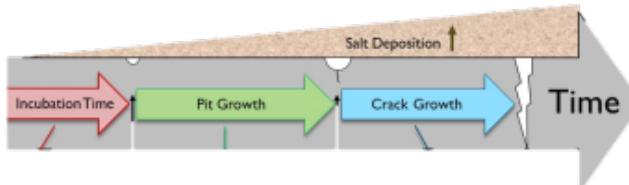




Stress Corrosion Cracking of Austenitic Stainless Steels in Concentrated Chloride Environments



PRESENTED BY

Ryan M. Katona

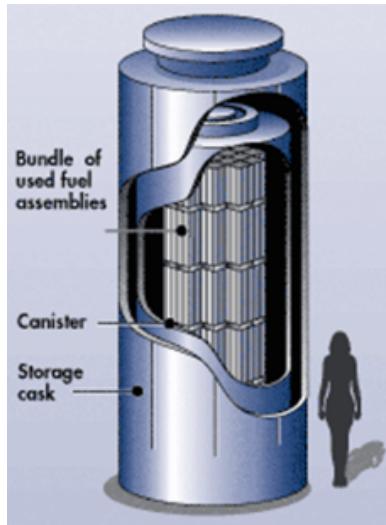
J. Taylor, E. Karasz, B. Nation, A. W. Knight, C. R. Bryan, and R. F. Schaller

Sandia National Laboratories, Albuquerque, New Mexico 87123,
USA

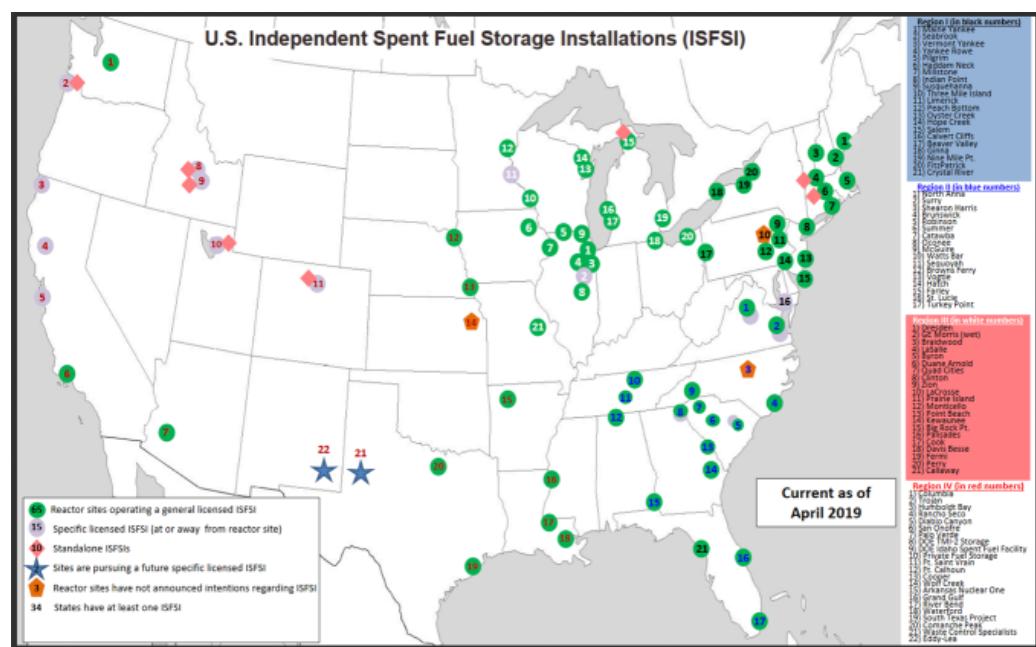
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.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



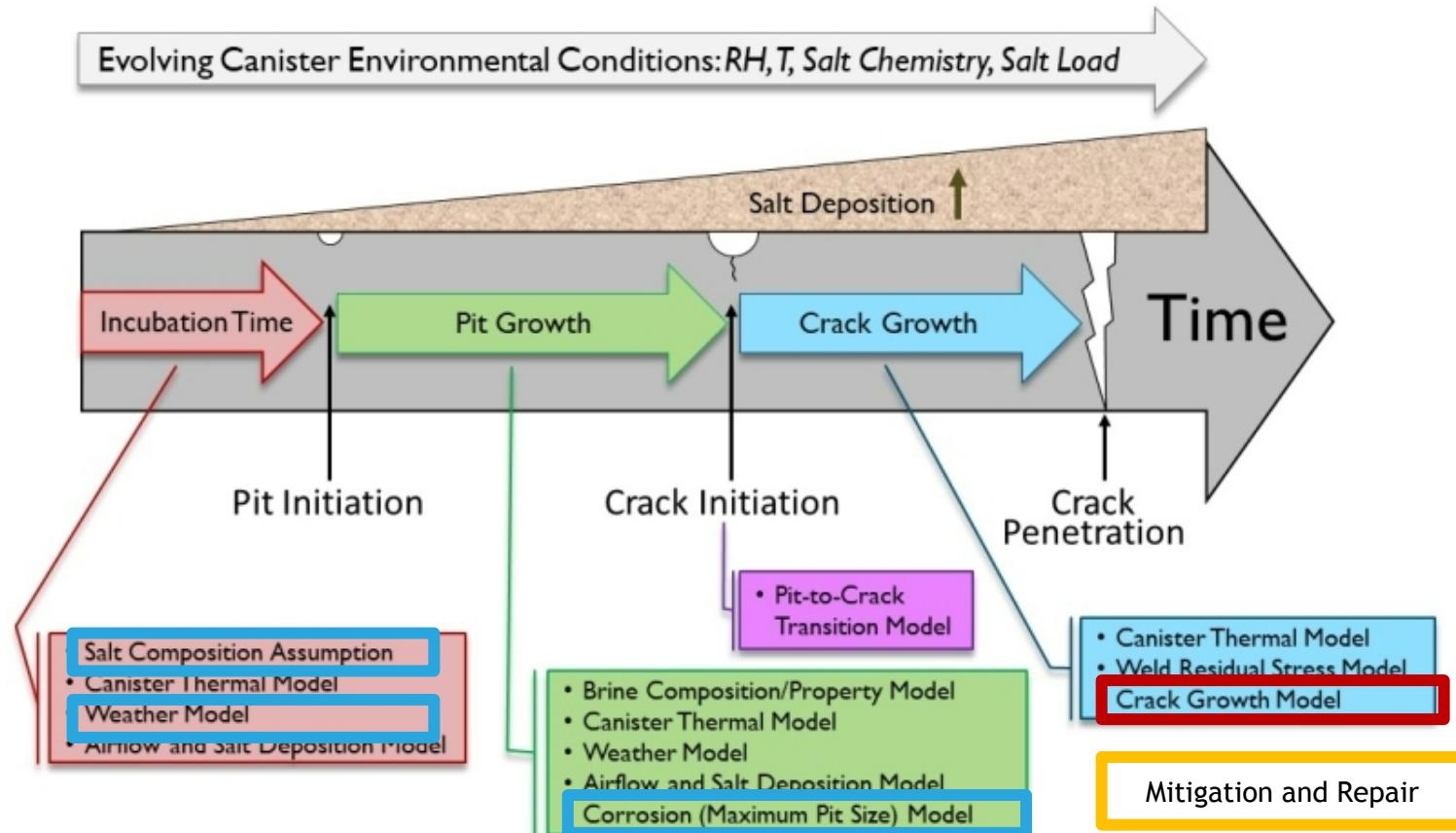
- US has over 86,000 metric tons of Spent Nuclear Fuel (SNF)
 - > 3600 stainless steel (SS) canisters
 - > 70 storage sites
- Interim storage sites being utilized longer than initially intended
- US has no permanent disposal site selected for SNF



SNF Canister inside concrete overpack

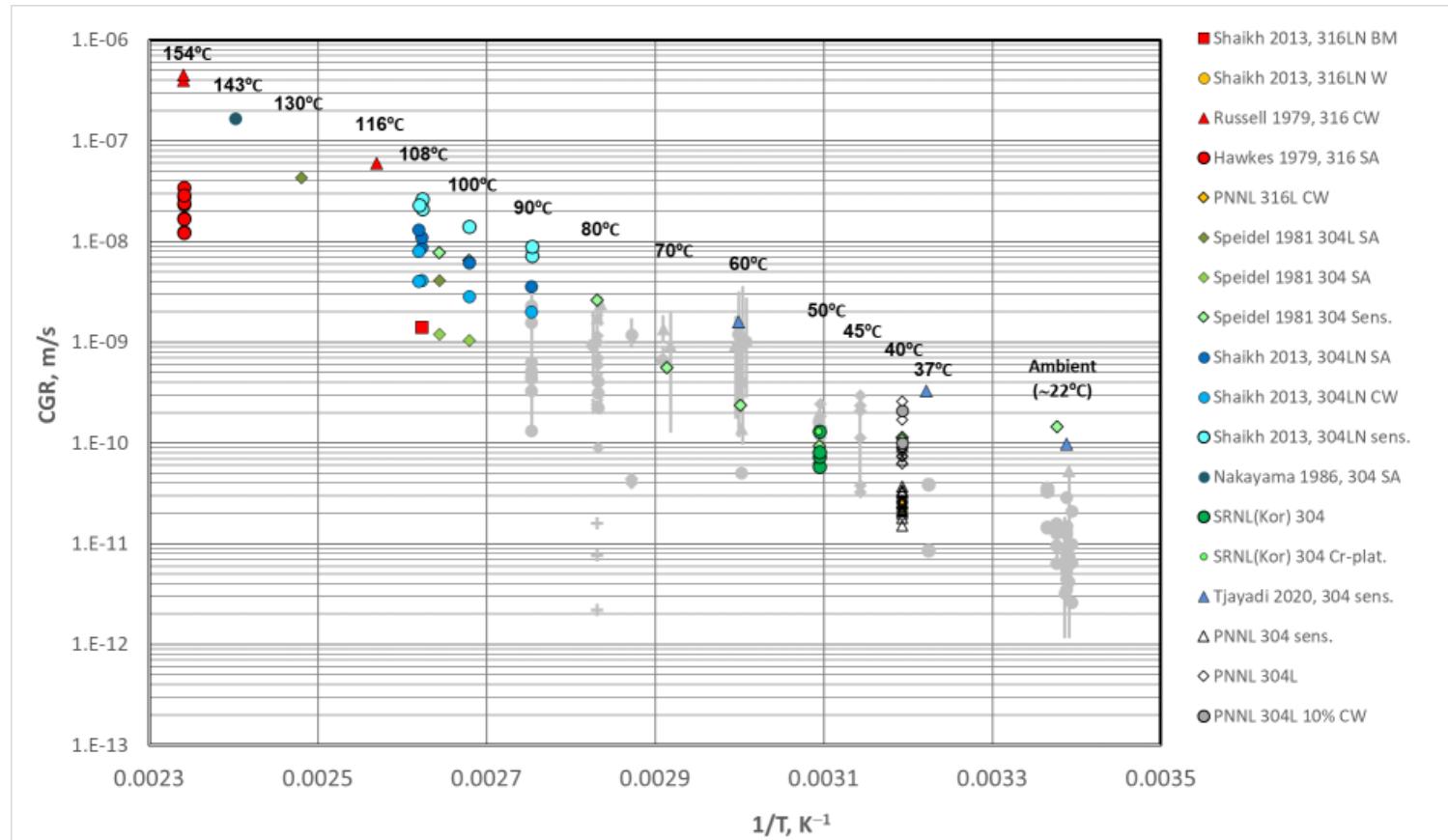


Integrated Mechanistic/Probabilistic Model for Canister SCC



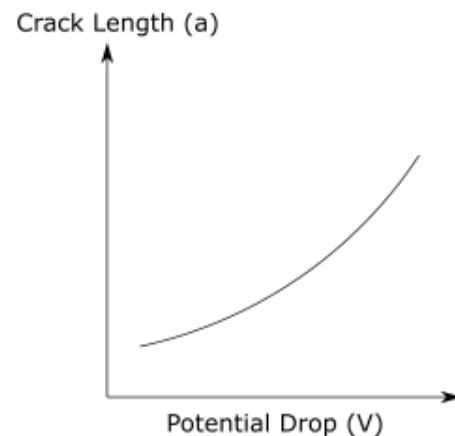
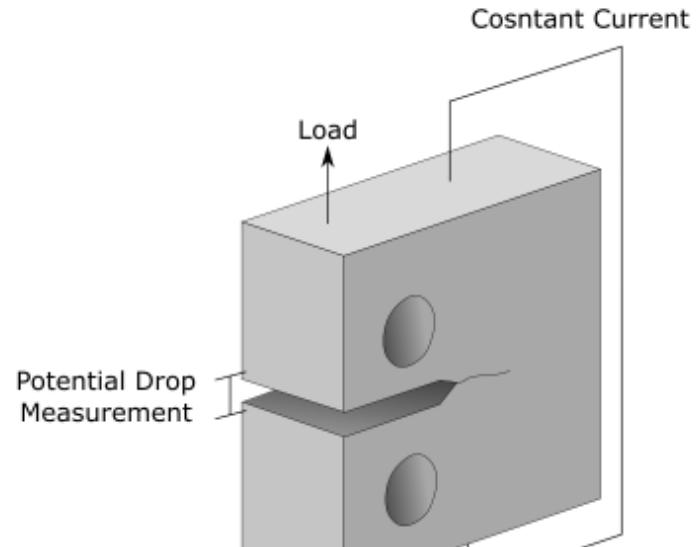
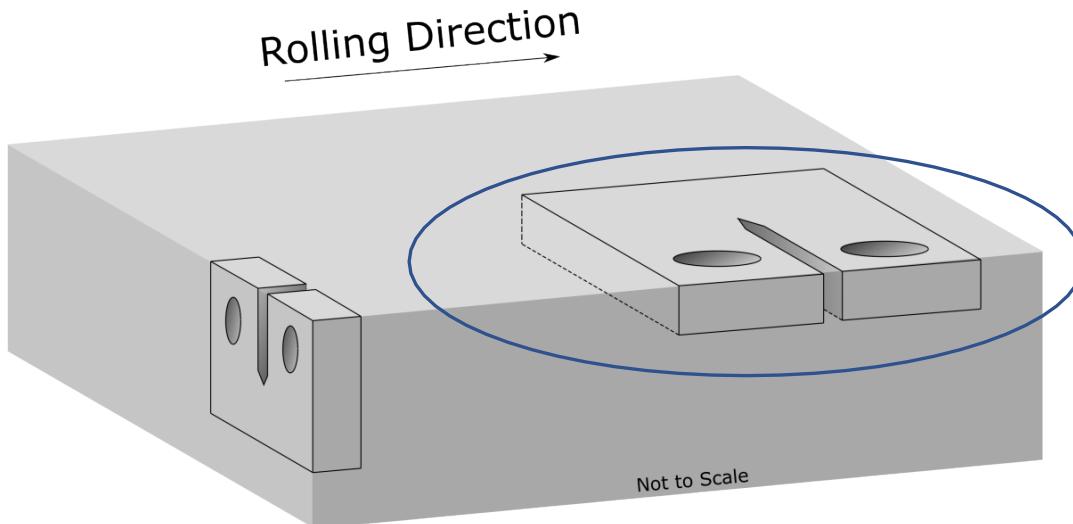
- Check out:
 - **Dr. Erin Karasz** (*Accelerated Corrosion Testing Of Cold Spray Coatings On 304L In Chloride Environments*)
 - **Dr. Ryan Katona** (*Environmental Influences on Maximum Pit Sizes for Austenitic Stainless Steels Utilized in Spent Nuclear Fuel Storage*)
 - **Timothy Montoya** (*Poster Session - Long term, simulated marine diurnal exposure of Austenitic Stainless Steel at elevated temperatures*) and **Armando Shehi** (*The Effect Of Sulfate-To-Chloride And Nitrate-To-Chloride Ion Ratio On The Kinetic Parameters For Pit Stability*)

