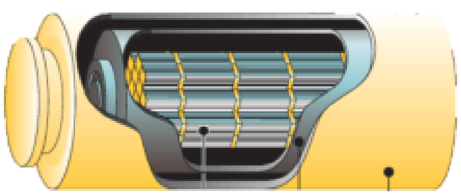
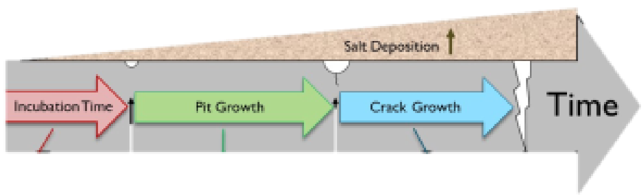
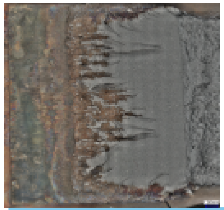
SAND2022-9203C

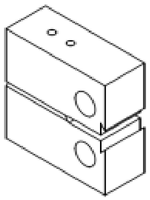
Sandia National Laboratories

Towards Understanding the Controlling Nature of Crack Tip Chemistry on the Stress Corrosion Cracking of Austenitic Stainless Steels









PRESENTED BY

Ryan M. Katona[1]

J. M. Taylor[1], E. K. Karasz[1], C. R. Bryan[1], R. G. Kelly[2], and R. F. Schaller[1]

[1]Sandia National Laboratories, Albuquerque, New Mexico 87123, USA

[2]University of Virginia, Charlottesville, Virginia 22904, USA

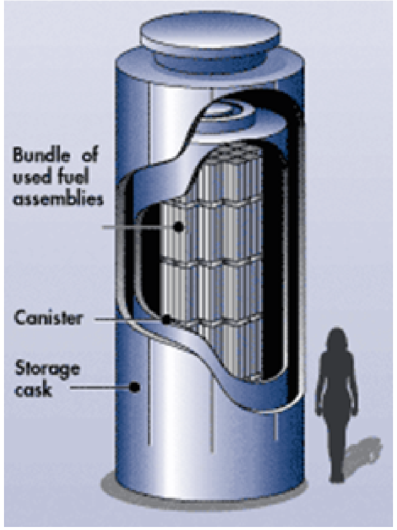
Gordon Research Seminar and Conference

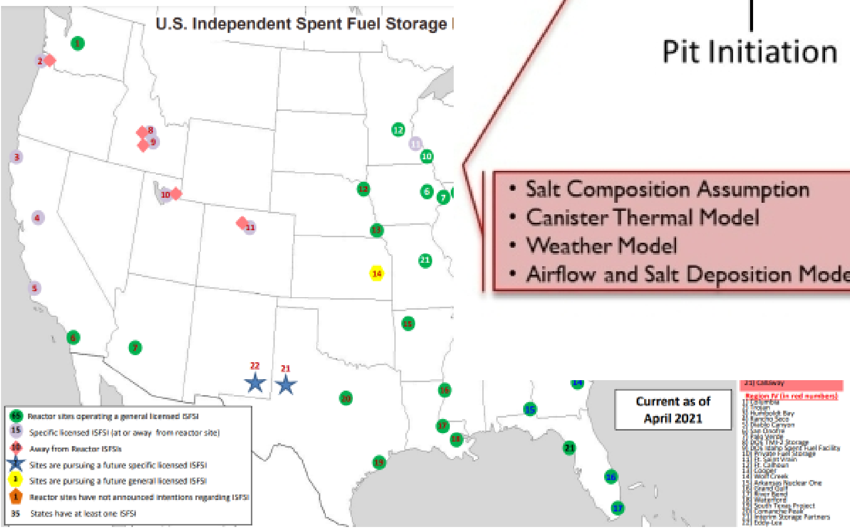
July 9-15th, 2022

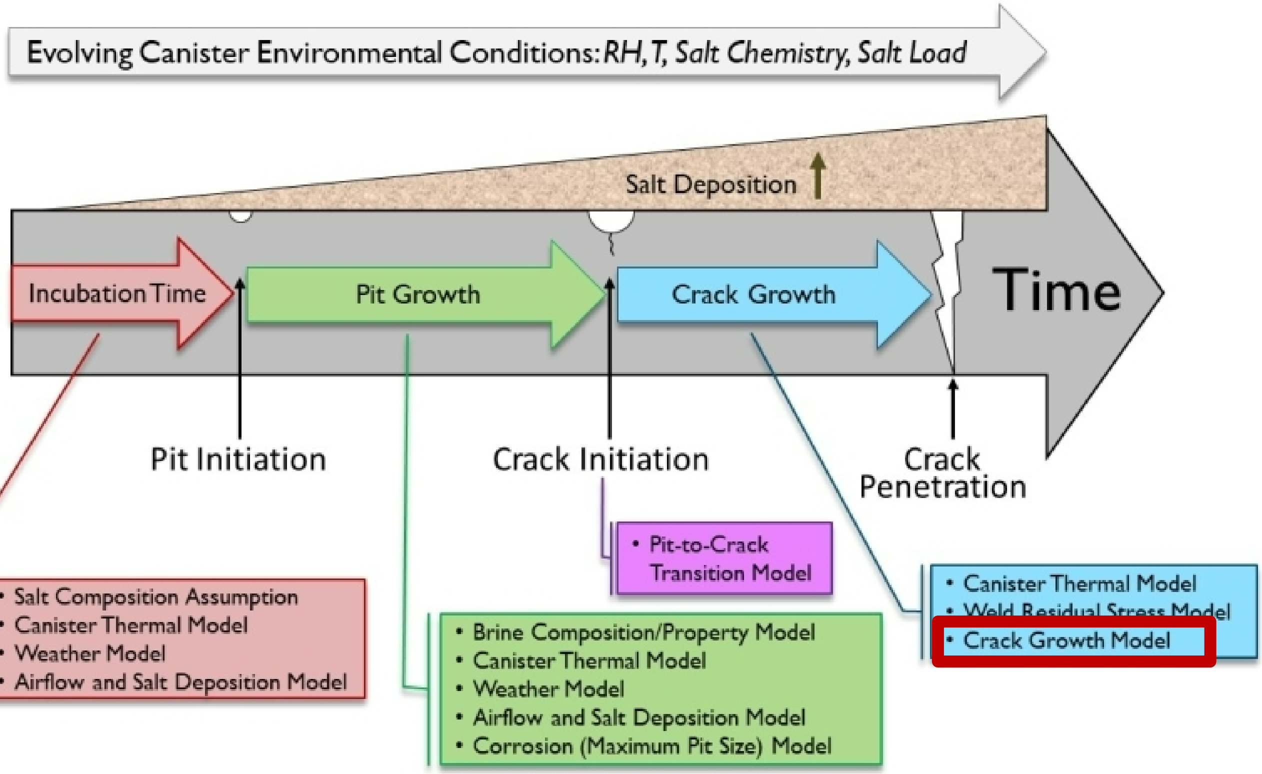
New London, NH, United States

Center 1800: Material, Physical and Chemical Sciences

Long Term Storage of Spent Nuclear Fuel in Austenitic Stainless Steels

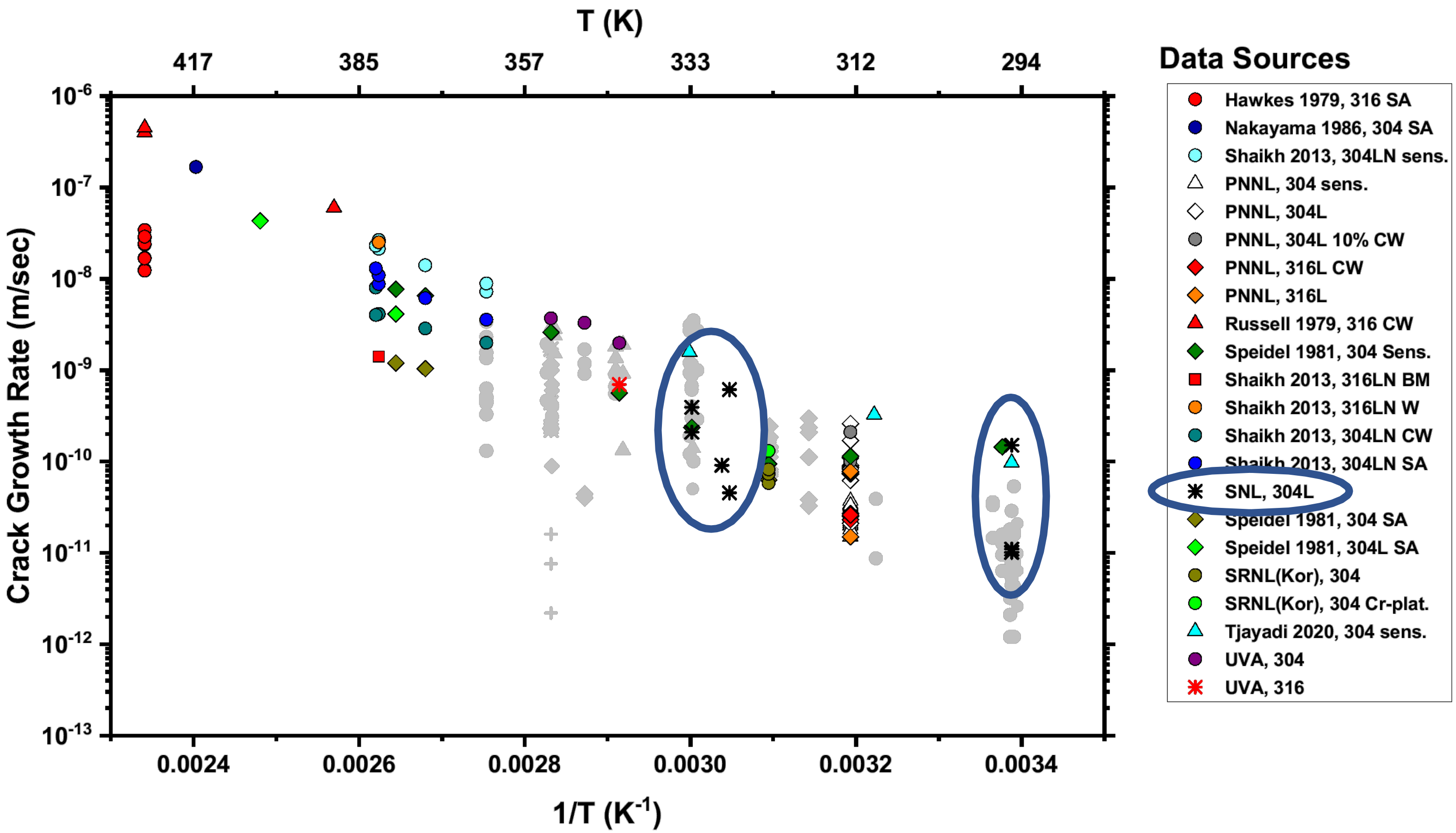






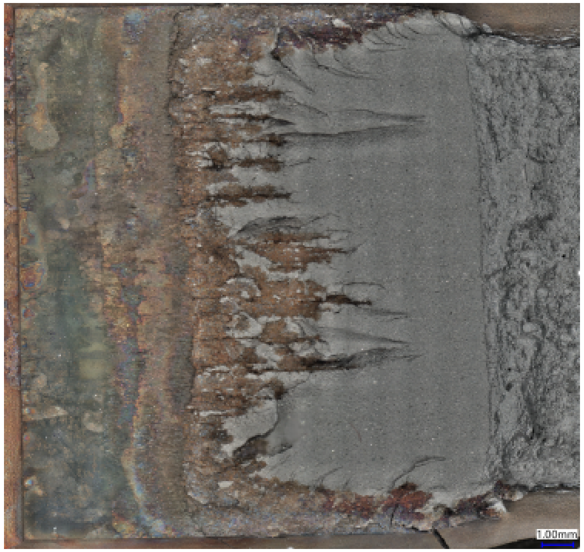
https://www.nrc.gov/docs/ML2111/ML21116A041.pdf

Arrhenius Temperature Dependence of Crack Growth for SS Alloys



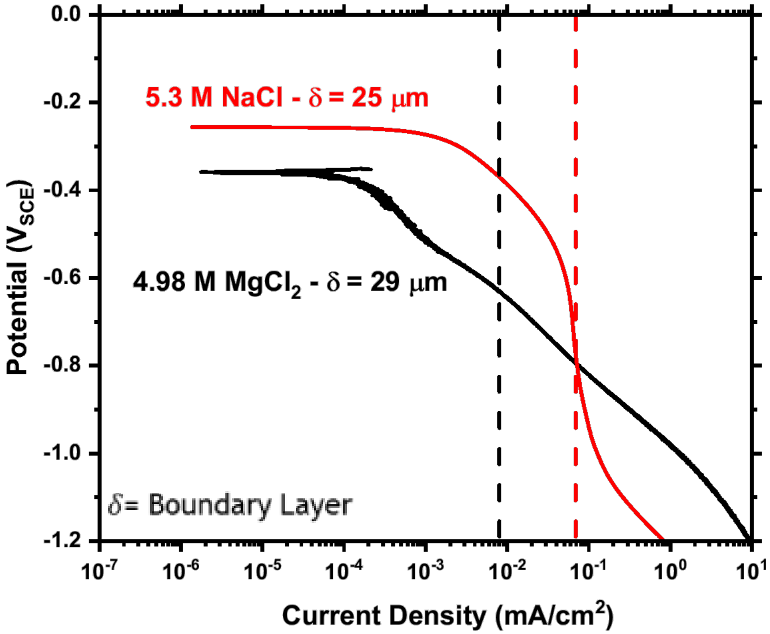
- Various collection methods, environments, material lots, sensitization state, etc.
- ***What are the governing factors and will certain factors accelerate growth?***

What Causes Different Morphology Between Solutions?



$MgCl_2$

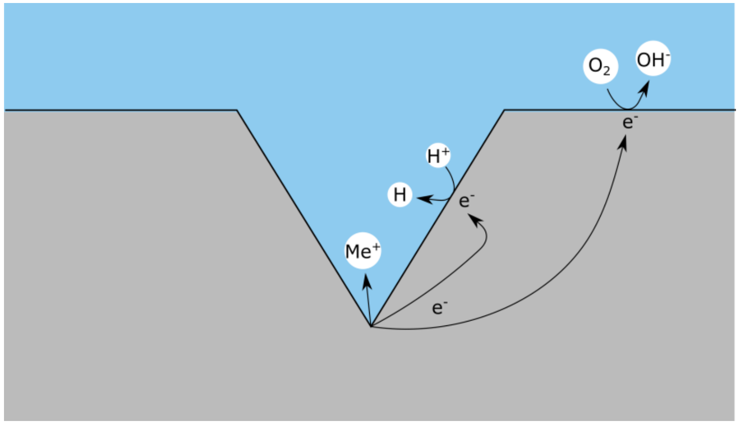
Lot 3 - 55 ˚C



NaCl

Lot 3 – 60 ˚C

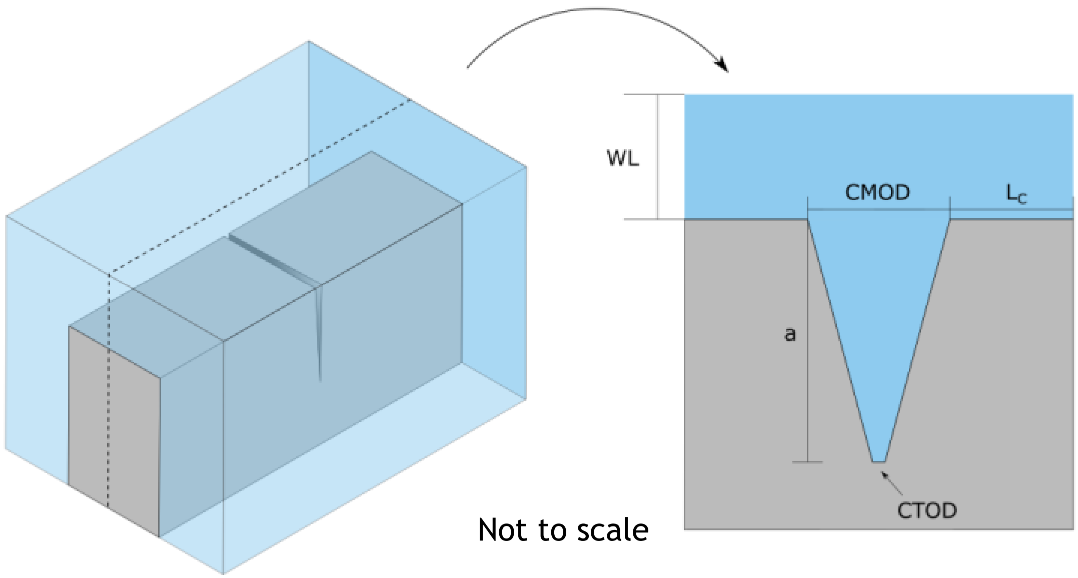
- Difference in cracking morphology as well as crack growth rates between NaCl and $MgCl_2$ solutions
- Potentially due to differences in cathodic reduction reaction
- Possibility for different crack tip chemistry changing pH and embrittlement

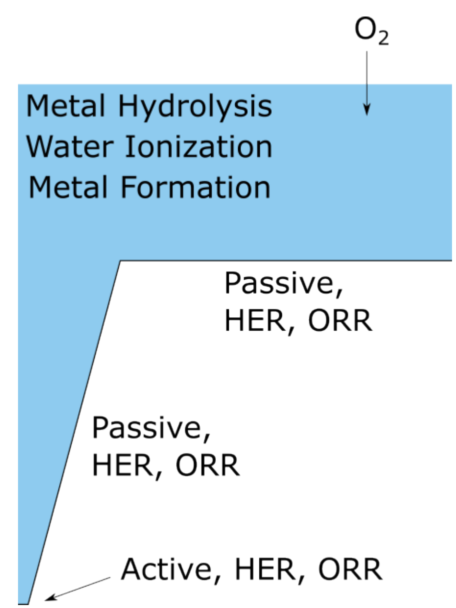


R.M. Katona et al., Journal of The Electrochemical Society, 168 (2021) 031512.
R.M. Katona et al., Corrosion Science, 177 (2020) 108935.

Proposed Finite Element Model

- Stress state and aggressive chemical/electrochemical conditions local to the crack tip control SCC



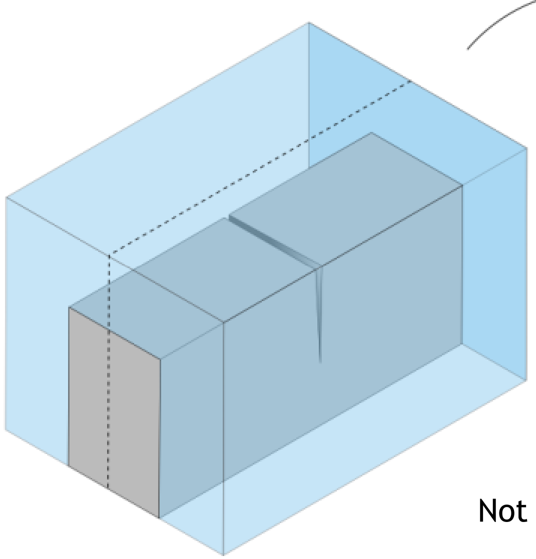


- Finite element reactive transport model looking for trends in electrochemical parameters (potential, current, chloride concentration, pH, etc.)

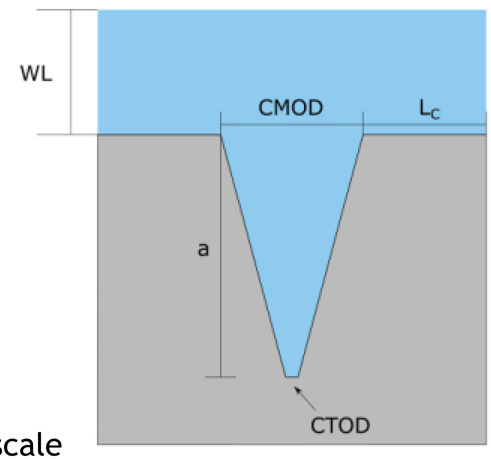
- Inferences about crack growth rates

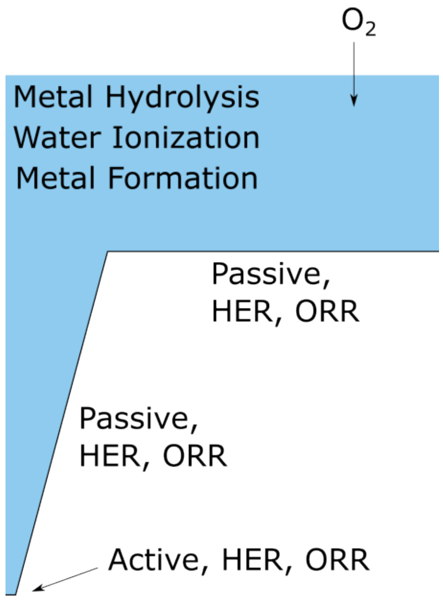
Proposed Finite Element Model

- Stress state and aggressive chemical/electrochemical conditions local to the crack tip control SCC



Not to scale

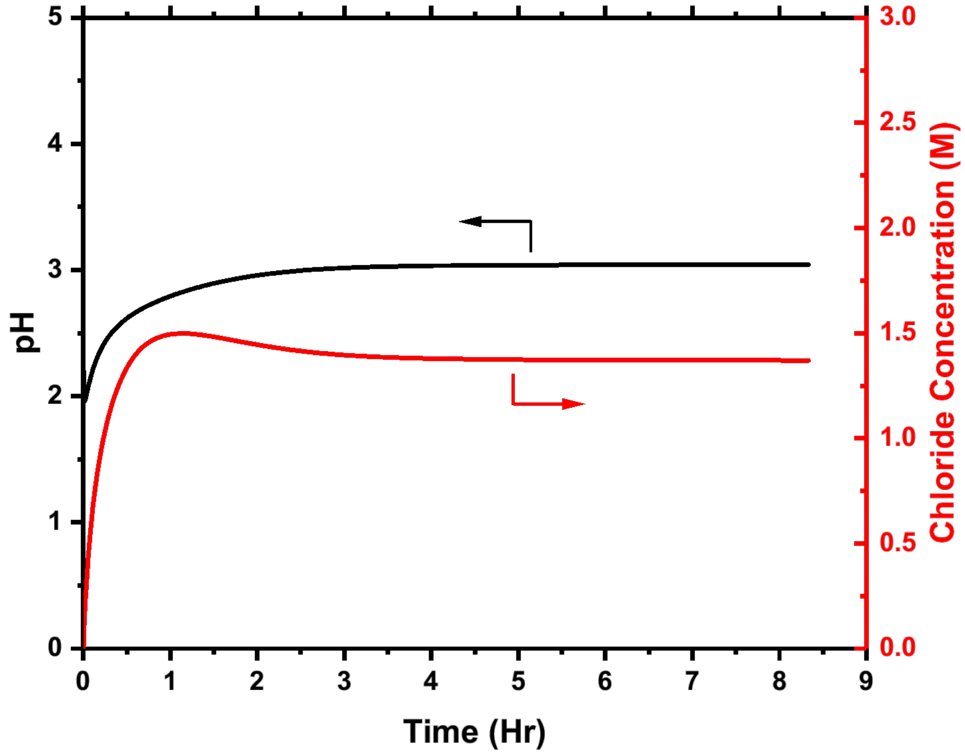




- Finite element reactive transport model looking for trends in electrochemical parameters (potential, current, chloride concentration, **pH**, etc.)

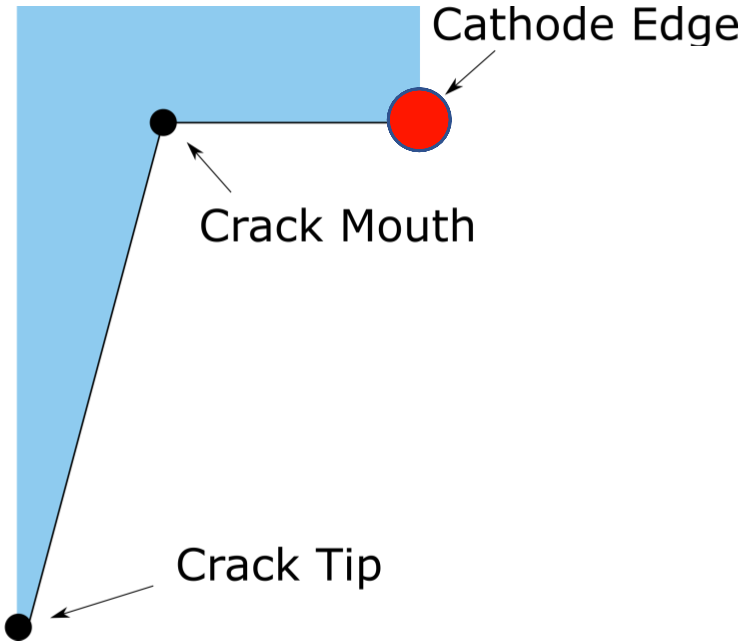
- Inferences about crack growth rates

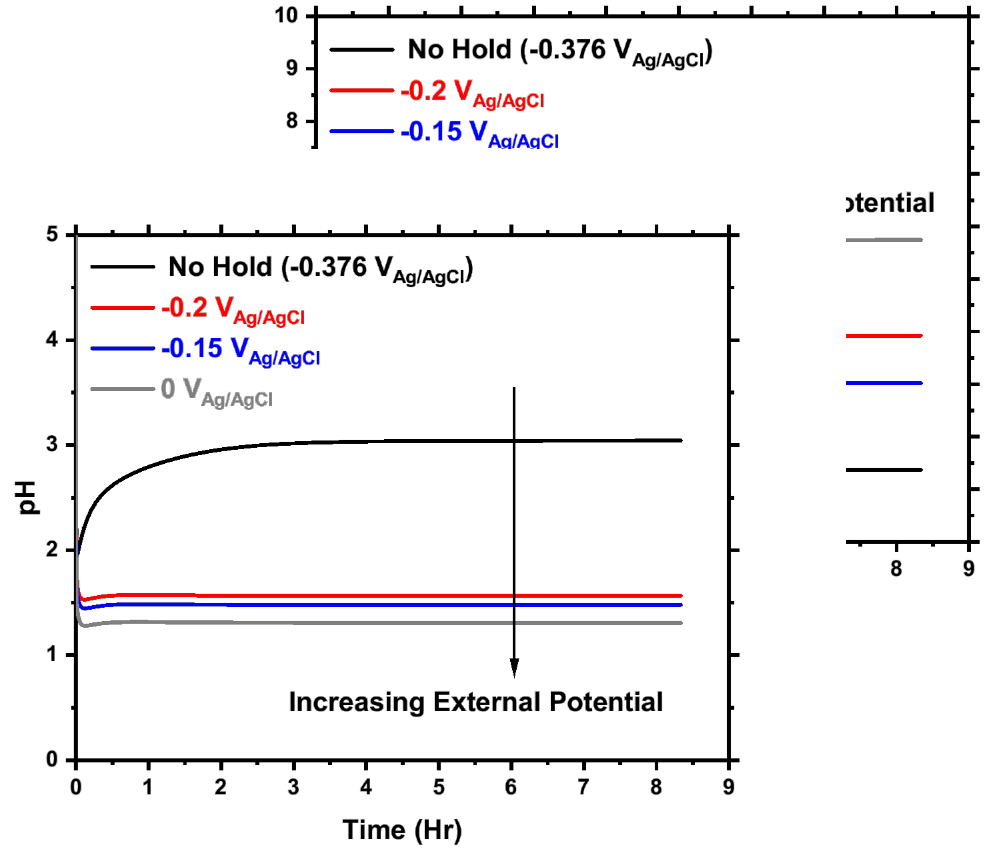
Crack tip pH Initially Decreases but Increases to Reach a Steady State



- Predicting chloride concentration and pH at the crack tip for SS304 Alloy (Fe, Ni, Cr species) in 3 M NaCl
- Increase in chloride concentration (due to metal cations) to steady state value
- Initial decrease in pH then subsequent increase to steady state

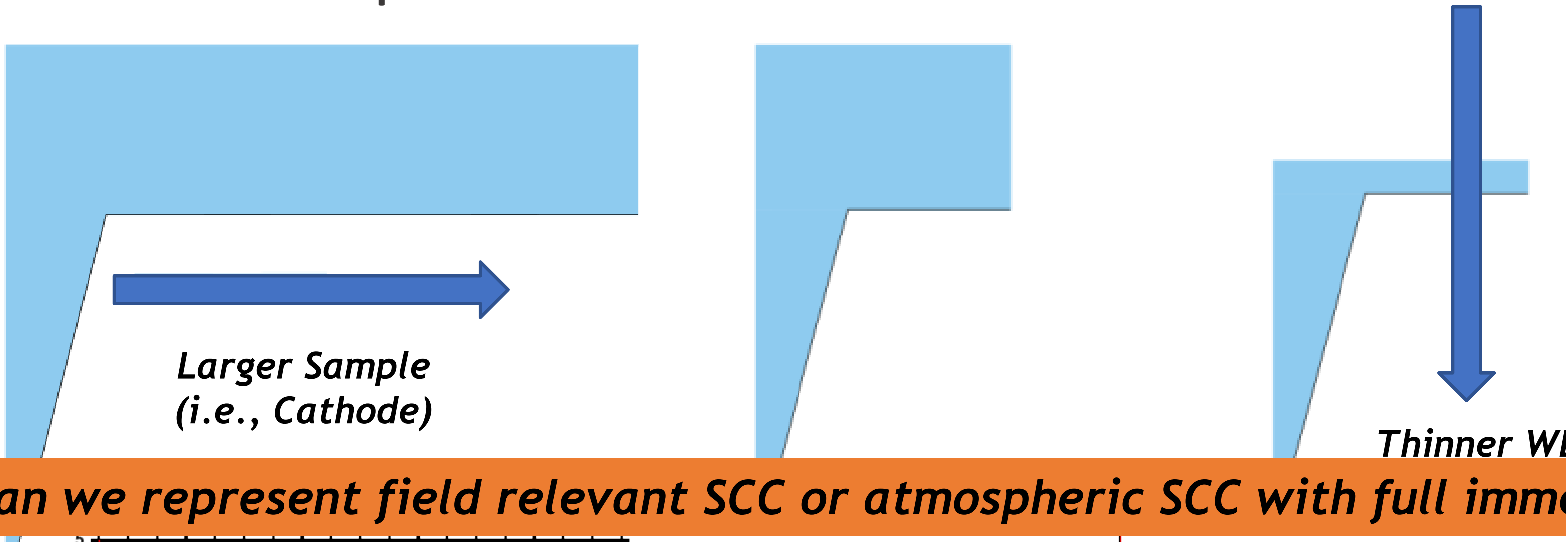
Increasing External Potential Increases Chloride Concentration and Decrease pH at Tip



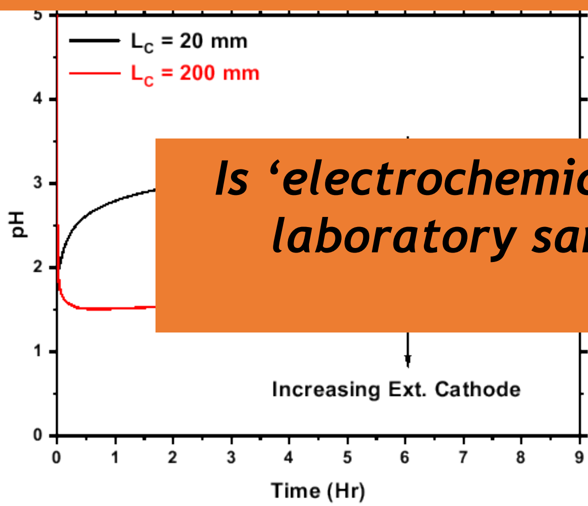


- Increasing external potential increases chloride concentration
- Increasing external potential decreases pH
- ***Modest polarization of external surface can greatly change crack tip conditions***

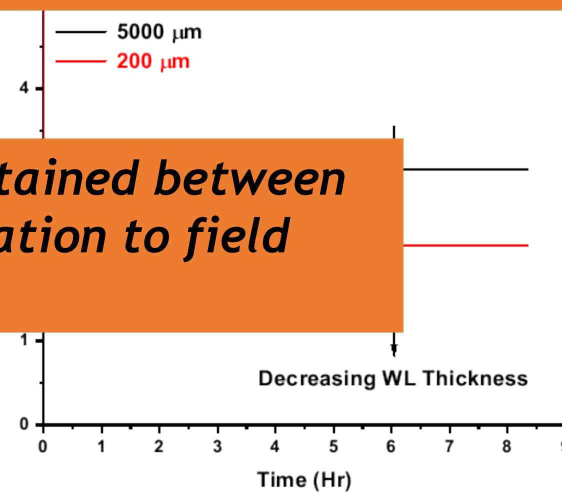
Increasing Cathode Length and Decreasing WL Decreases pH



Can we represent field relevant SCC or atmospheric SCC with full immersion?

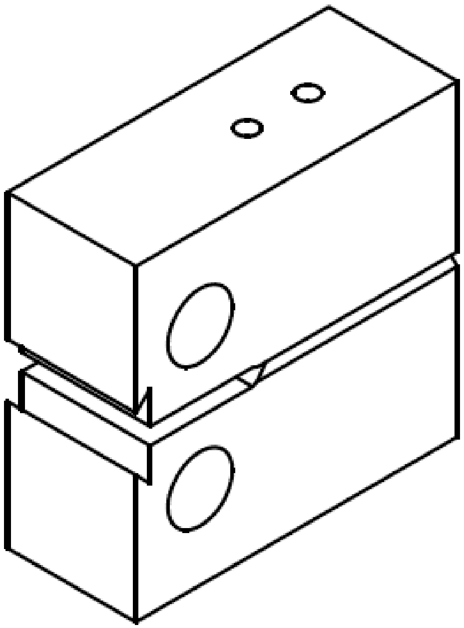


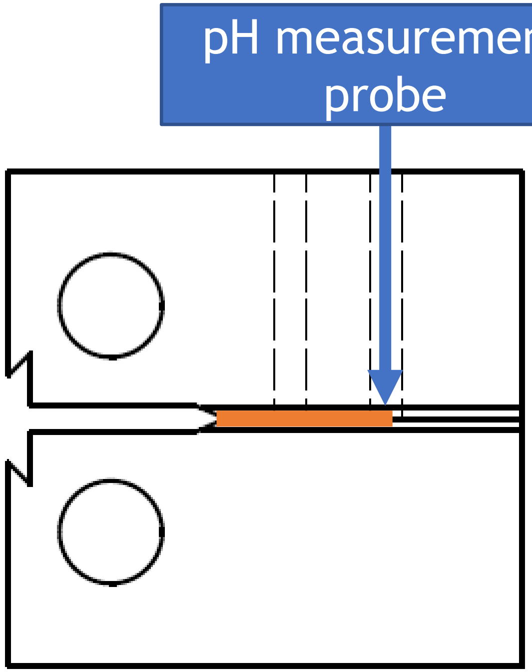
Is 'electrochemical similitude' maintained between laboratory samples and extrapolation to field applications?

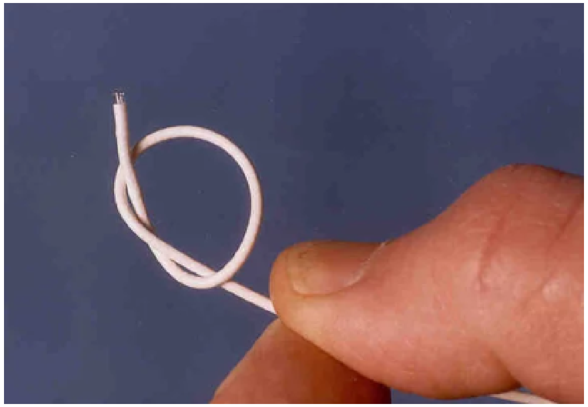


Driven by increase in external cathodic current

Can we confirm crack tip electrochemistry?

