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Atmospheric Corrosion Through a Multiphysics Lens

The Linkage between Surface Environment and Electrochemical Processes

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Acknowledgements: Rebecca Schaller, Harry Moffat, Charles Bryan, Carlos Jove-Colon, Rob Sorensen, Doug Wall

Discussion Outline

- Introduction
- Background on Atmospheric Corrosion
  - Challenges
  - Linking Environment to Corrosion Damage Distributions and Rates
  - Deterministic models
- How do surface environments evolve and what is impact?
  - Model systems at high humidity
  - NaCl on copper, NaCl on aluminum
- How does this translate to other engineering challenges?
  - spent nuclear fuel dry storage casks

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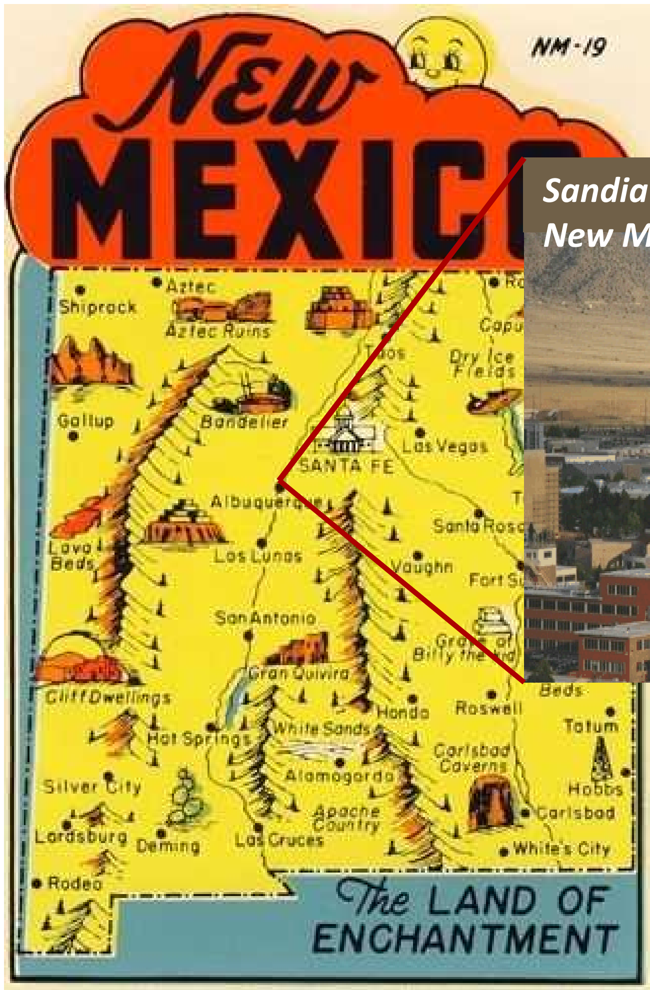


Established 1949: non-nuclear component engineering
Now: ~10,000 employees
6 sites
7 national security mission areas: NW to Energy

Center 1800:
Materials Science & Engineering

- **Our mission is to provide:**
  - Foundational materials expertise and innovation to enable Sandia success in its national security missions
  - Leadership in Sandia's Materials Science Research Foundation, ensuring that the R&D performed sustains and grows our expertise for the laboratory

- **Key Research Areas**
  - Fundamental understanding of mission critical materials and their processing
  - Materials discovery and materials-enabled technologies
  - Materials performance in mission environments
  - Materials aging and reliability
  - Predictive materials behavior – atomic-to-continuum length scales
  - Materials characterization, failure analysis, and forensics

- **Primary Customers**
  - Nuclear Weapons PMU – Legacy and Modernization
  - Defense Systems & Assessments PMU
  - Energy and Climate PMU
  - Engineering Campaigns – WS&T and SWPR
  - Advanced Simulations & Computing (ASC)

- **Research Challenges Support**
  - Engineering of Materials Reliability
  - Revolutionary Approaches to the Stockpile
  - Power On Demand

Aging of High Reliability, Long Life Systems

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

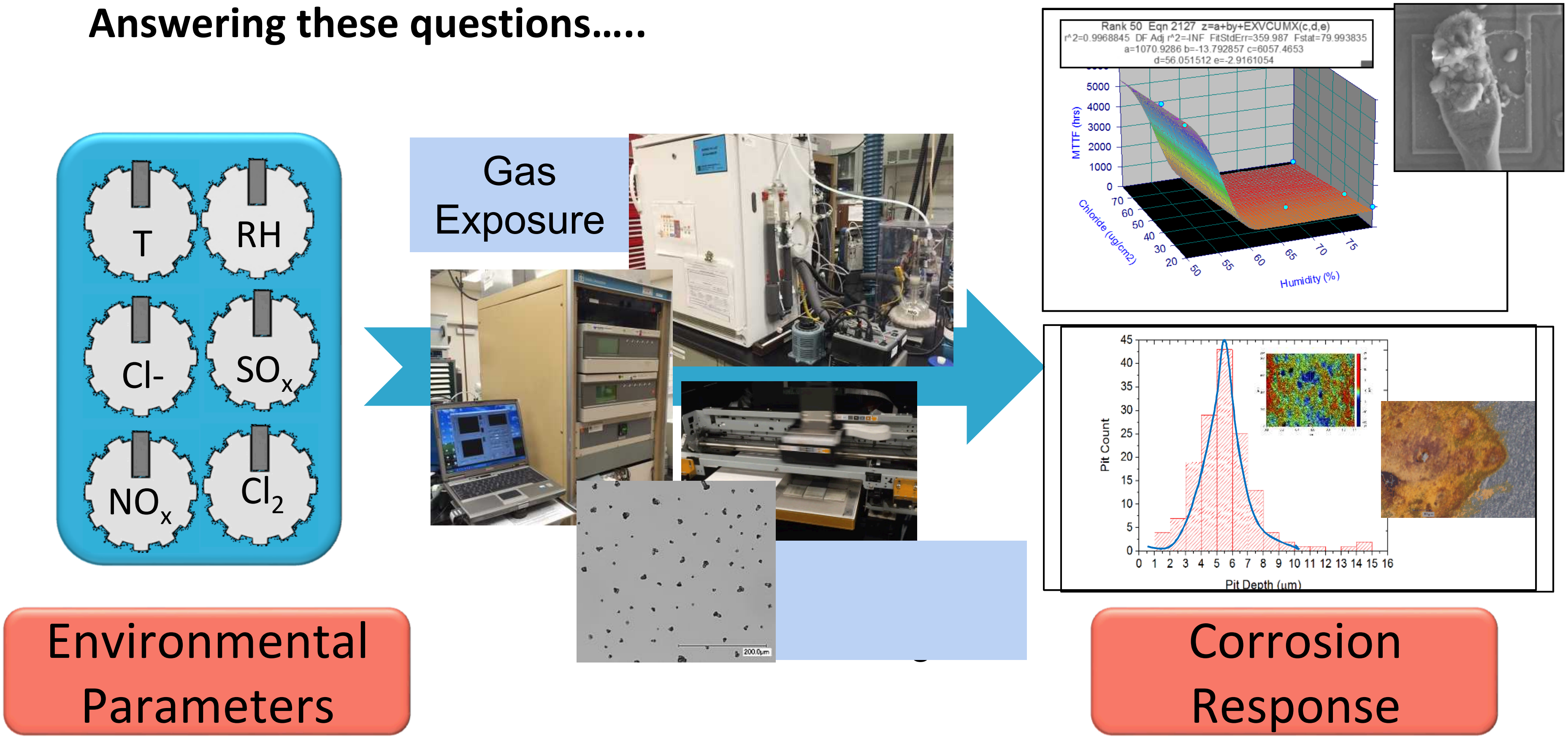
What frequency and where should we inspect?

How can we change environment to minimize corrosion?

How robust is this design against corrosion in expected environment? Where are corrosion hot spots?

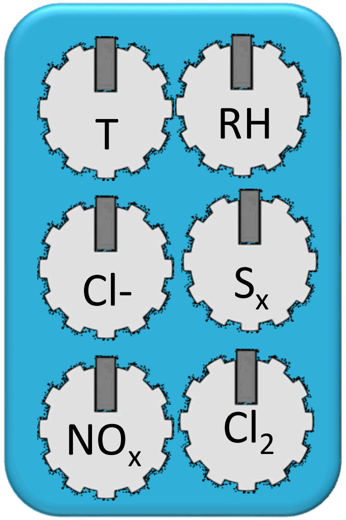
Current Engineering Approaches are Limited to Correlative Observations

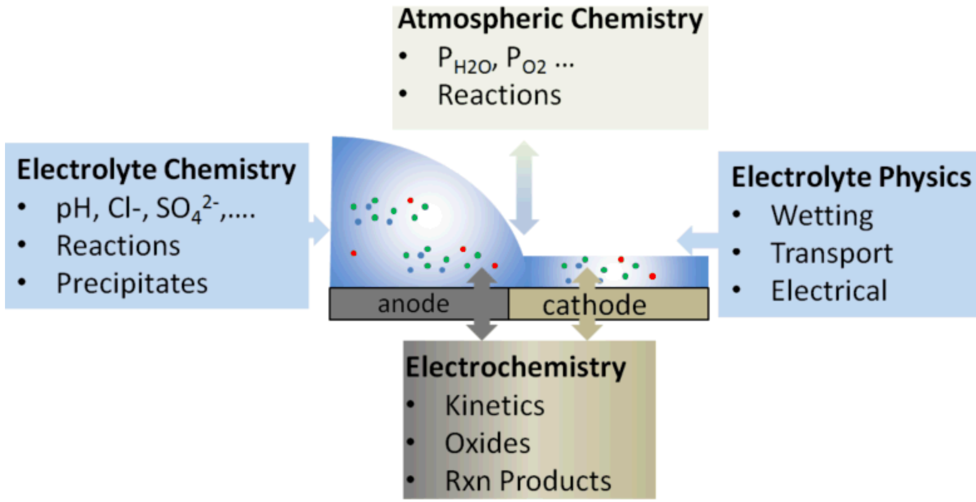
Answering these questions…..

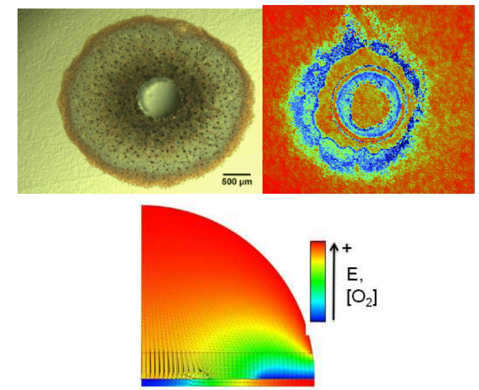


Limited prediction of extent or rate, Limited mechanistic insight

Linking Surface Environment to Corrosion Response







damage distributions and rates

Environmental Parameters ⟵ **System State** ⟶ **Corrosion Response**

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

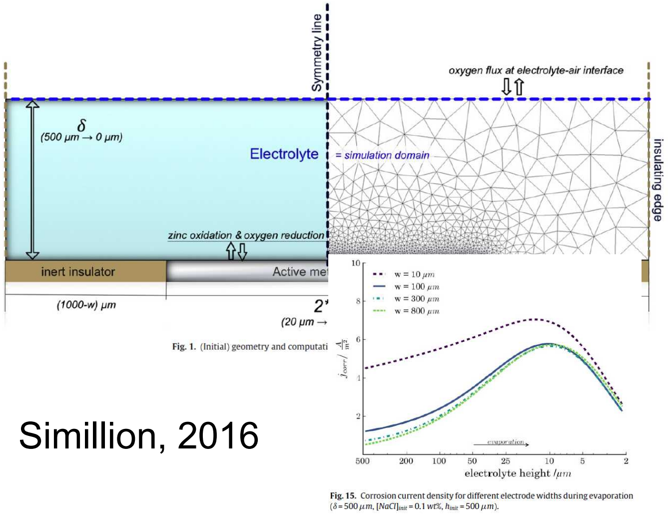
Quantitatively Linking Surface Environment to Corrosion Behavior

Deterministic Approaches

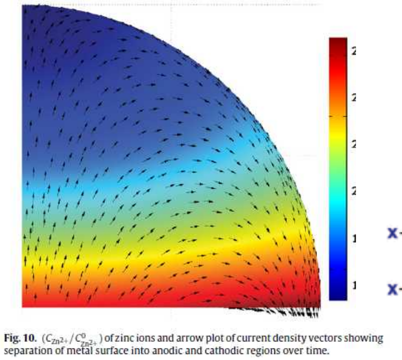
Variety of Assumptions

- static electrolyte- fixed geometry, chemistry or phases
- bulk electrolyte- electrochemical behavior

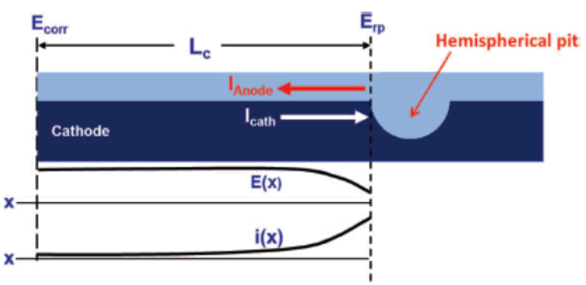
Assumptions are largely due to lacking definition of electrolyte and electrochemical kinetics



Simillion, 2016



Cole, 2011



Kelly group, 2009, 2014

Corrosion Processes and a *Dynamic* Surface Environment

How do saline electrolytes evolve once corrosion initiates in humid environments?

