A History of Accelerated Life Testing for Cathodic Debonding: 1978 to 2018

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Topics

• Introduction: What Is Cathodic Debonding?

• Accelerated Life Testing
  > Arrhenius Kinetics and ALT Design

• Cathodic Debonding ALT History
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  > 1985-1995: STRIP/NRL-USRD Orlando
  > 2010-2018: New Approaches/NUWC-NPT
  > The Future: ALTs without Heat?

• Summary
What Is Cathodic Delamination?

Cathodic Delamination is collateral damage from the Navy’s never ending war on corrosion.

- CD is driven by a corrosion reaction that occurs on cathodically polarized surfaces.
- The most common reaction is the reduction of oxygen to yield hydroxide ions:

\[ 2\text{H}_2\text{O} + \text{O}_2 + 4e^- \rightarrow 4\text{OH}^- \]

- The cathodic polarization comes from sacrificial anodes, ICCP systems, or galvanic couple mis-matches.
- CD is responsible for most of the U.S. Navy’s metal-polymer adhesion failures; remediation costs > $100M/year.
Some ALT Words of Wisdom

“Prediction is difficult… especially about the future”
and
“If you don’t know where you are going, you’ll wind up somewhere else.”

Lawrence “Yogi” Berra
Catcher, NY Yankees and World-Renowned Philosopher
The Theoretical Basis for Accelerated Life Testing

The Arrhenius Equation

\[ K = A e^{-E/kT} \]

- **K** = reaction rate constant
- **A** = constant; represents the frequency at which atoms and molecules collide in a way that leads to a reaction
- **e** = base of the natural logarithm system
- **E** = activation energy (energy required to generate the reaction transition state)
- **k** = Boltzmann’s constant
- **T** = absolute temperature

The Arrhenius equation is a mathematical expression that describes the effect of temperature on the velocity of a chemical reaction.
As temperature is increased, the average molecular speed also increases.

Molecular energy is related to molecular speed (kinetic energy = \( \frac{1}{2}mv^2 \))

**Activation Energy** is not affected by changes in temperature; however, at higher temperatures, more molecules have sufficient energy to engage in reactions.

In many cases, degradative (aging) processes can be accelerated by raising the temperature. Useful service lifetimes can be determined rapidly using ALT protocols.

The “participation area” ratio is directly proportional to the RAF.
**Activation Energy**: an energy barrier or hurdle that must be surmounted by the reacting molecules before a reaction can occur.

Activation Energy is the most important ALT parameter; it relates temperature to time (and vice-versa).

For most reactions, the Activation Energy must be determined by experimentation. There are few published values in the literature.
The Basic ALT Equation

In order to set up an accelerated life test (ALT) a parameter known as the reaction acceleration factor (RAF) must be calculated:

\[
\frac{TF_1}{TF_2} = RAF = e^{\frac{-E(T_2 - T_1)}{R(T_1T_2)}}
\]

E = activation energy
R = gas constant
T₁ = normal operating temperature of the item
T₂ = temperature at which the ALT is run
e = base of natural logarithm system
TF₁ = time to failure at temperature T₁
TF₂ = time to failure at temperature T₂

The RAF indicates how much faster a given process will occur in the ALT.
The Effect of Activation Energy ($E_a$) On Accelerated Aging

Because the Arrhenius Equation is exponential, small changes in $E_a$ can have large effects on the RAF!

The differences in activation energies is 2x, but the difference in accelerated ages is 6x!
The 1970s
The First ALT Experiments

- Began at Naval Ocean Systems Center (NOSC), San Diego, CA (1978).

- Included 40 hour immersion in fresh water at 60°C
  - Estimated 18,750 hours at 20°C with Ea = 30,000 calories/mole ("corrosion test")
  - Estimated 575 hours at 20°C with Ea = 13,000 calories/mole ("water permeation test")

- Also included:
  - "Dry heat" at 75°C for 475 hours to accelerate rubber degradation
  - Pressure cycling/pressure dwell
  - Thermal shock (-54°C to 0°C) in air

This early NOSC efforts used "generic" Ea values for metal corrosion and water permeation through "rubber". No attempt was made to calculate the real Eas for the materials actually used. With fresh water being used, one would expect very little "corrosion" to occur during the ALT.
The 1980s – 1990s: STRIP and NRL-USRD Orlando

- In-air thermal aging (66°C) for 31 hours
- Salt water soak (66°C) for 350 hours
- Thermal cycling (salt water) 66°C to 6°C 33 times (30 mins/each temperature)
- Pressure cycling in fresh water (13 cycles)
- Pressure dwell in fresh water (45 hours)

- This improved ALT protocol retains the major NOSC sections (heated air; heated water soak, thermal cycles; pressure cycles and pressure dwell). The maximum heated temperature is now 66°C.

- Heated water soak is now carried out in sea water. Appears to be a water into polymer permeation test. Ea is not stated but appears to be between 11,000 to 13,000 calories/mole. Note that no cathodic voltage/current is employed, nor is dissolved oxygen level maintained in test tank.

- Thermal cycling is now carried out in sea water (not air). Temperature range is 66°C to 6°C versus -54° to 0°C

- Pressure cycling carried out in fresh water – so again, no cathodic debonding is occurring.
What is actually being accelerated in the “water immersion” part of the ALT experiment?

The permeation of water into and through the polymeric overmolding compound was considered to be the rate-limiting step in the cathodic delamination process. Water is needed to make hydroxide ions and to form the blisters that cause debonding. However, with no cathodic voltage or current applied to the samples, cathodic debonding would not occur.