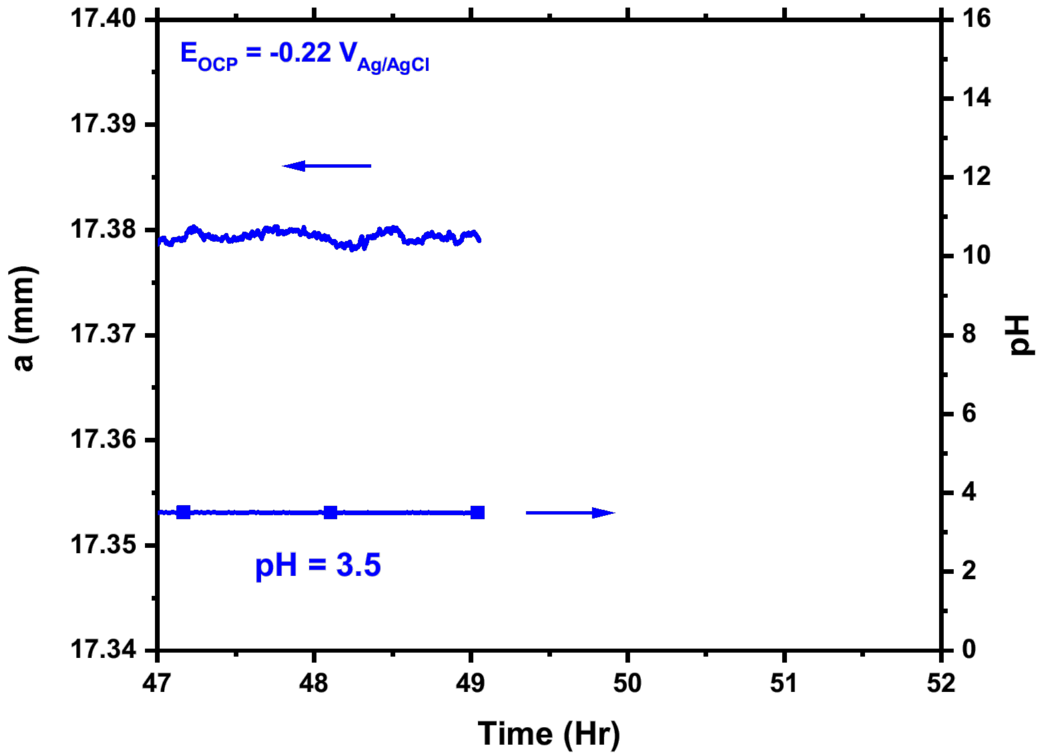




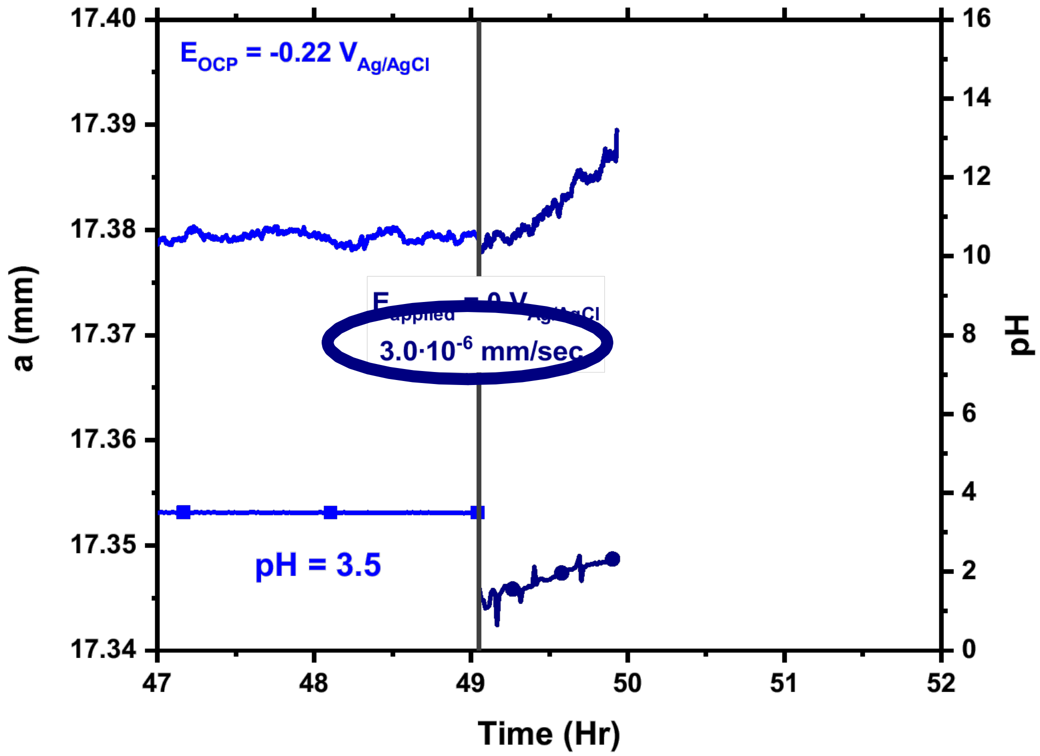


- Drilled holes in CT specimen to allow for placement of micro-pH probes
- Will the holes influence mechanical driving forces? – No
- Is there significant ohmic drop between the drilled holes and reference probe for pH measurement? – No

Anodic Polarizations Increase Crack Growth and Decrease Crack Tip pH

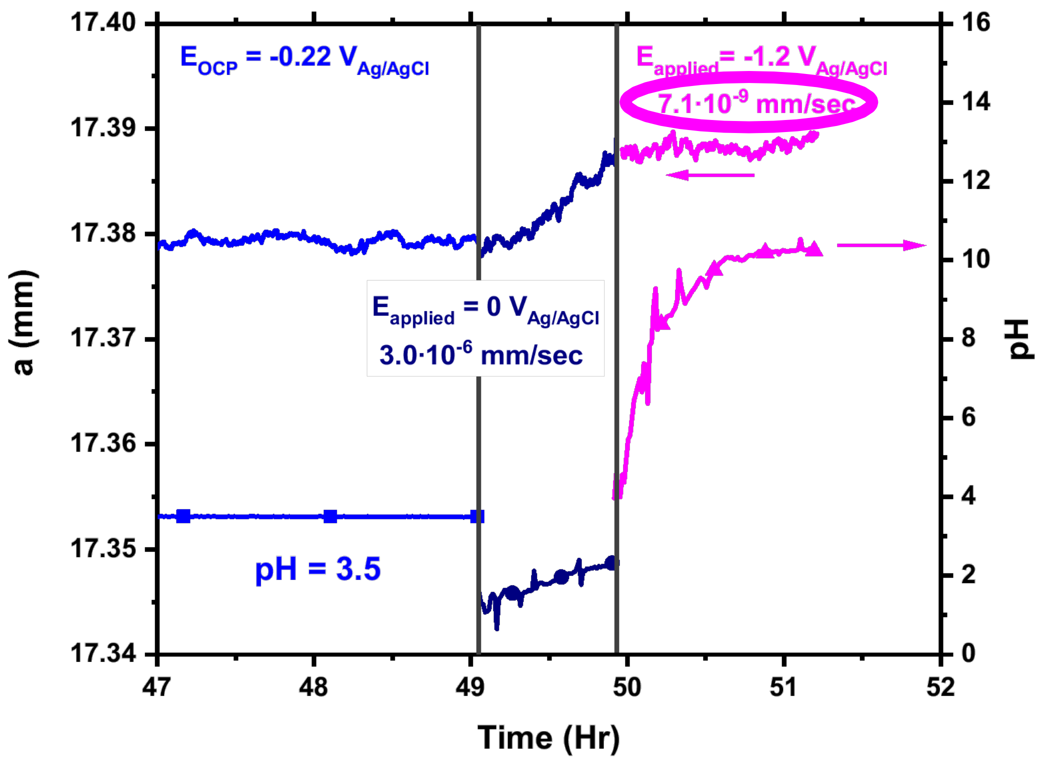


Anodic Polarizations Increase Crack Growth and Decrease Crack Tip pH



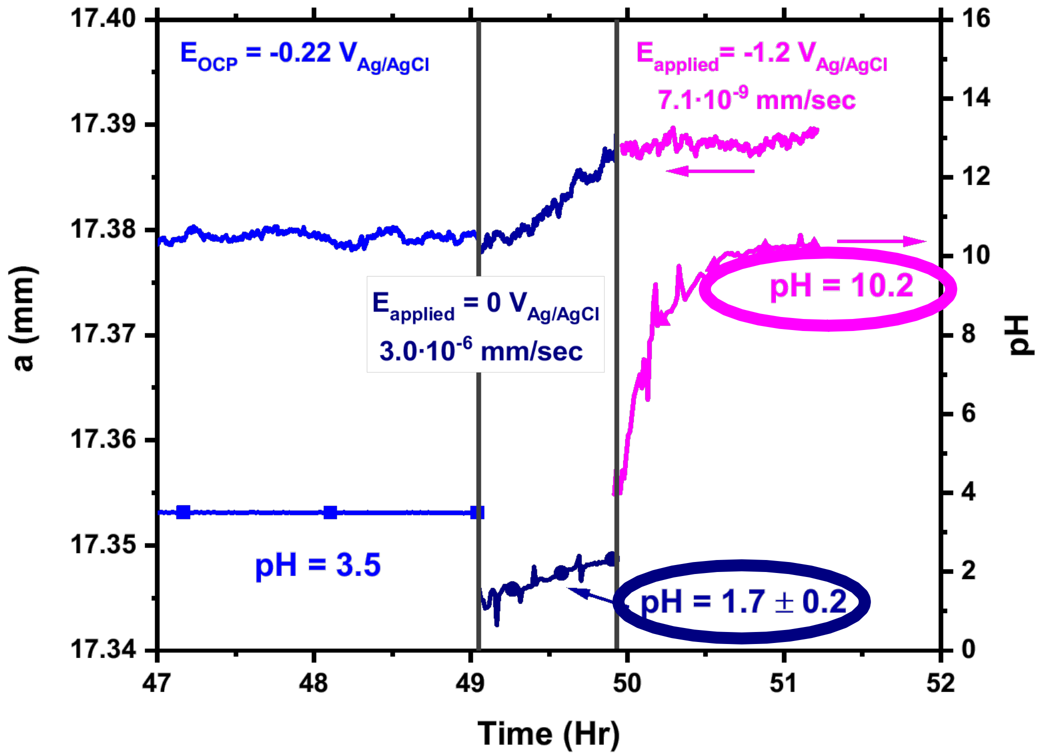
- Externally polarizing the sample increases crack growth ***31 fold*** in comparison to non-polarized conditions

Anodic Polarizations Increase Crack Growth and Decrease Crack Tip pH



- Externally polarizing the sample increases crack growth ***31 fold*** in comparison to non-polarized conditions
- Cathodically polarizing the crack tip decreases crack growth ***13 fold*** in comparison to non-polarized conditions

Anodic Polarizations Increase Crack Growth and Decrease Crack Tip pH

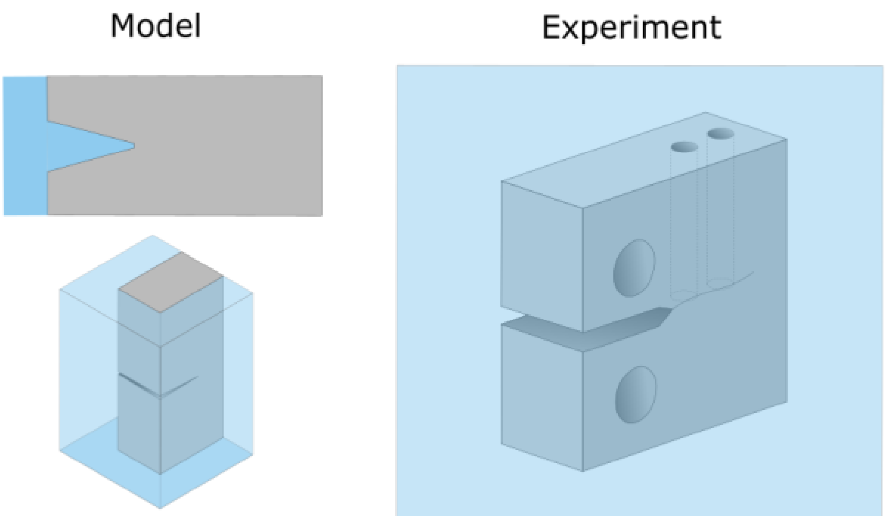


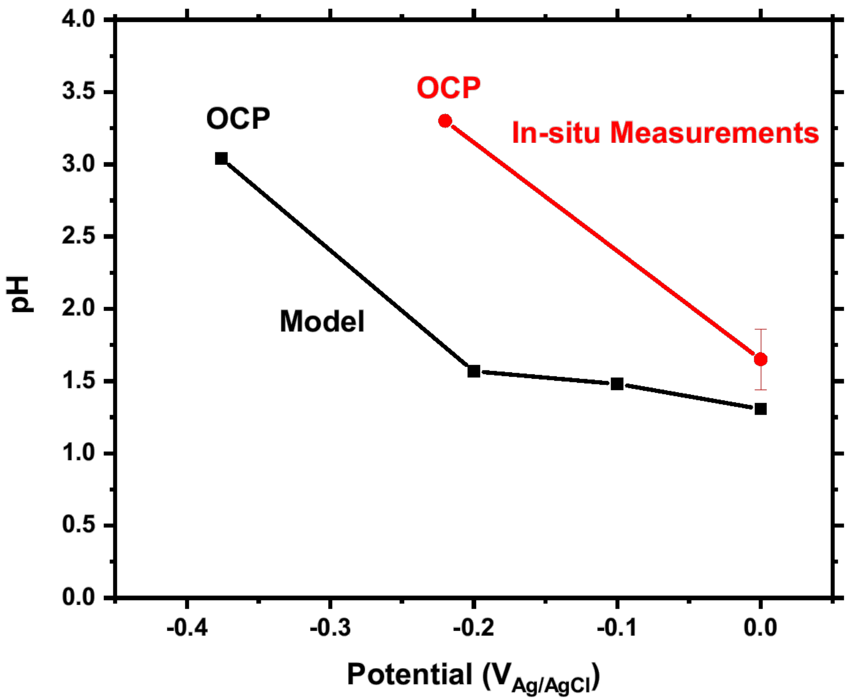
- Externally polarizing the sample increases crack growth ***31 fold*** in comparison to non-polarized conditions
- Cathodically polarizing the crack tip decreases crack growth ***13 fold*** in comparison to non-polarized conditions
- pH drops during anodic polarization (pH = 1.7)
- pH raises significantly during cathodic polarization (pH = 10.2)

- Preliminary investigations show that SS304L exposed to 3 M NaCl at room temperature is more susceptible to SCC under anodic polarization than cathodic polarization

Modest Polarization Influences Crack Growth Rate and Crack Tip Electrochemical Conditions

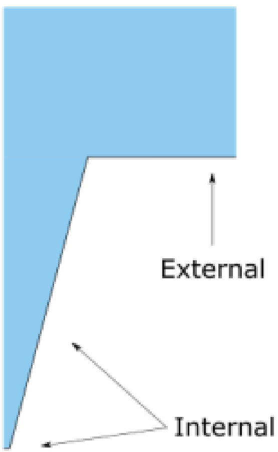
How does the model do?

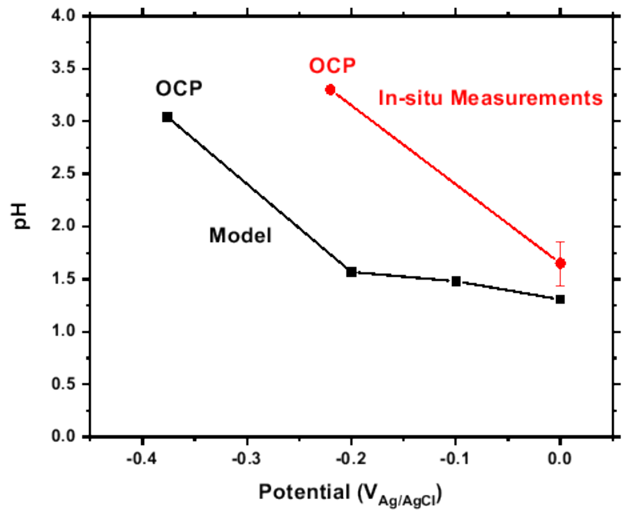




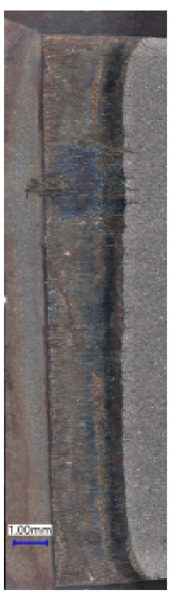
- Remember: Different geometries (2D/3D), longer crack length
- General trend is present between modeling and experimental results
  - Model appears to have more aggressive conditions
  - Not too surprising to have higher pH in measurements given a longer crack length (higher ohmic drop)

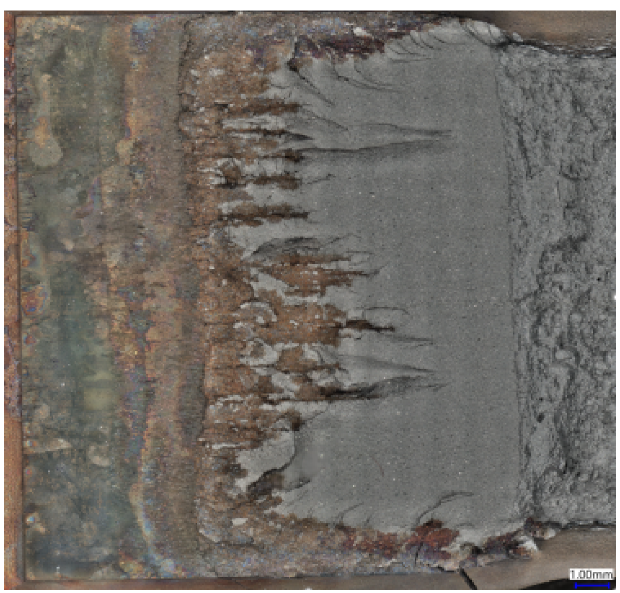
Overall Summary

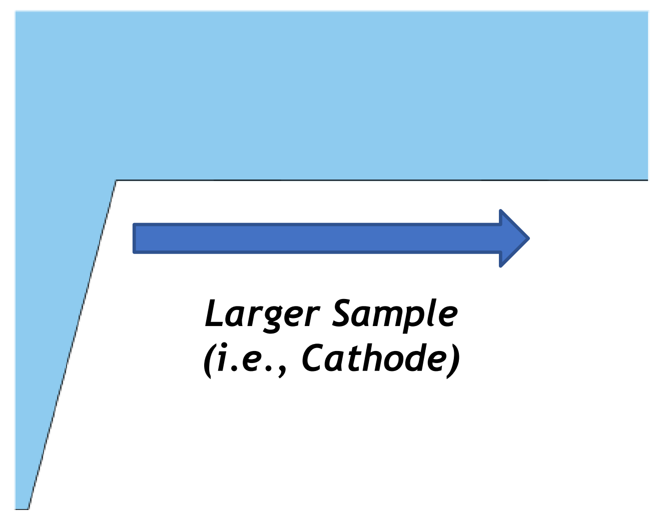




Is 'electrochemical similitude' maintained between laboratory samples and extrapolation to field applications?



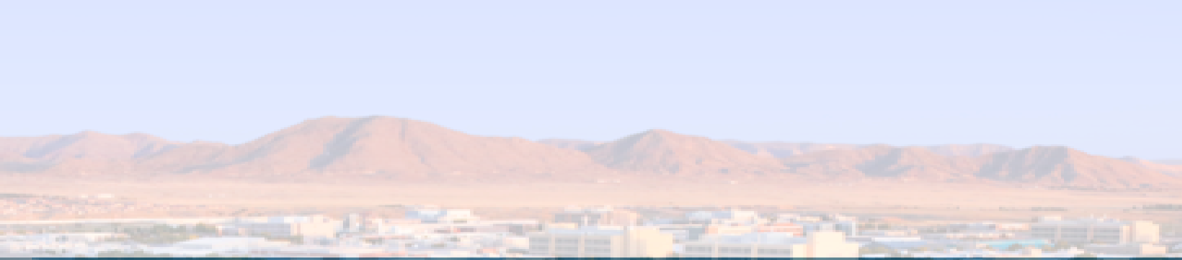




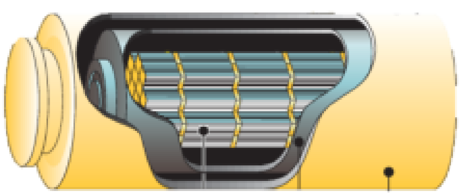
Is 'electrochemical similitude' maintained between solutions?

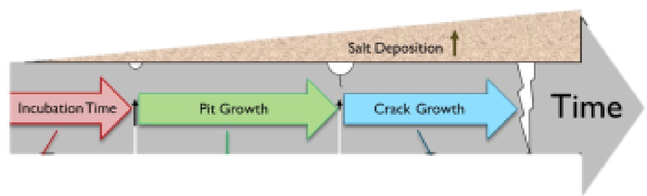
Acknowledgements

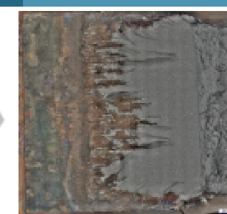
- Dr. Andrew Knight, Dr. Michael Melia, Dr. David Enos, Brendan Nation, Jason Snow
- Helpful conversations with Dr. Mychailo Toloczko (PNNL), Dr. James Burns (UVA), Sarah Blust (UVA), Trevor Shoemaker (UVA), Michael Roach (UVA) and Dr. Jen Locke (OSU) are appreciated
- Funding:
  - DOE's Office of Nuclear Energy's Spent Fuel and Waste Science and Technology program
  - Engineering Science Laboratory Directed Research and Development (LDRD)

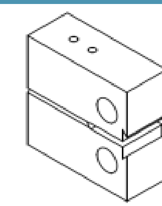


Towards Understanding the Controlling Nature of Crack Tip Chemistry on the Stress Corrosion Cracking of Austenitic Stainless Steels









PRESENTED BY

Ryan M. Katona[1] (rmkaton@sandia.gov)

J. M. Taylor[1], E. K. Karasz[1], C. R. Bryan[1], R. G. Kelly[2], and R. F. Schaller[1]

[1]Sandia National Laboratories, Albuquerque, New Mexico 87123, USA

[2]University of Virginia, Charlottesville, Virginia 22904, USA

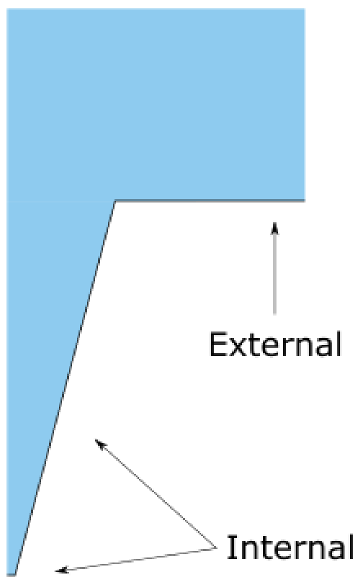
Gordon Research Seminar and Conference

July 9-15th, 2022

New London, NH, United States

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.
SAND No. SAND2022-8467 PE

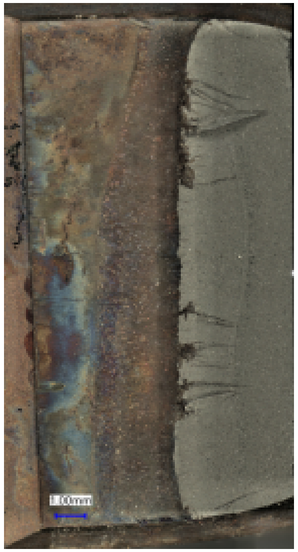
Proposed Finite Element Model

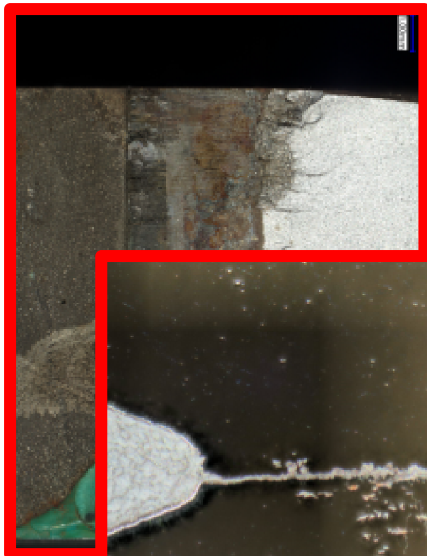


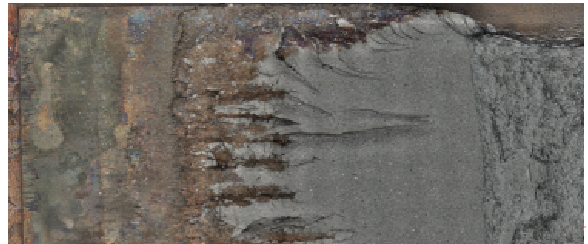
- In a freely corroding/cracking need to consider the following reactions:
  - Hydrogen Evolution (HER; $H^+ + e^- = H$)
  - Oxygen Reduction (ORR; $O_2 + 4e^- + 2H_2O = 4\,OH^-$)
  - Metal Oxidation ($Me_s = ne^- + Me_{aq}^{n+}$)
  - Metal Hydrolysis ($Me^{n+} + OH^- = MeOH^{n-1}$)
  - Metal Salt formation ($Me^{n+} + \mathrm{Cl}^- = \mathrm{MeCl}^{\mathrm{n-1}}$)
  - Water Equilibrium

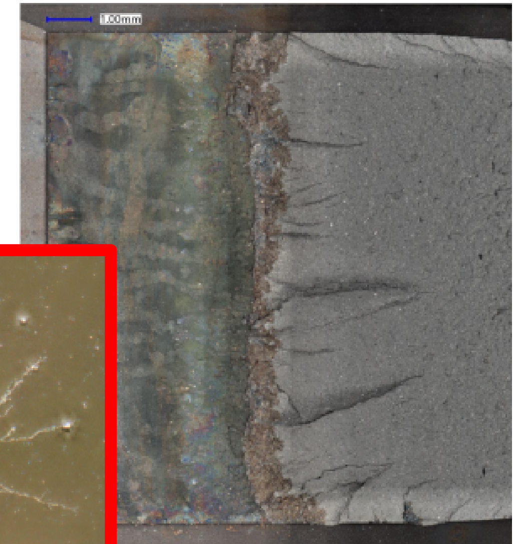
- Predicting chloride concentration and pH at the crack tip for SS304 Alloy (Fe, Ni, Cr species) in 3 M NaCl

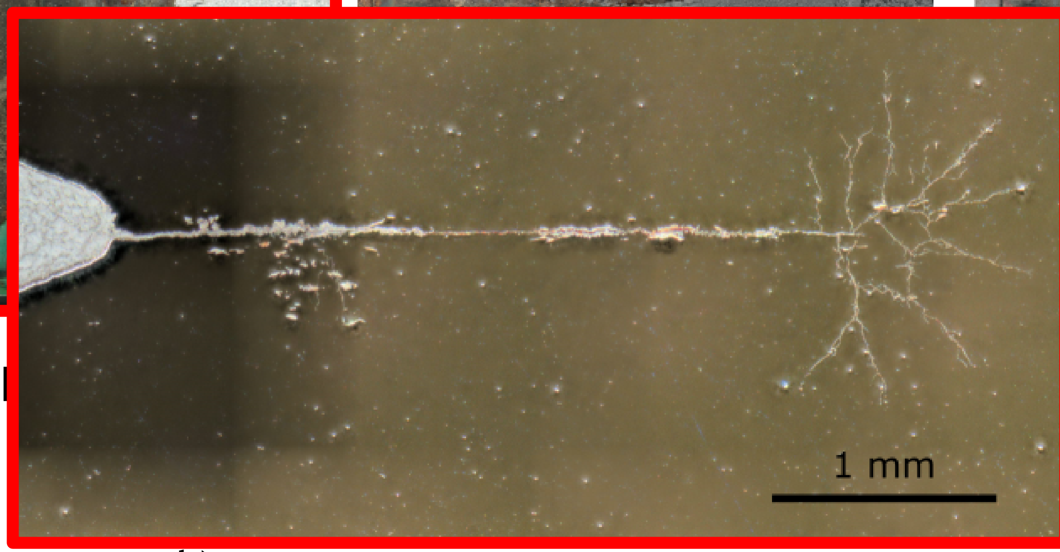
Overview of $MgCl_2$ Samples











Lot 1 – RT

(1218 hours)

3 - 55 ° C (T-S)

(800 Hours)

growth)

(Time under Constant K)

- Crack growth rates and morphologies show influence from temperature, lot, and direction

Overview of Saturated NaCl Samples

Lot 1 – 22 ˚C

Lot 3 – 60 ˚C

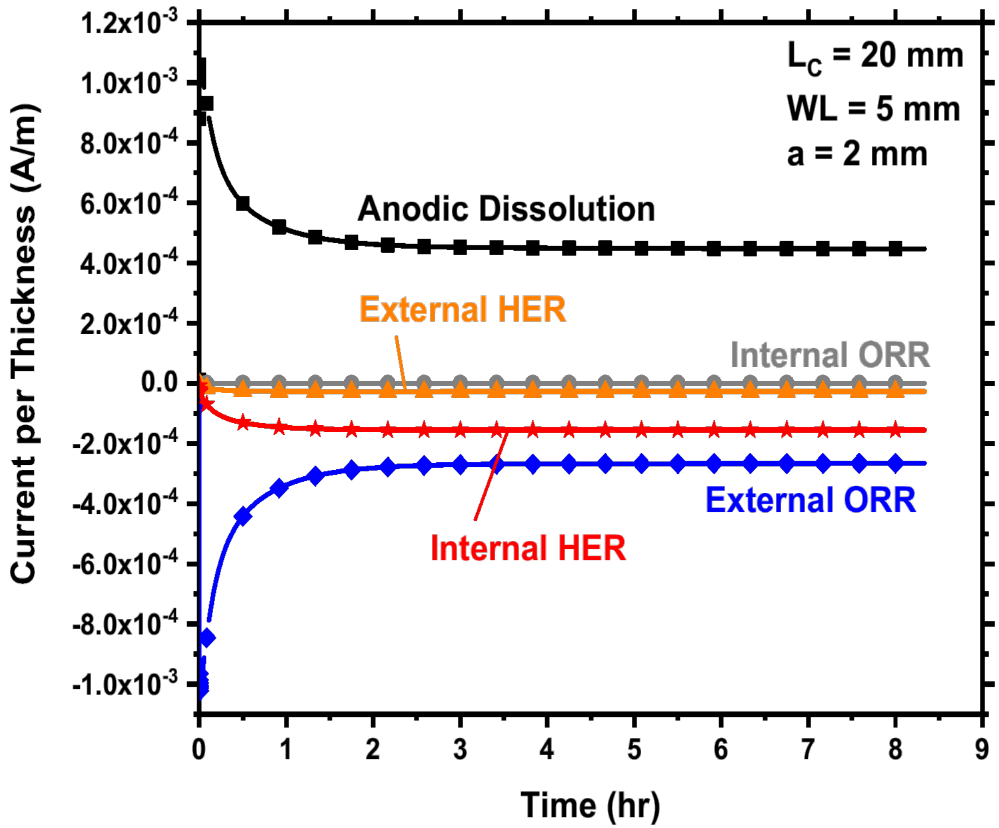
Difference in cracking morphology as well as crack growth rates between NaCl and $MgCl_2$ solutions

growth

50 μm of crack
on during
constant K

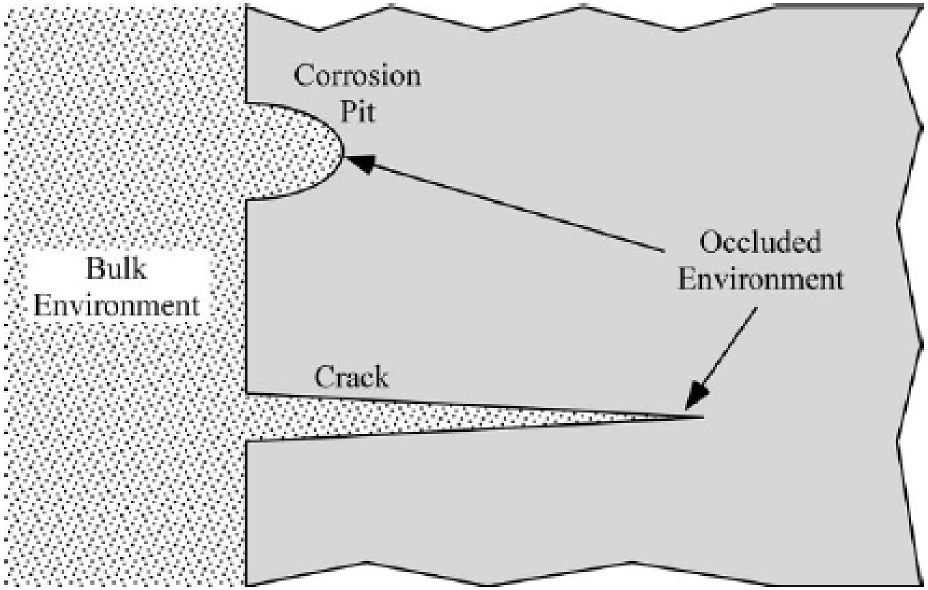
Crack growth rate of $2.1 \cdot 10^{-8}$ mm/sec

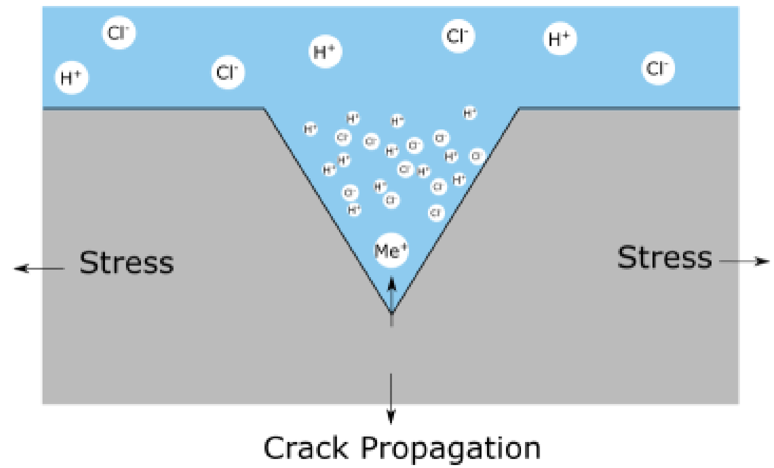
External ORR is Dominant Cathodic Reaction



- FEM provides decoupling of all reactions as a function of position (not previously done for SCC modeling)
- External ORR provides majority of cathodic current
  - Strong coupling between the external and internal surfaces

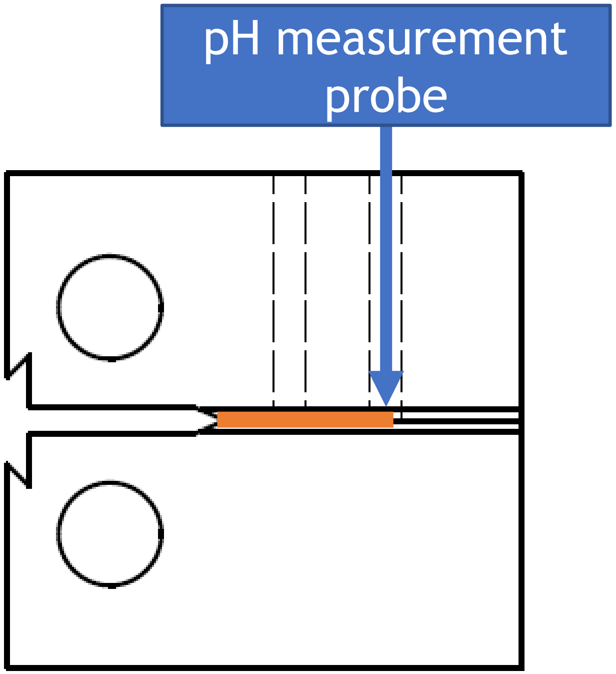
Crack Tip Electrochemistry Model

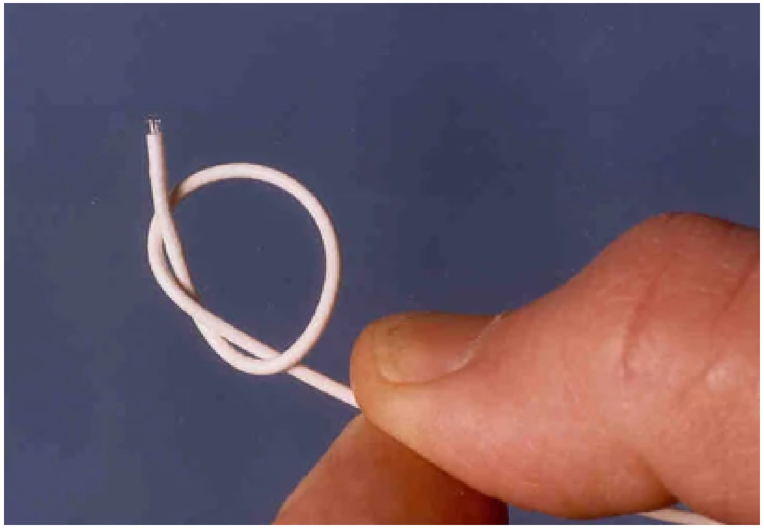




- Two things are generally accepted for SCC:
  - Bulk chemical and electrochemical conditions not maintained down the crack
  - Stress state and chemical/electrochemical conditions local to the crack tip control SCC
- Need to understand the occluded environment

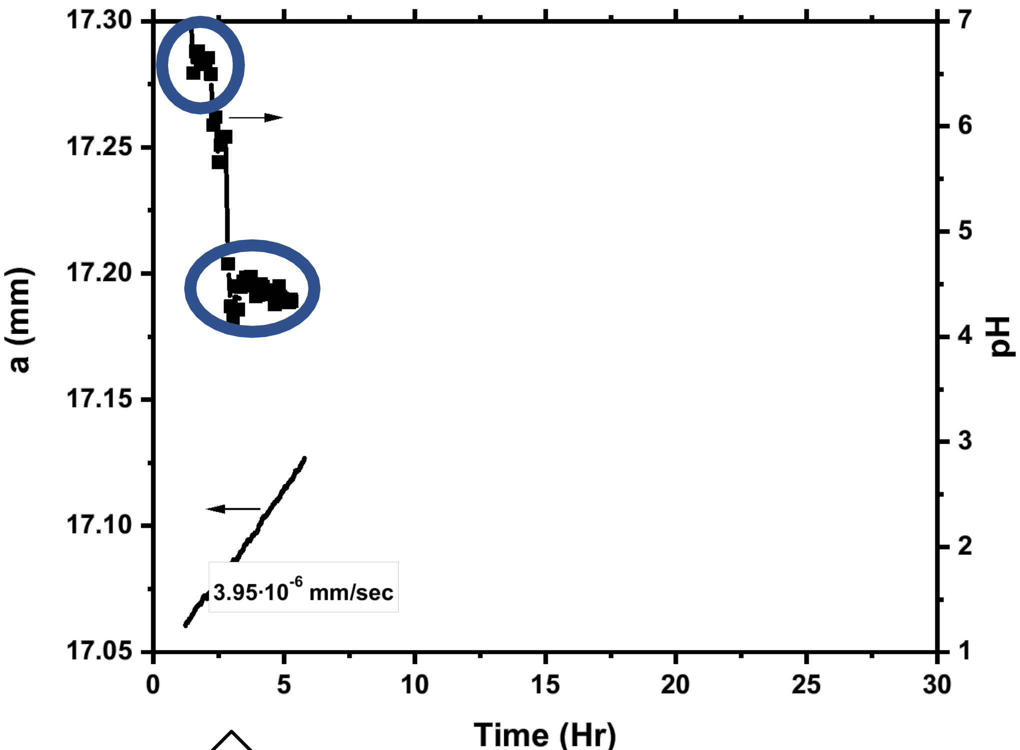
In-situ Crack Tip Measurements





- Measurement of crack tip chemistries in 3 M NaCl
  - Corresponds to model concentration
- Investigate fatigue, constant K conditions, and polarizations

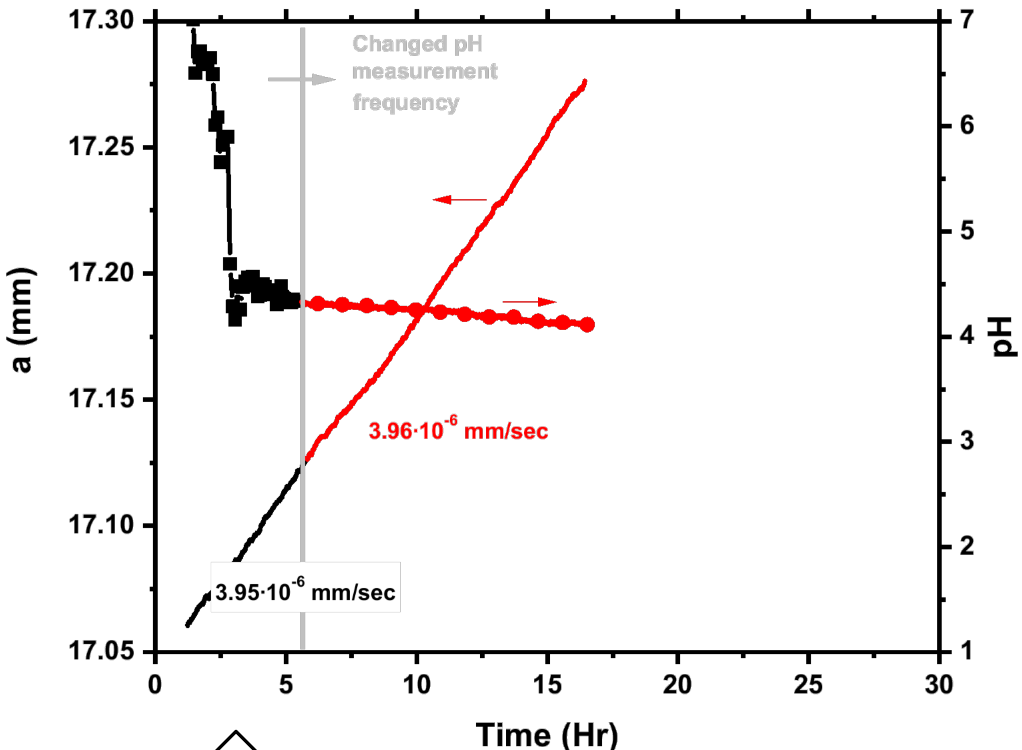
In-situ Crack Tip Measurements



Fatigue
(f = 1 hZ;
R = 0.1)

