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Deployable Sensors for Quantifying Corrosion in Natural and Laboratory Environments

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Introductory Thoughts

- Atmospheric corrosion is a ubiquitous issue with significant impacts for transportation, infrastructure, and energy applications
- Many sophisticated techniques are available for examining material behavior in laboratory conditions and examining materials following exposure to natural outdoor environments
- Quantitative electrochemical measurements are foundational to quantifying thermodynamic and kinetic properties but are often restricted to bulk aqueous environments
- Furthermore, electrochemical test equipment is not typically hardened for exposure to corrosive conditions, complicating how materials can be evaluated
- A goal of our work has been to create technology that enables electrochemical corrosion monitoring across a diverse set of exposure conditions

Outline

- Key aspects of a deployable corrosion monitoring system
  - Parameters of interest
  - Design considerations
  - Measurement approach, sensitivity & range
- Application of deployable sensors to corrosion monitoring and material evaluation
  - Corrosion and Environmental Monitoring
  - Coating Evaluation
  - Environmental Severity Classification
- Combined Effects Testing – Environmental Cracking in Natural Environments
- Concluding thoughts

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Aspects of a Deployable Corrosion Monitoring System

ANSI-AMPP TM0416-2023; ISO 22858-2020 Corrosion of metals and alloys—Electrochemical measurements—Test method for monitoring atmospheric corrosion

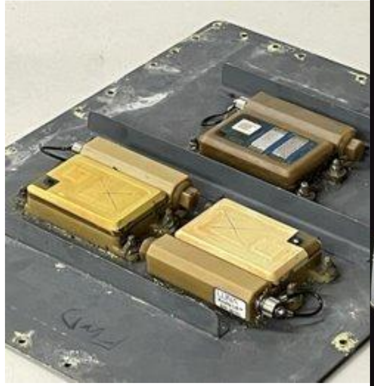
Enable corrosion measurements across diverse environments and applications

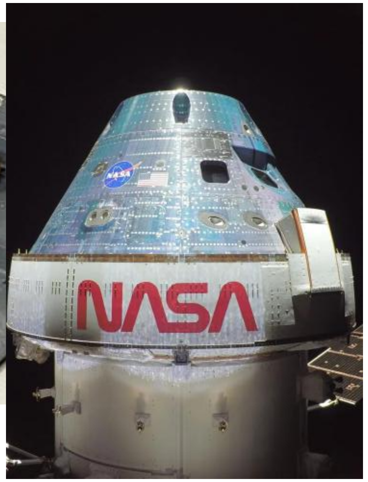
Laboratory (Environmental Chambers)

Natural outdoor environments

Remote locations

Deployed on-asset





- ❖ Instrumentation rigorous enough to withstand temperature, moisture, vibration, shock
- ❖ Operate without line power for remote deployment or on-asset
- ❖ Test materials and material combinations relevant to application

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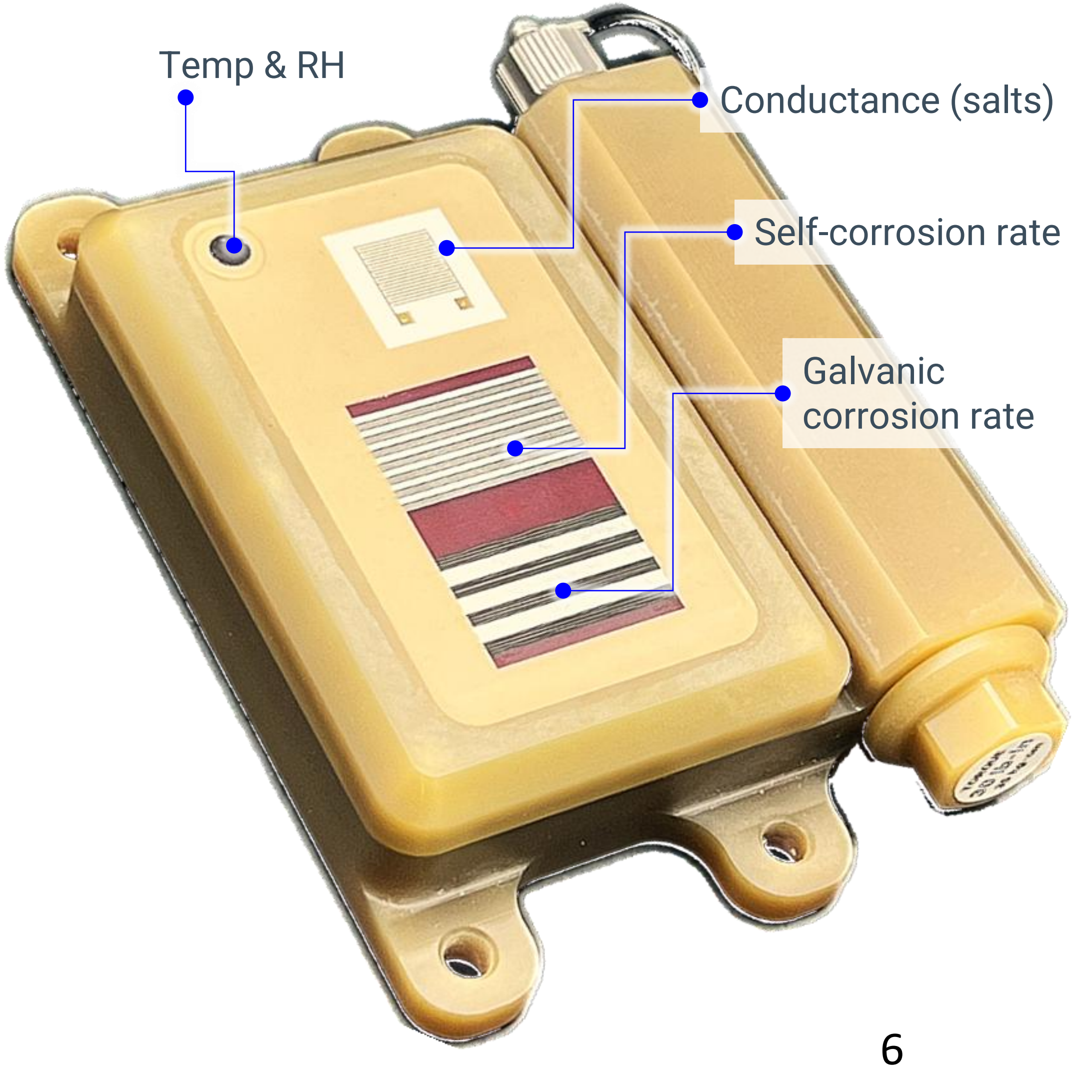
Quantify both environmental conditions and material behavior with a field-deployable device



Environmental characterization
- Temperature
- Humidity
- Contamination (salt loading)

Corrosion Processes
- Free corrosion
- Galvanic corrosion

- Small and lightweight
- Periodic measurements and data storage
- Autonomous, battery powered operation



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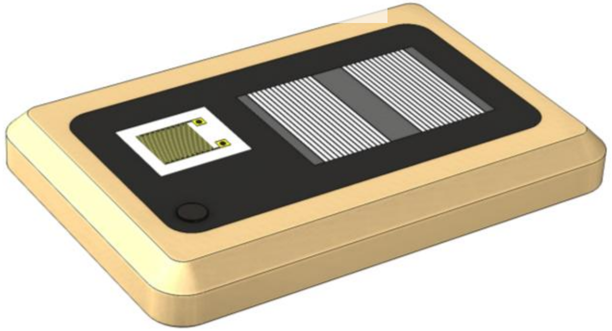
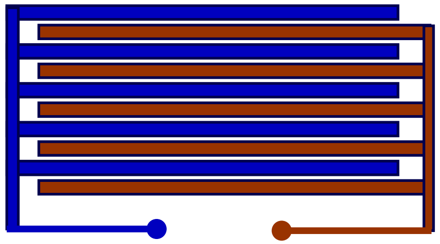
Electrochemical Measurements

Sensor panel – customizable for specific materials of interest

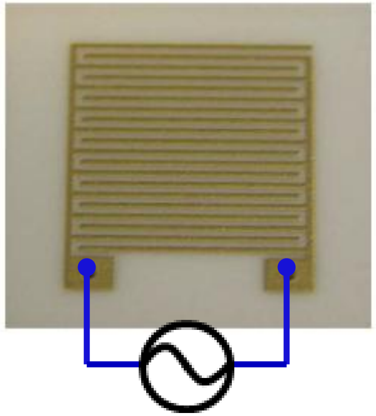


Interdigitated electrodes enable measurements in thin water layers or under droplets

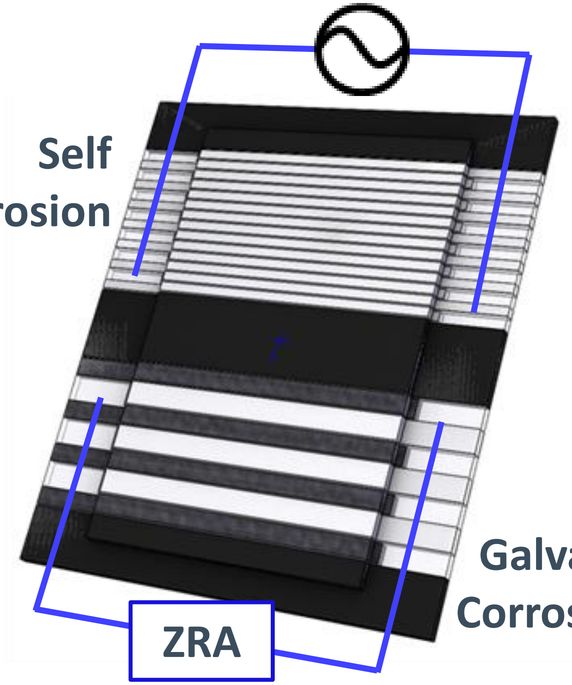


- Small separation minimizes solution resistance between electrodes
- Electrode area provides good signal to noise ratio and to gives representative material response

Electrolyte Conductance (gold electrode)



Measurement	Symbol	Range Min	Range Max	Units	Sensor Excitation
Air Temperature	T_a	-40	+85	°C	-
Relative Humidity	RH	0	100	%	-
Conductance (Low Freq)	G_L	0.005	1	µS	20 mV_{pp}, 10 Hz
Conductance (High Freq)	G_H	5	10,000	µS	20 mV_{pp}, 25 kHz
Galvanic Corrosion	I_g	0.01	100	µA	ZRA
Free Corrosion	I_c	0.005	100	µA	20 mV_{pp}, 0.5 Hz



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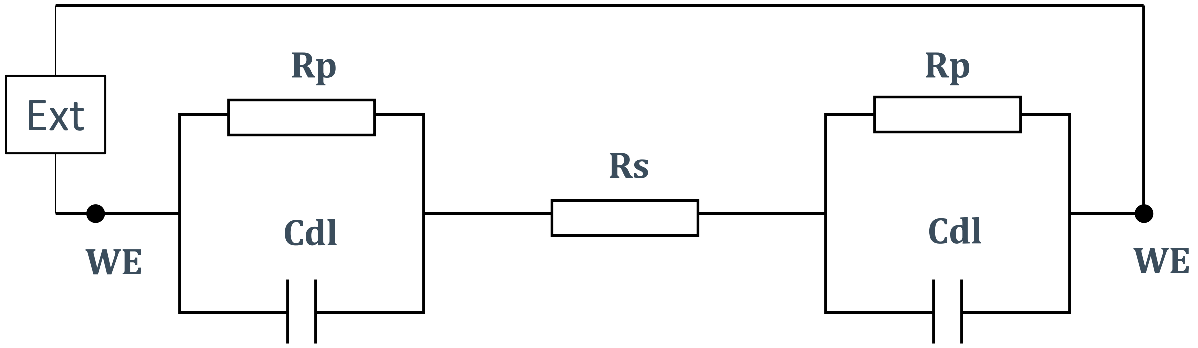
Measurement frequencies selected to characterize key material and environment characteristics



Low frequency (0.5 Hz)

- Capacitors have high impedance
- Measured signal is $R_S + 2R_P$
- For $R_P >> R_S$: $R_S + 2R_P \approx 2R_P$

$$Z_{\omega \to 0} = 2R_p + R_s$$

Polarization resistance measured with two electrodes of the same material is proportional to self corrosion rate

High frequency (25 kHz)

- Capacitors have near zero impedance @ high frequency
- Measured signal is R_S
- Used with gold electrode to measure solution conductance

$$Z_{\omega \to \infty} = R_s$$

Conductance is an indication of contaminant level and corrosivity of electrolyte

Integration of these signals over time gives an indication of total corrosivity and total corrosion for an exposure

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System configuration

Measurement systems for laboratory and usage environments need to be durable and capable of autonomous operation

Environment Severity Monitoring
- *Temp, RH, Conductance*

Environment and Corrosivity Monitoring
- *Temp, RH, Conductance*
- *Self and Galvanic Corrosion*

Environment and Corrosivity Monitoring
- *Temp, RH, Conductance*
- *Self and Galvanic Corrosion*

Acuity ES

Acuity LS

Acuity CR

Laboratory / Exposure Site / Asset Monitoring

Laboratory / Exposure Site

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Application of deployable sensors to corrosion monitoring and material evaluation