Arrhenius Temperature Dependence of Crack Growth



- Various collection methods, environments, lot of material, sensitization state, etc.
- ***What are the governing factors and will certain factors cause accelerated growth?***

Sample Orientation and *In-Situ* Testing Methodology

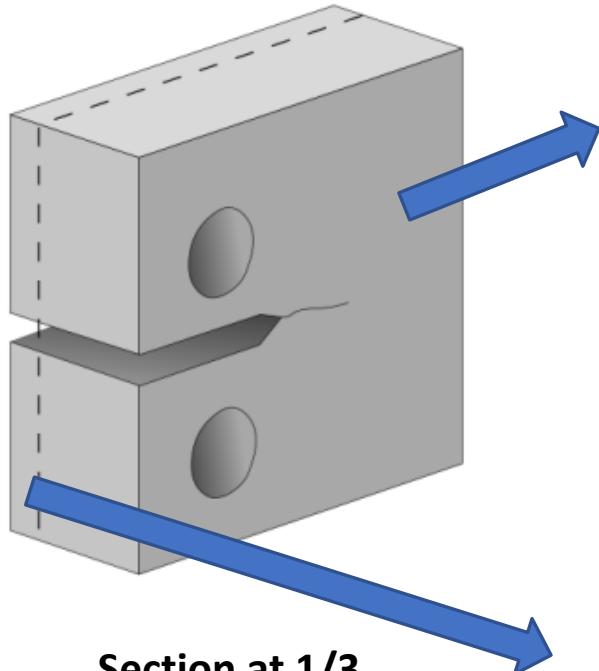


- Majority of samples presented will be in the L-T orientation
- Annealed ASTM SS304L (information in supplemental)
- Utilizing Direct Current Potential Drop (DCPD)

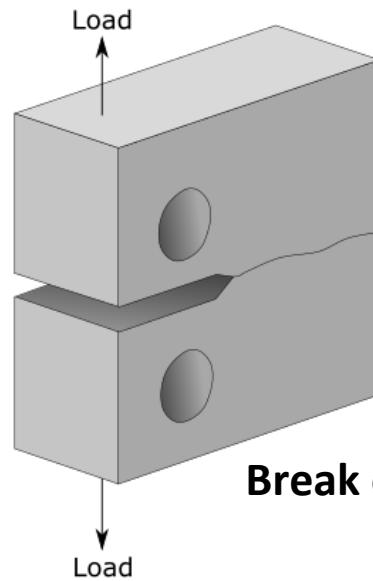
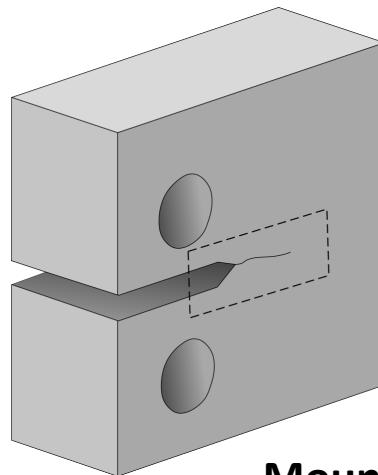
Methods for Post Test Sample Analysis



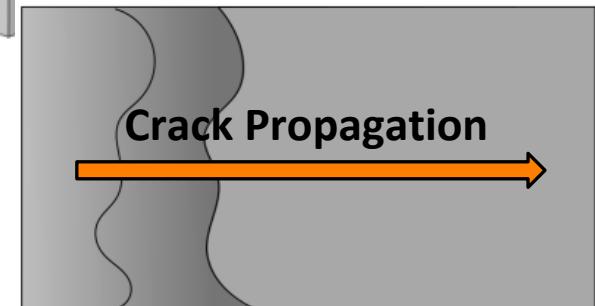
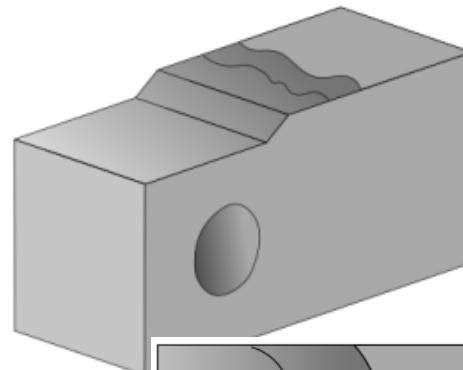
After Heat Tint