- Initial pH is near bulk solution pH
  - 3 M NaCl (pH = 6.5)
  - K_{max} = 20 $MPa\sqrt{m}$
- Initial chemistry (pH ~ 4) in crack develops over roughly 1.5 hours

In-situ Crack Tip Measurements

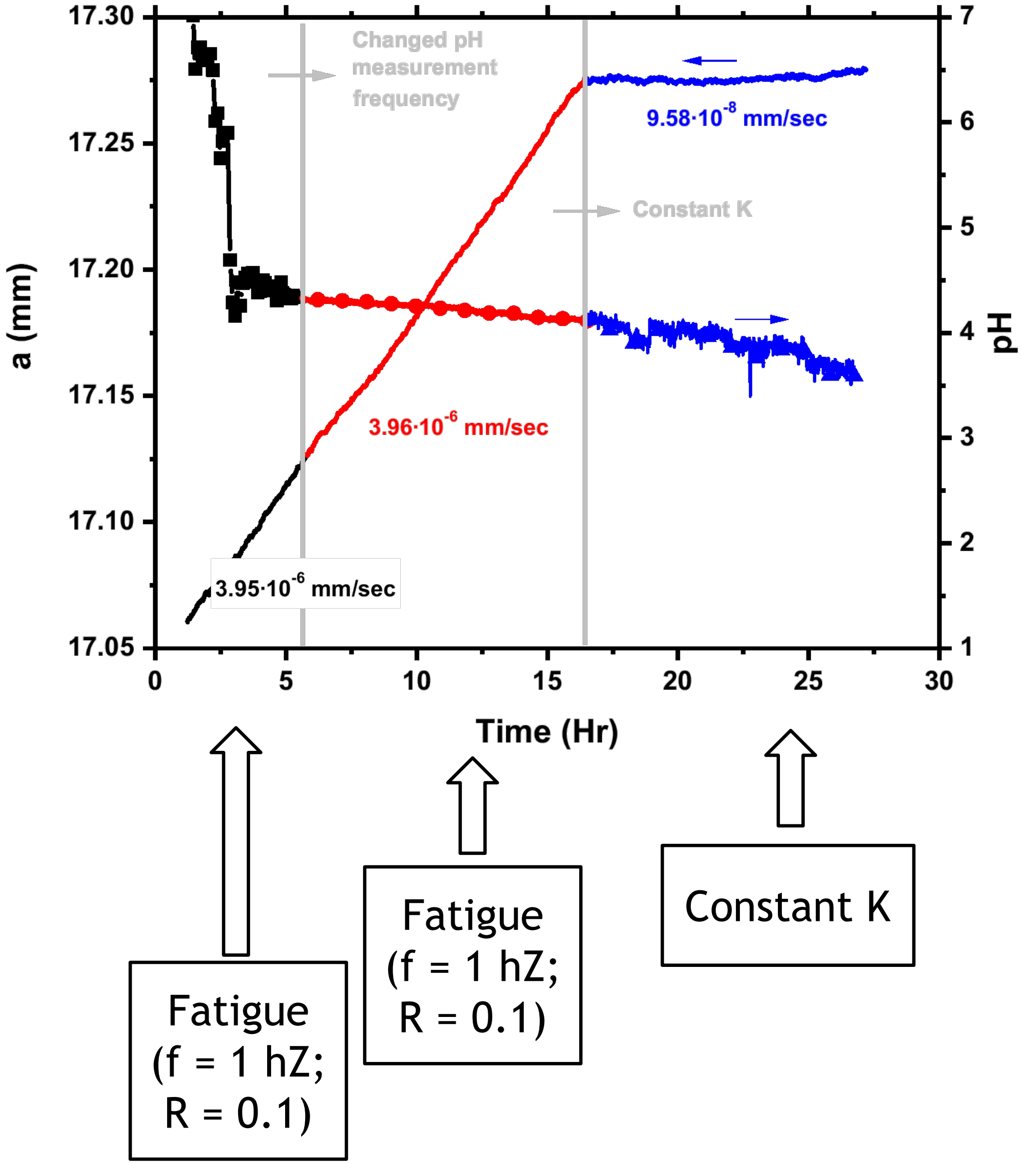


Fatigue (f = 1 hZ; R = 0.1)

Fatigue (f = 1 hZ; R = 0.1)

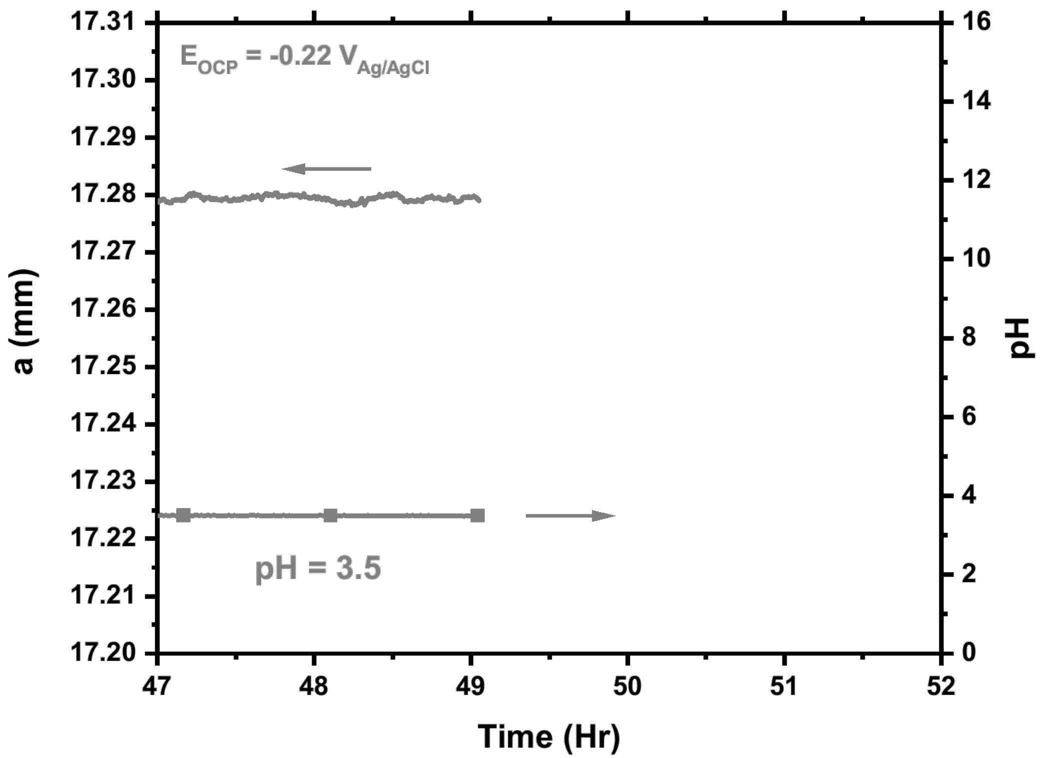
- Initial pH is near bulk solution pH
  - 3 M NaCl (pH = 6.5)
  - K_max 20
- Initial chemistry (pH ~ 4) in crack develops over roughly 1.5 hours

In-situ Crack Tip Measurements



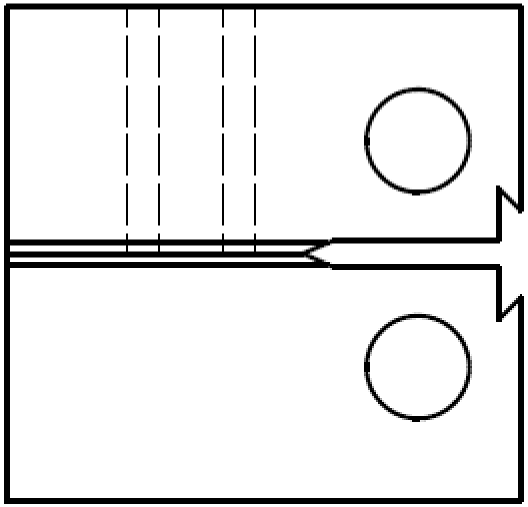
- Initial pH is near bulk solution pH
  - 3 M NaCl (pH = 6.5)
  - K_max 20
- Initial chemistry (pH ~ 4) in crack develops over roughly 1.5 hours
- pH slightly lower with no fatigue
  - Slight impact of advection on chemistry

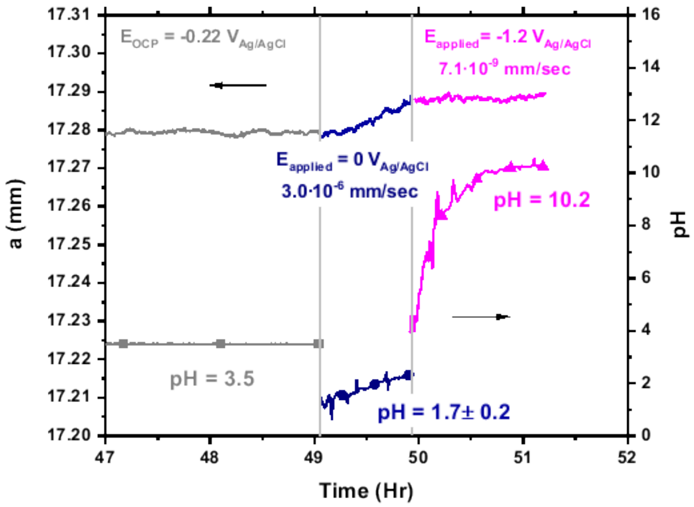
Anodic Polarizations Increase Crack Growth and Decrease Crack Tip pH



Conclusions and Implications

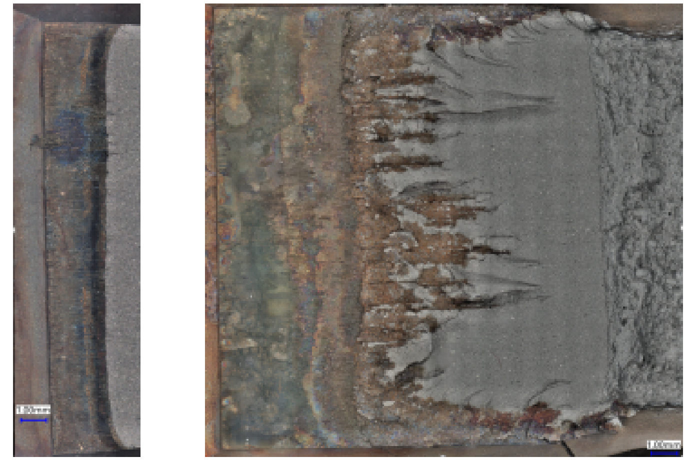
- Created set-up to actively measure crack tip pH and crack extension with DCPD
- Advection plays small role in determining crack tip pH
- Crack tip pH during constant K conditions is roughly 3.5
- Anodic polarization increases crack growth and decreases crack tip pH
    - Is austenitic stainless steel more susceptible to anodic dissolution?
- Same trend between modeled and measured pH values



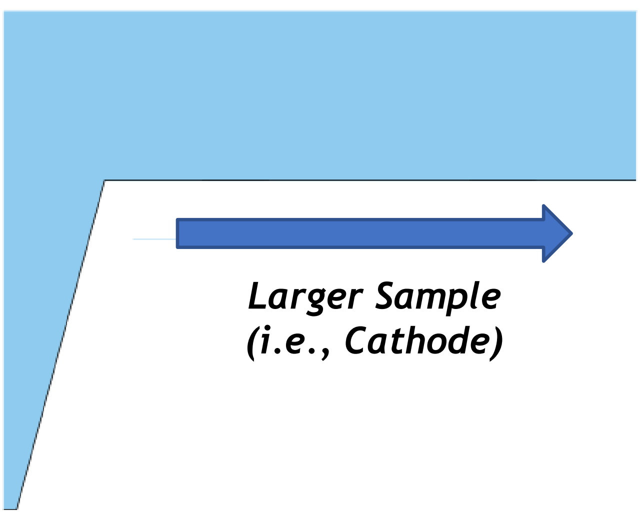


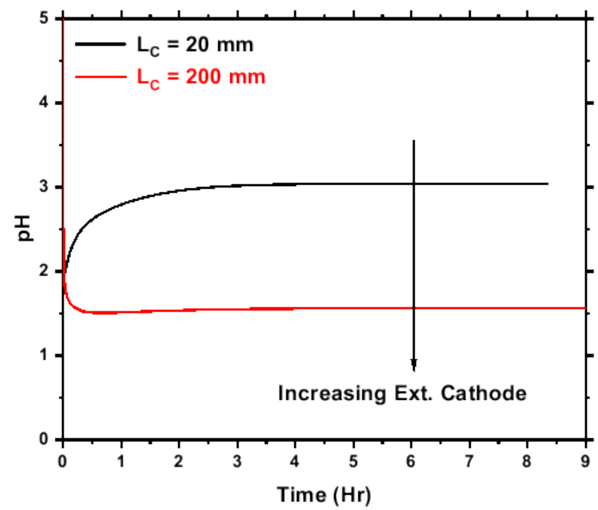
Next Steps

- 3D Model
- Measurement of crack tip pH as a function:
  - sample size (*i.e.*, cathode length)
  - solution composition (*i.e.*, $MgCl_2$)
- Measurement of crack tip potential, Na^+ concentration, and conductivity

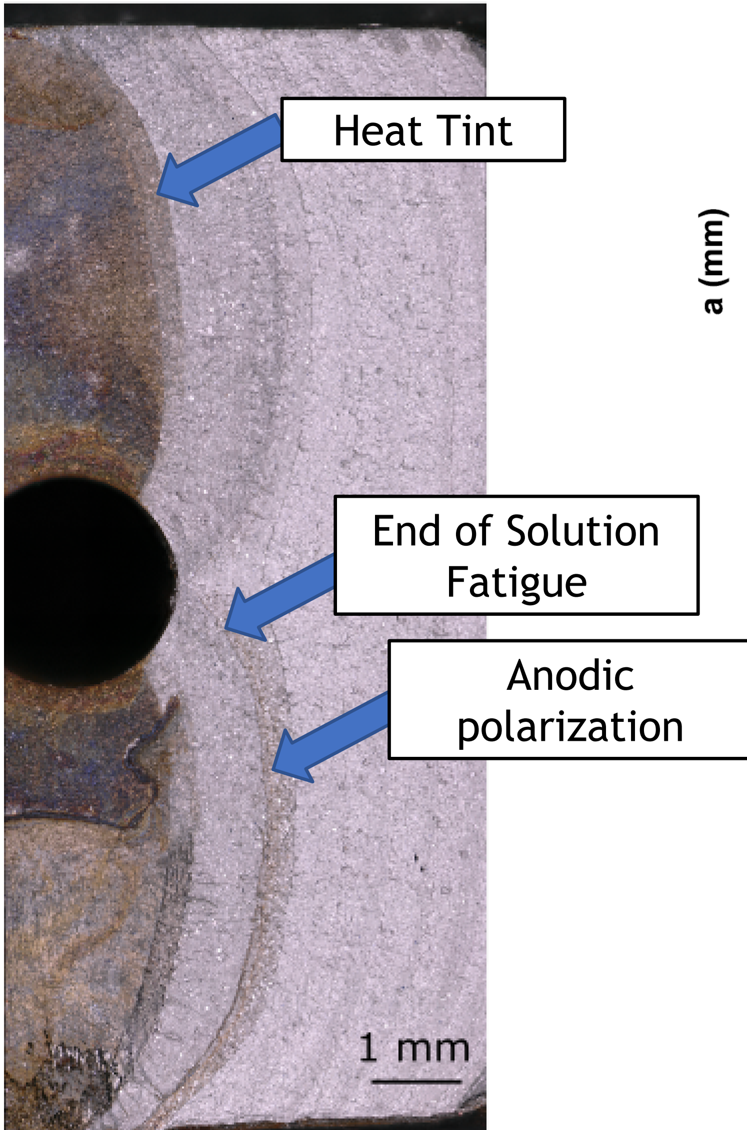


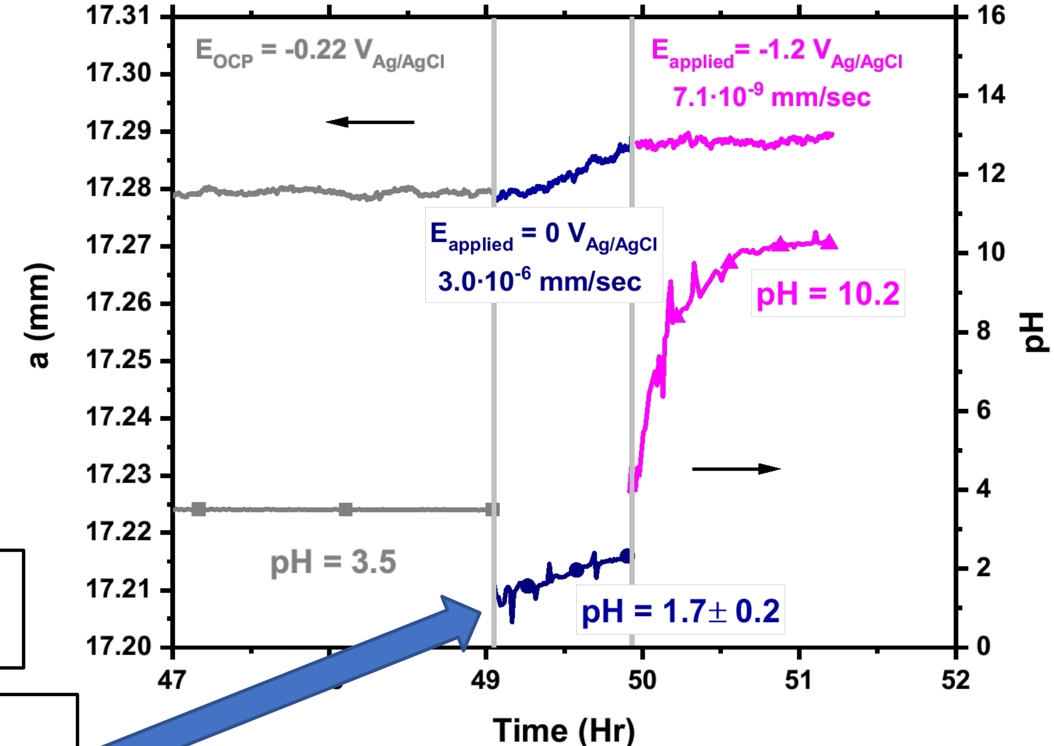
NaCl $MgCl_2$





Anodic Polarizations Increase Crack Growth and Decrease Crack Tip pH

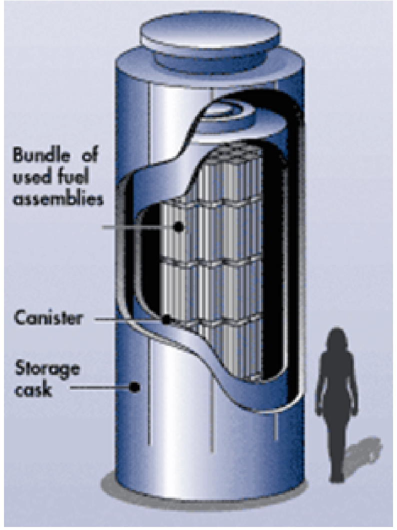




- Initial fractography investigation started

Spent Nuclear Fuel Storage

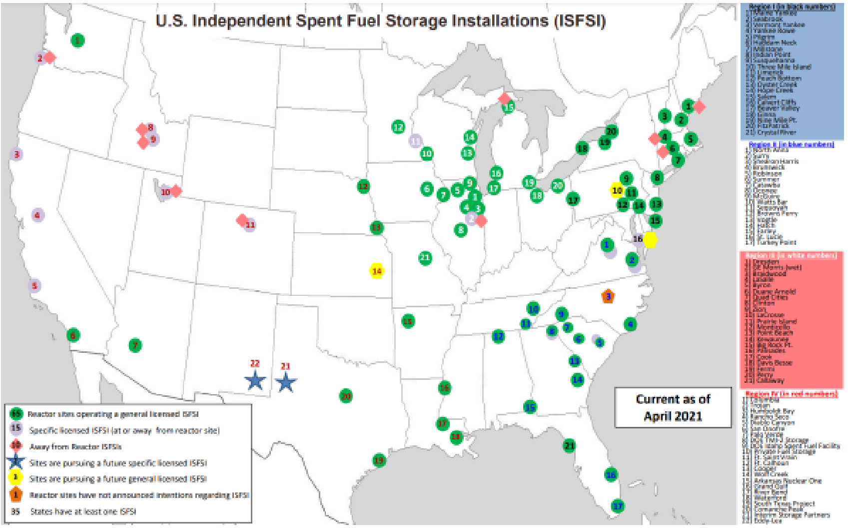
- US has over 86,000 metric tons of Spent Nuclear Fuel (SNF)
  - > 3600 stainless steel (SS) canisters
  - 77 storage sites



SNF Canister inside concrete overpack

- Interim storage sites being utilized longer than initially intended

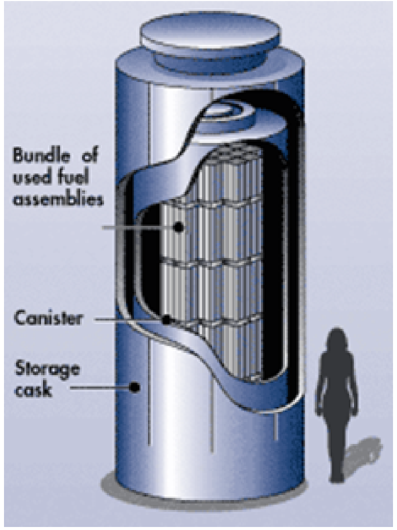
- US has <u>no</u> permanent disposal site selected for SNF

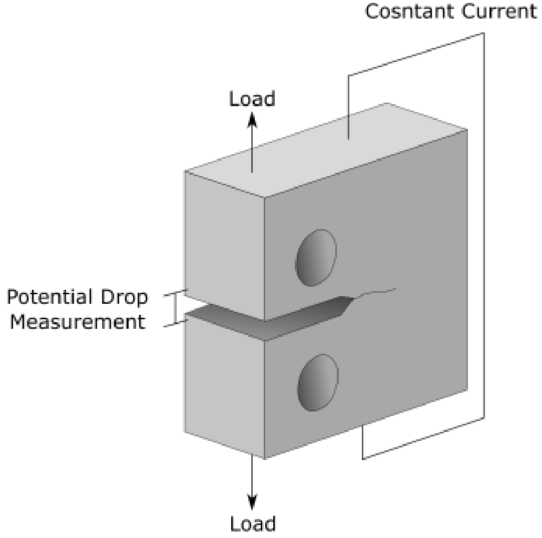


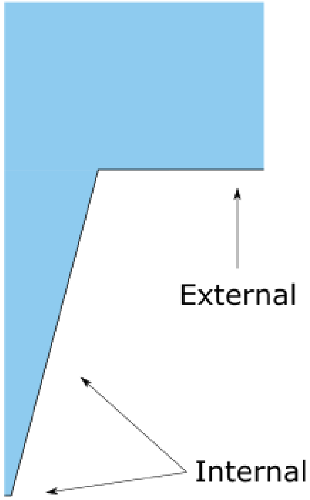
https://www.nrc.gov/docs/ML2111/ML21116A041.pdf

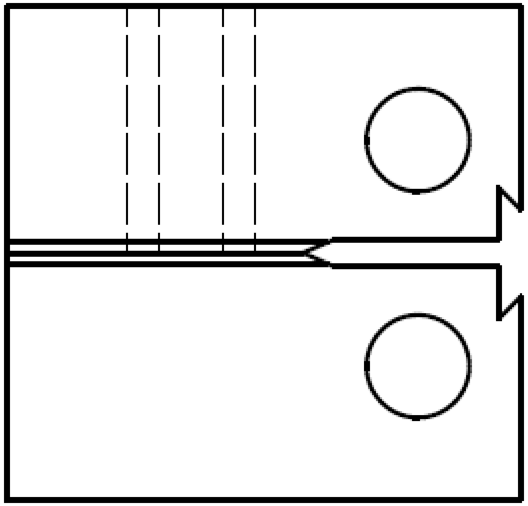
Towards Understanding Stress Corrosion

- Crack growth rate determination
- Crack tip chemistry modeling
- Crack tip chemistry measurement

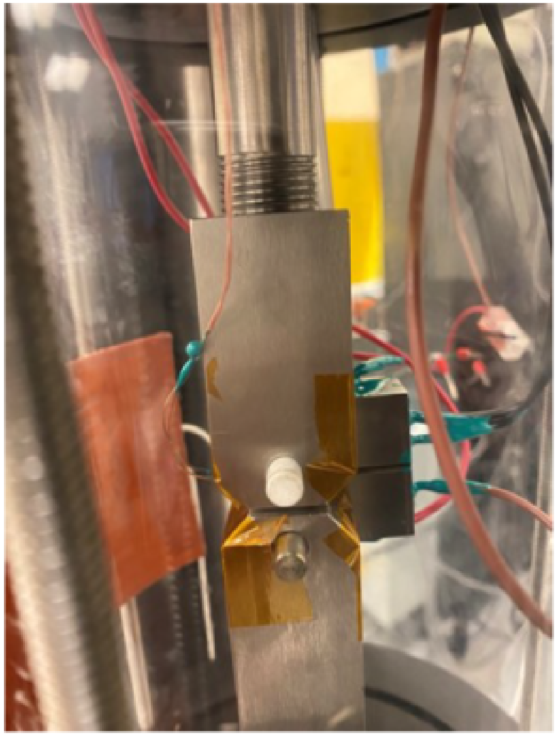


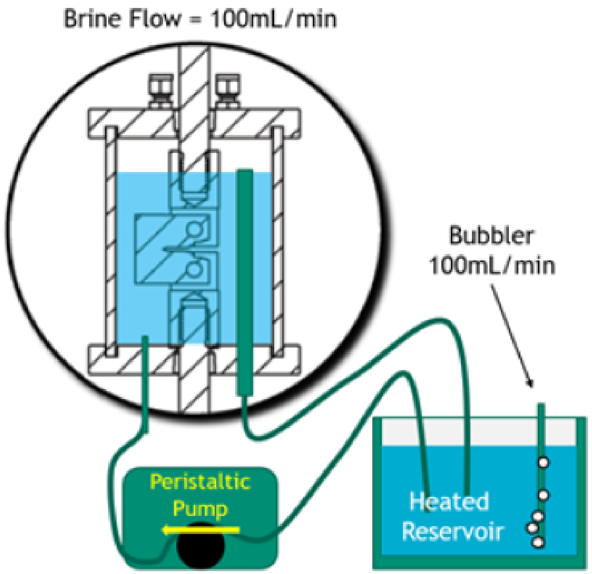






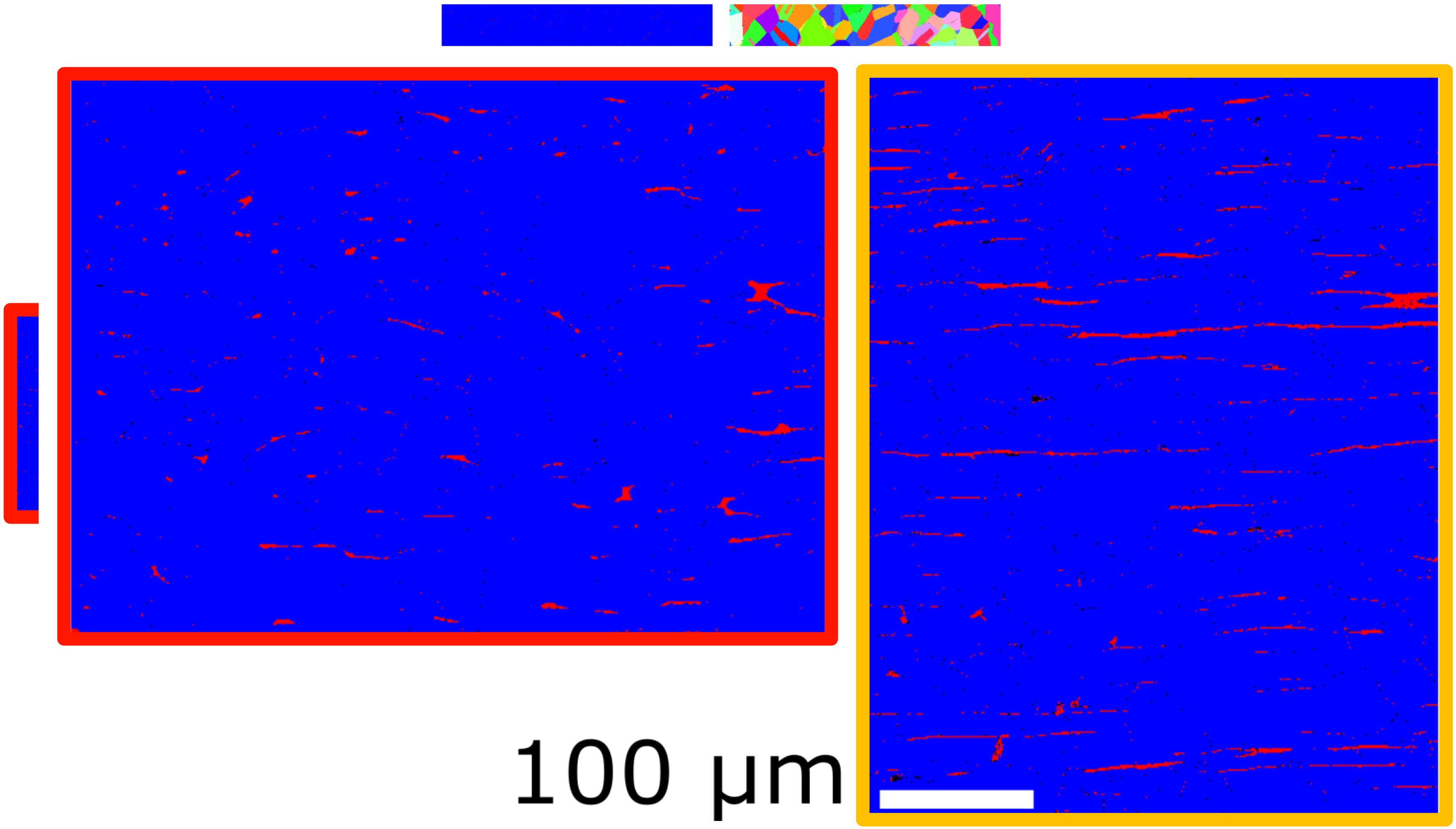
New SCC/CF Capabilities at SNL





- Compact tension specimen in heated cell allowing for fluid flow

Plate Microstructure

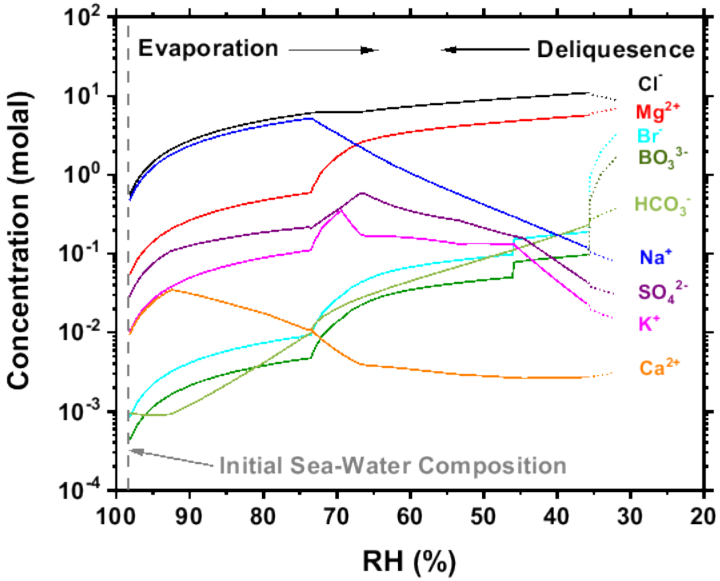


Lot Information

Lot ID	Plate #	Heat #	PNNL Reference #	UTS (Mpa)	YS 0.2% (Mpa)	Elong.(%)	HRB
LT001	206972	SD23822	n/a	647	267.516653	57.6	82.2
LT003	213104	04E28VAA	P304L1	623	292	62.9	81

	Composition													
	C	Co	Cr	Cu	Mn	Mo	N	Nb	Ni	P	S	Si	Ti	Fe
LT001	0.02	0.2	18.14	0.25	1.7	0.08	0.07	-	8.04	0.031	0.004	0.4	0.001	bal
LT003	0.017	0.234	18.1	0.412	1.782	0.414	0.08	0.014	8.03	0.037	0.001	0.236	0.002	70.7

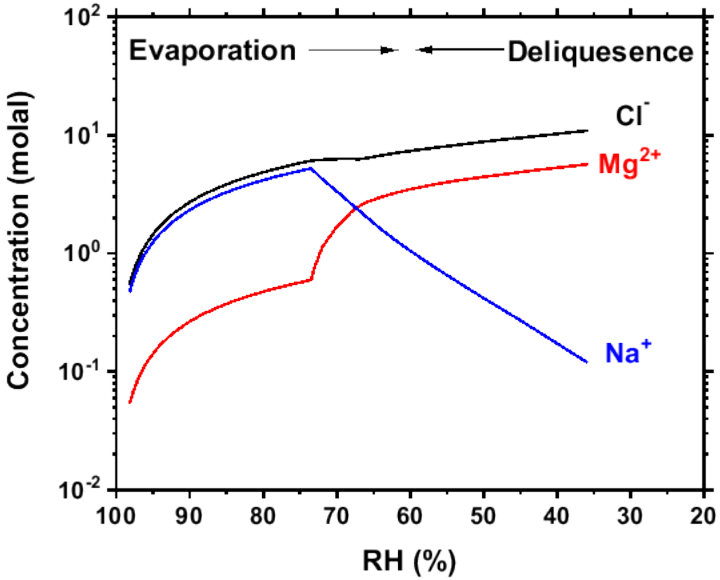
Salt Composition and Concentration Change with RH

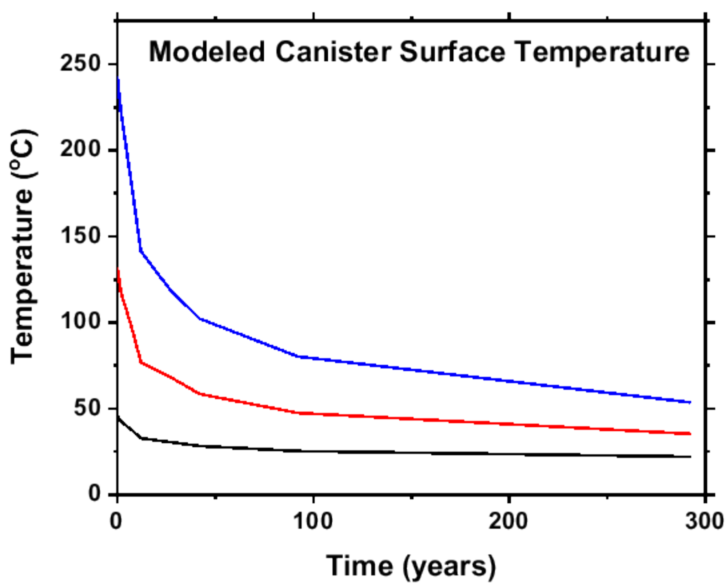


- Initial assumption of sea water brine

C.R. Bryan et al., Science of the Total Environment, Under Review, (2022)

Salt Composition and Concentration Change with RH





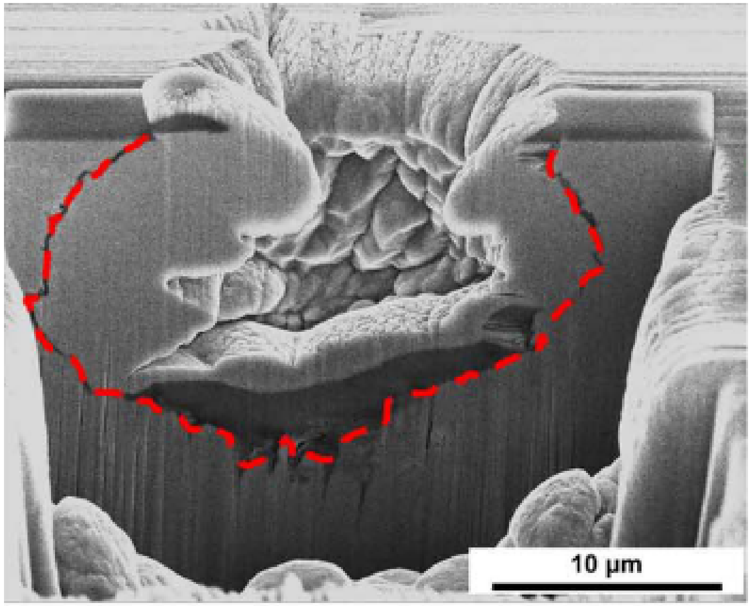
- Initial assumption of sea water brine
- Evaporation of sea water:
  - Concentration of chloride (Cl^-)
  - Change in brine composition (~ 75 % RH)
- Canister surface physically hot

Need to inform upon localized corrosion across a wide range of chloride concentration (dilute NaCl to saturated $MgCl_2$) and temperature (20 – 55 ˚C)

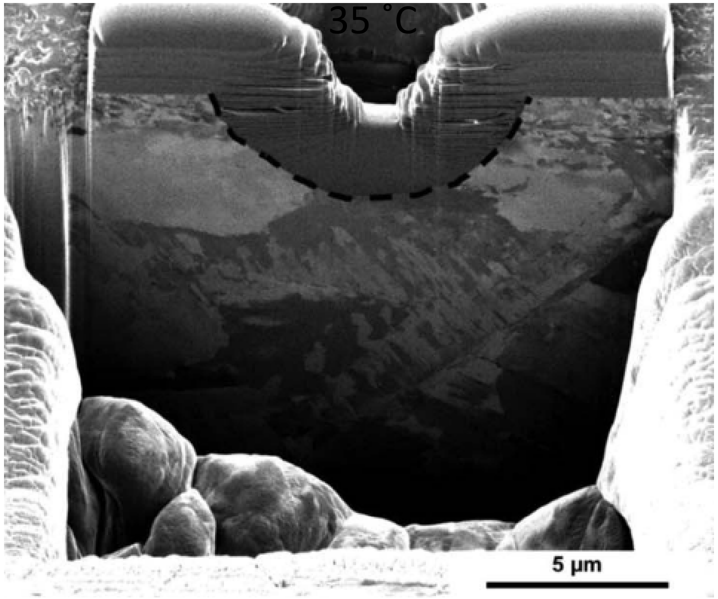
C.R. Bryan et al., Science of the Total Environment, Under Review, (2022)

Future Consideration of Anode Shape

Sample exposed at **40 % RH** and 35 ˚C



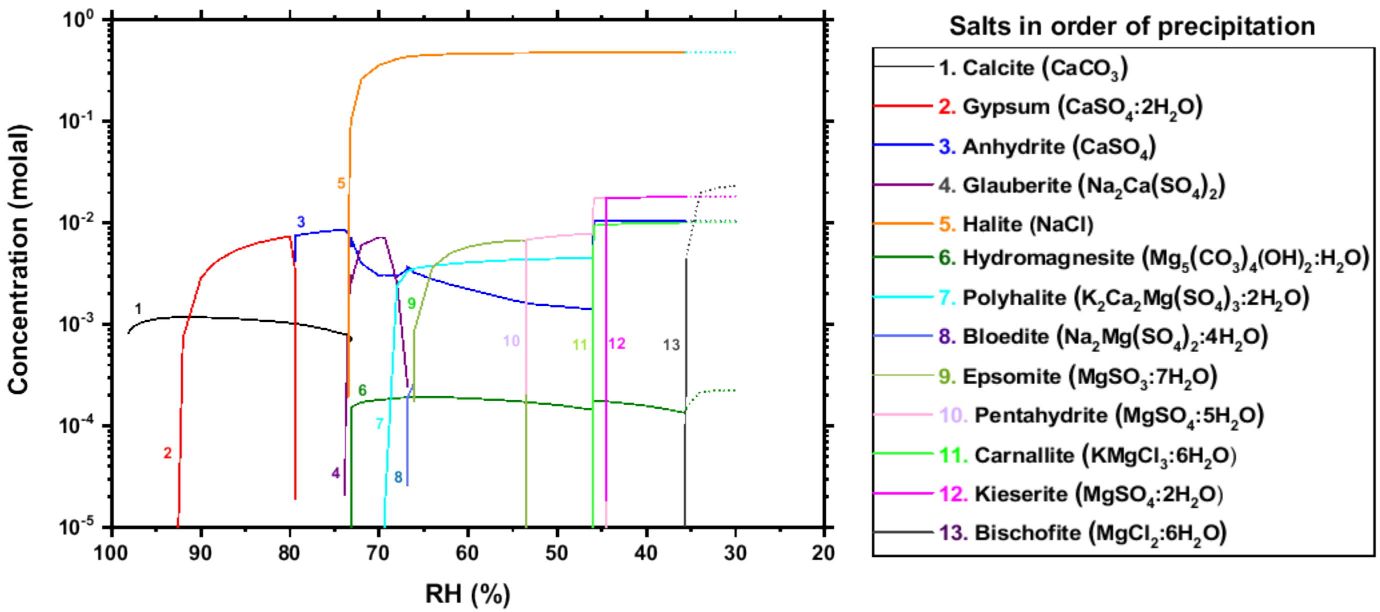
Sample exposed at **76 % RH** and 35 ˚C



- Anode shape dependent upon RH
- Potential influence on diffusion and whether or not propagation is under a salt film
- Pit kinetics are a function of position (what is the bounding case?)

