Accelerated Dynamic Corrosion Test Method Development

WP-1673

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Project Teams

- Government
- Industry/Academia

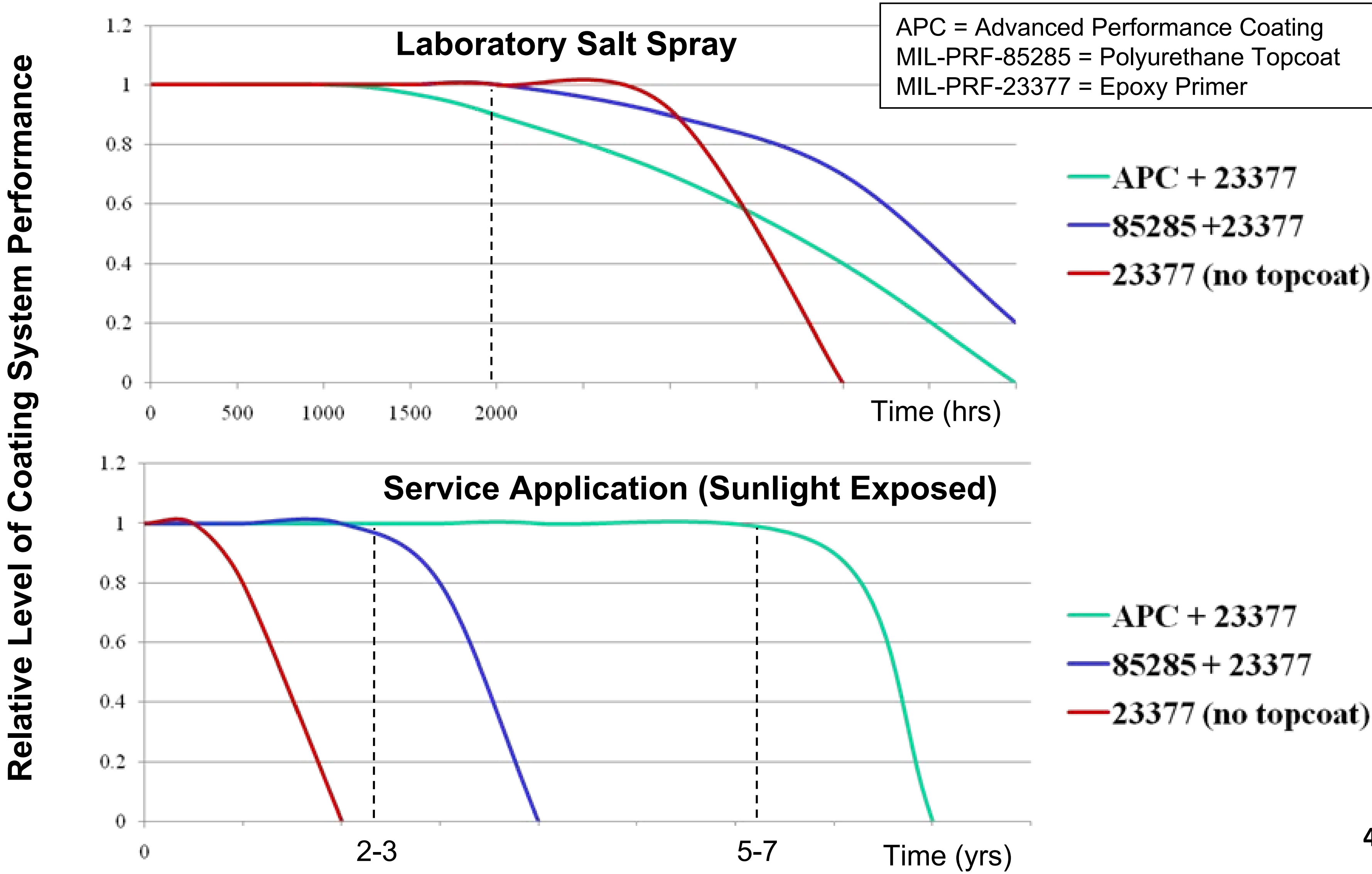
Problem Statement

- Advanced materials for improved performance are being implemented on new and legacy systems
- Limitations of current corrosion testing
  - Long term testing is rate limiting for technology implementation
  - Poor correlation between laboratory and field testing (i.e. promising technologies fail lab testing while poor technologies pass lab testing)
- Need to improve accelerated corrosion testing
  - Differentiate candidate materials
  - Accelerate “real world” failure modes

Lab vs. Outdoors

Disparity between outdoor and laboratory corrosion testing:

APC = Advanced Performance Coating
MIL-PRF-85285 = Polyurethane Topcoat
MIL-PRF-23377 = Epoxy Primer



Technical Objectives

- Characteristics of a comprehensive accelerated laboratory test protocol to accurately predict all aspects of the performance of DoD coatings
  - independent of substrate
  - Will accurately rank performance of coating systems in a particular service application
  - Is tunable to match multiple service environments and multiple service applications

Technical Objectives

- Develop an improved test method to assess corrosion of new systems
  - Integrate representative sample designs into accelerated corrosion testing
  - Integrate mechanical loading into accelerated corrosion testing
  - Characterize and compare the development of corrosive-electrolytes for “real world” and current accelerated corrosion tests
  - Determine the effect of critical environmental and mechanical parameters on degradation modes of system components

Technical Background

- Many accelerated environmental tests exist
  - Tests incorporate flat panel sample configuration with no loading component: **limits observable failure modes**
  - Developed by applying reasonable environmental conditions and ensuring resultant corrosion damage of a test system is realistic: **may or may not "excite" specific operational failure modes in other systems**
- Approach to new accelerated corrosion test
  - Thoughtful consideration of appropriate sample design
  - Make use of scientific understanding of corrosion mechanisms to develop exposure test cycle parameters

Technical Approach Overview

- How are current laboratory environments different from real world?

Task 1
- Laboratory Exposure Testing

Task 2
- Outdoor Exposure Testing

- Measure the evolution of chemistry and morphology
- Measure the relationship between RH, temperature, and TOW
- Identify differences between accelerated and outdoor environments

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- What are the critical variables that drive corrosion?
- What are the relationships between these critical variables and corrosion processes?

Task 3
- Laboratory studies of critical variables

- Determine critical electrolyte chemistry
  - Chemical composition
  - RH affects
  - UV affects
- Determine affects of environment
  - Environmental cracking
  - Corrosion at a coating defect
  - Coating fracture
  - Coating adhesion

