Comprehensive modeling, experimental and testing corrosion assessment for the substrate/coating system under marine environment

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Fast forward to 2013, with inflation the direct cost is now over $1 Trillion annually in U.S.

In 1998 a NACE study calculated the directed cost of corrosion at $276B

1 Trillion
$552B
$276B

“NCMRC includes state of the art facilitates to host leaders in corrosion and materials through mentoring and research that solves tomorrow’s industrial challenges”

National Corrosion and Materials Reliability Laboratory (NCMRL)

How can we help industry?

• Being a World Class Corrosion Education and Research Center
• Bridging the gap between fundamental research (science) and technology (engineering)
• Corrosion Minor and certificate
Corrosion Minor/Certificate

Core Courses

Intro Mat Science Eng (201/222)

Materials Electrochemistry and Corrosion
Fall

Corrosion and Electrochemistry Laboratory

Advanced Corrosion Control & Prevention

Electives

Mechanical Civil, Chemical Aerospace, Biomedical Petroleum, Industrial

Corrosion Engineering
Spring
Topics:

• VOC Reduction for Maritime Coatings
• Biofouling Technology in the Maritime Industry
• Anti-icing Coating for Maritime Exposures
• Effect of Ballast Water Treatment on PSPC-compliant Coating in Ballast Water Tanks
• Future Research topics for Maritime applications
Corrosion assessment for Marine applications

- Being used to preserve durability or delay corrosion
- It is inevitable for the existence of anodic and cathodic surface of metallic assets due to the difference in electrical potential.

Invasive marine conditions and environmental factors affecting the corrosion process in maritime conditions

- Moisture and oxygen availability at metal surface
- Relative humidity and Temperature
- Chloride ions from the external environment in winter
- Presence of bacterial microorganisms
- Salts on roads (deicing)
- Ultraviolet irradiation
Accelerating testing and characterization simulating sea-water conditions

At 16 h
At 136 h
At 232 h

Laboratory testing
Dynamic Corrosivity Map based on Macro-parameters
Different samples exposed in the Gulf of Mexico for validation
Corrosion control and protection for Maritime coatings

Trends for anti-corrosion-performance of substrates/coatings

State of the art of corrosion monitoring technology

• Most common non-destructive technologies:
  – Visual inspection, Ultrasonic, X-ray and so on

  – Visual inspection has been usually used as the most basic inspection method for corrosion engineering.

  – However, the results are **not reproducible** because they are dependent on one’s individual viewpoint and could not explain the mechanistic damage evolution.
Advanced characterization and quantification for coatings in corrosion

- **Electrochemical Impedance Spectroscopy (EIS)**
  - A powerful non-destructive technique
  - EIS with open circuit potential (OCP) allows the user to monitor, characterize, and determine the coating performance in different environments
  - Corrosion assessment with EIS.
Electrochemical measurements are performed for three coating conditions: intact, pre-damage, and pre-exposed coating by following:

<table>
<thead>
<tr>
<th>TEST</th>
<th>CONDITION</th>
<th>PURPOSE</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>A dry condition - two-electrode</td>
<td>In-situ monitoring of pre-exposed automobile samples</td>
</tr>
<tr>
<td>B</td>
<td>A constant immersed condition three-electrode</td>
<td>To develop a predictive experimental model to understand the corrosion damage/performance. To correlate laboratory with field testing.</td>
</tr>
<tr>
<td>C</td>
<td>Wet-dry cyclic condition with EIS three-electrode</td>
<td></td>
</tr>
</tbody>
</table>

• Critical parameters affecting the coating performance;
  ✓ The thickness and composition
  ✓ The interface properties and combination of top coating/primer layer
  ✓ The thickness
  ✓ Exposure time
  ✓ Ocean environment
Monitoring coating system on site

- Exposure time and environment on EIS response at dry condition

  ✓ Electrical resistance is used to quantitatively describe coating performance

  ✓ The result reveals automobiles in Halifax experienced more severe corrosion than other regions

The change of resistance of the metallic asset band coating
Wet-dry cyclic test with EIS (Fog chamber)

- Key points: Reliable quantitative results on wet-dry cycle,

- Various pre-damaged samples (galvannealed steel)
  - Main function for anti-corrosion: **Cathodic protection**
  - The changes of OCPs and EIS describe the difference of various pre-damaged samples
Various pre-damaged samples for life cycle model

• Full immersion
  ✓ Main anti-corrosion principle: **Barrier protection**
  ✓ OCPs describe active corrosion
The schematic of 2D networks of electrochemical impedance elements for layer-by-layer composite coating system based on charge and energy conservation.
Cr (VI) coating/metallc substrate system

Stage I
- Intact Coating
  - Electrolyte
  - Topcoat
  - Primer
  - Pre-treatment
  - Al substrate
  - SrCrO₄

Stage II
- Water Uptake
  - Electrolyte
  - Topcoat
  - Primer
  - Pre-treatment
  - Al substrate

Stage III
- Lixiviation of Cr⁶⁺
  - Electrolyte
  - Topcoat
  - Primer
  - Pre-treatment
  - Al substrate
  - Cr⁺⁺⁺

Stage IV
- Self Healing
  - Electrolyte
  - Topcoat
  - Primer
  - Pre-treatment
  - Al substrate
  - Cr₂O₃/Cr(OH)₃