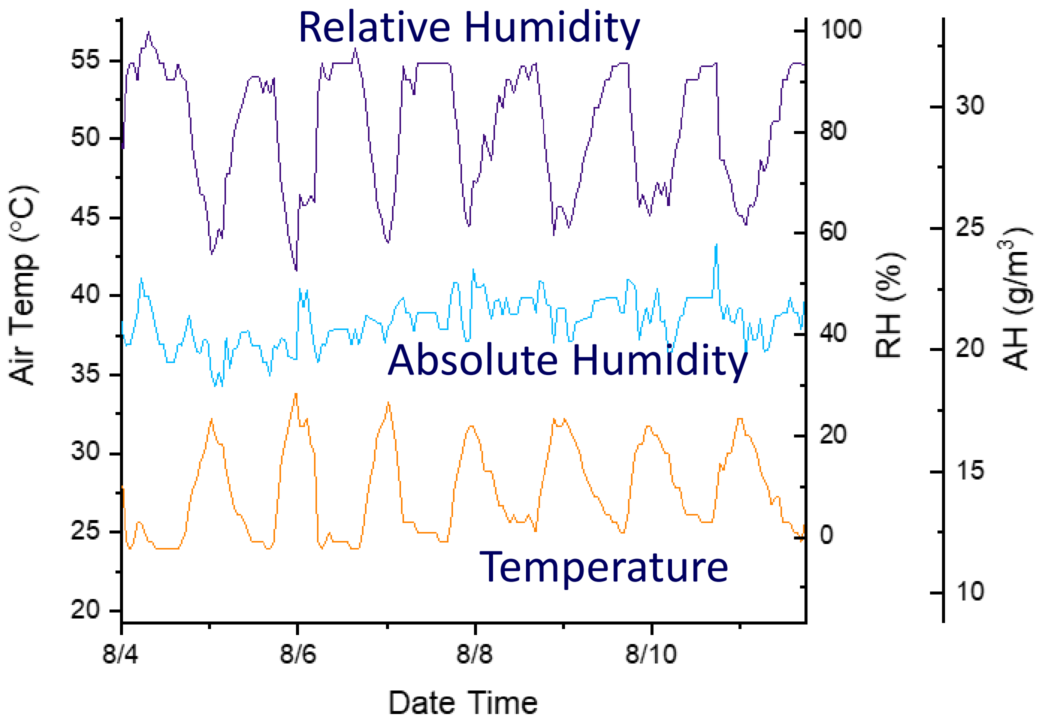
Environment and material monitoring

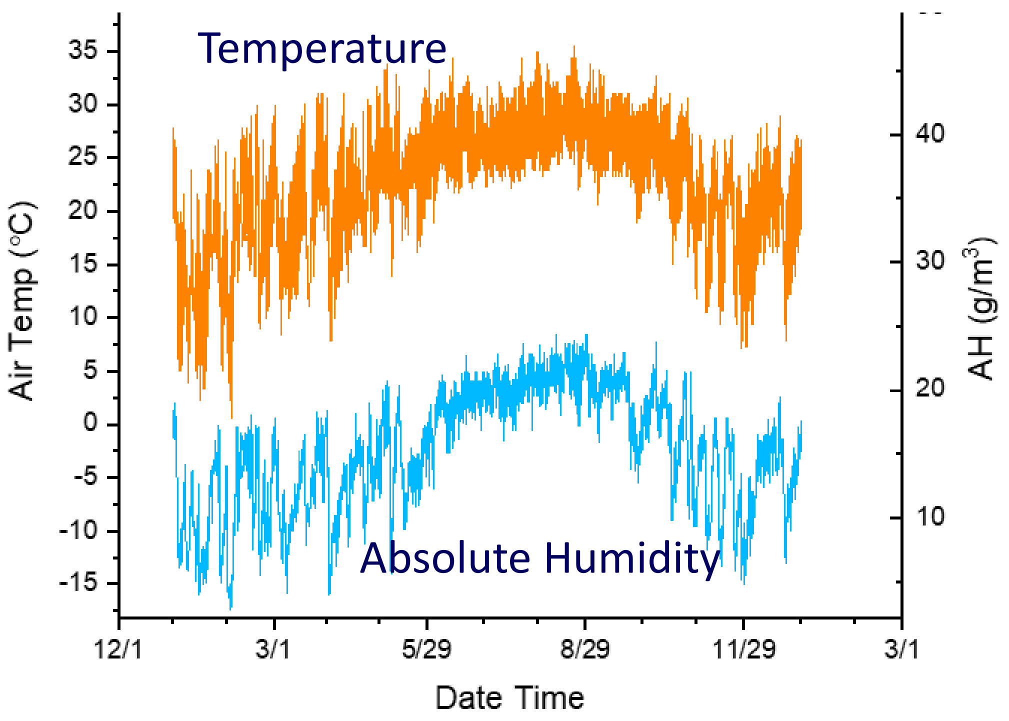
Environment Spectra: T and RH

Environmental parameters used to assess corrosion severity: temperature, relative humidity, and contaminants (solution conductance)

Environment severity and corrosion vary over a broad range of time scales

- Operation and use • Weather events • Diurnal cycle • Seasonal variation • Climate change

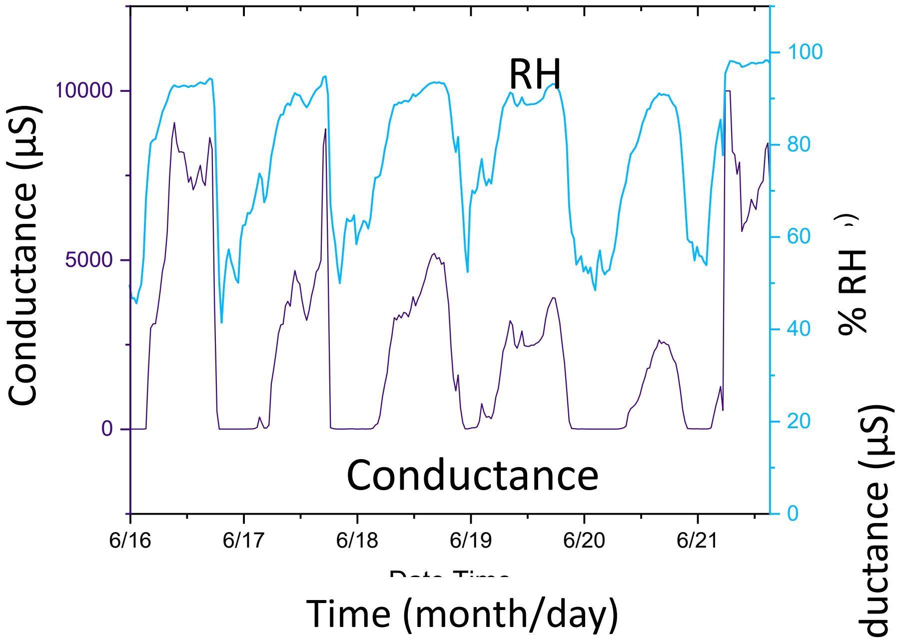




Environment Spectra: Conductance

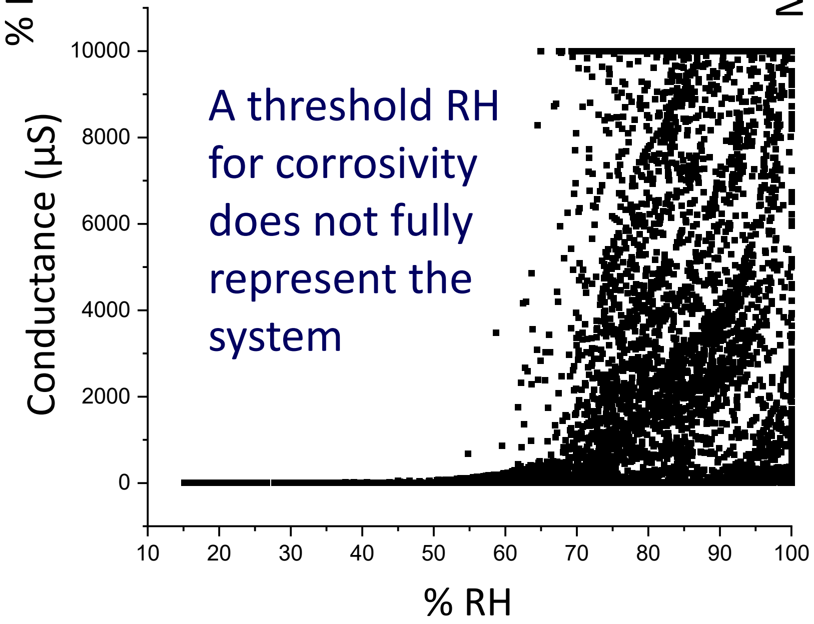
- ❖ Conductance versus RH has discernable regions of wet/dry behavior
- ❖ Dependent on salt chemistry

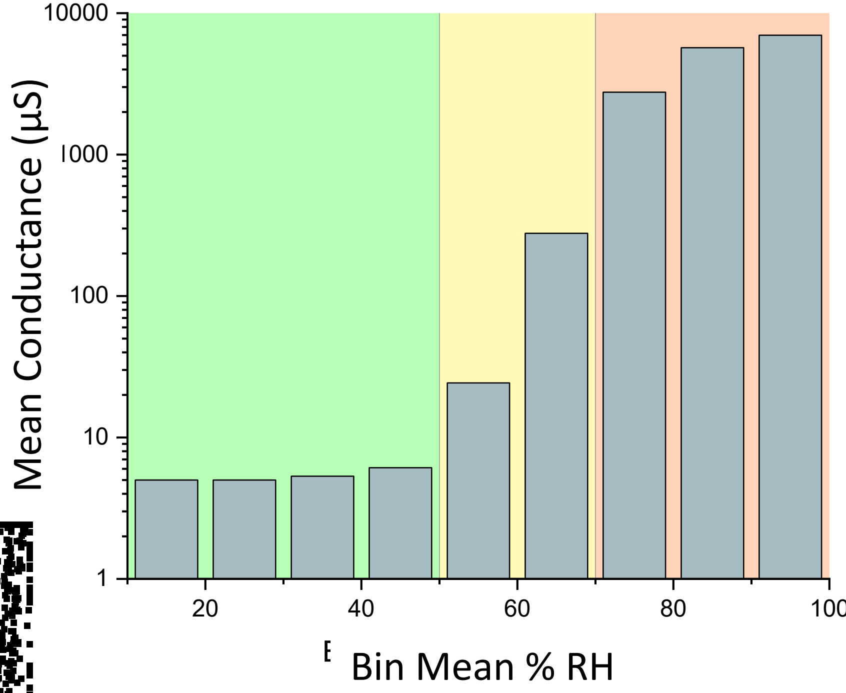
Conductance versus time follows diurnal wet/dry cycles



The mean conductance can be used to define wet and dry conditions for a given environment and provide additional context to RH data

A threshold RH for corrosivity does not fully represent the system





Dry < 50%
50% ≤ Semi-wet < 70%
Wet ≥ 70% RH

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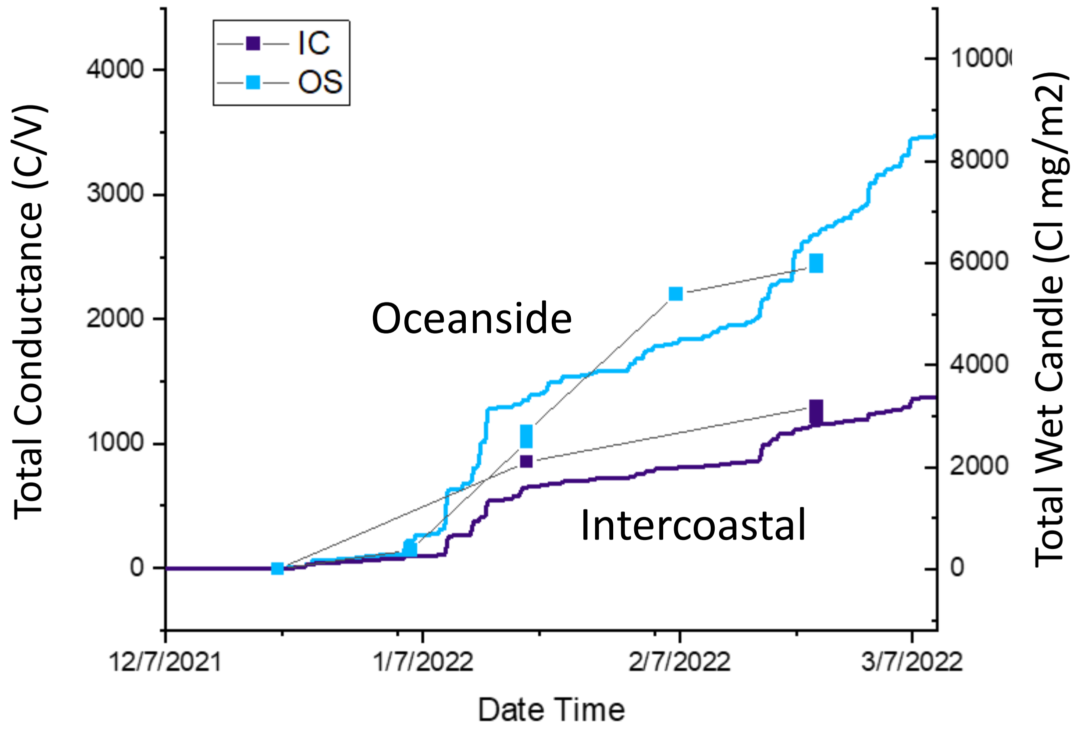
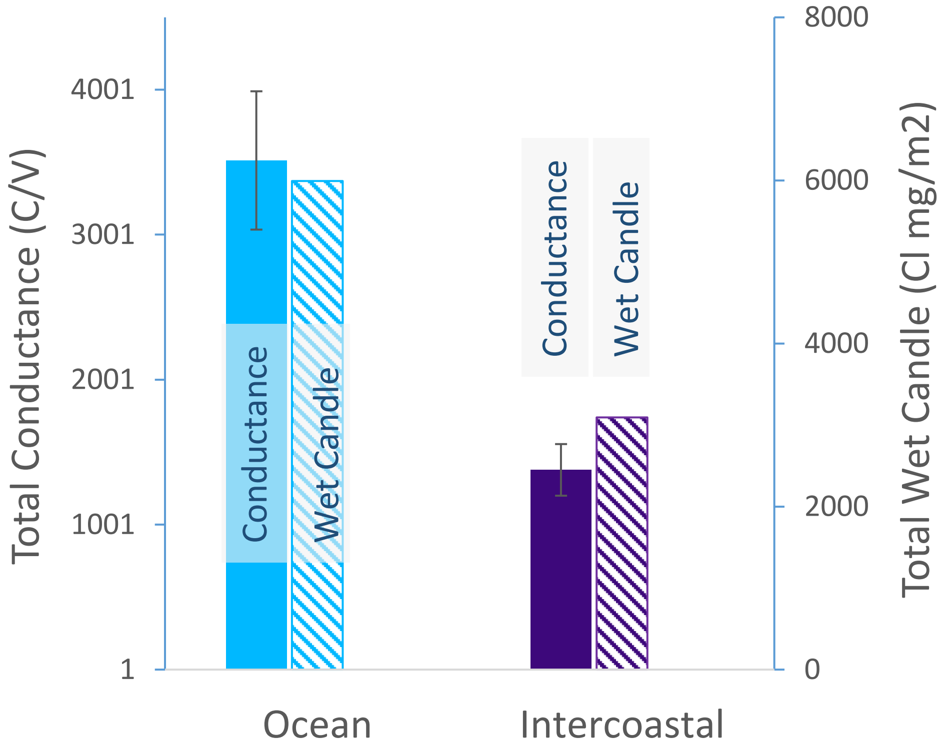
Comparison of conductance and chloride for two coastal environments