What is the interplay between electrolyte dynamics and corrosion damage distributions and rates?

Studies under highly simplified conditions:

(1) NaCl droplets on Cu: role of alkaline films and computationally capturing the evolving system

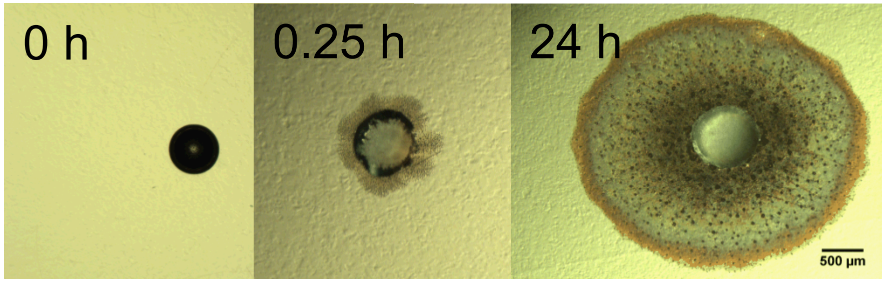
(2) NaCl on 1100 Al: relationship between salt loading and damage extent

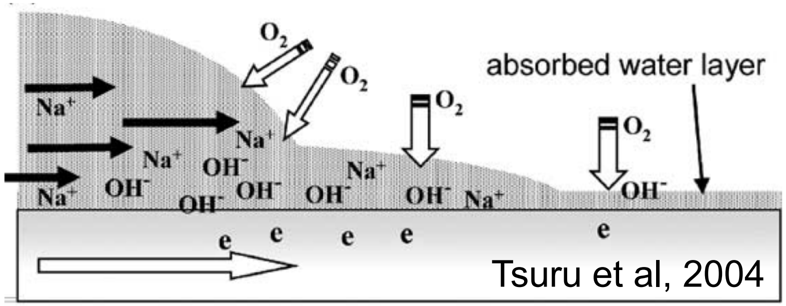
Cu-NaCl-H2O: Secondary Spreading

How does electrolyte evolution impact electrochemical processes?

rate and extent of spreading
- initial drop size and chemistry
- substrate alloy
- environment (P_{CO2}, RH)

Secondary Spreading

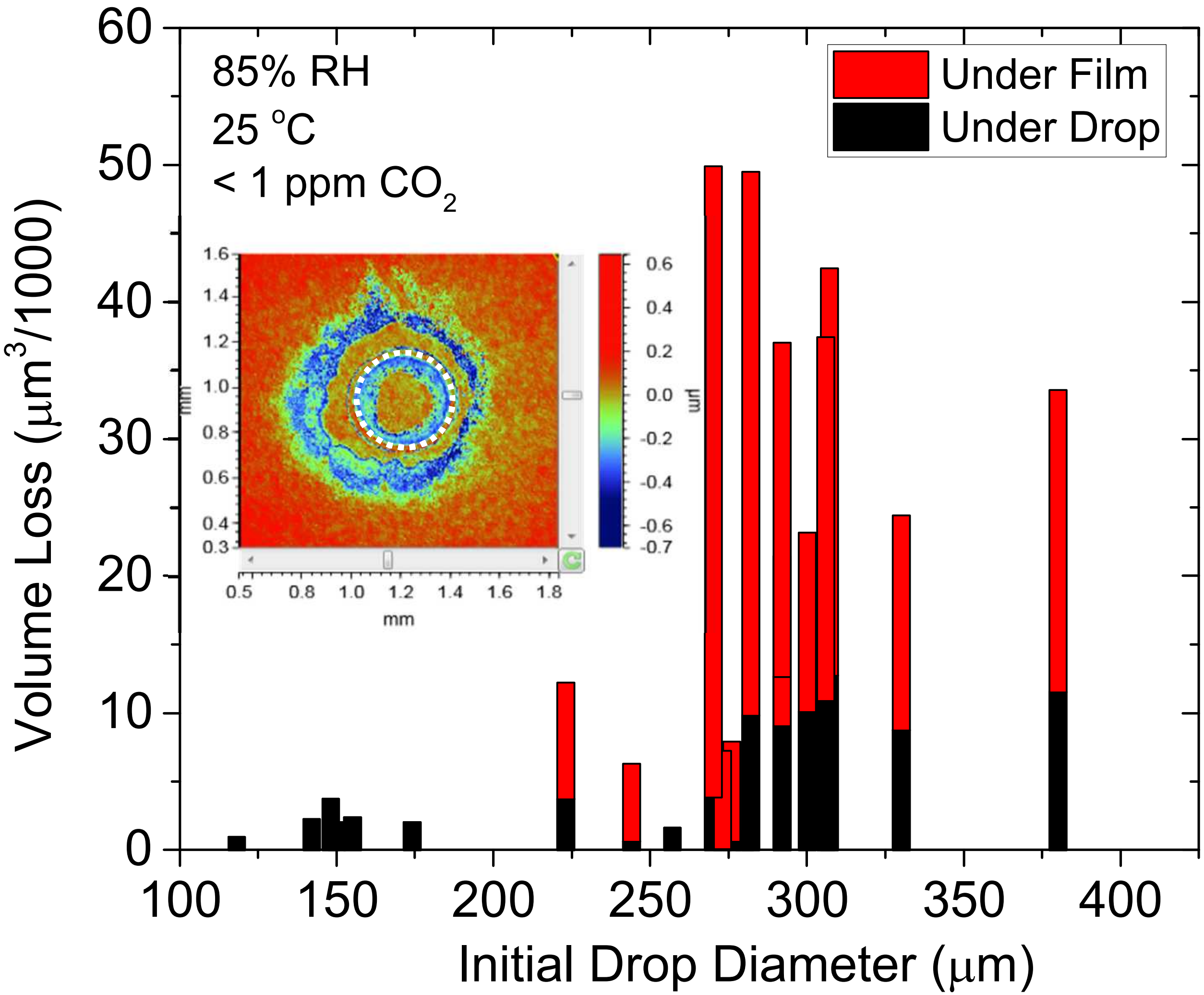




$$I_{m,drop} = I_{O_2,drop} + I_{O_2,film}$$

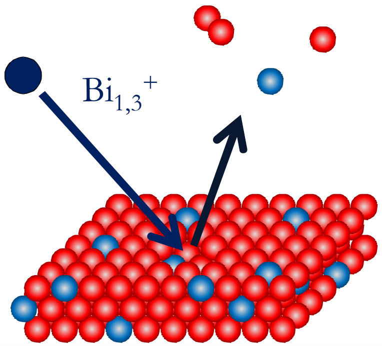
Chen, 2005

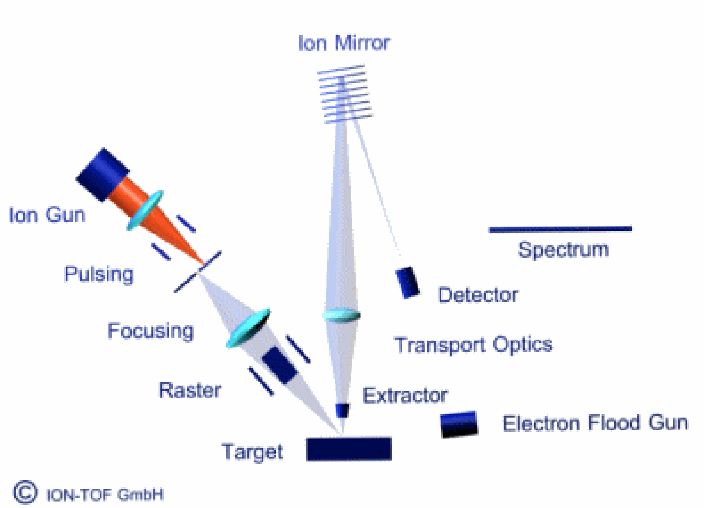
Damage Relation to Initial Drop Size and Spreading