T.D. Weirich, et al., Journal of The Electrochemical Society, 166 (2019) C3477-C3487.

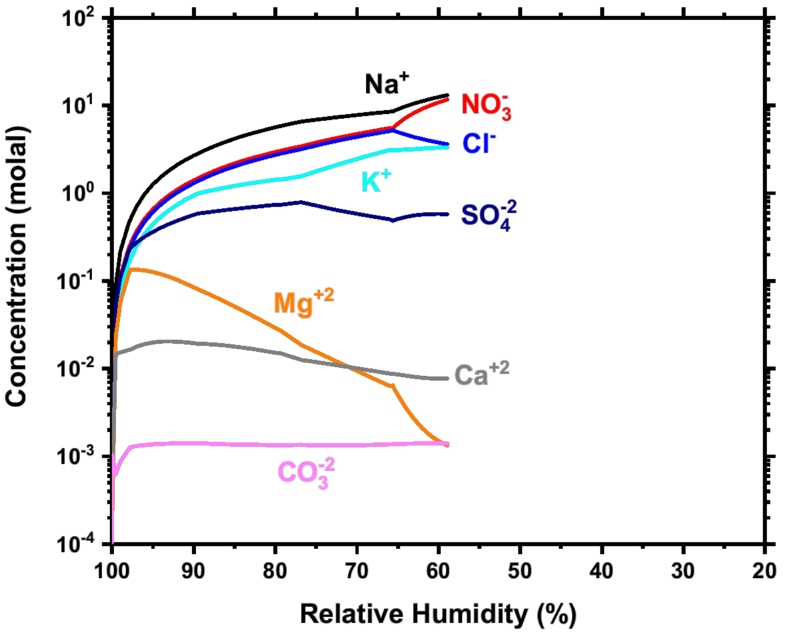
Future Consideration of Precipitated Species in Cathode

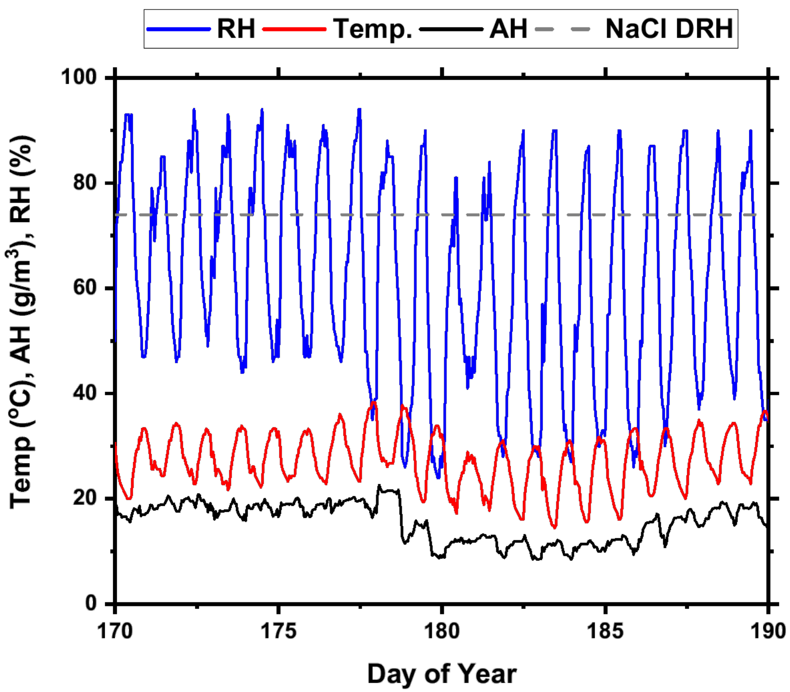


C.R. Bryan et al., Science of the Total Environment, Under Review, (2022)

R.M. Katona et al., Electrochimica Acta, 370 (2021) 137696.

Salt Composition and Temperature Vary by Location



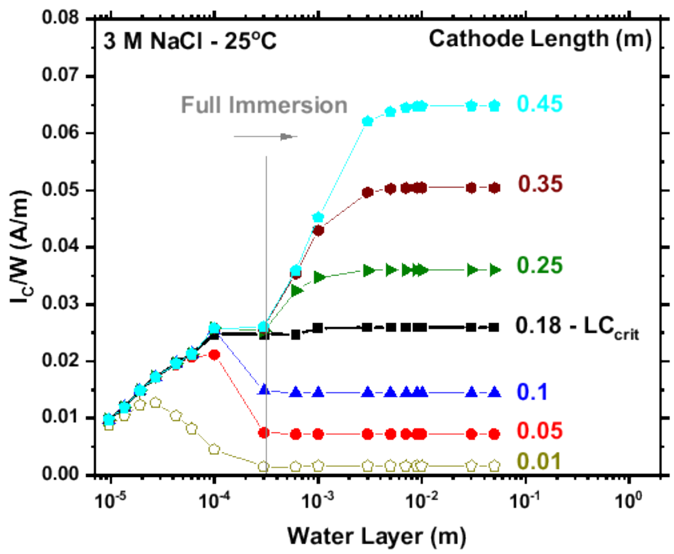


- Composition and deliquescence RH change by geolocation
- Daily/Seasonal temperature and RH changes

Model can be adapted to predict pit size as a function of location and daily fluctuations

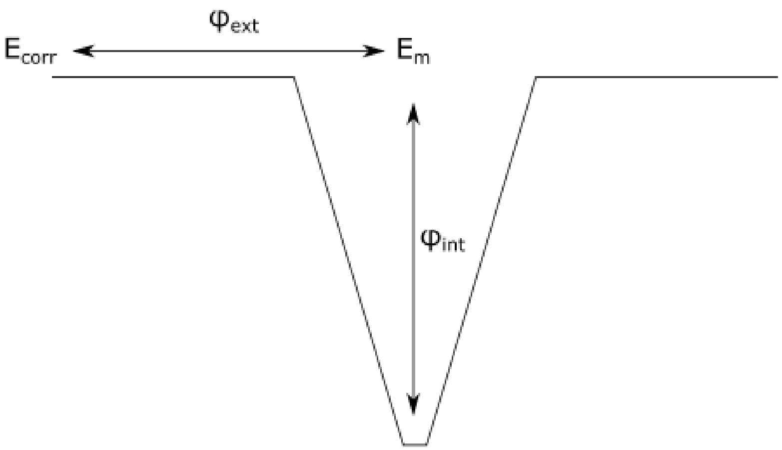
Framework can be combined with kinetic information

What We Know from Galvanic Couples

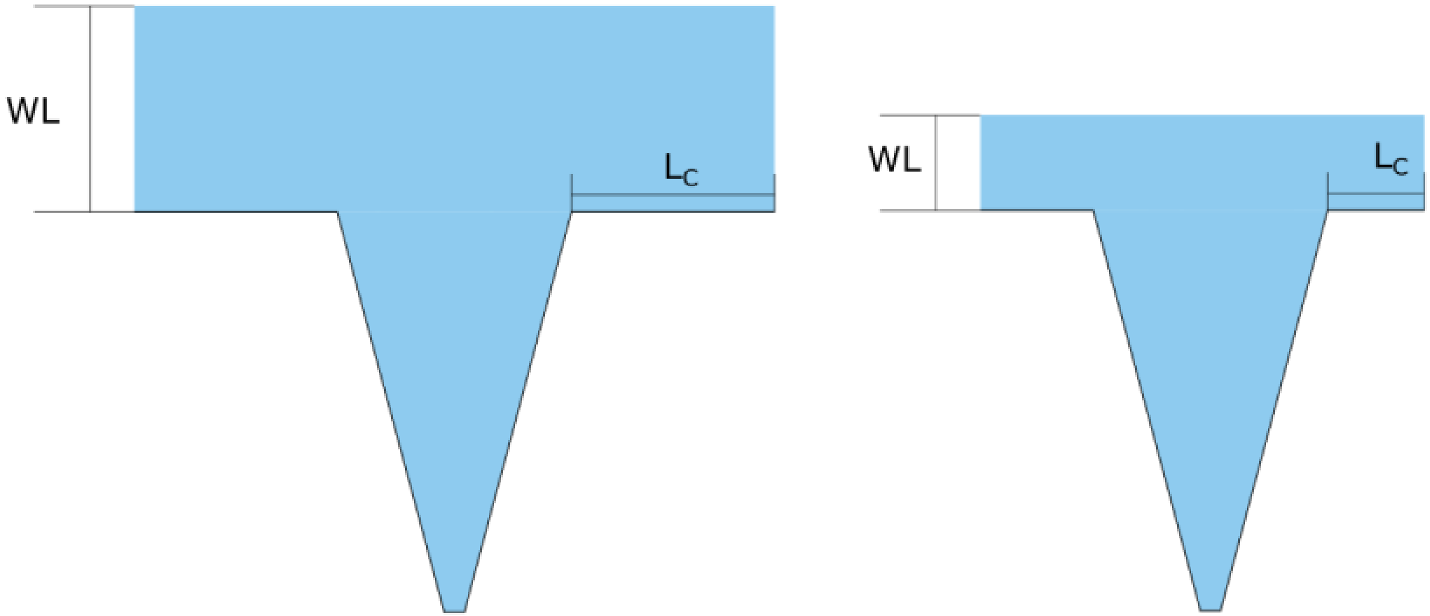


- Galvanic coupling model with fixed boundary conditions
- ***Strong coupling of the WL thickness and cathode length***
- Delineation between thin film and bulk conditions

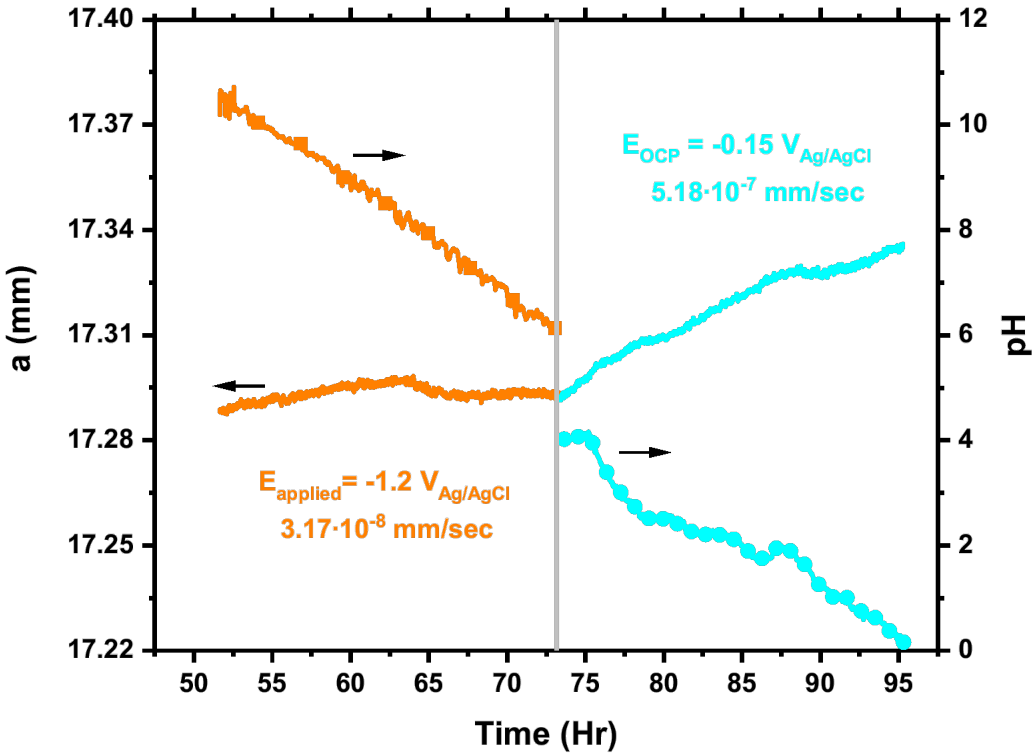
What's Missing in SCC models?



- Chemistry dependent boundary conditions
- Diffusion limited ORR
- Influence of external environment
  - Size sample
  - WL thickness



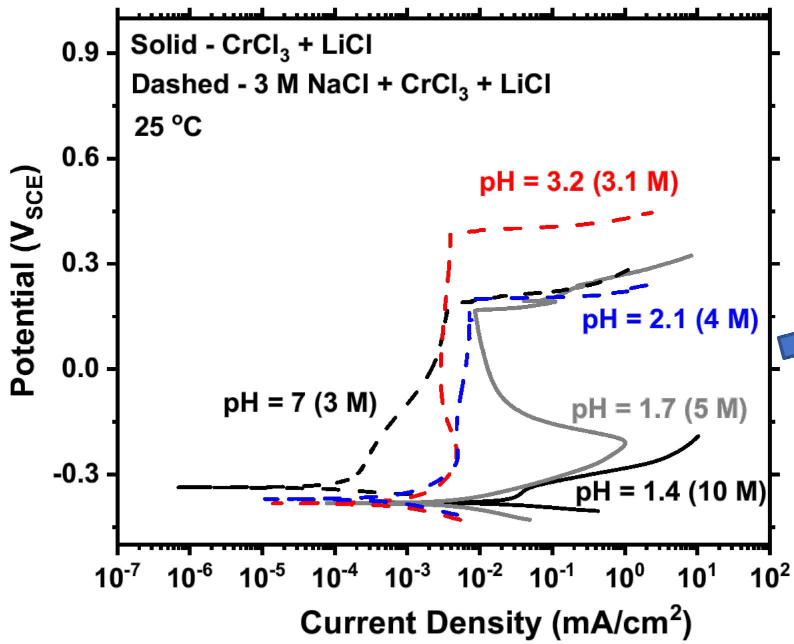
In-situ Crack Tip Measurements

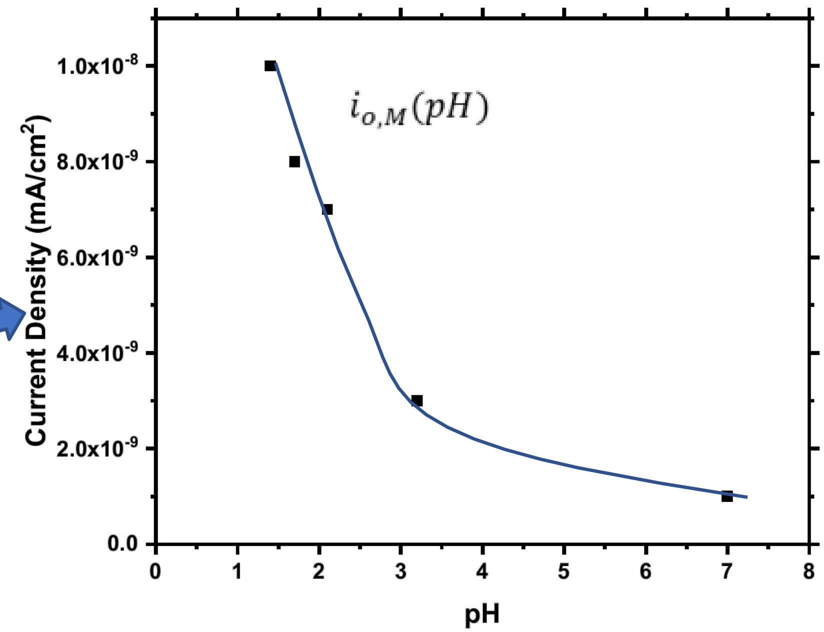


- Cathodic charging over long time periods has a low crack growth rate and pH decreases
- Changing from cathodic polarization to floating conditions, increases crack growth and decreases the crack tip pH significantly

- Minor anodic polarizations increase crack growth rates, more than cathodic charging
  - Further suggests susceptibility to anodic dissolution

Current Model Accounts for Changing Electrochemistry



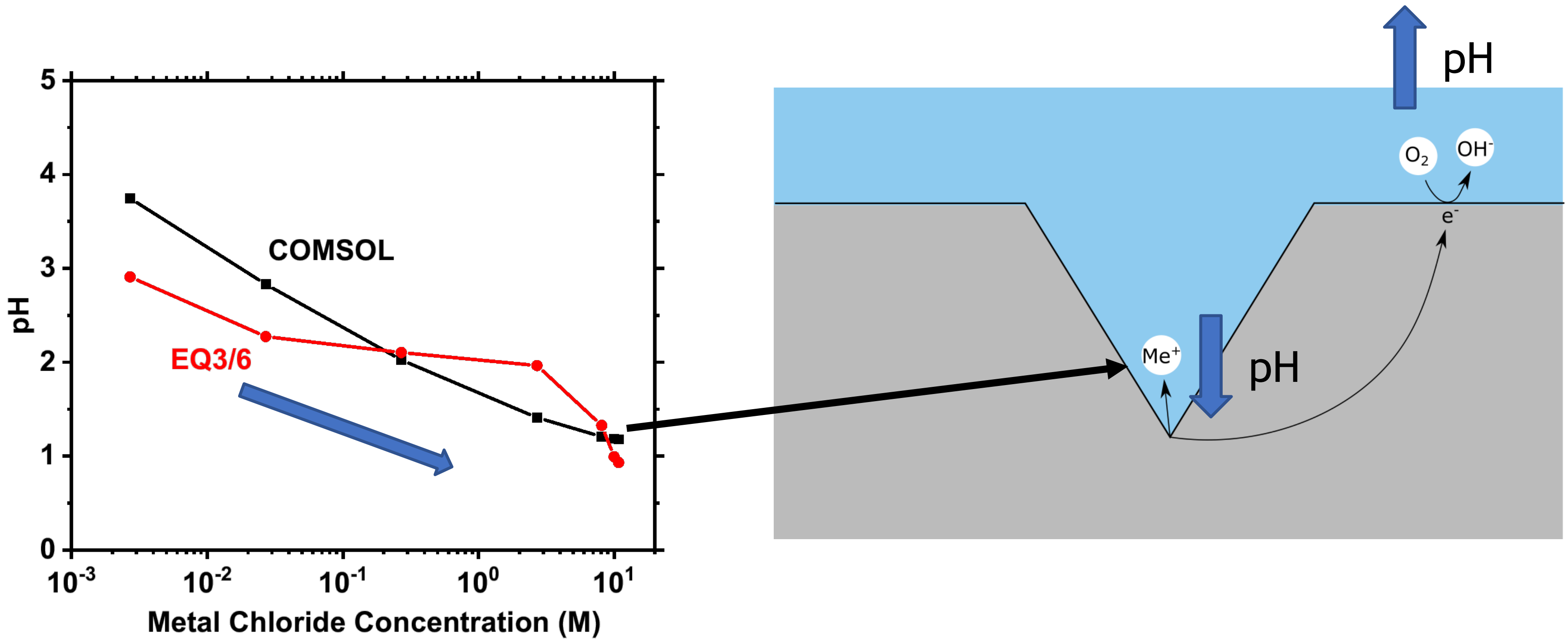


- Measured electrochemical parameters as a function of pH

$$i_{act,M}(pH) = i_{o,M}(\mathrm{pH}) \cdot 10^{\frac{\eta_M}{A_M}}$$

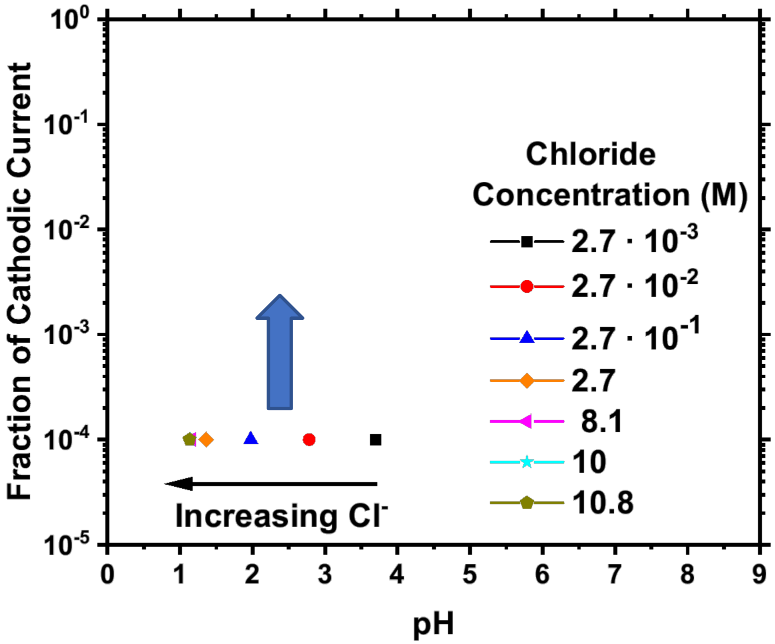
$$i_M(pH) = \frac{i_{act,M}(pH)}{1 + \frac{i_{act,M}(pH)}{i_{pass,M}(pH)}}$$

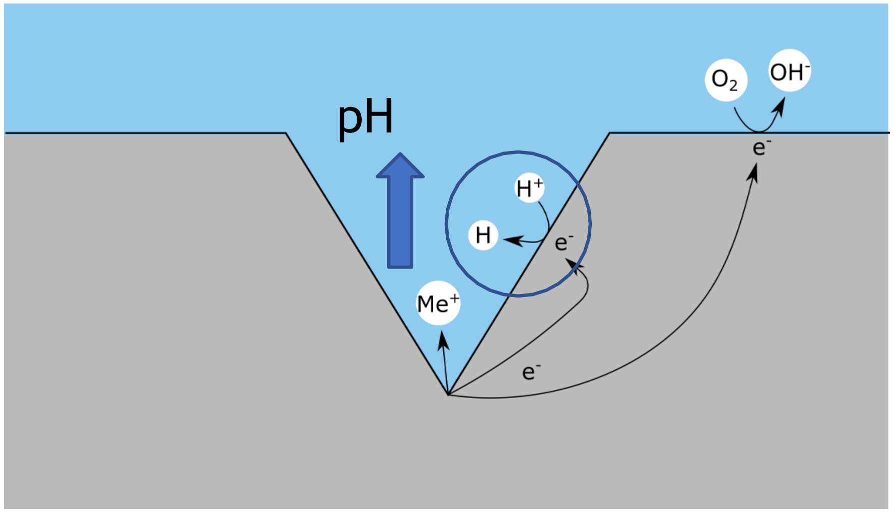
Local Cathodic Current Influences Solution pH



- Similar pH's when comparing concentration (COMSOL) and activity based calculations (EQ3/6)
  - Just metal chloride concentration (*i.e.,* $FeCl_2$, $CrCl_3$, $NiCl_2$)

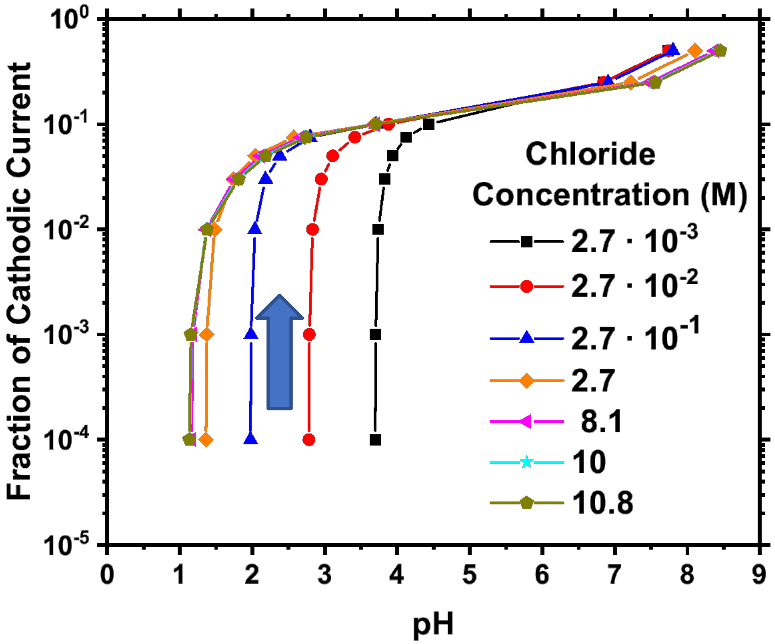
Local Cathodic Current Influences Solution pH

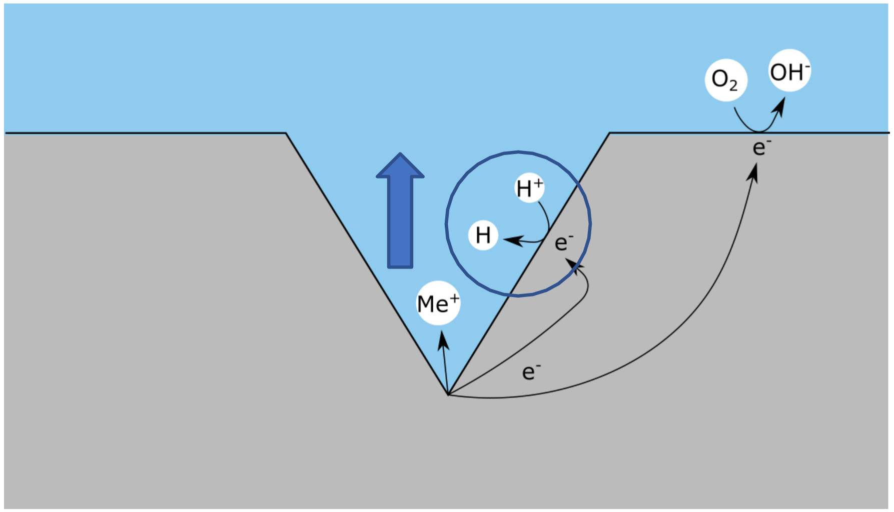




$$\text{Fraction of Local Cathodic Current} = \frac{i_{cathodic}}{i_{anodic}}$$

Local Cathodic Current Influences Solution pH



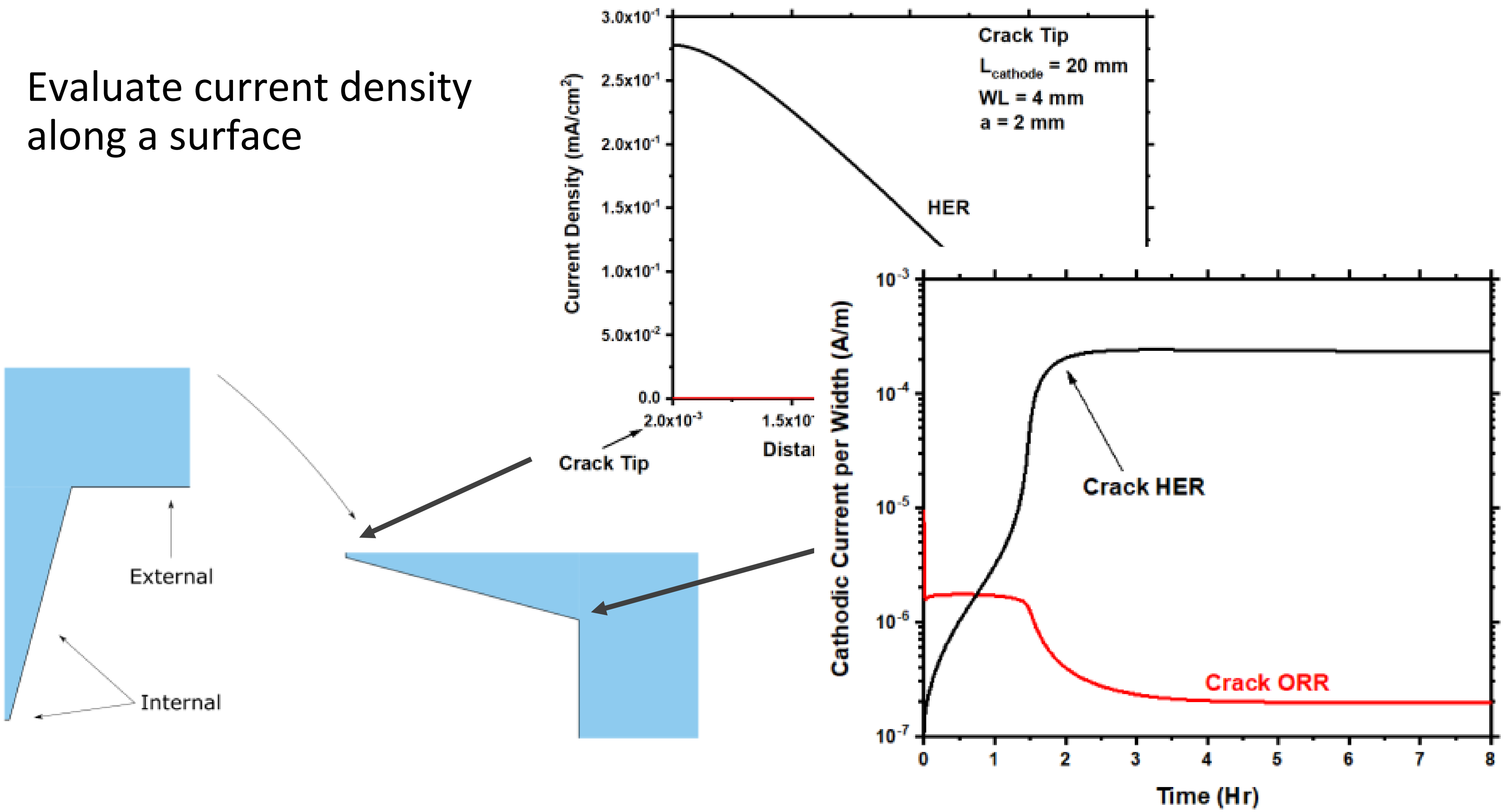


$$\text{Fraction of Local Cathodic Current} = \frac{i_{cathodic}}{i_{anodic}}$$

- pH is a function of both anodic dissolution and local cathodic reactions which are both a function of time

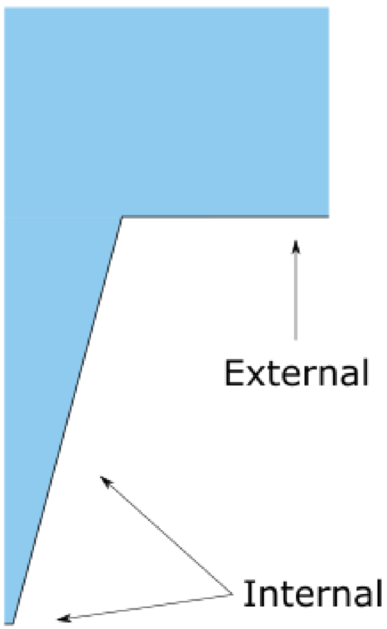
Current per Width Allows Evaluation Over Time

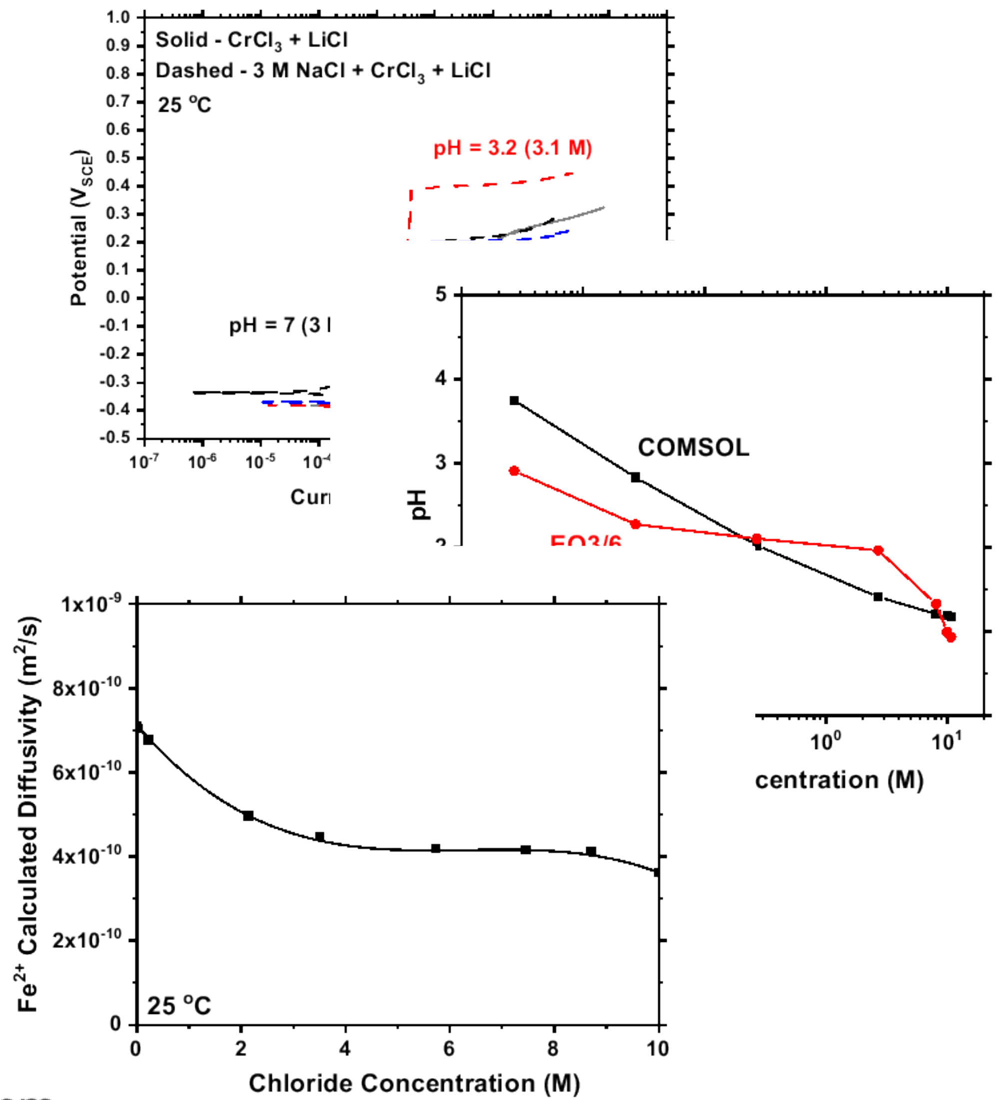
Evaluate current density along a surface