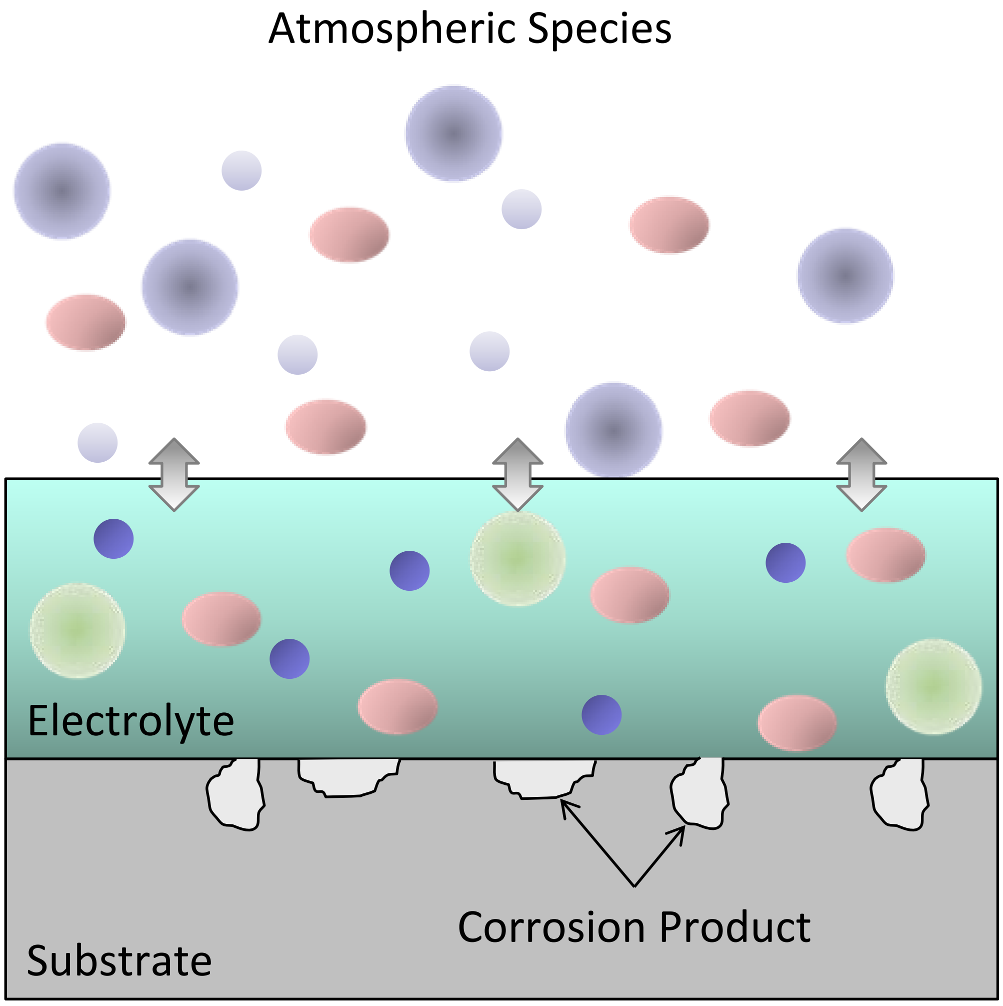
- What geometry can be used for a universal corrosion test samples?
- Can we develop test criteria that can be used to tailor lab test methods to replicate damage in the field?

Task 4
- Sample design
- Data mining

- Develop a corrosion test sample that simulates component geometries and materials
- Use data mining tools to model relationships between environment and corrosion failure modes
- Based on these models, develop an accelerated corrosion tests

Technical Background

- Corrosion reactions are a function of electrolyte chemistry
- Atmospheric particulates and/or gasses partition into adsorbed water layer
  - Form reaction products with water
  - Substrate/particulate interaction
  - Substrate/reaction product interaction
- Corrosion products affect electrolyte chemistry



Tasks 1 & 2 Approach

Type of Exposure	Site	Team Participation
Coastal	Daytona	Luna + AF
Industrial	Alcoa rack	Luna + AF
Shipboard	Navy System	Luna + AF
Desert	?	Luna
	Arizona	AF

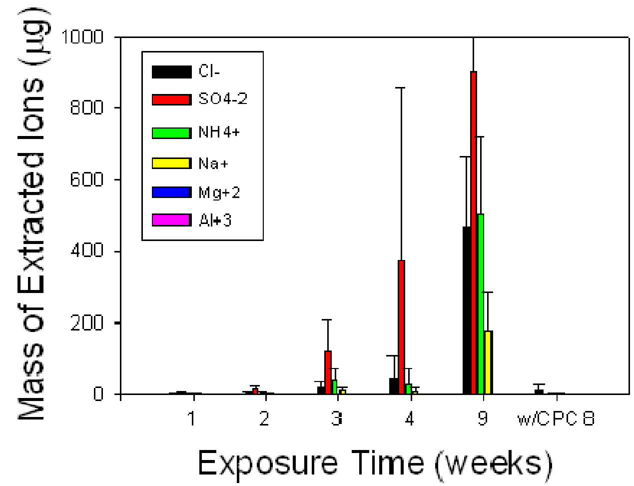
Accelerated Test	Test Facility
Neutral Salt Spray	AMCOM
SO_2 Salt Spray	NAVAIR
Cyclic Automotive	ARL
Acid Salt Spray	Alcoa

- Outdoor testing compared with accelerated testing (4 samples / system)
  - Evolution of electrolyte chemistry
  - TOW, temperature, and duty cycle
  - Evolution of morphology
- Outdoor testing coordinated with AF team
  - Luna – electrolyte chemistry
  - AF – corrosion product
  - Overlapping exposure sites and sample design allows data leveraging

Tasks 1 & 2 Approach

UVA

- Corrosion product sampling
- HPLC for ionic analysis
- Evolution of electrolyte over time

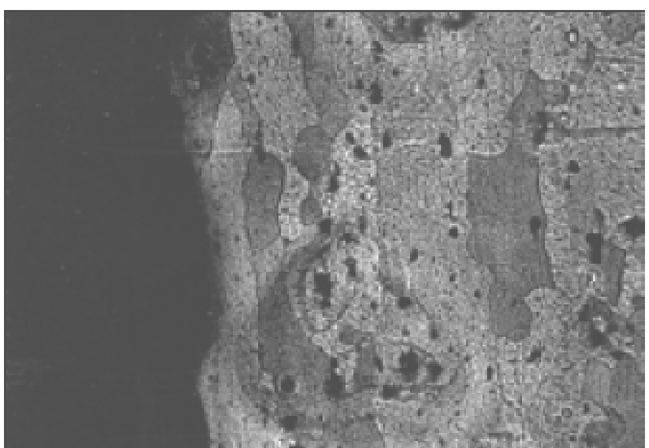


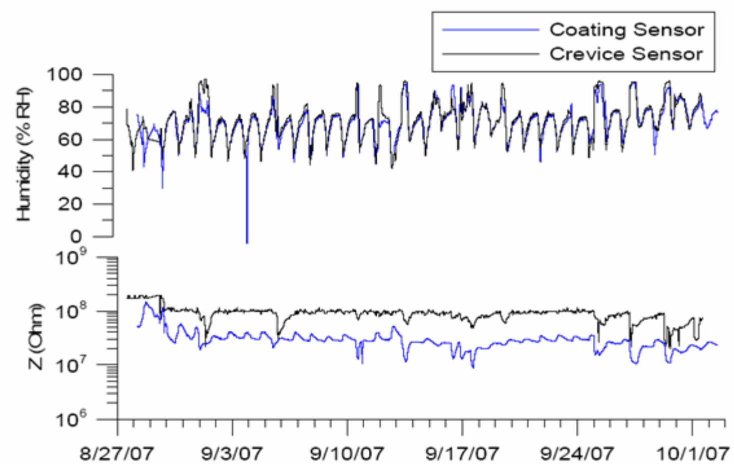
Boeing

- Characterization
  - o Develop metrics
  - o Metallographic analysis
  - o Evolution of morphology

Luna

- Procure sensor suite
- Monitor RH, TOW, UV, and oznone at sites
- Quantify metrics and compare with lab tests





Surface Chemical Analyses

- **Determine ionic composition of deposits, corrosion products present, and their morphology**

Analysis	Purpose
Auger Electron Spectroscopy (AES)	Determine chemical composition of metal oxides and ions
X-Ray Photoelectron Spectroscopy (XPS)	Determine chemical composition of metal oxides and ions
Time of Flight Secondary Ion Mass Spectroscopy (ToF – SIMS)	Determine chemical composition of deposits; provides molecular information
Raman Spectroscopy	Determine chemical composition, molecular structure, and molecular interactions of corrosion products and chemical species
Environmental Scanning Electron Microscopy (ESEM)	Image the morphology of panel surfaces w.r.t. corrosion product; provide elemental analysis below coating surface
Energy Dispersive X-Ray (EDX) Analysis	Characterize chemical composition