Chemistry Distribution after Exposure

TOF-SIMS

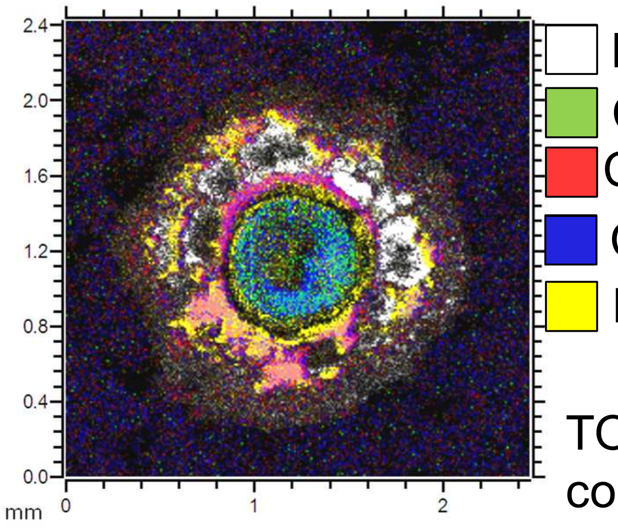




~ 1 nm interaction depth
ppt to ppb resolution

85%RH
25 °C
< 1ppm CO_2

After 24 h, prior to drying



TOF-SIMS composite map after N_2 drying

Chemistry Distribution after Exposure

TOF-SIMS

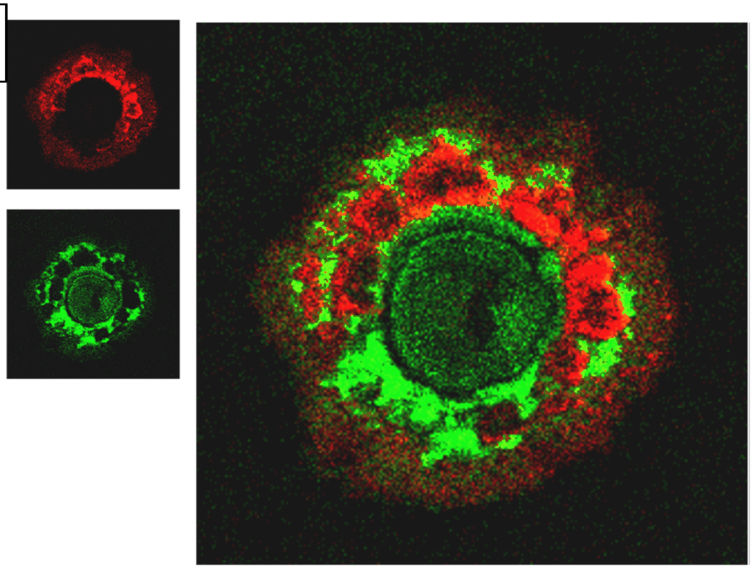
NaOH

NaO_2H_2

NaCl

Na_2Cl

2.5 x 2.4 mm²



collocation of NaCl and NaOH is minimal

red indicates cathodic activity

$O_2 + 2H_2O + 4e^- = 4\ OH^-$

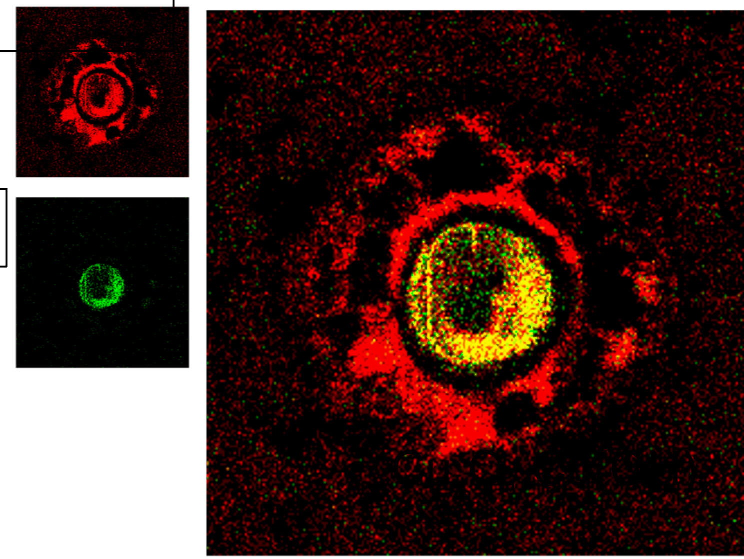
Cu_xO, $Cu(OH)_x$, CuOHCl

CuOHCl

$CuCl_x$

$Cu_2Cl_3^-$

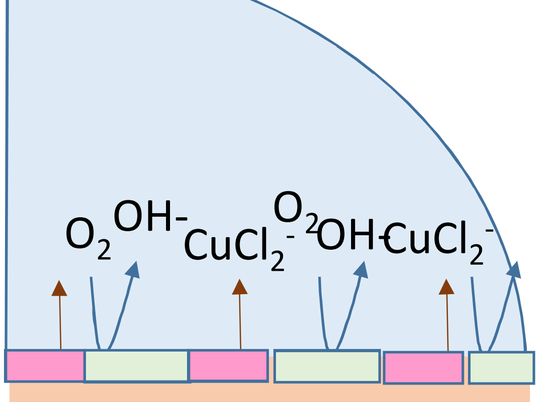
2.5 x 2.4 mm²



Copper chlorides concentrated in drop, lacking in spreading zone

Electrolyte and Damage Evolution

Initiation



pH 2-10

$$O_2 + 2H_2O + 4Cu + 8Cl^- = 4CuCl_2^- + 4OH^-$$

$4Cu + 8Cl^- = 4CuCl_2^- + 4e^-$ *Tromans, 1991,1992

$O_2 + 2H_2O + 4e^- = 4OH^-$

pH 12,13

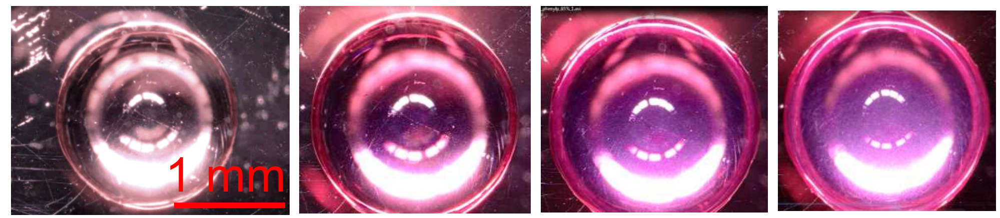
$$4CuCl_2^- + 6H_2O + O_2 + 4OH^- = 4Cu(OH)_2 + 8Cl^-$$

$4CuCl_2^- + 2H_2O = 2Cu_2O + 4H^+ + 8Cl^-$

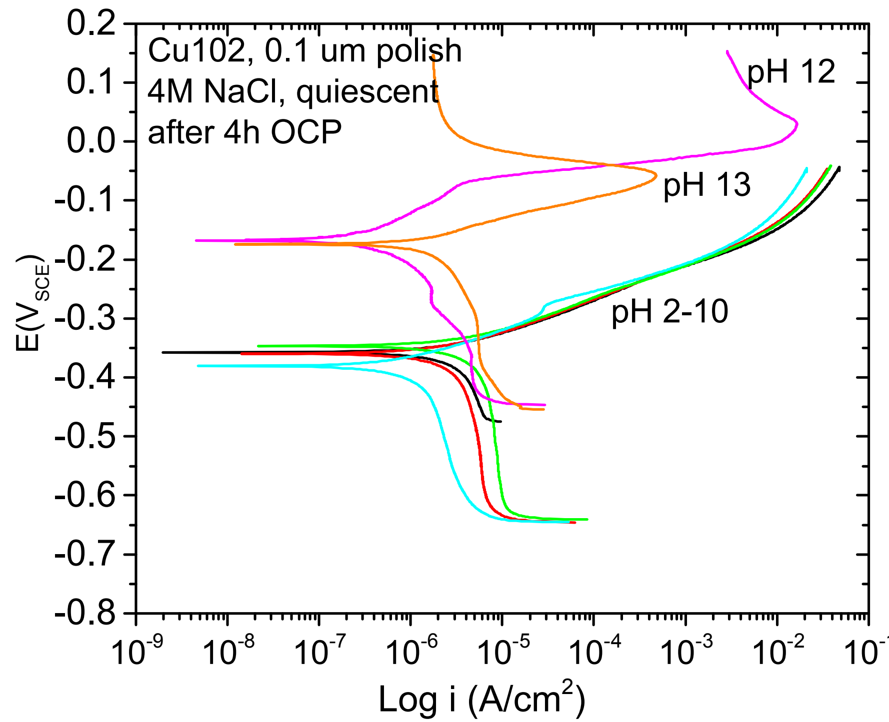
$2Cu_2O + 4OH^- + 2H_2O = 4Cu(OH)_2 + 4e^-$

$O_2 + 2H_2O + 4e^- = 4OH^-$

pH 6 | pH > 8 | pH ≥ 10



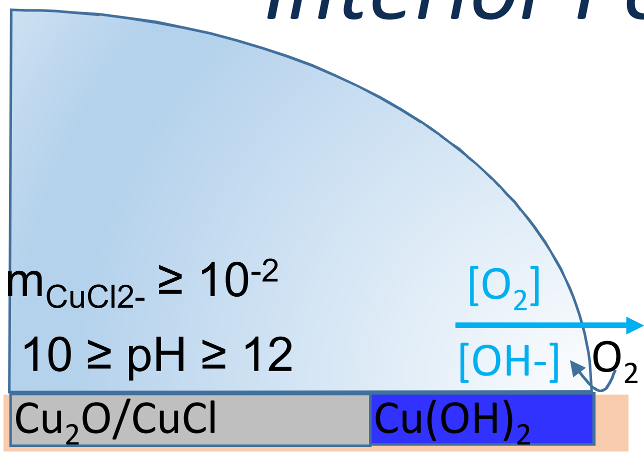
20s | 2 min | 7 min | ≥ 30 min

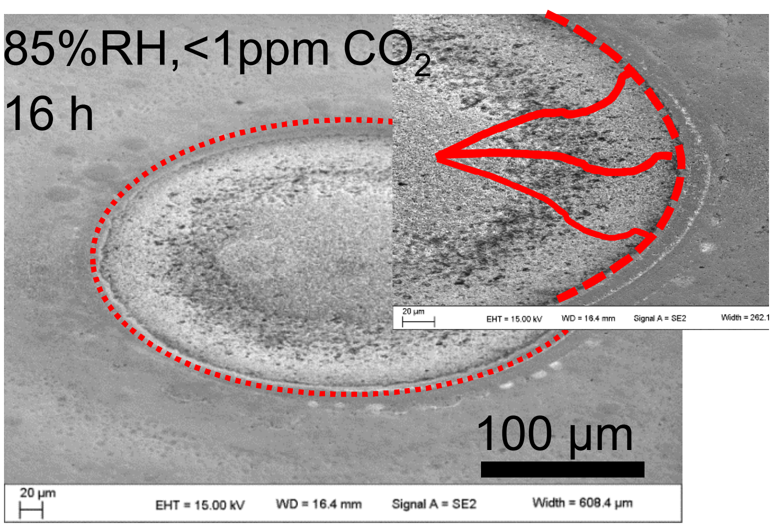


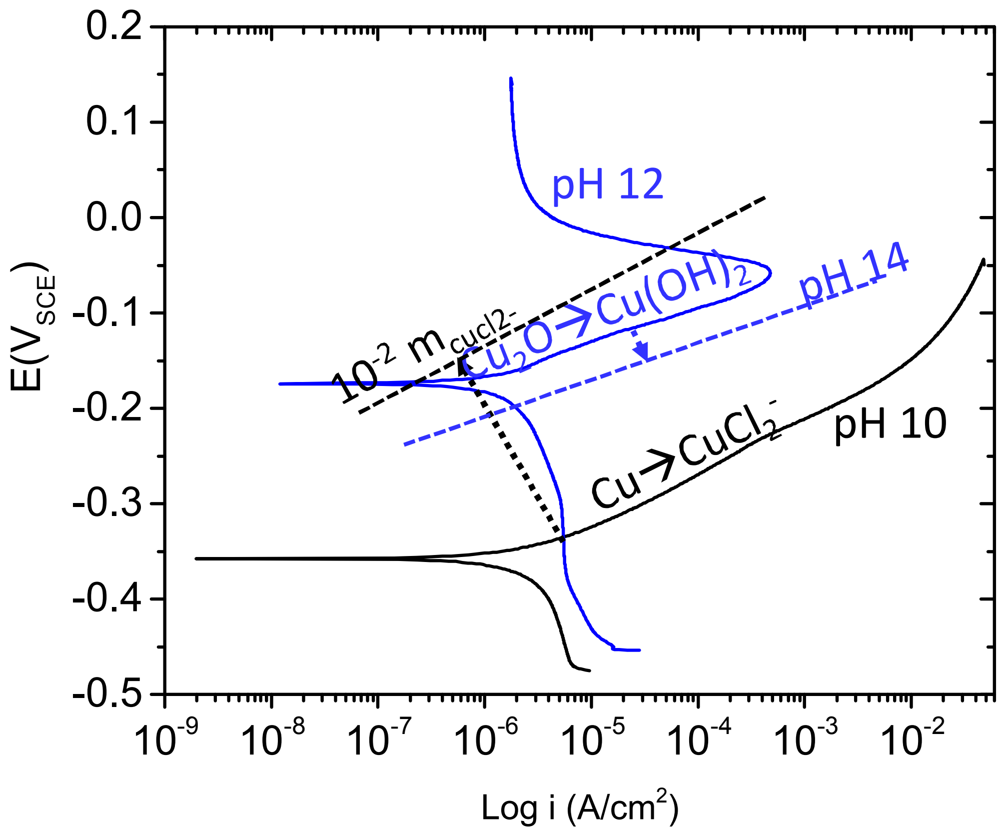
pH likely buffered by $CuCl_2^- \leftrightarrow Cu_2O \leftrightarrow Cu(OH)_2$