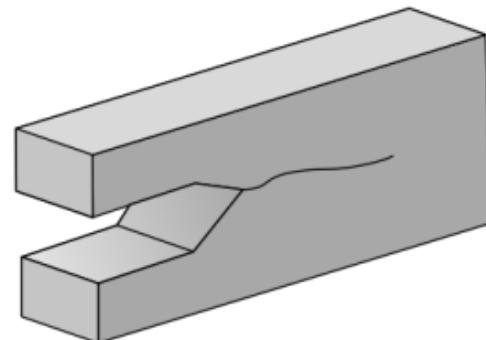
Section at 1/3 thickness



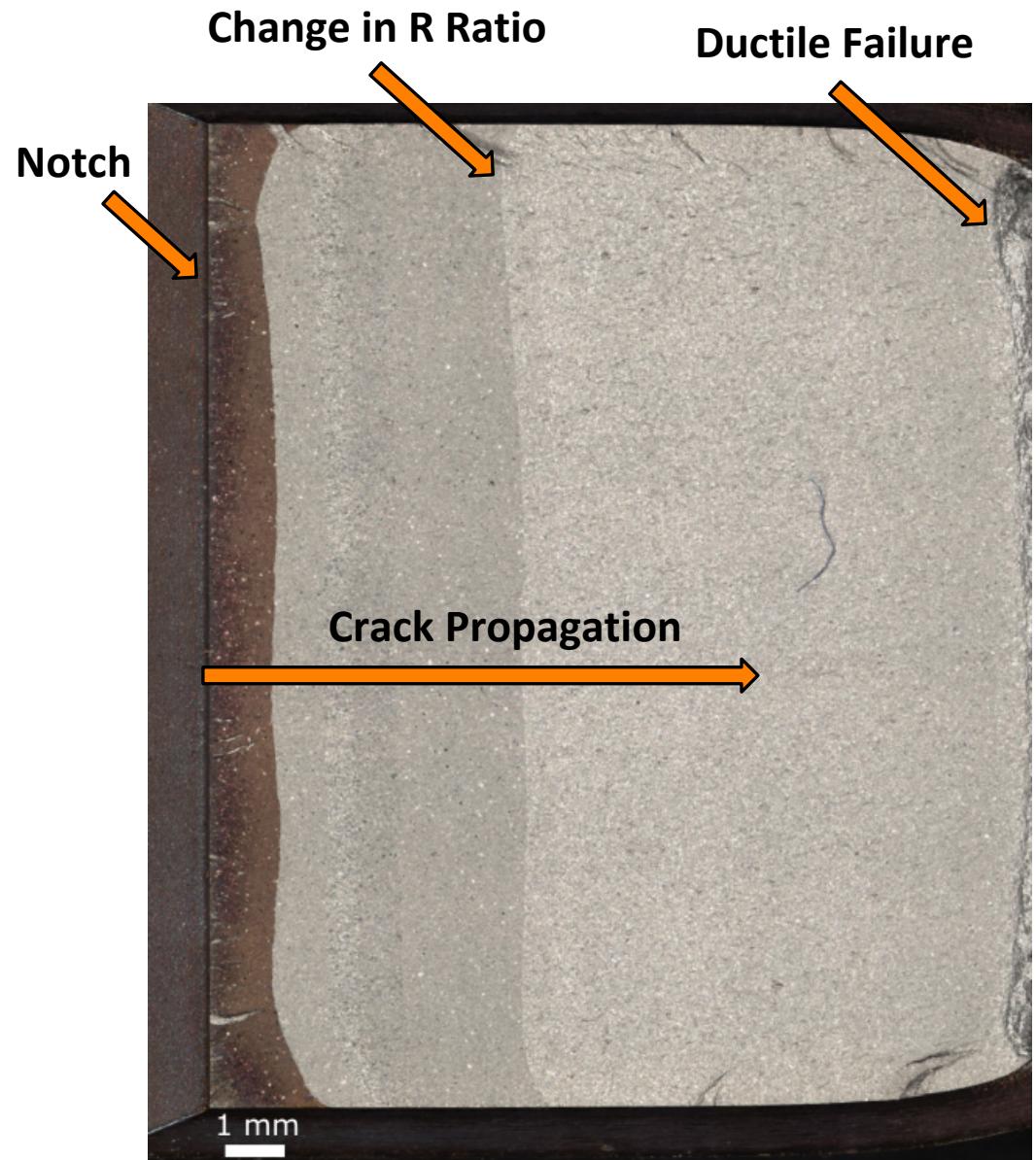
Break open 2/3



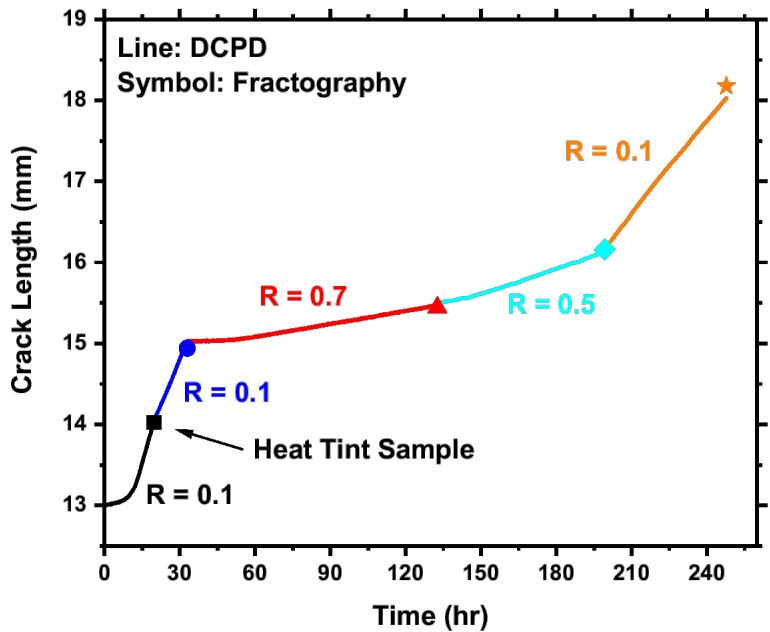
Mount Polish 1/3



Calibration of DCPD Set-up

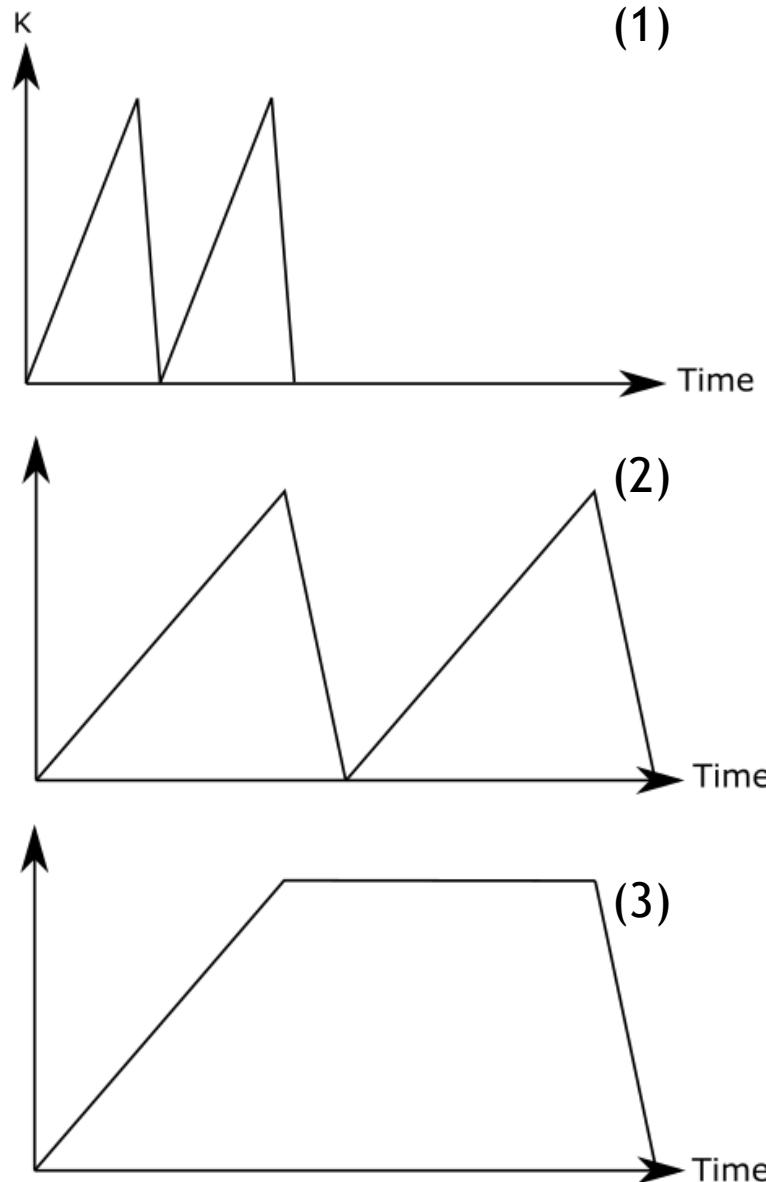
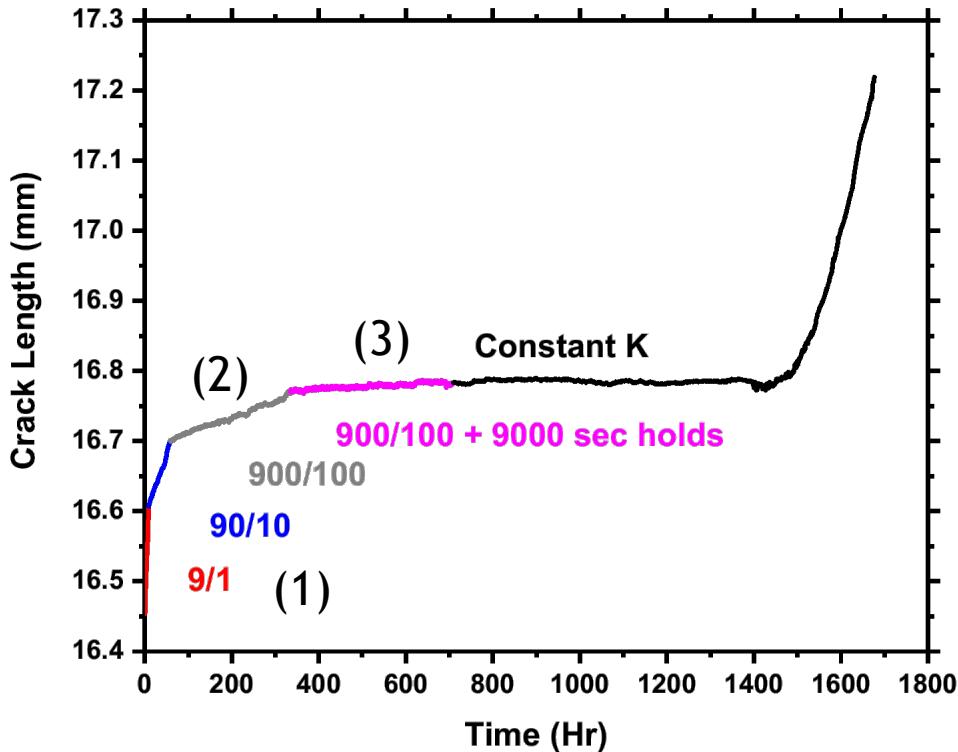


Calibration of DCPD Set-up



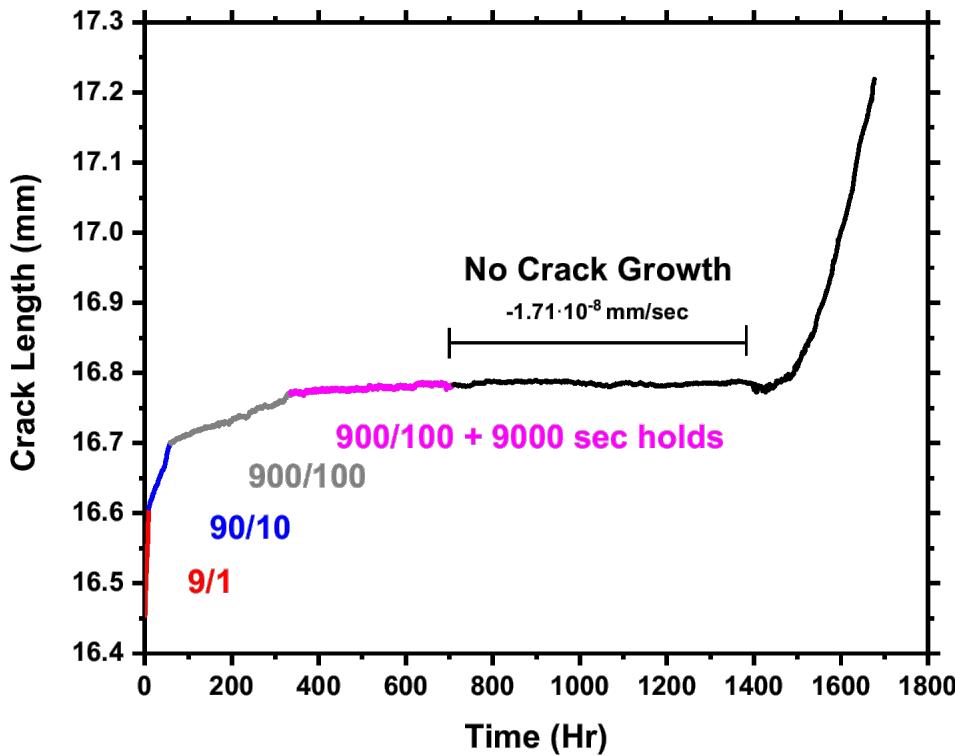
- Performed on two different load frames
- Confidence DCPD system is set-up correctly

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



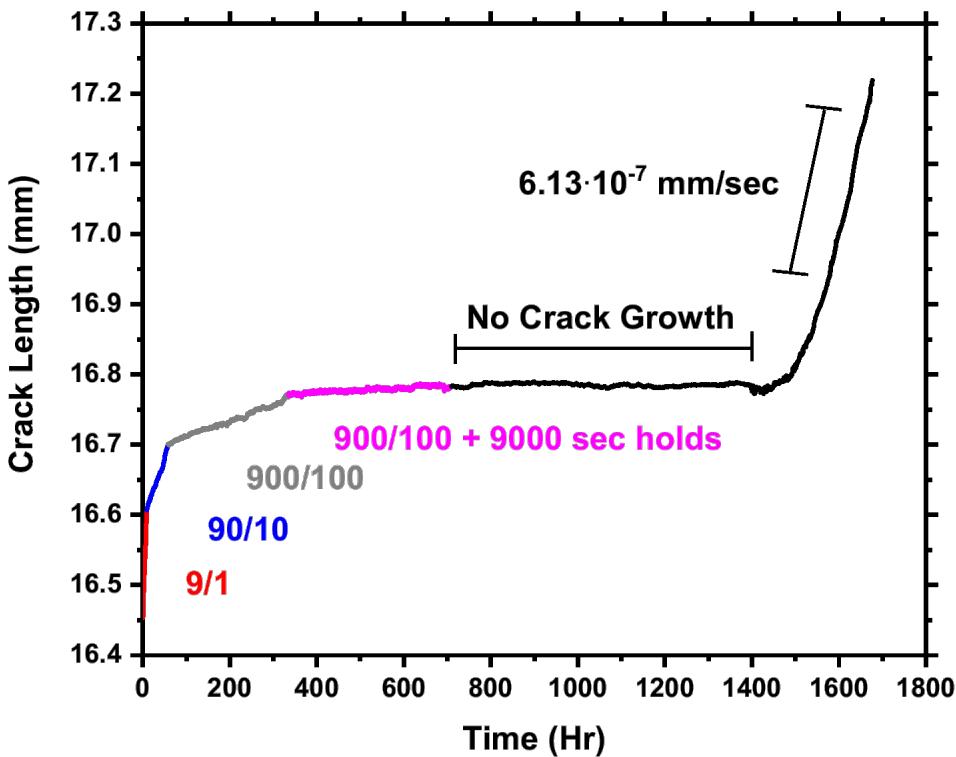
- Decreasing frequency under K control to constant K state
 - 'True' crack plane for constant K SCC
- $K_{max} = 20 MPa\sqrt{m}$

SS304L Exhibits Delayed Crack Growth Under Constant K in MgCl₂ at 55 °C



- No growth for ~ 700 hours

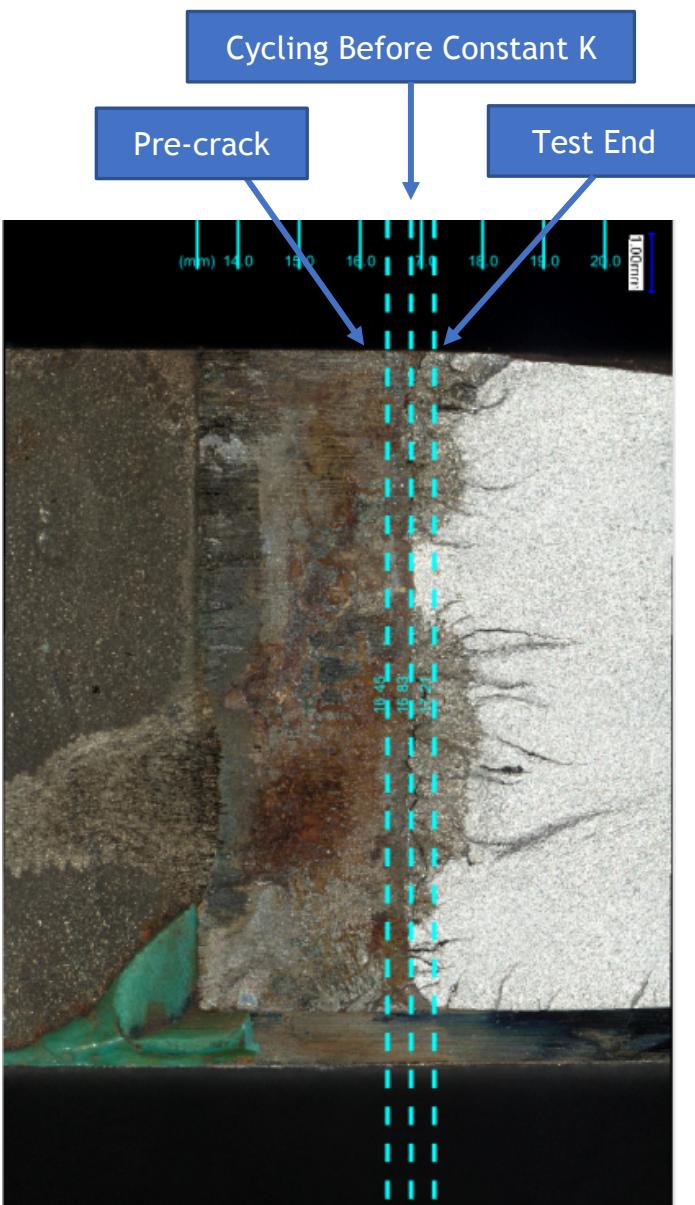
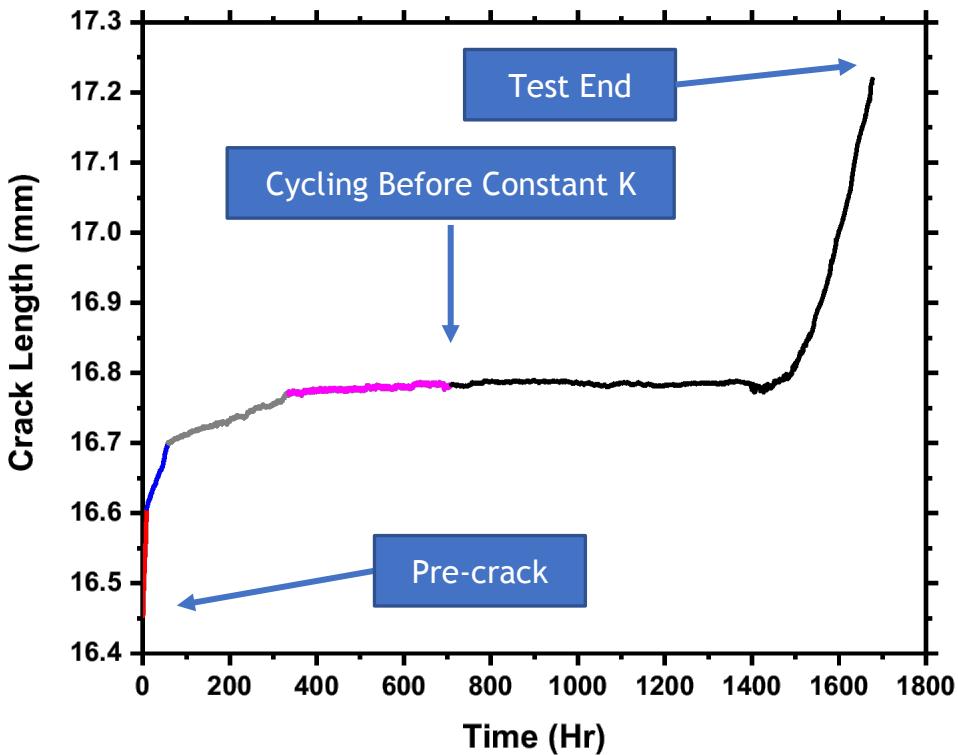
SS304L Exhibits Irregular Crack Front in Saturated MgCl₂ at 55 °C



