SAND2022-2466C

Why Low Humidity is Detrimental to Stainless Steel in Marine Atmospheres

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U.S. DEPARTMENT OF ENERGY

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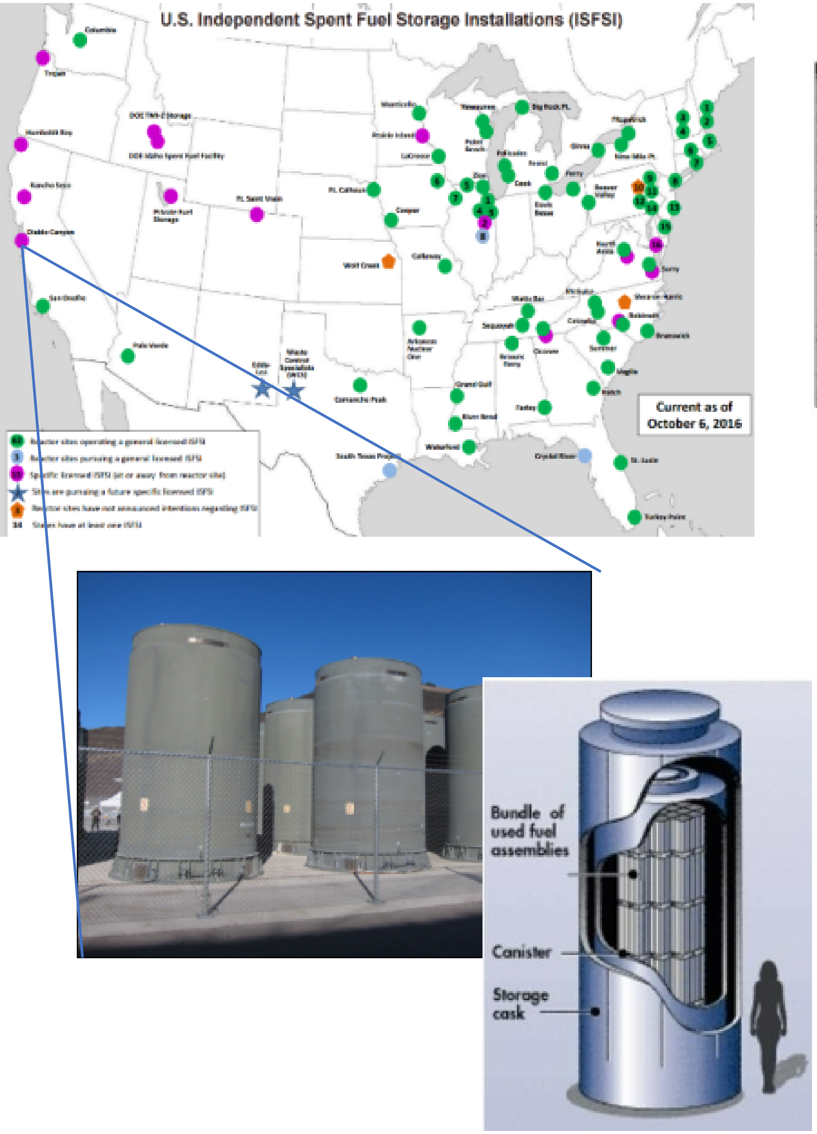
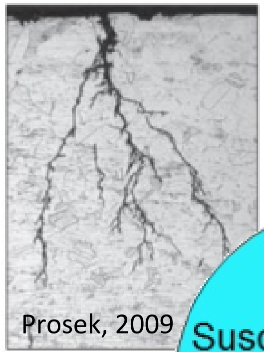
WASTEPD Performance and Design

Motivation: SCC Risk of Spent Fuel Dry Storage Canisters





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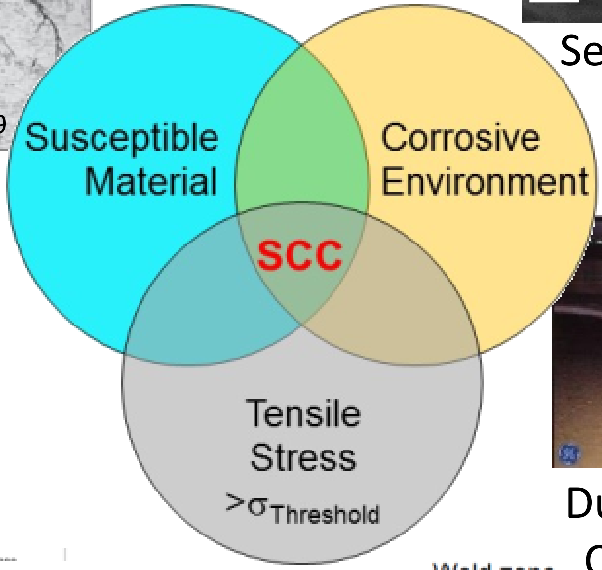
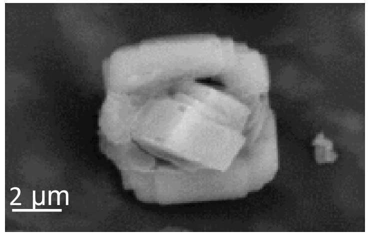
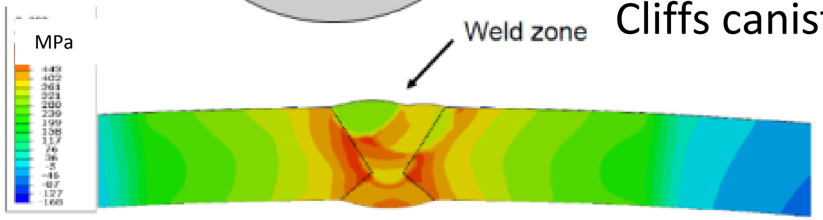




Sea-salt particle on Diablo Canyon canister

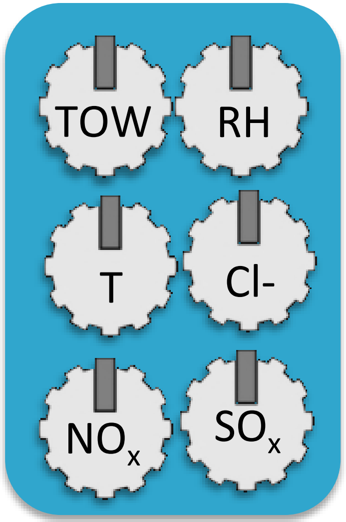
Dust on Calvert Cliffs canister



NRC, 2013

Assessing Risk: Empirical/Probabilistic Approach

At what rate and to what extent will corrosion damage propagate?



Environmental Parameters, f(t)

Field Exposure

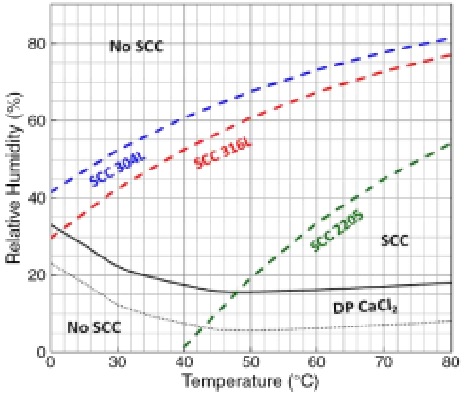
years

Lab Exposure

weeks

$$V_{corr} = kt^n \times 10^{[a(SO_2)+b(Cl-)+c(TOW)]}$$

Rodŕiguez, J. *et al. Corr. Sci.*, 2003, *45* (4), 799-815

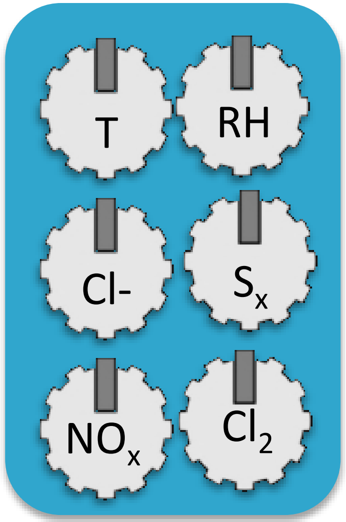


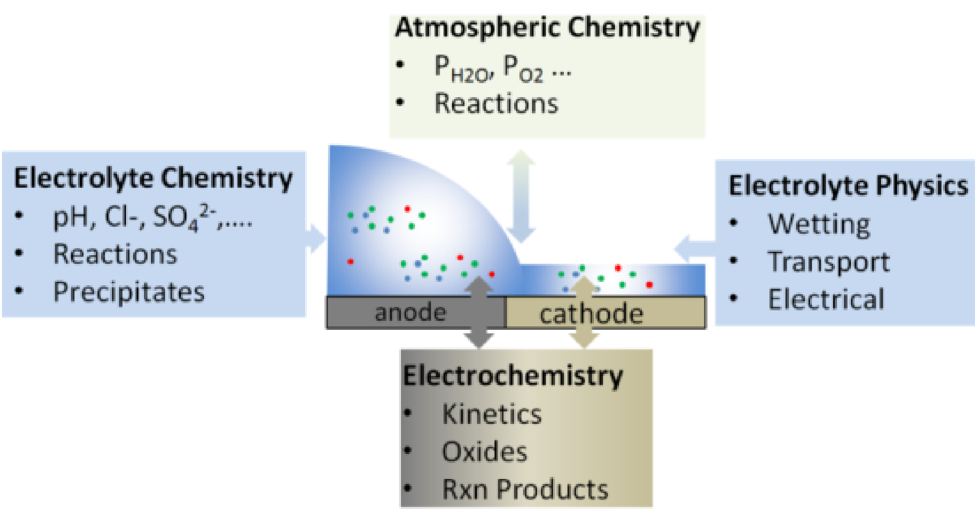
Prosek, et al., *Corrosion*, 70 (10): 1052–1063

