



SOUTHWEST RESEARCH INSTITUTE

Cyclic Corrosion and Failure Mechanisms

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SERDP • ESTCP
SYMPOSIUM
2018 | Enhancing DoD's Mission Effectiveness



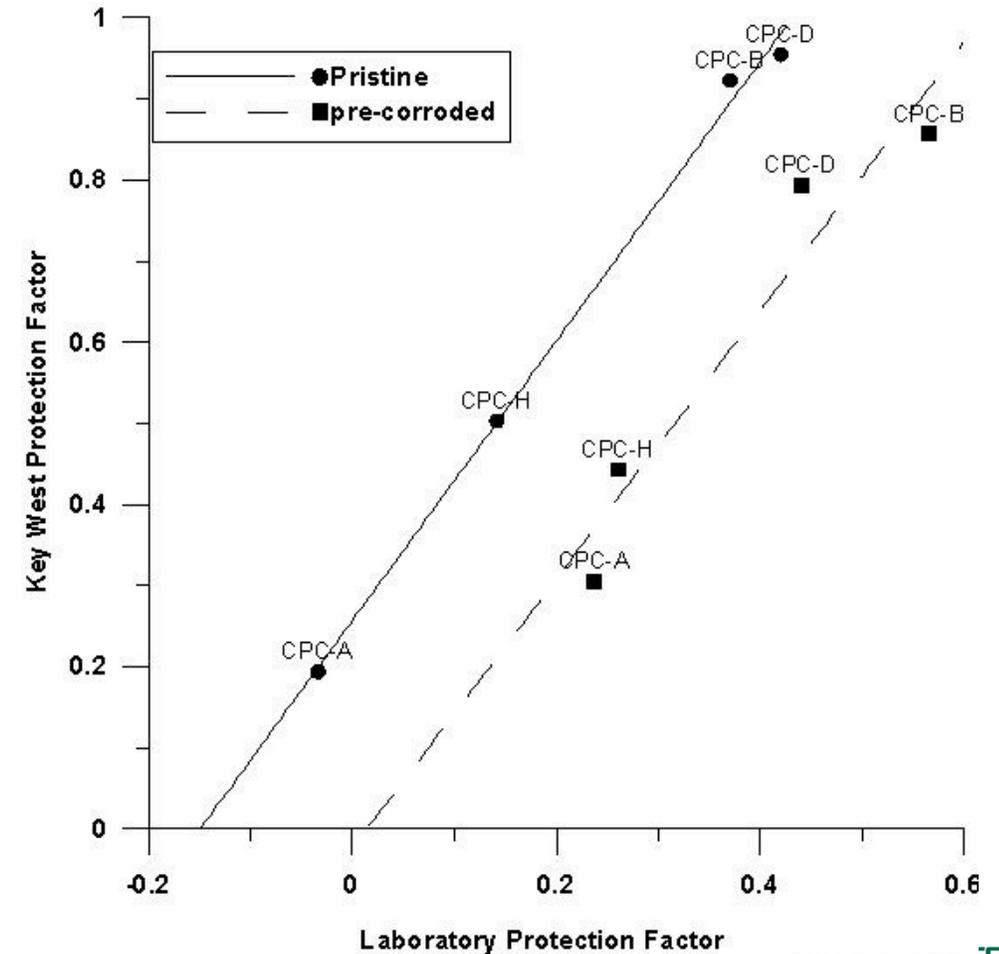
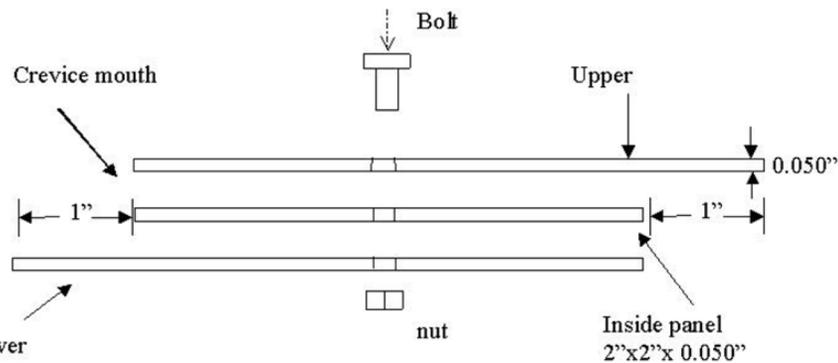
Background

- Problem Statement

- Hexavalent chromium (Cr6+) is particularly effective in reducing corrosion but is a known carcinogen and environmental toxin, and it is facing increased regulation.
- The need to identify and qualify alternatives to formulations based on hexavalent chromium (Cr6+)
- Outdoor exposure testing is the most effective at replicating field damage, but it is time-consuming and not widely accessible.
- Although several accelerated corrosion tests (ACT) are available for DoD use, none of them fully replicate damage observed in field environments (e.g., ASTM B117, ASTM G85, ASTM 810, etc.).

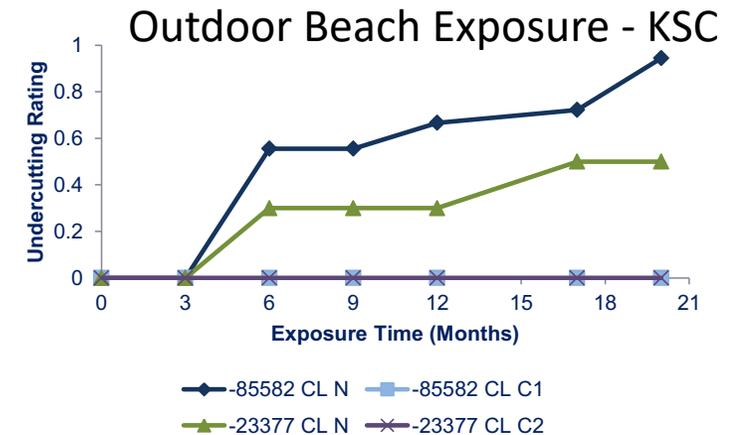
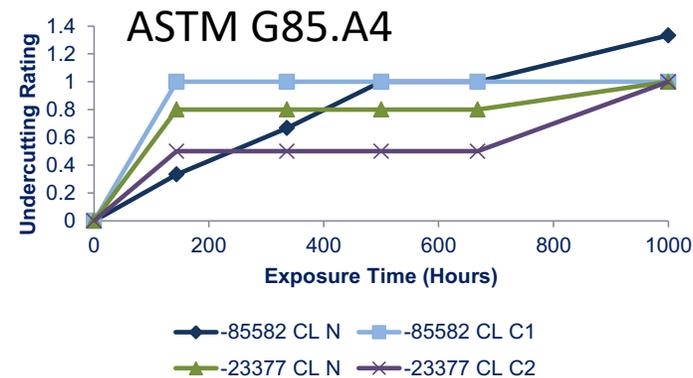
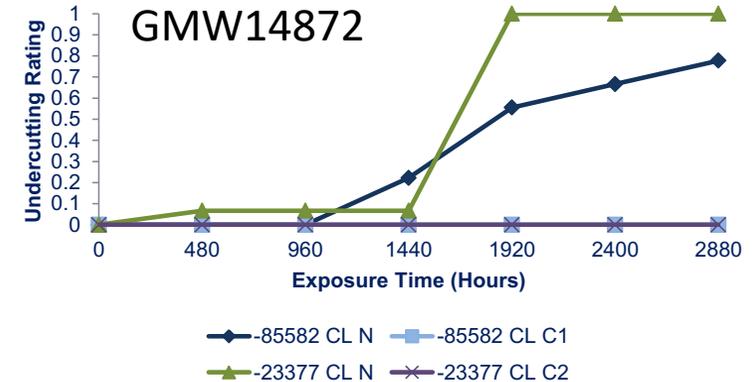
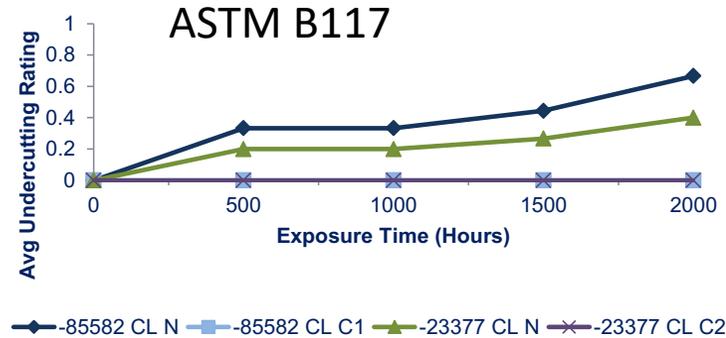
USMC Ranking of CPC Performance