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

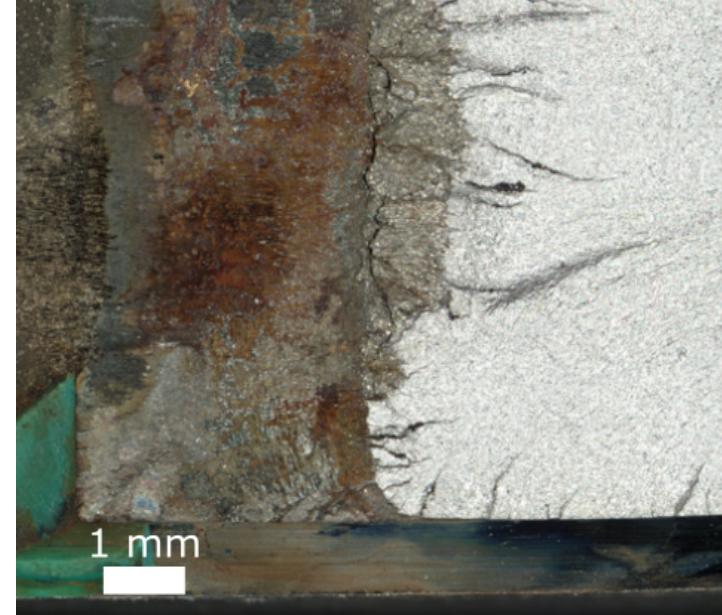
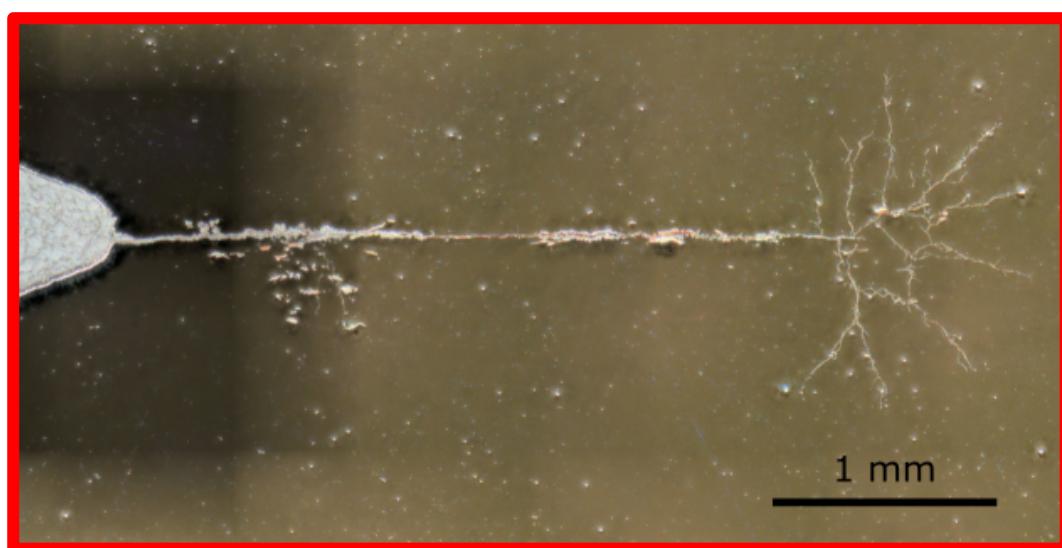
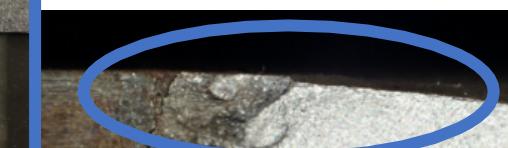
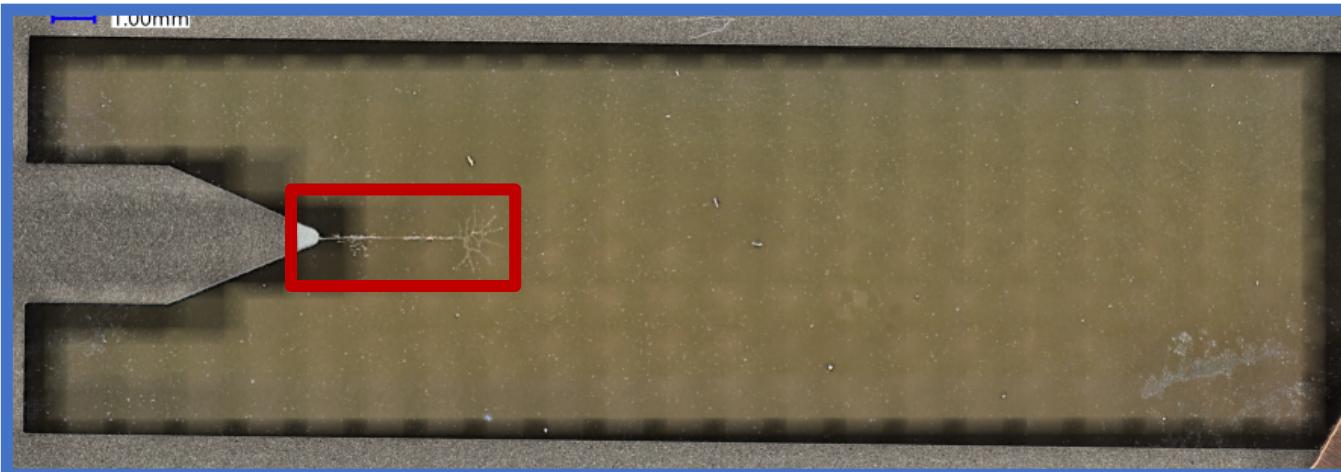


SS304L Exhibits Irregular Crack Front in Saturated $MgCl_2$ at 55 °C

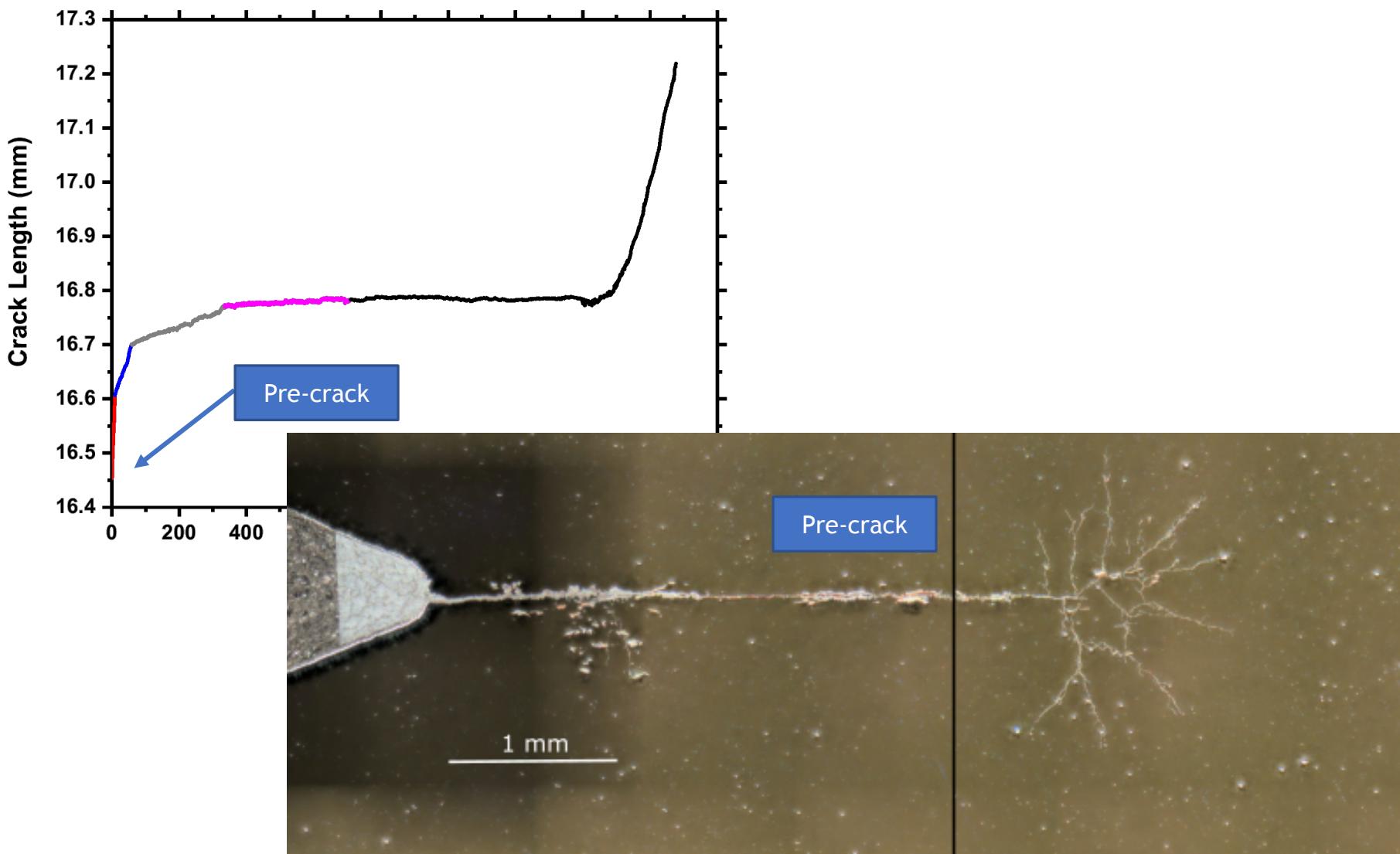


- Overlay of DCPD on fractography potentially suggests cracking halted at the uniform 'ledge'

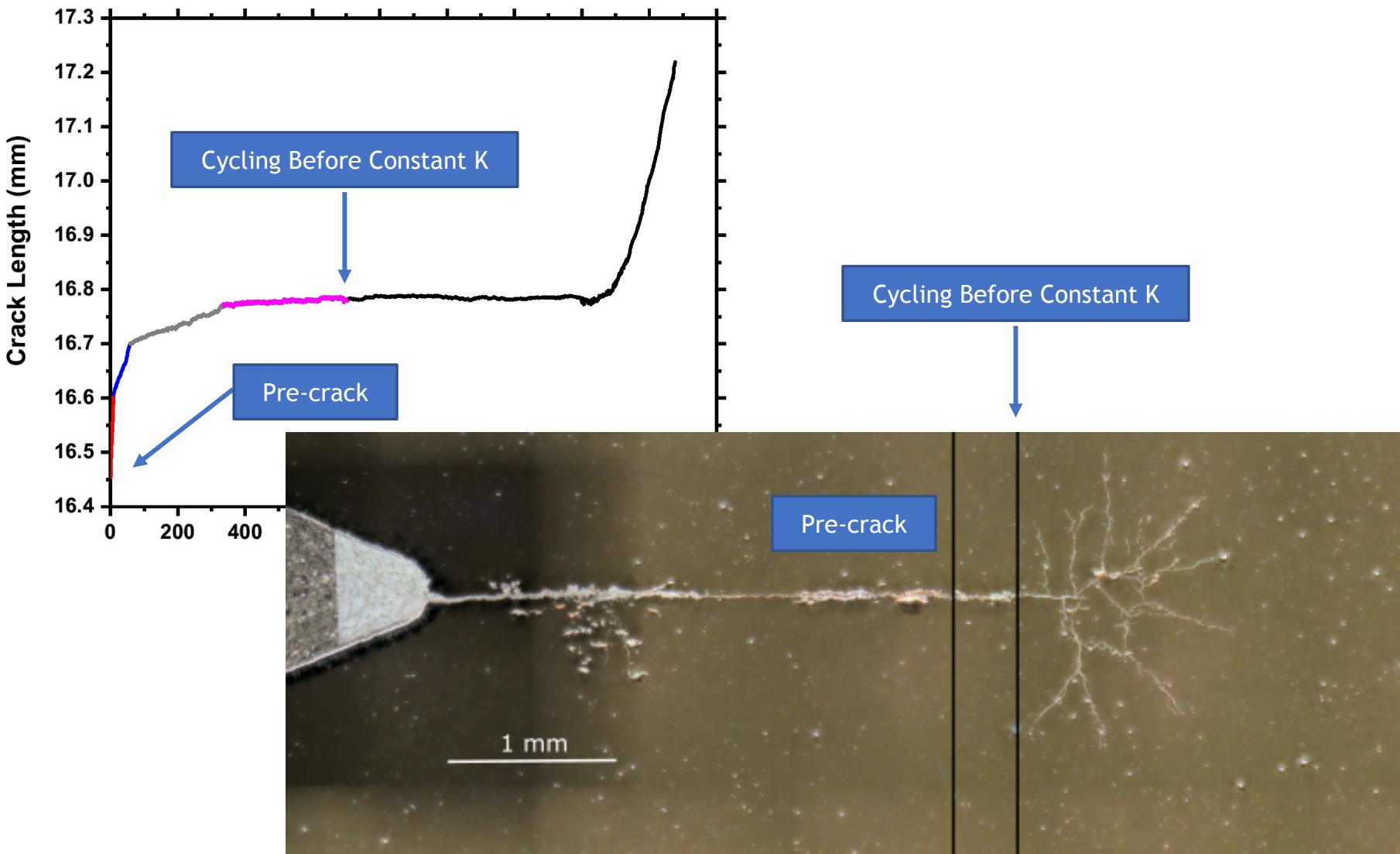
SS304L Exhibits Crack Branching in Saturated MgCl_2 at 55 °C