Electrolyte and Damage Evolution

Interior Perimeter Trenching



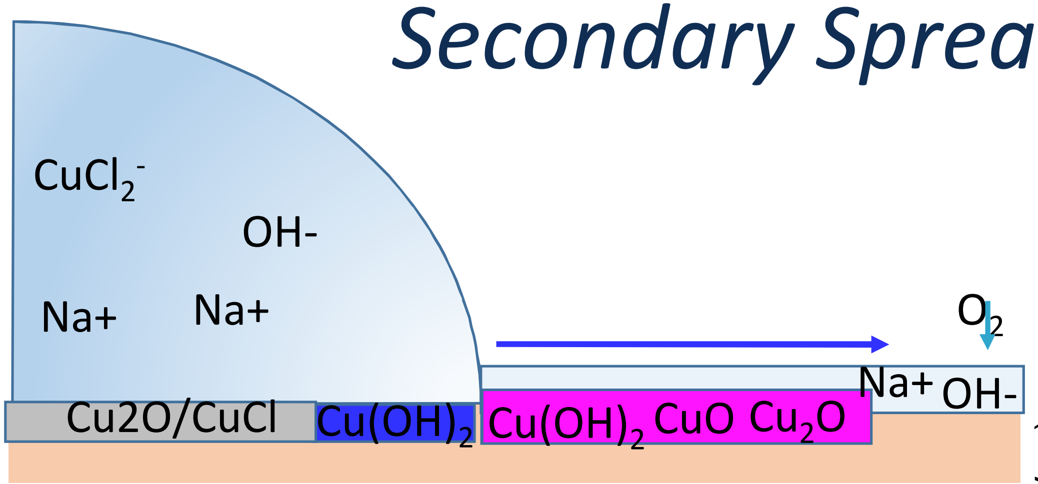


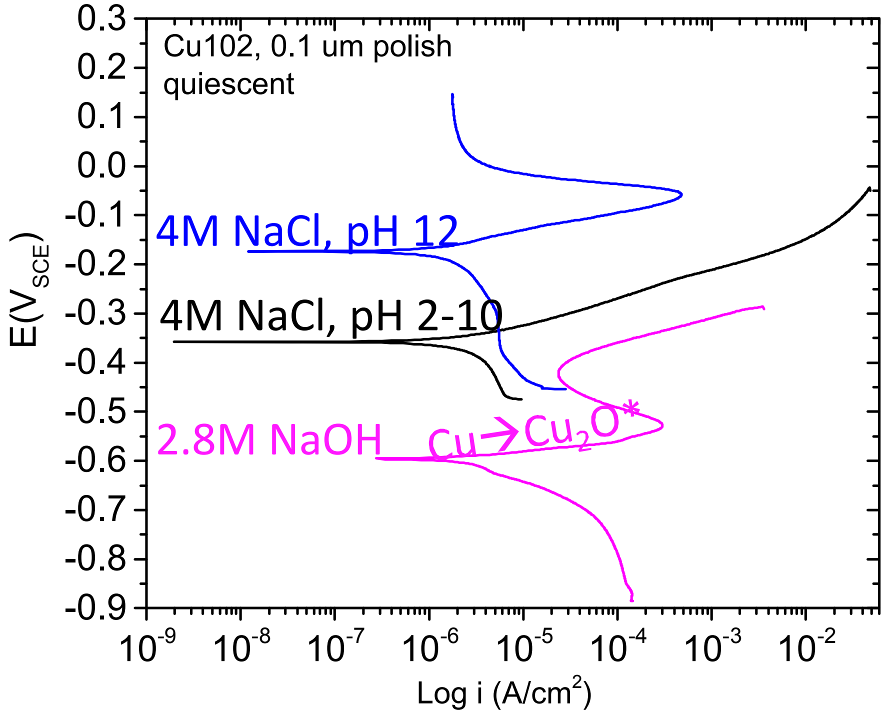


$[O_2]$ gradient may cause trenching near drop edge

Electrolyte and Damage Evolution

Secondary Spreading





*Biton *et al.*, 2006

Trenching in spreading film region due to Cu→Cu_2O, $Cu(OH)_2$

0D Reactor Network Model for Evolving Electrolyte

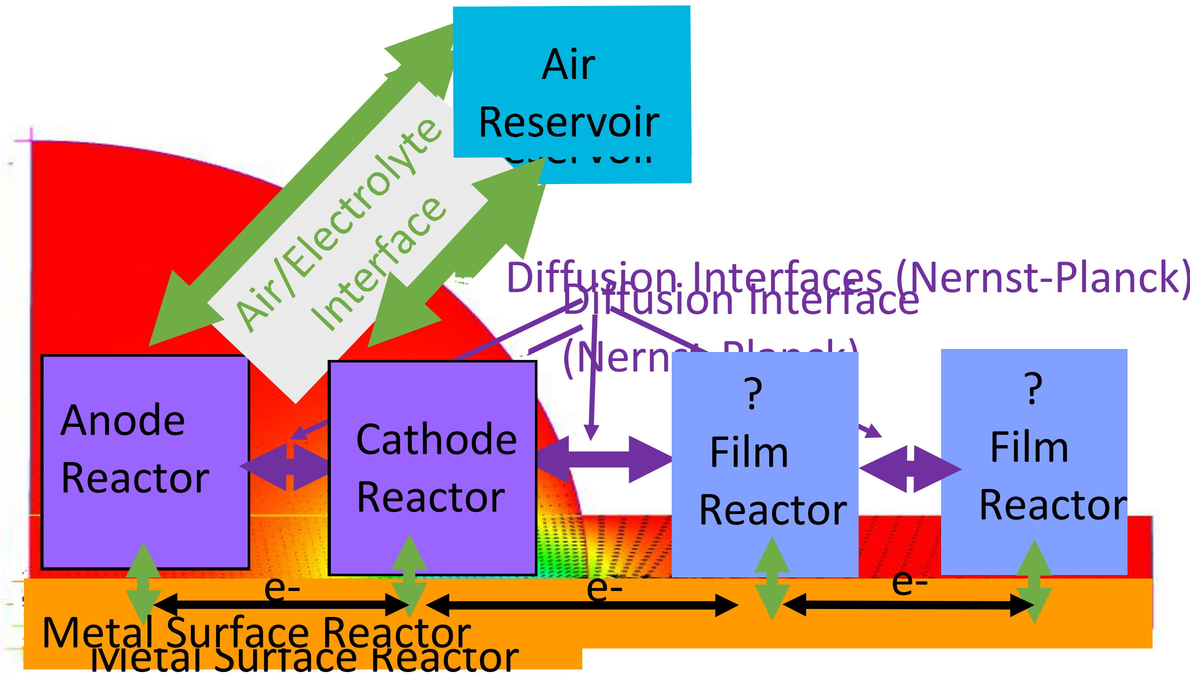
Sandia National Laboratories

Cantera/Zuzax

Non-Ideal Solution Thermodynamics, Electro/Chemical Kinetics, Transport

Reactors

- Pitzer non-ideal thermo.
- Mass balances: homogenous and interfacial chemistry, and diffusion interfaces
- Precipitation of salts, oxides
- Potential



Interfaces

- Air-Brine Equilibrium
- Diffusion between reactors
- Redox Reactions-charge transfer

0D Reactor Network Model

$$\frac{d\left(\Xi_{R,k}\right)}{dt} = V_R \dot{W}_k + \sum_I A_{R,I} \dot{S}_{R,I,k} + \sum_D A_{R,D} \dot{N}_{R,D,k}$$

$\Xi_{R,k}$ = Total moles of species k in Reactor R (multiple phases allowed)

$\dot{S}_{R,I,k}$ = Source term for species k in Reactor R due to Interface I

$\dot{W}_{R,k}$ = Source term for species k in Reactor R due to homogeneous and hetergenous Rxns

$\dot{N}_{R,D,k}$ = Source term for species k in Reactor R due to diffusional interface D

$$\dot{N}_{R,D,k}\left(L\right) = -D_k C_T \frac{\Delta X_k}{L} + D_k C_k z_k \frac{F}{RT} \frac{\Delta \phi_R}{L}$$

Electric Potential for brine in each Reactor solved via an Algebraic Constraint:

$$0 = \sum_k z_k \left(\sum_I A_{R,I} \dot{S}_{R,I,k} + \sum_D A_{R,D} \dot{N}_{R,D,k} \right)$$

0D Reactor Network Model of Evolving System

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Homogenous Species included in Brine (Moffat, Jove-Colon 2009)

H2O(L), Cl-, H+, Na+, OH-, Cu++, ClO4-, Cu+, CuOH+, CuCl+, CuO(aq), CuCl(aq), CuCl2-, CuCl2(aq), HCuO2-, CuCl3, CuCl3--, Cu(OH)2-, Cu(OH)(aq), CuO2--, O2(aq)

Solid Species included in Precipitation Mechanism

Cu2O(S) Cu(OH)2 (s)

Charge Transfer Reactions (B-V kinetics)

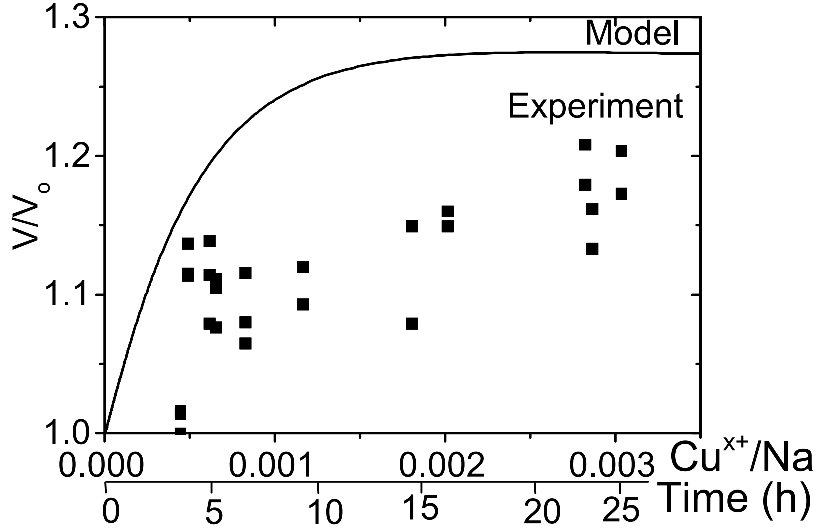
$$0.5\,\mathrm{O}_2 + \mathrm{H}_2\mathrm{O(L)} + 2e^- \rightleftarrows 2\mathrm{OH}-$$

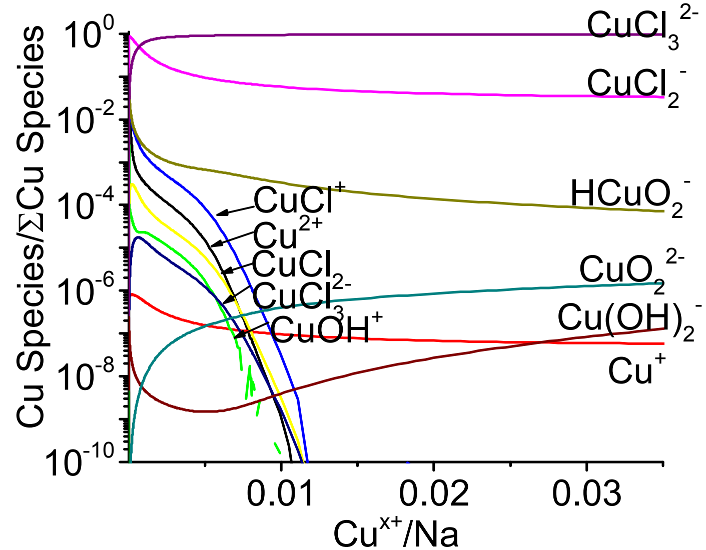
$$0.5\,\mathrm{Cu(S)} \rightleftarrows \mathrm{Cu}^{++} + 2e^-$$