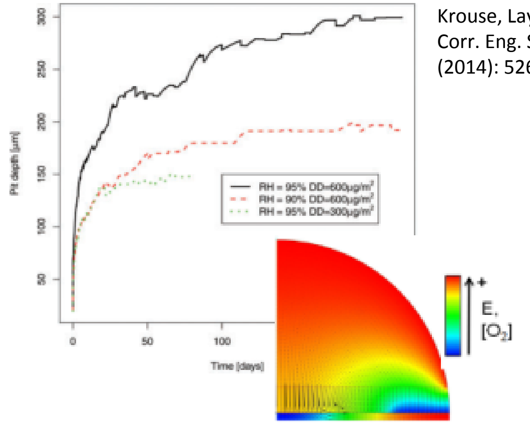
Damage

limited prediction capability, mechanistic insight lacking; development of realistic accelerated tests and predictive models is a grand challenge

Opening the Black Box: A Deterministic Approach







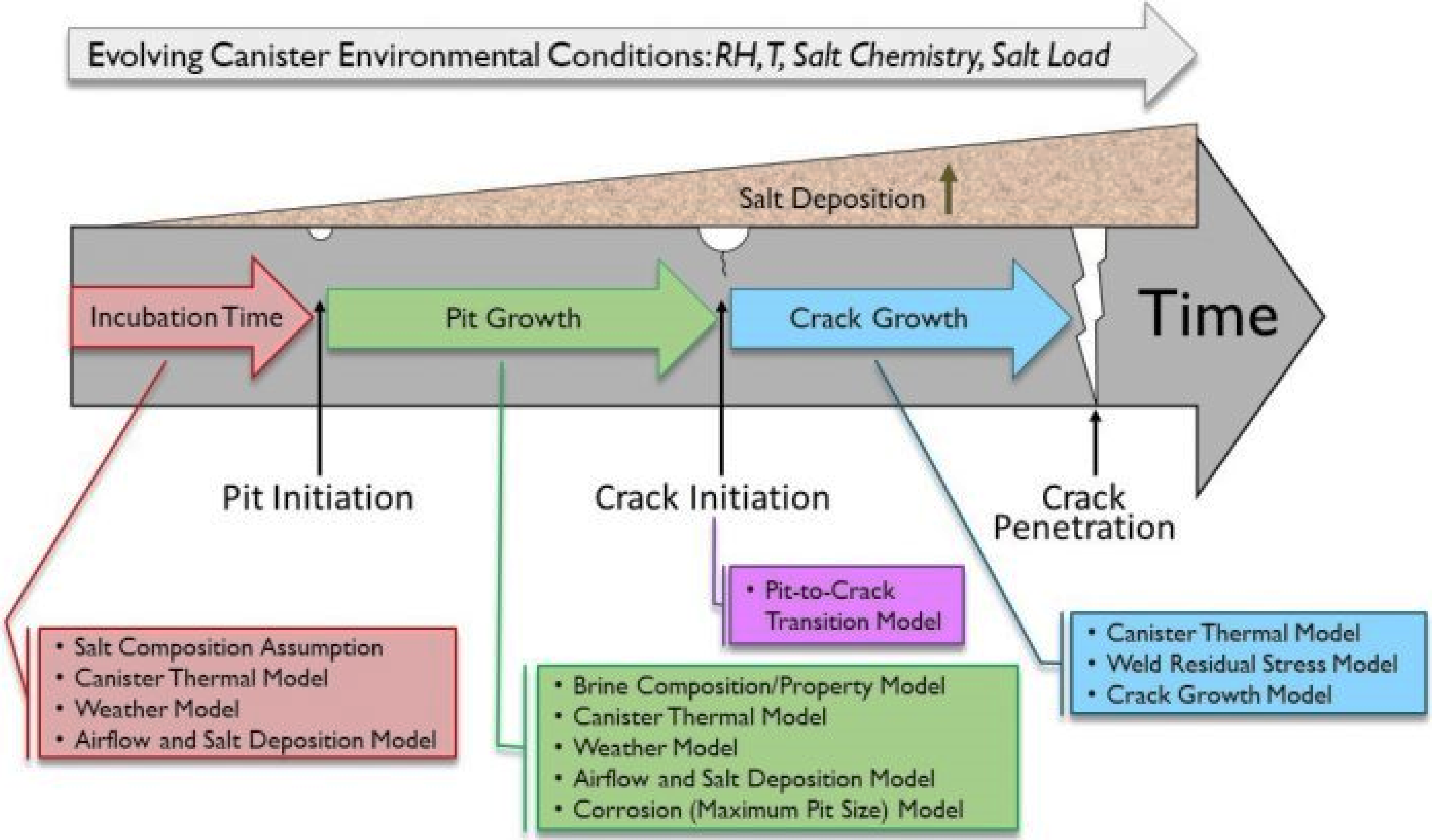
Krouse, Laycock, Padovani, Corr. Eng. Sci. Tech 49 (2014): 526-529

damage distributions and rates

Environmental Parameters ⟷ **System State** → **Corrosion Damage**

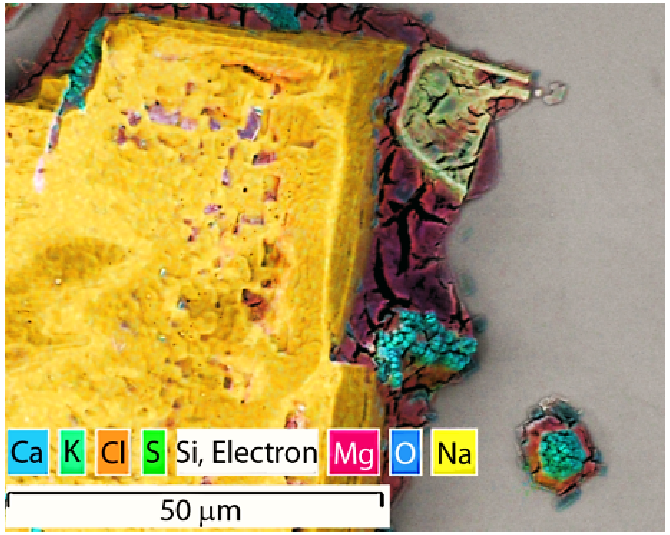
Foundational challenge inhibiting fundamental understanding is the limited ability to directly probe surface environment and corrosion processes

Integrated Deterministic/Probabilistic Model Concept for Canister SCC

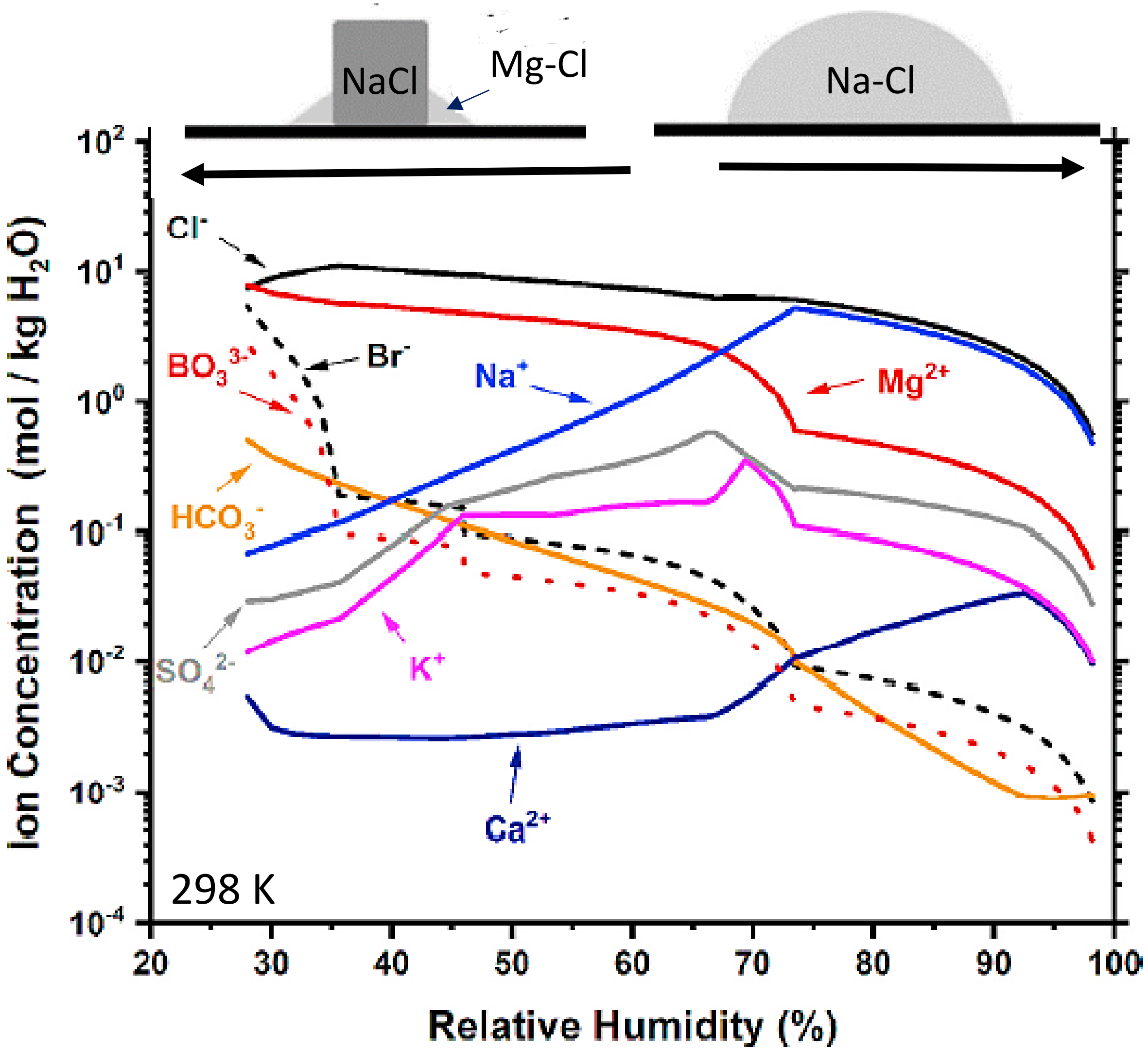


Schindelholz, Bryan, Dingreville et al., SAND2019-6240PE,675986

Sea Salt Brine Chemistry and Properties f(RH,T)