- Integrate to get current per width of a surface over time

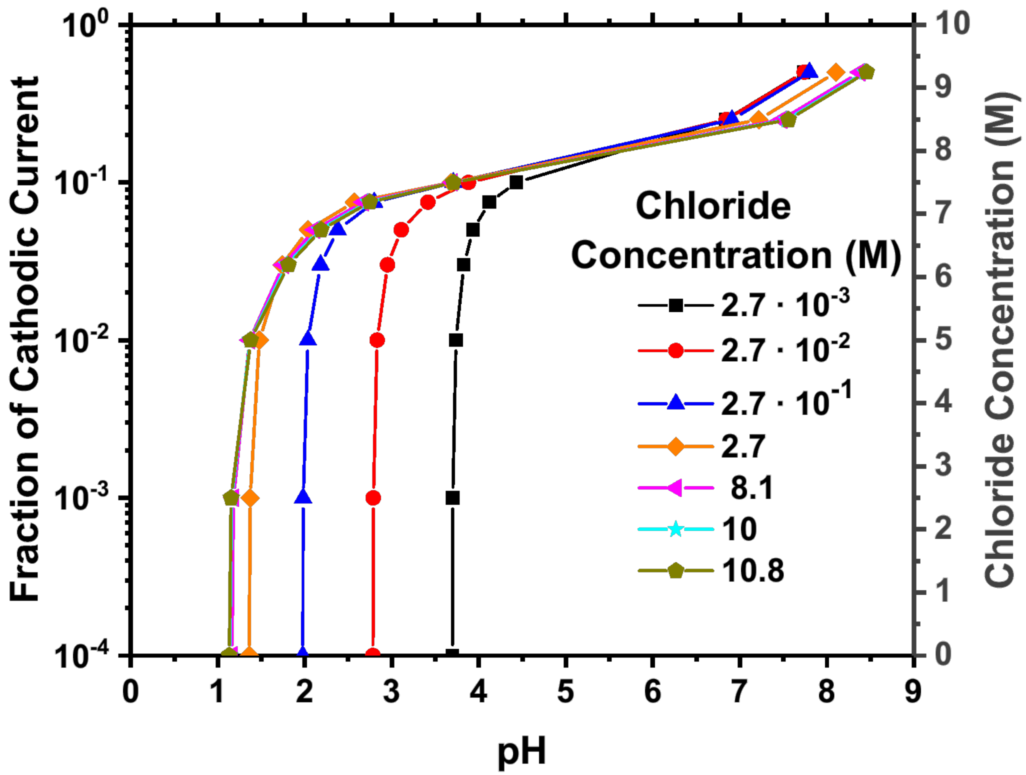
Model Summary



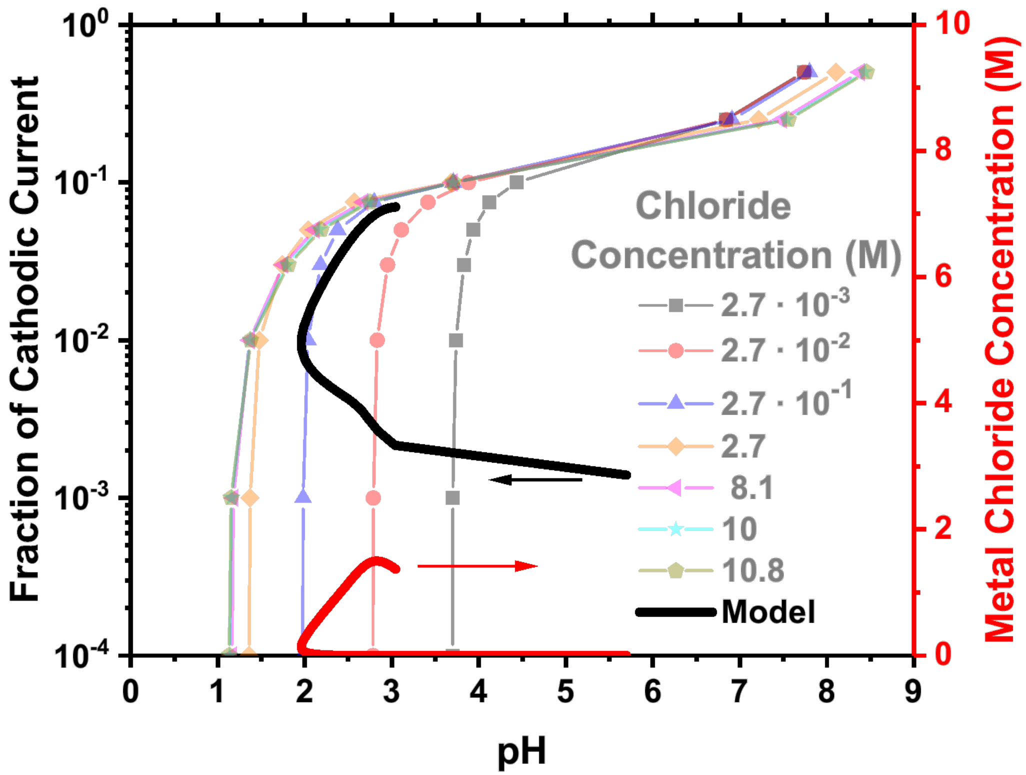


- SS304L in 3 M NaCl, 25 ˚C
  $K = 10\ MPa\sqrt{m}$
- WL = 5 mm, L_C = 20 mm, a = 2 mm

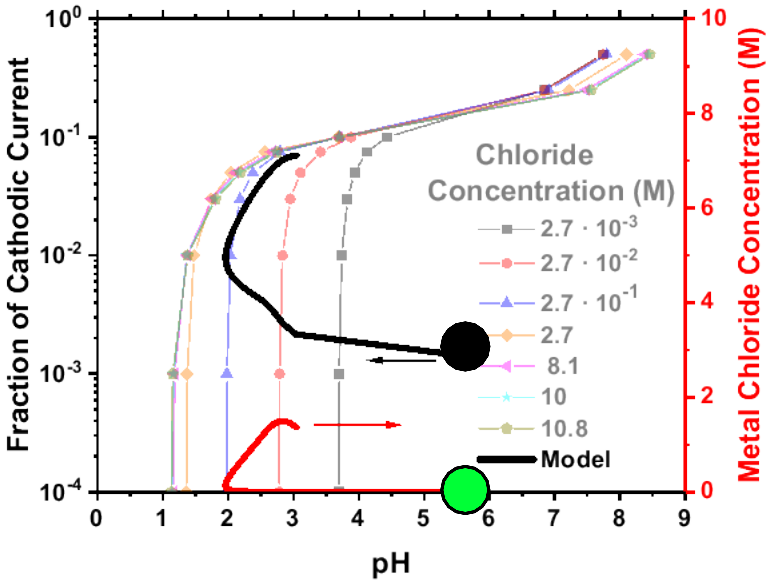
Crack tip pH Initially Decreases but Increases to Reach a Steady State

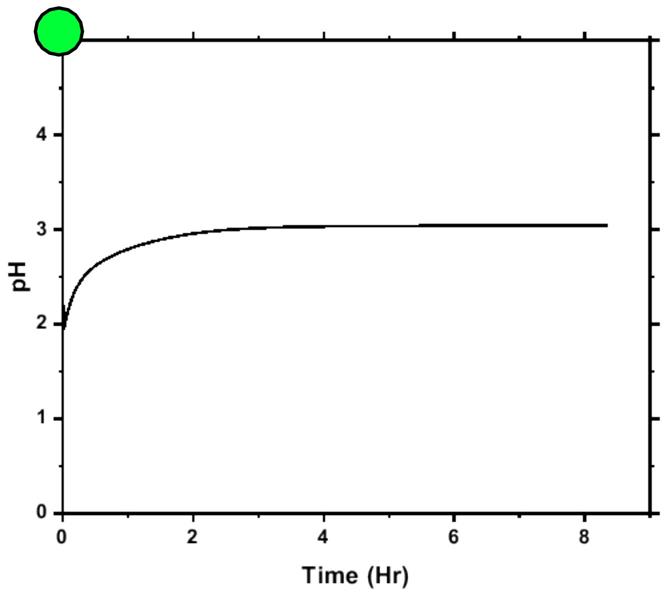


Crack tip pH Initially Decreases but Increases to Reach a Steady State

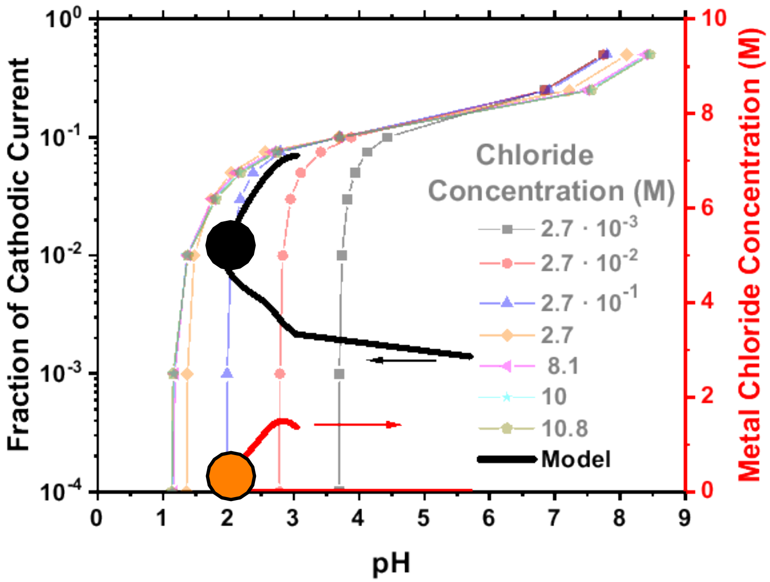


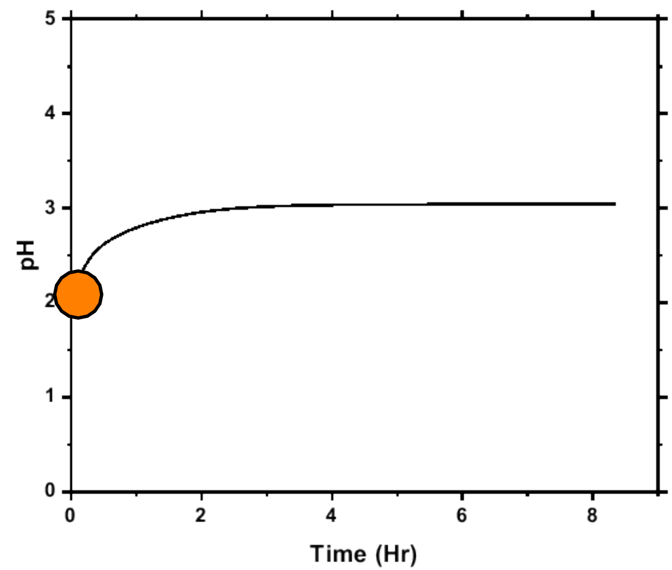
Crack tip pH Initially Decreases but Increases to Reach a Steady State





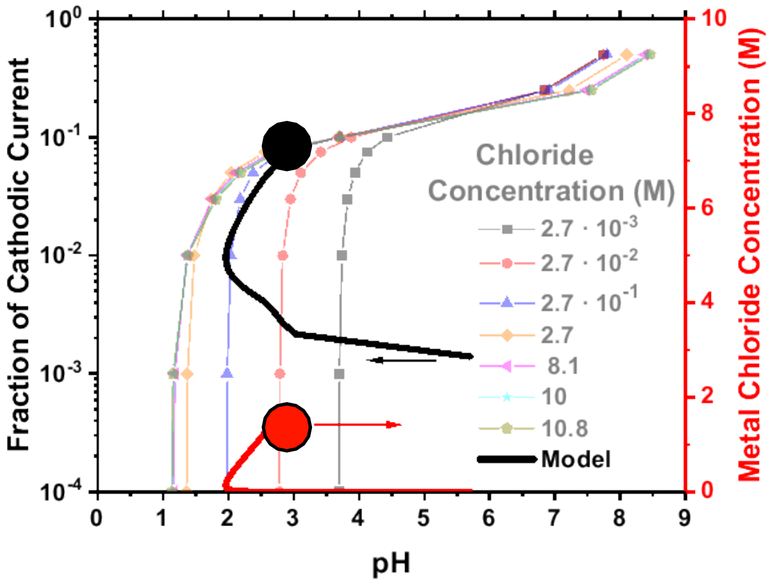
Crack tip pH Initially Decreases but Increases to Reach a Steady State

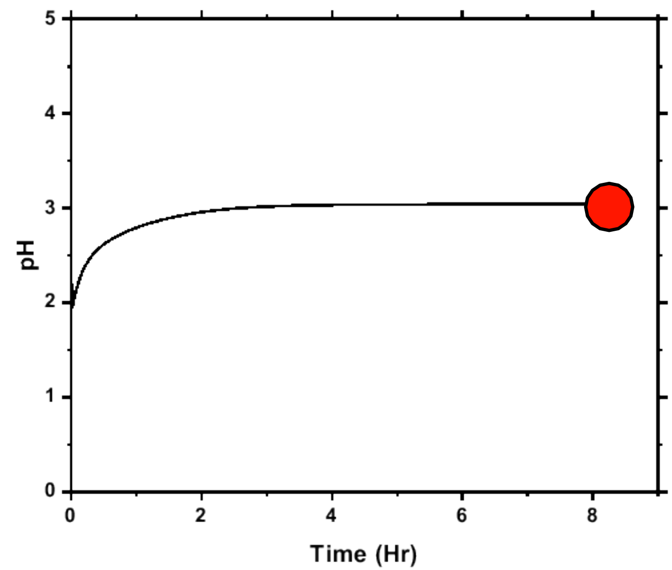




Decrease in pH, increases local cathodic reactions, causing for a subsequent pH rise

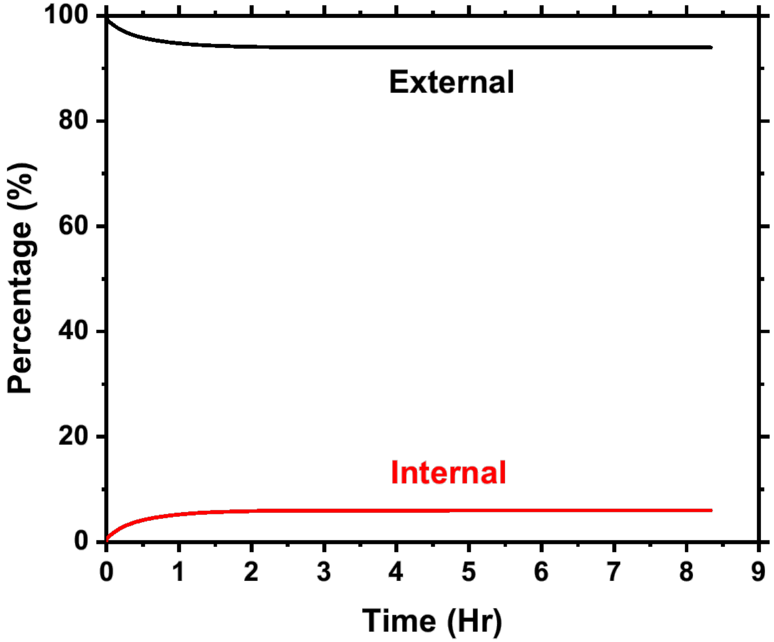
Crack tip pH Initially Decreases but Increases to Reach a Steady State

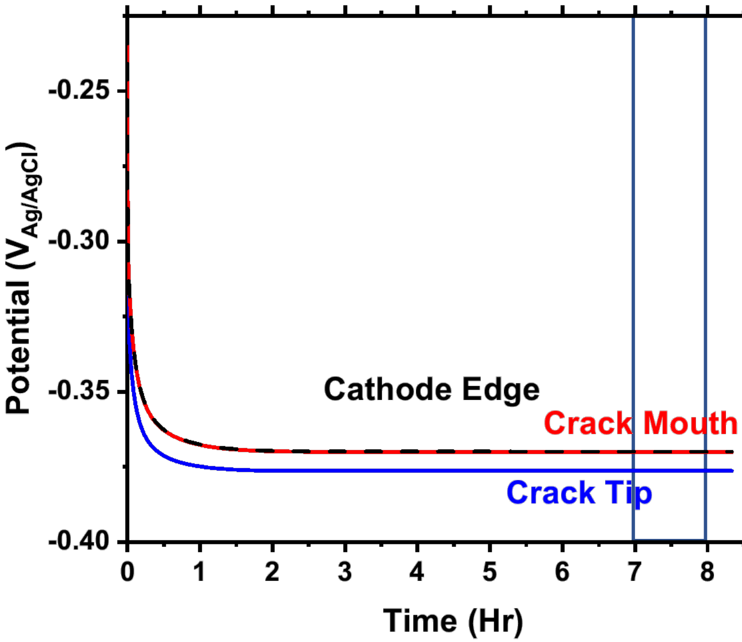




'High' pH due to significant contribution from local cathodic current

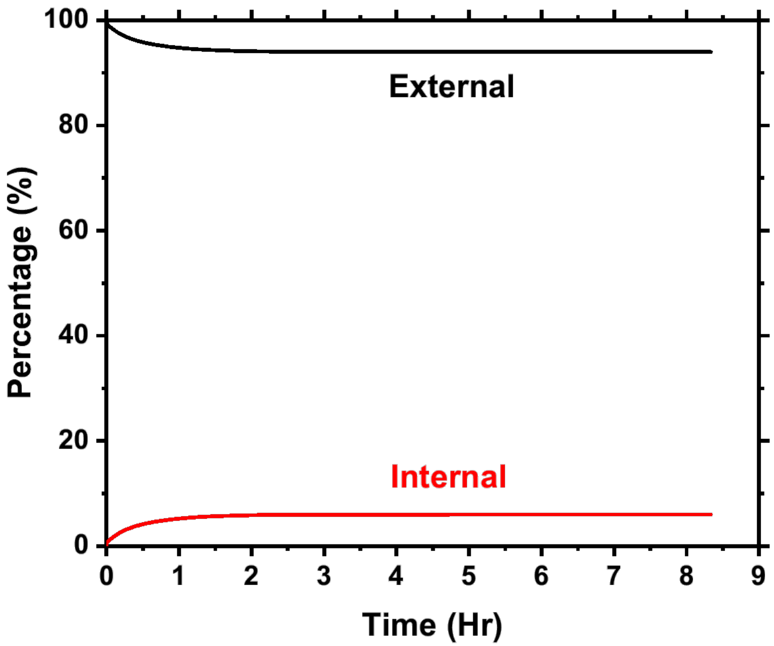
Cathodic Current External to Crack and Crack Tip Polarized Negatively compared to Cathode

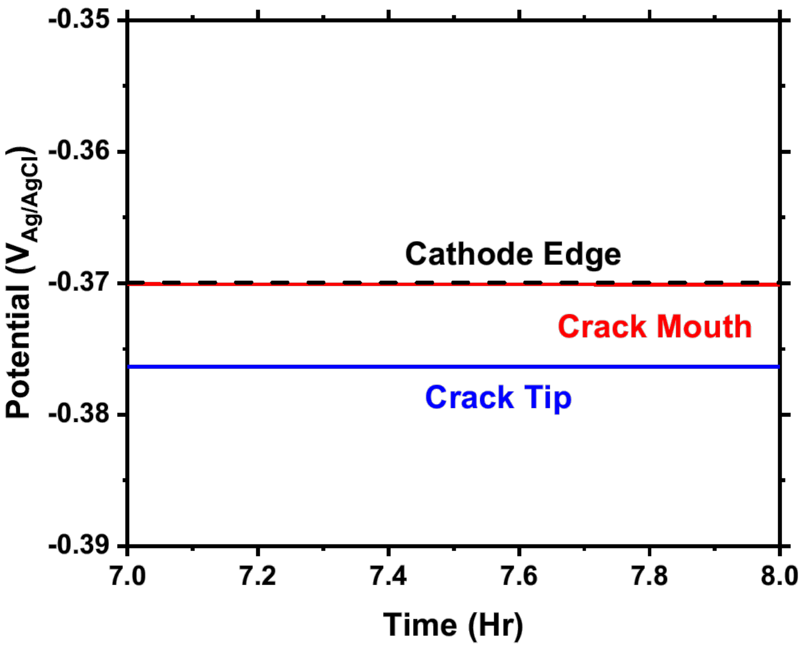




- Majority of cathodic current on external surface due to oxygen reduction reaction (ORR)
- Crack tip polarized negatively with respect to cathode edge

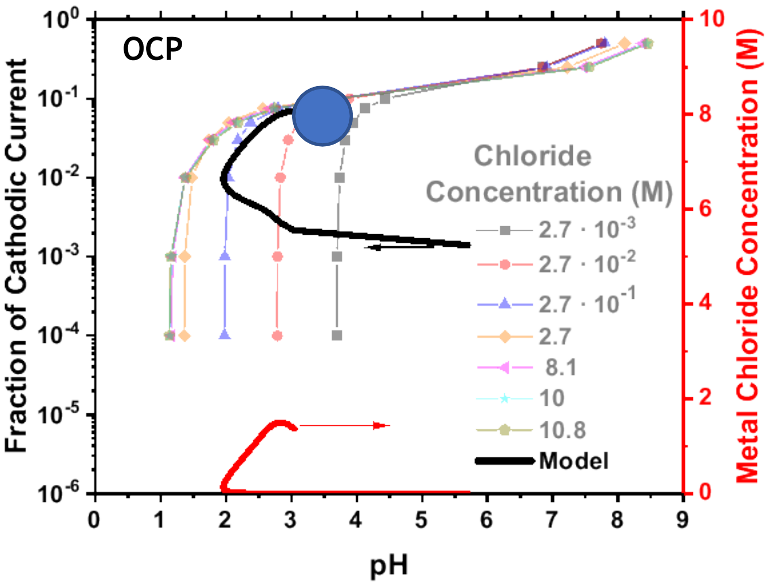
Cathodic Current External to Crack and Crack Tip Polarized Negatively compared to Cathode

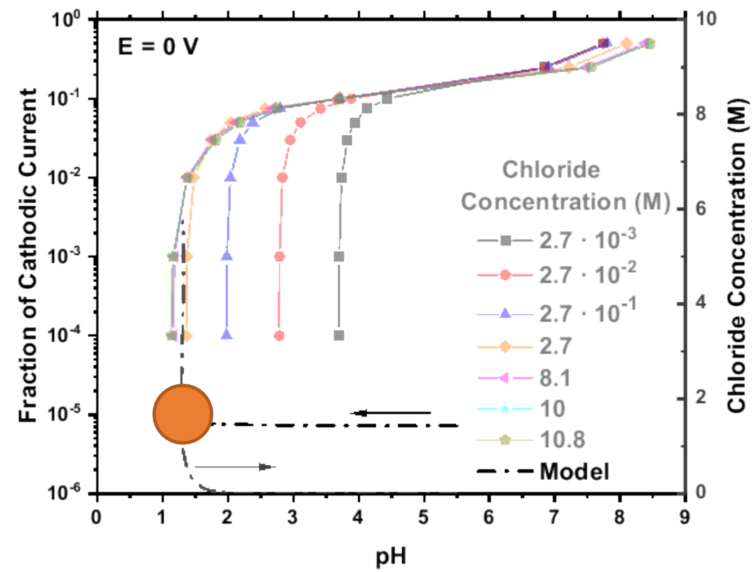




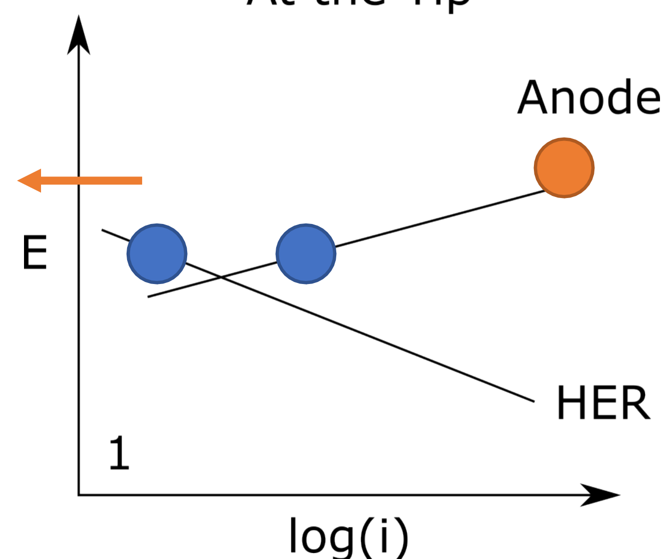
- Majority of cathodic current on external surface due to oxygen reduction reaction (ORR)
- Crack tip polarized negatively with respect to cathode edge
- Cathode edge and crack mouth near same potential
  - ***Limited potential drop on the external surface***

Increasing External Potential Decreases Local Cathodic Reactions



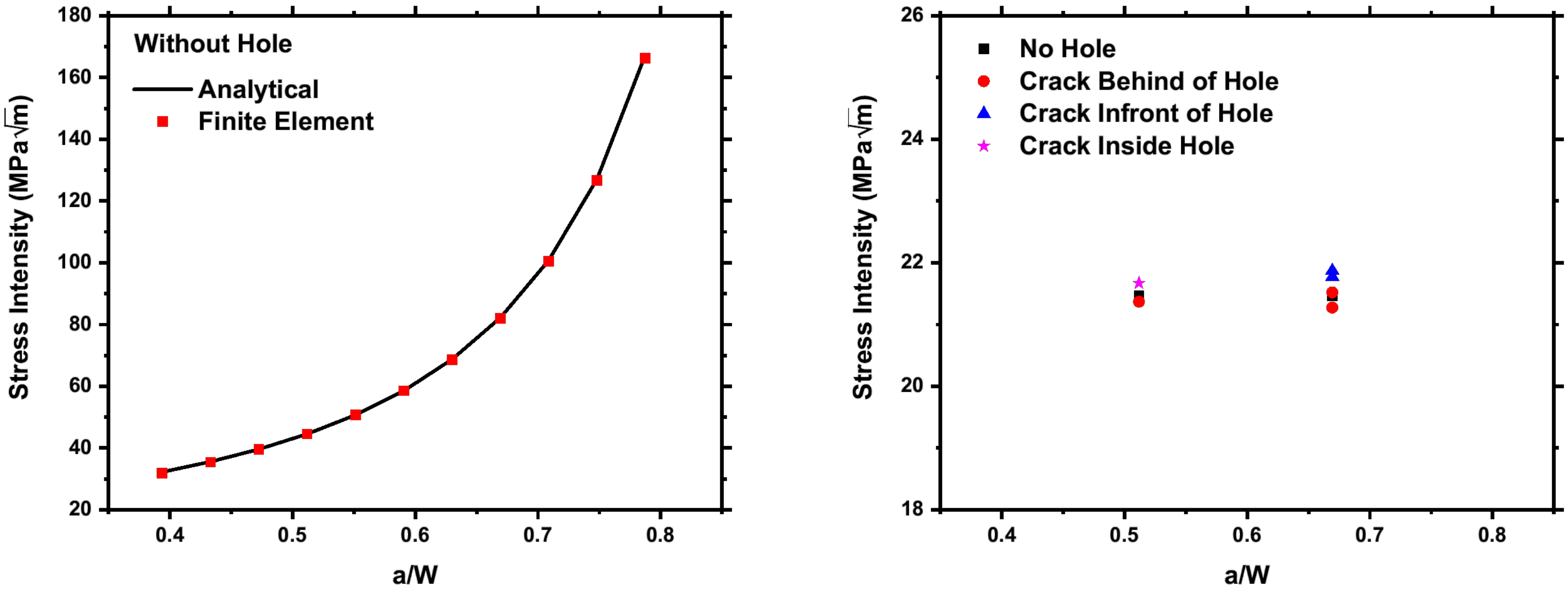


At the Tip



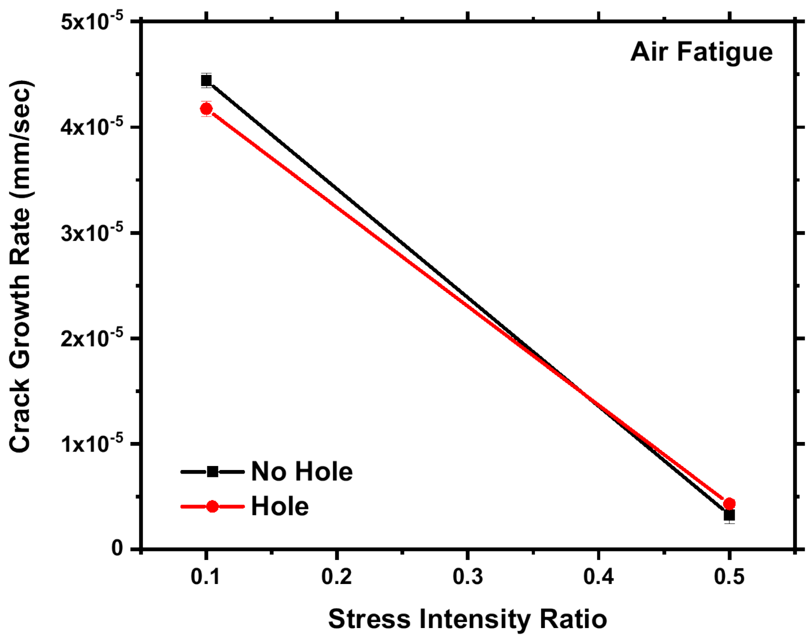
- Increasing external potential increases crack tip potential
- Decrease in local cathodic current
- ***Overall increase in crack tip severity***

Holes do not change mechanical driving force

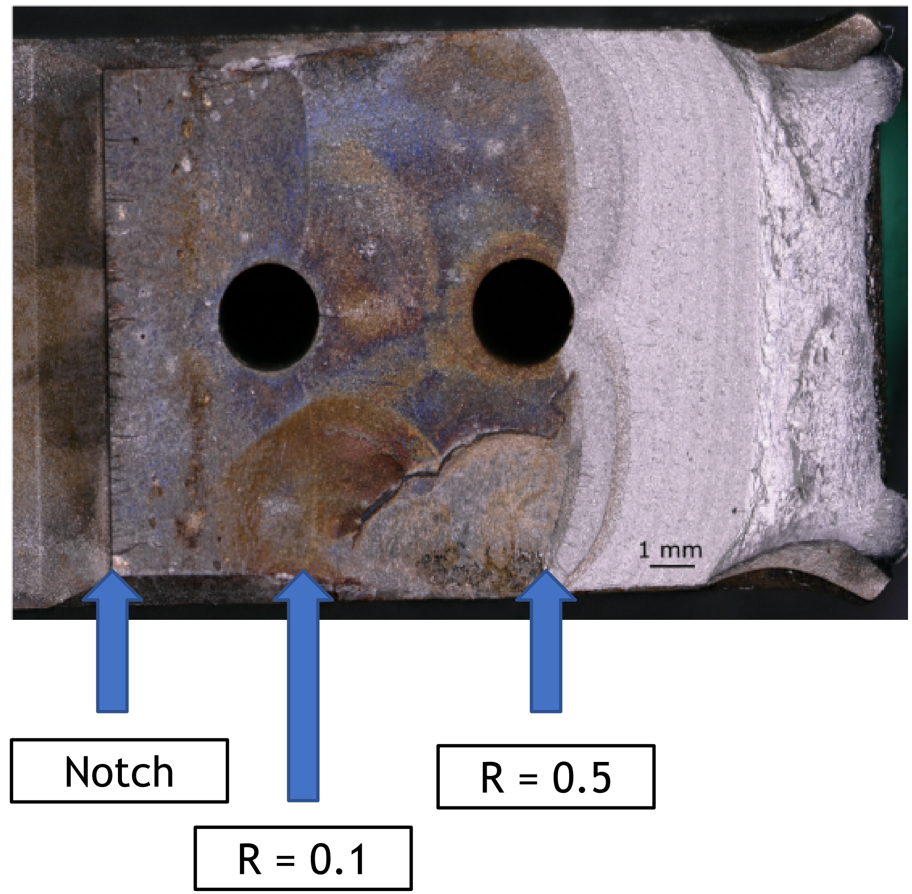


- Without hole, 3D simulations of stress intensity match analytical solution
- Hole location causes variation in stress intensity of ± 0.2 $MPa\sqrt{m}$ at the stress intensity values of interest
  - ***Hole location should not change mechanical driving forces***

Holes do not change air fatigue crack growth rate

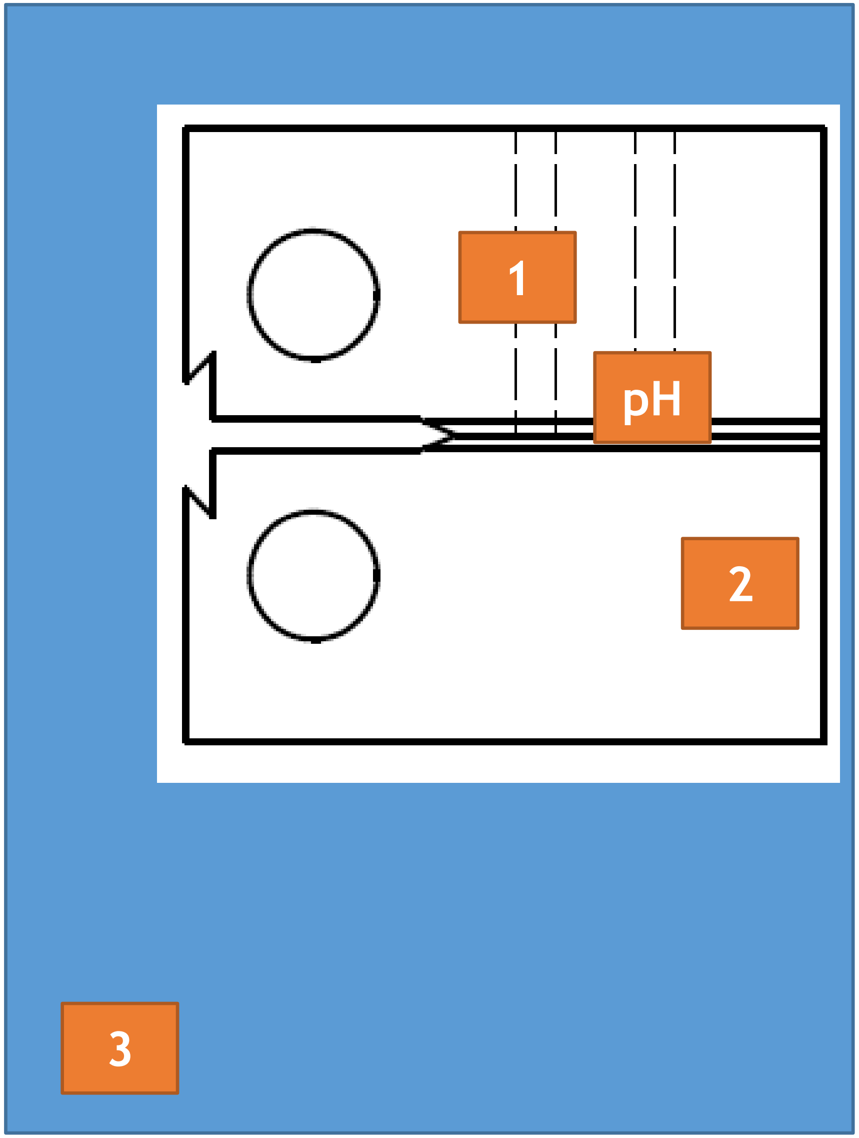


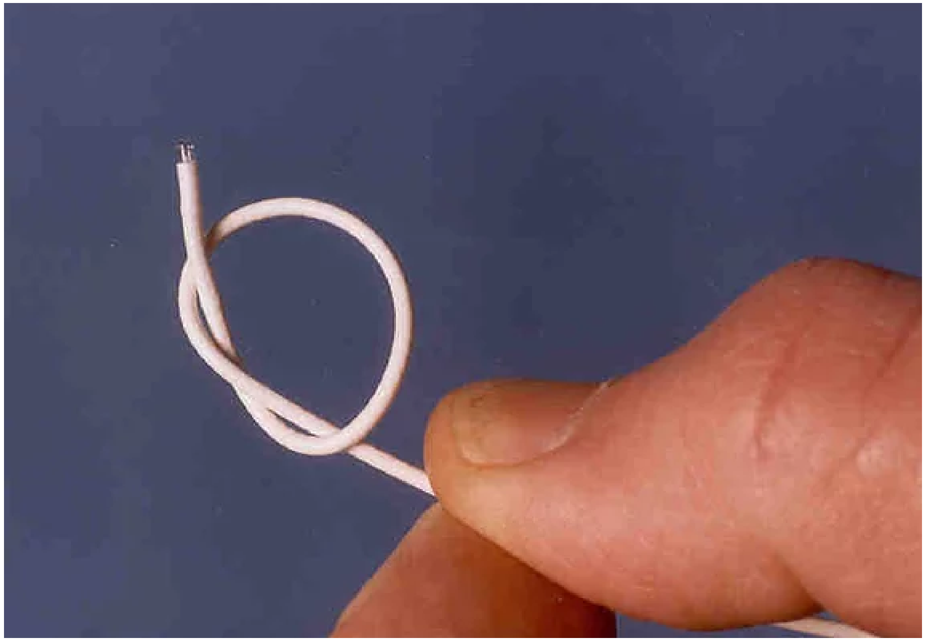
- Air fatigue of specimens with and without holes
- No difference in CGR



- Minor influences on crack propagation from holes

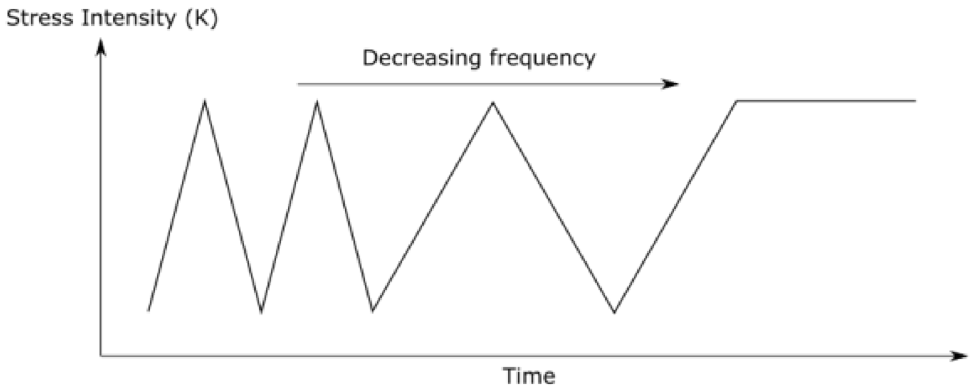
Calibration of Micro pH Probe

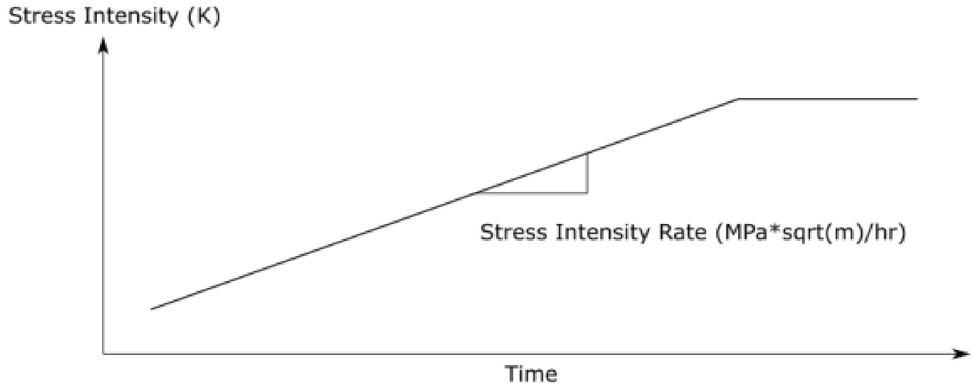




- Half cell pH electrode
- Measuring pH as a function of reference probe location
  - Very little differences in ohmic drop between the different reference probe location