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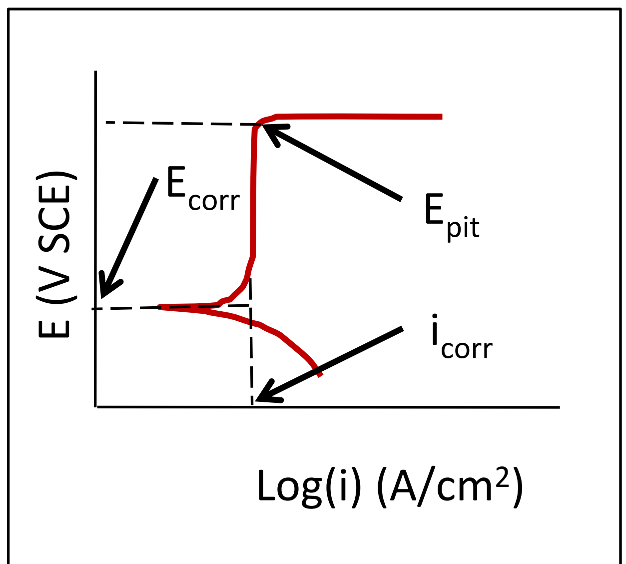
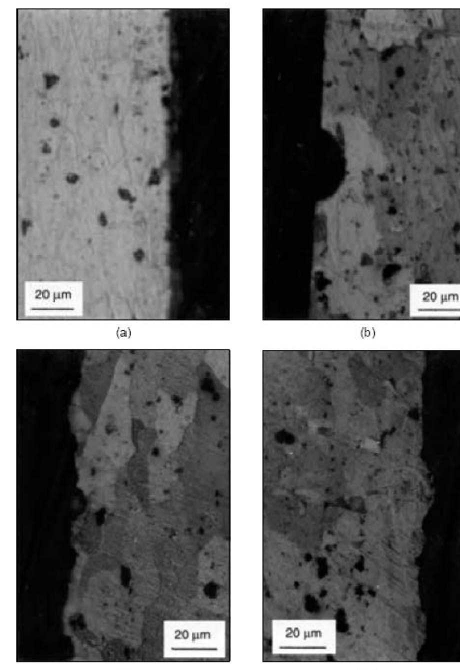
Task 3 Approach – Critical Chemistry

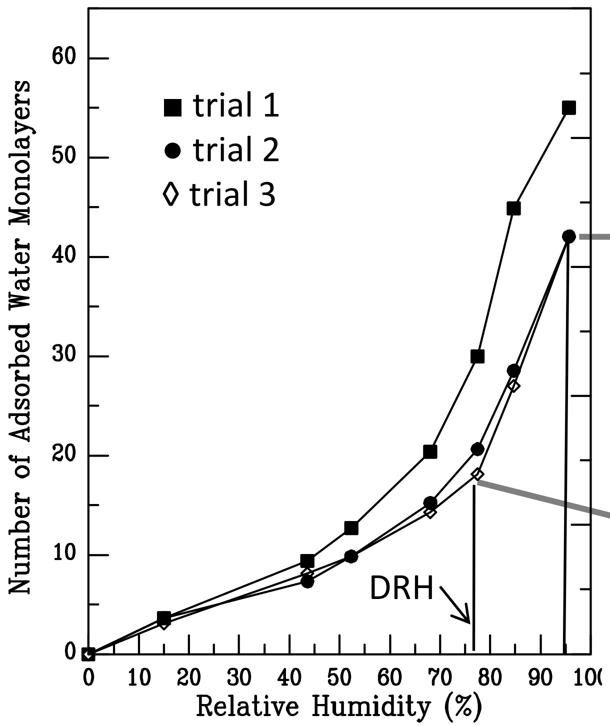
- Identified speciation in Tasks 1 & 2
- Use electrochemical parameters to determine statistical importance of each species relative to corrosion
- Develop chemistry appropriate to each environment
- Compare corrosion morphology in new chemistry to outdoor exposure samples
- Determine relationship between chemistry on exposed surface and in occluded site

Ions found	Significance
Chloride	Increase E_{corr}
Nitrite	Increased E_{corr} and i_{corr}
Nitrate	---
Sulfate	---
Fluoride	Increased i_{corr}
pH	Increased i_{corr}
Bicarbonate	Increased E_{corr}
acetate	---