- Relationship of CPC performance between GM9540P (14 days) and Key West
- Triple lap configuration where middle panel mass loss was measured
- Protection Factor (PF) is a measure of CPC performance vs. a control with no CPC
- GM Test is an excellent predictor of CPC performance at coastal site



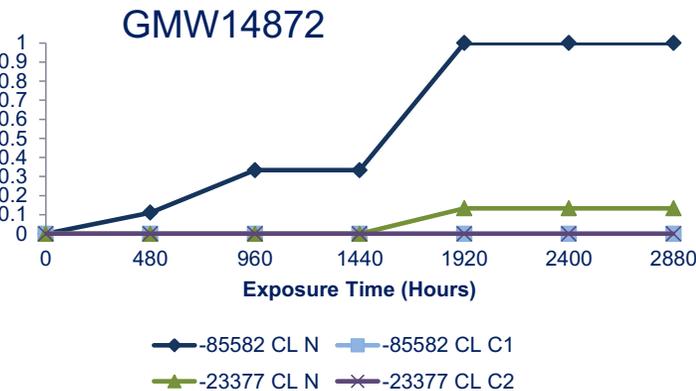
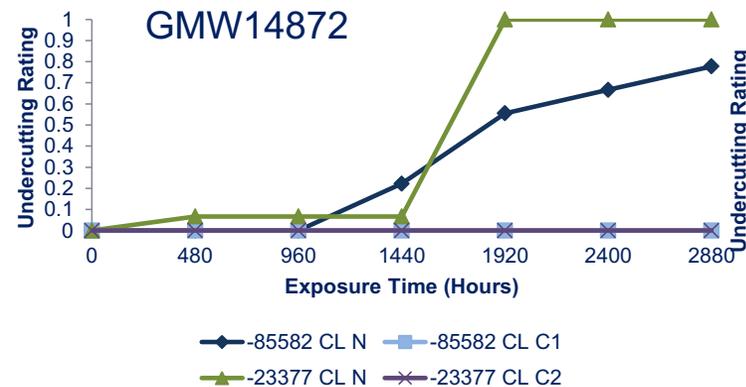
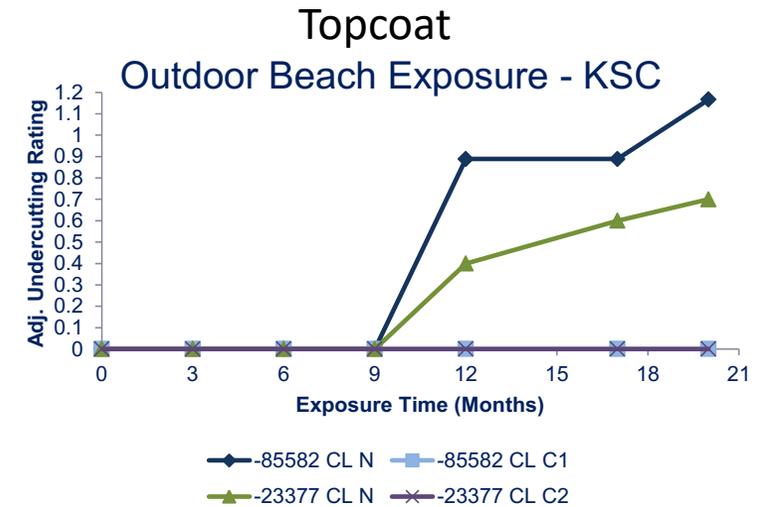
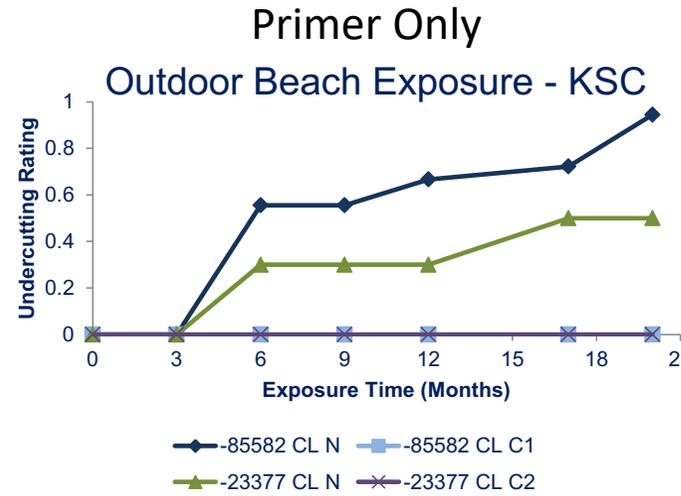
NAVAIR Testing of Non-Chrome Systems

- Looking at coating performance
- What method best replicates field exposure
- Note small amount of scribe creep (1 = 1/16") for primer only systems
- ASTM B117 predicts order but corrosion starts immediately
- GMW14872 shows incubation period (although order not correct).