Influences of Loading Protocol

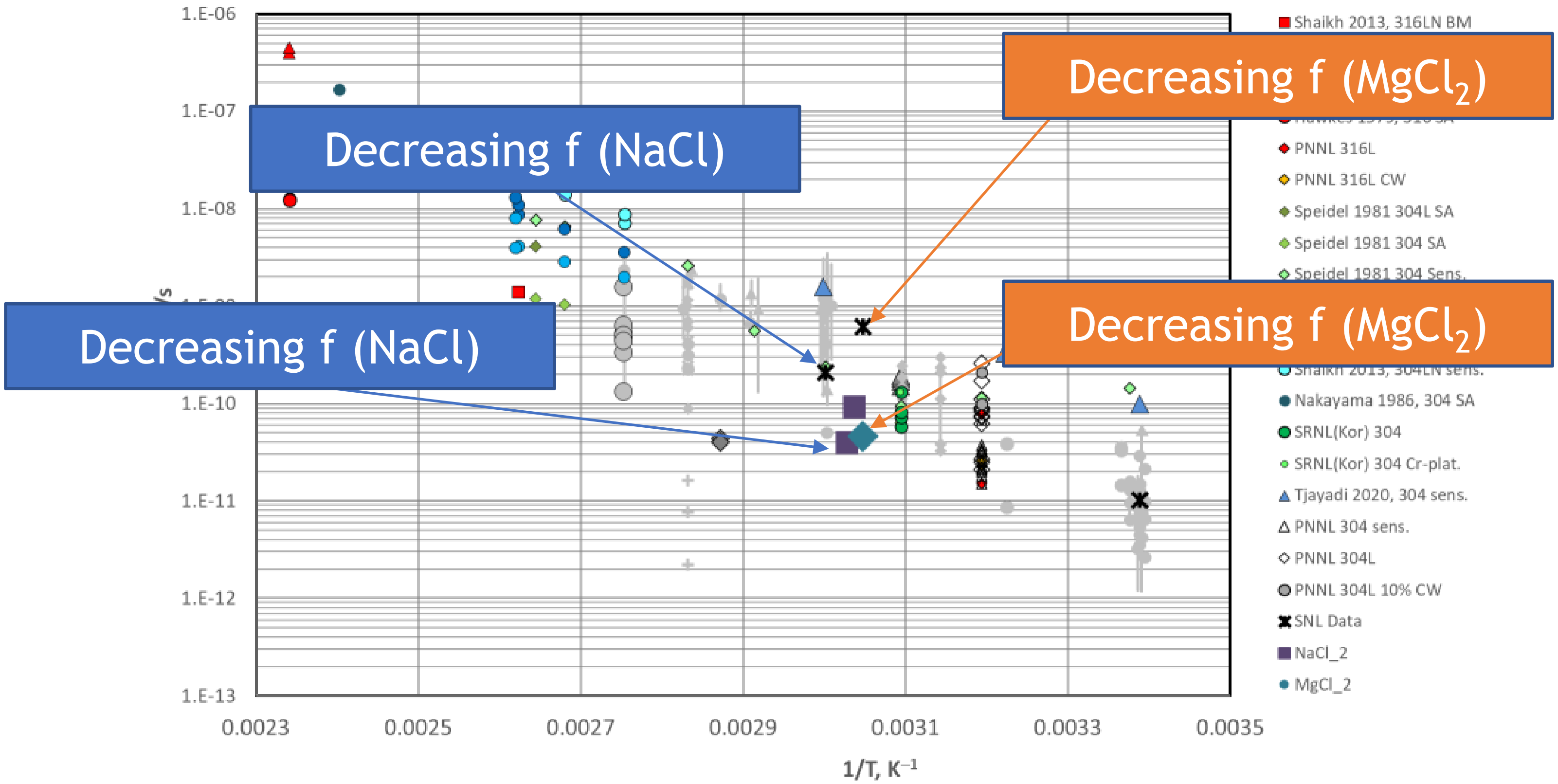




- Decreasing frequency
  - Widely accepted as testing method for BWR environments (Andresen)
  - Promotes SCC behavior of crack by transitioning from transgranular pre-crack to intergranular SCC during constant K
  - Very time consuming (300+ hrs to transition)
- Rising K
  - Used to quickly assess hydrogen embrittlement susceptibility
  - CGR during ramping period dependent on ramp rate
  - Not widely applied
  - Much quicker tests (~ 60 hrs to constant K)

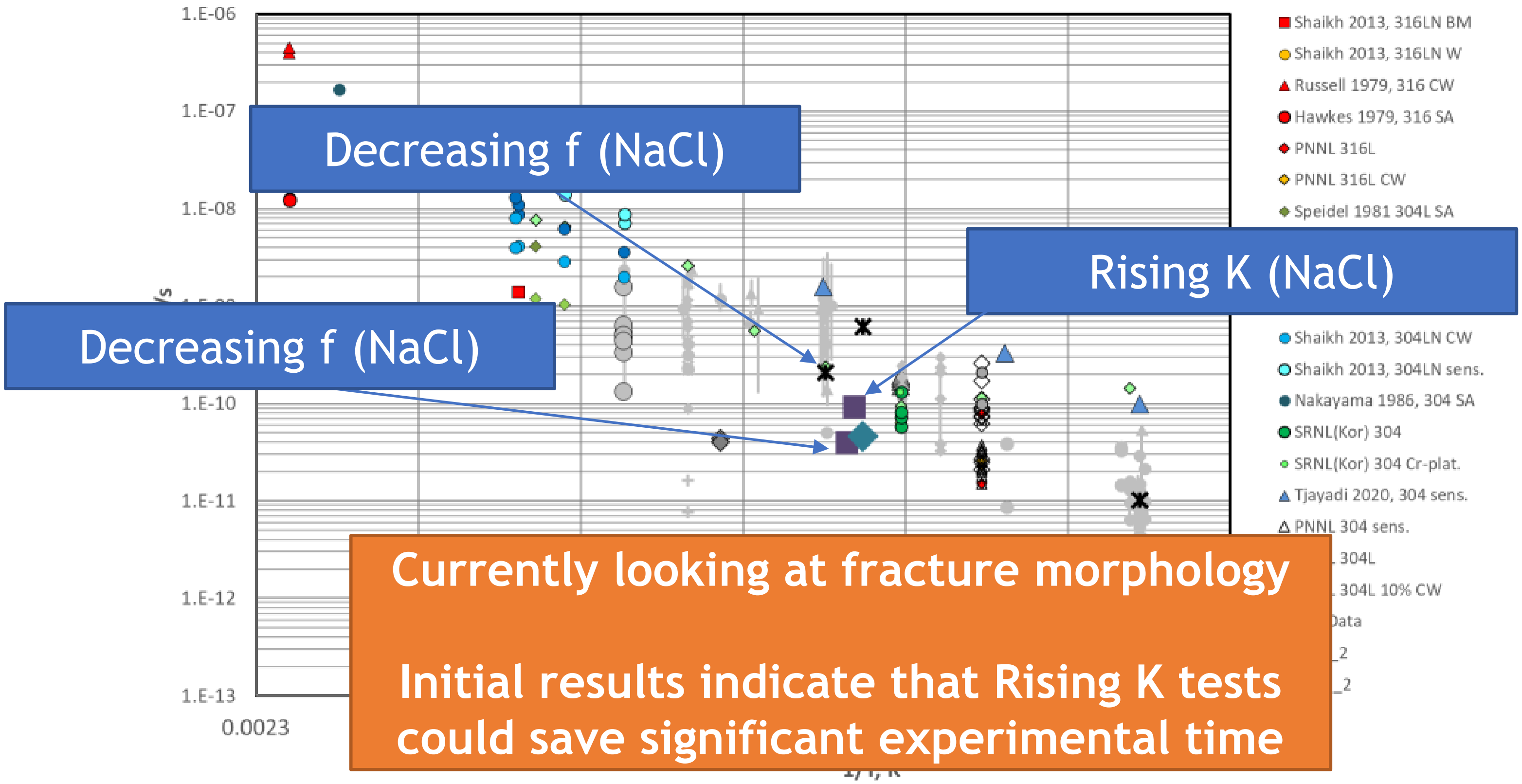
Do both tests produce the same CGR and cracking mode (*i.e.*, inter/intra-granular)?

Comparison of Loading Protocol



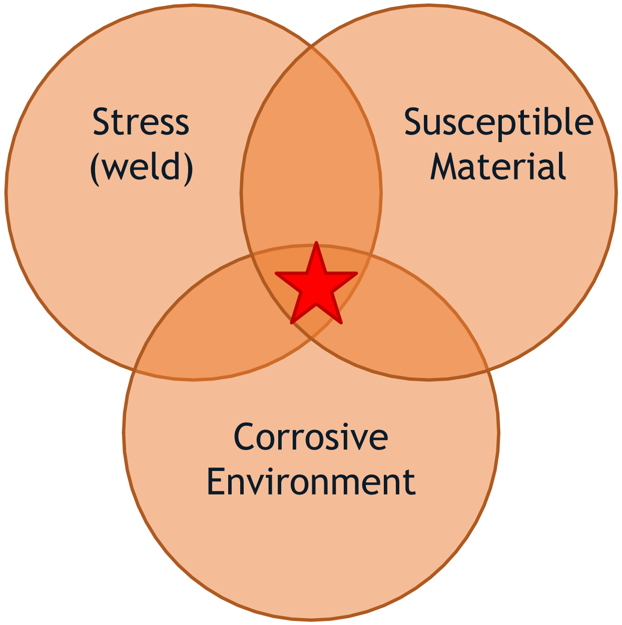
- Scatter within decreasing f tests

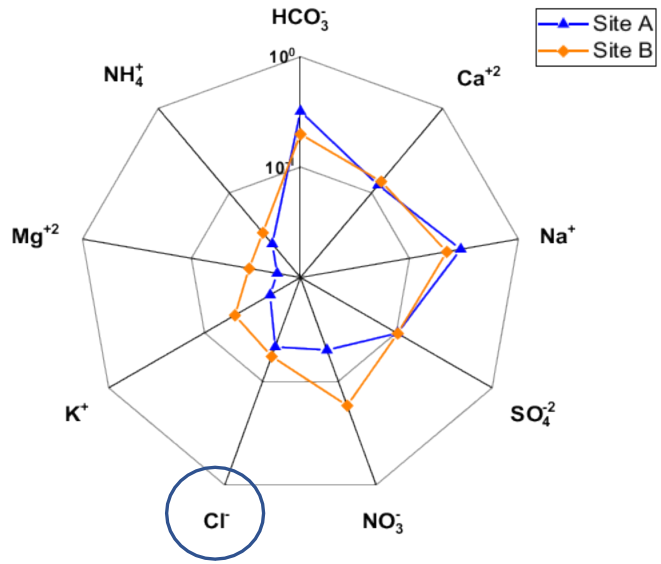
Comparison of Loading Protocol



- Scatter within decreasing f tests
- Rising K is in between the scatter of decreasing f tests

What is Stress Corrosion Cracking (SCC)?

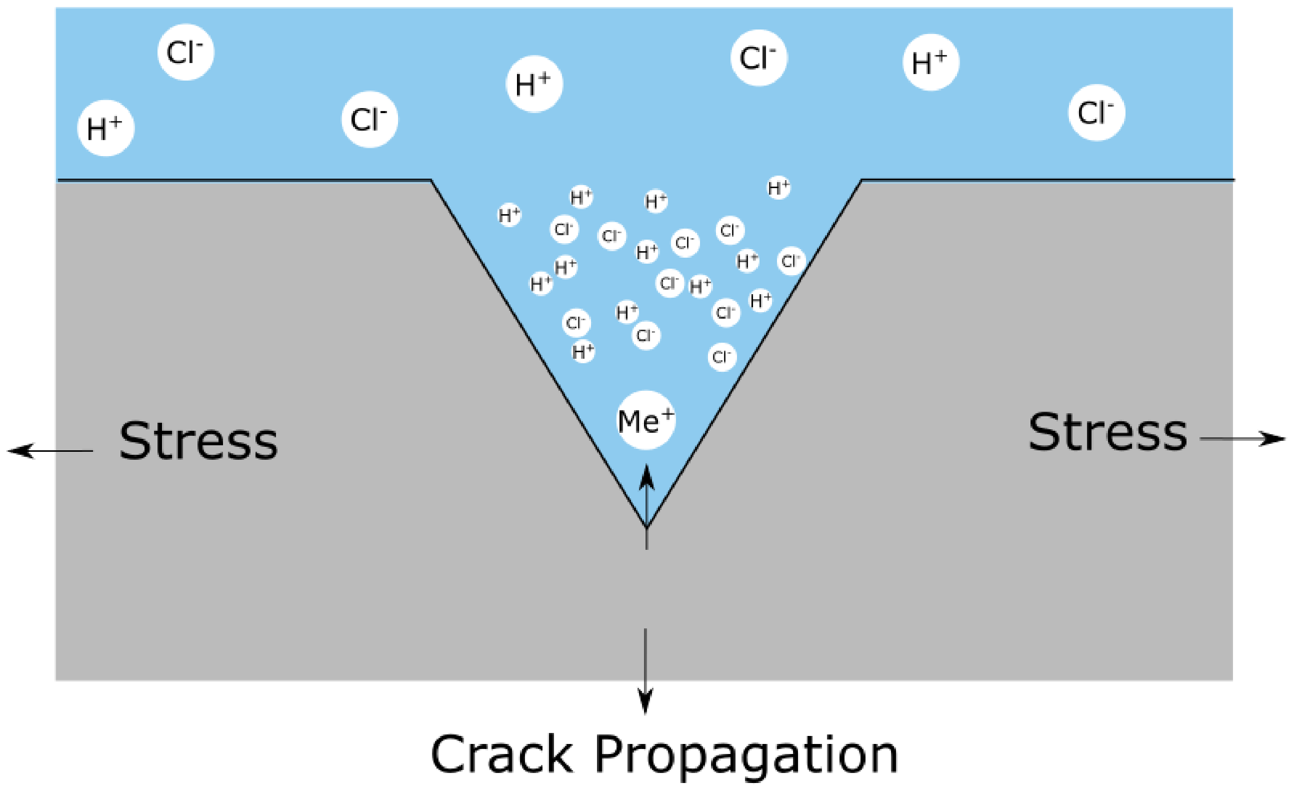




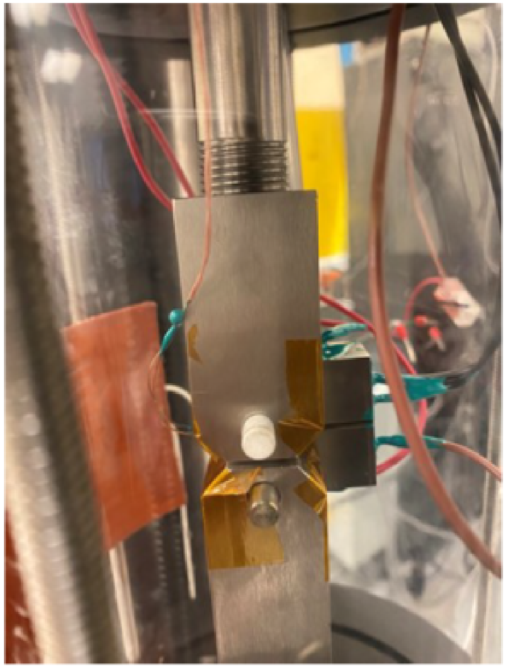
- Stable crack growth of a susceptible material in a corrosive environment below the material's fracture toughness
  - Environmentally assisted cracking, corrosion fatigue, chloride induced stress corrosion cracking, hydrogen embrittlement (sometimes), sulfide induced stress corrosion cracking
  - Mechanisms vary by environment/material system

What is Stress Corrosion Cracking (SCC)?

- *Chloride induced stress corrosion cracking of austenitic stainless steel will be the focus*
  - Generally accepted that H^+ and chloride concentration is elevated in the crack tip

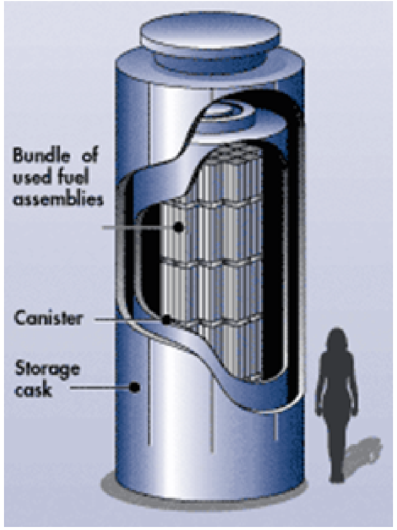


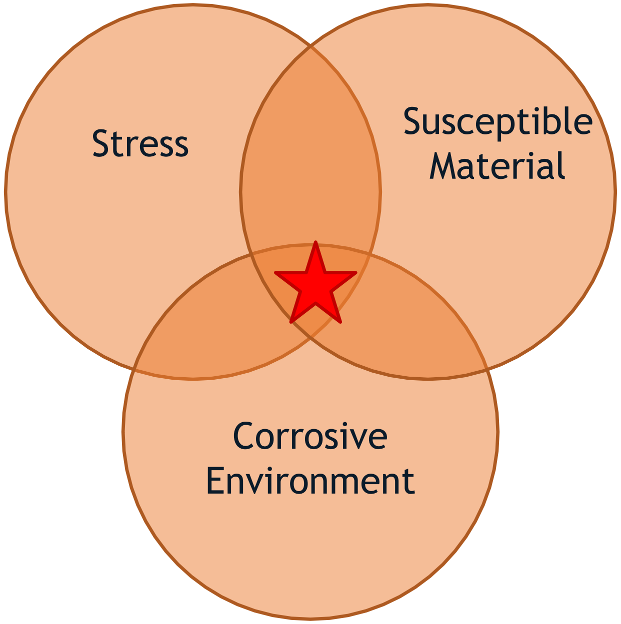
New SCC/CF Capabilities at SNL

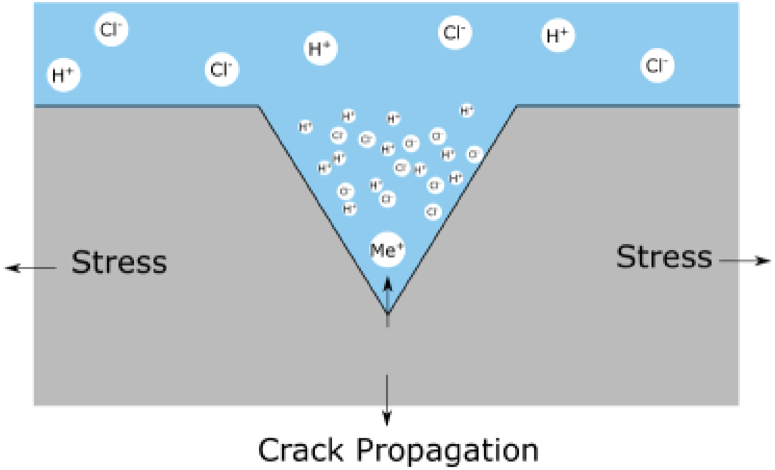


- Measure in-situ crack growth rate in a corrosive solution under flow
  - ~10^{-12} m/sec; 15 kip (66 kN); 1 Hz (10 Hz intermittently) max frequency
- Ability to interface with fluid and gas flow (originally built for H_2S environments)
  - Temperatures over 150 ˚C (flow only up to ~75 C at this point)
- RH/T chamber for atmospheric SCC

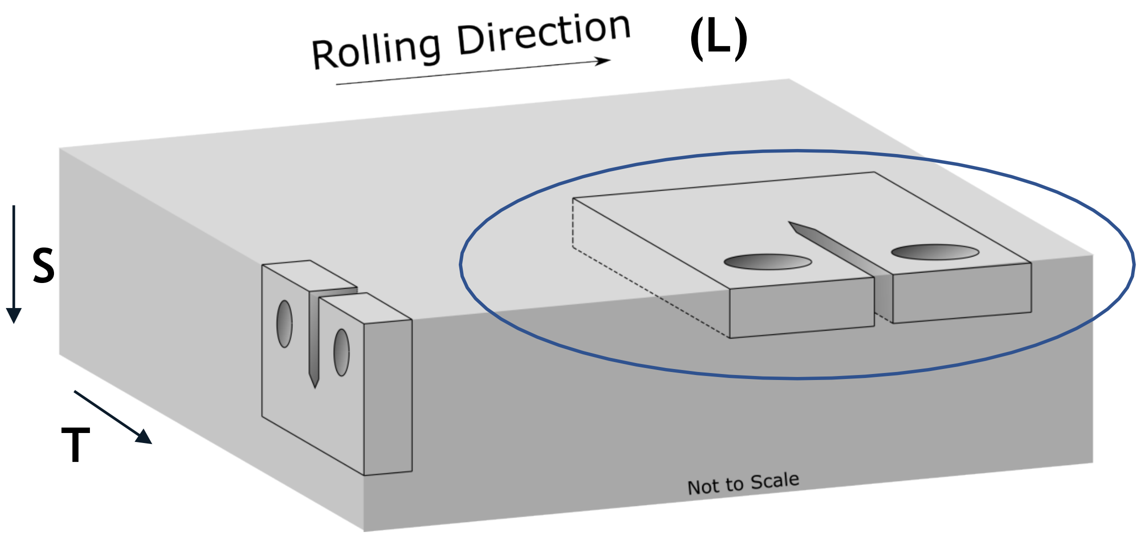
Quick Summary

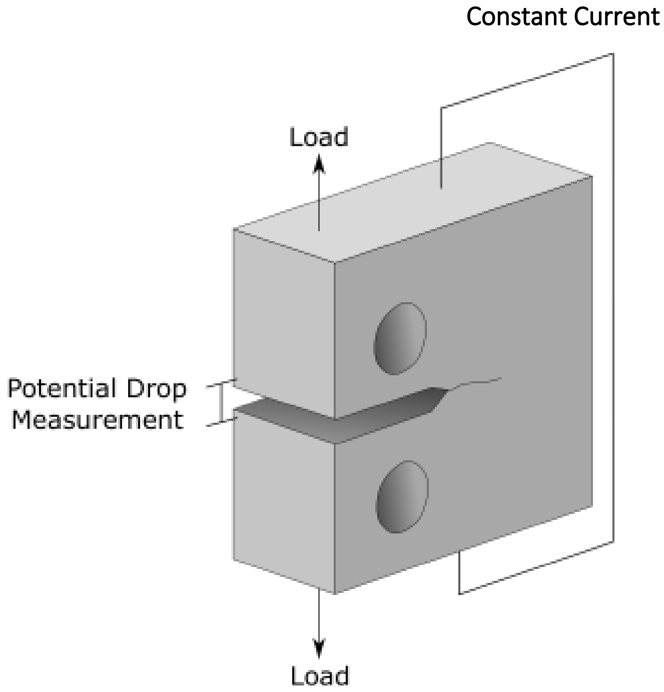


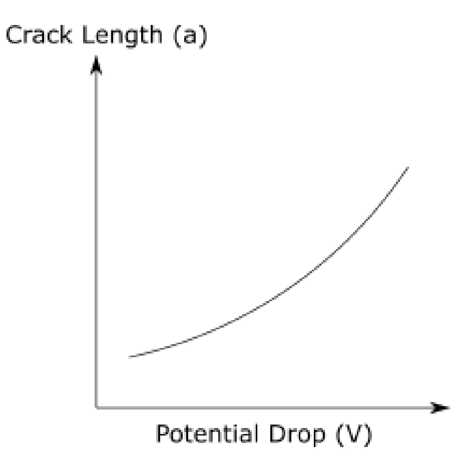




Sample Orientation and *In-Situ* Testing Methodology

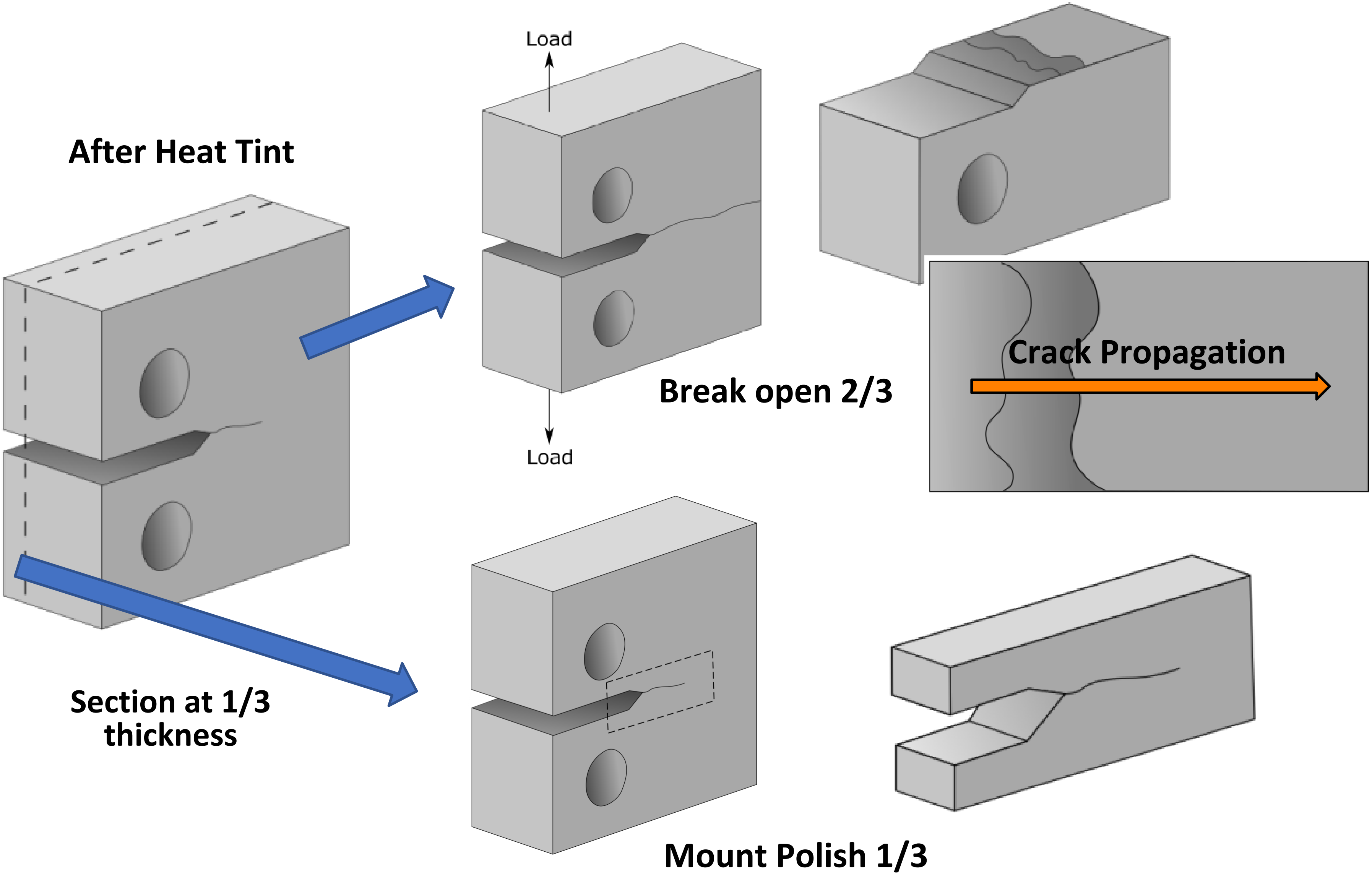




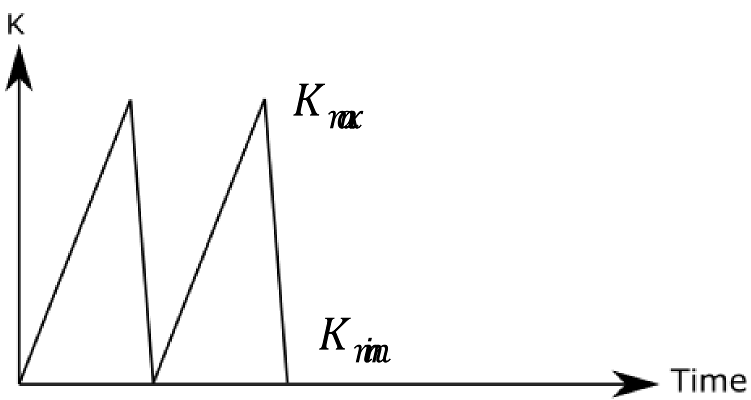


- Majority of samples presented will be in the L-T orientation
- Annealed ASTM SS304L (information in supplemental)
- Utilizing Direct Current Potential Drop (DCPD)
  - Measure of *average* crack growth

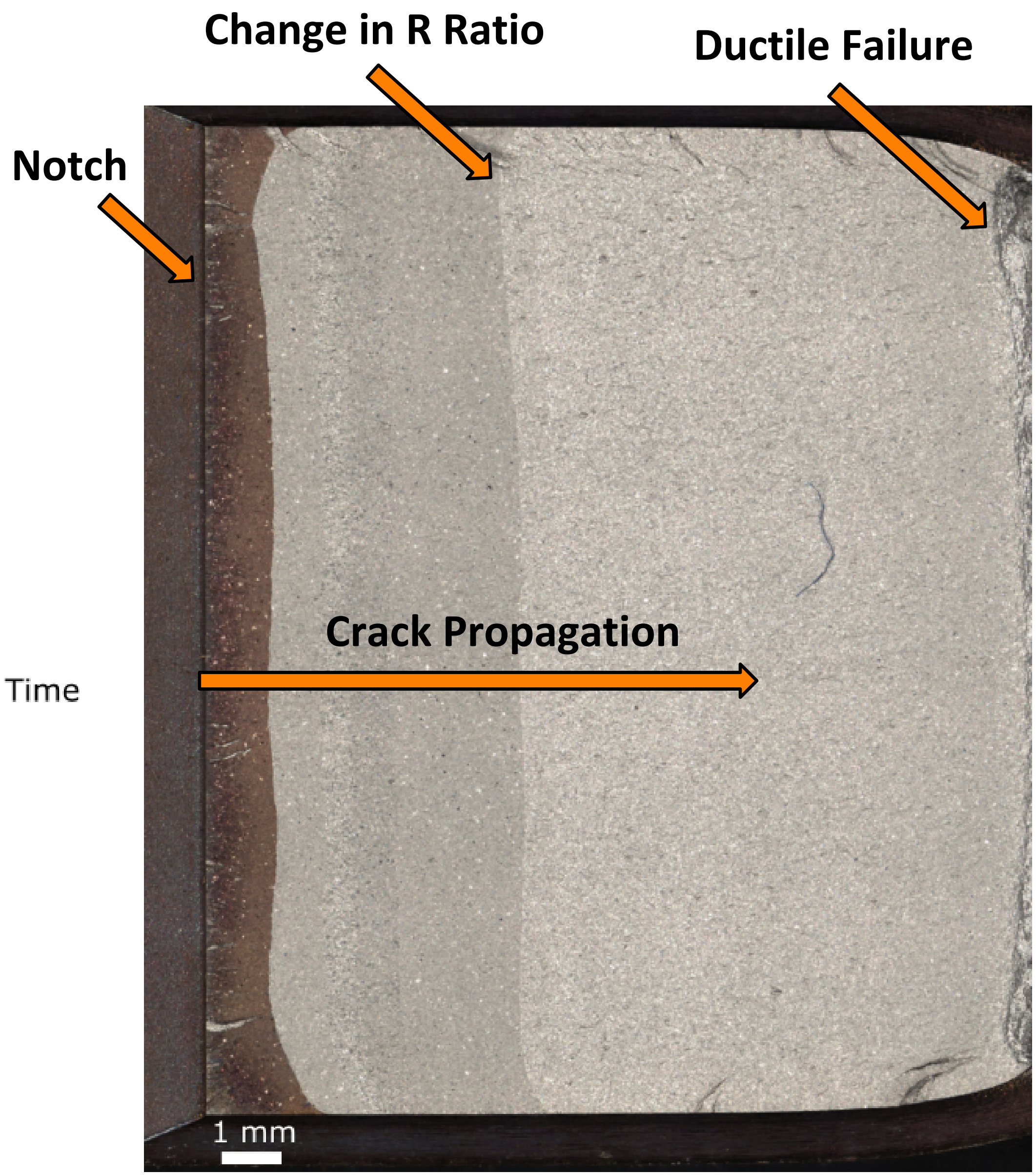
Methods for Post Test Sample Analysis



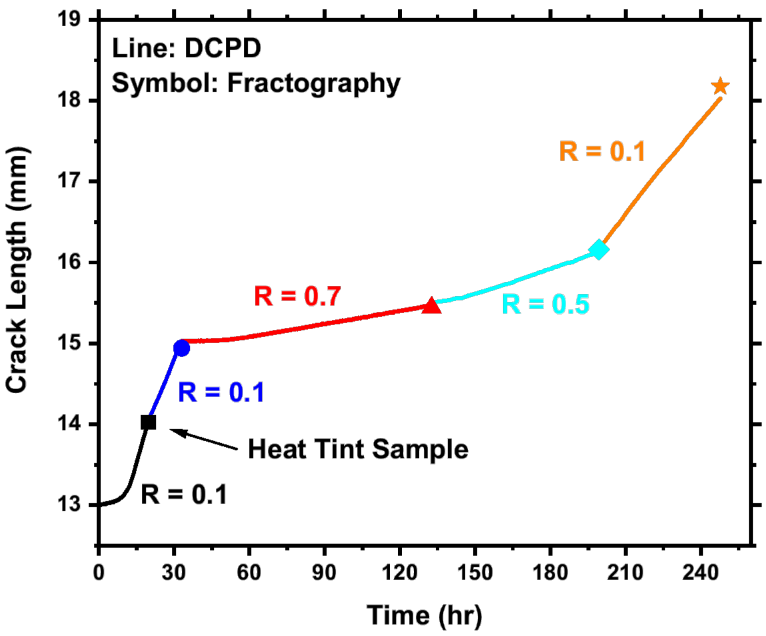
Calibration of DCPD Set-up



$$R_{ratio} = \frac{K_{min}}{K_{max}}$$

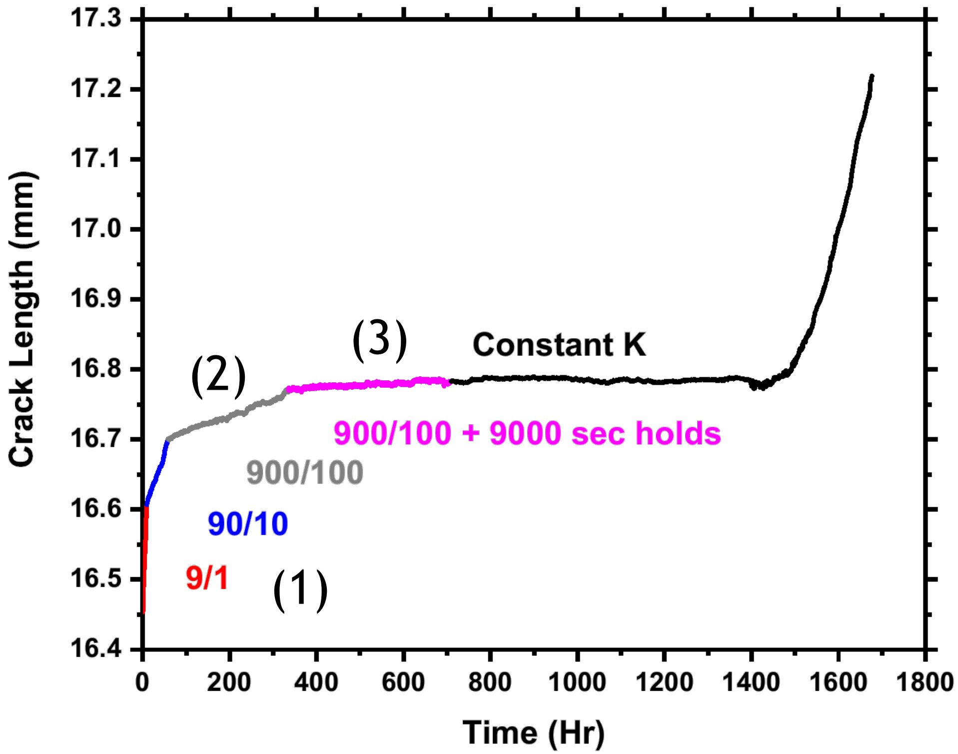


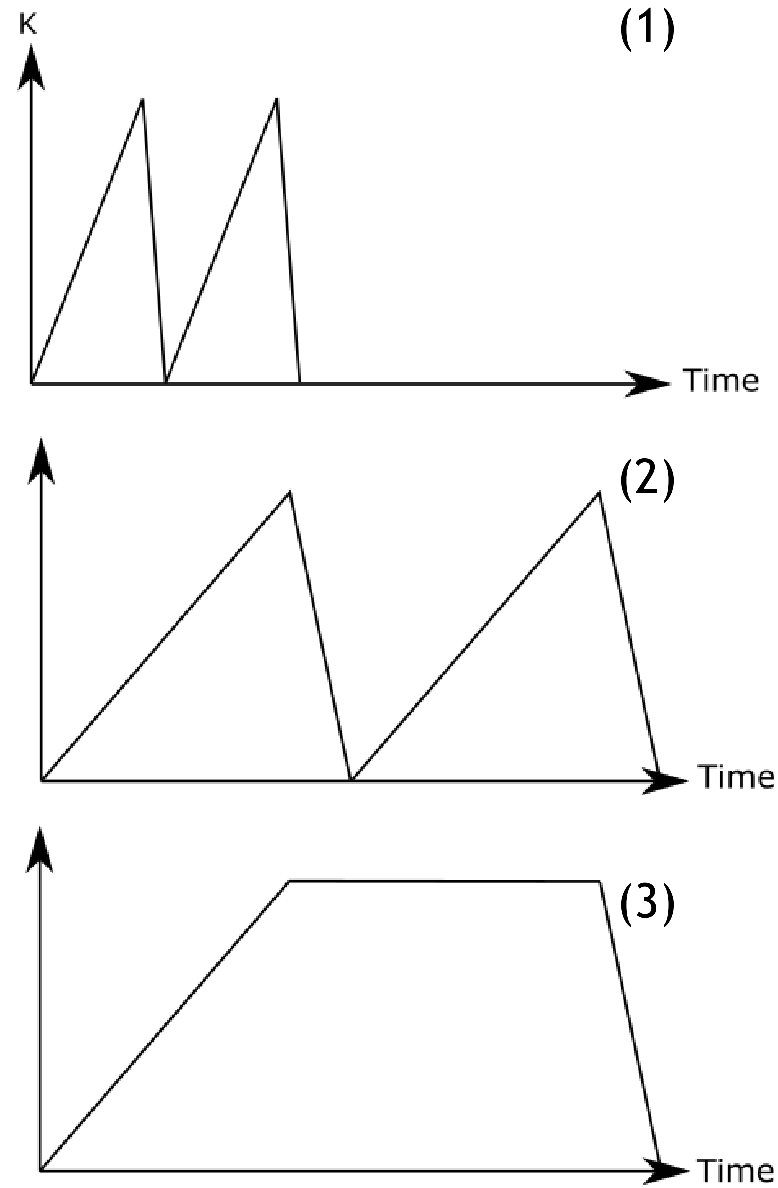
Calibration of DCPD Set-up



- Performed on two different load frames
- Confidence DCPD system is set-up correctly