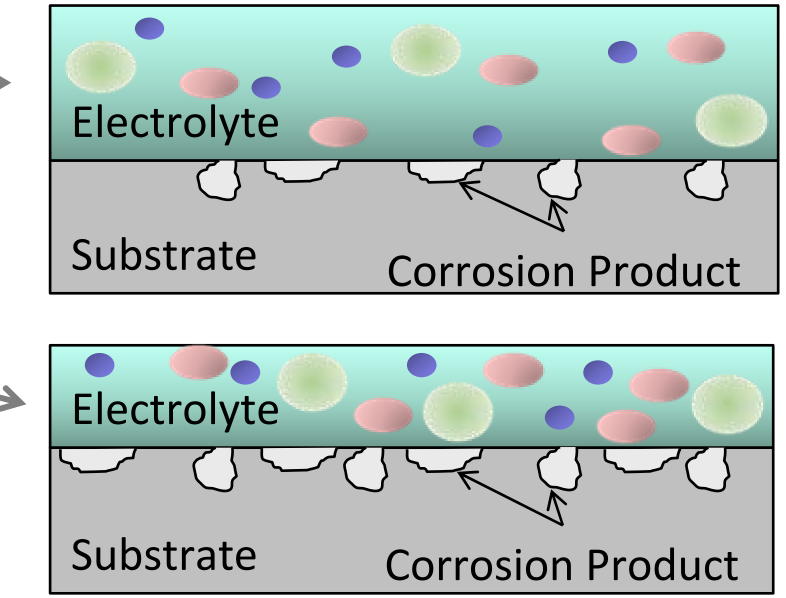




Technical Background

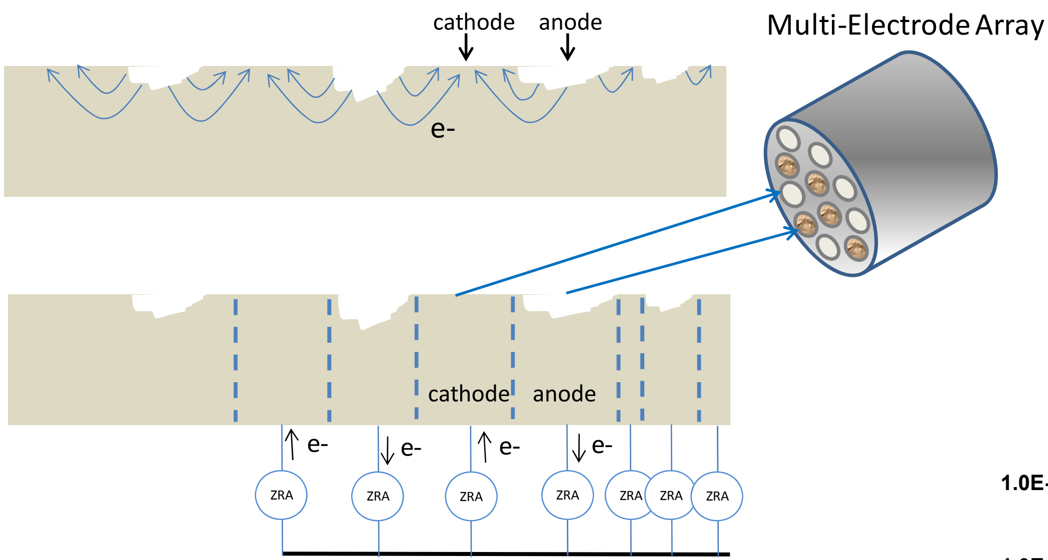


Electrolyte is most concentrated at deliquescence RH



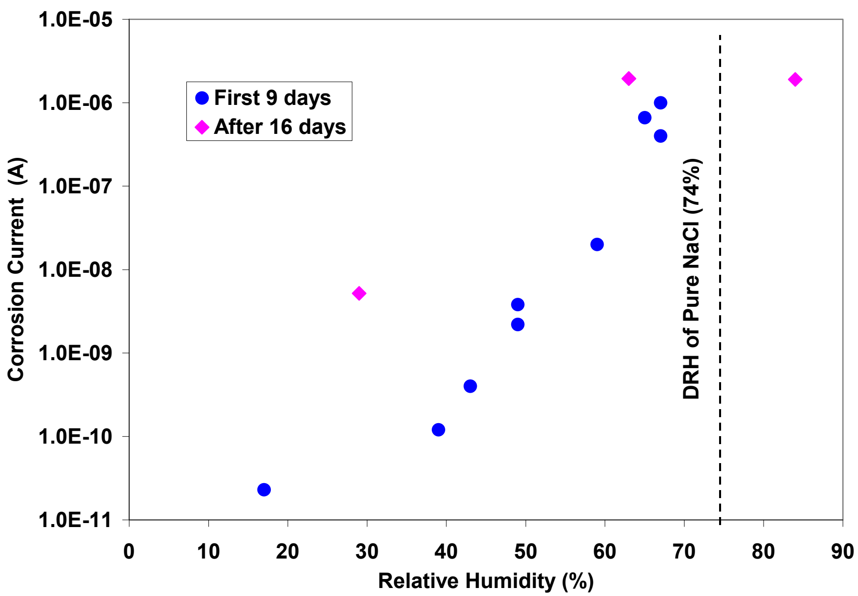
- Relative humidity affects the amount of adsorbed water
- Above a critical RH corrosion occurs
- Salt deposition produces deliquescence and increased corrosion rate (76% for NaCl and 35% for MgCl deposits)

Task 3 Approach – Critical RH



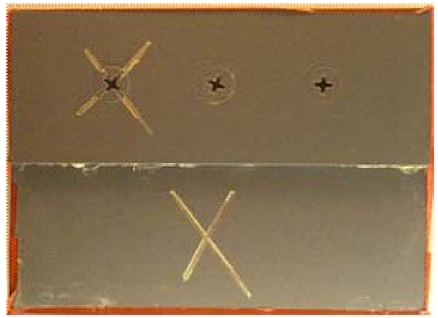
- Corrosion (anodic site) and reduction (cathodic site) occur at the same rate
- Electrons flow from anode to cathode
- Multiple isolated anodes or cathodes develop
- Measure current at each electrode gives corrosion rate at the corrosion potential

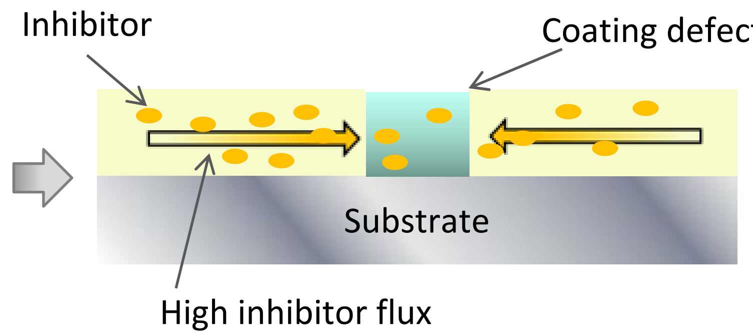
- Multi-electrode sensor allows measure of corrosion under thin electrolyte
- Measure corrosion as function of immersion and RH for different salt chemistries (from Tasks 1 – 3)
- How does salt and corrosion product affect TOW



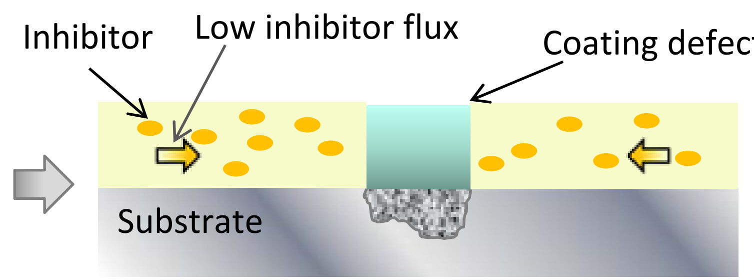
Technical Background

Continuous salt fog



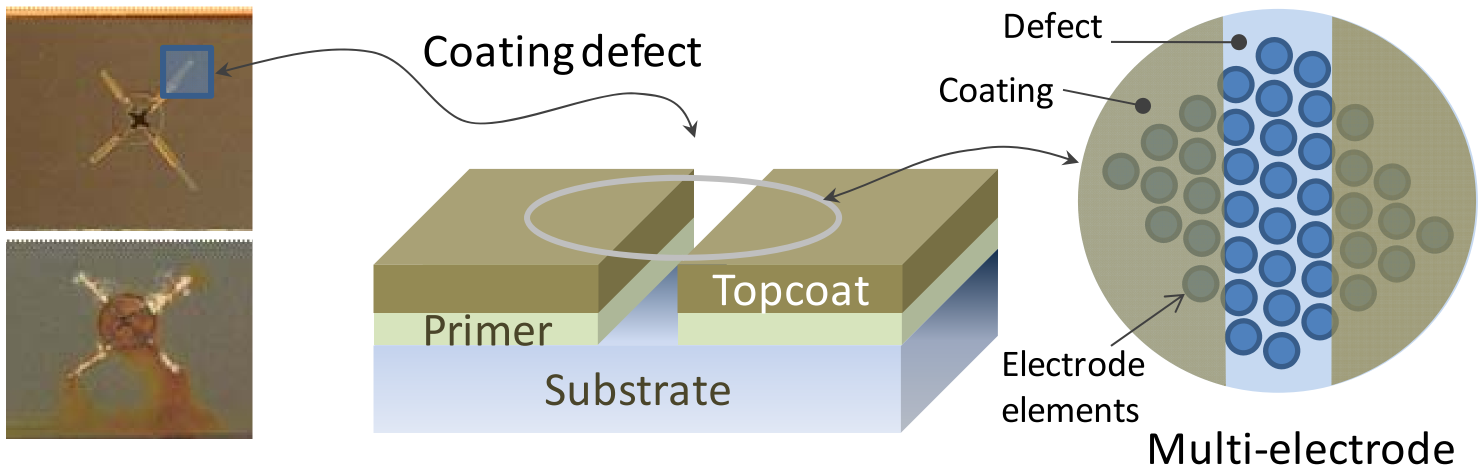


Dilute cyclic salt fog



- Ability to protect substrate at a coating defect depends on connectivity between defect and mode of inhibition
- Moisture can promote inhibitor migration in the coating. For a given test method, wet and dry times will influence inhibitor mobility, and thus corrosion rate
- In the case of galvanic coatings, galvanic connectivity and protection is reduced under dry conditions; however, under aggressive wet conditions, inhibitor will be depleted more rapidly.