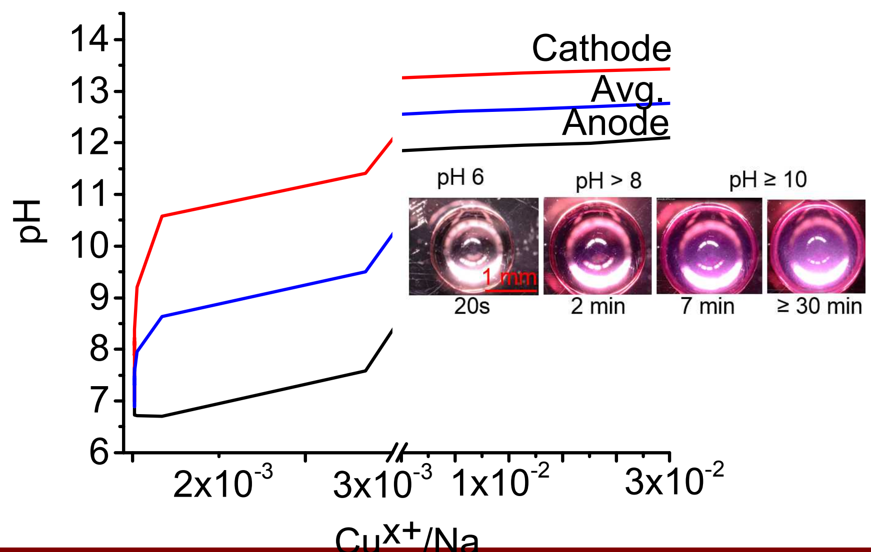
$$\mathrm{Cu(S)} + 2\mathrm{Cl}\text{-} \rightleftarrows \mathrm{CuCl}_2^- + e^-$$

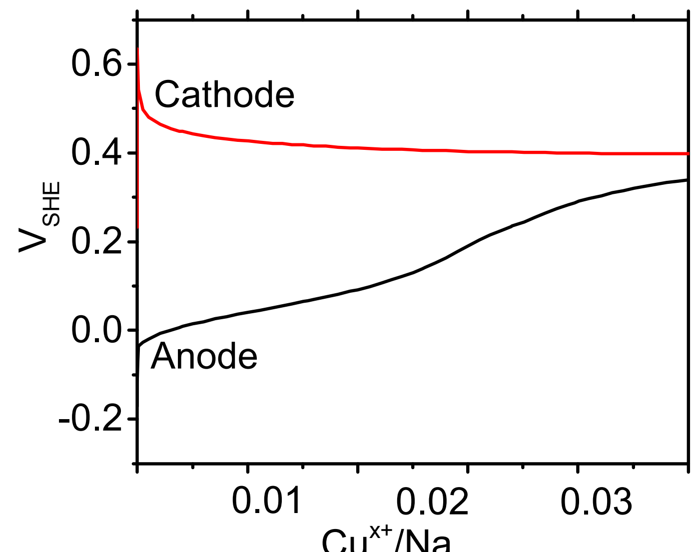
$$2\mathrm{Cu(S)} + \mathrm{H}_2\mathrm{O} \rightleftarrows \mathrm{Cu}_2\mathrm{O(S)} + 2\mathrm{H}^+ + 2e^-$$

0D Reactor Network Model of Droplet: Proof of Concept









Summary: Cu-NaCl in humid zero air

- Greatest damage occurred external to original droplet geometry – secondary spreading zones not strictly a cathode – evolution must be considered
- Hypothetical process proposed via mixed potential theory in analogous bulk electrolyte solution- preferential, high pH anodic dissolution
- Computational approach being developed to capture chemophysical electrolyte evolution and impact on electrochemical processes.
- How does anode-cathode distribution evolve and how does it relate to spreading and chemistry distribution?
- How does behavior vary with environmental parameters (salt load, RH, CO_2, etc.)?

Corrosion Processes and a *Dynamic* Surface Environment

How do saline electrolytes evolve once corrosion initiates in humid environments?

What is the interplay between electrolyte dynamics and corrosion damage distributions and rates?

Studies under highly simplified conditions:

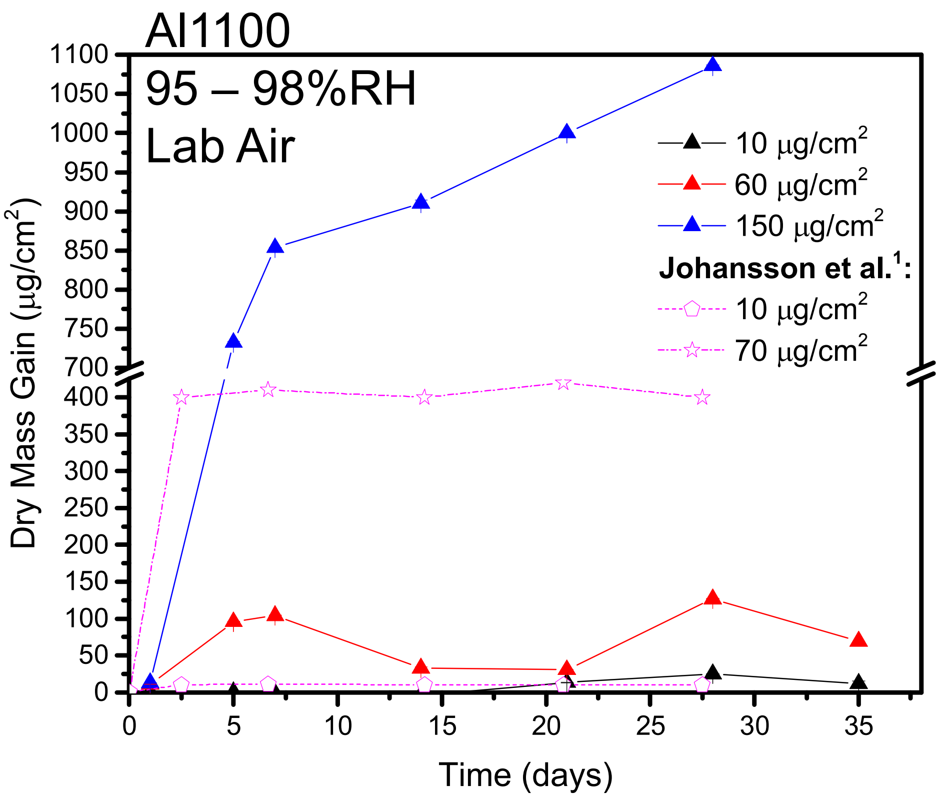
(1) NaCl droplets on Cu: role of alkaline films and computationally capturing the evolving system

(2) NaCl on 1100 Al: relationship between salt loading and damage extent

Influence of NaCl Loading on Aluminum

Can we predict a maximum effective extent of corrosion based on initial salt loading?

- Laboratory exposures:
  - Extent of corrosion increases with increasing NaCl loading
  - "Stifling" or bendover in rate occurs at lower loadings
  - Johnsson et. al (2005) attribute to CO_2
    - pH buffering of electrolyte

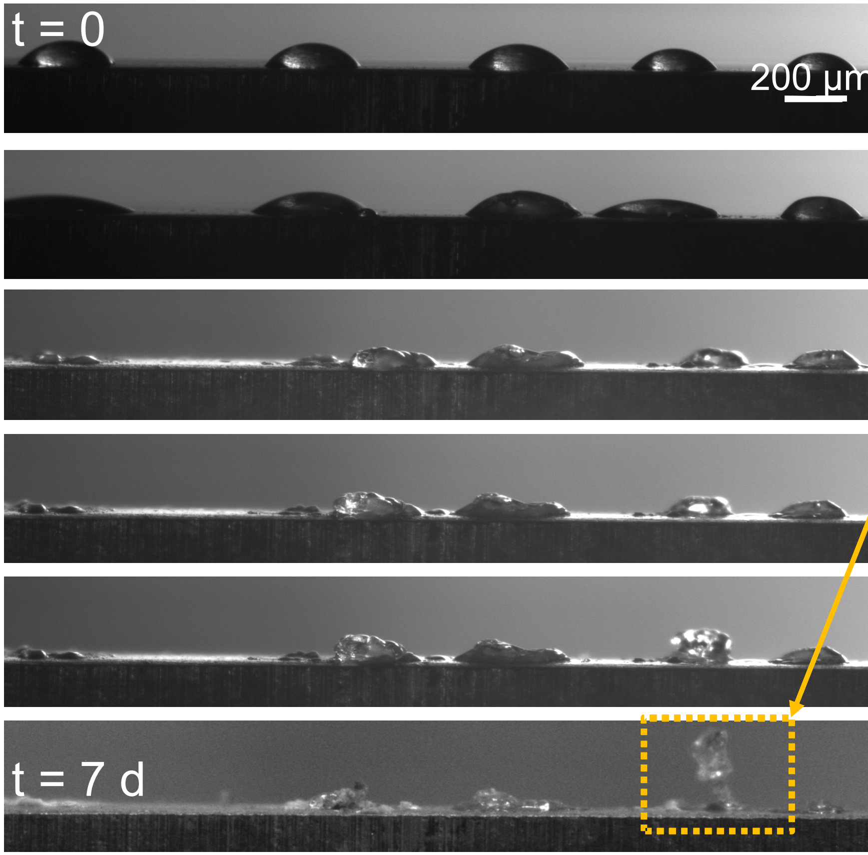


What is causing apparent "stifling" at relatively short times?

Hypothesis: gettering of NaCl by corrosion product

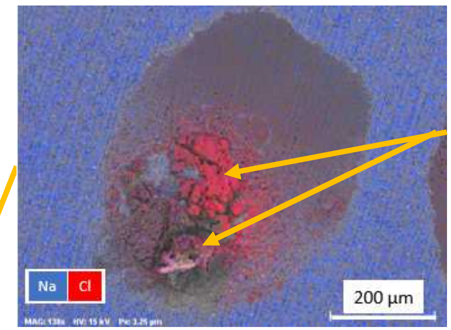
Bend over in corrosion rate ~ drying

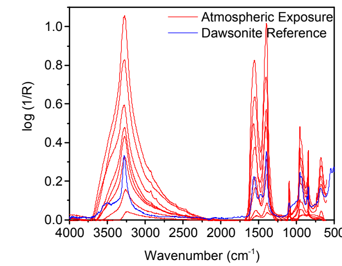
98 %RH, 298K, Lab Air



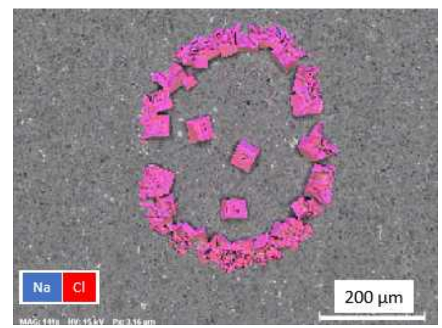
Electrolyte volume dramatically shrinks and replaced by gel-like solid within days