Total conductance can be used to quantify corrosion severity of outdoor sites

- The total chloride deposition, measured by wet candle, at the intercoastal site was approximately 50% of the ocean site
- The intercoastal site produced approximately 40% of total conductance of the ocean site





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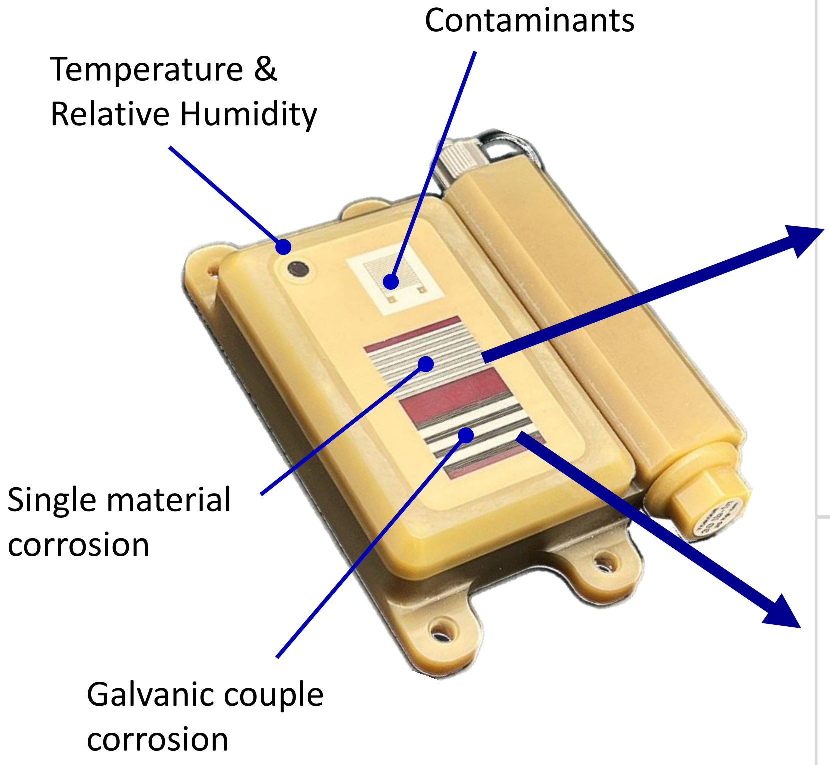
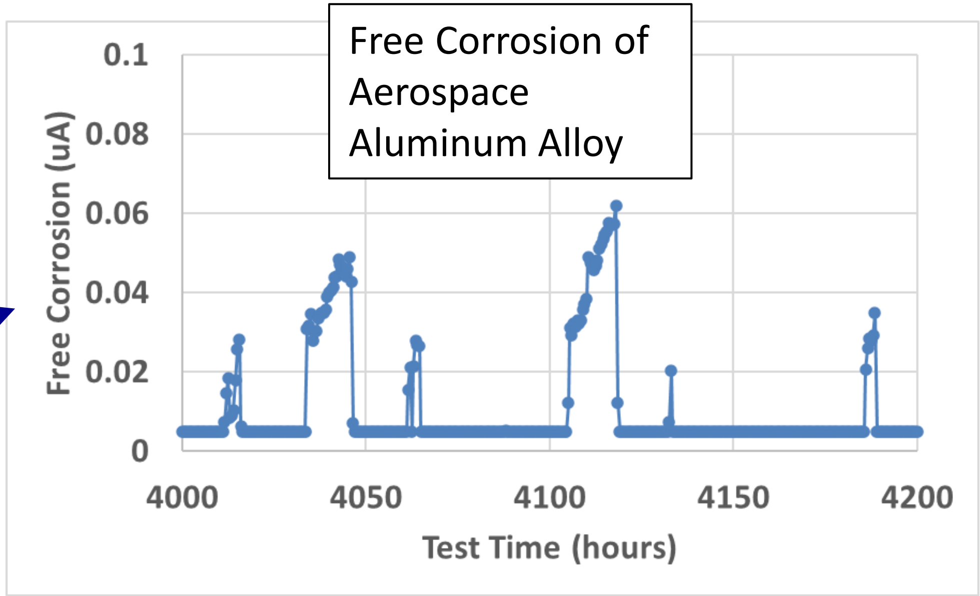
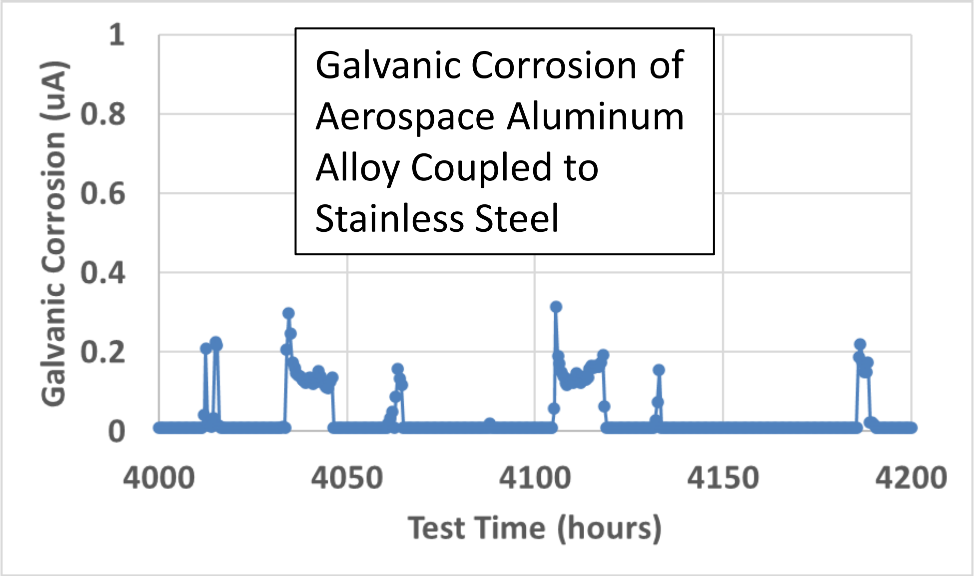
Corrosion Measurements







Measured RMS current is proportional to corrosion current

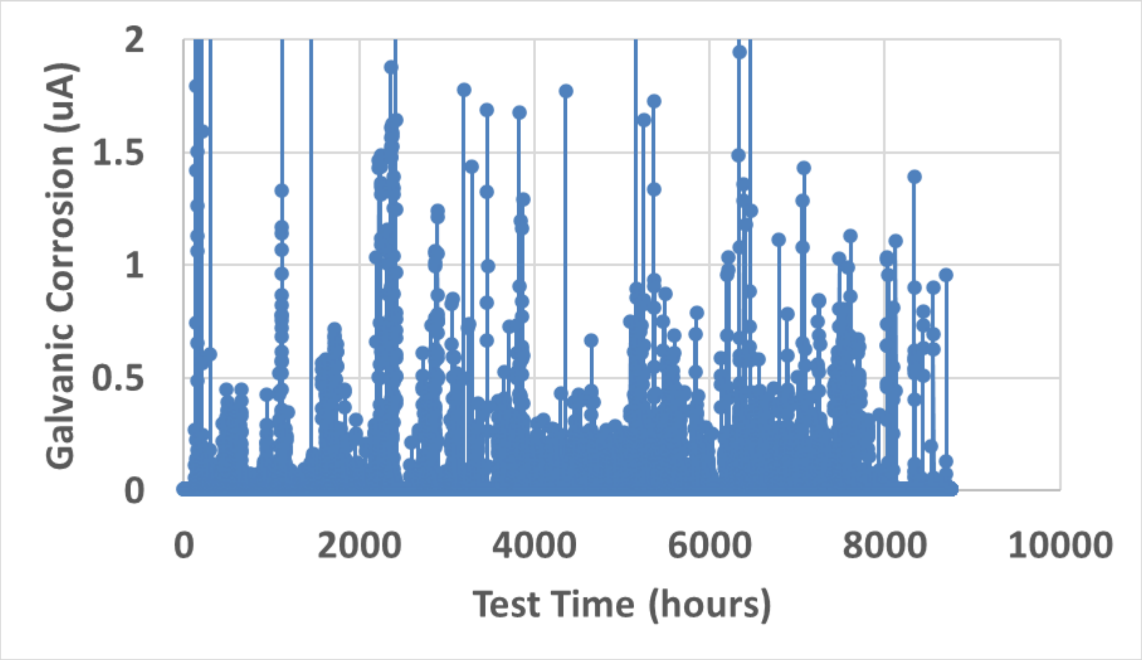
$$R_p = 0.5 \cdot \frac{V_{rms}}{I_{rms}} \cdot A \qquad i_f = \frac{\beta}{R_p}$$

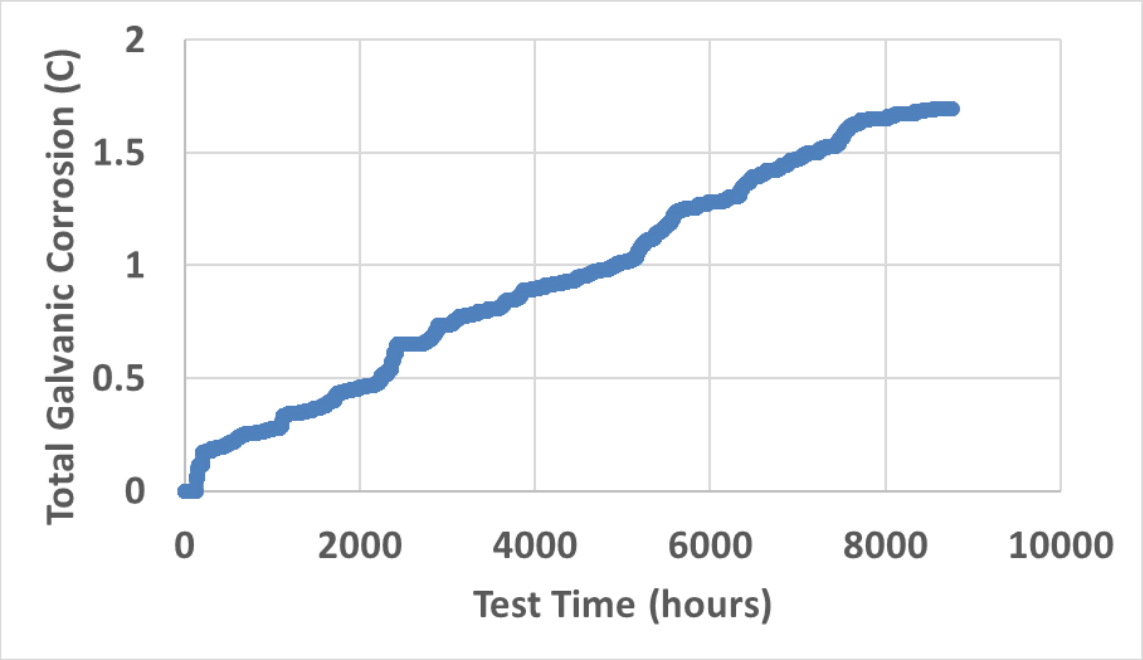
$$\beta = \frac{\beta_a \cdot \beta_c}{2.303(\beta_a + \beta_c)}$$

Corrosion current is measured directly with ZRA

$$i = \frac{I}{A}$$

Integration of corrosion current determines total material loss





- Charge can be converted directly to mass loss via Faraday's law

$$m = \frac{Q \cdot M}{nF}$$

- Converting to a penetration rate requires estimate of active surface area

$$Penetration\ Rate = \frac{m}{\rho \cdot A \cdot t}$$

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Use Case – Coating Evaluation

Applying coatings to electrochemical sensors

Coating systems can be applied to electrochemical sensors using processes developed for standard test panel preparation

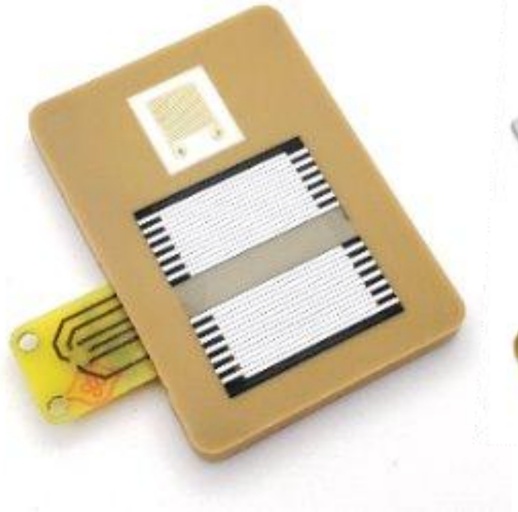
- Clean, Pretreatment, Primer, Topcoat, Scribe

Applicable to liquid, ambient cure coating systems

Quantify coating degradation processes

Develop models of coating property & performance relationships

Evaluate replacement options for hexavalent chromate coatings in aerospace applications