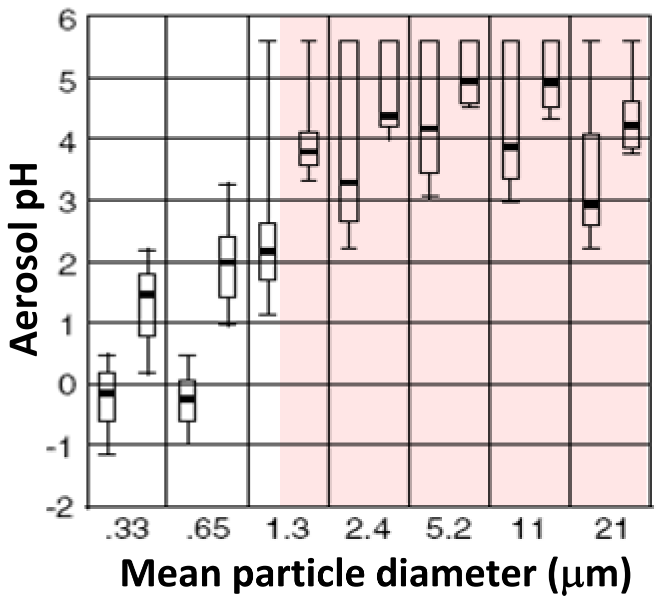
Task 3 Approach – Corrosion at a Defect

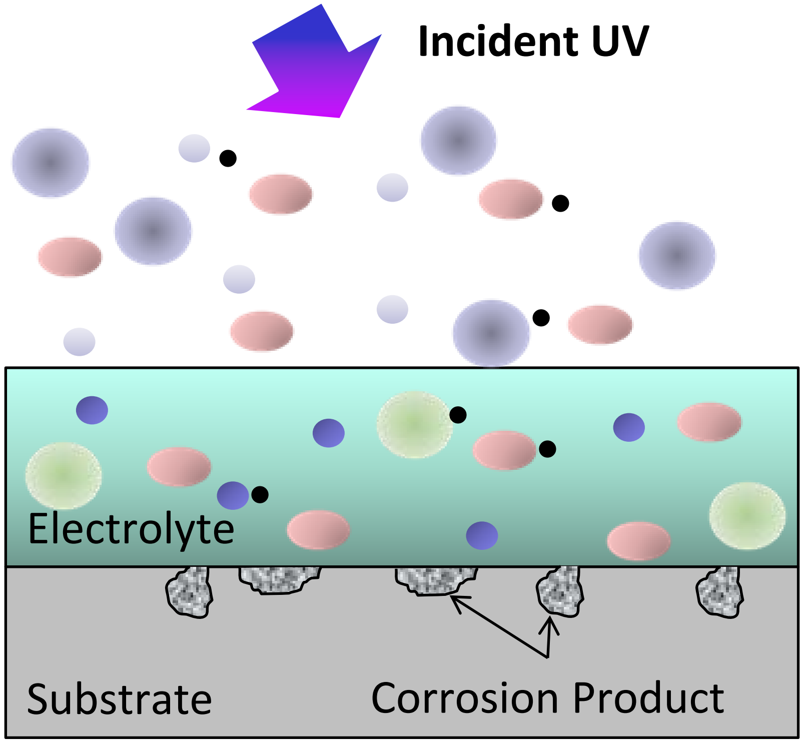


- Multi-electrode technique
  - Coated and un-coated samples
  - Vary the RH and measure
    - Corrosion rate
    - Location of anodes and cathodes
- Electrochemical Impedance Spectroscopy (EIS)
  - Measure coating barrier properties of as a function of RH
  - Use 2 pins of the multi-electrode as leads for EIS to measure barrier properties simultaneously

Technical Background

- Electrolyte pH is governed by
  - UV generation of oxidizing free radicals
  - Aerosol size
  - Acid gasses (HCl, H_2SO_4, SO_2, NO_x)
  - Presence of corrosion products
- Electrolyte pH control may be key factor in explaining the differences between tests
  - >6 for neutral salt spray test
  - <3 for SO_2 and acidified salt fog test
  - **3 < pH < 5** for coastal and shipboard environments (aerosol size > 1.3μm)

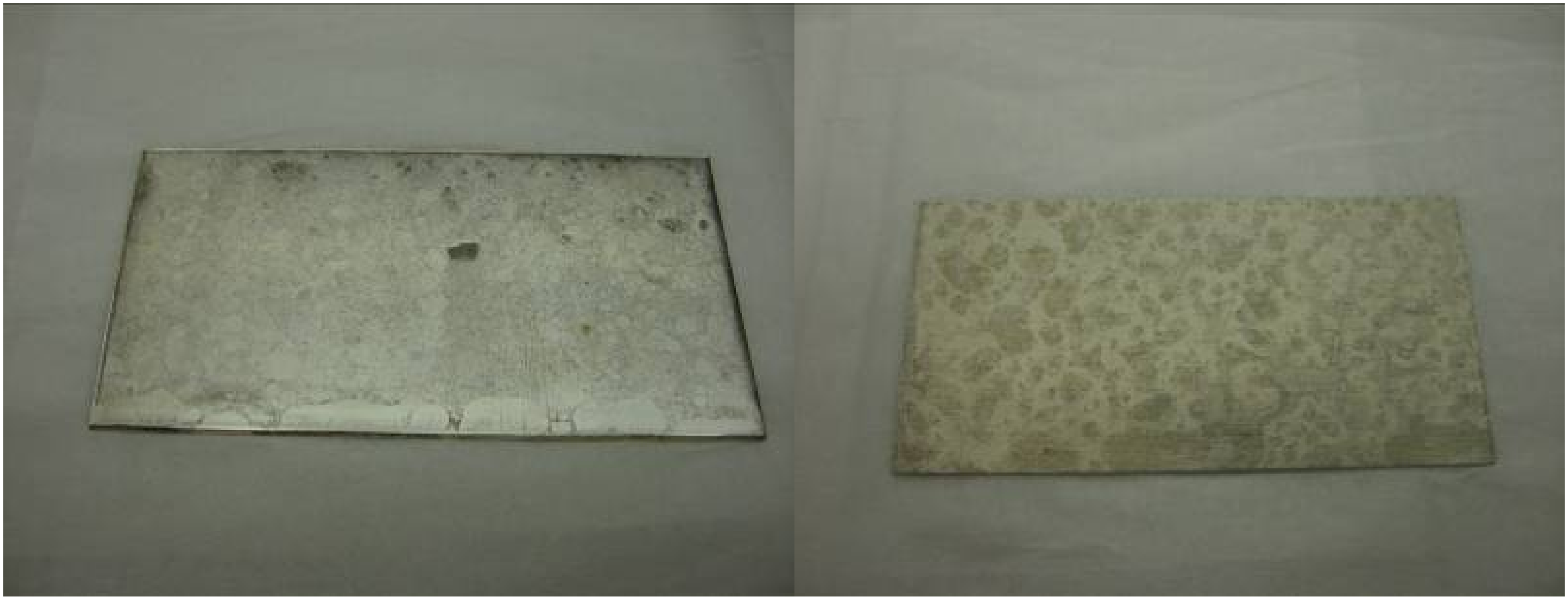




Increases in aerosol particle size and volume percent corrosion products tend to increase pH