Schindelholz, E.J., Risteen, B.E., Kelly, R.G., J. Electrochem. Soc. (2014): C450



Bryan, C.R. and Schindelholz, E.J., SAND 2017-11231

Higher Chloride (lower humidity) Increases Pitting Susceptibility

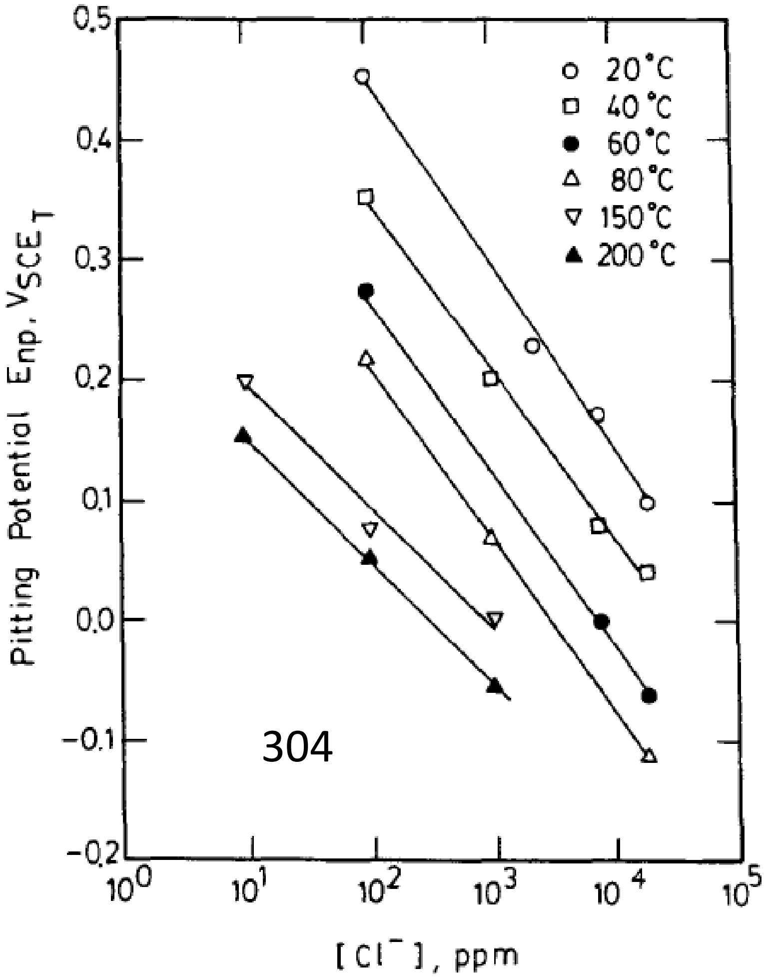
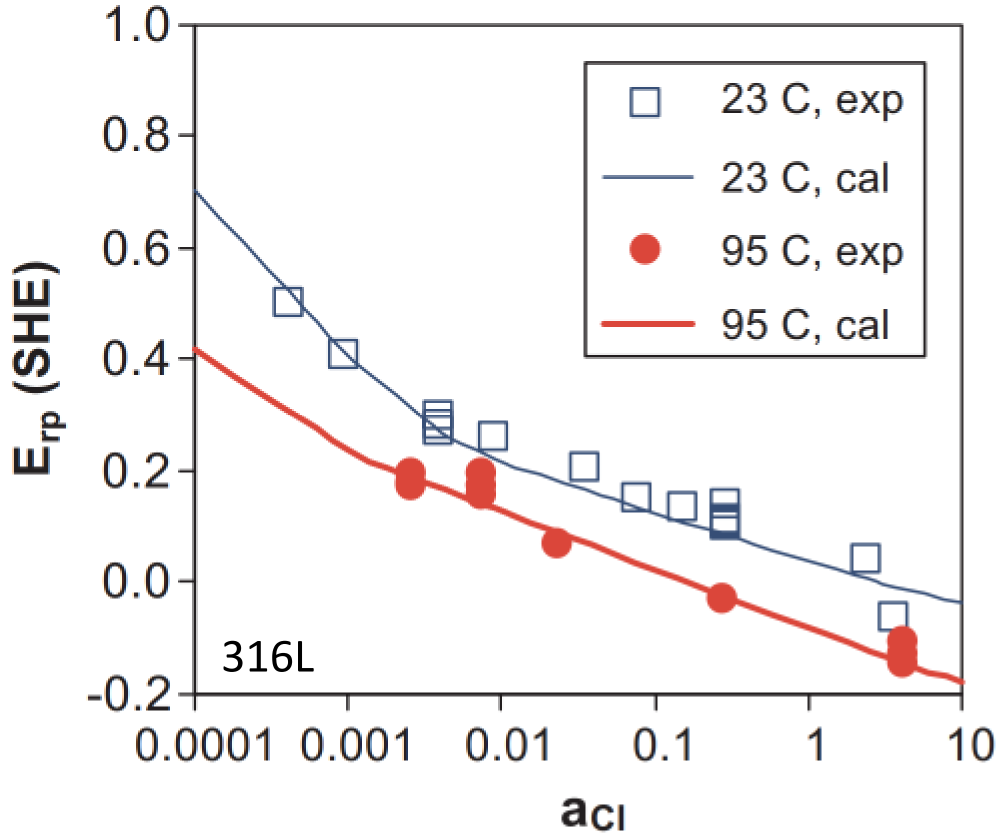


FIGURE 1. *Pitting potential vs log Cl⁻ concentration in aerated solutions at various temperatures.*

Wang, Su, Szklarska-Smialowska, Corrosion, 44, (1988): 732-737



Anderko, Sridhar, Dunn, Corr. Sci. 46 (2004):1583-1612

Lower Humidity (higher chloride) increases SCC Susceptibility

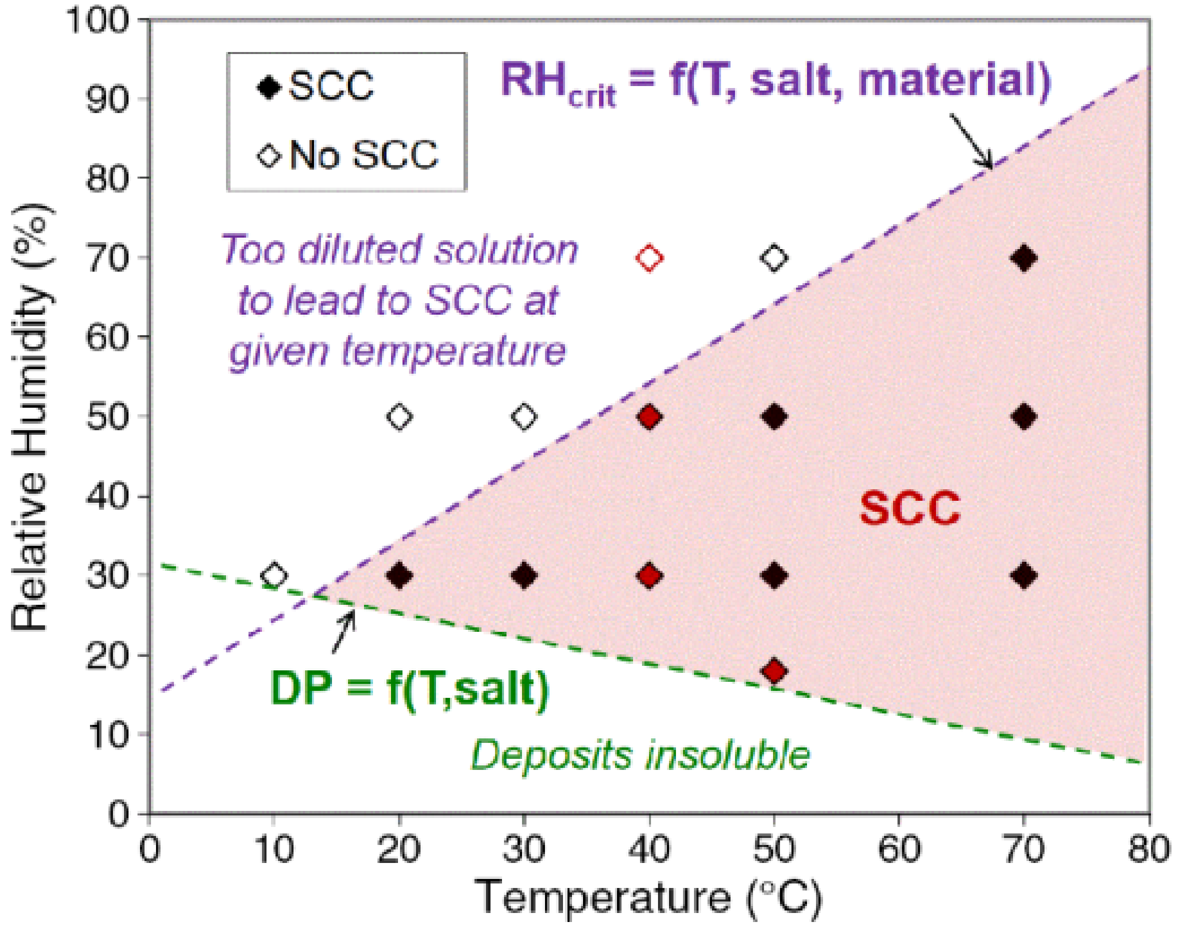


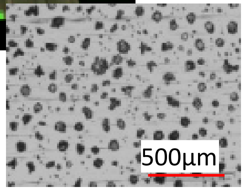
FIGURE 14. *Schematic presentation of RH limits for SCC initiation.*