Chromium Conversion:
\[ Cr₂O₇^{2⁻} + 8H^+ + 6e^- \rightarrow 2Cr(OH)_3 + H_2O \]

Aluminum Oxidation:
\[ Al \rightarrow Al^{3⁺} + 3e^- \]

SEM morphology of CCC in the Interface of primer/substrate after exposure for 260 days

Cr oxide layer after exposure

Breakdown of the Cr oxide layer and self-healing process

Randomly structured model

- The position distribution of electrolyte percolation

Log-Normal probability density function

- The distribution of electrolyte percolation length

\[ P(z, \mu, \sigma) = \frac{1}{z\sigma\sqrt{2\pi}} e^{-\frac{(\ln(z)-\mu)^2}{2\sigma^2}} \]

\[ m = \exp(\mu + \sigma^2/2) \]

\[ \nu = \exp(2\mu + \sigma^2)(\exp(\sigma^2) - 1) \]

where the mean \( m \) and variance \( \nu \) of a lognormal random variable are functions of \( \mu \) and \( \sigma \) that can be calculated.
Extracting the electrical properties of each layer

- The polyurethane topcoat served as good barrier
- At the condition of pH 4

Day 15

- 75% electrolyte penetration of multi-layered coating thickness
- The uptake area is extended
Day 45

- The electrolyte penetrates the multilayered coating
- The solution reaches the aluminum substrate
- Electrochemical reaction
Self Healing and Stable Oxide Layer

Day 100

Day 125

Day 160

(a) $-Z''$ vs. $Z'$ for Al 2024 at pH 4:
- Day 45
- Day 60
- Day 100
- Day 125
- Day 160
- 2D-Modeling
- Day 100
- Day 125
- Day 160

(b) $|Z|$ vs. $f$ for Aluminum 2024 at pH 4:
- Day 45
- Day 60
- Day 100
- Day 125
- Day 160
- 2D-Modeling @ Day 100
- 2D-Modeling @ Day 125
- 2D-Modeling @ Day 160
Simulation and design of Performance

1. maximum percolation length/coating length

M=0.002809, V=6.7E-5
M=0.377192, V=1.207585
M=0.687289, V=4.009323
Localized Impedance Spectroscopy with Defect LEIS for the effect of probe position

Experimental Result

- Probe z-direction position @ 18 h Immer., 62400 μS/cm, and -1.040 (V vs SCE)
  - Reference position
  - +100 μm
  - +300 μm
  - +500 μm
  - +1000 μm
  - +1500 μm
  - +2000 μm
  - +3000 μm

Computational Result

$|Z|$ dependent on probe position

Probes Position

<table>
<thead>
<tr>
<th>Distance</th>
<th>Probe Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 μm</td>
<td>1, 13, 26, 39</td>
</tr>
<tr>
<td>40 μm</td>
<td></td>
</tr>
<tr>
<td>60 μm</td>
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<td>80 μm</td>
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<td>100 μm</td>
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<td>200 μm</td>
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<td>300 μm</td>
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<tr>
<td>400 μm</td>
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LCM 3D Image
The modeling by using damage evolution concept
• The change in electrochemical active area
• The change in Charge transfer phenomenon

The probabilistic approach considers the laboratory and field exposure samples correlation.

The image of an anticipated final outcome for probabilistic life prediction model
Repairing criteria

Effect of different intervention strategies on expected service life for maritime applications

Reliability vs. Time
Corrosion under hydrodynamic conditions Flow loops with MIC capabilities

- Hydrodynamics conditions inside the pipeline can accelerate considerably the corrosion attack due to higher diffusion of aggressive species and presence of MIC.
- Corrosion inhibitors with different chemical structures are used for preventing internal corrosion.
- Biofouling simulation conditions.
Biofouling monitoring


Biofilm with Microbiological induced corrosion
Marine environments

Atmospheric Conditions

Atmospheric Testing Vs Salt Fog Chamber Testing

Before Exposure

Environmental exposure

Salt Fog Chamber Testing

SKP- Exposed Galvanized sample

Corrosion products and corresponding EDX

Microbiology induced Corrosion

Zn+CNT coated substrate exposed to MIC
Facility: Pier side Atmospheric Test Facility
The test facility was established in 2017 with an objective of providing in-situ corrosion experiments. The corrosion test bed is located on a raised pier 50 feet above the Ocean elements.

Facility: Seawater Submersion Testing
System Capability: The facility along the pier has been dredged ~100 feet deep to allow the capability to test specimens that require complete immersion in natural seawater. This is critical especially when studying coatings and concrete coupons in an ever changing seawater kinematics and chemical conditions.

Payoff: Seawater Submersion Testing can be used to study the impacts of tidal velocity and environmental changes over a given season on erosion corrosion, cavitation & impingement corrosion etc.

Data Collection Approach: 1) Gravimetric Weight loss 2) Microscopic and Spectroscopic techniques.
R/V Trident:
- 70ft long, has a draft of 4ft and a cruising speed of 17 knots & equipped with scientific sampling gear.
- It has a capacity of 12-44 persons and can operate 24hrs per day for up to 5 days between port calls
- Saltwater pump to supply a flow through system
- For shallow water and offshore research

R/V Earl L Milan:
- A versatile 47 ft vessel for offshore deployment
Sensor technique for in-situ monitoring

Manufactured ship with Sensor

Docking platform

The coating and corrosion evaluation test

1) E. David (2017) – Nace Corrosion Conference #8834
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QUESTION?