Bare Panel Corrosion Test

Ozone and DI Water (no UV) for 20 minutes

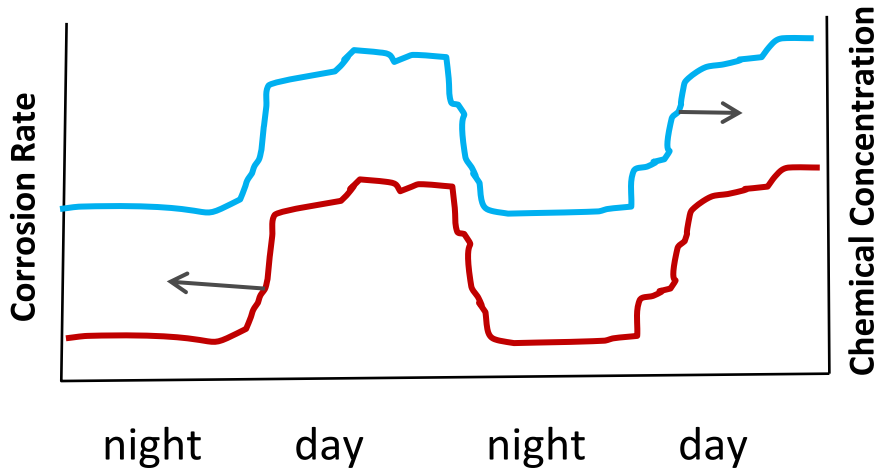


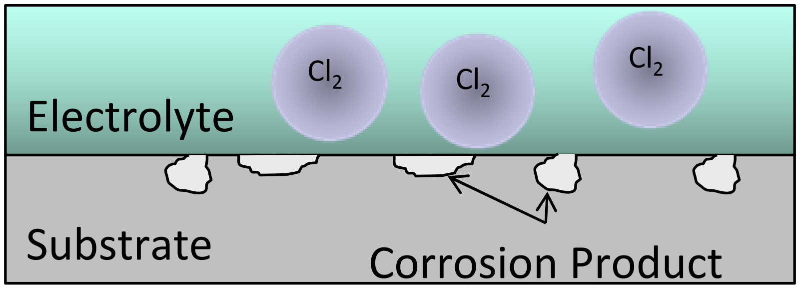
Silver
- shows corrosion almost instantly

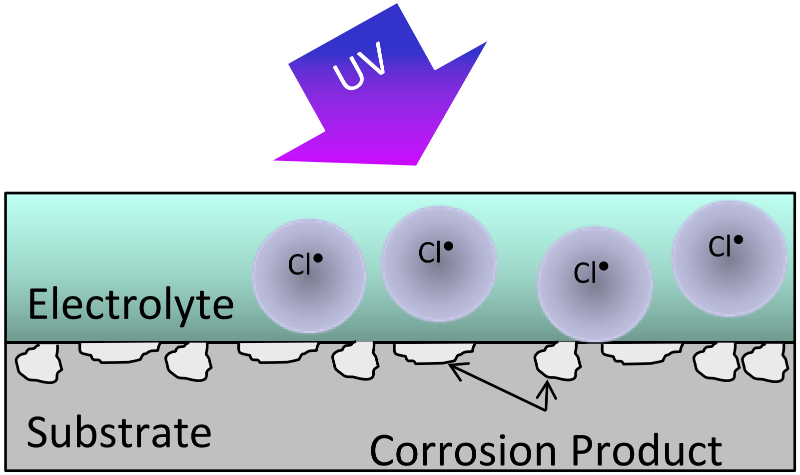
AA2024-T3
- shows corrosion
- potentially worse than ozone and salt spray?

Task 3 Approach – Effect of UV

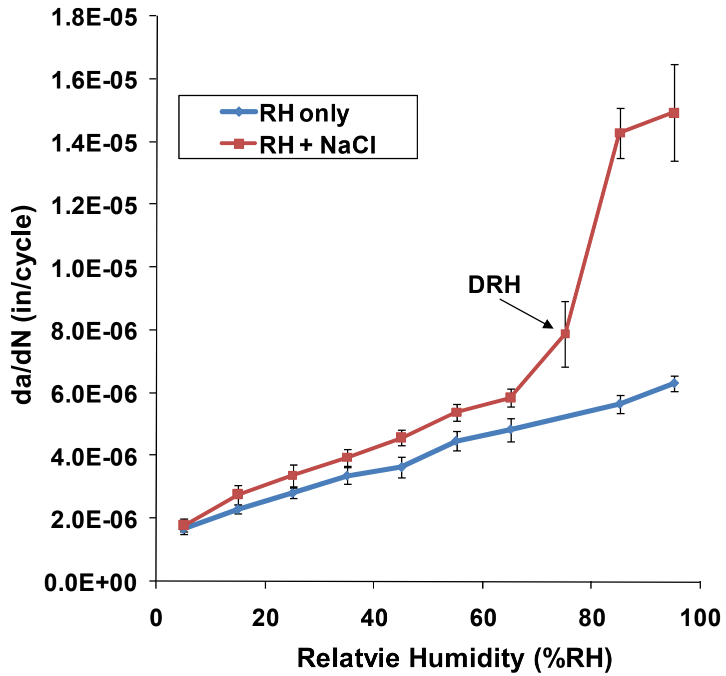
- UV affects
  - free radicals from chlorine, bromine, and organic matter causes decrease in pH and increased oxidation potential
  - oxide energy levels to enhance corrosion
- Outdoor exposure in Miami FL
  - Expose samples for 24 hours and measure 1/hour
  - Use multi-electrode to measure corrosion rate
  - Sample chemistry (pH, organics, oxidizers)
  - **Correlate corrosion rate with chemistry**
- Laboratory exposure
  - Verify corrosion rate/chemistry relationship
  - **Is UV needed in accelerated test or can chemistry be simulated?**







Task 3 Approach – Crack Growth

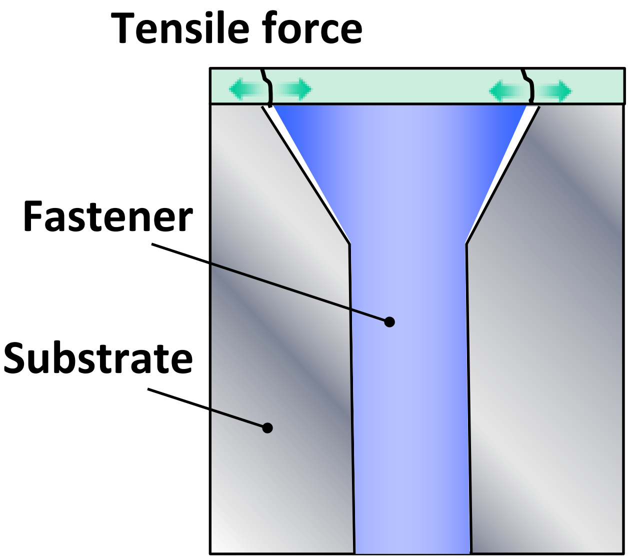


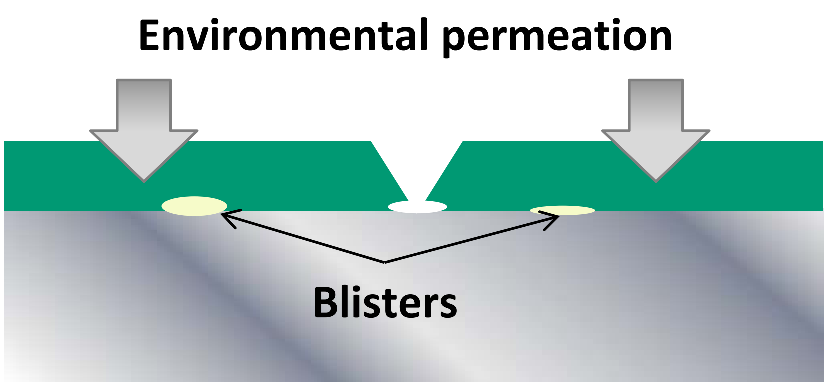
- Crack initiation and growth of Al7075 T-6 is dependant on salt composition and RH
- Using identified salt chemistries and deliquescence data (Tasks 1-3), examine SCC as a function of RH and cyclic RH