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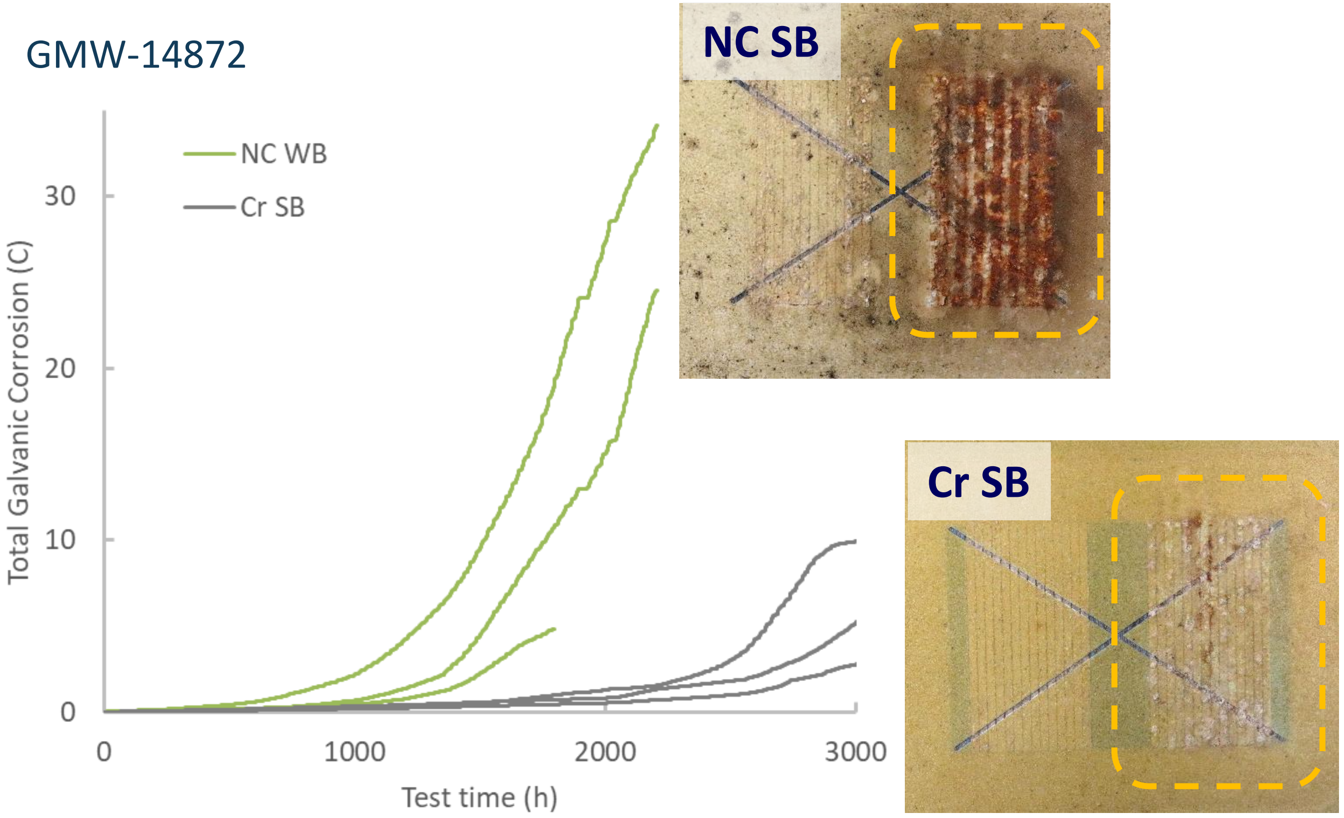
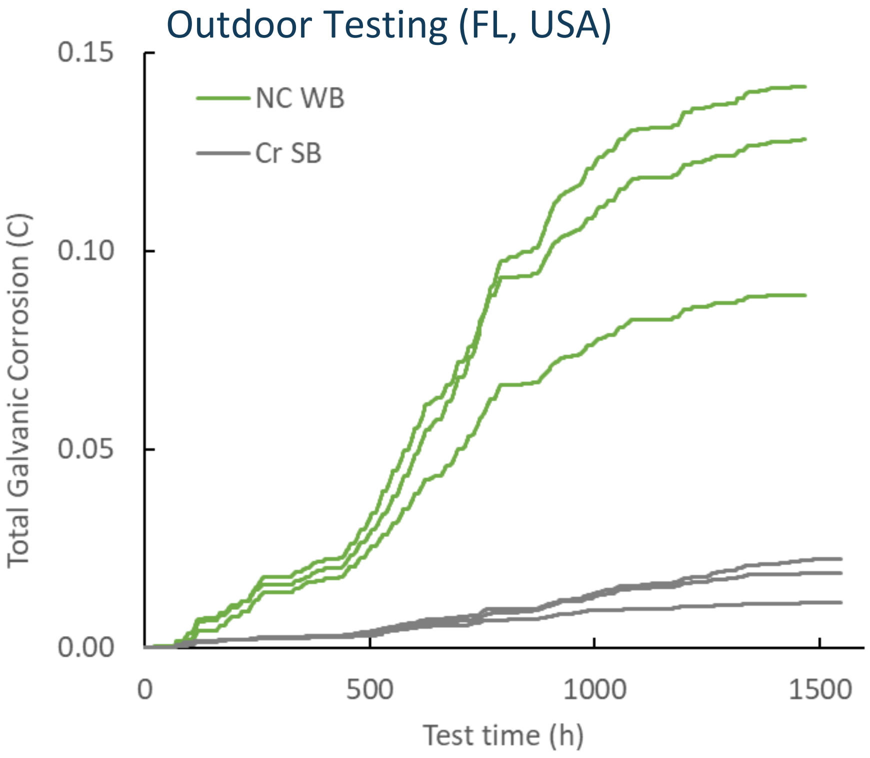
Galvanic corrosion measurements differentiate coating degradation





Galvanic corrosion measurements provide clear separation between chromate and non-chromate primers in laboratory and outdoor tests

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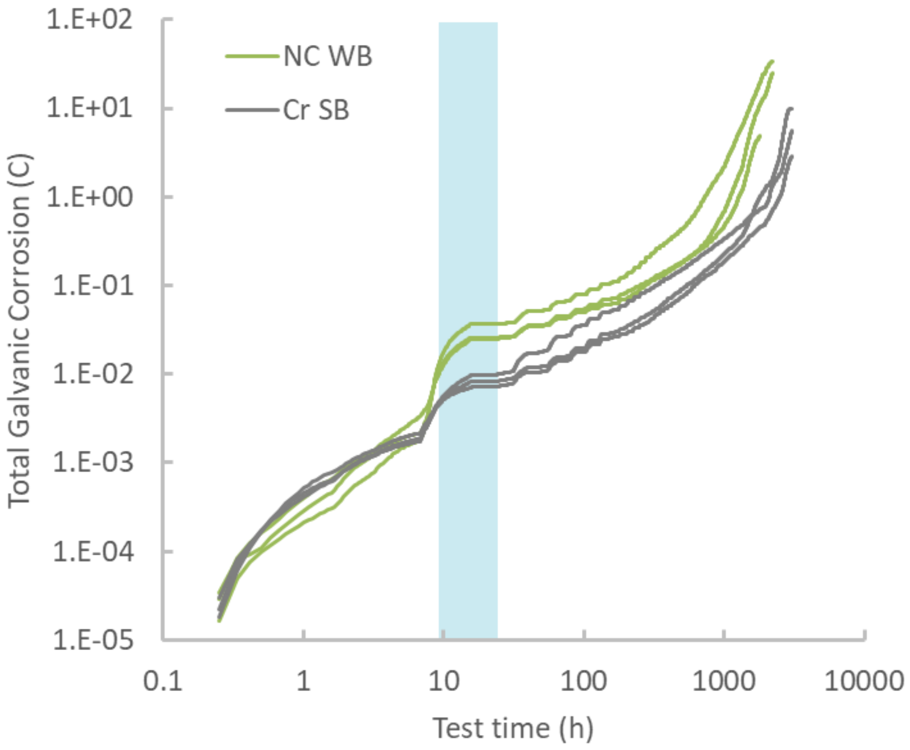
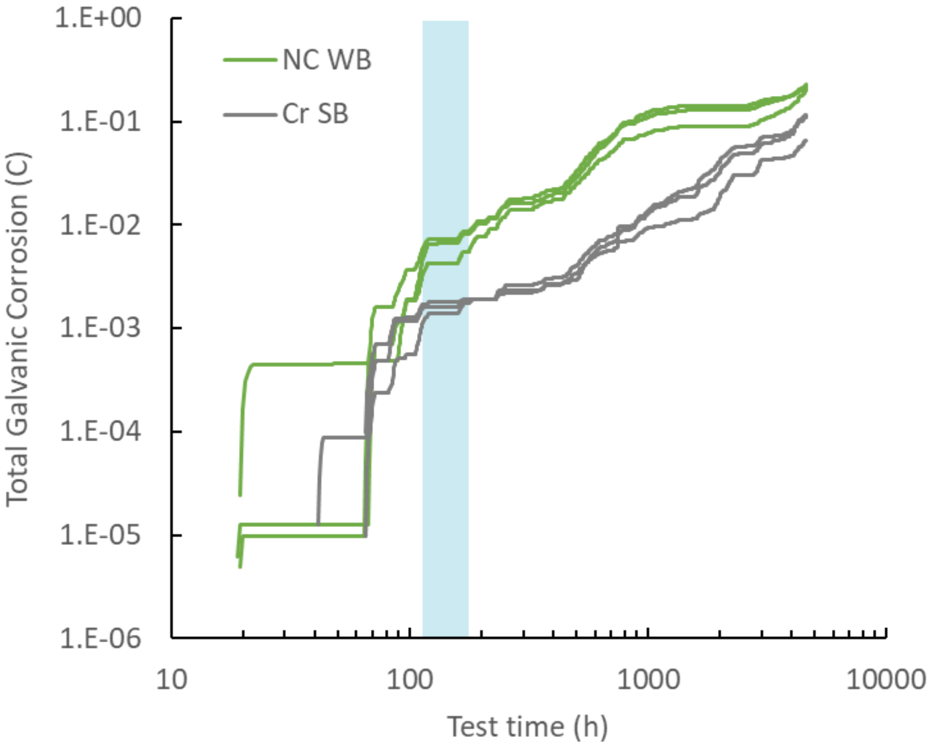
Electrochemical techniques are sensitive to early stages of coating breakdown





Coating performance differentiated during first 10 – 20 hours in accelerated lab test

Coating performance differentiated during first 100-200 hours in natural outdoor exposure

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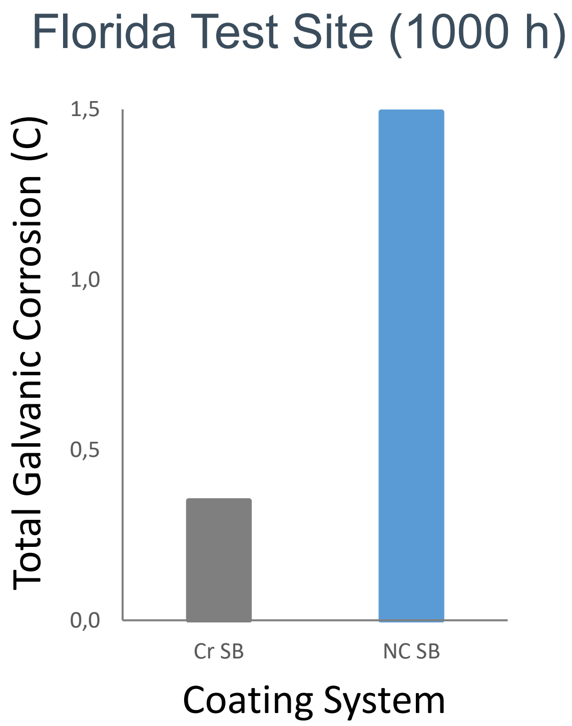
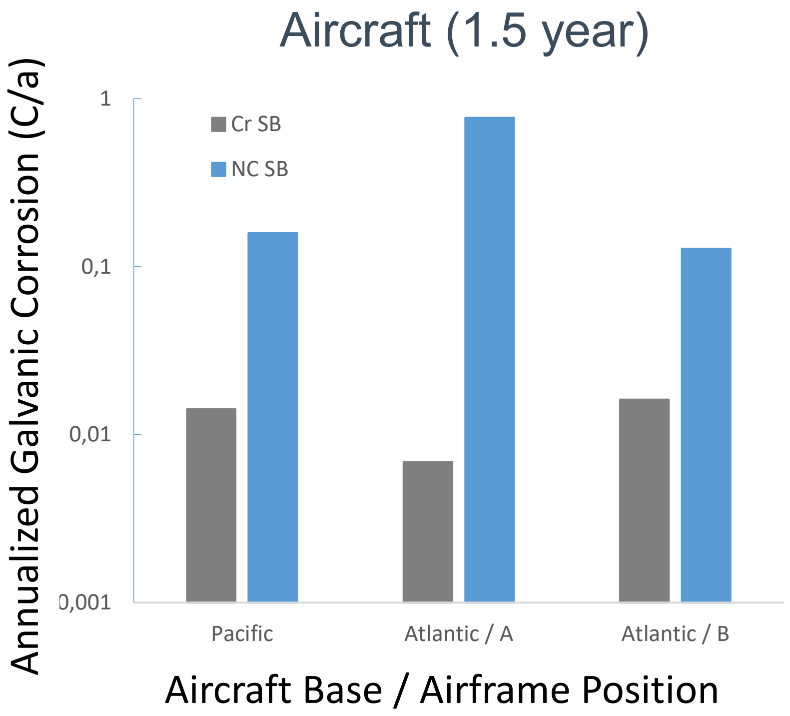
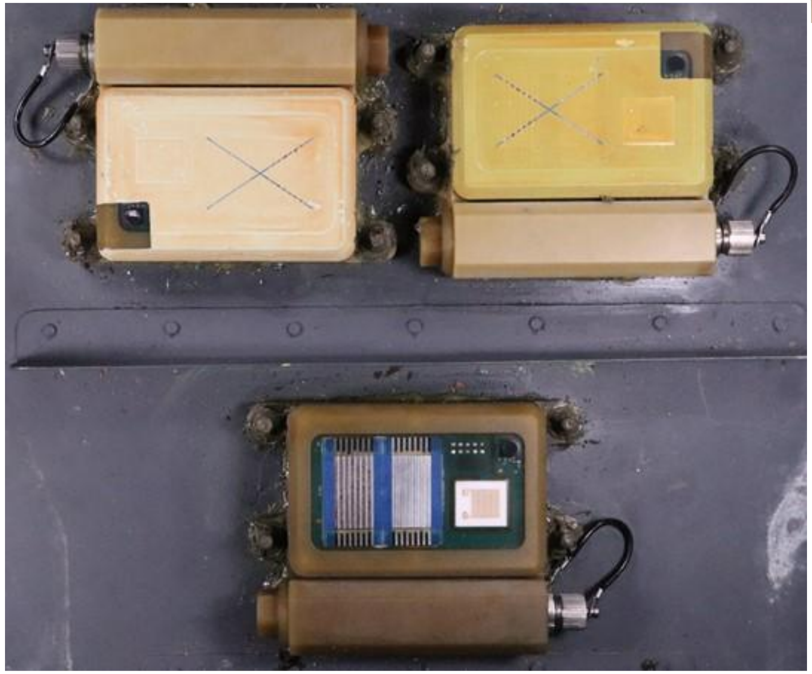
On-asset coating evaluation