Prosek, et al., *Corrosion,* 70 (10): 1052–1063

Pitting Kinetics and Damage Distributions: Baseline Data

Salt Load

120 grit finish 304H SS coupons



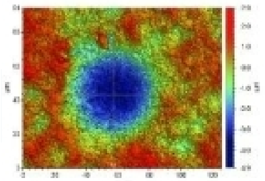
300µg/cm^2
ASTM D-1141
sea salt

Expose

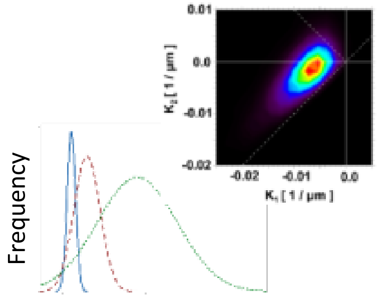
RH %	Temperature (°C)			
76	35			
70	35			
65	35			
60	35			
55	35	40		
50	35	40		
45	35	40	45	
40	35	40	45	
35	35	40	45	50
30	35	40	45	50

Duration: 1 week to 2 years

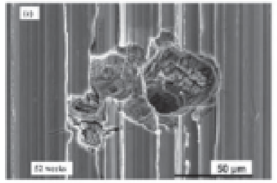
Post-Exposure Analysis



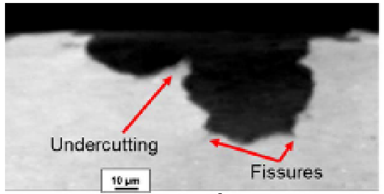
Profilometry



Pit Size and Shape Distributions



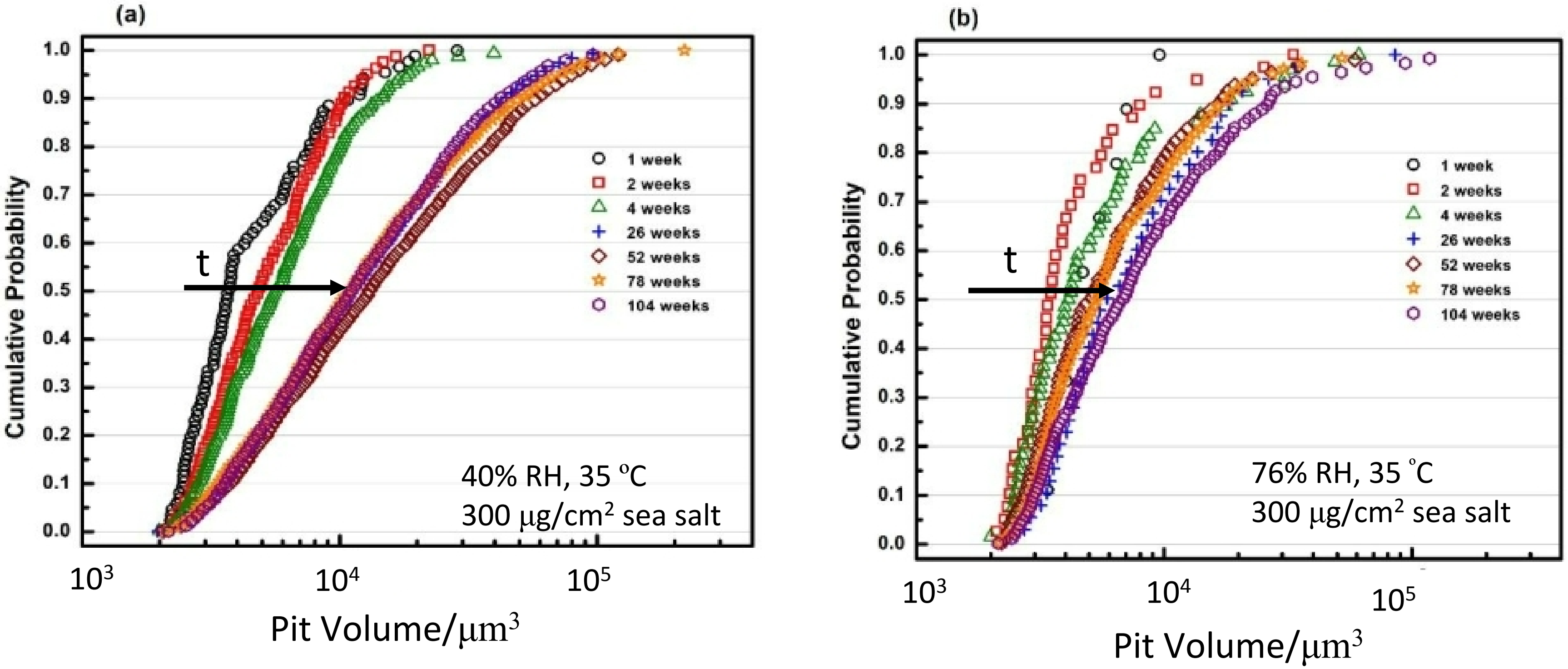
FIB/SEM



Tomography

Weirich, T.D., Srinivasan, J., .. Schindelholz, E.J. J. Electrochem. Soc. 166 (2019): C3477-C3487
Srinivasan, J., Locke J., Schaller R., … Schindelholz, E.J. J Electrochem. Soc. 168 (2021): 021501

Pit size and frequency on 304H reach limiting values; 40% RH produces larger pits



What about other RH, T, salt loads, alloy, material conditions?.....Fluctuating RH, salt loads?.....

Srinivasan, J., Locke J.S., Schaller R.F., … Schindelholz, E.J., J Electrochem. Soc. 168 (2021): 021501

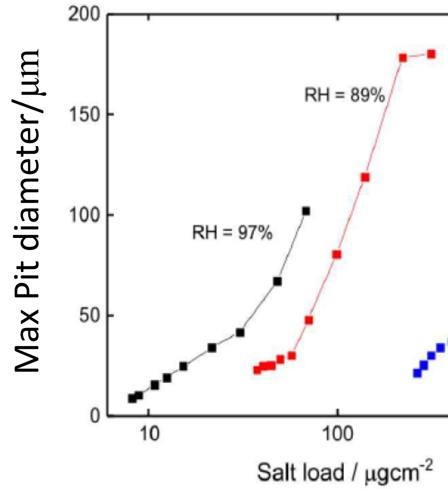
Maximum Pit Size Model: Deterministic Approach

Electrochemical model for predicting maximum pit size possible for a given material and environmental condition

Model Inputs:
salt chemistry, salt load, RH, T, alloy

Challenge:
Information on electrochemical parameters lacking for expected canister brine conditions

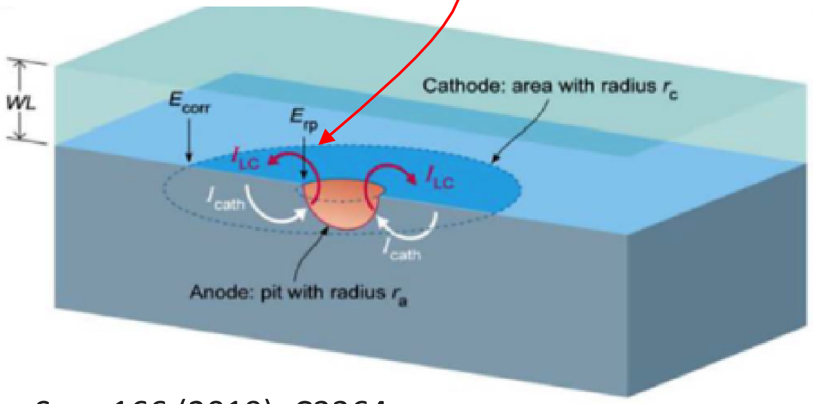
Assumptions:
1. Continuous and uniform brine film
2. Hemispherical pits
3. Cathodic and anodic kinetics are time independent (fixed electrolyte conditions)