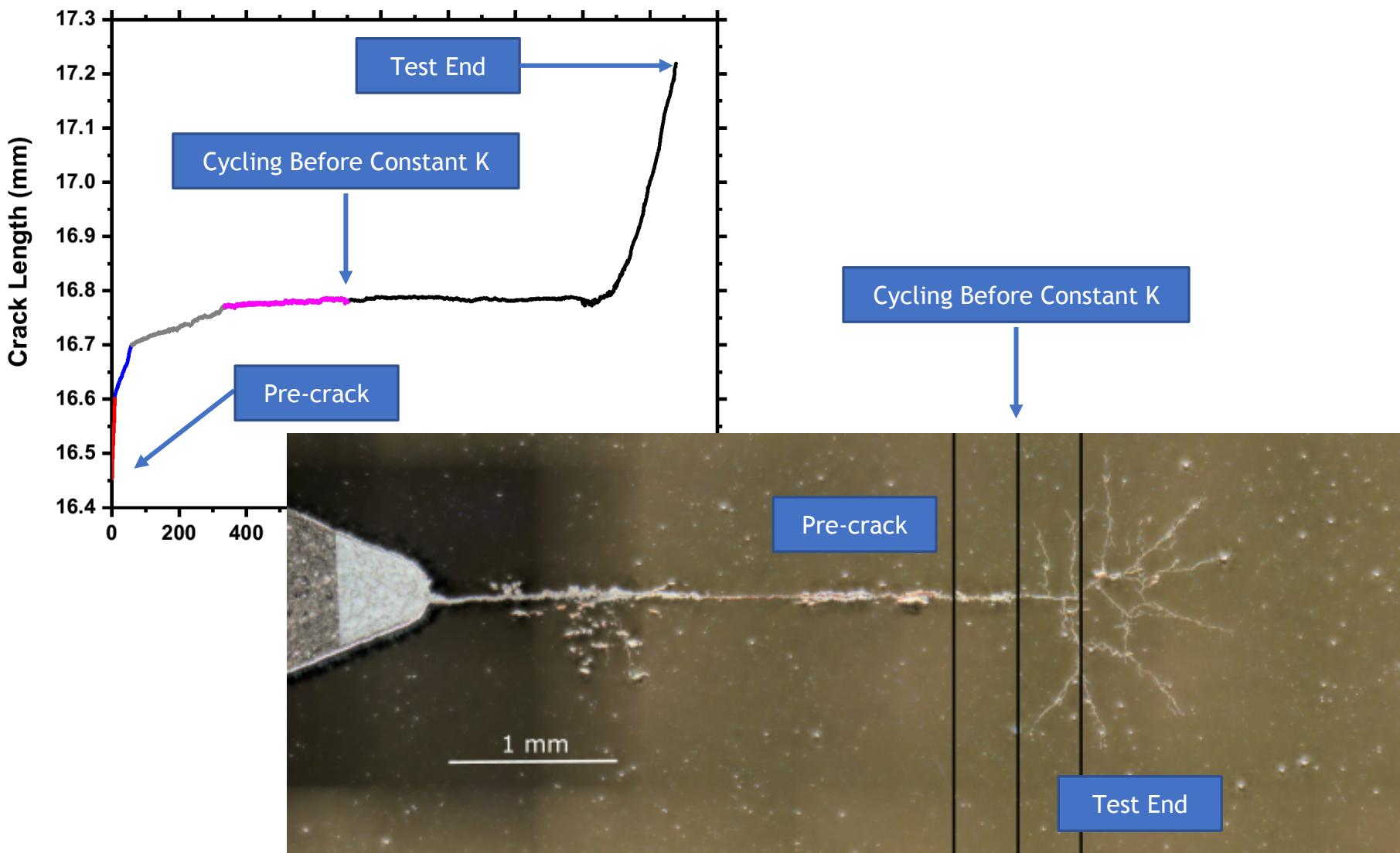
SS304L Exhibits Crack Branching in Saturated MgCl_2 at 55 °C



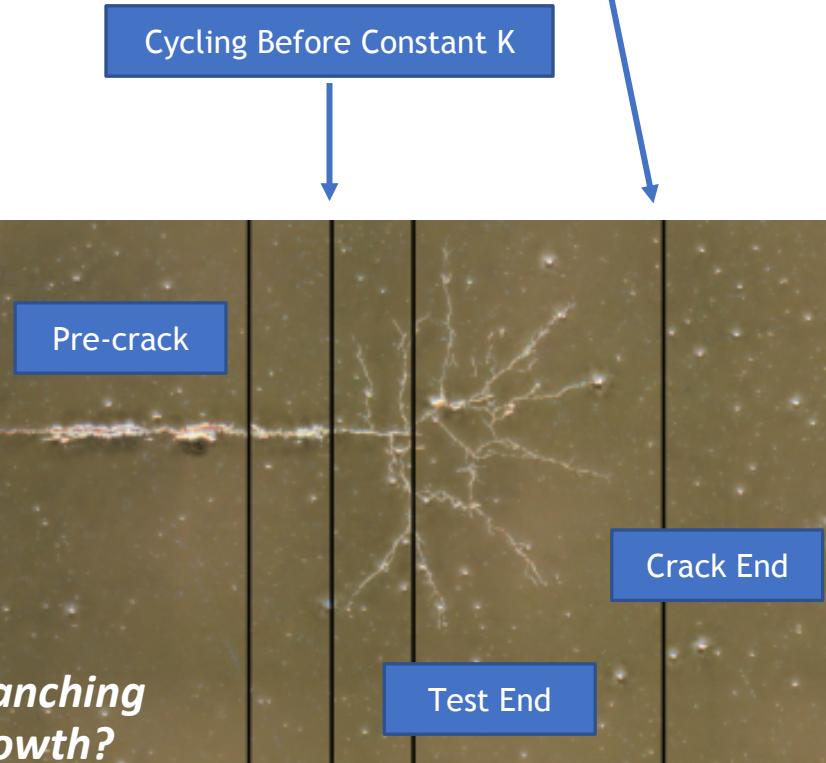
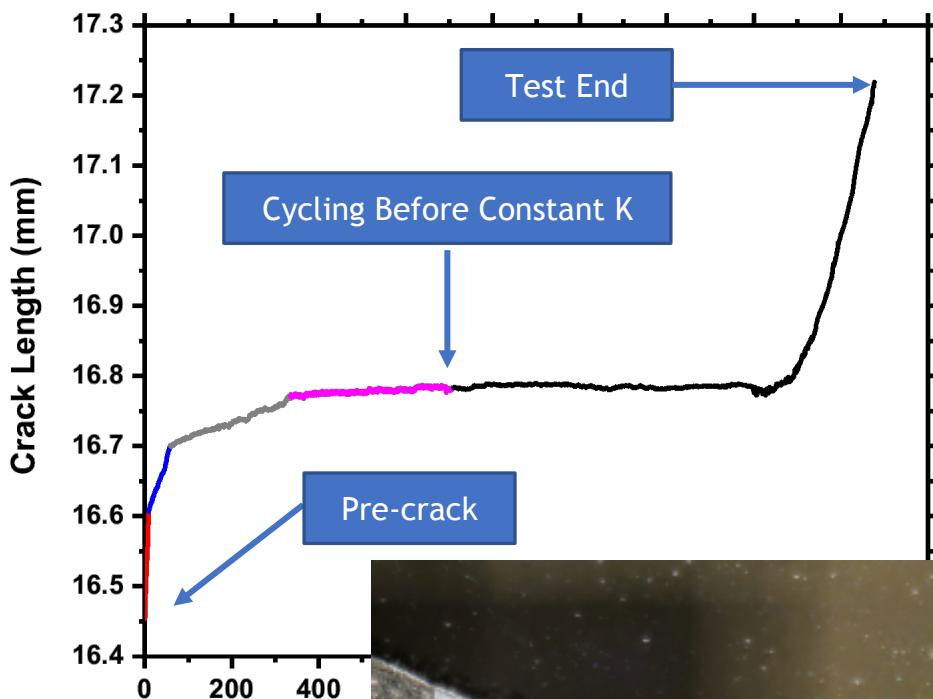
SS304L Exhibits Crack Branching in Saturated MgCl_2 at 55 °C



SS304L Exhibits Crack Branching in Saturated MgCl_2 at 55 °C

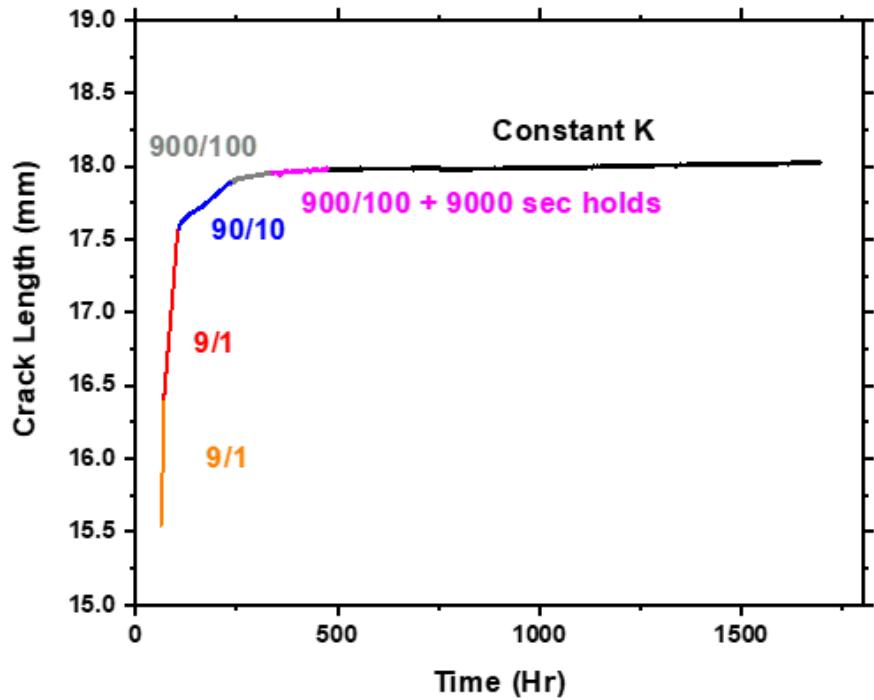


SS304L Exhibits Crack Branching in Saturated $MgCl_2$ at 55 °C

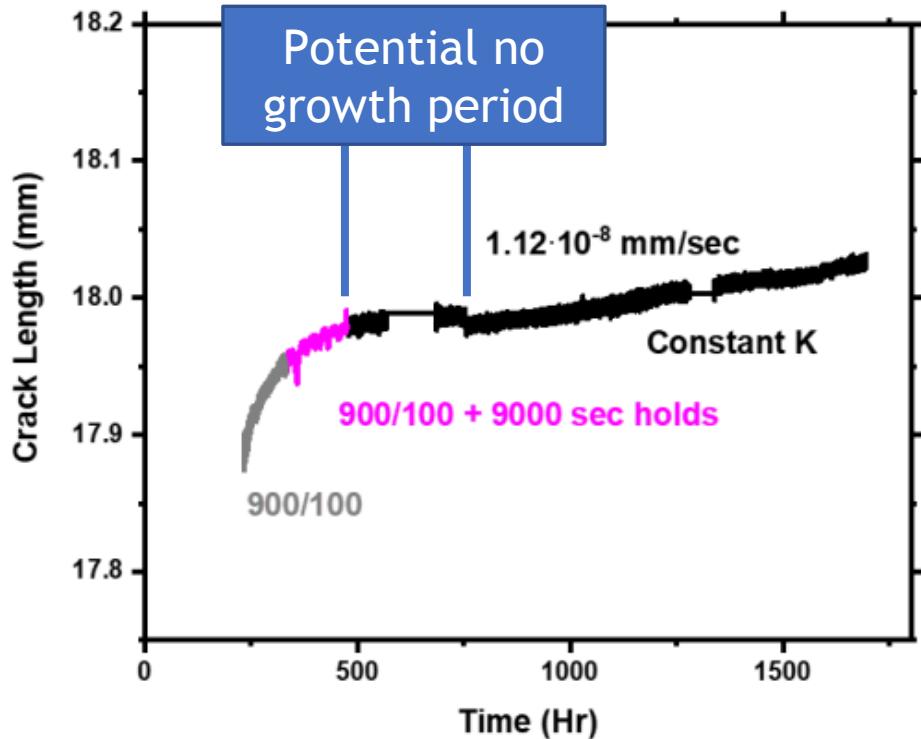


Is it possible that crack branching caused delayed crack growth?

Low Crack Growth Rate for in Saturated MgCl_2 at 25 °C



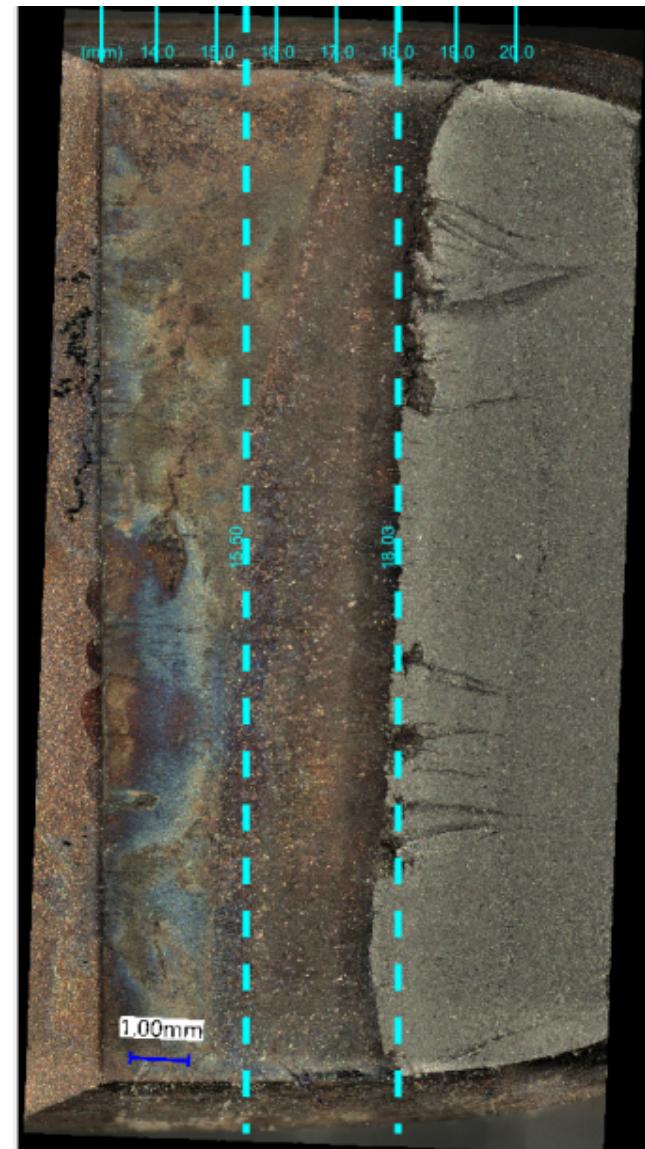
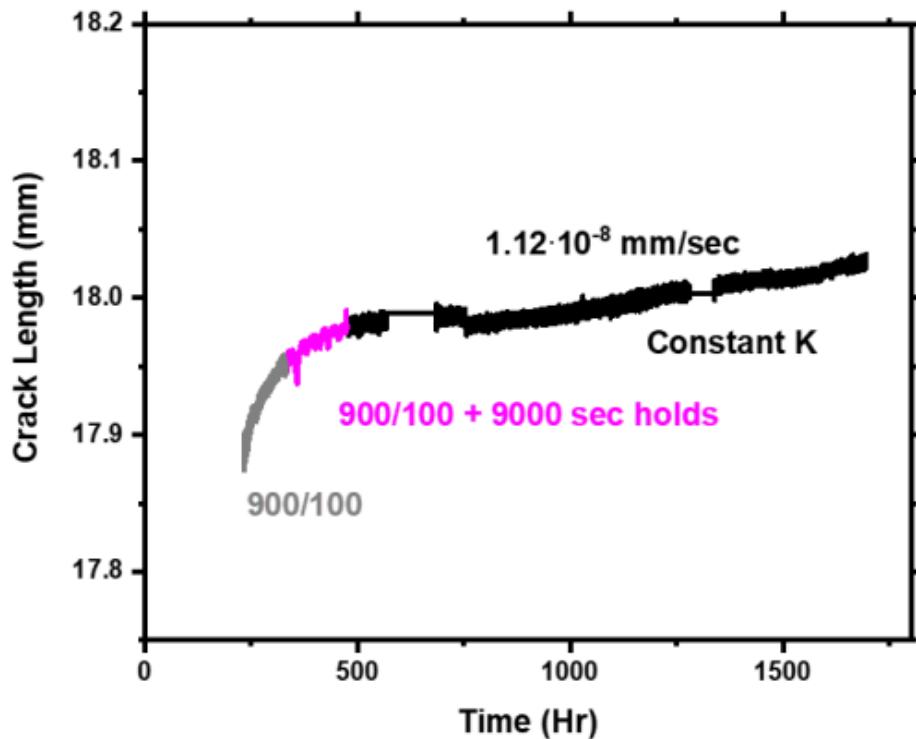
Low Crack Growth Rate for in Saturated MgCl₂ at 25 °C Experienced Localized Cracking