On-aircraft monitoring produces differentiation of coating systems consistent with performance in accelerated tests and outdoor exposures







Coated and Scribed Sensor on Aircraft Interior

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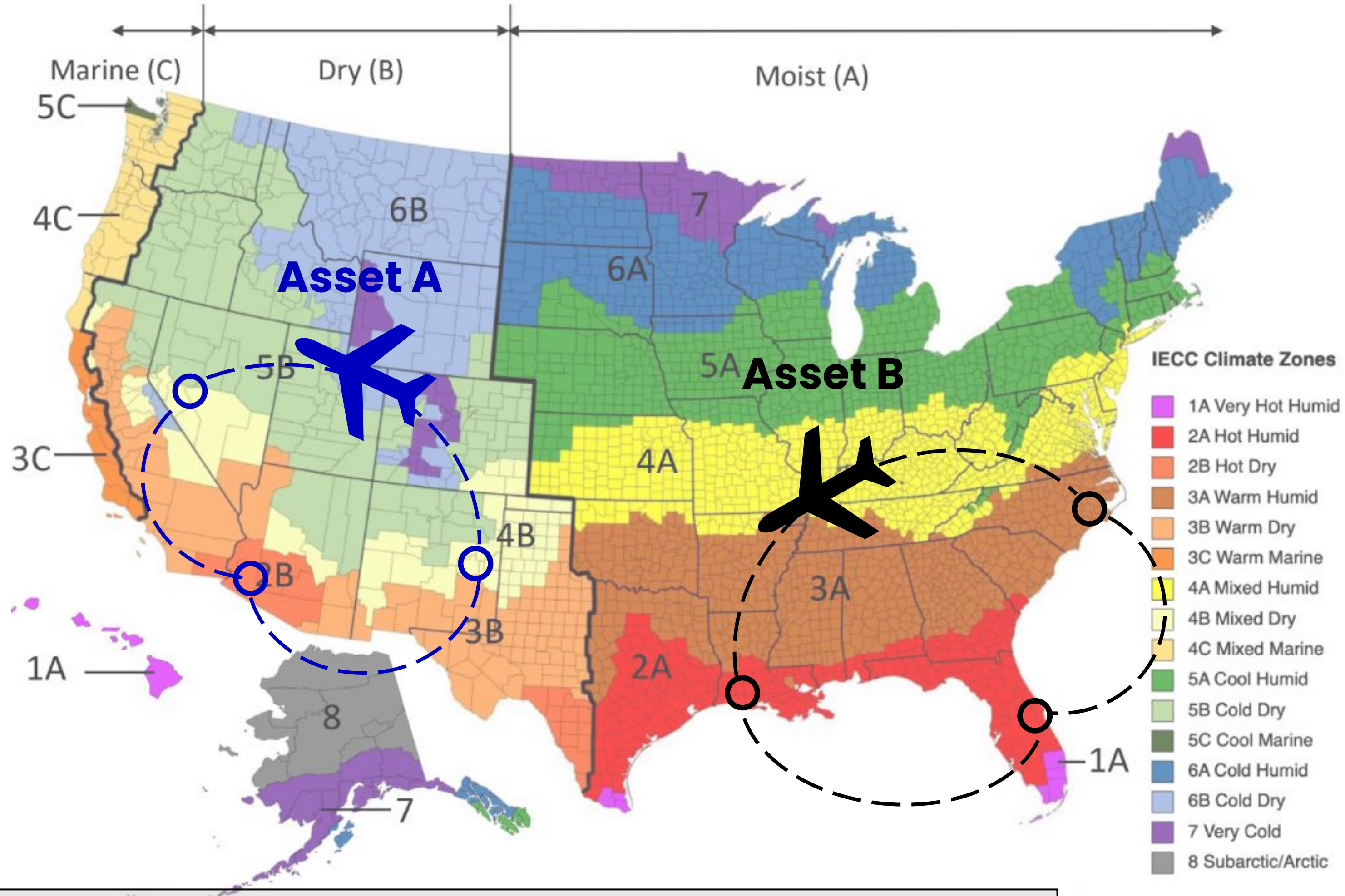
Use Case – Site Severity Assessment and Classification

Need for site severity assessment

- ❖ Understanding corrosion rates in a service environment is critical to design and maintenance decisions

- ❖ Mobil assets such as aircraft are subjected to a wide range of environments associated with basing and operations
  - Asset A: Nevada to Arizona to New Mexico - Low severity location history
  - Asset B: Florida to Louisiana to North Carolina - High severity location history



There are over 30 climate categories and countless metal alloys, making **individual measurements of all material-environment combinations infeasible**

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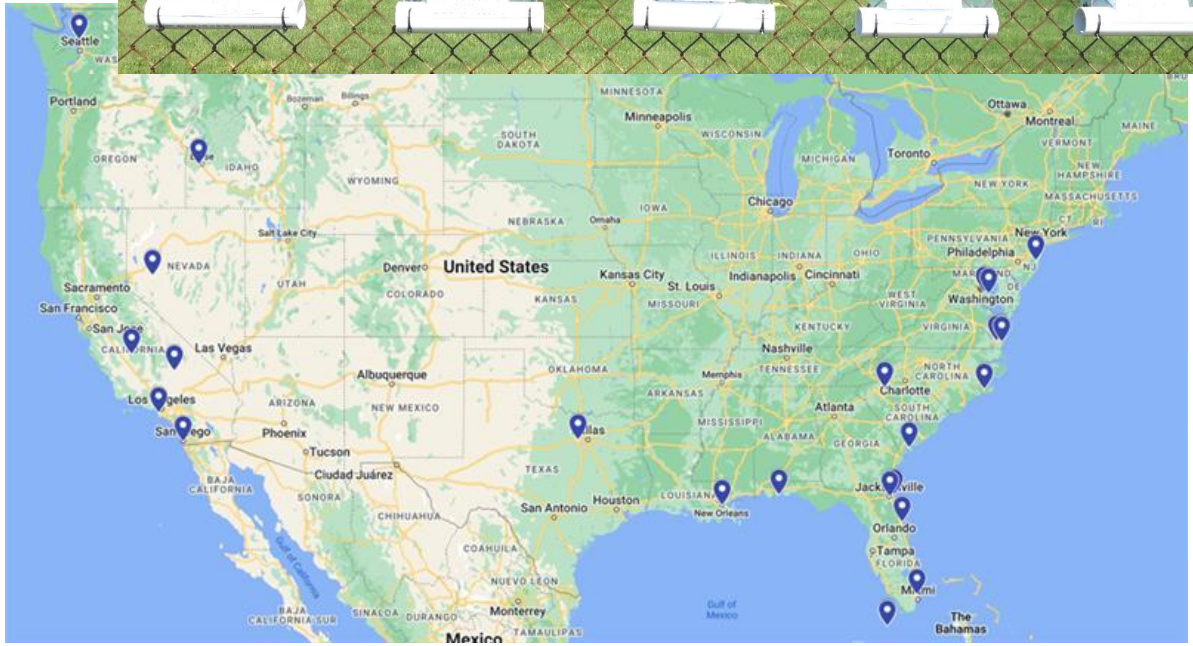
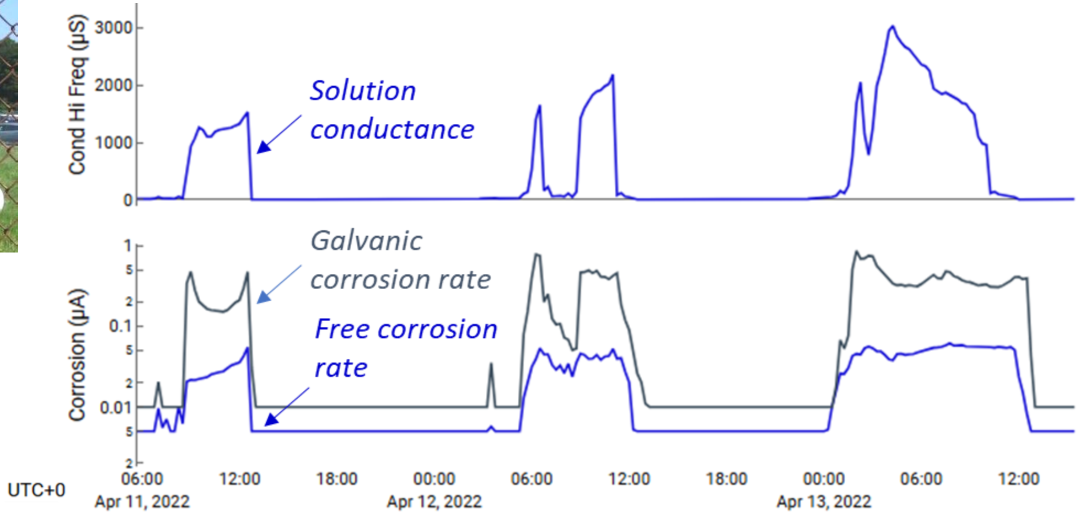
Site Survey and Severity Assessment

- A large dataset from 25 domestic and international sites has been collected by the Naval Air Warfare Center Aircraft Division (NAWCAD)
- Electrochemical corrosion and environment measurement devices were co-located with mass loss coupons



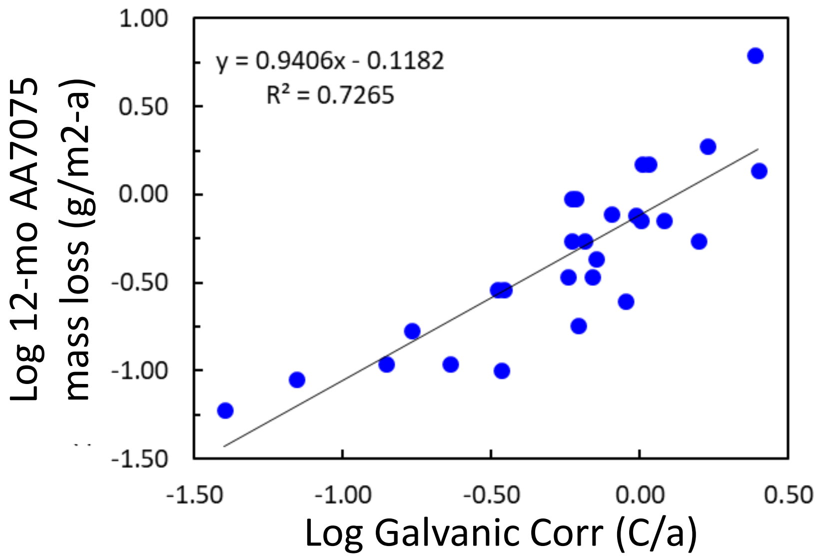


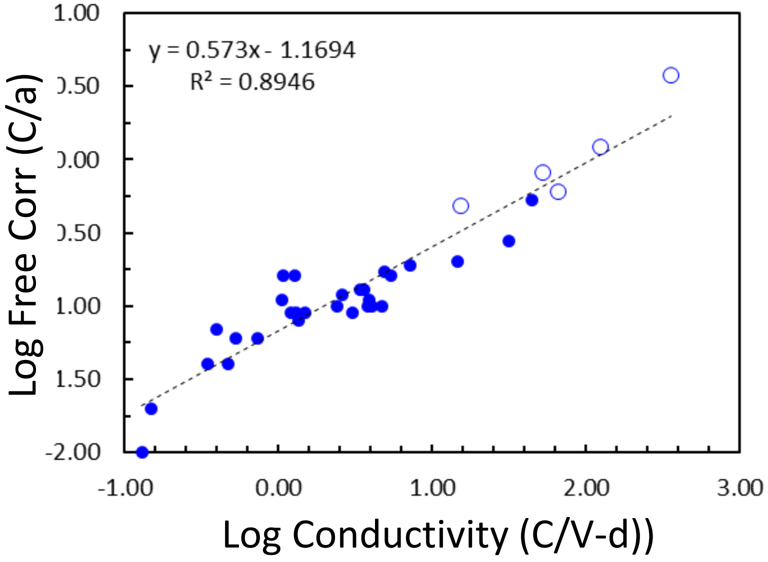
Continuous measurements of conductance, AA7075-T6 self corrosion, and AA7075-T6 / A286 galvanic corrosion for one year are used to quantify severity

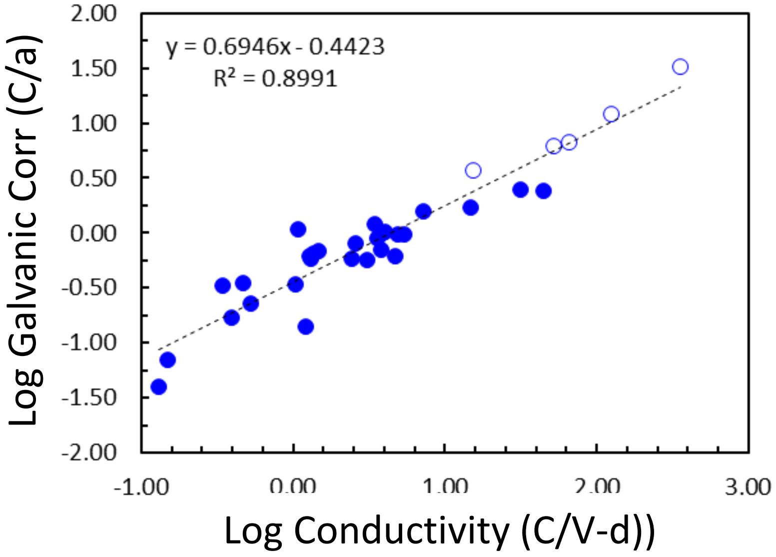
Steven Kopitzke, Alexander Lilly, Ian Long, Kaylee Canales, Allison Muenzer; A Comprehensive Characterization of Environmental Severity Across 25 Sites in Nine Climactic Zones. Part 1: Witness Coupon Evaluation. *CORROSION* 2024; 4505. doi: https://doi.org/10.5006/4505