- SCC testing will be performed in accelerated test chambers
- The Luna team has developed a portable instrumented load cell that can be used for in-situ crack growth monitoring

Technical Background

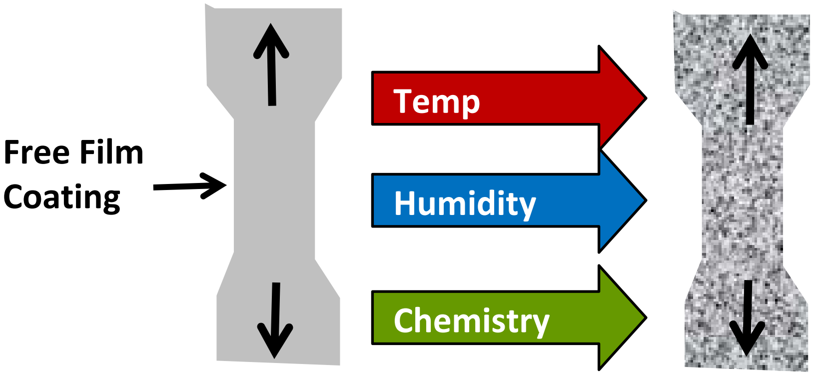
- Blisters form as moisture + chemistry penetrates coating barrier creating osmotic pressure
- Adhesion failures occur at site of environmental ingress, mechanical defect, or blister site
- Both oxidation and reduction reactions cause coating delamination



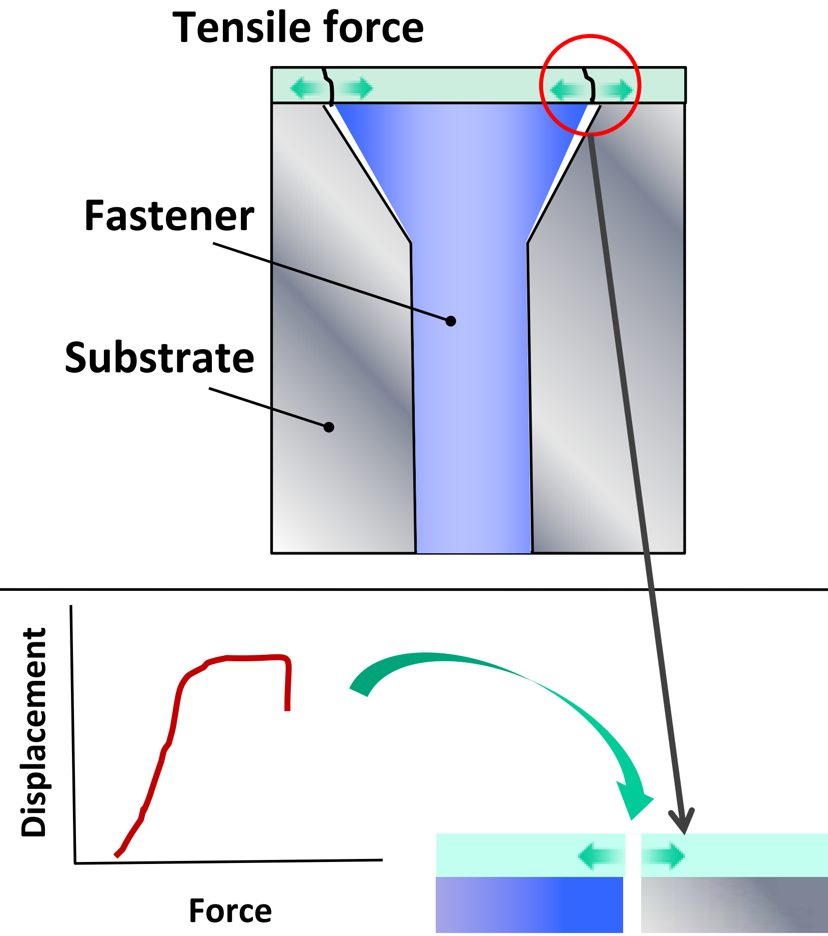


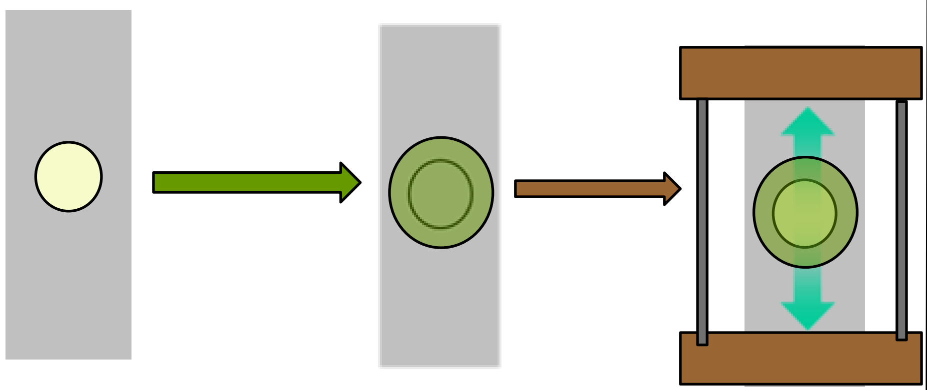
- Paint over surface discontinuity results in tensile load in coating
- Environment affects physical properties of coating
- With time coating will crack

Task 3 Approach – Coating Fracture



Design of Experiments to determine environmental affects on mechanical properties