- 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 MgCl₂ at 25 °C



- Slightly curved crack front makes overlay of DCPD difficult

SS304L Exhibits Irregular Crack Front in Saturated MgCl₂ at 25 °C



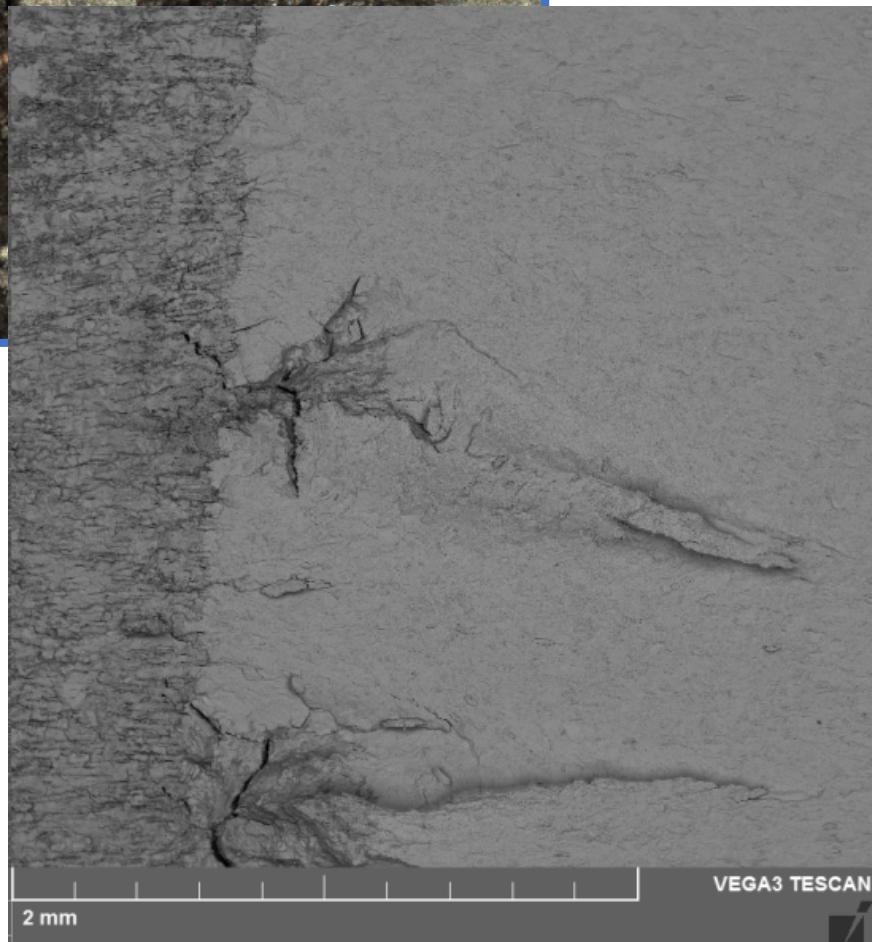
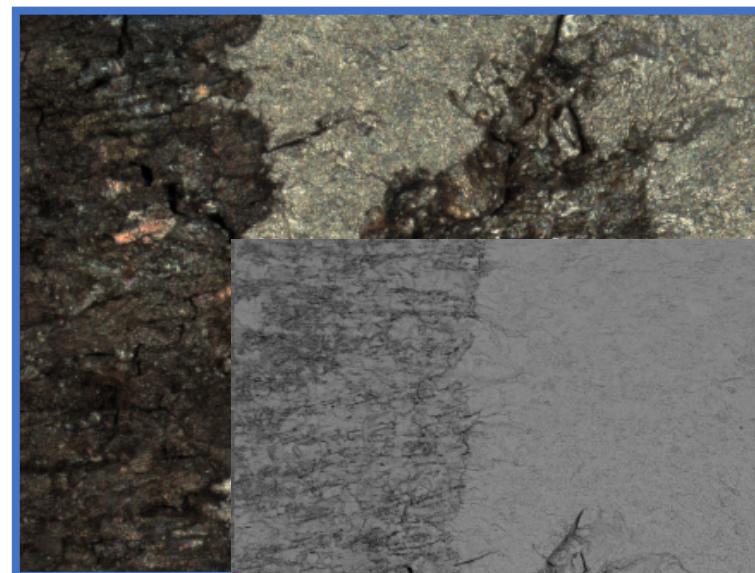
- Measured 100 points of extension from the drawn blue line and averaged
 - Integration of crack extension by hand

Method	Δa
DCPD	53.8 mm
Fractography	60.1 mm

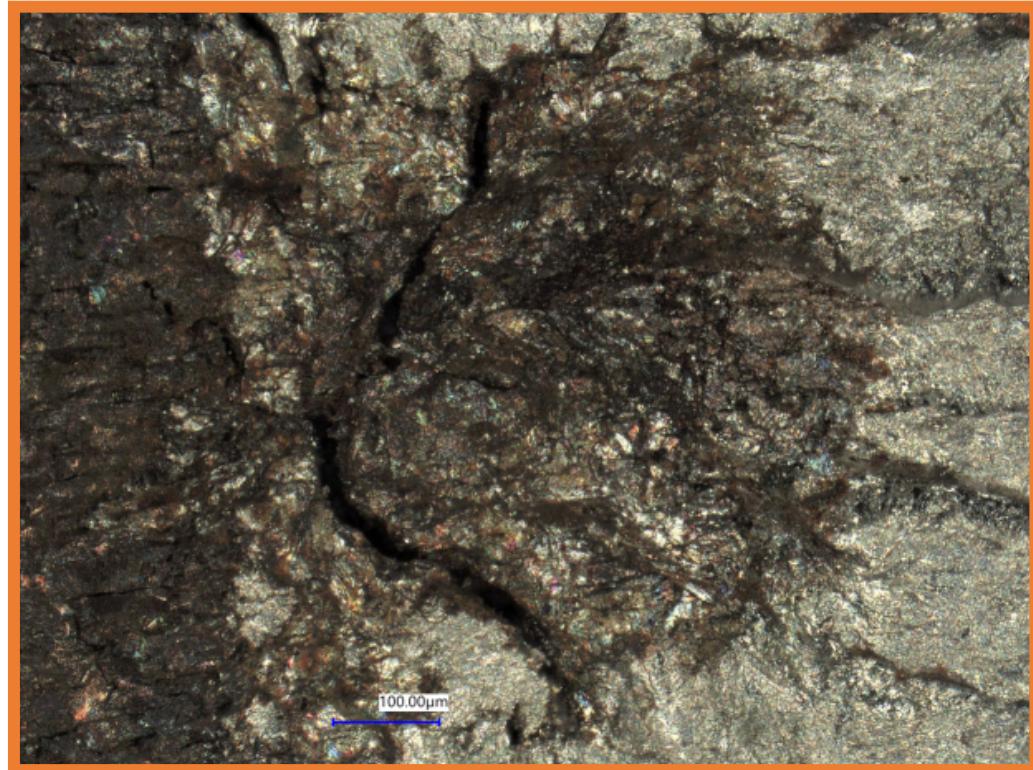
- Compared to total crack extension during constant K portion
- Possible that growth in 'protrusions' ahead of blue line occurred during the constant K portion



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

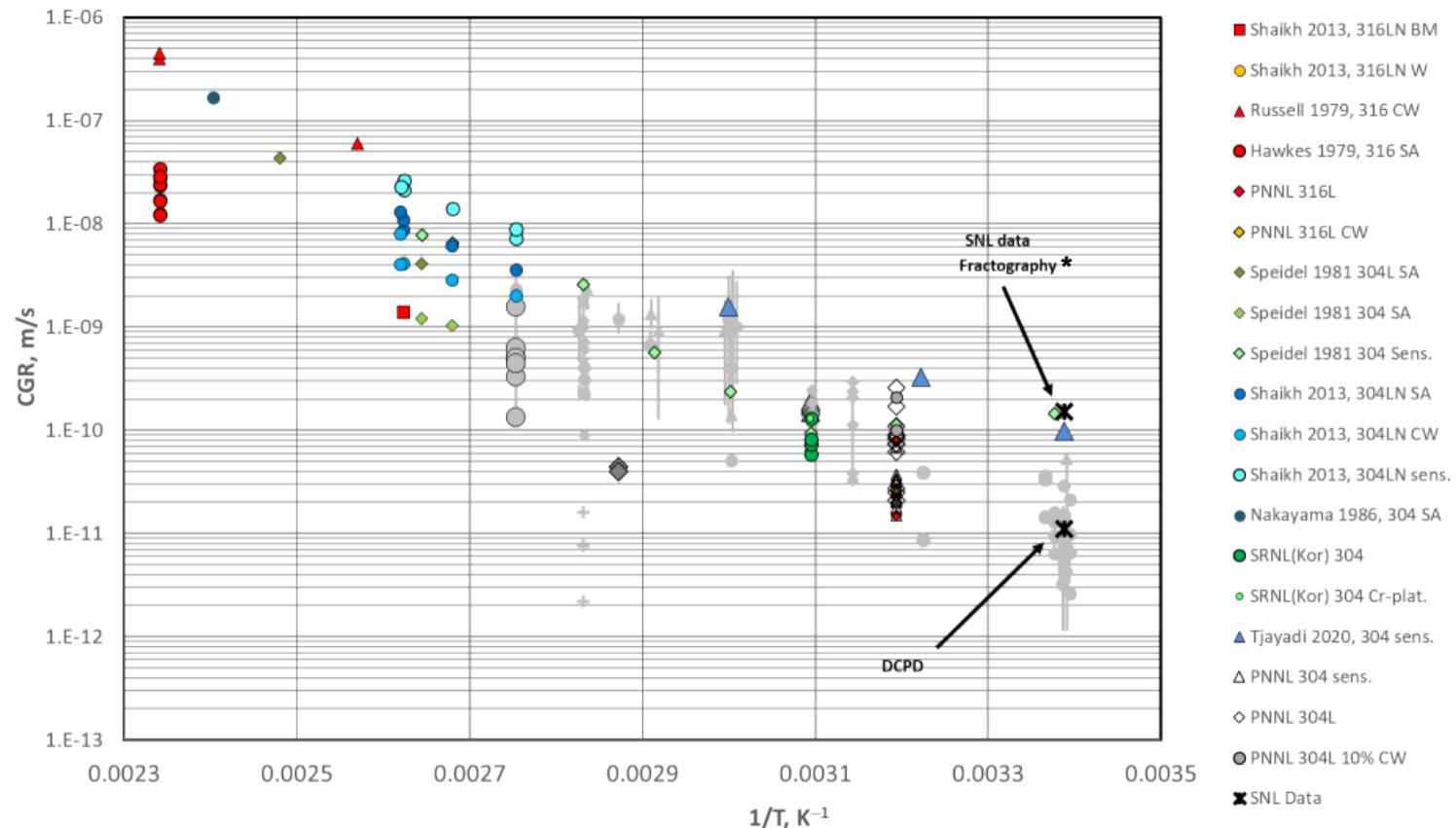


SS304L Exhibits Irregular Crack Front in Saturated MgCl₂ at 25 °C



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

Crack Growth of Furthest 'Protrusion' Potentially Order of Magnitude Higher Than DCPD

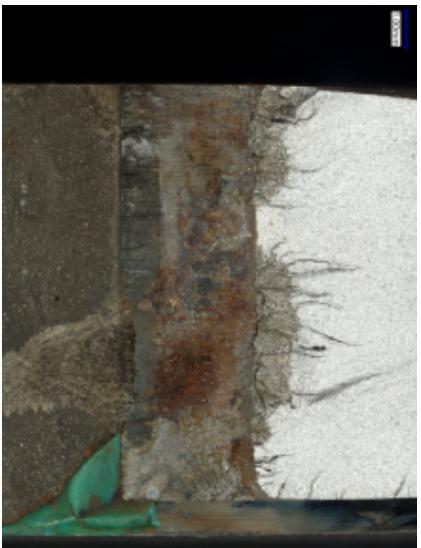


- Considering protrusion occurs during constant K portion of the test, an increased crack growth rate is calculated
 - *measured from deepest point of protrusion

Overview of MgCl₂ Samples



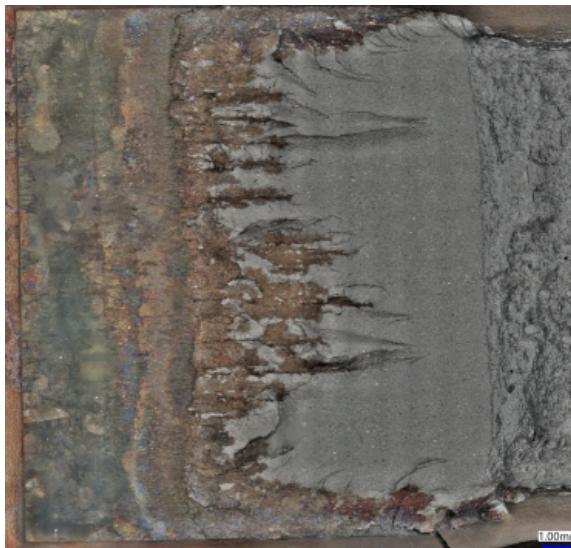
Lot 1 – RT
(1218 hours)



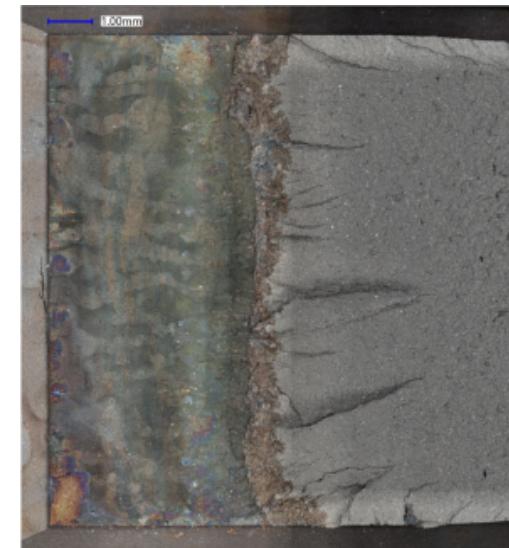
Lot 1 - 55 °C
(709 Hours)

(450 hours of
growth)

(Time under Constant K)



Lot 3 - 55 ° C
(650 Hours)



Lot 3 - 55 ° C (T-S)
(800 Hours)

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

Overview of Saturated NaCl Samples



No indicated crack growth

Lot 1 – RT



Roughly 50 μm of crack extension during constant K

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

Lot 3 – 60 °C

What Causes Different Morphology Between Solution?