***Ex-situ* surface analysis**



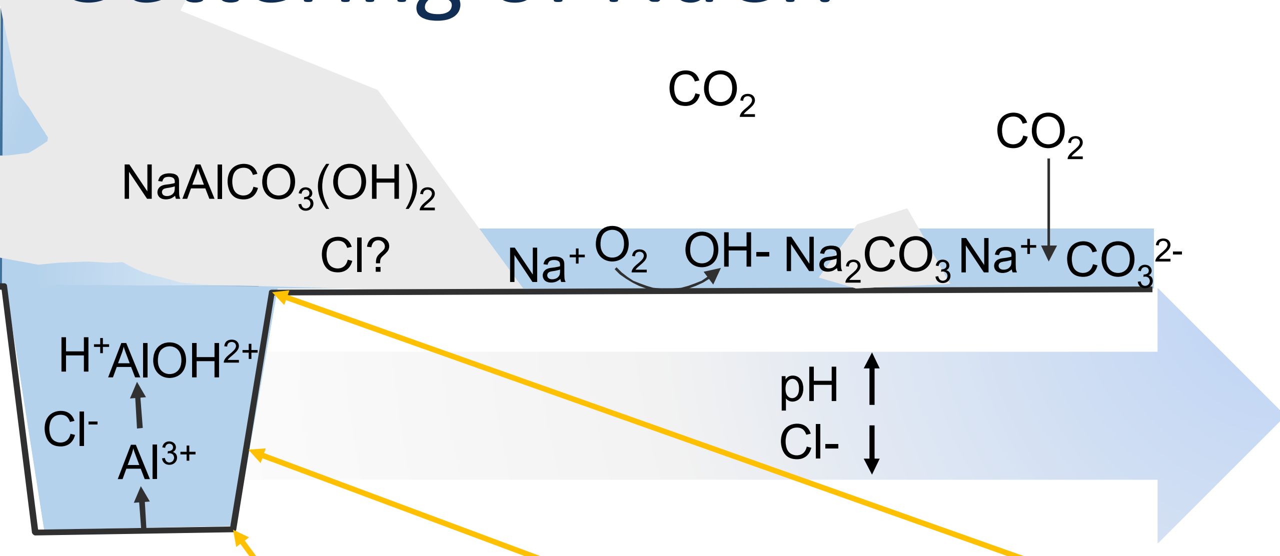


$NaAl(OH)_2CO_3$

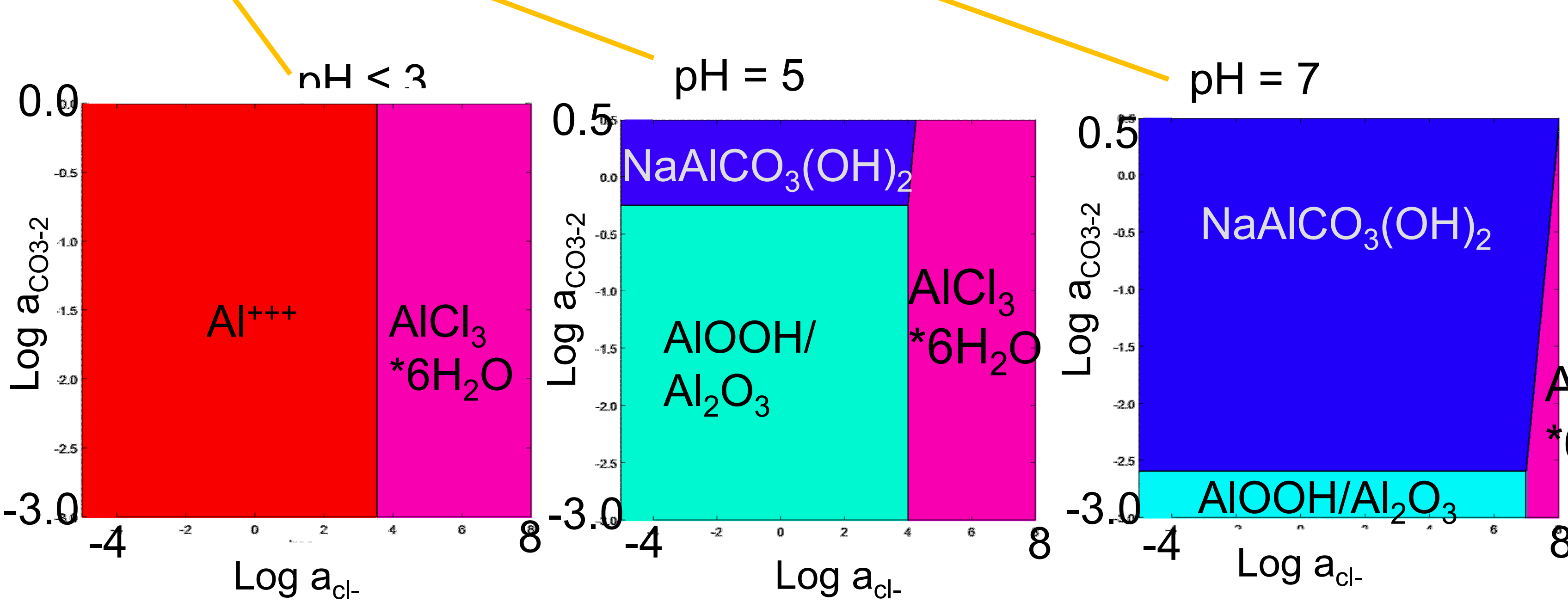


droplet dried immediately after deposition

Gettering of NaCl?



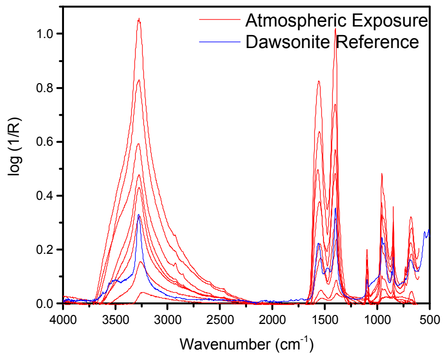
State of Cl
in this system?



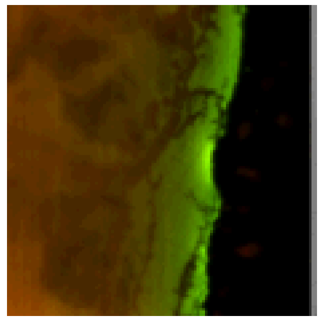
Summary: Al-NaCl in humid air

- "Stifling of corrosion correlated with considerable electrolyte volume loss and growth of corrosion products
- Only detectable corrosion product was $NaAlCO_3(OH)_2$, a low solubility compound able to getter Na
- The presence of NaCl crystals, to varying degrees, after all exposures suggests that either exposure times were insufficient to consume all Na or that it is mobile to some extent
- The state of Cl in the system – free versus bound has not been established
- Phase field thermodynamic modeling and in-situ correlation of corrosion rate to electrolyte chemistry and corrosion products under way.

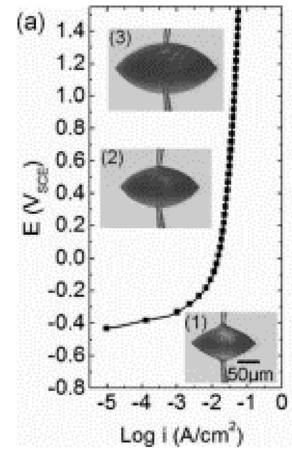
Multiresolution, in-situ chemical/electrochemical approaches



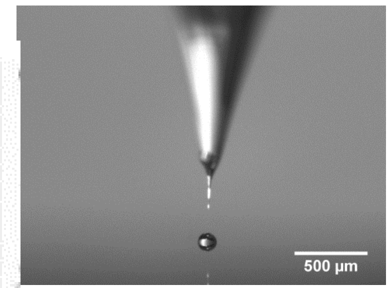
in-situ Raman



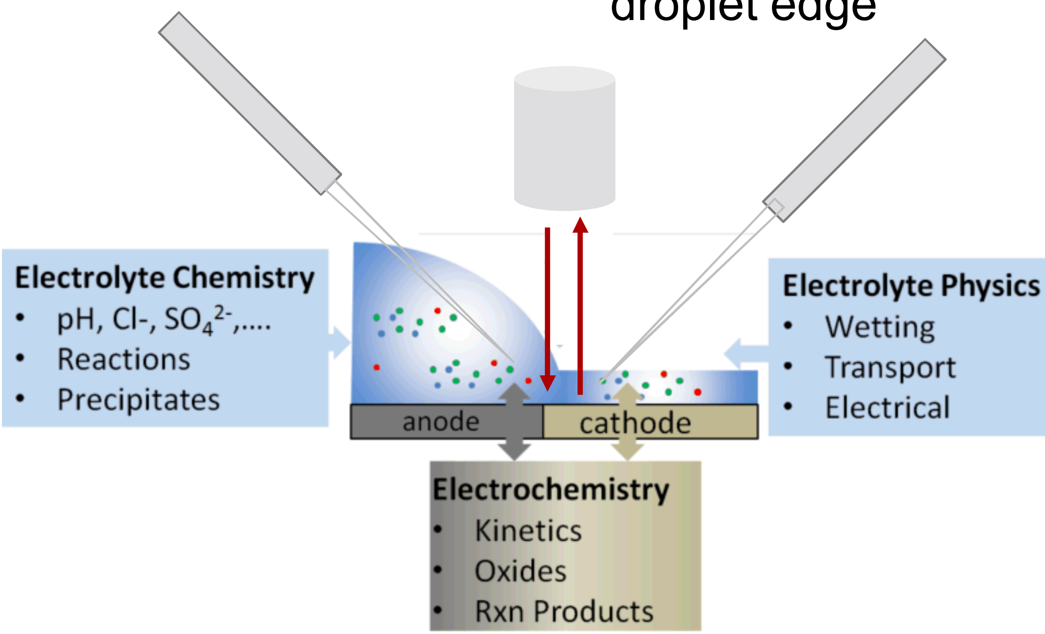
fluorescent pH marker droplet edge

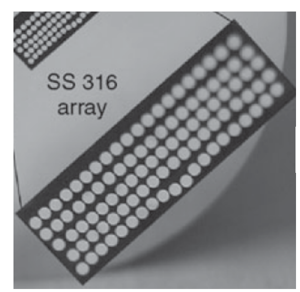


Li, 2012

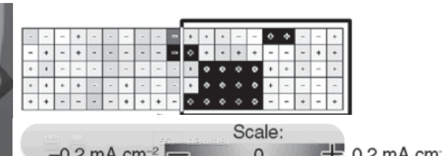


capillary electrochemical probing



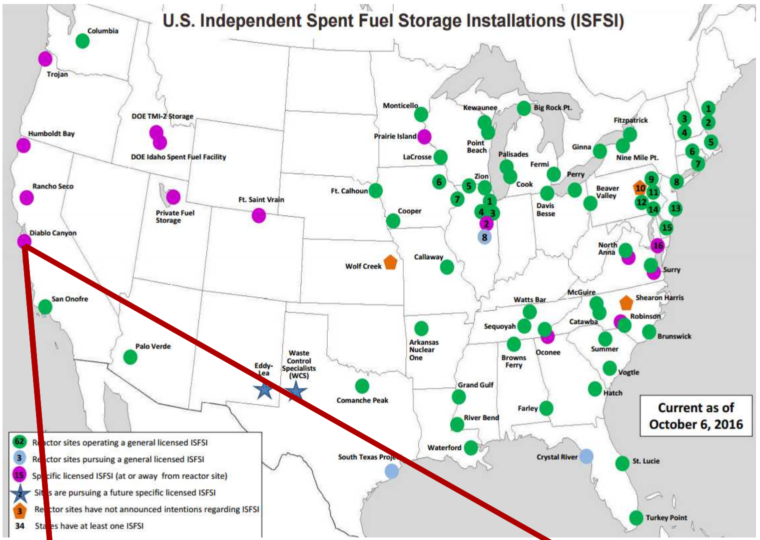


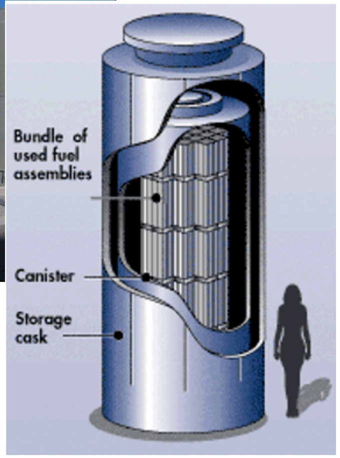
Budiansky, 2007



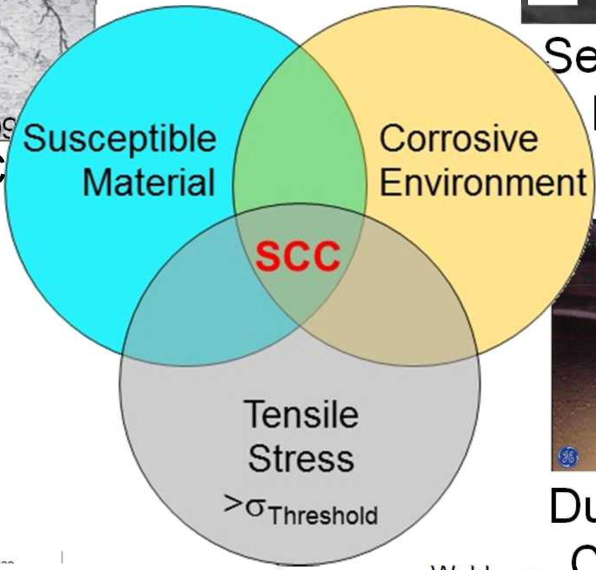
Spatially resolved kinetics via multielectrode array