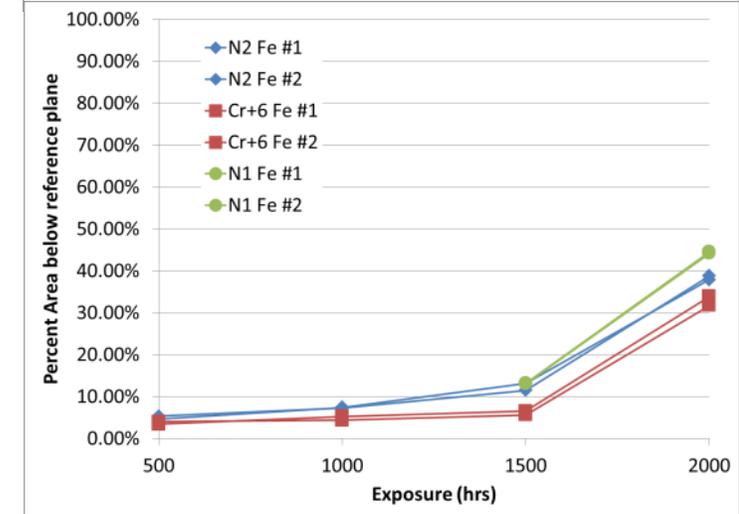
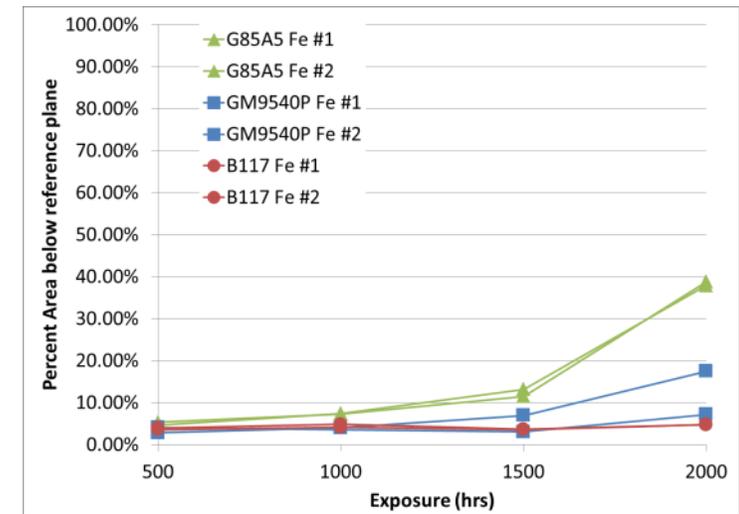
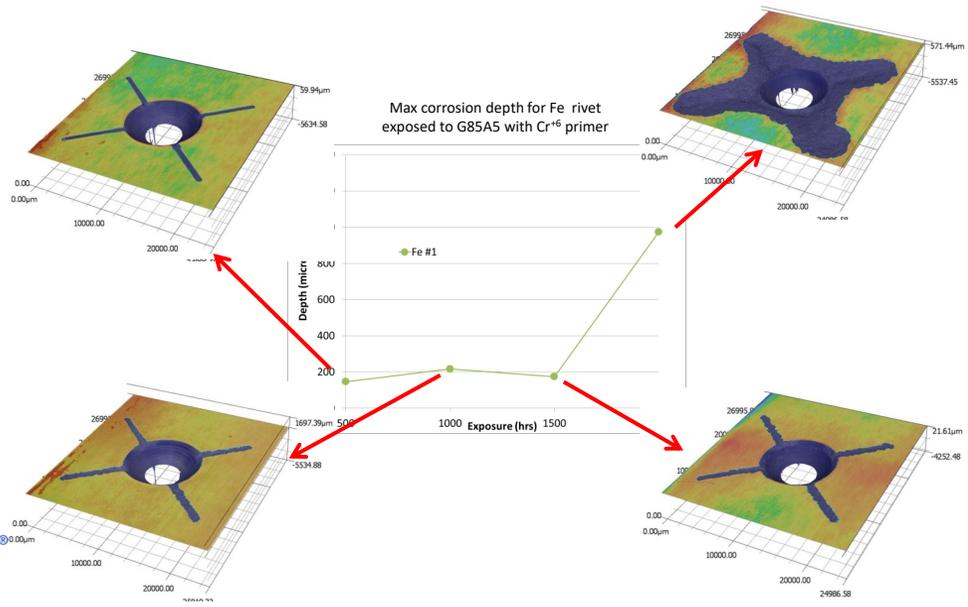
NAVAIR Testing of Non-Chrome Systems

- GMW14872 seems like a good fit for accelerated testing of Al alloys
 - Minor/slow corrosion rate
 - Steep increase in corrosion rate after approximately 1/2 duration of test interval
 - Plateau for corrosion performance
 - Show decreased performance with topcoat
- Gets Class N vs. Class C correct but issues with water borne vs. solvent borne



Accelerated Test Performance for Coated Samples with Galvanic Fasteners

- Used image analysis to quantify scribe undercutting (Percent Area)
- Like NAVAIR, SwRI data showed GM testing is more aggressive than B117 (result of cycles)
- ASTM G85-A5 is even more aggressive (more cycles, more salt, lower pH)
- Need aggressive testing to distinguish performance



G85A5 Exposure for steel rivet holes

Zinc Rich Coating

- Cyclic testing can distinguish performance of Zn-rich systems from non Zn-rich systems

**TABLE 2
USE OF A ZINC RICH ORGANIC PRIMER TO EXTEND
THE LIFETIME OF A COATING SYSTEM**

System	DFT	ASTM D5894 (Creep)	ASTM B117 (Creep)	ISO 20340 (Freeze) (Creep)	Norsok Rev 4 (Creep)	5 Years C5-M (Creep)
Zinc Rich Primer Hydrocarbon Modified Epoxy (MIO)	75 200	1.1mm	3.7mm	0.2mm	1.0mm	0mm
Hydrocarbon Modified Epoxy (MIO)	200	3.3mm	4.2mm	3.3mm	3.3mm	40mm

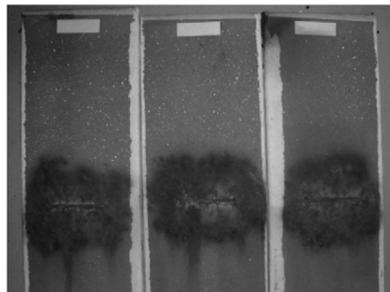


FIGURE 3 – Non-Zinc Primed System

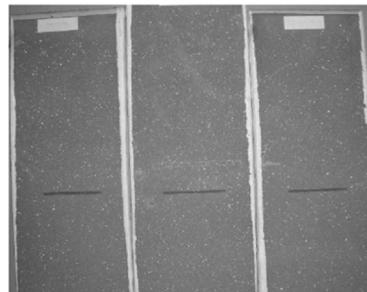


FIGURE 4 – Zinc Primed System

**TABLE 1
ACCELERATED CORROSION TESTS**

Test	Type	Cycle	Scribe Dimensions
ASTM D5894	Cyclic	<ul style="list-style-type: none"> • 168 hours Prohesion [ASTM G85, Annex A] • 168 hours QUV-A (4 hours UV at 140°F (60°C)/ 4 hours at 122°F (50°C)) • Total duration 4,032 hours (24 weeks) 	2mm x 50mm Horizontal
ISO 20340	Cyclic	<ul style="list-style-type: none"> • 72 hours QUV-A • 72 hours Salt Fog at 95°F (35°C) [ISO 7253] • 24 hours freeze at -4°F (-20°C) • Total duration 4,200 hours (25 weeks) 	2mm x 50mm Horizontal
Norsok M-501, Rev 4	Cyclic	<ul style="list-style-type: none"> • 80 hours QUV-A • 72 hours Salt Fog at 95°F (35°C) using artificial sea water as electrolyte • 16 hours dry at 73°F (23°C) • Total duration 4,200 hours (25 weeks) 	2mm x 50mm Horizontal
NACE TM0304 Rust Creepage Test	Cyclic	<ul style="list-style-type: none"> • 168 hours Prohesion [ASTM G85, Annex A] using artificial sea water as electrolyte • 168 hours QUV-A • Total duration 2,016 hours (12 weeks) 	2mm x 90mm Vertical
ASTM B117	Static	<ul style="list-style-type: none"> • Continuous Salt Spray at 95°F (35°C) (5% sodium chloride electrolyte) 	2mm x 50mm Horizontal

From Ward, CORROSION 2008, Paper #: 08003

Zinc Rich Coating

- Current cyclic testing has limited predictability of Zn-rich systems
 - Can distinguish the worst performers
 - Most do not pick the best
- Cyclic testing does not distinguish the performance of non Zn-rich systems
 - No test predicts the worst system
 - Only 1 predicts the best system
 - For multifunctional protection mechanisms, current methods struggle to accurately predict performance.