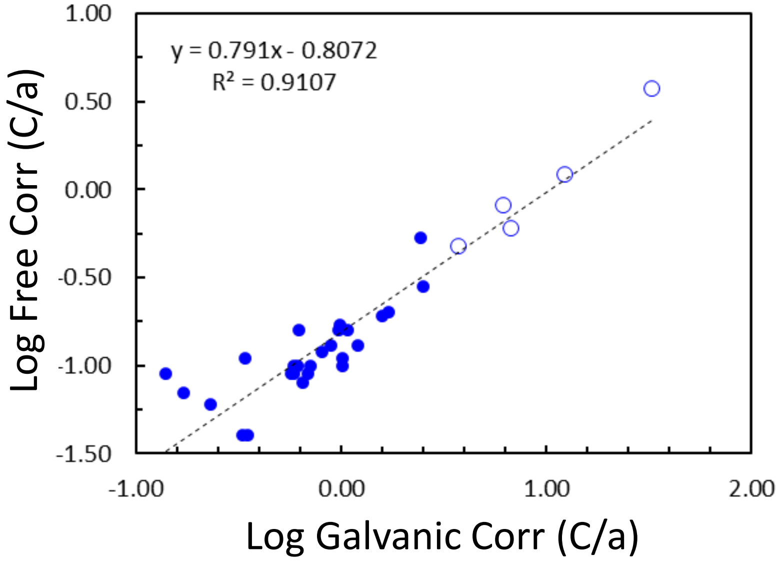
Correlation between corrosion metrics

- ❖ Data accumulated from 25 domestic and international sites in NAWCAD site survey, as well as additional data from related projects
- ❖ Strong power-law correlations for galvanic and free corrosion, conductance, and mass loss
- ❖ Functional relationships can be used to convert data across all parameters









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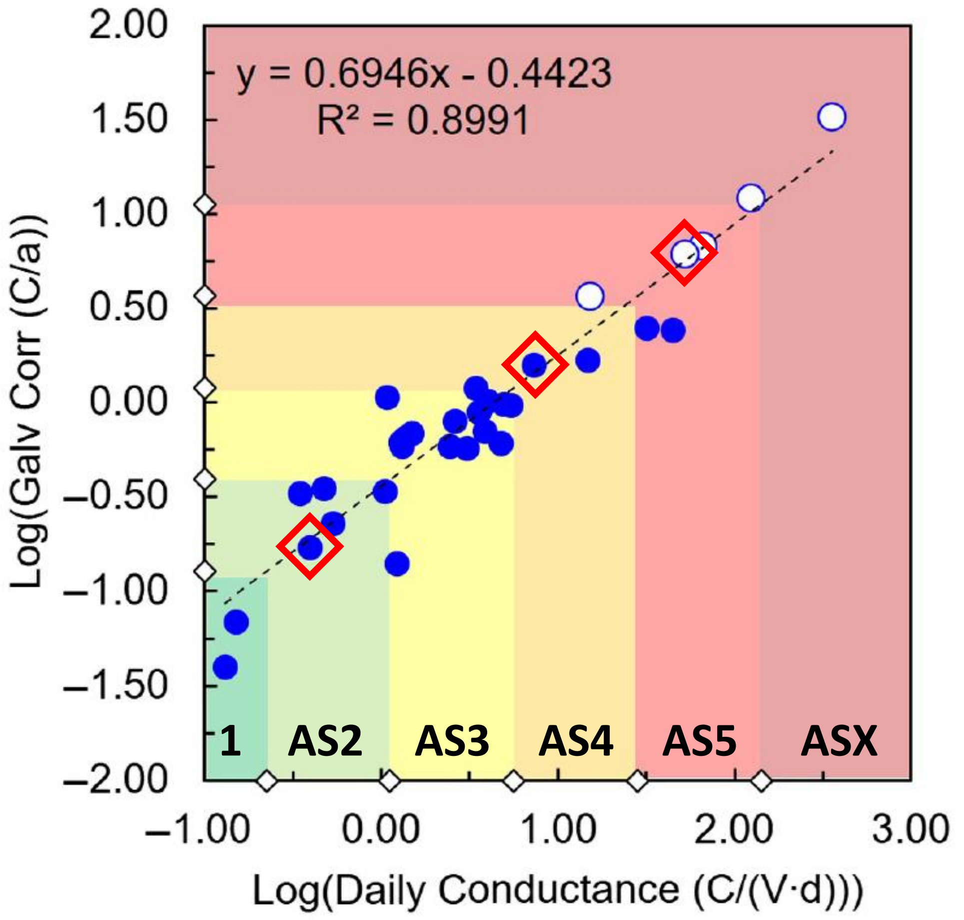
AA7075 free corr
AA7075/A286 galv. corr

Severity Classifications Categories

- Strong power-law correlations for galvanic/free corrosion, conductance, and mass loss
- Bounds of varying severity classifications can be identified and correlated
  - Annual Severity (AS) Scale, AS1-AS5, ASX
  - Consistent with ISO 9223 six-category classification

The severity classification can be determined from solution conductance or corrosion (free or galvanic)

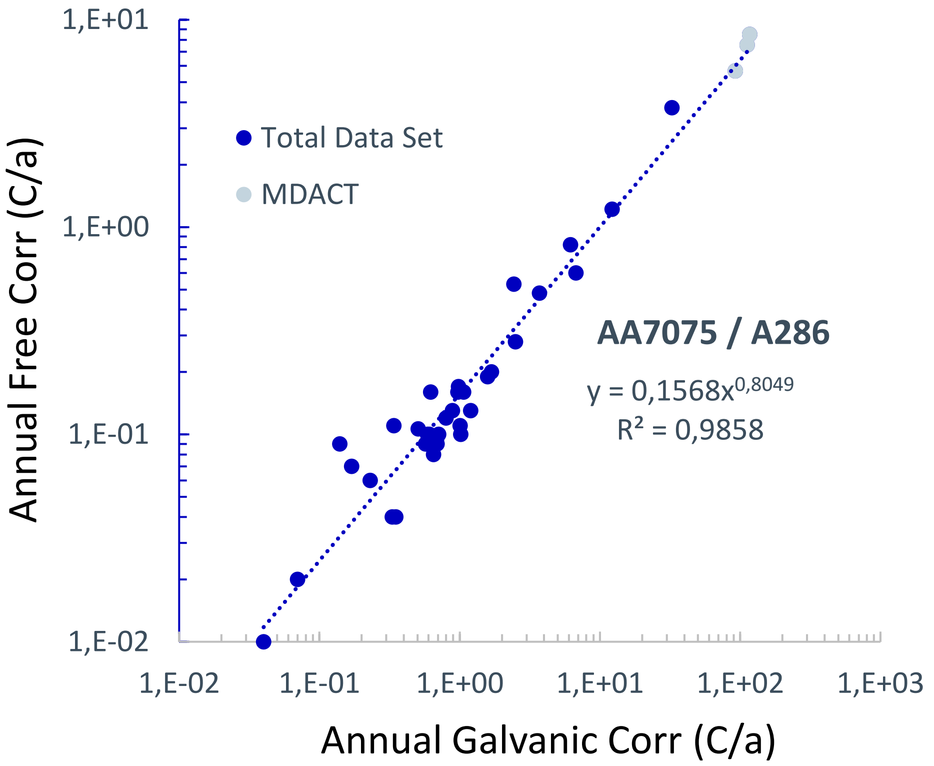
Adding new locations or alloys requires only targeted deployments to span the severity range

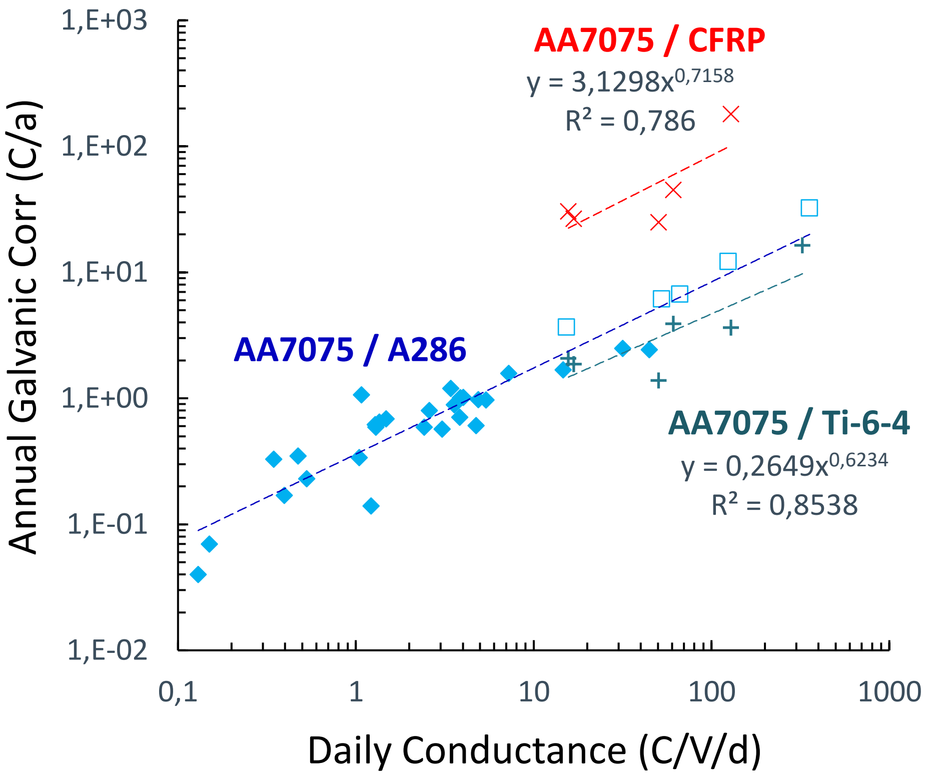


R.S. Marshall, V. Avance, L. Askew, F. Friedersdorf, Environmental Severity Classification of Atmospheric Corrosion Using Electrochemical Monitoring, Materials Performance and Characterization by ASTM Undergoing publication (2024).

Severity ranking is extensible to accelerated testing and additional materials

- Measurements allow severity mapping for assets, sites, and accelerated tests
  - Multivariable accelerated corrosion test (MDACT AMPP TM21559 SC 07 Ballot)
- Severity assessments can be done with other engineering alloys and galvanic couples





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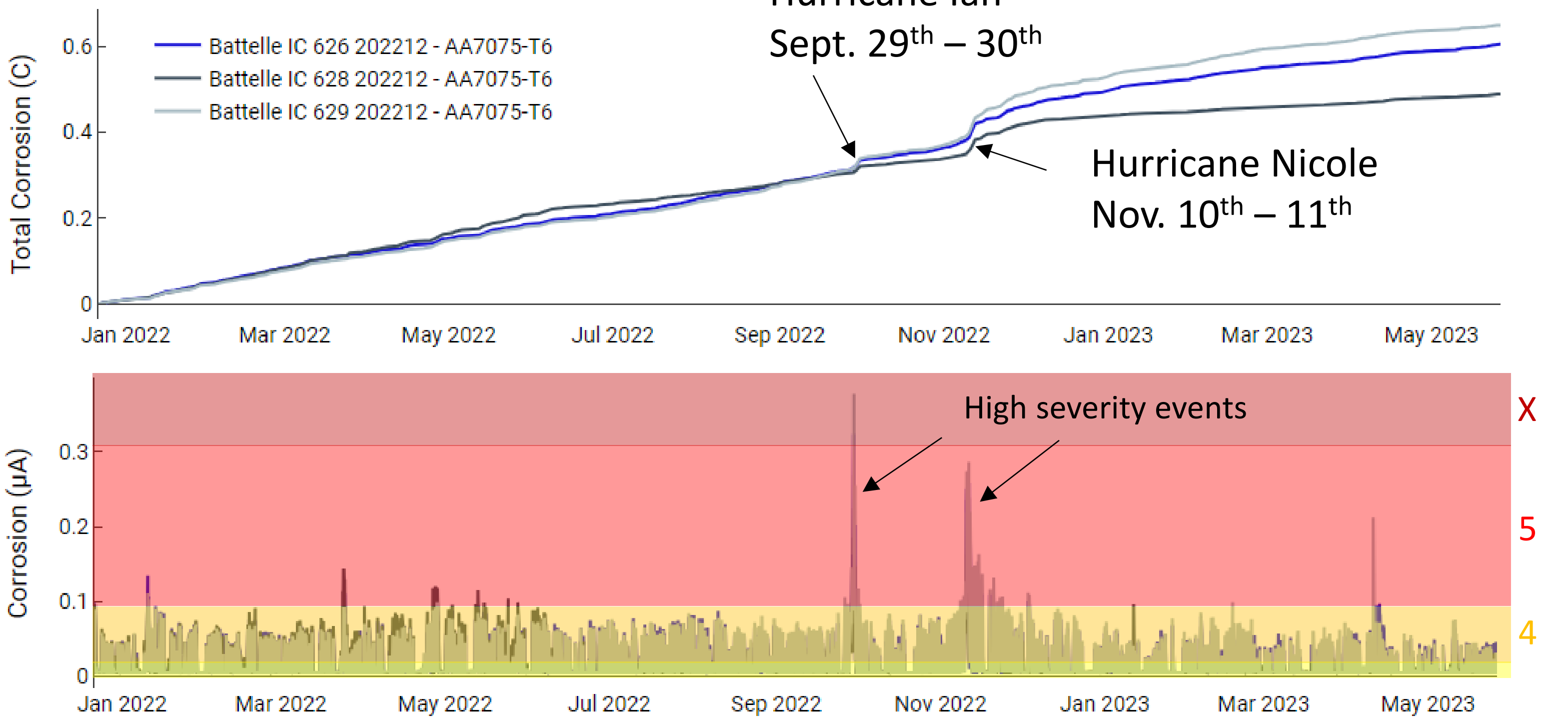
Time Dependent Severity