Conceptual schematic

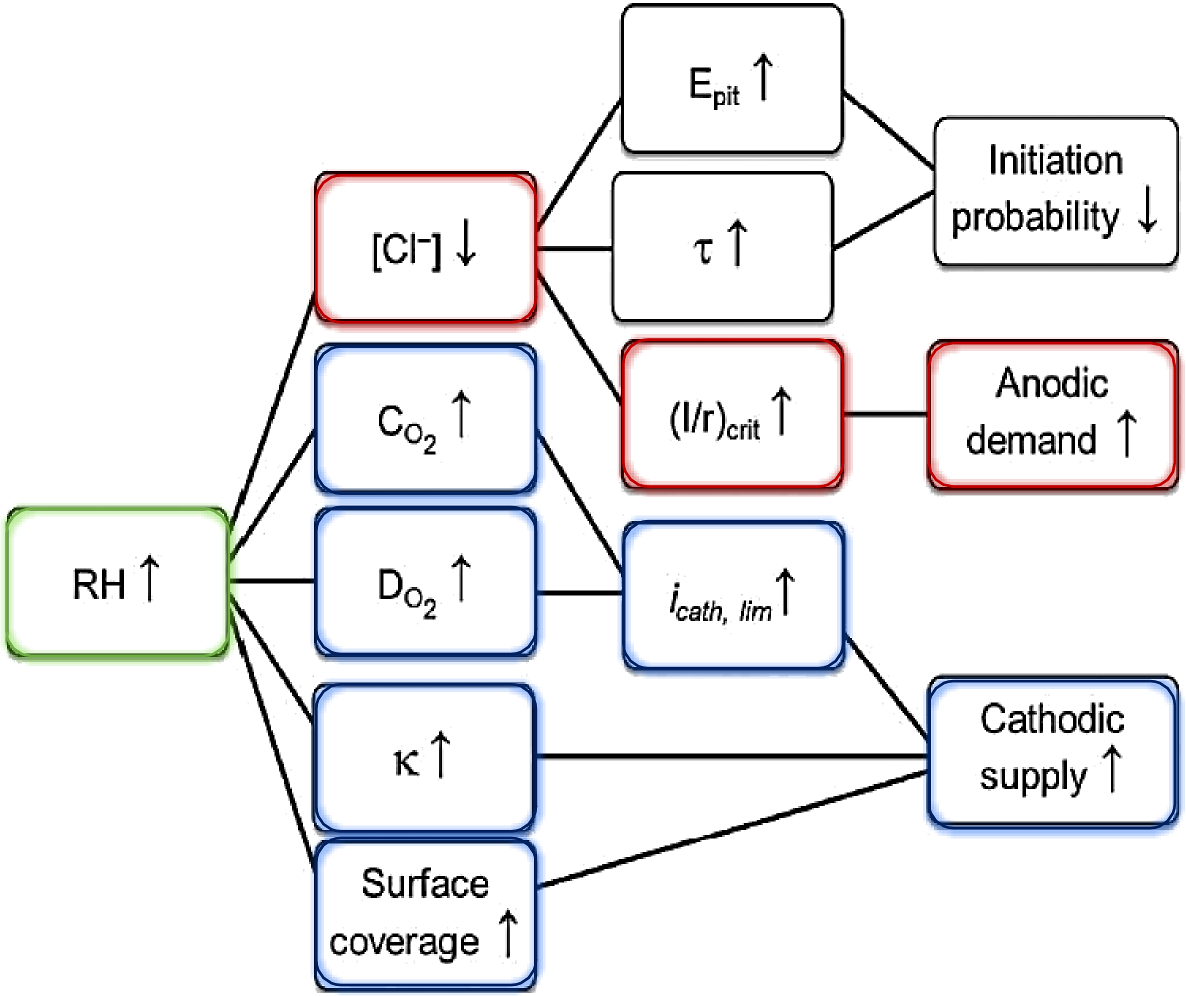
Max. cathode current — Brine conductivity — Brine layer thickness — Cathodic Kinetics

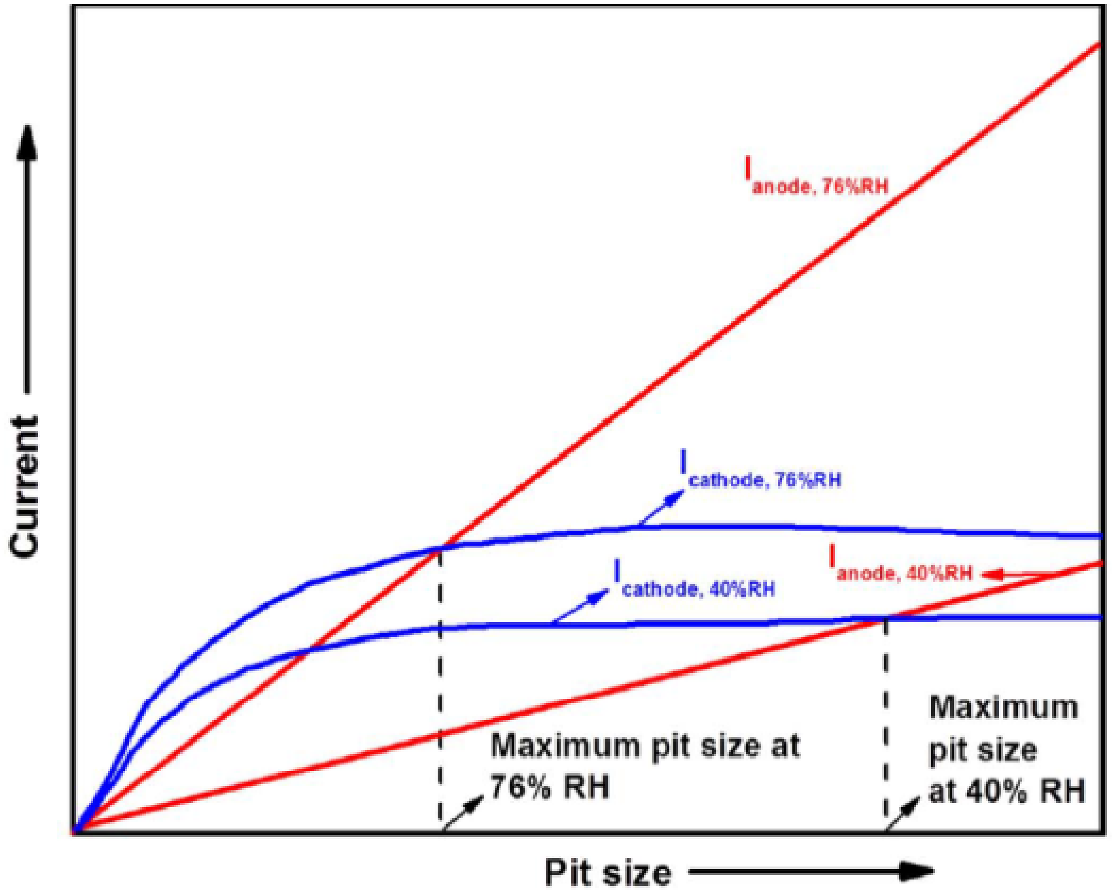
$$\ln I_{c,max} = \frac{4\pi k W_L \Delta E_{max}}{I_{c,max}} + \ln\left[\frac{\pi e r_a^2 \int_{E_{corr}}^{E_{rp}} (I_c - I_p)\, dE}{\Delta E_{max}}\right]$$



Katona, R. M., Carpenter, J., Schindelholz, E. J., Kelly, R. G. , *J. Electrochem. Soc.,* 166 (2019): C3364.

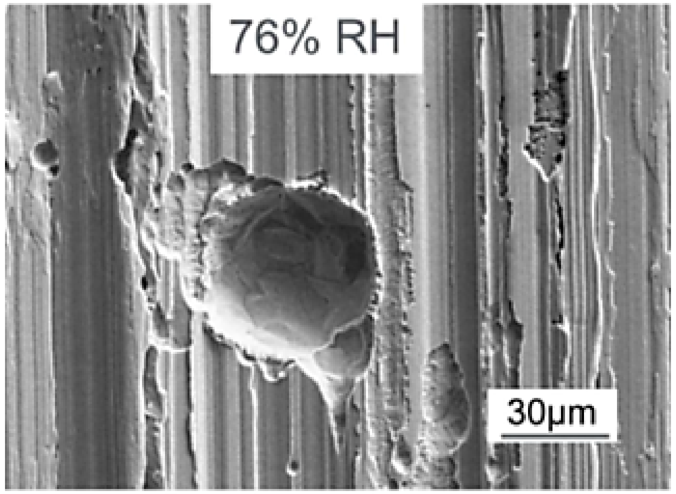
Several Humidity-Dependent Brine Characteristics Control Pit Growth



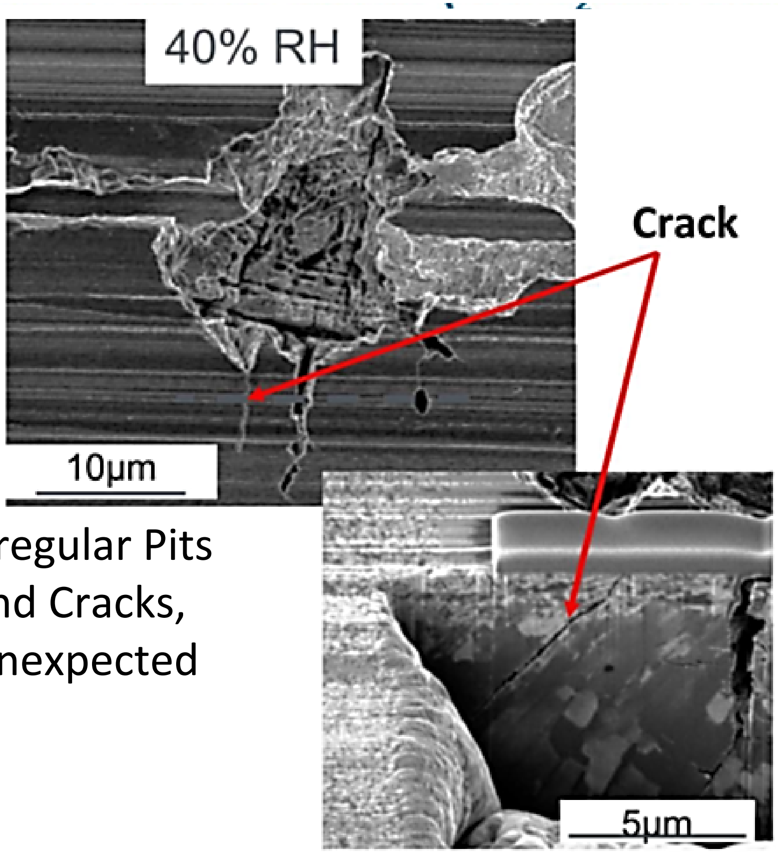


Weirich, T.D., Srinivasan, J., .. Schindelholz, E.J. J. Electrochem. Soc. 166 (2019): C3477-C3487