TABLE 3
EFFECT OF USING DIFFERENT ORGANIC ZINC RICH PRIMERS ON COATING PERFORMANCE

System	DFT	ASTM D5894	ASTM B117	ISO 20340	Norsok Rev 4	NACE TM0304	6 Years C5-M
Zinc Rich Primer (1) Hydrocarbon Epoxy Polyurethane	75 200 60	0.9	2.2	1.1	0.9	0.2	1
Zinc Rich Primer (2) Hydrocarbon Epoxy Polyurethane	75 200 60	1.5	2.4	3.2	3.9	1.9	30
Zinc Rich Primer (3) Hydrocarbon Epoxy Polyurethane	75 200 60	1.1	2.0	1.0	1.0	0.1	1
Zinc Rich Primer (4) Hydrocarbon Epoxy Polyurethane	75 200 60	0.7	2.5	1.7	1.1	0.4	0

TABLE 4
HIGH SOLIDS EPOXY SYSTEMS

System	DFT	ASTM D5894	ISO 20340	Norsok Rev4	NACE TM0304	6 Years Outdoor Exposure
Hydrocarbon Modified Epoxy (1)	2 x 200	5.4	13.0	7.3	4.2	0
Hydrocarbon Modified Epoxy (2) [High Solids]	2 x 200	4.4	4.2	5.0	6.8	12
Hydrocarbon Modified Epoxy (3) [Solvent Free]	3 x 150	9.9	7.7	8.0	4.3	30
Hydrocarbon Modified Epoxy (4) [Solvent Free]	2 x 200	6.4	6.5	7.0	6.0	40

SERDP WP-1673

- Technical Objective
 - Create an improved accelerated corrosion test method that can
 - Accurately replicate corrosion damage modes
 - Accurately rank material performance under atmospheric conditions
 - Control severity
 - Reduce development time for new corrosion mitigation technologies
- Technical Approach
 - Integrate representative sample designs into accelerated corrosion testing
 - Determine the effect of critical environmental and mechanical parameters on degradation modes of system components
 - Characterize and compare the development of corrosive environments for “real world” and current accelerated corrosion tests

Corrosion Rate of Steel vs. RH

- ASW and $MgCl_2$ provide considerable conductance to <2% RH for up to 24 h
- Sustained corrosion detectable down to 11% RH for $MgCl_2$ and 23% for AS
 - DRHs of contaminant salts do not serve as threshold for wet-dry or significant corrosion
- Large disparity in attack between 33% and 53% RH for NaCl and ASW (Critical RH): linked to ERH and the presence of other salts
- Above DRH, continuous electrolyte forms
 - cathode moves away from single drop edge
 - Large cathodic drives fewer but deeper pits

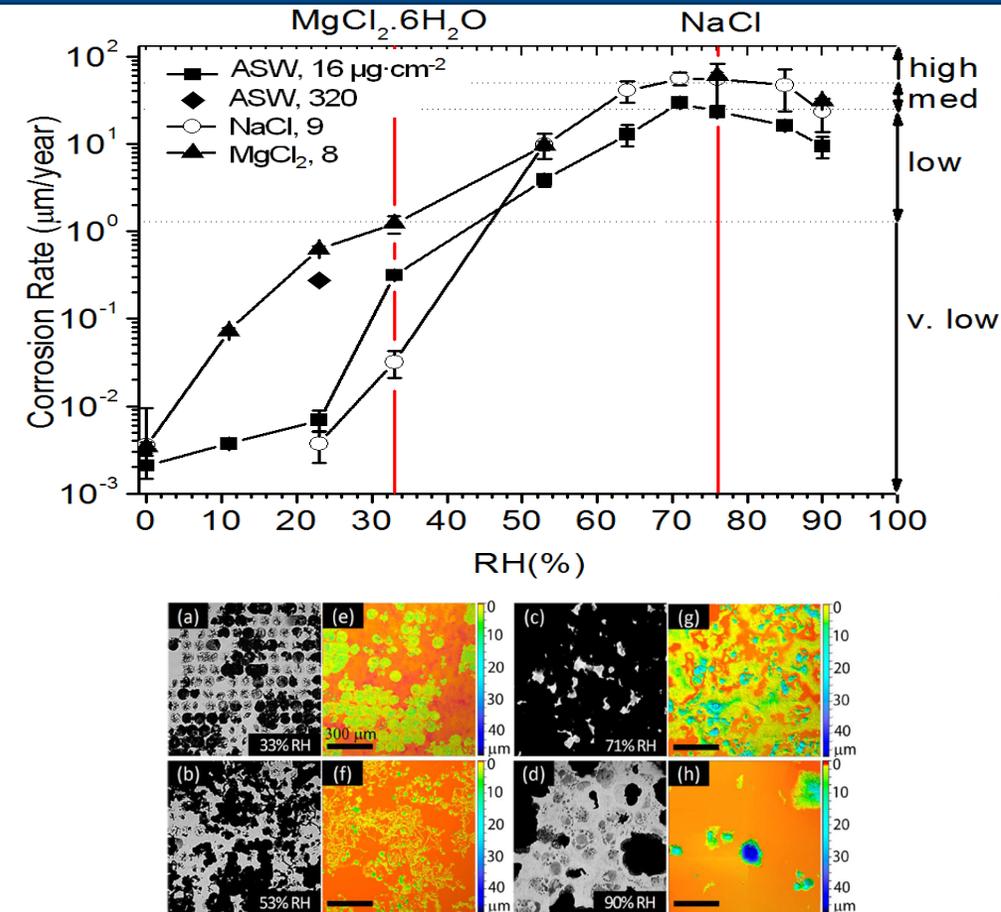
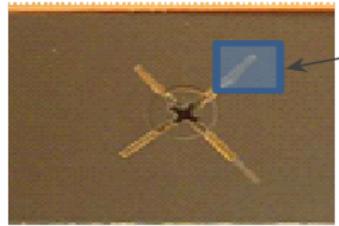