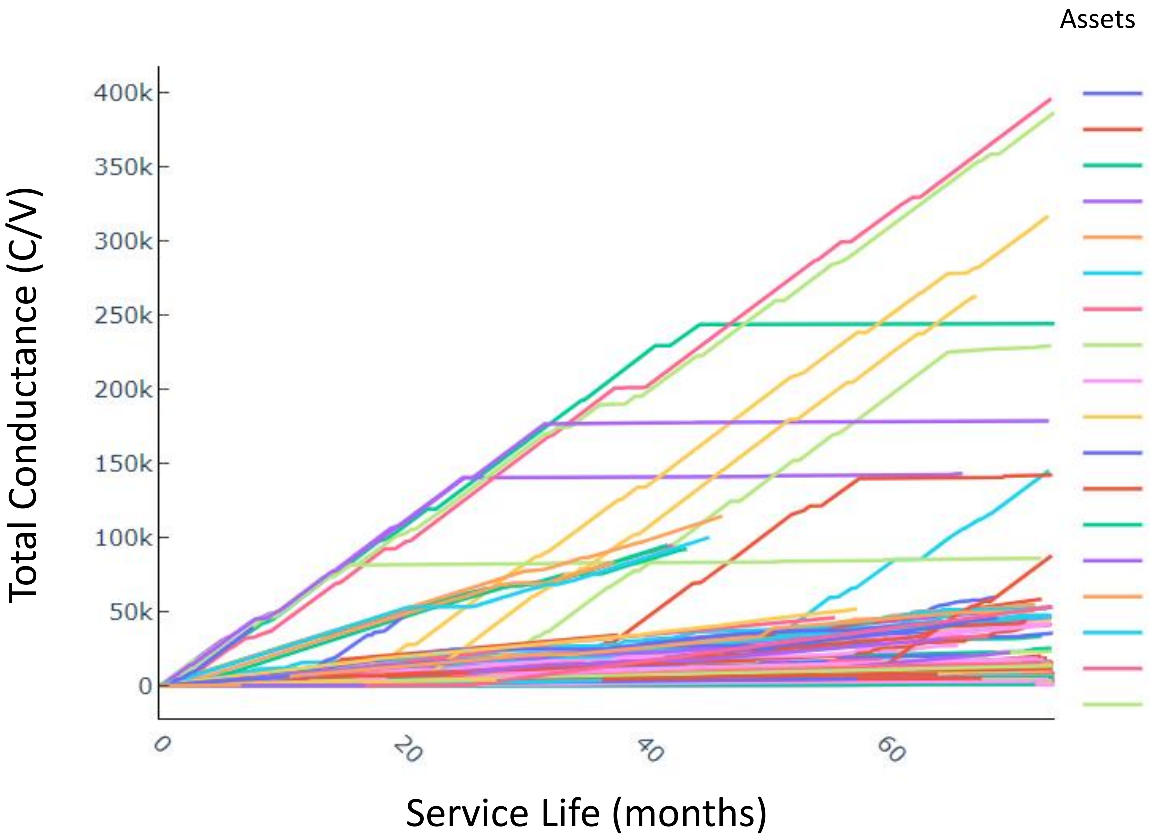
Continuous electrochemical measurement of environment severity and corrosivity can be used to characterize processes contributing to corrosion

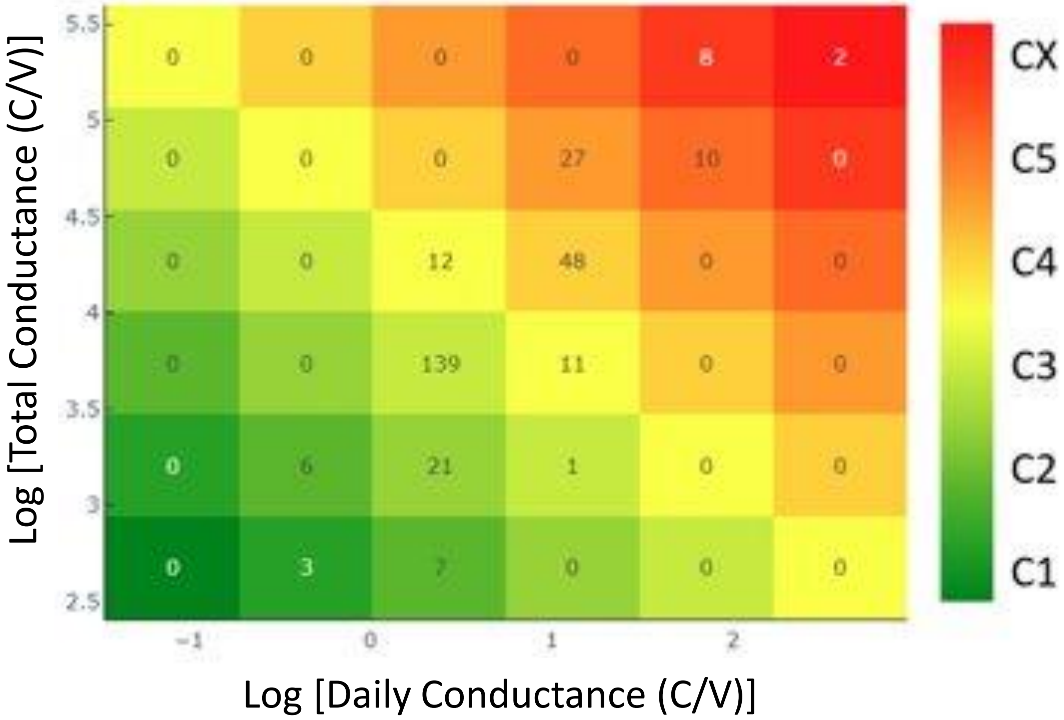
- Accelerated test conditions, operations, and weather events

Daytona Beach, intracoastal



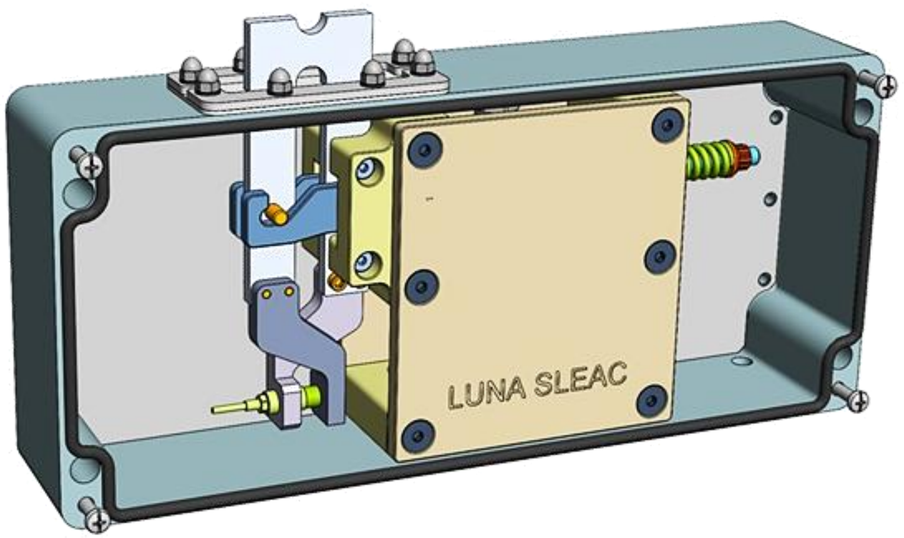
Using severity classification across sites or assets allows for system-level risk management





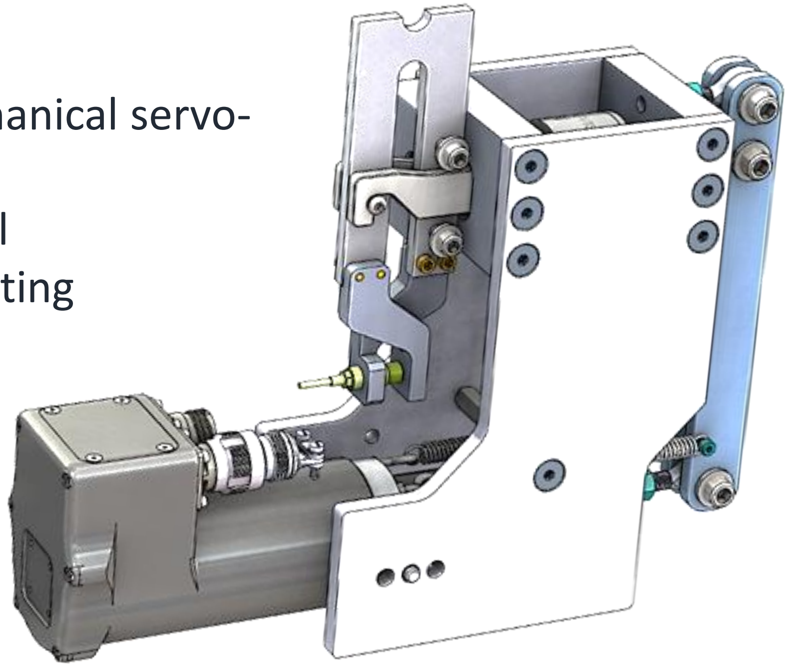
Combined effects testing – Environment Assisted Cracking

Combined effects testing – mechanical stress & corrosive atmosphere



- Spring-loaded system
- Static testing

- Electromechanical servo-actuator
- Load-control
- Dynamic testing



Compact load frames control mechanical environment and are suitable for aggressive test environments

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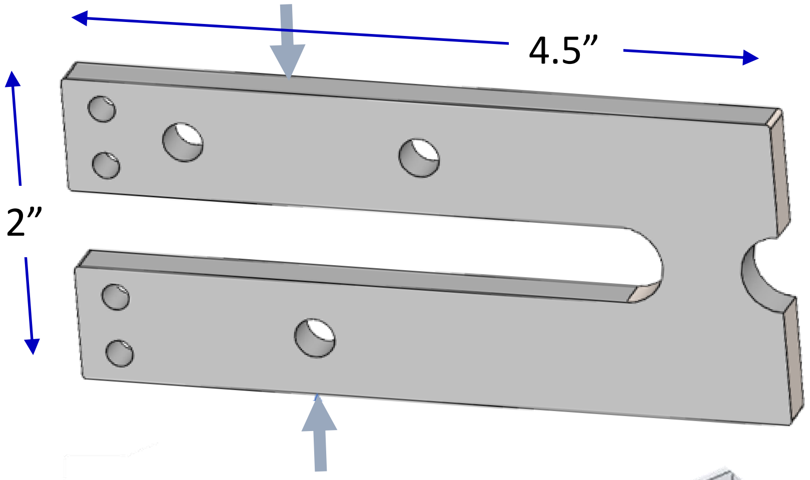
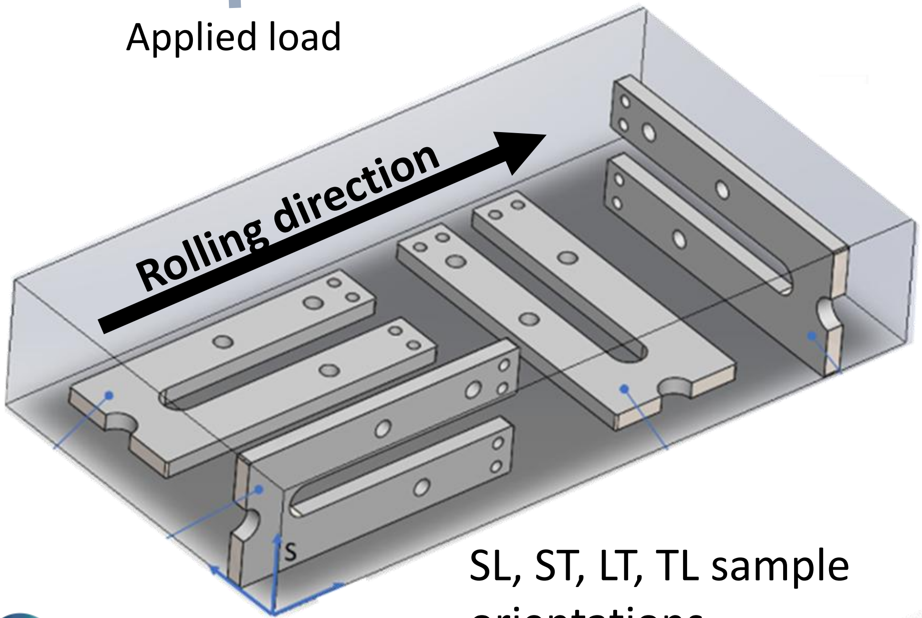
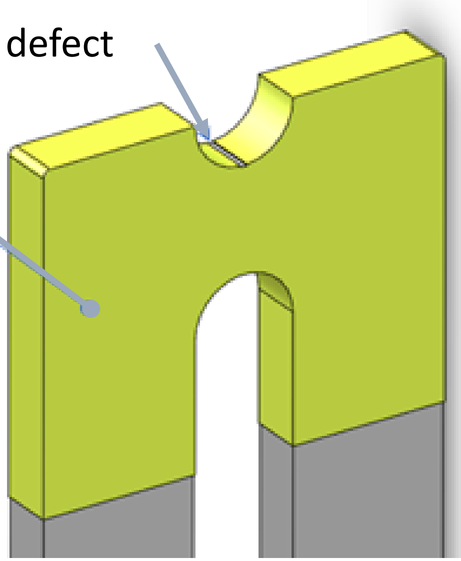
Sample design

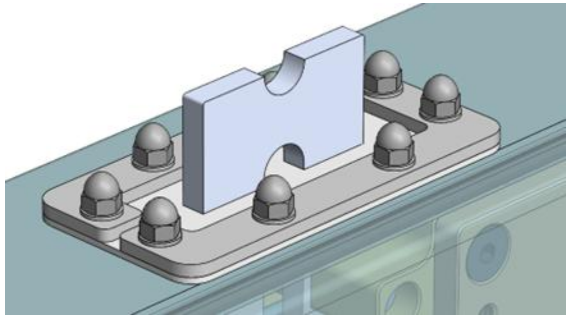
Smooth notch geometry allows for surface modification and evaluating crack initiation