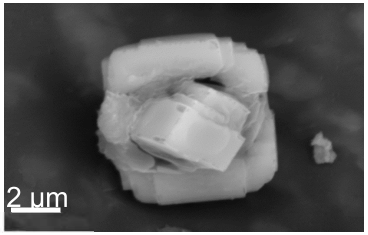
Interim Spent Fuel Dry Storage Containers



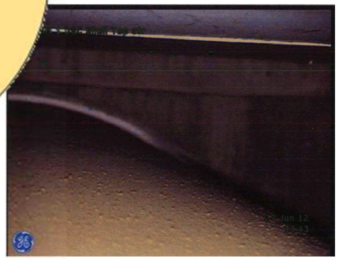


Prosek, 2009
304 SCC

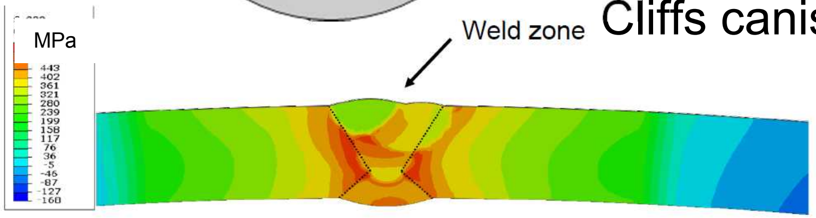




Sea-salt particle
Diablo Canyon canister



Dust on Calvert Cliffs canister



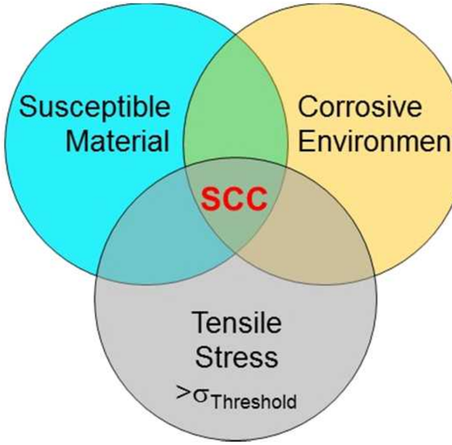
NRC, 2013

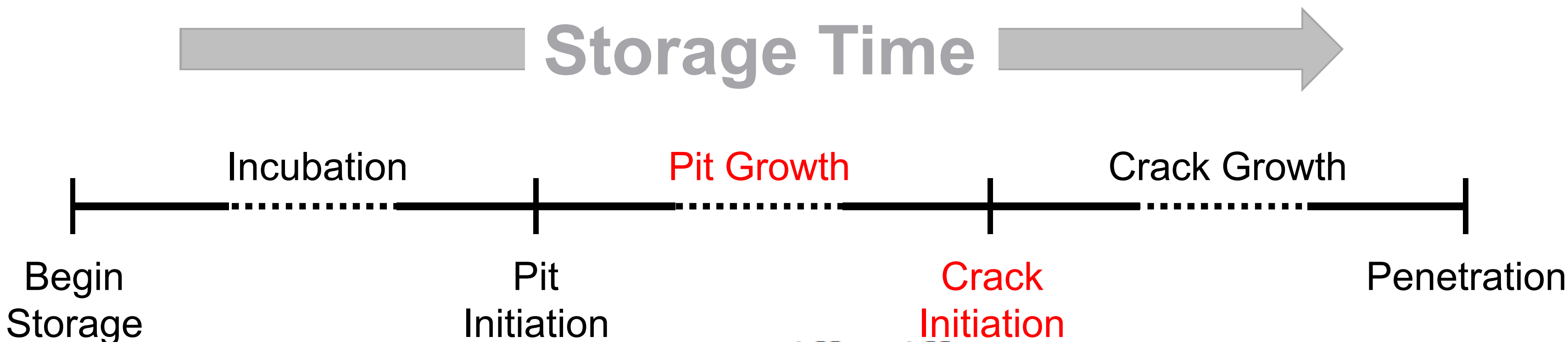
Addressing the Risk of SCC

What is risk and when and where should we inspect?

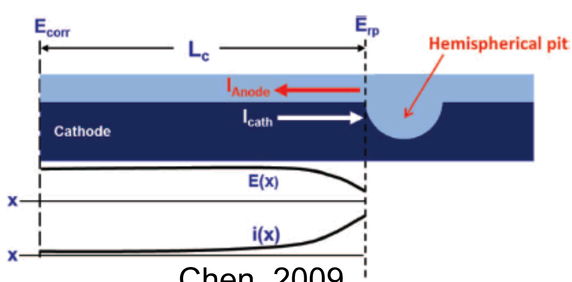
statistical and deterministic approaches –relevant conditions

What are the relevant and accessible limits of pitting and SCC models relative to canister conditions and timescale?

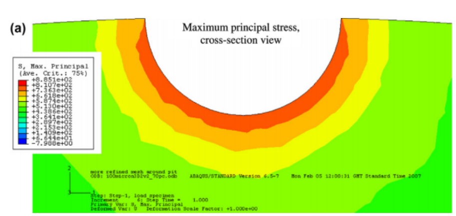




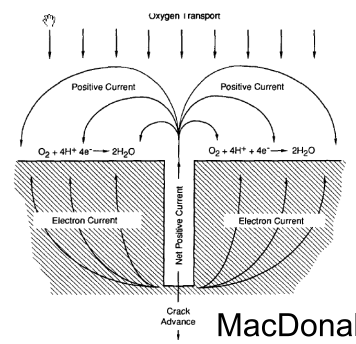
$\Delta K \geq \Delta K_{th}$



Chen, 2009



Horner, 2011



MacDonald, 1991

Maximum Pit Size Model : Environment

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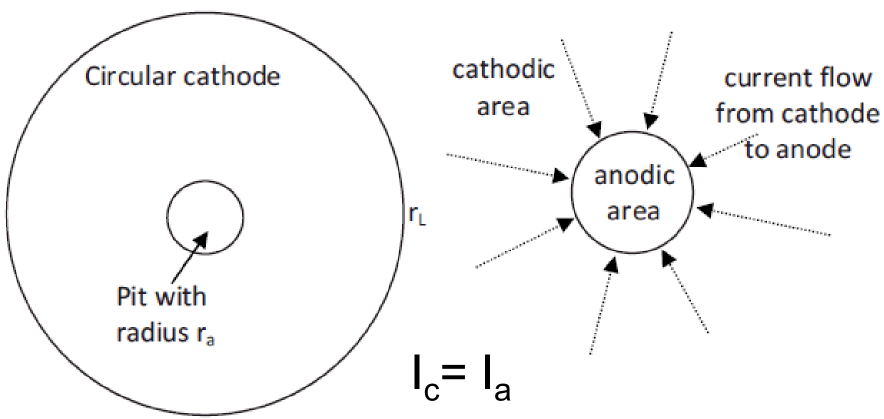
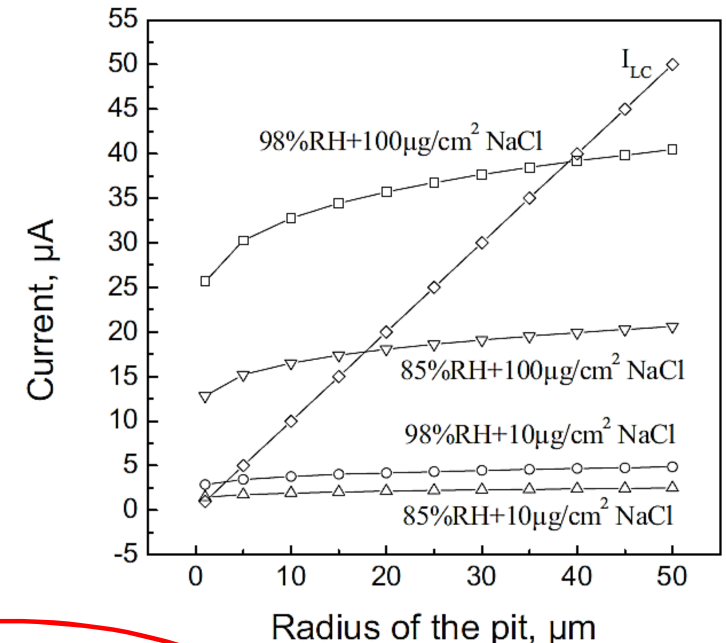
Chen and Kelly (2010): Max pit size is a function of the maximum cathode current, in turn a function of brine film properties.





Max. cathode current

Brine conductivity

Brine layer thickness

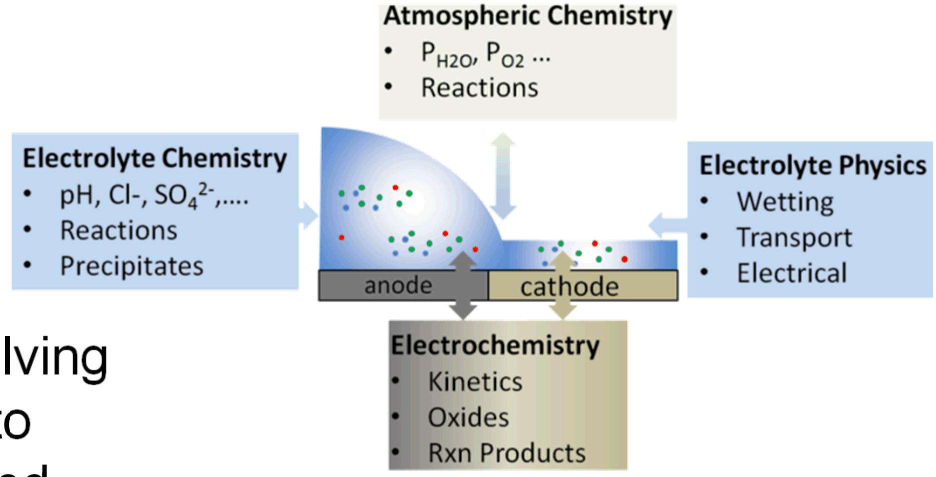
$$\ln I_{c,max} = \frac{4\pi k W_L \Delta E_{max}}{I_{c,max}} + ln\left[\frac{\pi e r_a^2 \int_{E_{corr}}^{E_{rp}} (I_c - I_p)\, dE}{\Delta E_{max}}\right]$$

Cathodic kinetics

How does surface chemistry evolve and what is impact to electrochemical kinetics?