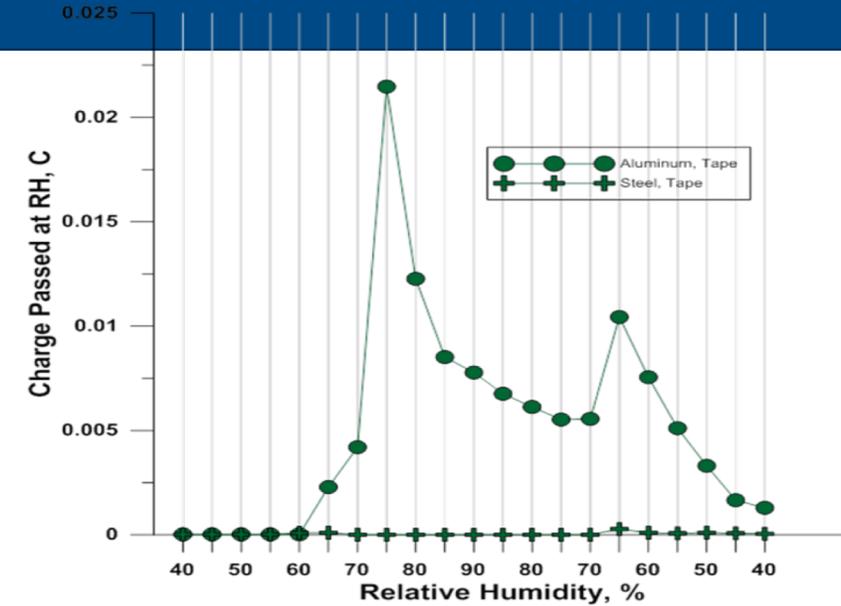
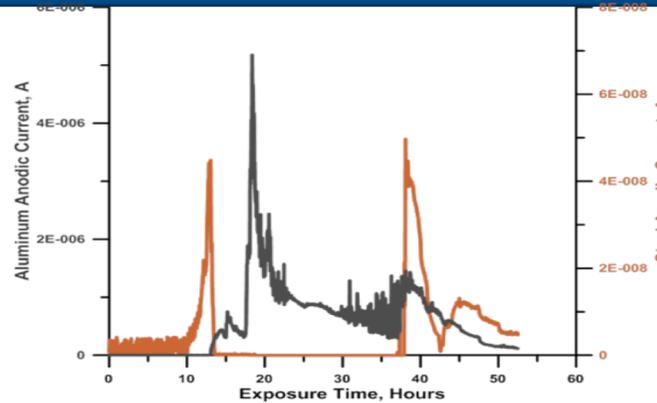
Figure 7. Optical micrographs of ASW-loaded coupons ($16 \mu\text{g}\cdot\text{cm}^{-2}$) after 7 d of exposure at the humidity indicated and before rust removal (a-d). Measured surface profiles after rust removal for the same exposure period are also shown (e-h). All images are the same scale.

Uninhibited Galvanic Electrode

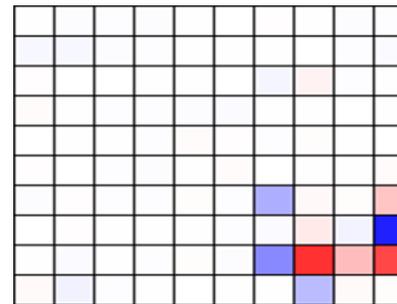
ASTM B117
Constant fog



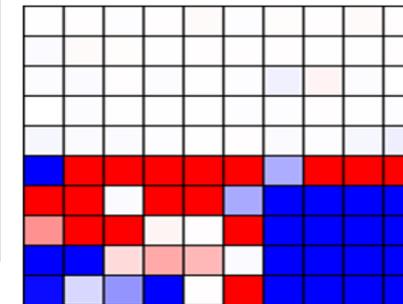
ASTM G85-A5
Cyclic wet/dry



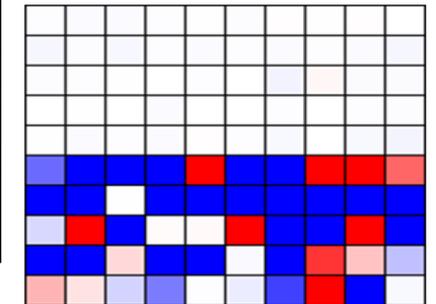
- Mimicking aircraft corrosion is not easy
- Steel is anodic ONLY when anodic Al current activity is low (during wetting and drying transitions)
- Above DRH, steel becomes a cathode and Al an anode
- Suggests RH governs galvanic coupling
- Most charge is passed during transition between wet and dry



60% RH



90% RH



65% RH

RH Affects Surface Morphology of Coated Aluminum

- Degradation mechanisms can be triggered by the right combination of humidity cycling:

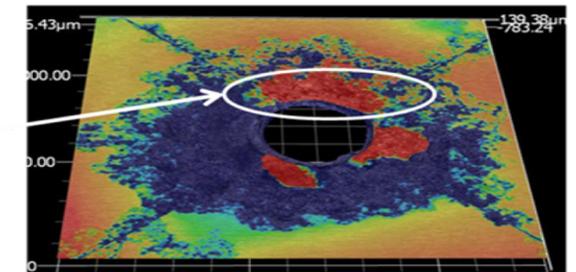
- Accelerated Test Cycle Conditions, $T = 49^\circ \text{C}$
- TOW (RH > 76%) = 67% of total exposure time
- Salt deposition: 0.6M NaCl, pH = 3, salt dip = 15 minutes

	Cycle 1	Cycle 2	Cycle 3
Max RH	90%	90%	90%
Min RH	40%	65%	40%
Max RH Time (hr)	2	2	8
Min RH Time (hr)	1	1	4
Salt Dip Frequency (per wk)	1	1	1

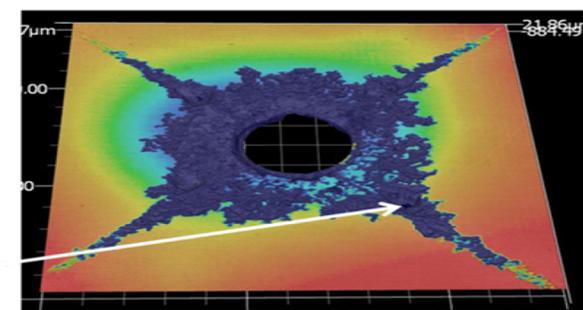
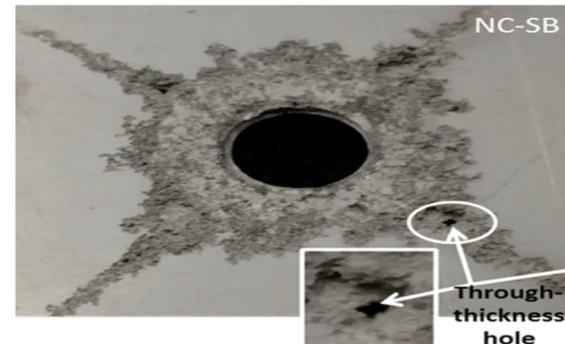
Effect of degree of drying