SL, ST, LT, TL sample orientations





Sample pass-through separates control and measurement from test environment

Crevice former / galvanic couple

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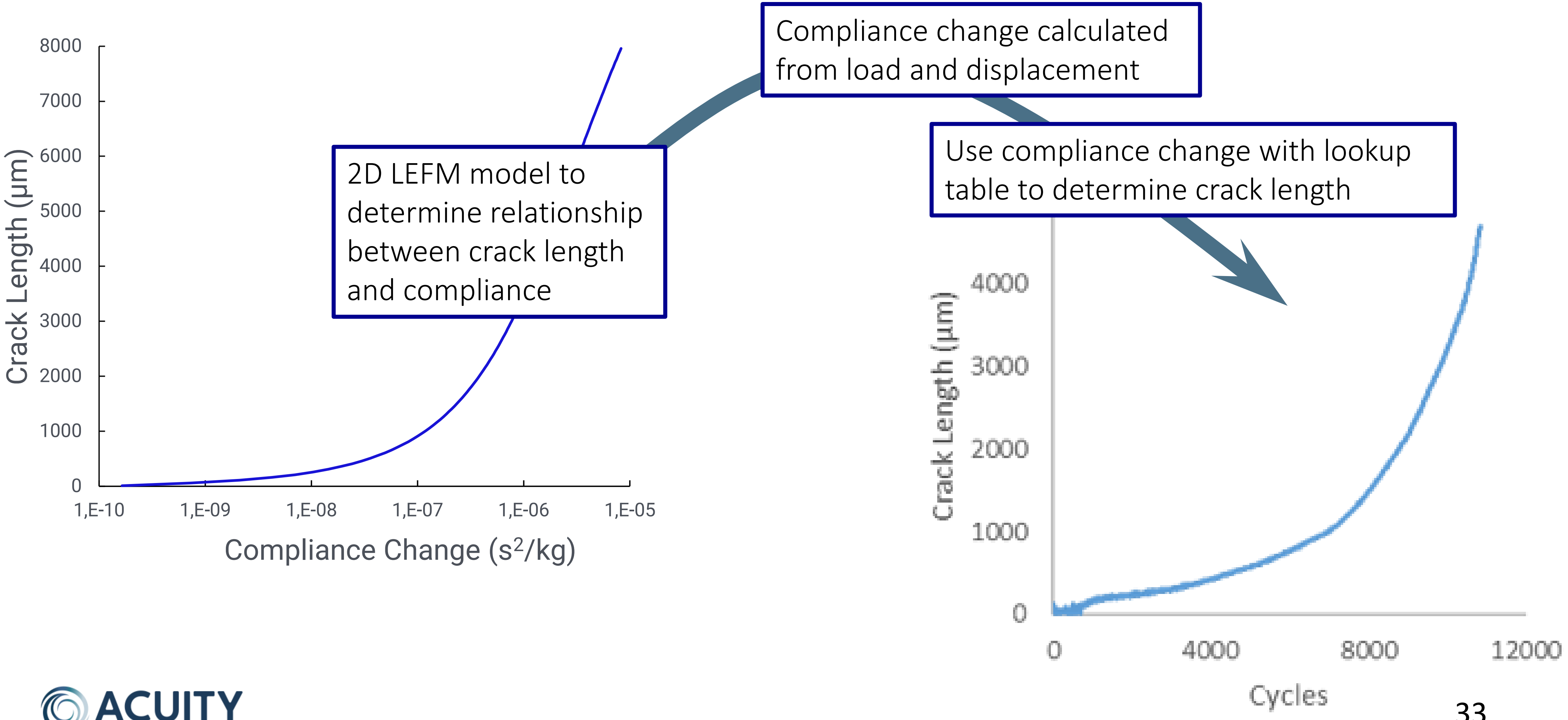
In-situ crack length measurement based on compliance change



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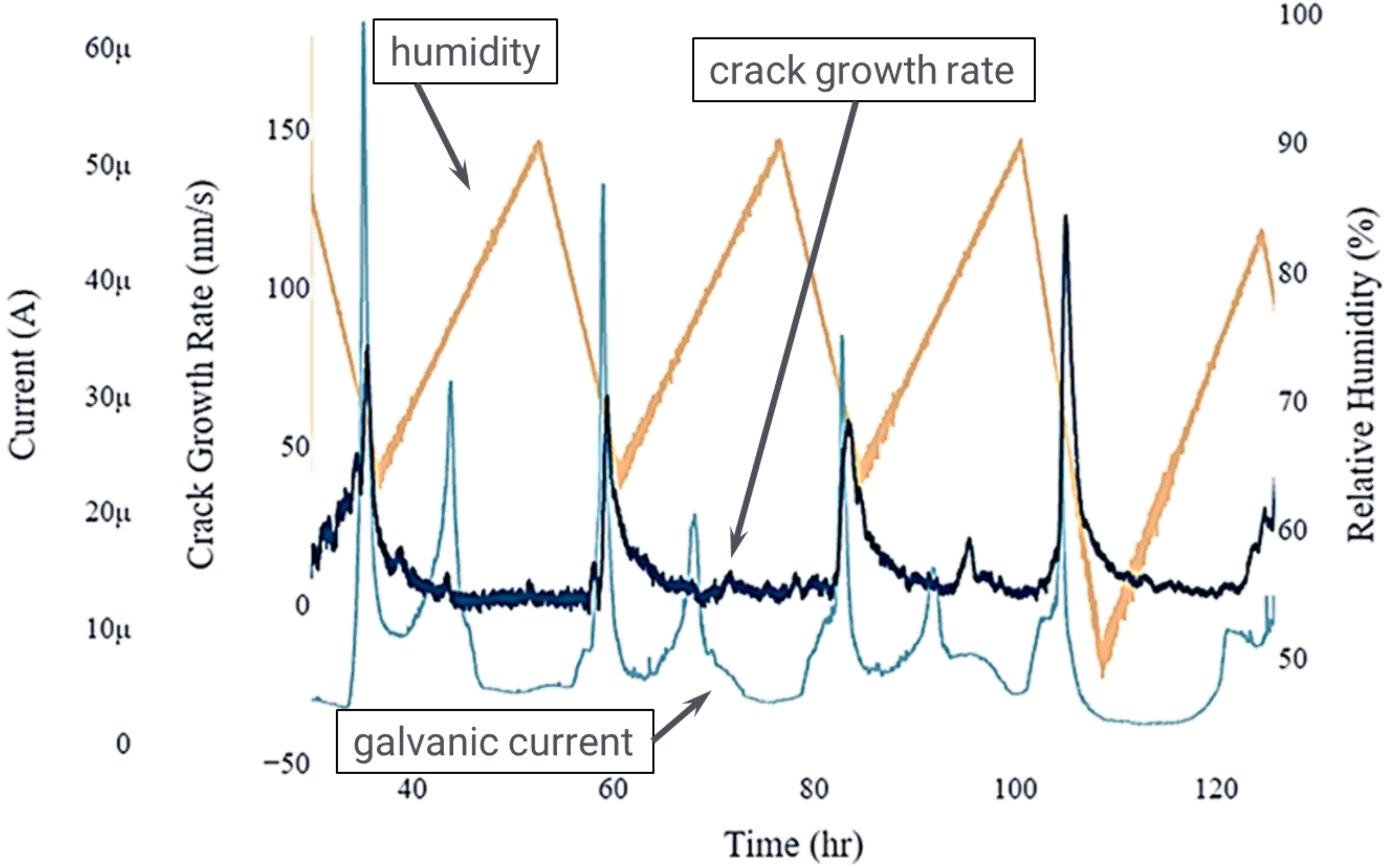
Static load laboratory testing

7075-T651 SL
SS 316 crevice former, glass membrane separator
2.4M NaCl preconditioning
RH cycle developed by NAVAIR -statistical representation of low and high time-of-wetness weather conditions at Beaufort SC, 25C
Initial load: 40% YS



Environmental cracking in outdoor environments

Charlottesville, VA

- **Single-load frame**

Daytona, FL

- **Battelle Florida Materials Research Facility (FMRF)**
- **6 load frames**

Bring the load frame to the environment instead of bringing the environment to the load frame

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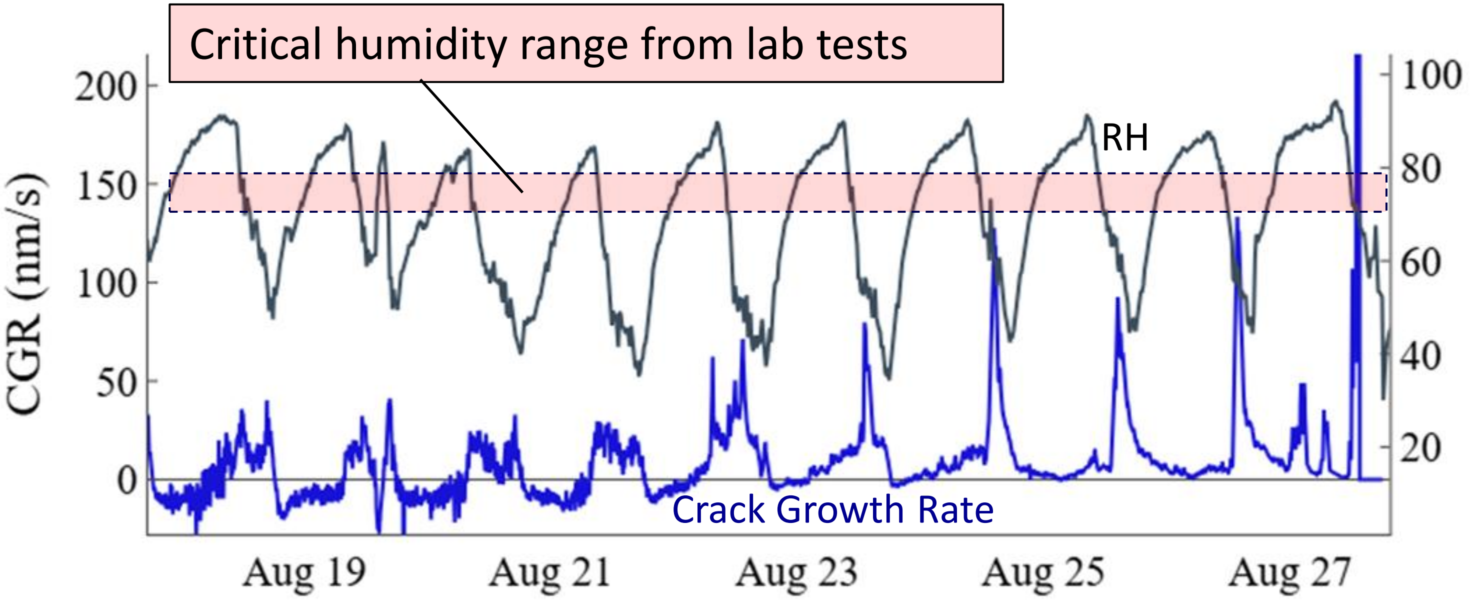
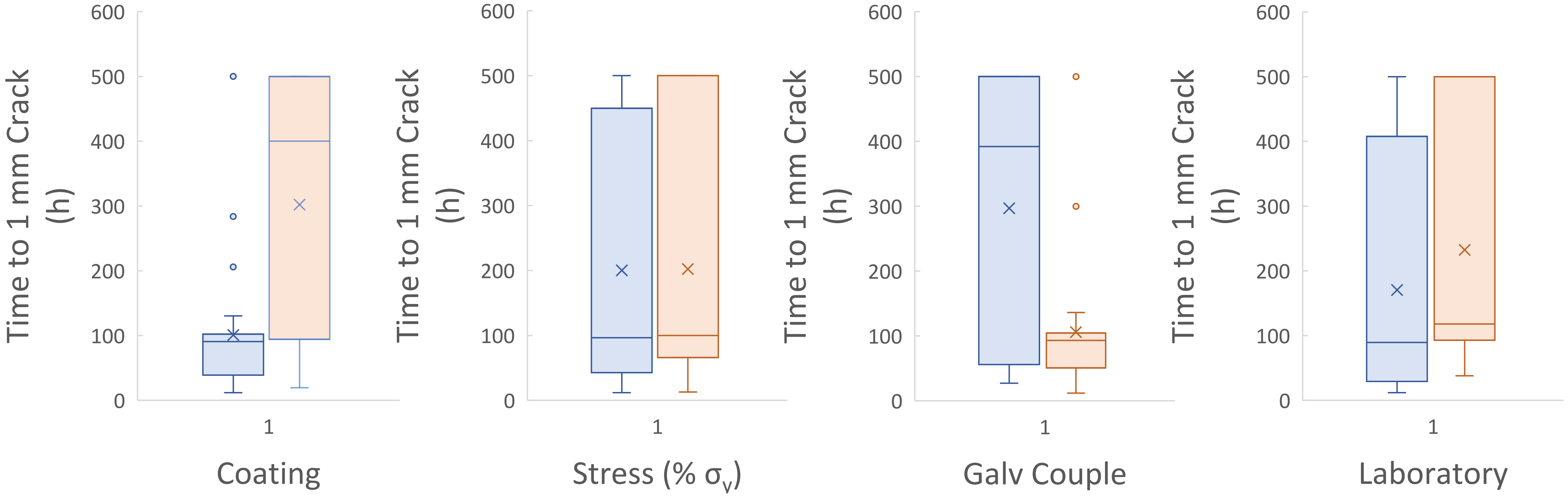
Cracking behavior during outdoor exposure

7075-T651 SL
SS 316 crevice former, glass membrane separator
ASTM Seawater contamination prior to test
Initial load: 35% YS
Outdoor exposure in Charlottesville, VA
Test performed inside louvered shelter



ACUITY corrosion technology

Crack growth rate used to differentiate factors affecting SCC of coated samples



- The DOE factors of coating and galvanic couple were most significant
- Although stress was expected to accelerate cracking, it was not a significant factor
- Both laboratories produced similar results

ACUITY corrosion technology

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Summary

Deployable, self-contained environmental and corrosion sensors are an enabling technology for evaluating:

- Material corrosion rate
- Environment severity
- Asset-specific damage accumulation
- Corrosion mitigation efficacy (coatings)

Deployable load frames with the capability to monitor crack growth and loading conditions offer the ability to perform combined effects testing in natural and service environments

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