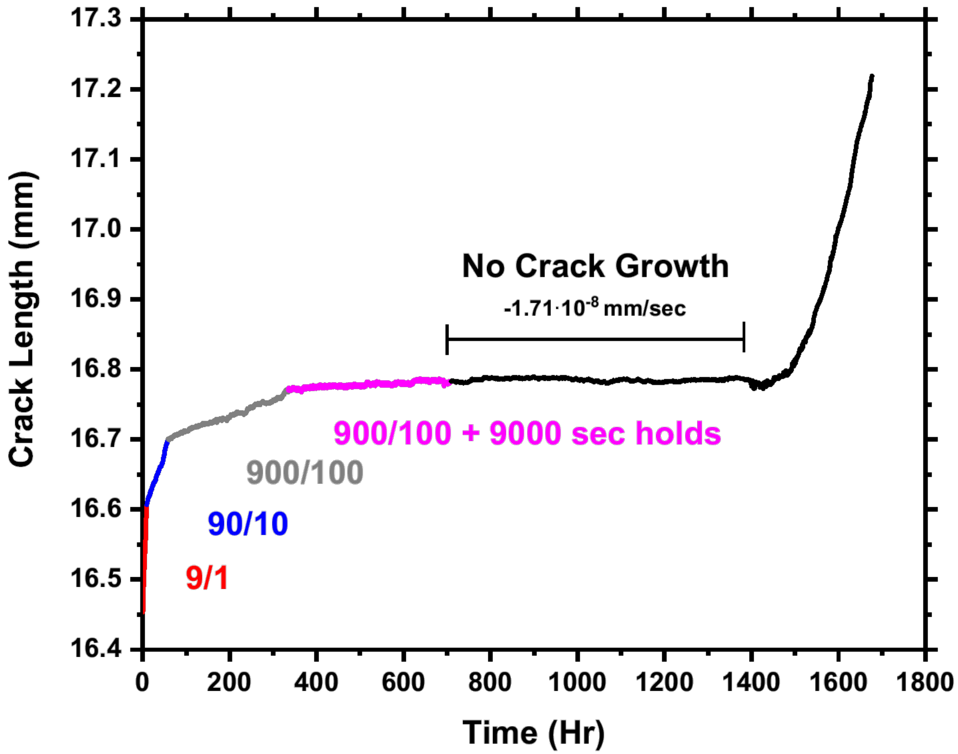
SS304L Testing Methodology





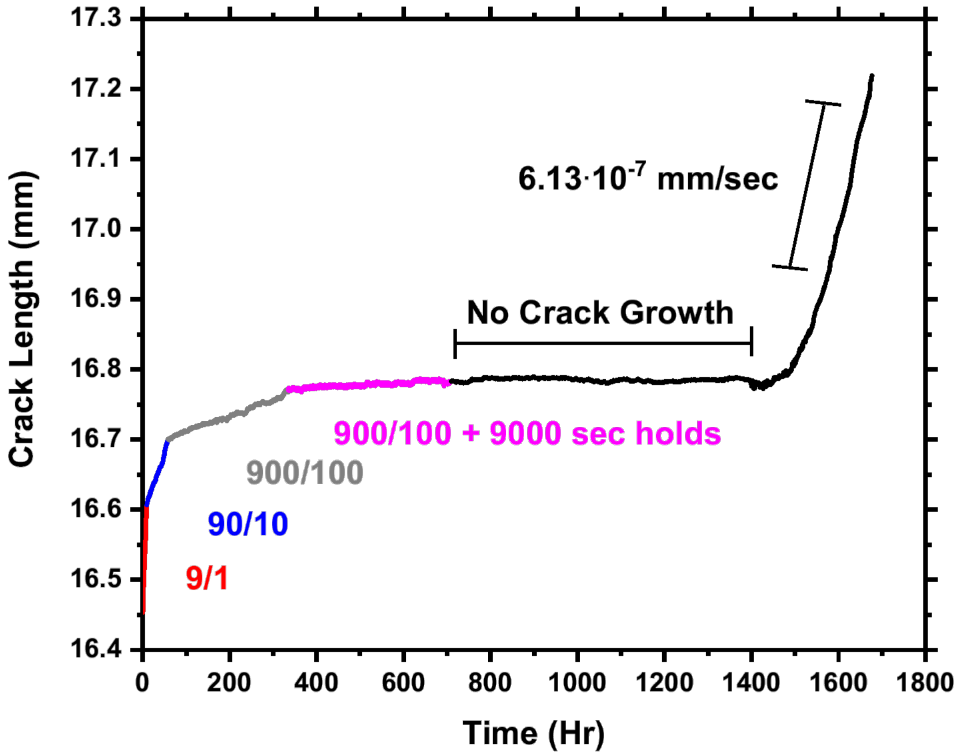
- Decreasing frequency under K control to constant K state
  - 'True' crack plane for constant K SCC
- $K_{max} = 20\ MPa\sqrt{m}$

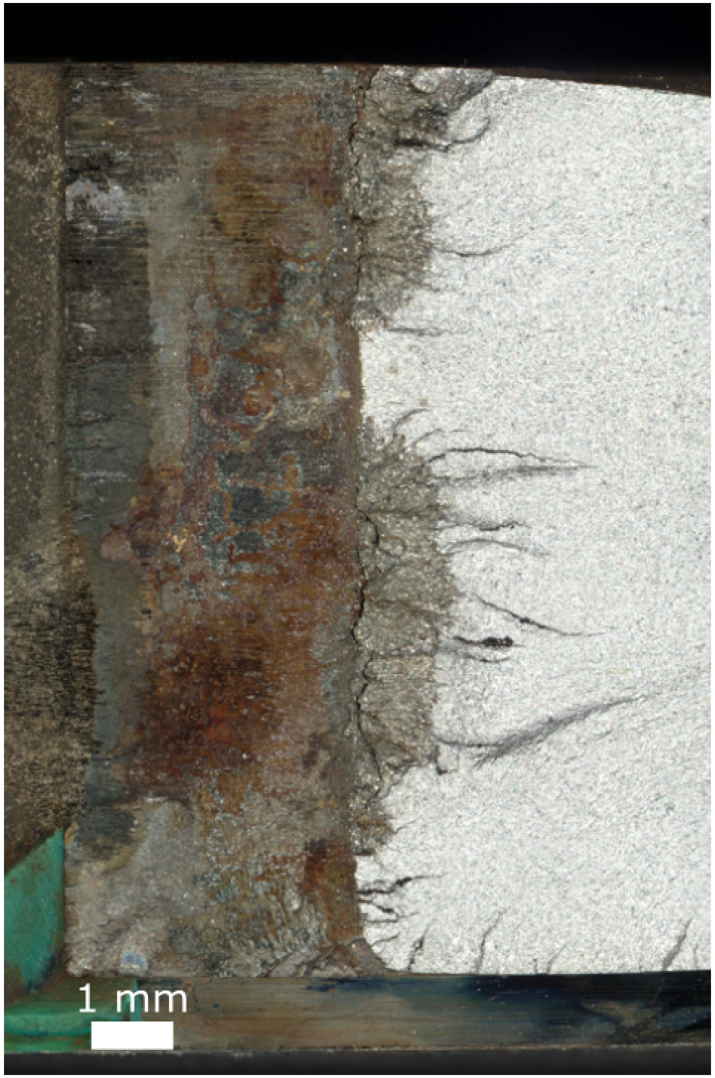
SS304L Exhibits Delayed Crack Growth Under Constant K in $MgCl_2$ at 55 ˚C



- No growth for ~ 700 hours

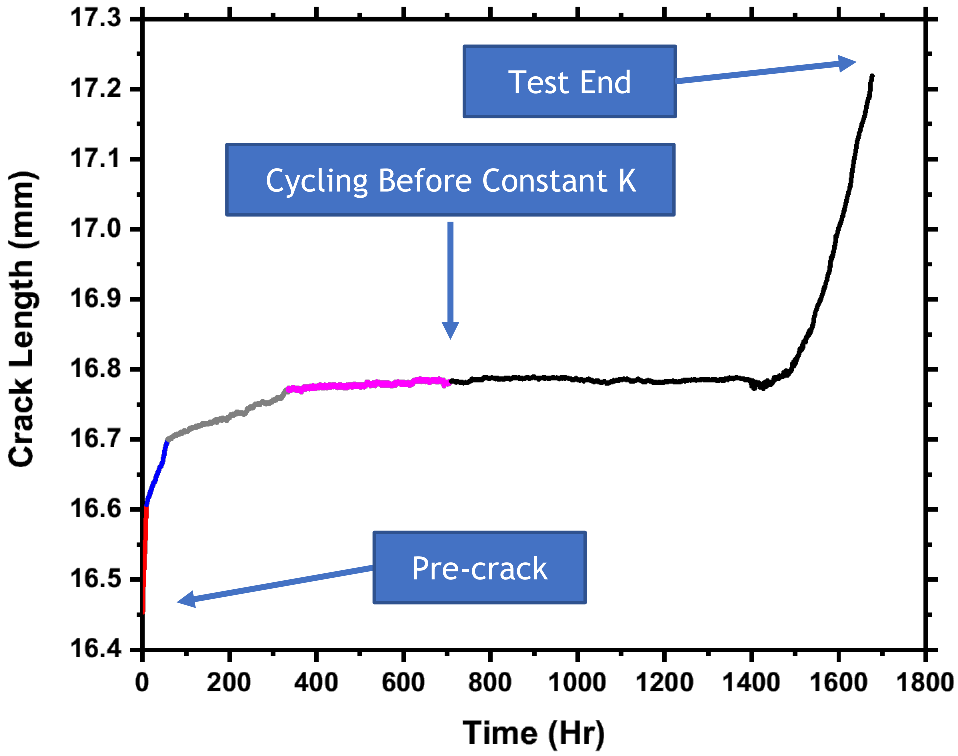
SS304L Exhibits Irregular Crack Front in Saturated $MgCl_2$ at 55 ˚C

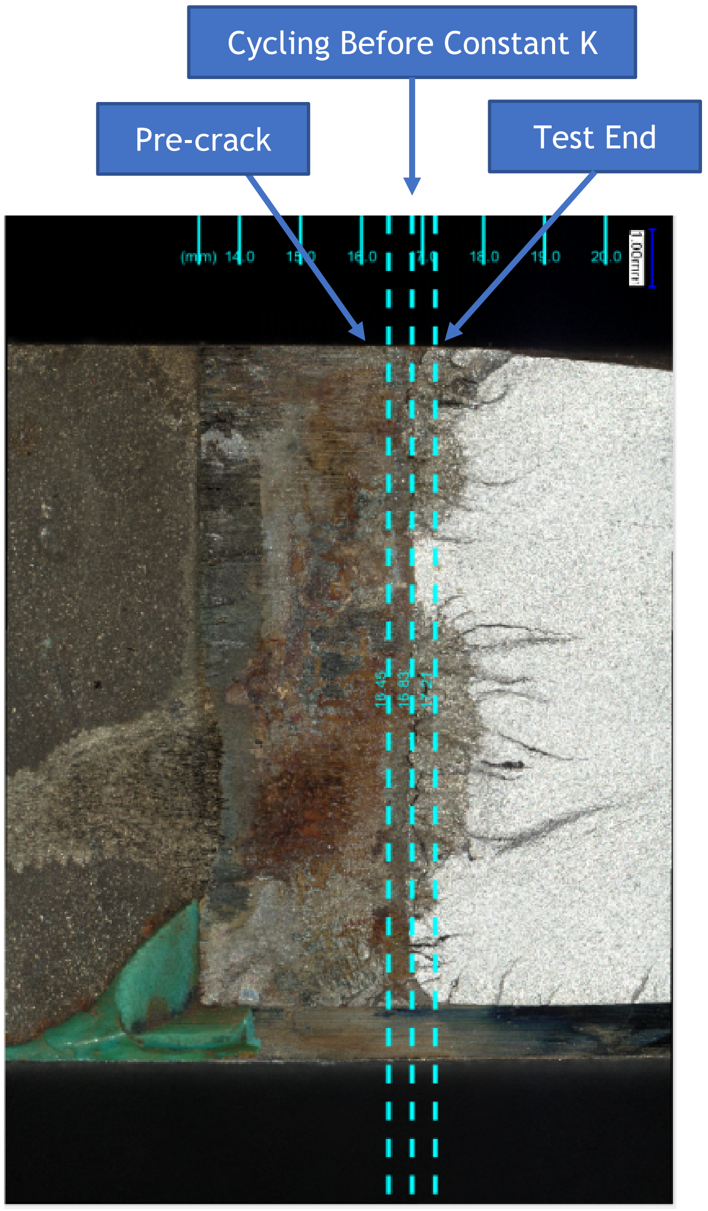




- After roughly 1500 hours of total test time, cracking ensues
- Sample was cut at 1/3 of thickness

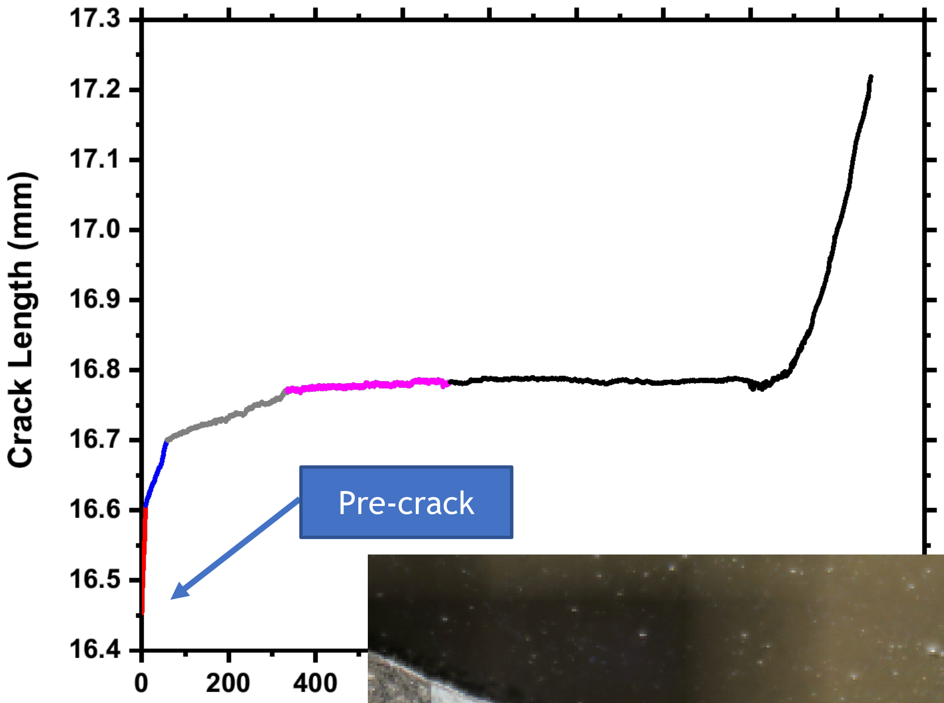
SS304L Exhibits Irregular Crack Front in Saturated $MgCl_2$ at 55 ˚C

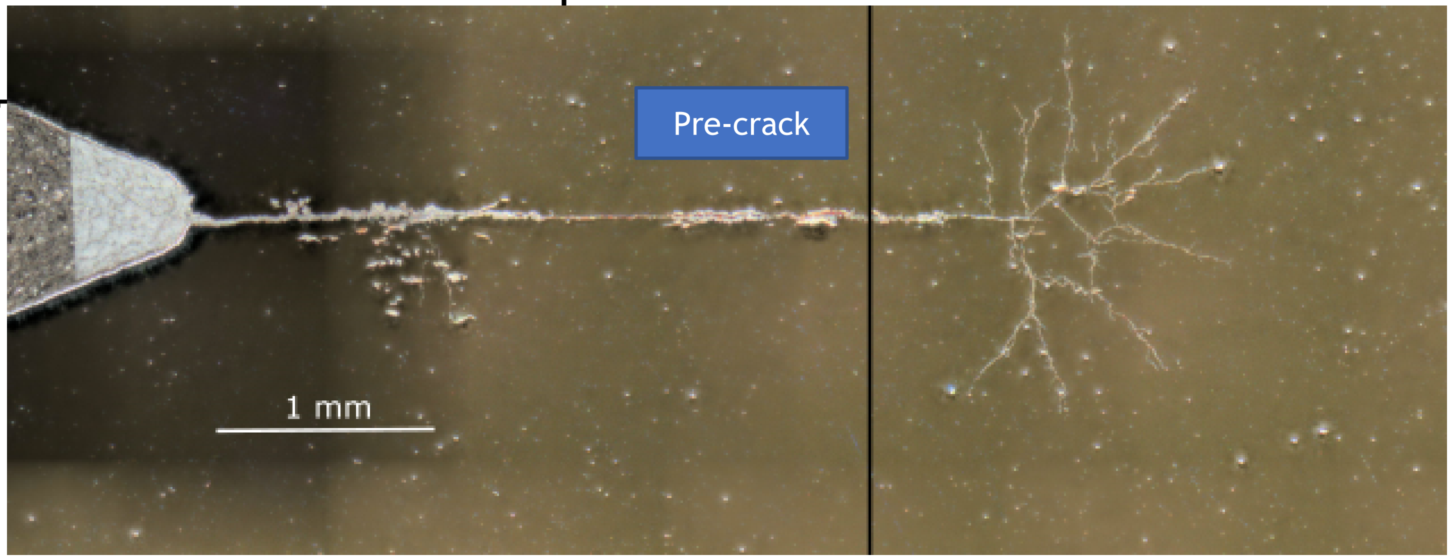




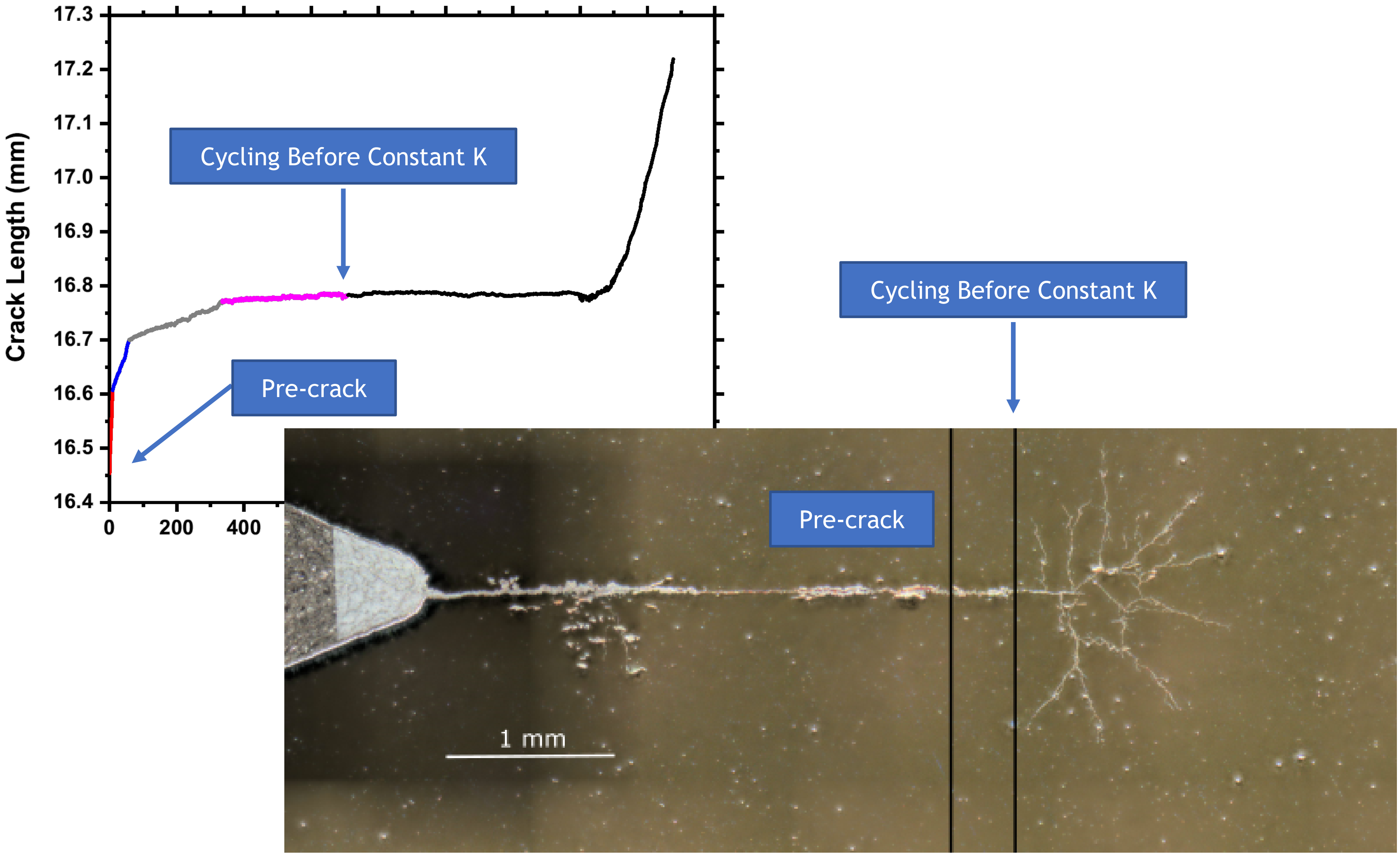
- Overlay of DCPD on fractography potentially suggests cracking halted at the uniform ‘ledge’

SS304L Exhibits Crack Branching in Saturated $MgCl_2$ at 55 °C

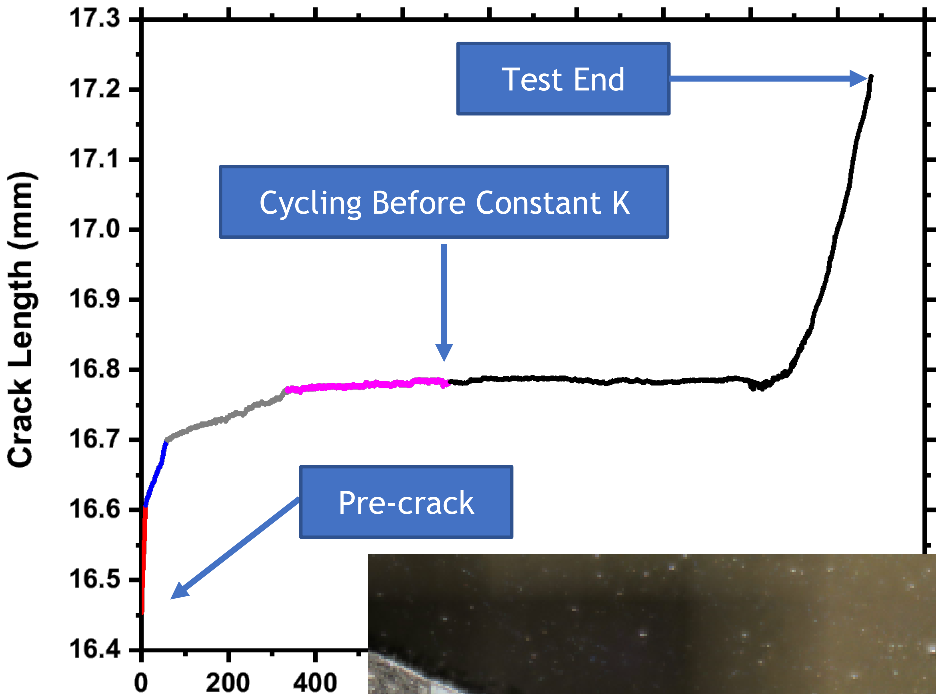


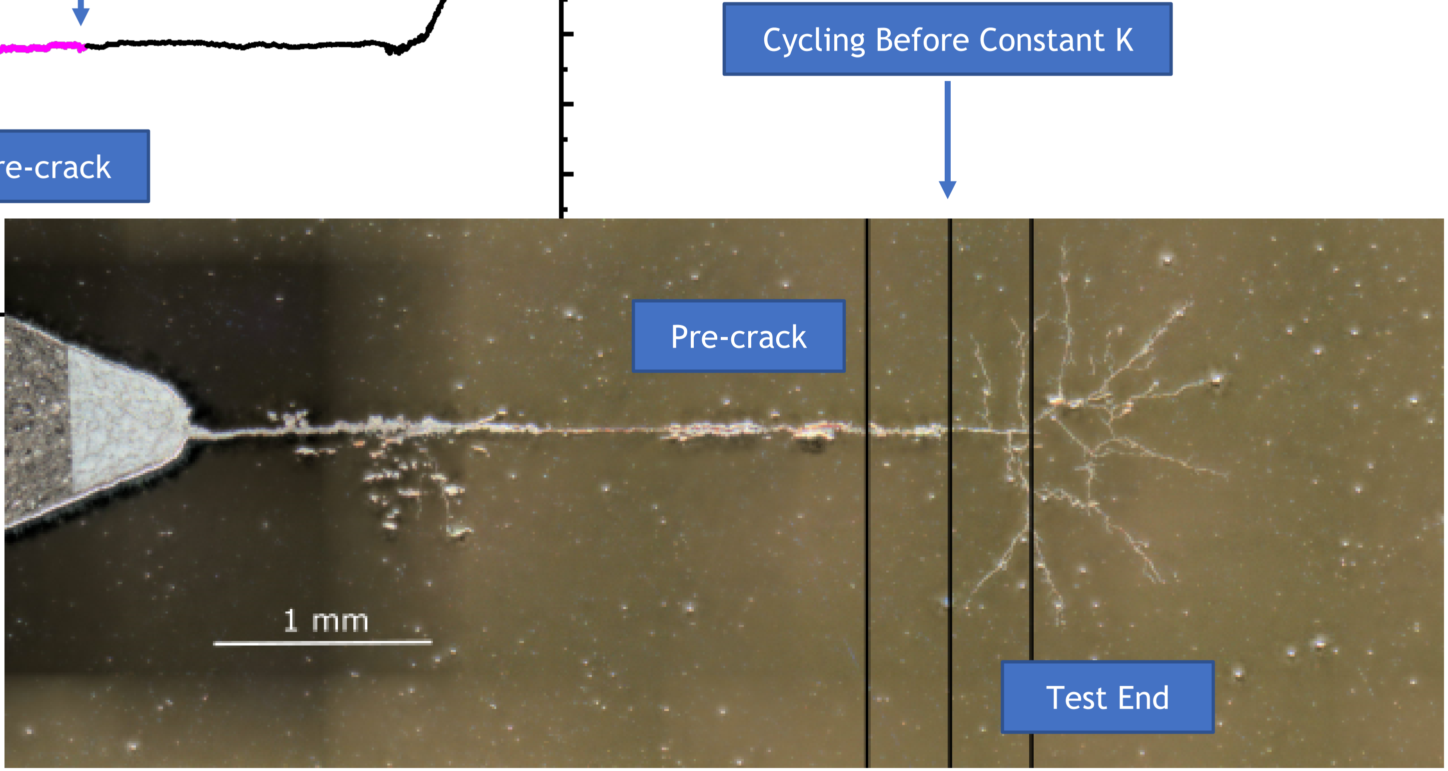


SS304L Exhibits Crack Branching in Saturated $MgCl_2$ at 55 °C

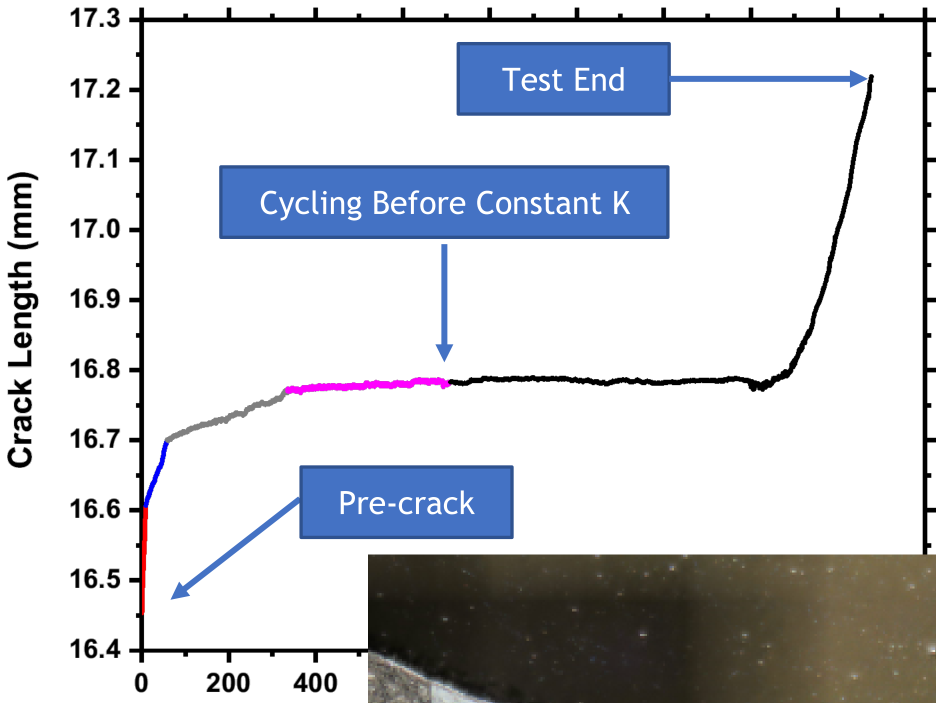


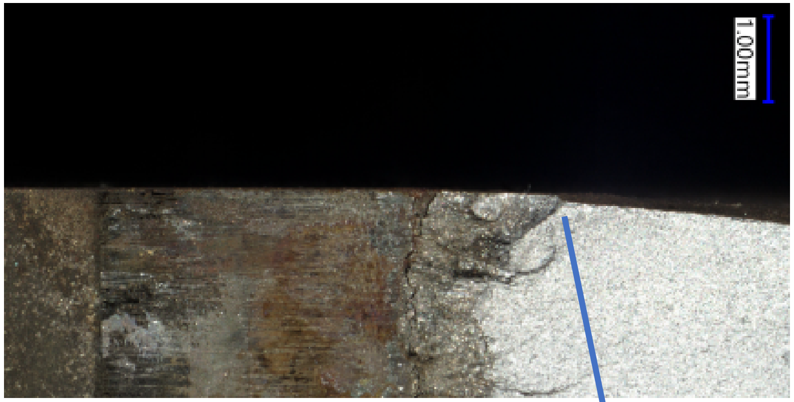
SS304L Exhibits Crack Branching in Saturated $MgCl_2$ at 55 °C

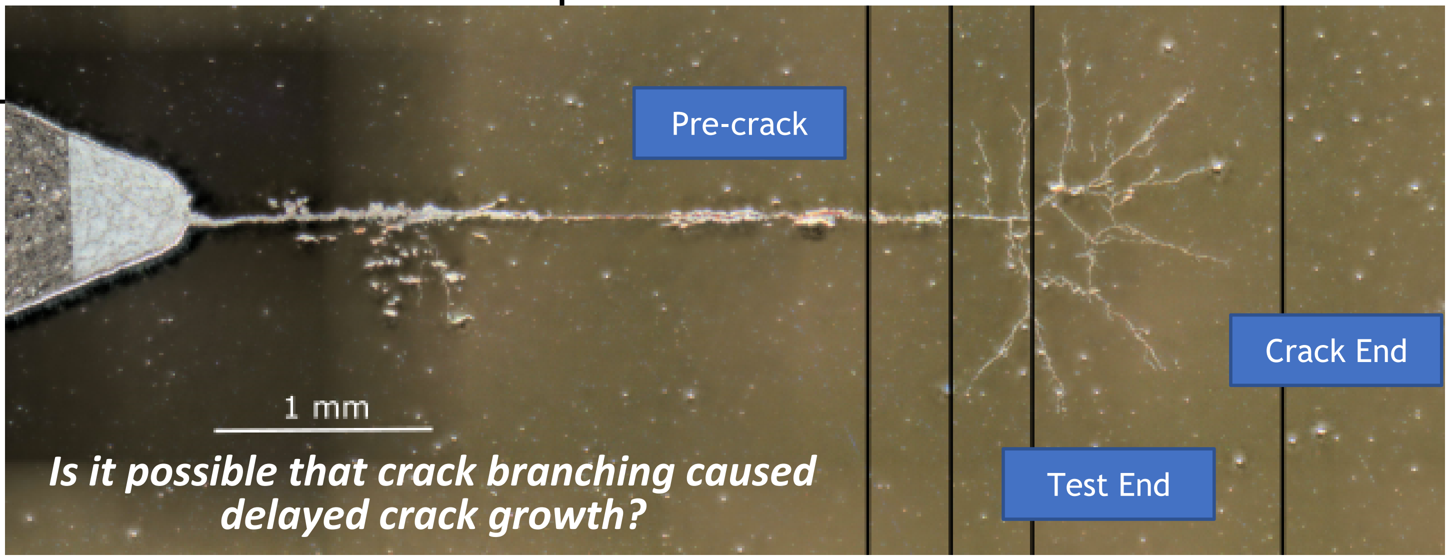




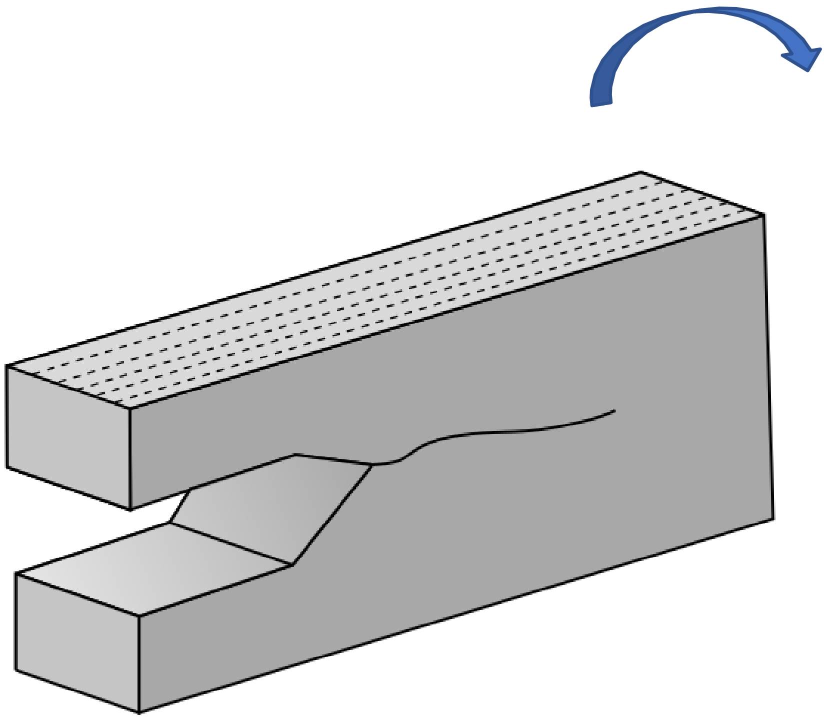
SS304L Exhibits Crack Branching in Saturated $MgCl_2$ at 55 ˚C

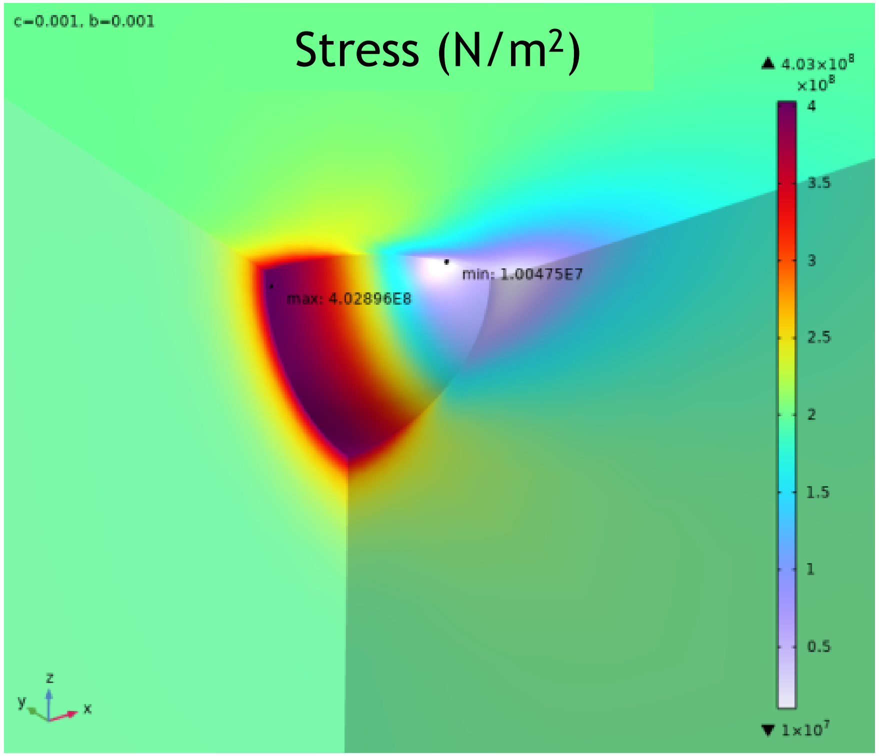






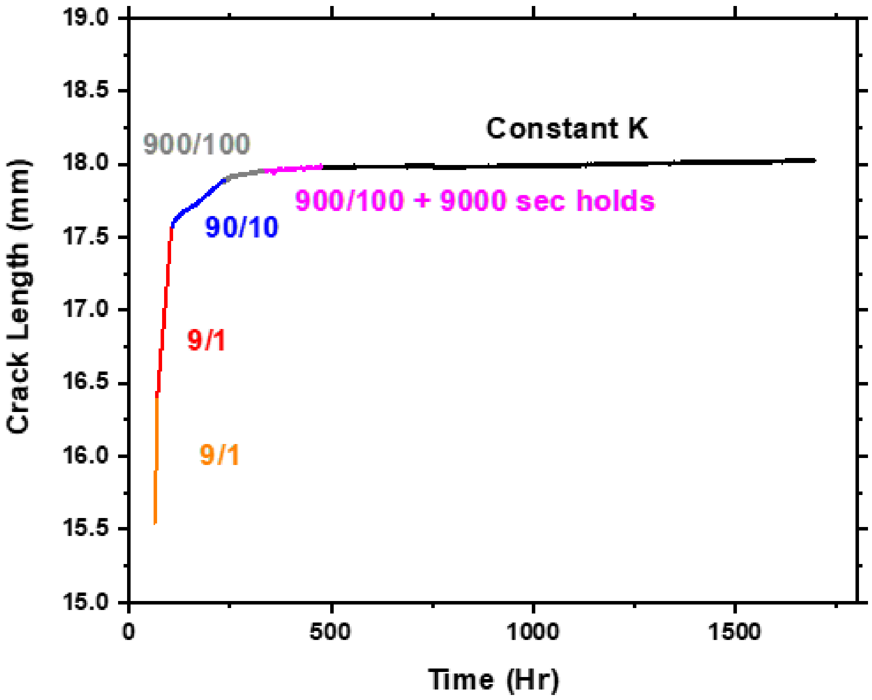
Next Steps



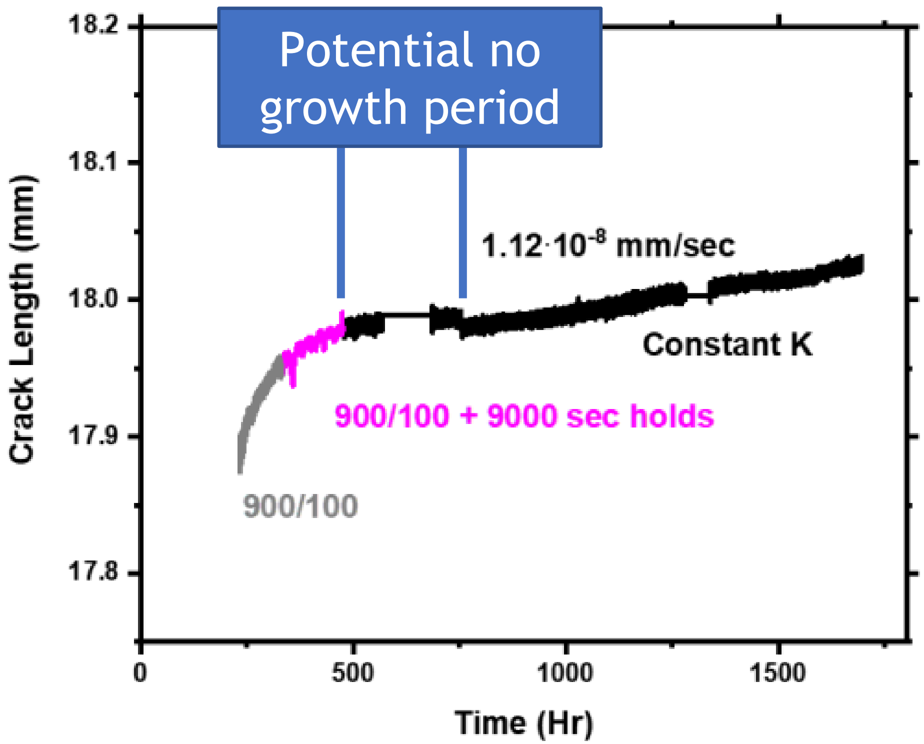


- Serial sectioning of the 1/3 slice
  - Understand crack propagation (repeat EBSD)
  - Reconstruct serial sectioning into 3D image and look at driving forces for branched crack
- Understand driving force for branched cracking