Effect of frequency of cycles and high RH dwell time

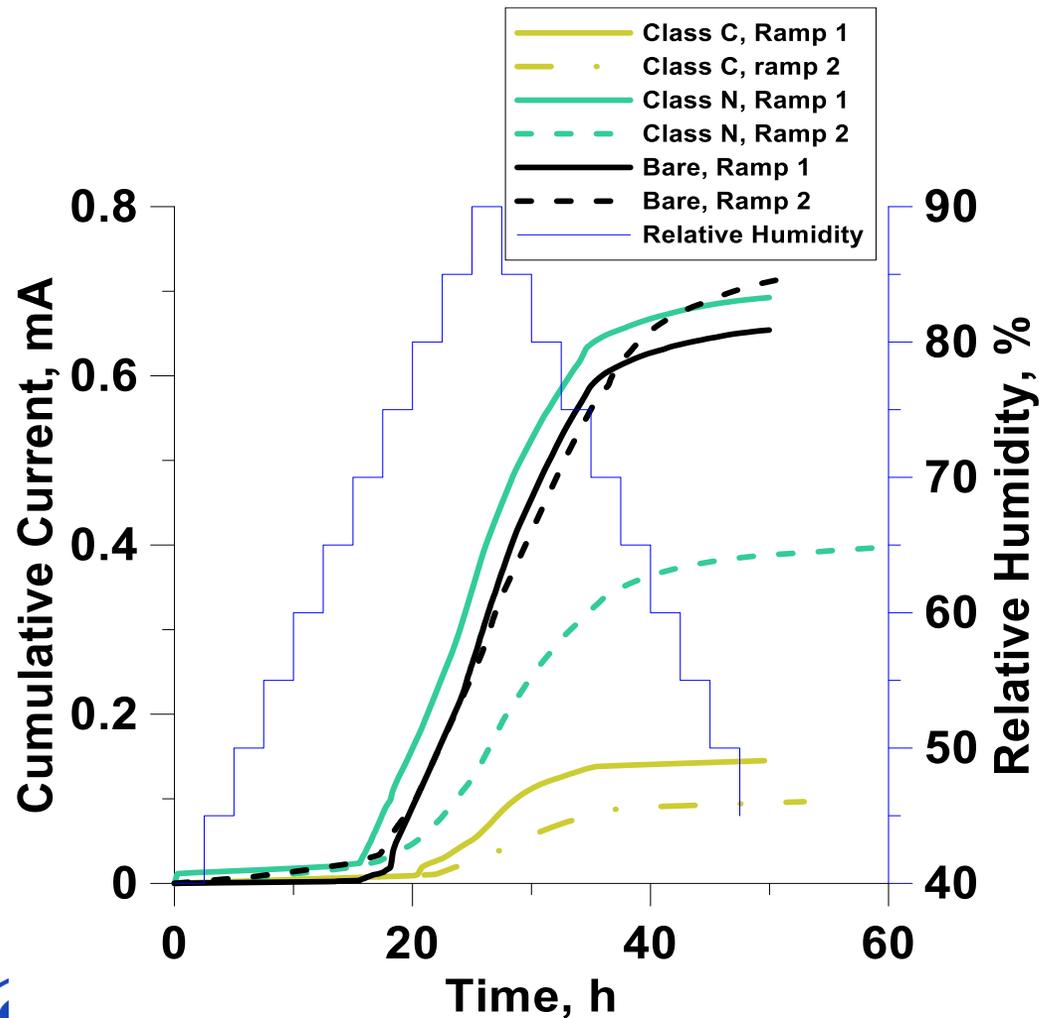
- **Cycle 1:** very shallow damage restricted to the uppermost surface layer with significant coating delamination.
- **Cycle 2:** Exfoliation, extensive coating delamination and material volume loss.



- **Cycle 3:** Deep corrosion trenches along fastener and significant pitting.



RH Effect on Inhibitor Release

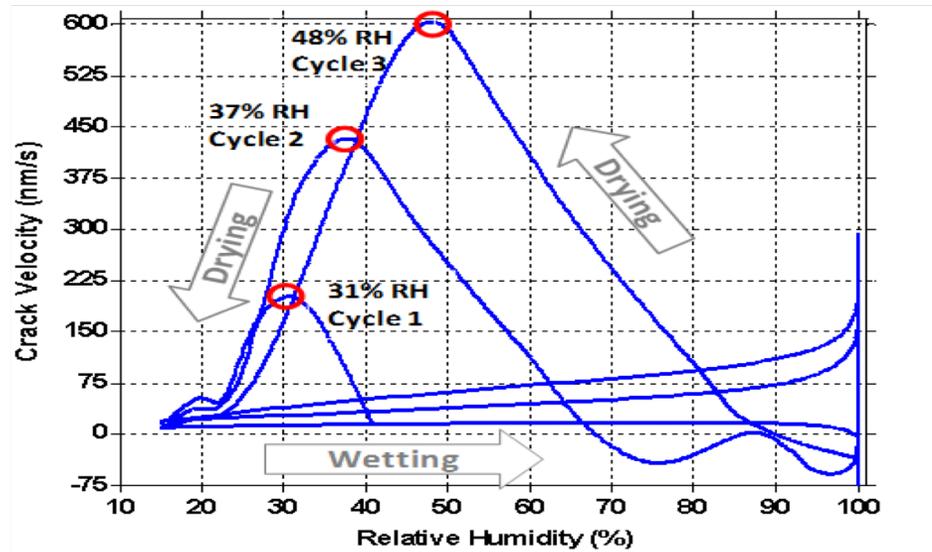


- Cumulative currents are lower for the second ramp than for the first ramp in the presence of a primer, but remain relatively unchanged for bare MEA
- Initial wetting of the surface during the high RH periods of the first ramp initiates inhibitor release which protects the surfaces during subsequent wetting events.

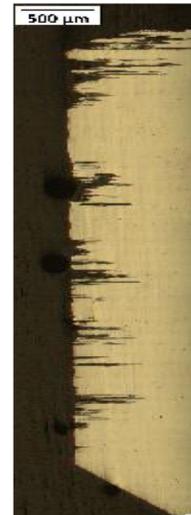
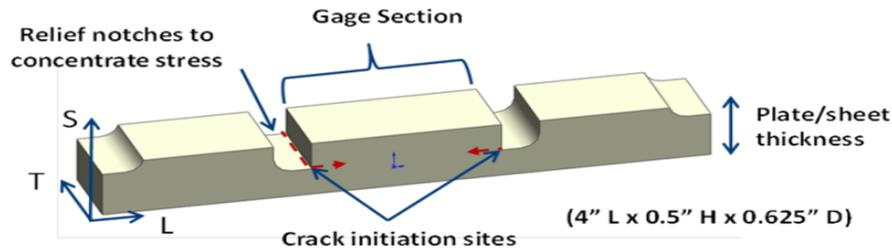
	Bare	Class C	Class N
Charge Passed 1st Cycle (C)	0.078	0.017	0.083
Charge Passed 2nd Cycle (C)	0.085	0.011	0.047
Percent of charge passed in 2nd Cycle vs. 1st	109%	66%	56%

RH Affects IGC and SCC of Aluminum

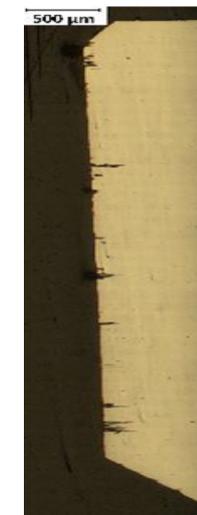
- Cyclic RH strongly affects SCC: CGR increase during drying
- Chemistry and RH strongly affect degree of corrosion within a fastener hole



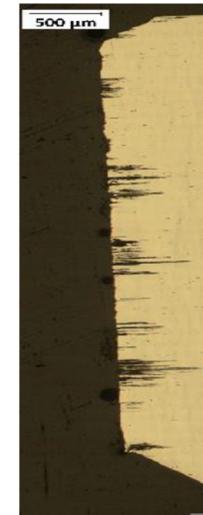
Sensitized AA5083 in modified
ASTM G85-A5.