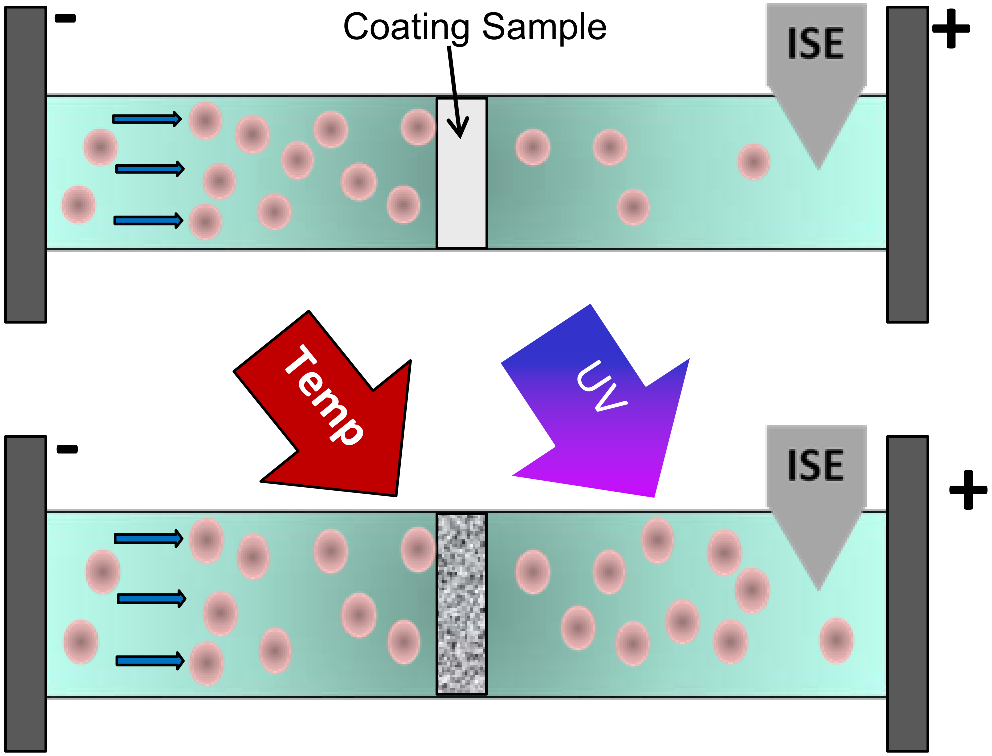


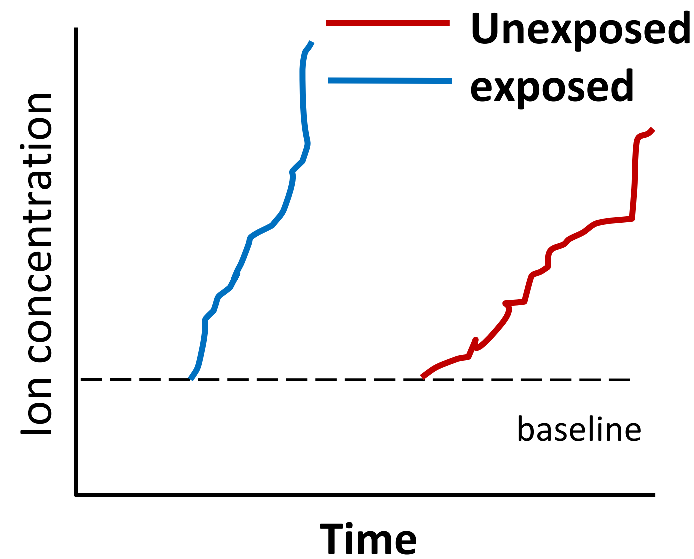


Apply coating over bolt specimen and place loaded sample into test chamber under conditions that cause mechanical failure

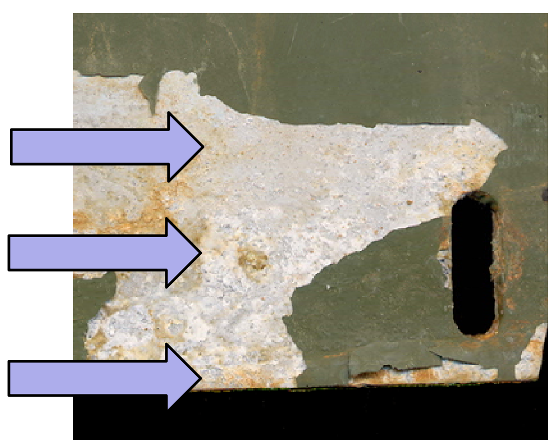
Measure mechanical response of new and aged coating samples; Is there enough residual stress to cause failure upon aging?

Task 3 Approach – Coating Adhesion





- Air flow shear force lifts coating at blister or scribe creep region



- Measure diffusion of ions through free film coating after exposure to various environments
- Relate change in diffusion to propensity to cause adhesion failure or form blisters
- Define exposure conditions for accelerated testing
- Implement shear mode paint delamination into accelerated testing (ARMY)

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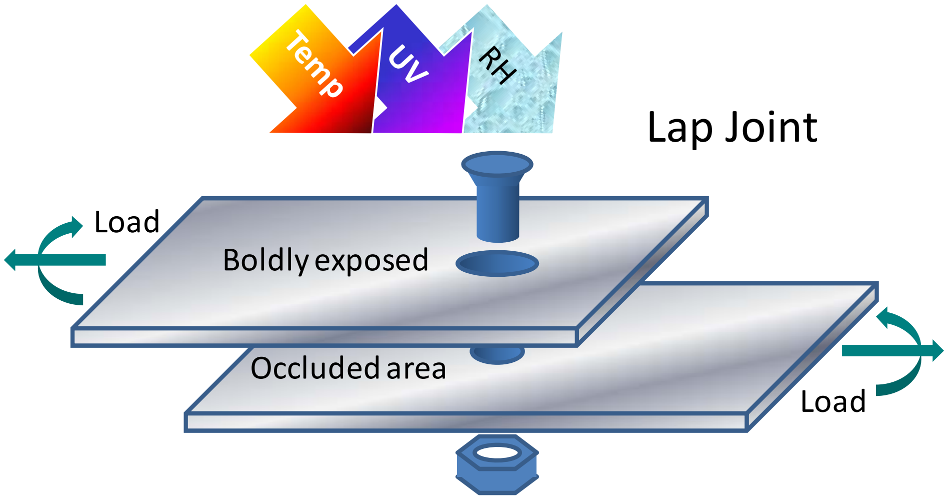
Task 4 – Sample Design



Component	Material
Paint	Pretreatment / Primer
	Mg based primer
	Topcoat
Substrate	Aluminum alloys (Al 2024, Al7075, Al5083), composites
Fasteners	Titanium, Steel, Aluminum

- Sample design needs to simulate:
  - Geometry with exposed and occluded areas
  - Galvanic couples between substrates and fasteners
  - Coating across discontinuities
  - Coating defects
- Sample design needs to allow for:
  - Selection of paint, fastener materials, and substrate alloys
  - External mechanical loading
  - May require multiple samples
- Select sample geometries based on relevant structural designs
- Develop guidelines and definitions for selection and characterization of exposed panels

Define Test Protocol

- Based on 2 different models
  - CTIO - Enable prediction of coating system lifetime based upon an accelerated test in a relatively short timeframe using multivariate approach employing Eyring equation
    - Vary lab test parameters to identify rate coefficients for kinetic models
    - Calibrate model coefficients to field observations
  - Luna - Artificial Intelligence framework to tailor the accelerated corrosion test to real world failure modes
    - Use datamining techniques to identify relationship between input variables and corrosion state (from lab and field exposures)
    - Scientific data used to prevent overfit (what is truly important)

Deliverables

- Accelerated corrosion test method that more accurately predicts component failure modes as a function of environment and can discriminate relative performance of material systems
- A means to implement mechanical loading into accelerated corrosion tests to simulate coating and structural material failures
- Improved understanding of the relationship between environmental parameters and corrosion failure modes
- Modeling tools that can be used to tailor laboratory tests to excite various combinations of failure modes and predict life expectancy

Transition Plan

- Transition to DoD
  - NAVAIR and **ARL** and **AFRL** have governance over coating specifications. Thus, they have authority to instigate and complete changes to specs as well as qualification of materials to the specs. **NAVAIR and AMCOM have engineering/technical authorization authority to approve new material systems for use.** As participating partners in the effort, developed technology can be directly applied as enhanced selection criteria beyond active specifications.
  - AMCOM sits on OSD Corrosion specifications working group. This ensures widest dissemination throughout DoD corrosion community
- Transition to industry
  - Alcoa currently chairs the SAE task to develop improved corrosion testing for cosmetic corrosion of Aluminum. This involvement will facilitate the transition of the accelerated corrosion test through SAE towards development of an industry specification.
  - Auto-Technology has expressed interest in incorporating the improved corrosion test protocol into their test chambers
- Accelerated corrosion test method validation
  - It is anticipated that “round robin” testing will be performed to validate the test protocol. This will be facilitated by strong ties within both the military and industry communities
  - It is anticipated that at least some funding from ESTCP will be required for organization of test labs and data analysis (including populating the data mining tool)