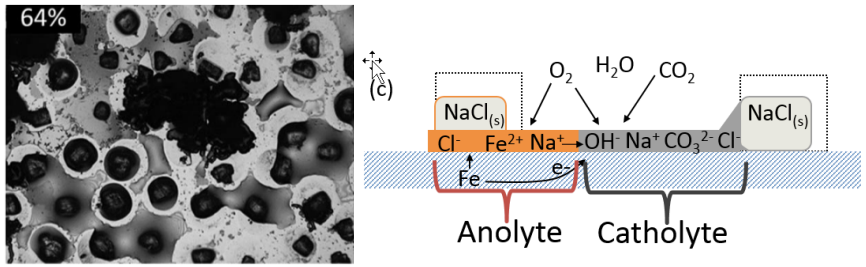
1) Characterize electrolyte coverage and chemistry distribution during exposure in ISFSI-relevant environment
2) Quantify impact on electrochemical processes driving pitting and SCC

SNL: Eric Schindelholz, Charles Bryan, Chris Alexander

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

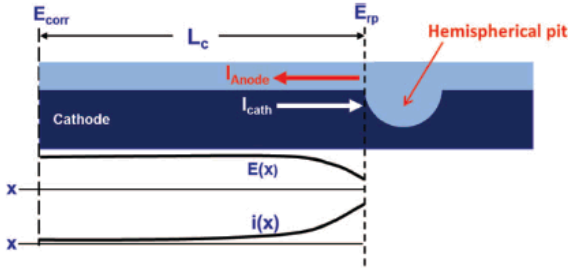
CSM Zhenzhen Yu, Xin Wu

NaCl on steel

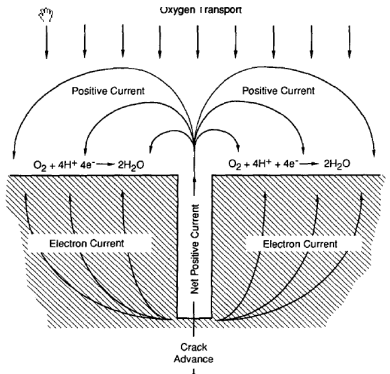


Schindelholz, 2014

maximum pit size *crack growth rate (?)*



Chen et al. 2008



MacDonald, 1991

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

Inkjet printing for high-throughput salt loading

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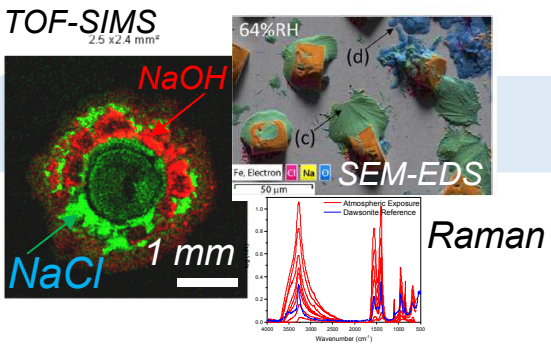
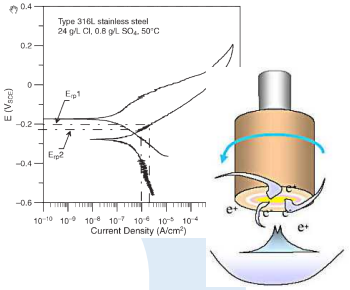
ISFSI-Relevant Conditions



Extent of electrolyte coverage and chemistry distribution



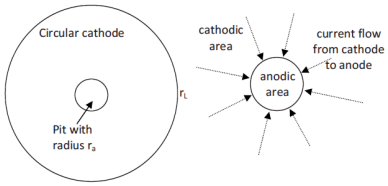
Cathodic and anodic kinetics in analog surface chemistries

Approach:

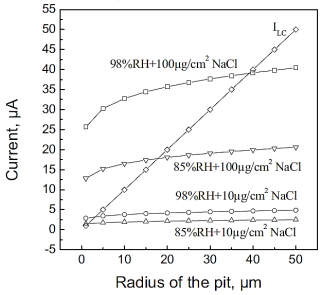
- *Post-exposure surface analyses of coupons from pitting experiments:*
- *TOF-SIMS, MicroRaman/FTIR, Auger Spectroscopy*
- *Cathodic kinetics of 304 in analog surface chemistries (sea-salt brines, carbonate brines)*
- *Establish variance in max pit size model predictions due to evolving electrolyte,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



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

Knowledge Gap:

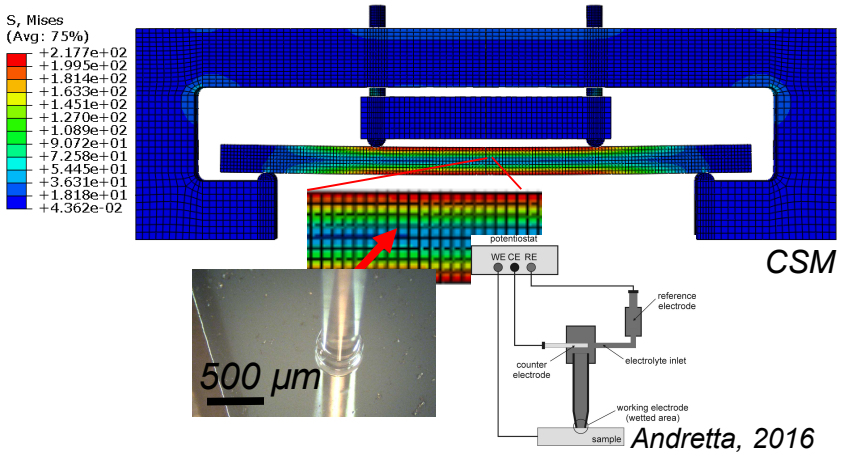
How material characteristics (microstructure, stress/strain) and environment (T, RH, salt load) impact electrochemical processes governing SCC

Goal:

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

Approach:

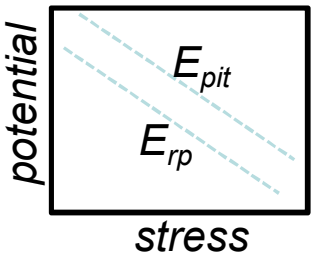
- Microelectrochemical mapping of CSM 4-point bend test specimens as a function of stress load
- Develop model to capture pitting characteristics as function of stress/strain with correlation to CSM 4-point bend atmospheric exposures



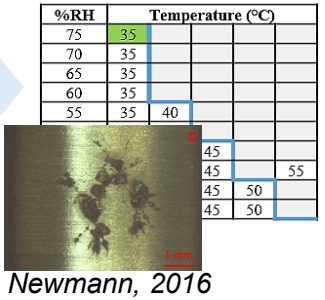
CSM

Andretta, 2016

Microelectrochemical mapping (SNL)



Stress effect on localized corrosion susceptibility



Newmann, 2016

Pit distribution on atmospherically exposed samples (CSM)