Pt. Judith
7075-T6
Al/SS
12 months



G85-A5
7075-T6
Al/SS
1,000 hrs



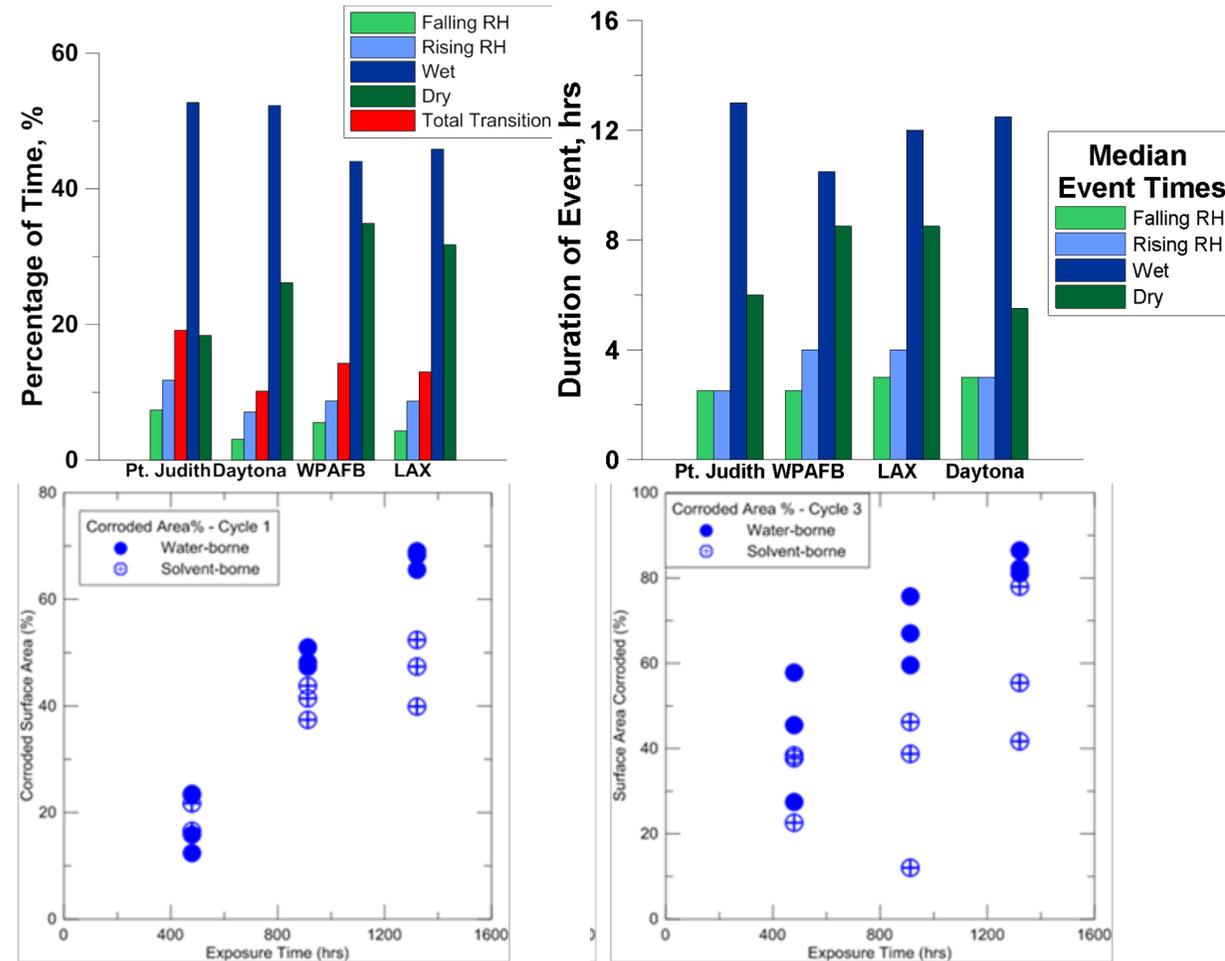
Experiment 1
7075-T6
Al/SS
1,000 hrs

RH Breakdown

	RH > DRH	50% < RH < DRH	RH < 50%	Comment
Point Judith* (3 years)	53	29	18	Sea salt exposure, saturated
Daytona* (3 years)	52	23	25	Sea salt exposure, saturated
WPAFB* (3 years)	45	20	35	Very low chloride
LAX* (3 years)	46	21	33	high chloride, industrial
ASTM G85-A5* (2000 hrs)	39.5	26.7	34	Dilute NaCl fog, pH = 5, 12 cycles/day
GM9540P (2000 hrs)	56.3	18.3	25.4	High NaCl brief spray, pH=5, 1 cycle/day, diluting fog
ASTM B117 (2000 hrs)	100	0	0	High NaCl, no cycles
Adhesion Testing (Cycle 1) (1400 hrs)	66	0	34	High NaCl, pH=3, dip applied 1/week, 8 cycles/day, high temp, RH controlled
Adhesion Testing (Cycle 2) 1400 hrs)	66	34	0	High NaCl, pH=3, dip applied 1/week, 8 cycles/day, high temp, RH controlled
Adhesion Testing (Cycle 3) (1400 hrs)	66	0	34	High NaCl, pH=3, dip applied 1/week, 2 cycles/day, high temp, RH controlled
UVA Trial 1 (1000 hrs)	33	34	33	High NaCl fog, pH=3, 16 cycles/day, high temp (49° C), modified ASTM G85-A2
NE#1	45	13	42	Mod sea salt exposure, 15 min spray, RH control, 12 cycle/day, pH = 3
NE#2	25	43	32	Mod sea salt with nitrate, 30 min fog, wet bottom RH, 12 cycles/day, pH = 3

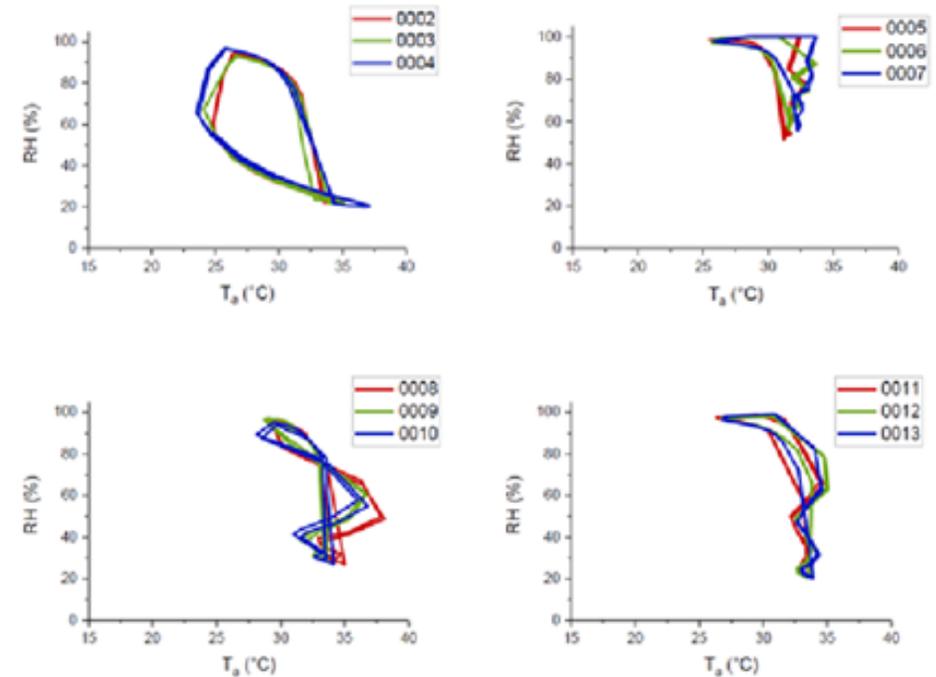
Mimicking Coating Delamination: Criteria for Accelerated Method

- RH > DRH for > 50% of the time in natural environments
- Coating delamination is a strong function of the time of wetness within a given cycle. This will also likely reduce time for inhibitor depletion
- Trade off between solution aggressiveness and percent of time wet and absolute time wet (less aggressive solutions need longer absolute wet time)
- Increase aggressiveness of delamination
 - pH < 5 (G85-A5 and UVA Trial 1 have high absolute dry time but very aggressive damage)
 - Increase salt deposition (most dilute spray has 10x – 100x more than coastal)
 - RH > DRH for longer periods of time



What's Next?