Something Unexpected: Pit Morphology f(RH)



Hemispherical Pits, Assumed



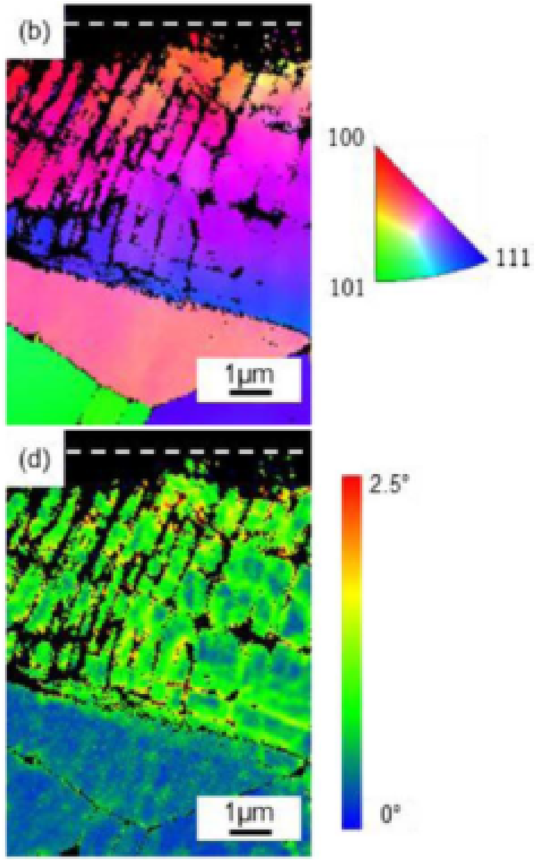
Irregular Pits and Cracks, Unexpected

cross-section through cracked region

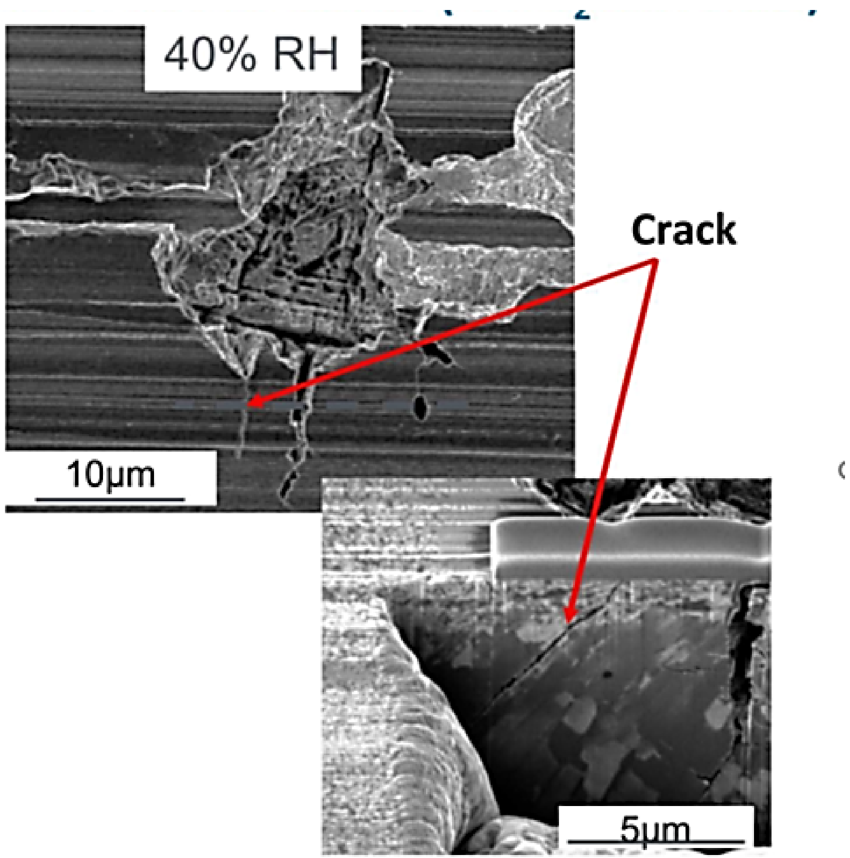
What is going on here?

Weirich, T.D., Srinivasan, J., Locke, J.S., …. Schindelholz, E.J., J. Electrochem. Soc. 166 (2019): C3477-C3487

Low Humidity (40% RH) Produces Irregular Pits Reflective of Surface Condition



EBSD maps of cross-section through 304 SS coupon surface



Weirich, T.D., Srinivasan, J., Locke, J.S., …. Schindelholz, E.J., J. Electrochem. Soc. 166 (2019): C3477-C3487

Irregular Pit Morphology at Low RH Near Critical Pit Stability?

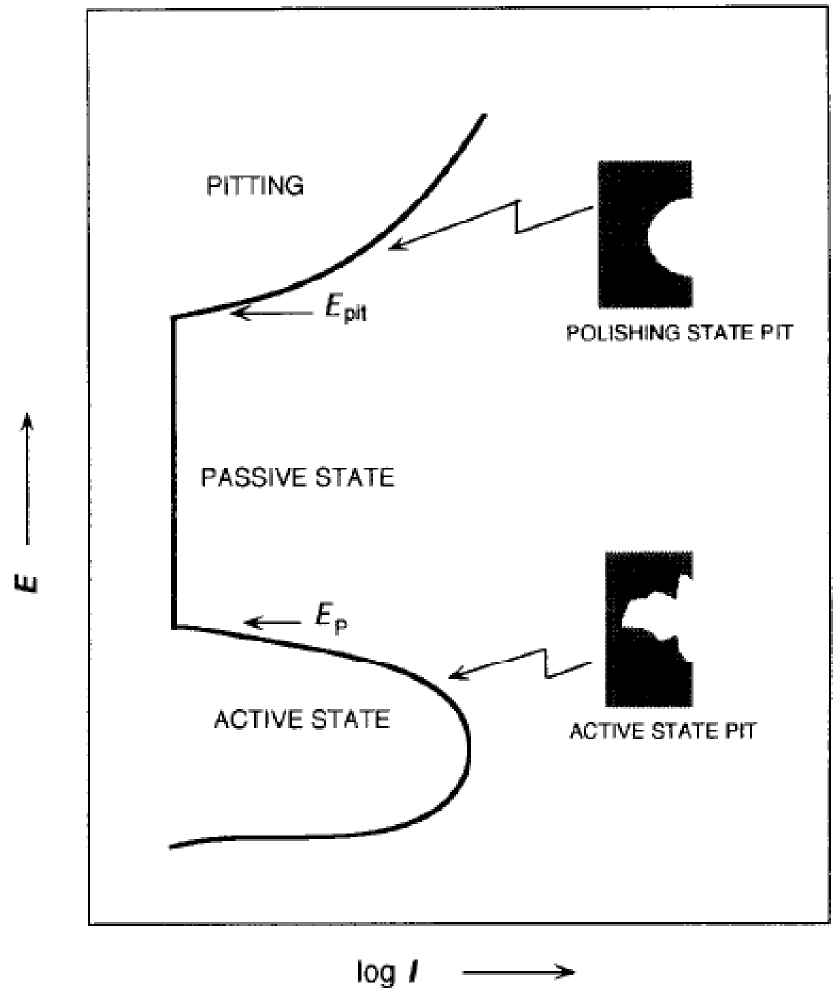
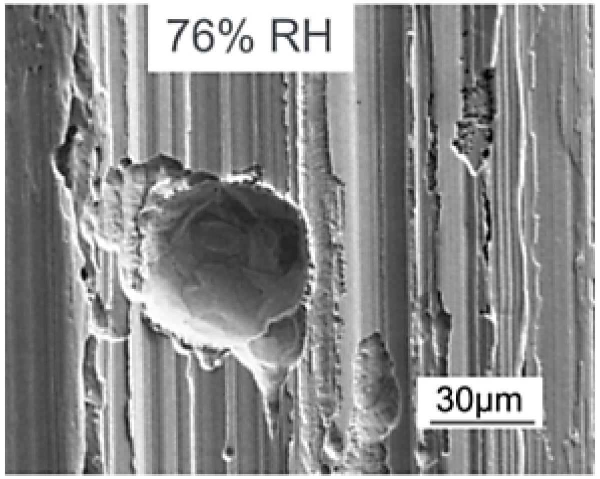
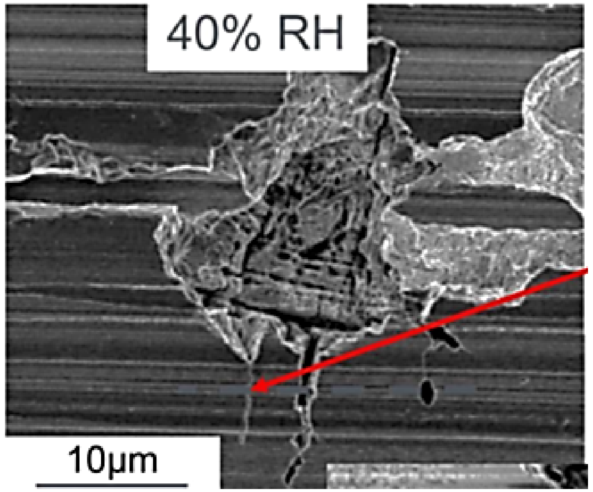