Summary and Conclusions

Electrolyte can rapidly evolve in finite volumes, with considerable impact on damage distributions and rates

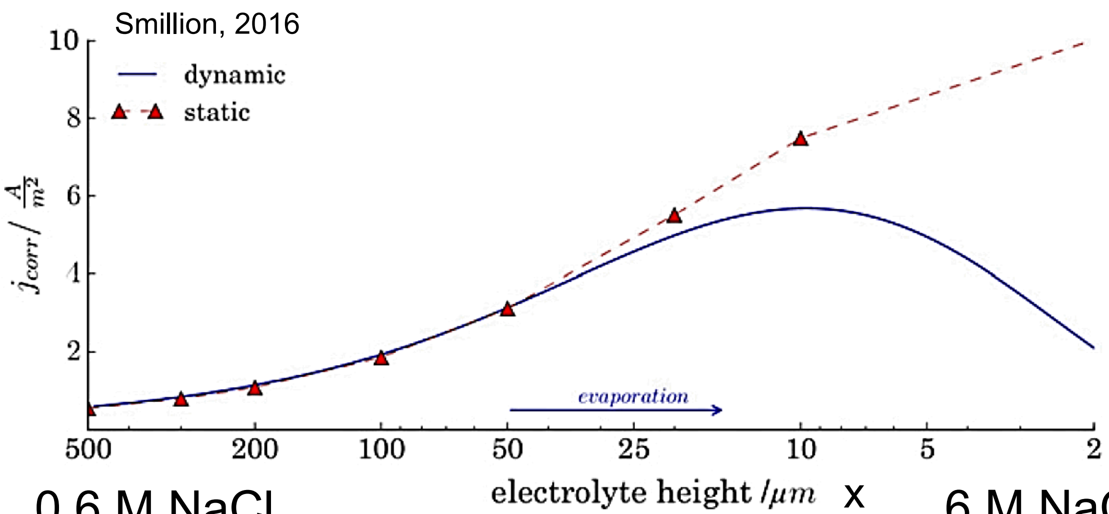


Need for more detailed definition of evolving surface environments and relationship to electrochemical processes- move beyond bulk solution assumptions

Need for computational and experimental tools and approaches aimed at surface environment-electrochemical linkage

Extras

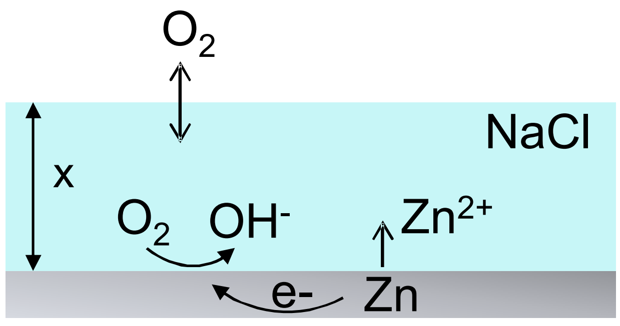
Corrosion Processes and a *Dynamic* Surface Environment: Evaporation



0.6 M NaCl
98% RH

Evaporation

6 M NaCl
76 % RH



$Zn = Zn^{2+} + 2e^-$

$O_2 + 2H_2O + 4e^- = 4\ OH^-$

$$i_L = zFD\frac{\partial C}{\partial x} = \frac{zFDC}{x}$$

Assumptions
fixed geometry (thin film)
fixed [species] (e.g., OH^-, Zn^{2+})
No homogenous,precipitation
fixed anodic kinetics

0D Reactor Network Model of Evolving System

Homogenous Species included in Brine (Moffat, Jove-Colon 2009)

H2O(L), Cl-, H+, Na+, OH-, Cu++, ClO4-, Cu+, CuOH+, CuCl+, CuO(aq), CuCl(aq), CuCl2-, CuCl2(aq), HCuO2-, CuCl3, CuCl3--, Cu(OH)2-, Cu(OH)(aq), CuO2--, O2(aq)

Solid Species included in Precipitation Mechanism

Cu2O(S) Cu(OH)2 (s)

Charge Transfer Reactions (B-V kinetics)

$$0.5\ \mathrm{O_2} + \mathrm{H_2O(L)} + 2e^- \rightleftarrows 2\mathrm{OH}-$$

$$0.5\ \mathrm{Cu(S)} \rightleftarrows \mathrm{Cu}^{++} + 2e^-$$

$$\mathrm{Cu(S)} + 2\mathrm{Cl}\text{-} \rightleftarrows \mathrm{CuCl}_2^- + e^-$$

$$2\mathrm{Cu(S)} + \mathrm{H_2O} \rightleftarrows \mathrm{Cu_2O(S)} + 2\mathrm{H}^+ + 2e^-$$

Description of Nucleation Modeling of Phases:

$\mathrm{A} + \mathrm{B} \rightleftharpoons [\mathrm{S}] + \mathrm{C}$

For nucleation of a solid, from the liquid phase, the following form leads to abrupt transitions in source terms

$$ROP = k_f a_f \left[\gamma_A \mathrm{c}_A\right]\left[\gamma_B \mathrm{c}_B\right] - k_r a_r \left[\mathrm{a}_s = 1\right]\left[\gamma_c \mathrm{c}_c\right]$$

We avoid the abrupt transitions by changing the effective area of the reverse reaction to linear in the total area

$$a_f \neq a_r \qquad a_r = a_f \min\left(\frac{\Xi_k^S}{\Xi_{cutoff}^S}, 1\right) \quad \text{where } \Xi_{cutoff}^S \text{ is small}$$

Description of Morphology of solid oxides and connectedness to Cu coupon

Short answer is that we cheat, because we have no idea. Passive layer models to be implemented later

Pourbaix Diagrams for system demonstrate the complexity of the phenomena

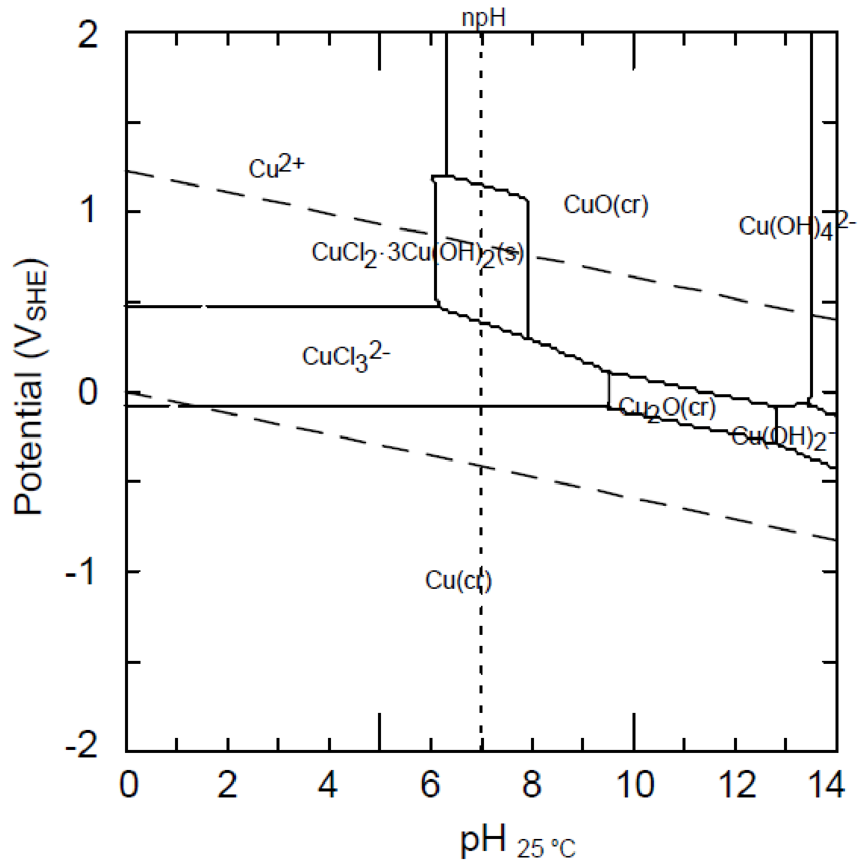


Figure 7B
Pourbaix diagram for copper species in the copper-chlorine-water system at 25 °C and $[Cu(aq)]_{tot} = 10^{-4}$ molal and $[Cl(aq)]_{tot} = 1.5$ molal.

(Puigdomenech, Taxen (2000))

SCC of Austenitic SS

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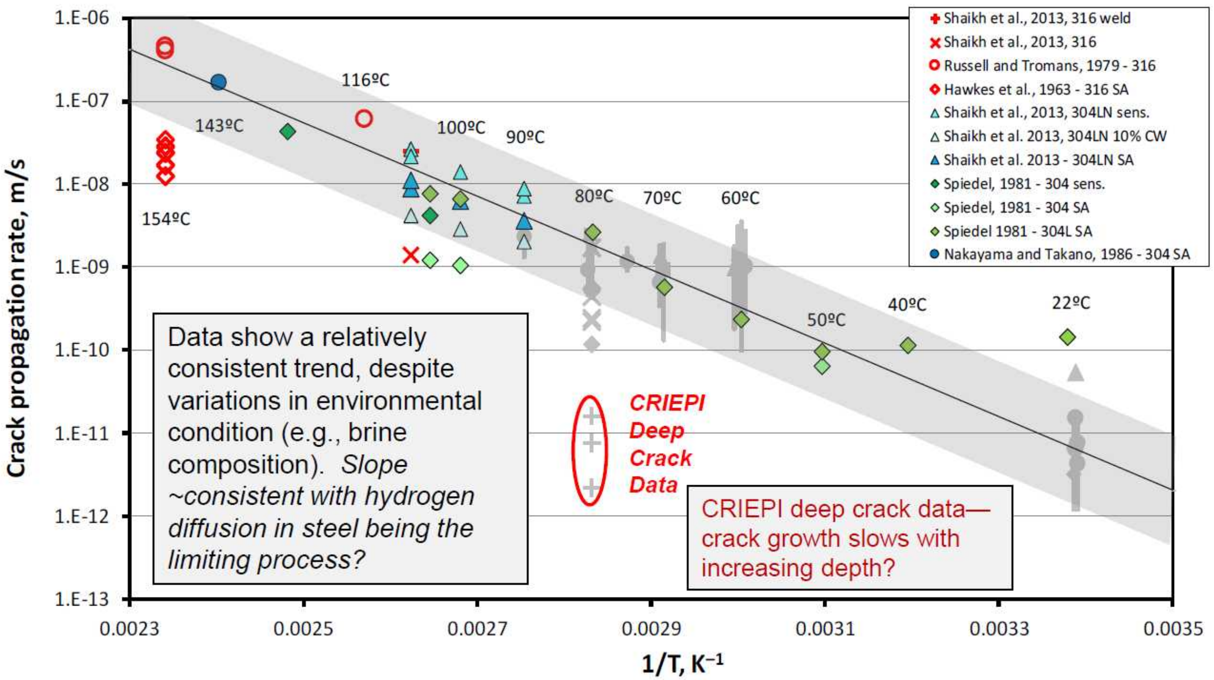

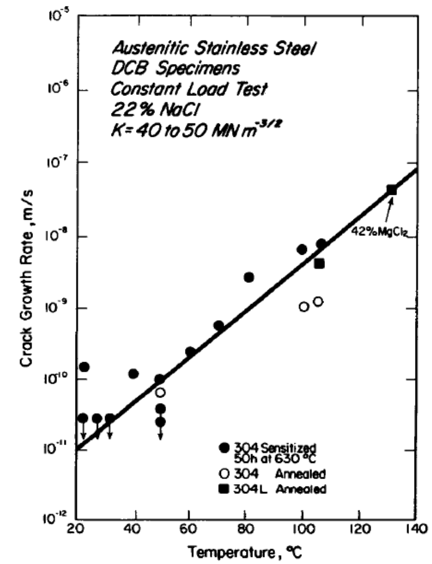

FIGURE 4 — Effect of temperature on SCC velocity for austenitic stainless steel in concentrated chloride solutions (Ref. 26).

28. S. Kaneko, A. Kurimoto, and S. Ooki. Boshoku Gijutsu, Vol. 29, p. 128 (1980).

$K_{IC} = \sigma_c\sqrt{\pi a}$

σ_c = crit. stress for crack prop.

a = crack length

How big of a crack must be present for KISCC vs. KIC given 500 Mpa?