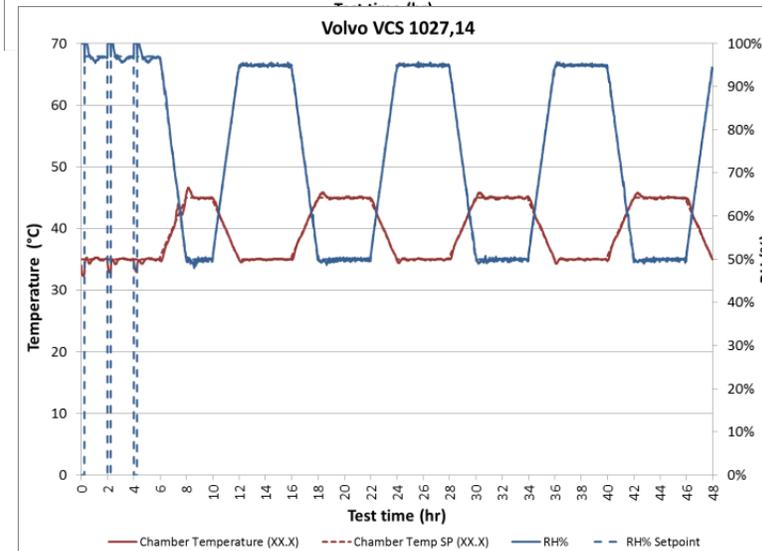
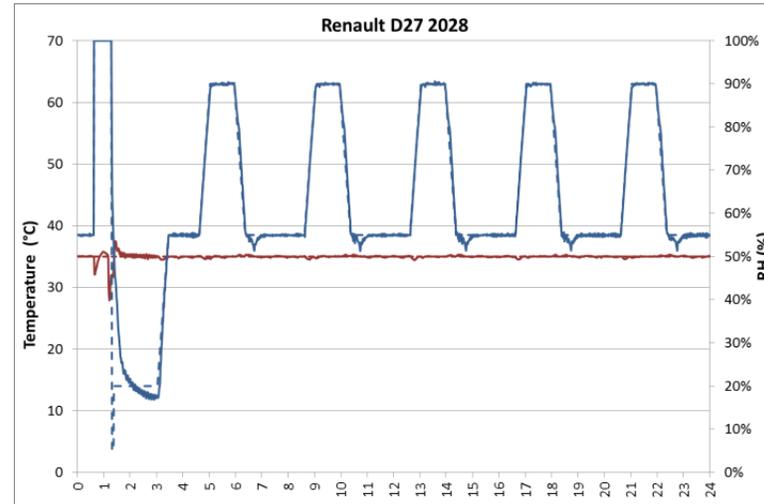
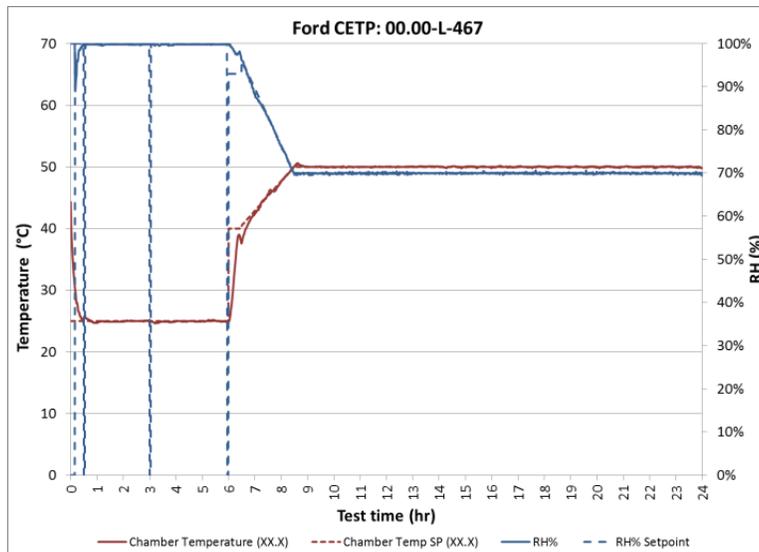
- The innovative aspect of this work is the control of cyclic variation of relative humidity and the periodic salt deposition of salt solution within each cycle
- Traditional DoD cyclic tests do not include this degree of control, limiting their usefulness and introducing a high degree of variation in test results
- A proposed ESTCP effort is designed to develop existing corrosion tests sufficiently to allow its widespread use in testing labs across the DoD, original equipment manufacturers, DoD contractors, and other testing labs.
 - **Objective 1:** Mature the accelerated corrosion test protocol developed during the SERDP WP-1673, WP-1674, and SERDP WP-2521 efforts*.
 - **Objective 2:** Characterize protocol variability by means of round robin testing with participation from DoD laboratories, contractors, and private industry.
 - **Objective 3:** Establish a national standard to be used throughout the acquisition life cycle for testing and qualification of corrosion prevention schemes.



Luna LS2A sensor monitoring ASTM G8-A5 chamber RH and Temperature in 4 laboratories (funding from AFCPO))

Automotive Testing

- Automotive testing summarized by S. Fowler (DoD Corrosion Conference, paper#: 789123)
- RH is specified in several tests
- Many tests do not promote full drying



Automotive Testing

- VDA 233-415 and Volvo VCS 2017.14 have %time above DRH similar to operational environments
- Volvo and Renault both have aggressive pH = 4
- Ford and Renault have similar RH profiles but different profiles of absolute time in each region (Renault has many cycles)
- Volvo has 1 daily cycle and minimizes salt deposition (2/week via spray):
 - Propose adding an additional RH step
 - Using sea salt using nitric acid to pH

Cycle	Solution	Spray Type	RH < 50%	50%≤RH <76%	RH≥76%
Ford L-467/Volvo 1027,1449 (ACTII)	NaCl 0.5% pH uncontrolled	Shower	0%	66%	34%
GMW 14872	NaCl 0.9% CaCl ₂ 0.1% NaHCO ₃ 0.075% pH uncontrolled	Shower	46% (22% below RH30%)	16%	38%
Renault D17 2028 (ECC1)	NaCl 1.0% pH =4.0 (H ₂ SO ₄)	Fog	8%	62%	30%
VDA 233-415	NaCl 5.0% pH neutral	Fog	1%*	39%	60%
Volvo VCS 2017,14	NaCl 1.0% pH =4.2 (H ₂ SO ₄)	Shower	17%	31%	52%

*RH below 50% is due to fluctuation of chamber conditions around a set point of 50%.

Acknowledgements

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- Teamed with Government Labs, University, and Industry