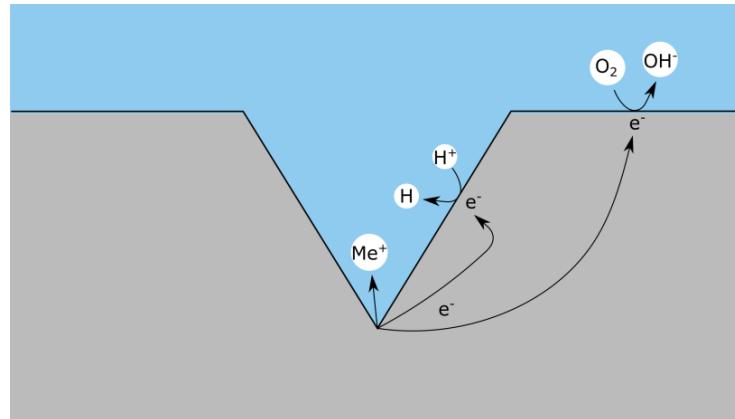
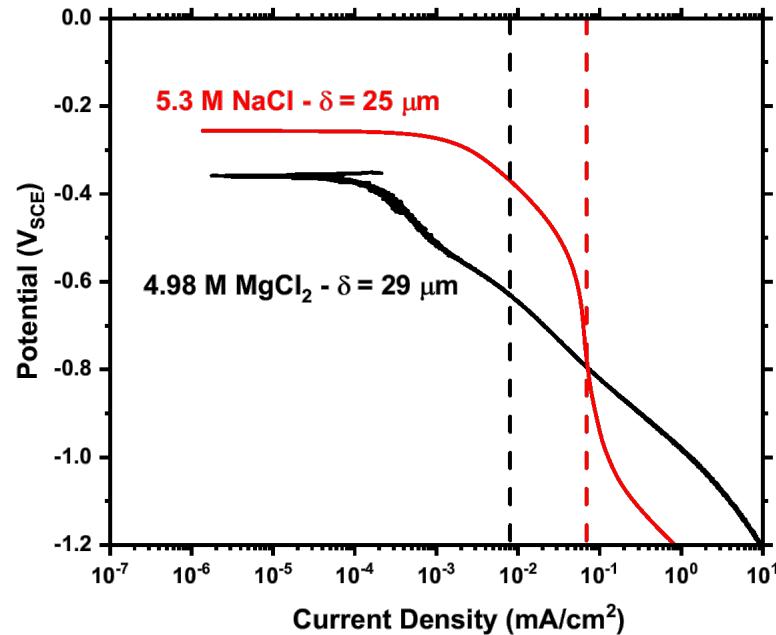
NaCl
Lot 3 – 60 °C



MgCl₂

Lot 3 – 55 °C

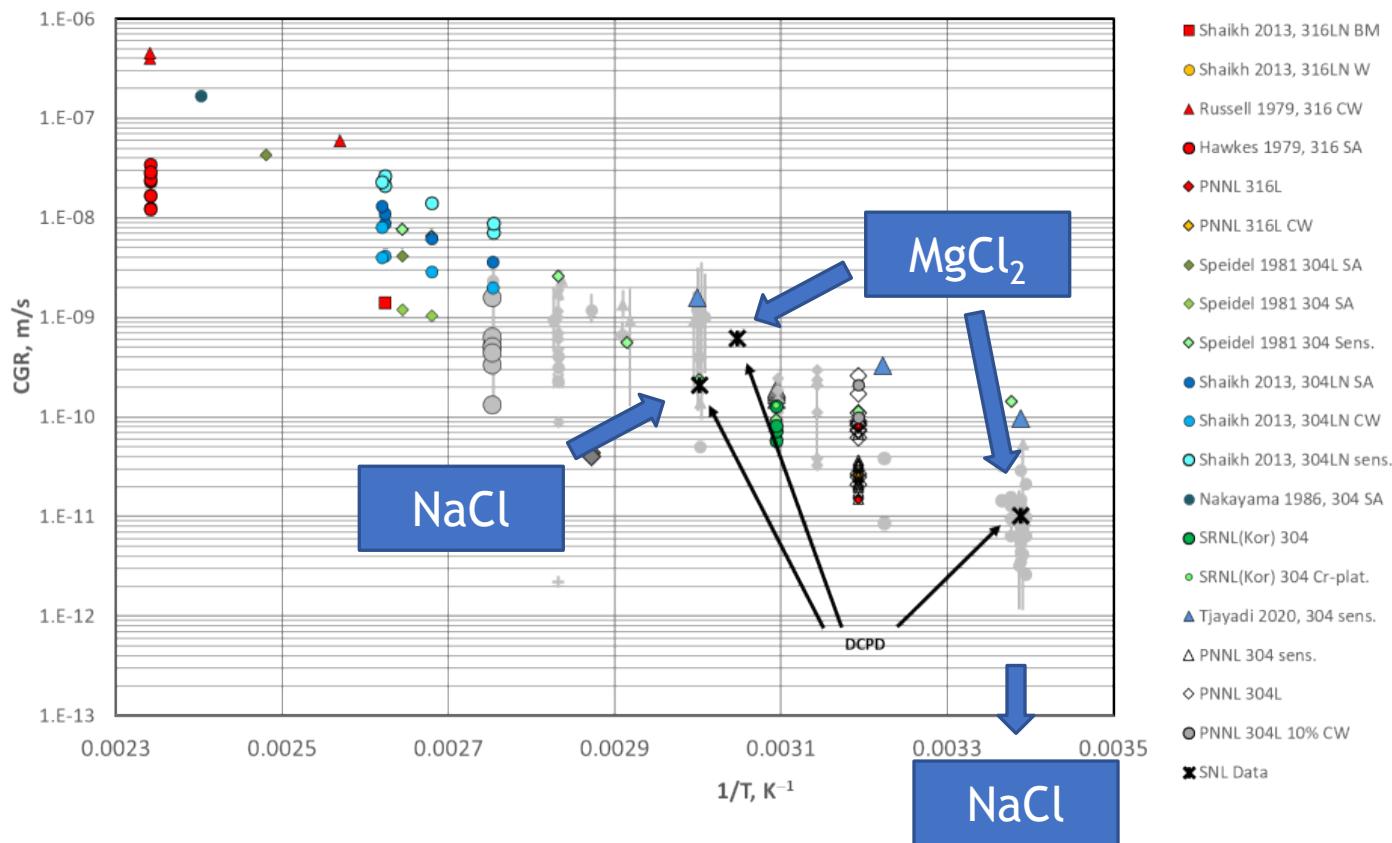
- Similar to differences in morphologies from corrosion exposures
- Potentially due to differences in cathodic reduction reaction
- Possibility for different crack tip chemistry changing pH and embrittlement



R.M. Katona et al., Journal of The Electrochemical Society, 168 (2021) 031512.

R.M. Katona et al., Corrosion Science, 177 (2020) 108935.

Measured Crack Growth Agrees with Literature Trends

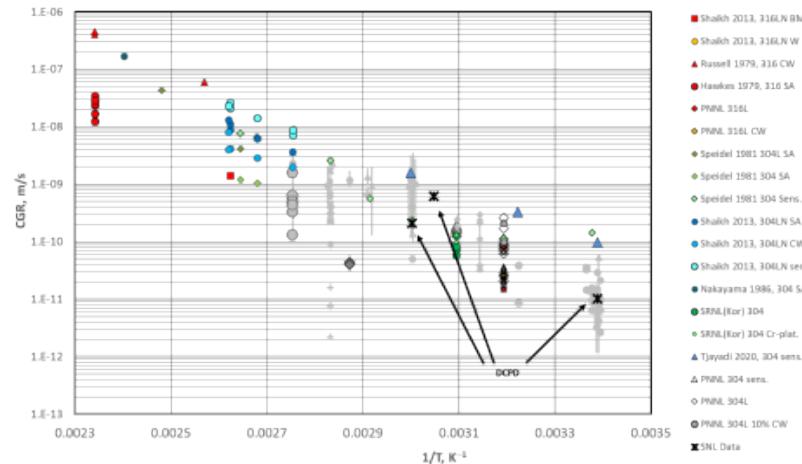


- Similar crack growth rate trend with temperature to other studies in literature
- Potential influence of solution composition on crack growth rate but does influence morphology

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.?

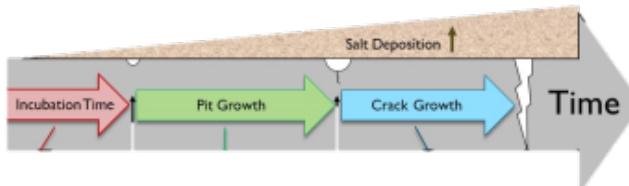


Acknowledgements



- I would like to thank Timothy Montoya (SNL) for helpful feedback
- Helpful conversations with Dr. James Burns (UVA), Dr. Robert Kelly (UVA), Dr. Mychailo Toloczko (PNNL), Sarah Blust (UVA), Trevor Shoemaker (UVA), and Michael Roach (UVA) are appreciated

Stress Corrosion Cracking of Austenitic Stainless Steels in Concentrated Chloride Environments



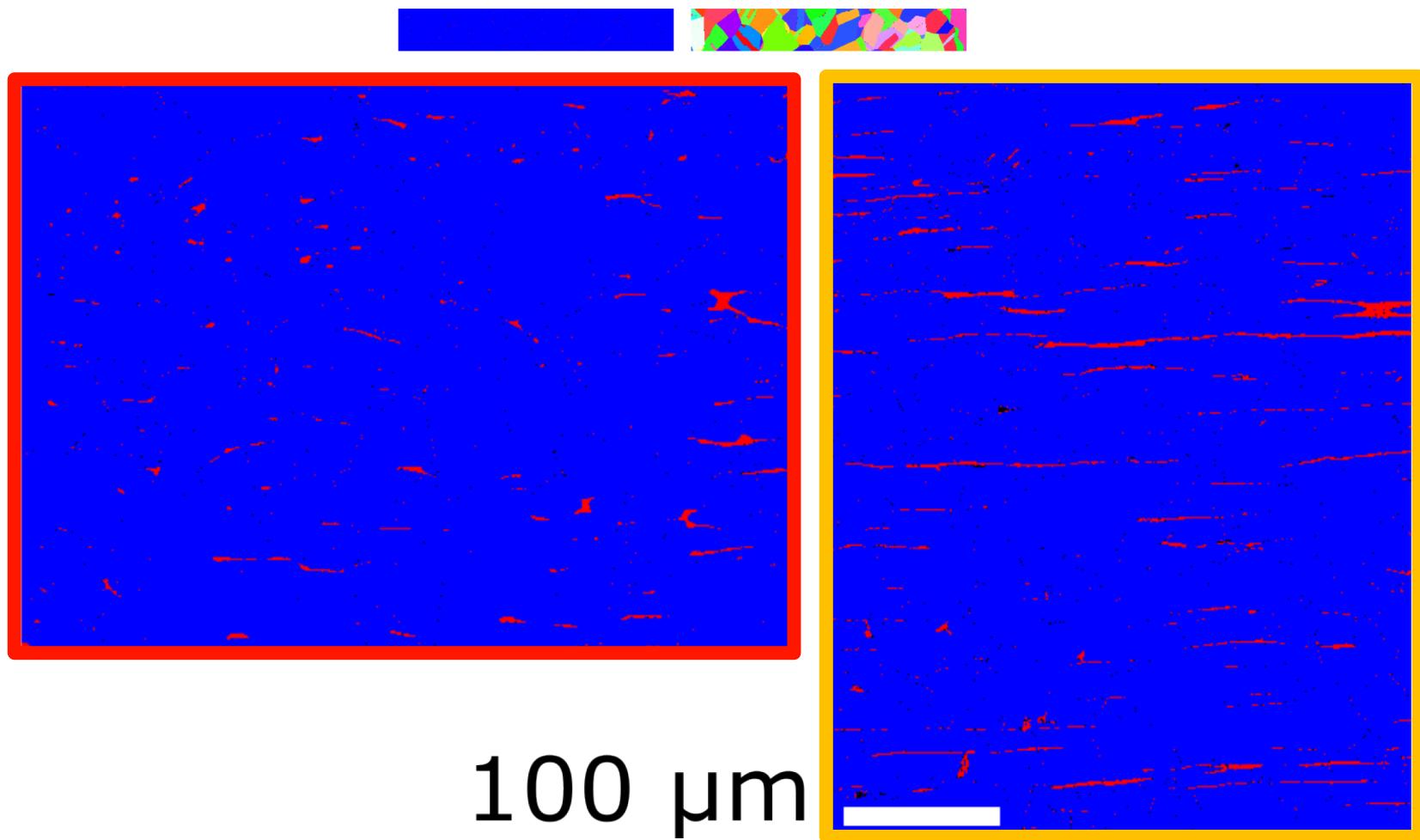
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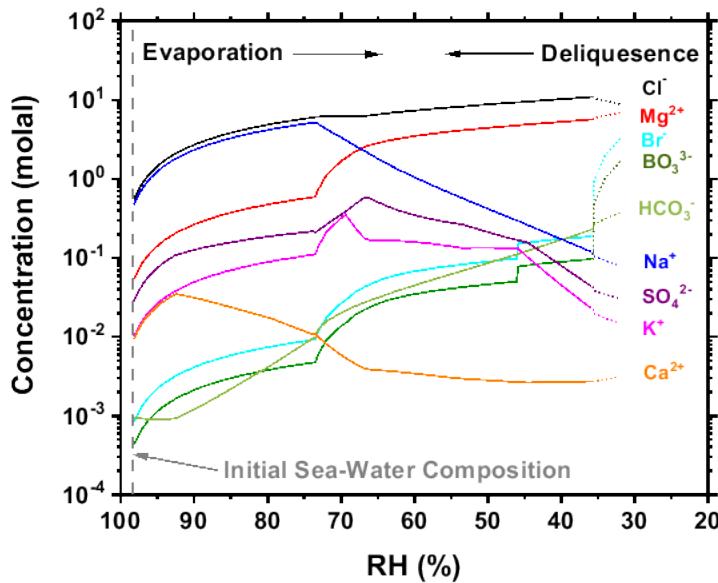
Lot Information