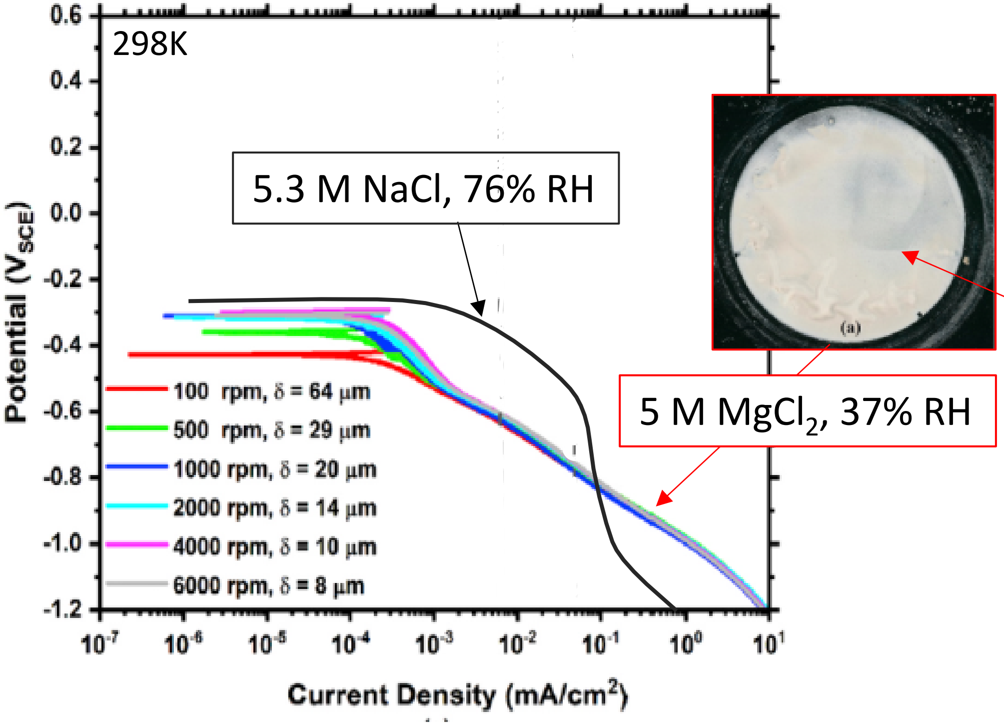
Fig. 1. Anodic polarization curve of metal showing potential regions for polishing state and active state pitting. E = electrode potential; I = metal dissolution current; E_{pit} = the pitting potential; E_P = the passivation–depassivation potential.





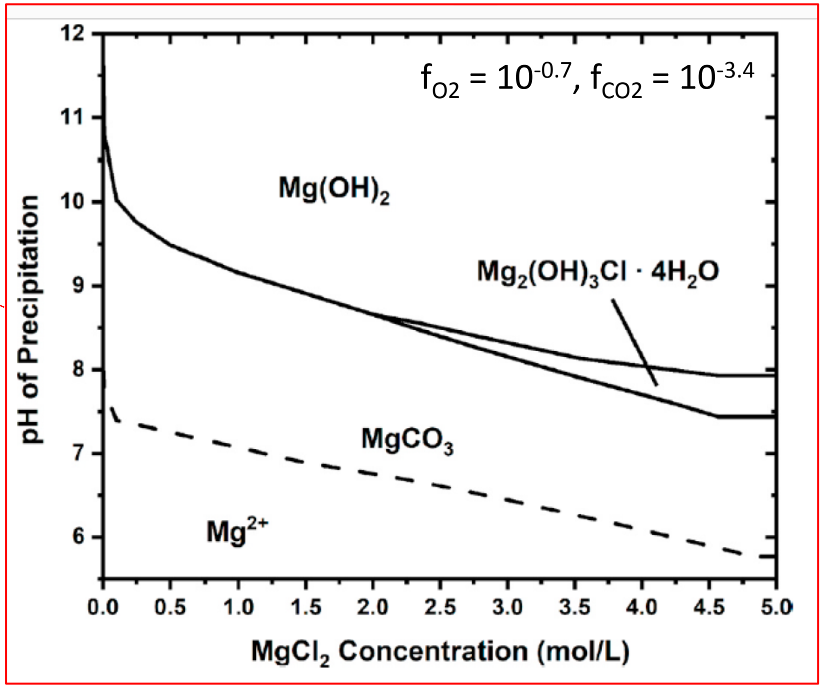
Sato, J. Electrochem. Soc. 129 (1982): 260

Precipitation of Mg Species May Limit Cathodic Supply and Promote HER in Low Humidity Brines



HER Dominates Cathodic Polarization Behavior in $MgCl_2$

H_2O-$MgCl_2$-O_2-CO_2, 298K



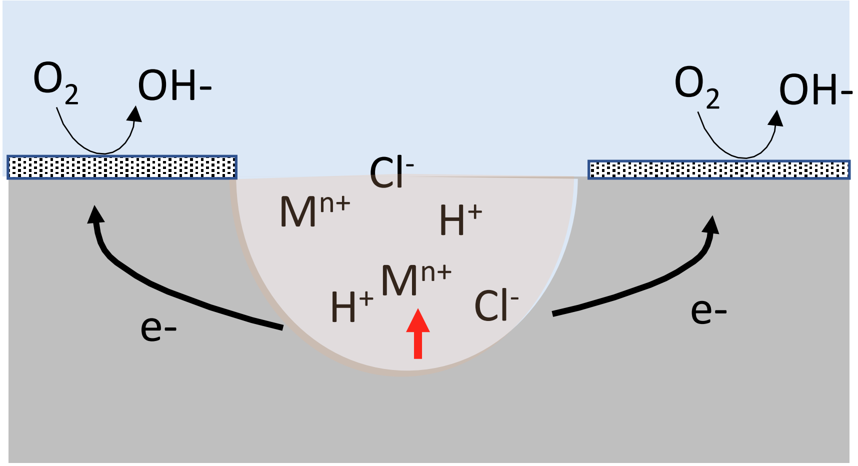
Mg precipitates buffer pH and promote HER

Katona, R.M., Carpenter, J., …, Schindelholz, E.J., *Corr. Sci.*,177 (2020): 108935

Alexander C.L., Liu, C., … Schindelholz, E.J., J. *Electrochem. Soc.*, 165 (2018): C869-C877

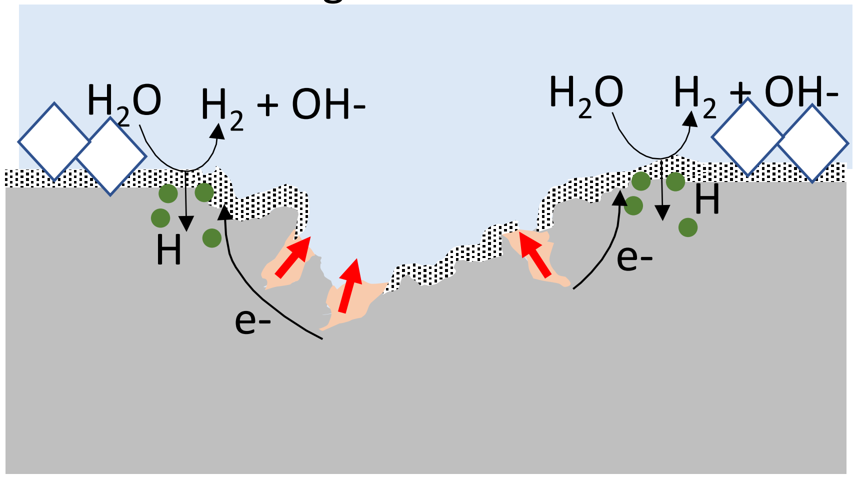
To What Extent does Low RH Sea Salt Brine Diminish Cathode Power and Embrittle Pit Area?