Low Crack Growth Rate for in Saturated $MgCl_2$ at 25 ˚C

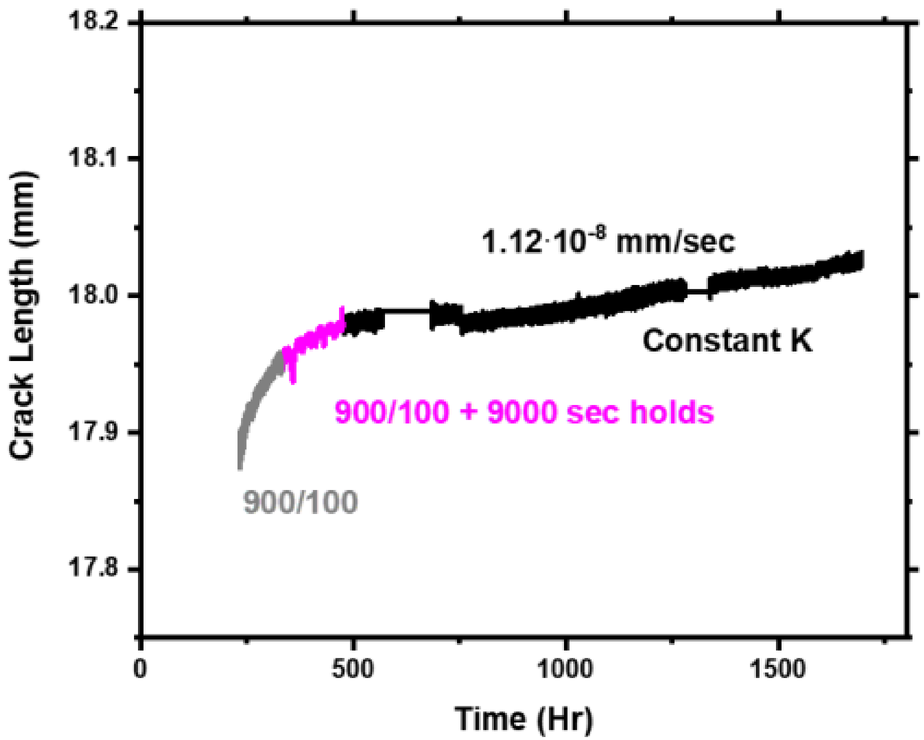


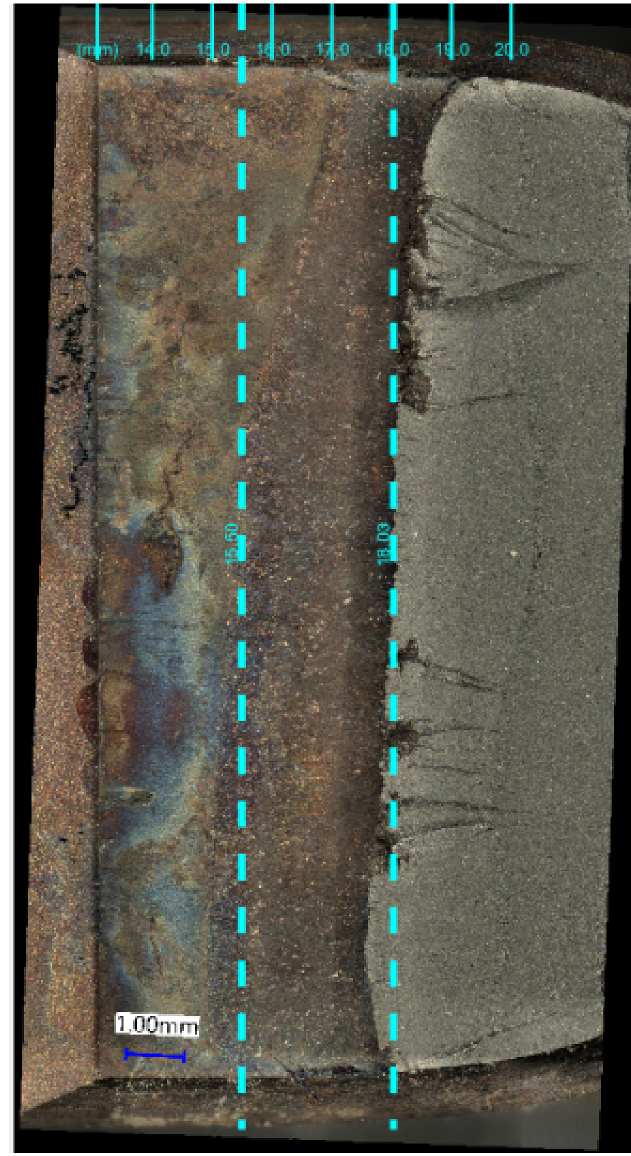
Low Crack Growth Rate for in Saturated $MgCl_2$ at 25 ˚C Experienced Localized Cracking



- Similar delay in indicated crack growth to 55 ˚C
- Sample was not sliced but fractured open
- Similar crack morphology to 55 ˚C however are thinner regions

SS304L Exhibits Irregular Crack Front in Saturated $MgCl_2$ at 25 °C





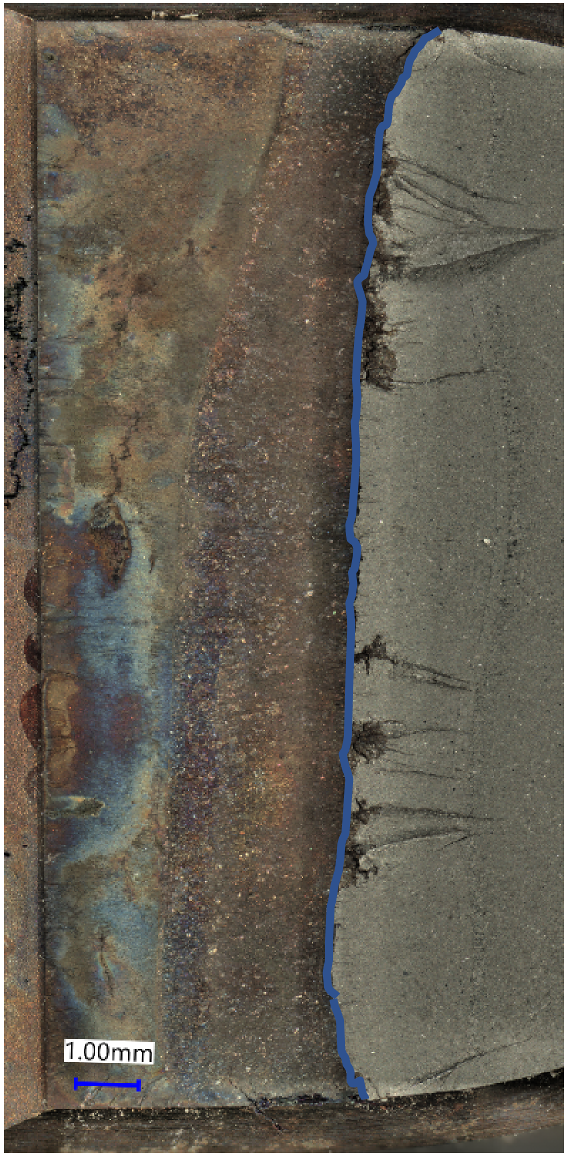
- Slightly curved crack front makes overlay of DCPD difficult (very small growth during constant K hard to decipher)

SS304L Exhibits Irregular Crack Front in Saturated $MgCl_2$ at 25 °C

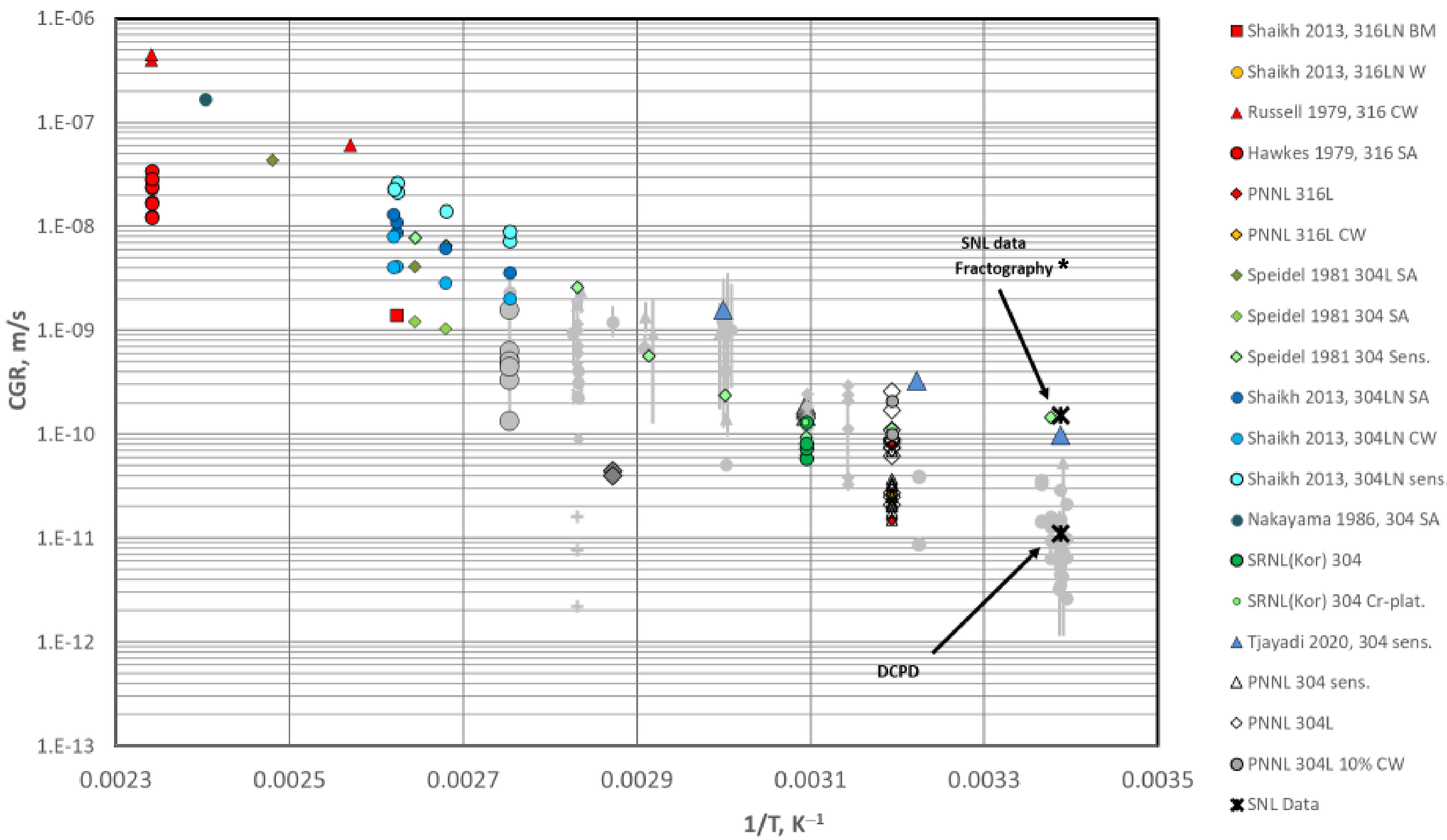
- Measured 100 points of extension from the drawn blue line and averaged
  - Integration of crack extension by hand
  - Similar to area integration
  - End goal to have image analysis

Method	Δa
DCPD	53.8 µm
Fractography	60.1 µm

- Compared to total crack extension during constant K portion confirming DCPD growth was correct
- Possible that growth in 'protrusions' ahead of blue line occurred during the constant K portion

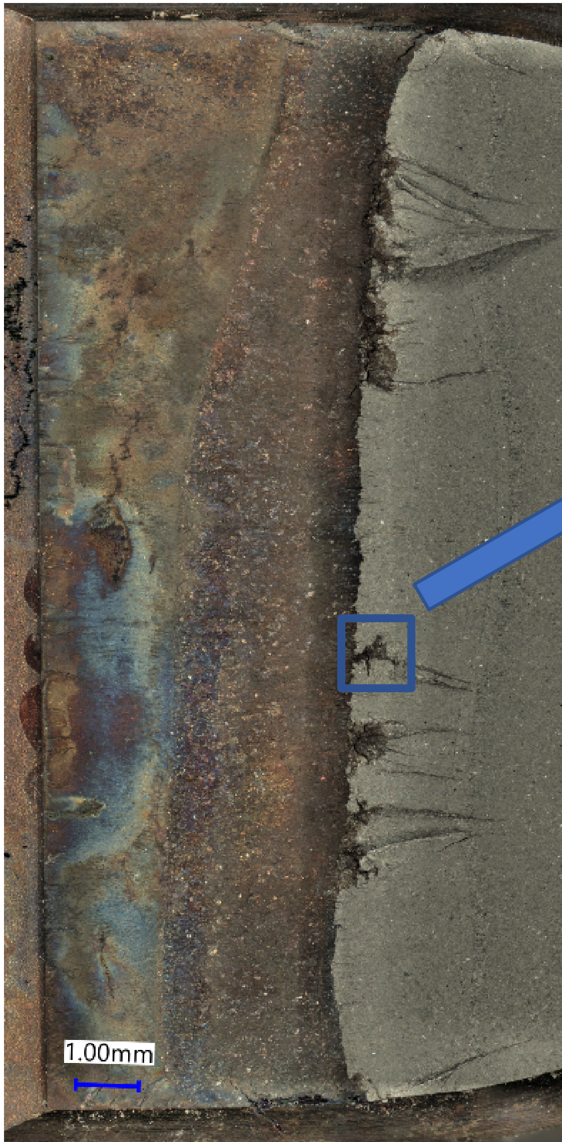


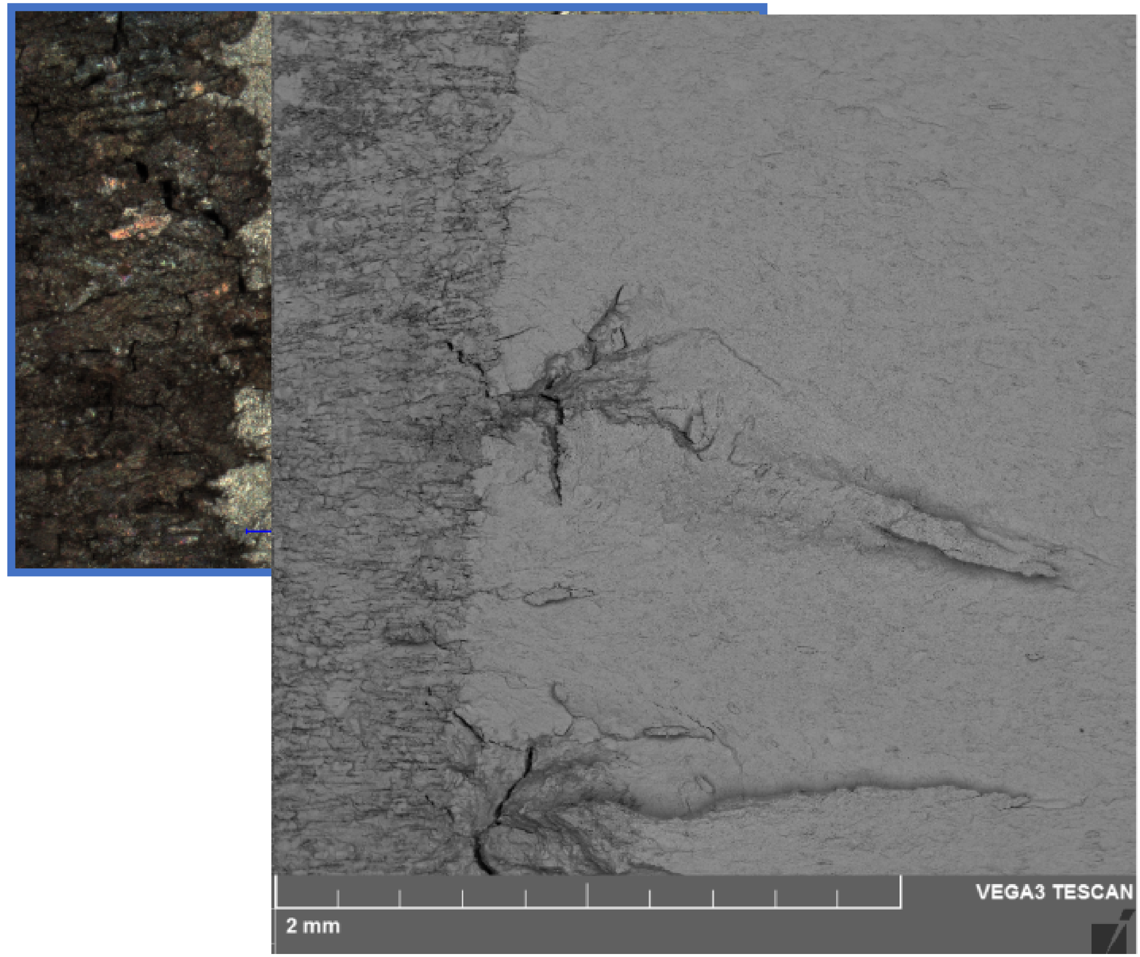
Crack Growth of Furthest ‘Protrusion’ Potentially Order of Magnitude Higher Than DCPD



- Considering protrusion occurs during constant K portion of the test, an increased crack growth rate is calculated
  - *measured from deepest point of protrusion

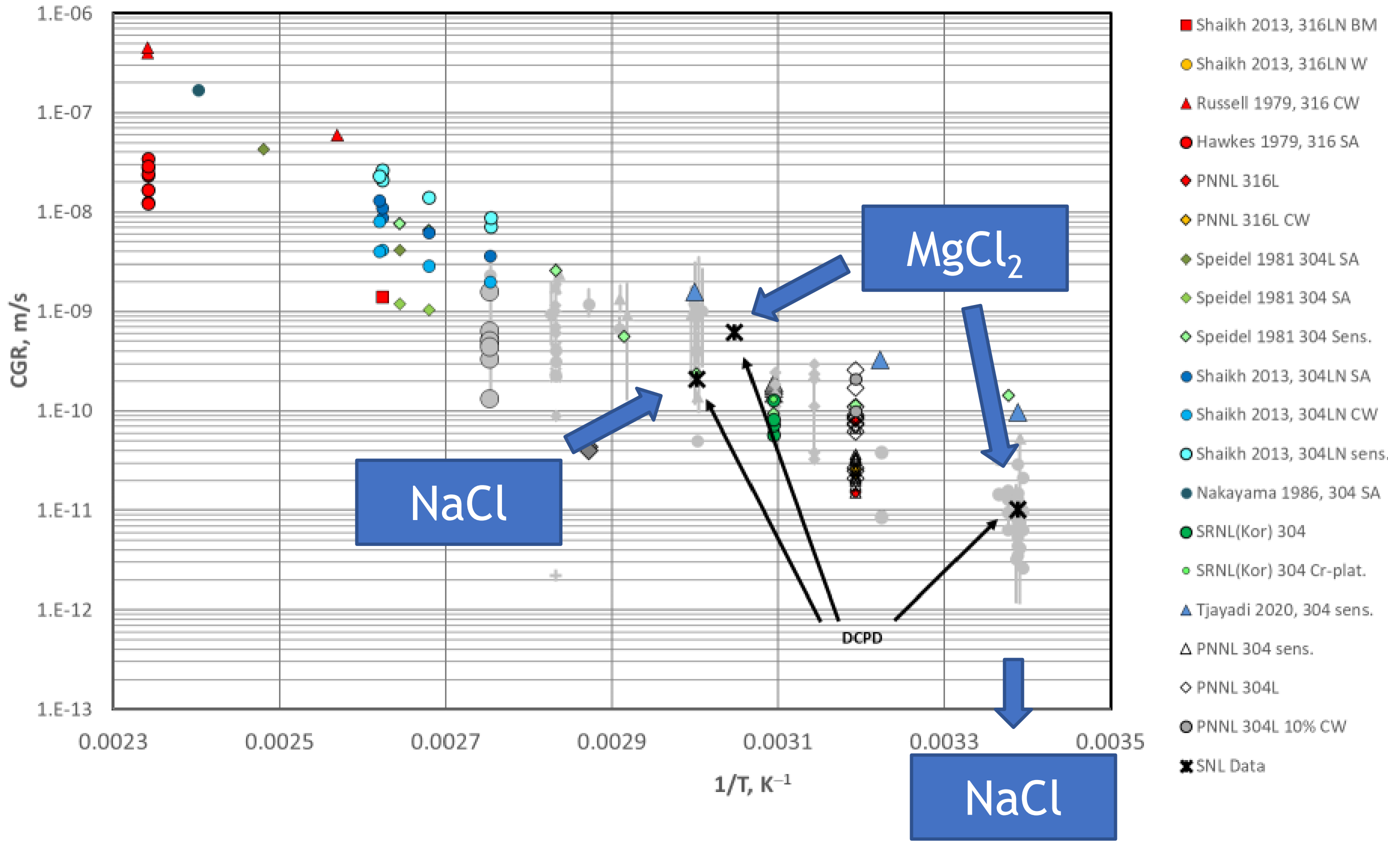
SS304L Exhibits Irregular Crack Front in Saturated $MgCl_2$ at 25 °C





- Significant corrosion products on the surface
- Enhanced cleaning needed, however, crack wake corrosion could be eliminating features of interest
  - Looking for intergranular/transgranular fracture

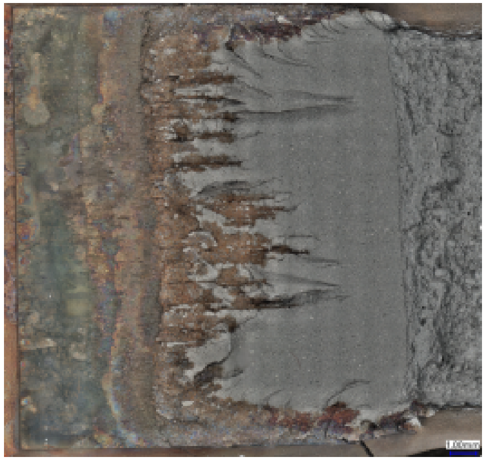
Measured Crack Growth Agrees with Literature Trends

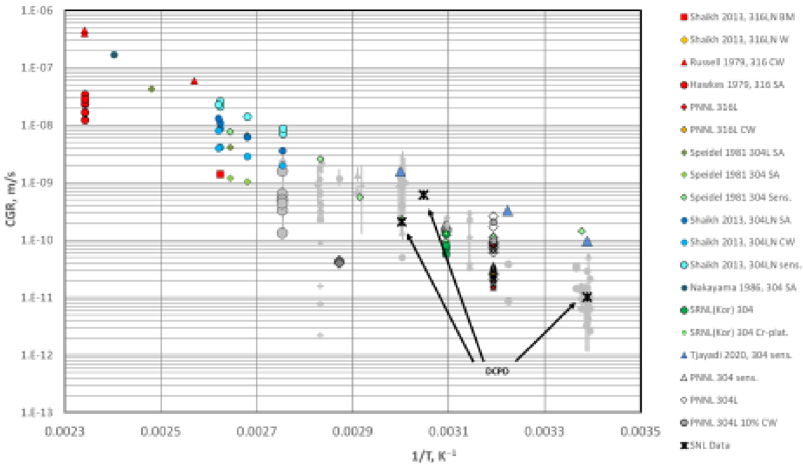


- Similar crack growth rate trend with temperature to other studies in literature
- Potential influence of solution composition on crack growth rate but does influence morphology

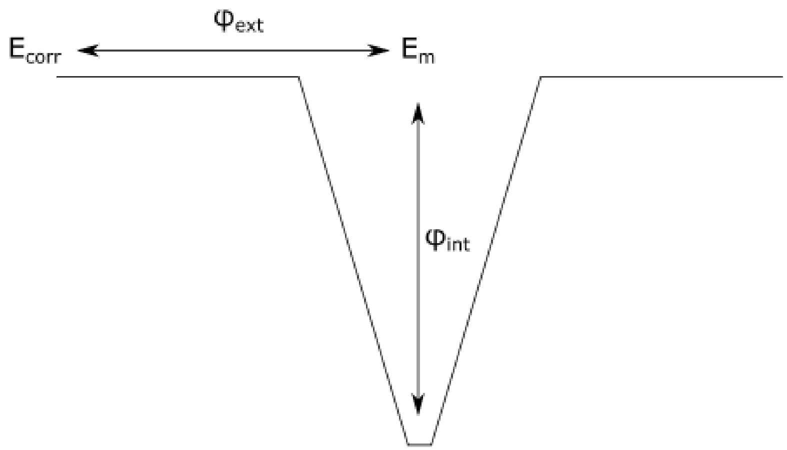
Key Take-a-ways

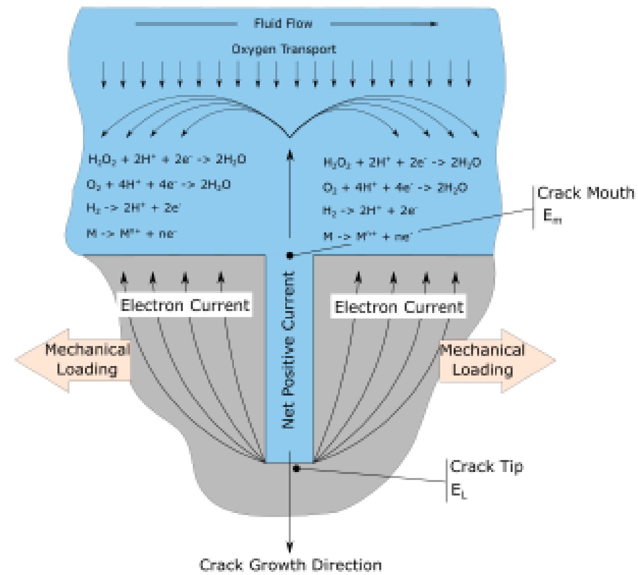
- Importance of fractography combined with DCPD
  - Can impact crack growth rate if taking DCPD average or growth of furthest protrusion
  - Can multiple tests be performed on the same sample given the ‘weird’ fracture morphologies?
- Solution, sample orientation, and material lot appear to impact crack growth and crack morphology
- Temperature has an impact on crack growth
- Is scatter due to these morphologies, **environment**, material, measurement technique, etc.?





Current Literature SCC Models

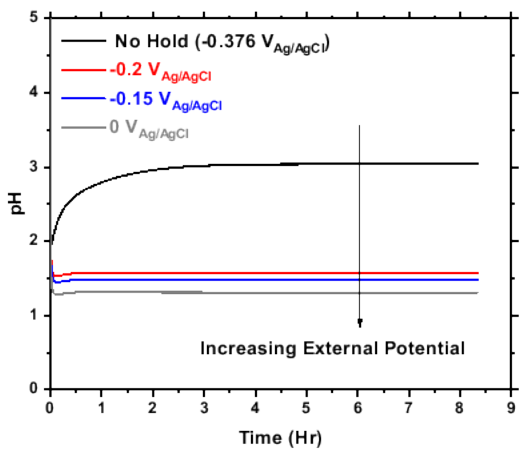


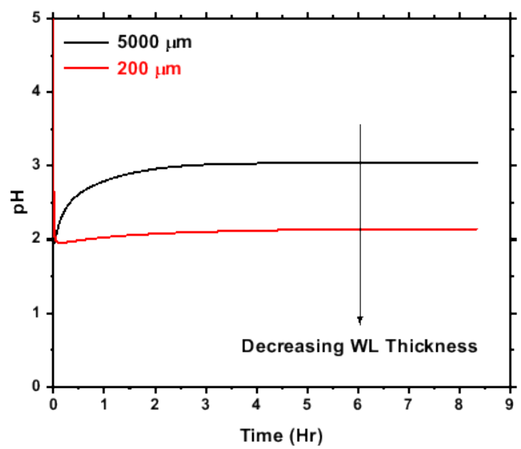


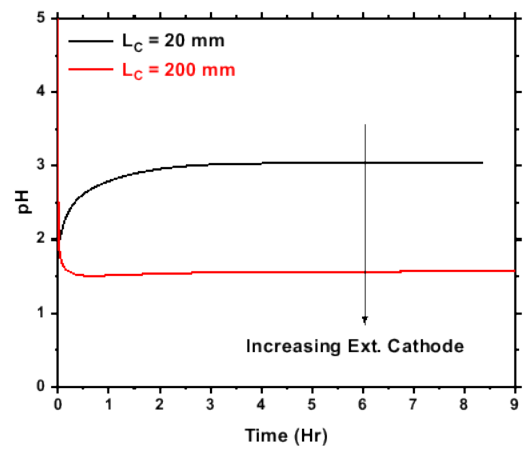
- Current models assume crack tip current density and external potentials to determine electrochemical conditions in the crack
  - ***Static boundary conditions***
  - **Size of external cathode and WL not explicitly considered**
  - **No consideration of diffusion limited oxygen reduction reaction (ORR)**

Conclusions and Implications

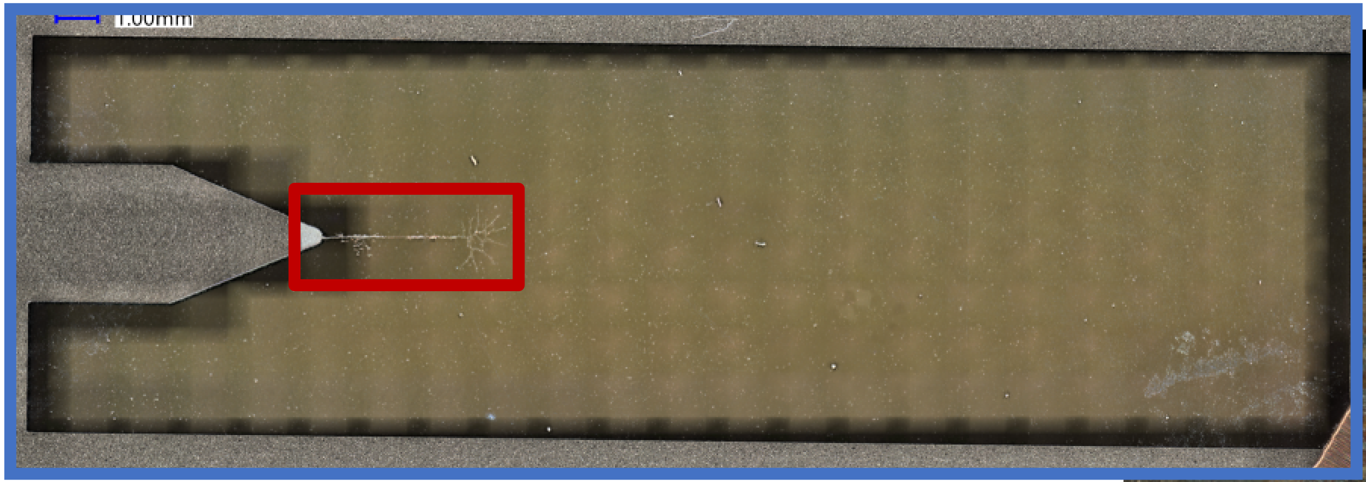
- Created model to accommodate changes in sample size, external environment (WL thickness and solution) and sample geometry
  - Results follows trends in literature
- Modest anodic polarization of samples can increase electrochemical severity at the crack tip
  - Are polarizations representative of real life scenarios?
  - Are laboratory scale specimens representative of field conditions?
- Strong influence of external surface on crack tip electrochemistry
  - Will this change in 3D?
- ***Important to understand internal and external impacts on crack tip environment***

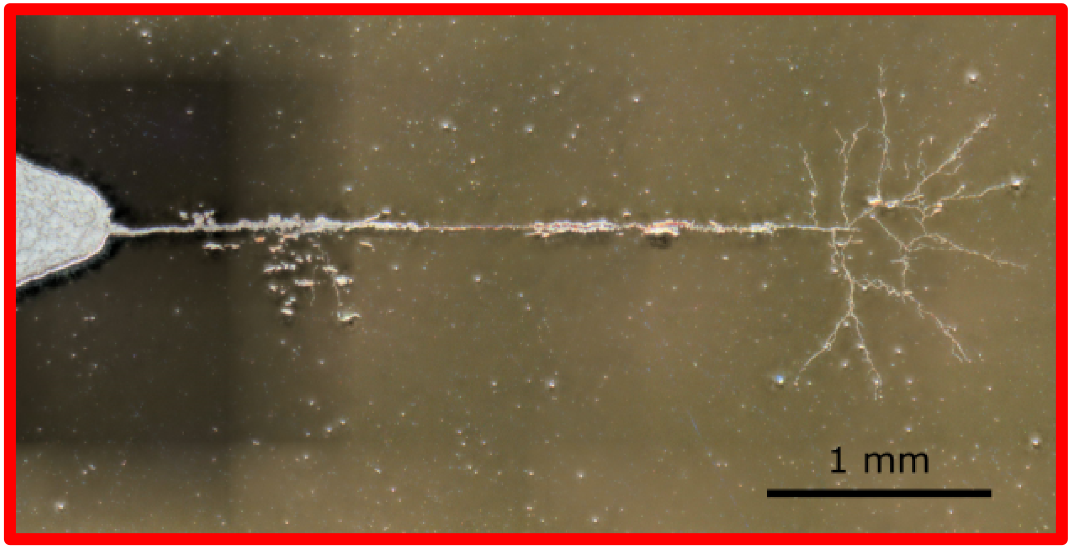




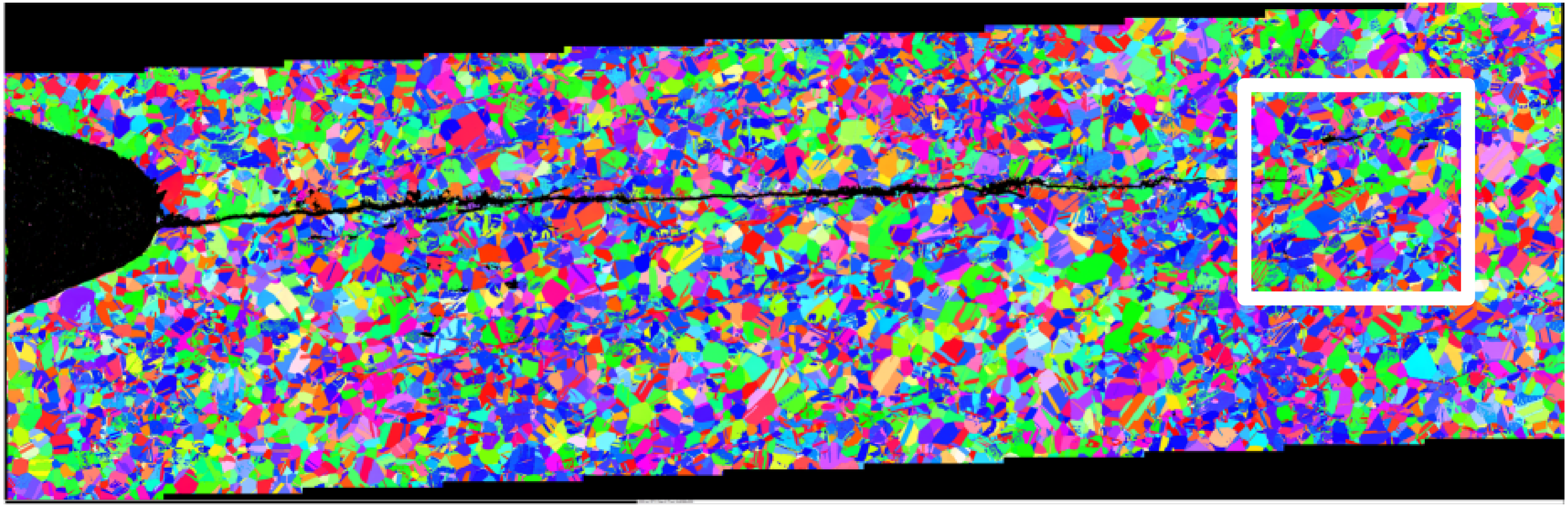


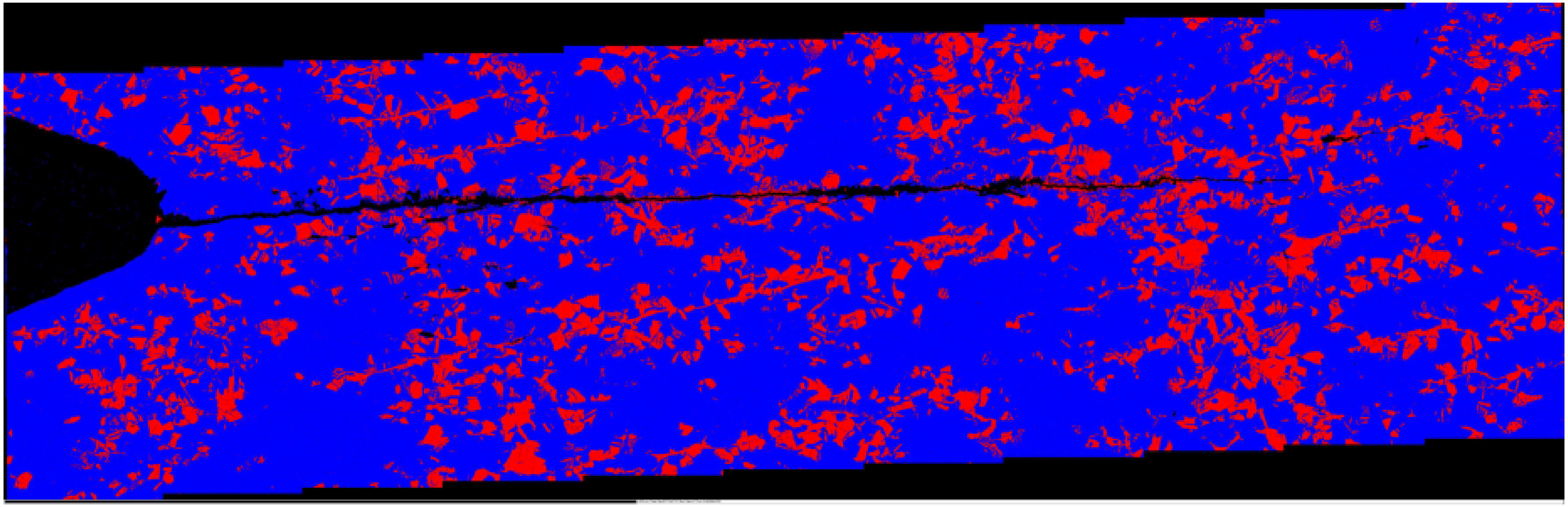
SS304L Exhibits Crack Branching in Saturated $MgCl_2$ at 55 °C





EBSD of Crack Tip





Mixed SCC Cracking Modes in $MgCl_2$