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

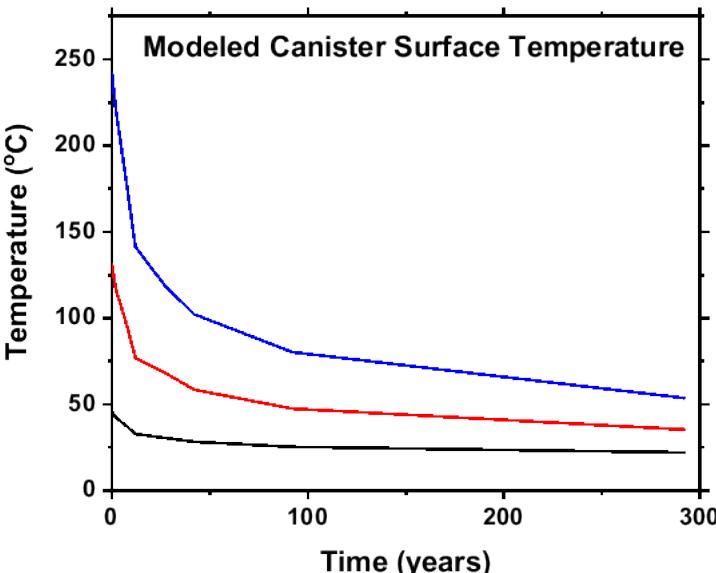
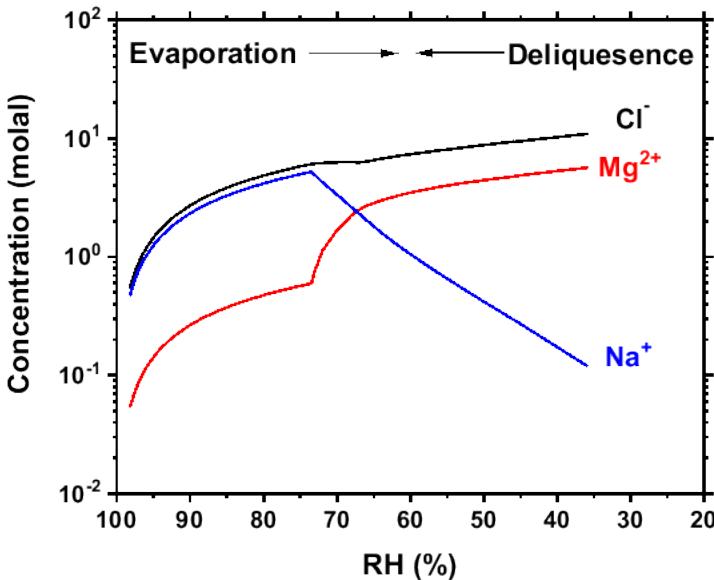
	Composition														
	<u>C</u>	<u>Co</u>	<u>Cr</u>	<u>Cu</u>	<u>Mn</u>	<u>Mo</u>	<u>N</u>	<u>Nb</u>	<u>Ni</u>	<u>P</u>	<u>S</u>	<u>Si</u>	<u>Ti</u>	<u>Fe</u>	
LT001	0.02	0.2	18.14	0.25	1.7	0.08	0.07	-	8.04	0.031	0.004	0.4	0.001	bal	
LT003	0.017	0.234	18.1	0.412	1.782	0.414	0.08	0.014	8.03	0.037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

Salt Composition and Concentration Change with RH



- Initial assumption of sea water brine

Salt Composition and Concentration Change with RH

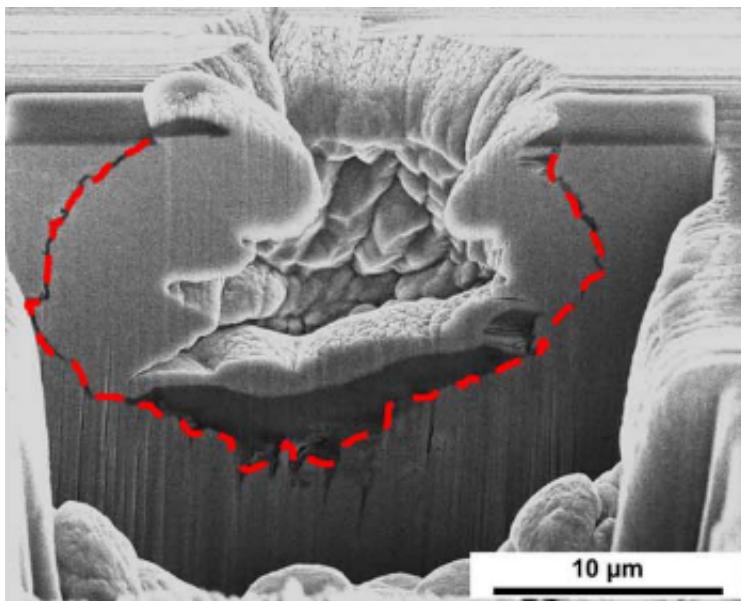


- Initial assumption of sea water brine
- Evaporation of sea water:
 - Concentration of chloride (Cl^-)
 - Change in brine composition ($\sim 75\% \text{ RH}$)
- Canister surface physically hot

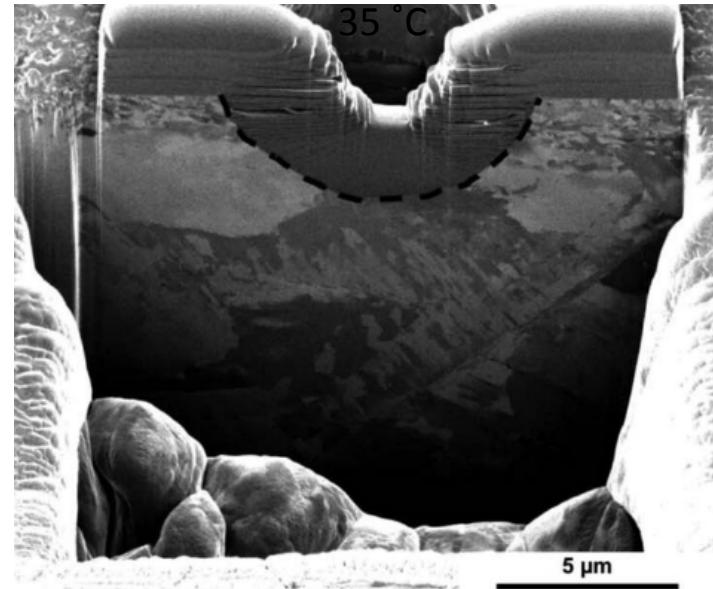
Need to inform upon localized corrosion across a wide range of chloride concentration (dilute NaCl to saturated MgCl_2) and temperature ($20 - 55^\circ\text{C}$)

Future Consideration of Anode Shape

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

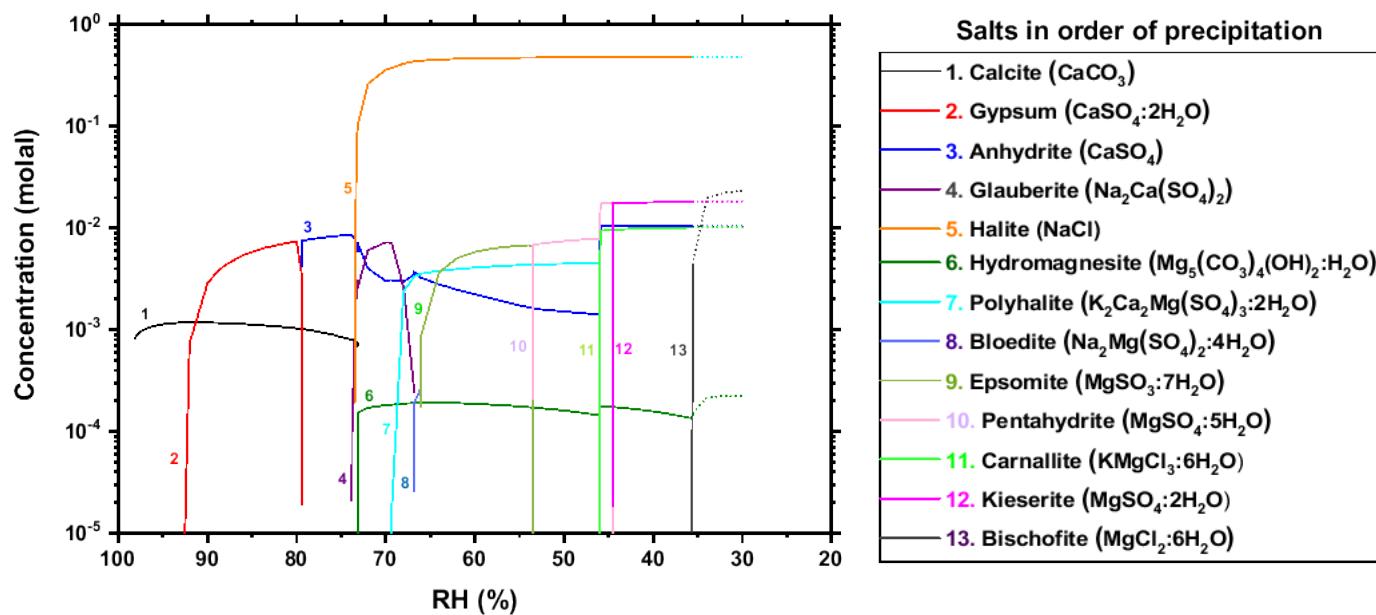


Sample exposed at **76 % RH** and



- 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?)

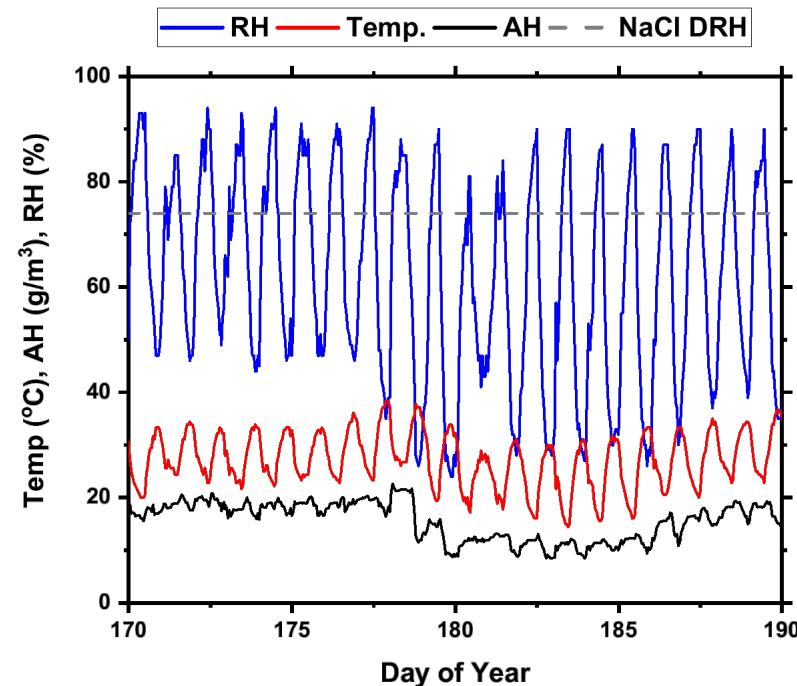
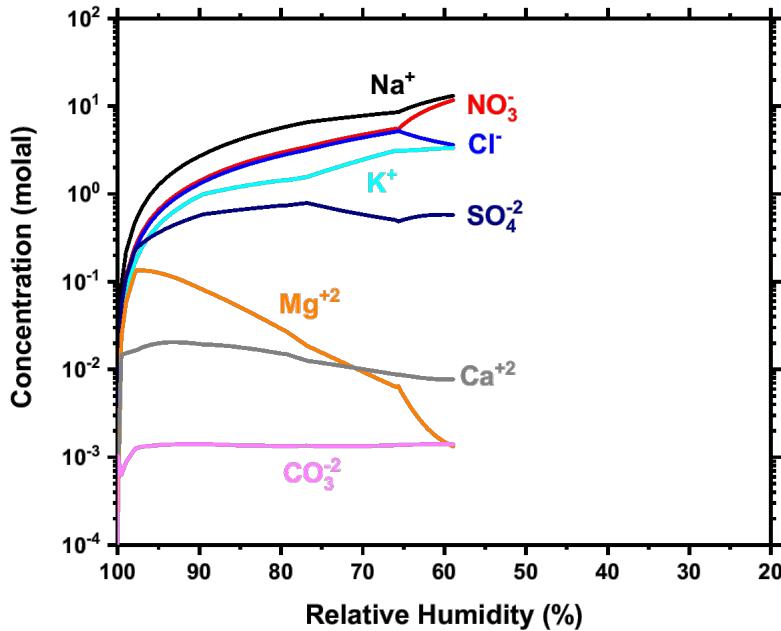
Future Consideration of Precipitated Species in Cathode



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