> 76% RH
Na-Cl Rich Brine



pH at cathode sites increases with hydroxyl production

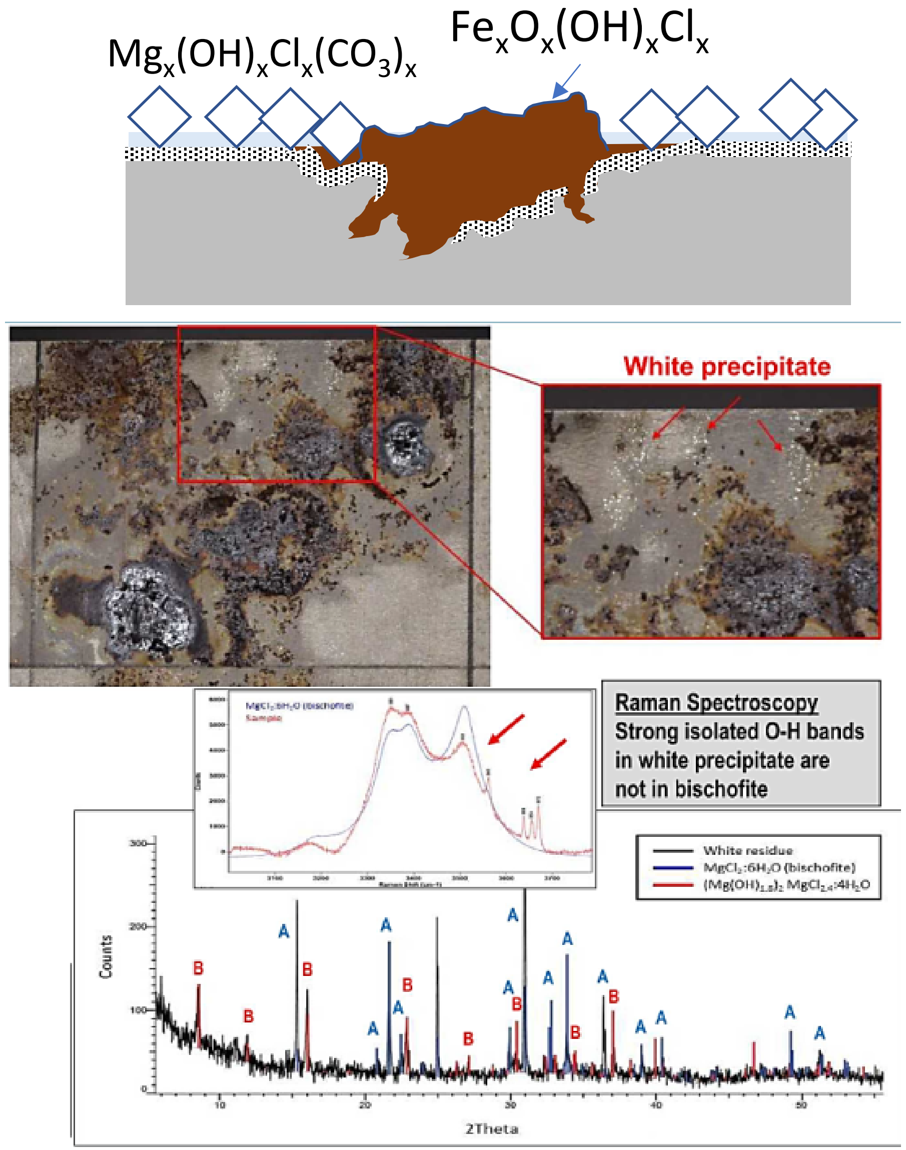
40% RH
Mg-Cl Rich Brine



Mg precipitates buffer to neutral pH and promote HER. H absorption embrittles area around pit?

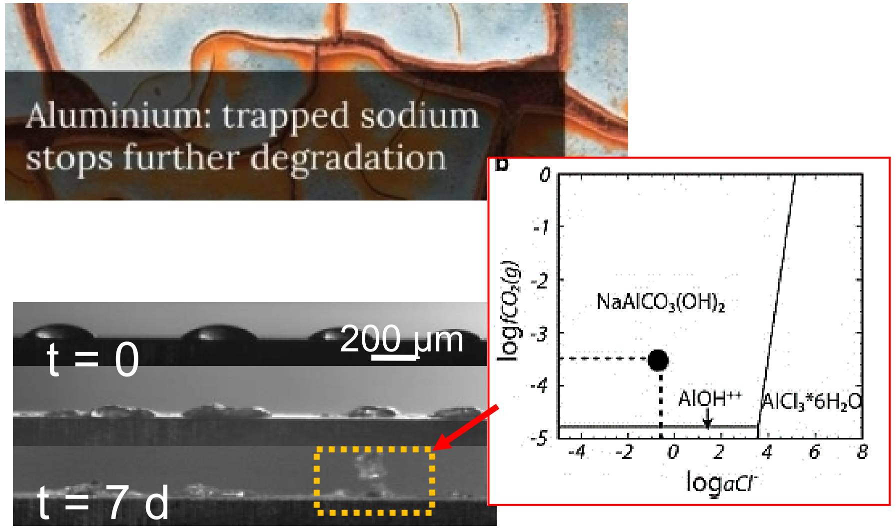
To What Extent do Low Humidity Precipitation Reactions Dry Out Brine and Limit Corrosion?

- Cathodic reactions produce hydroxides promoting Mg precipitates
- Corrosion products sequester Cl- from the brine
- Precipitation removes brine components, reducing brine volume at a given RH



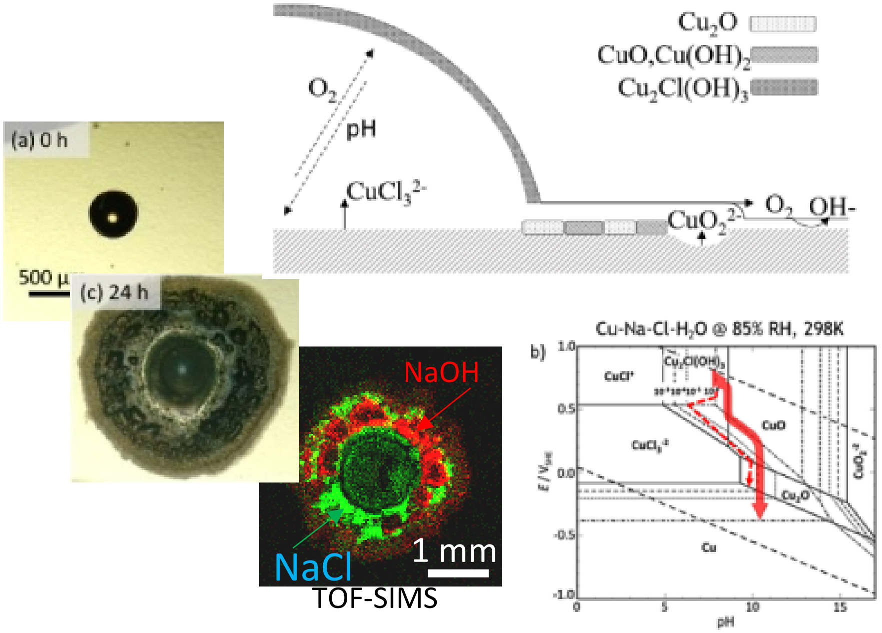
SAND2019-5032PE

Brine Evolution is a Critical Factor Controlling Corrosion Kinetics and Damage Distributions



98% RH, 298 K, Lab Air

Corrosion-induced drying of NaCl electrolyte stops aluminum corrosion



Copper corrodes in alkaline brine produced by cathodic reactions outside of salt droplets

Schaller, R.F., Jove-Colon, C., Taylor, J.S., Schindelholz, E.J., *Mat. Deg.* 1 (2017): 20

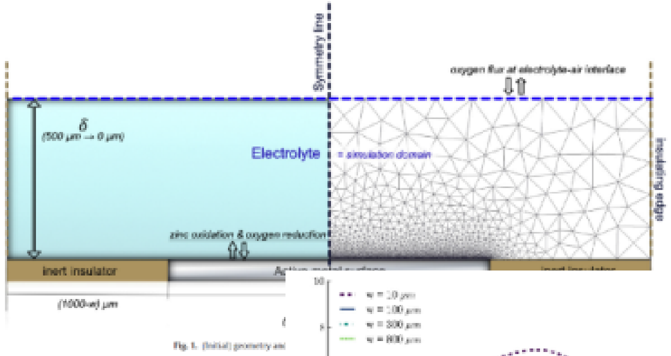
Schindelholz, E.J., Cong, H., Jove-Colon, C., Moffat, H.K., *Electrochimica Acta* 276 (2018): 194-206.

Broader Implications for Electrochemical Atmospheric Corrosion Models

Variety of Assumptions

- static electrolyte- fixed geometry, chemistry or phases
- electrochemical behavior in bulk electrolyte, “dilute” solutions

Assumptions are largely due to lacking definition of electrolyte and electrochemical kinetics



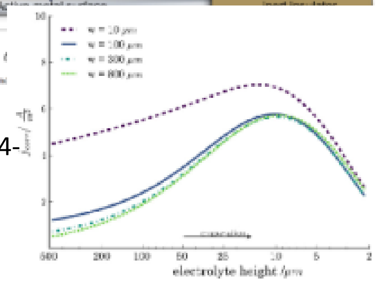


Fig. 15. Corrosion current density for different electrode widths during evaporation

Van den Steen, N., et al., Electrochim. Acta (2016): 714-723

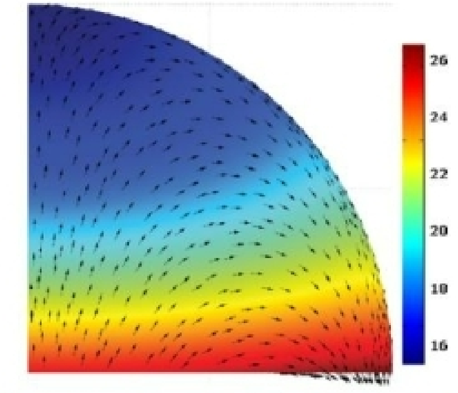
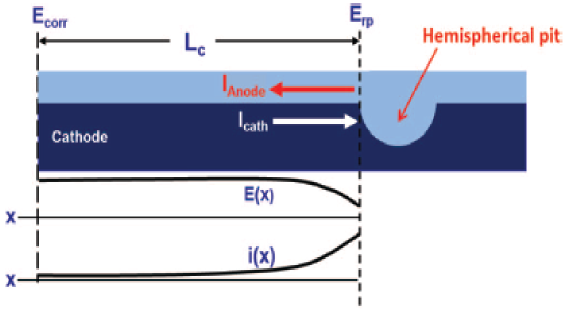


Fig. 10. $(C_{Zn^{2+}}/C^0_{Zn^{2+}})$ of zinc ions and arrow plot of current density vectors showing separation of metal surface into anodic and cathodic regions over time.

Cole, Ivan S., et al., Electrochim. Acta (2011): 1856-1865



Chen, Z. Y., and R. G. Kelly, J. Electrochem. Soc. (2009): C69

Conclusions

Pitting and SCC are promoted by low humidity conditions in the presence of sea salt deposits.

Why?

- Shift in brine conditions – high volume of Na-Cl rich brine at high humidity to low volume of more concentrated Mg-Cl rich brines below ~ 75 % RH

- High [Cl-] can promote pitting – anodic processes are well studied

- Concentrated Mg-Cl rich brines lead to irregular/jagged pits and microcracks in rough finish SS 304 that could promote SCC - limit cathode power and support HER?

Elucidating the relationship between evolving brine characteristics and the cathodic processes driving atmospheric corrosion and SCC would further the development of deterministic electrochemical models.