The activation energy used for the 1980s -1990s ALT was the permeation of water into the polymeric overmolding compound.
**Determination of Ea for Water Diffusion into Polymers**

Calculate diffusion constants (D) at three different temperatures.

\[ \ln D = -\frac{E_a}{RT} + \ln A \]

Plot ln(D) versus 1/T. The slope of the resulting line is \(-\frac{E_a}{R}\).
Two Different CD Degradation Pathways

THICK, FINITE COATING
- Has exposed bond-lines
- Macroscopic thickness
- Attack is via exposed edges

Example: Painted Surfaces

THIN, INFINITE COATING
- No edges/exposed bond-lines
- Microscopic thickness
- Attack is through the coating

Example: Cable Connectors
A New/Improved 21st Century ALT Protocol for Cathodic Debonding

Issues to be addressed:

- Need to standardize samples
- Need short-term screening test and long-term test
- Need to ensure cathodic debonding conditions are maintained
- Need to calculate Arrhenius activation energy based upon “something else” related to the cathodic debonding issue (diffusion of water through the polymeric encapsulant does not play a major role in the debonding process for outboard connectors)
Rectangular “Flat-Bar” Peel Test Coupons

Sample dimensions:
- 1” x 4” x 0.25” (metal)
- 1” x 6” x 0.25” (PU)

Only the two center square inches of the metal coupon is bonded to the polyurethane.

These samples are used in a quick, two-week long “screening” ALT.

Samples mounted in rack

ALT in progress
Cylindrical “Simulated Connector” Long-Term ALT Samples

Monel 400 cylinder “simulated connector”

Cylindrical “Simulated Connector”

Cylinder encapsulated in ¼” layer of polyurethane

Encapsulated cylinder with zinc attached

Encapsulated cylinder with zinc attached

Used for coatings that have passed the short-term “screening” ALT. These samples can be used to test technologies that do not work on flat-bar samples (e.g., internal and external bands).
Preparing the Cylindrical Samples for Peel Testing

Before they could be peel tested, the cylindrical samples had to be cleaned up and then machined. Two parallel circumferential cuts were made to generate three circumferential peel strips. The bottom quarter inch of PU was machined off, and ¼ of the PU was machined from the side of the samples.

The zinc anode is removed and the sample is cleaned prior to machining. Two parallel cuts are made through to the DGO-1 layer. A 1” wide gap in the PU is machined off down the DGO-1 layer. The ¼” thick PU layer on the bottom of the sample is machined off.
Cylindrical Sample Peel Testing

Peeling of the PU layer on a cylindrical sample showing how the sample was cut, the Instron grip, and the special holder that allows the sample to rotate as the grip is moved upwards.
Small “boat-rudder” sacrificial zinc anodes are attached to each individual sample before the sample is placed into the ALT. The sacrificial zinc anodes are bolted tightly to a bare metal surface on the sample using a nylon screw. These zinc anodes ensure the sample remains under a cathodic voltage and current during the ALT.
Maintaining CD Conditions During the ALT: Dissolved Oxygen Levels

The ALT tank being oxygenated.

2H₂O + O₂ +4e⁻ → 4OH⁻ (on cathodic surface)
No dissolved oxygen, no cathodic reaction and no cathodic delamination

The diffuser stone attached to the end of the ALT tank oxygen line.

Beware of “false positives” caused by a lack of dissolved oxygen in the ALT tank.
Maintaining CD Conditions During the ALT: pH Balance

The reduction of dissolved oxygen generates hydroxyl anions; over time this will cause the pH of the ALT tank water to increase.

In ALTs run with zinc anodes, a white precipitate will form inside the ALT tank. This material is zinc oxide (ZnO):

\[
\text{Zn}^{\text{+2}} + 2(\text{OH})^- \rightarrow \text{Zn(OH)}_2 \rightarrow \text{ZnO} + \text{H}_2\text{O}
\]

The generation of ZnO in the ALT tank indicates the zinc anodes are working (dissolving) and also keeps the pH of the ALT tank water from increasing significantly during the test.

If a battery is used rather than zinc anodes, acid will need to be added periodically to the ALT tank to prevent its pH from rising.
How do We Calculate Ea for the Cathodic Delamination Process (I)?

- Failure mode for sample not under CD conditions. Polyurethane debonds from the primer.
- Failure mode for sample under CD conditions. Primer debonds form the metal substrate.

Bare Metal Surfaces

Temperature increasing
How Do We Calculate Ea for the Cathodic Delamination Process (III)?

The strong temperature sensitivity of the CD data suggest that the CD process can be modeled using Arrhenius kinetics:

\[
\ln(S) = \ln(S_0) - \frac{E_a}{RT}
\]

A plot of the natural log of the CD “window-frame” slopes versus the reciprocal temperature (in Kelvin) should be linear with a slope equal to the Arrhenius activation energy (Ea) divided by the gas constant, R.

\[
y = -4212.5x - 1.5855
\]

\[R^2 = 0.9771\]

PR-1547/PR-420 primer

Ea = 8.4 kcals/mole
While the method just described “works” for some coatings, it does not work for all coatings.

In particular, it does not work for coatings that are very resistant to the CD process (the very coatings we would really like to test)!

Also, it is coating specific, because different coatings debond at different rates.

How do we move forward???

We know the rate of the CD reaction increases as the ALT temperature rises. Let’s treat the Cathodic Delamination as a corrosion reaction.

\[ 2H_2O + O_2 + 4e^- \rightarrow 4(OH^-) \]

The CD reaction consumes current. The more current that is consumed, the more hydroxyl anions are produced, and the more severe the attack on the metal-polymer bondline becomes.

Does an increase in temperature cause an increase in current consumption?
CD Current Consumption as a Function of Temperature

A Gamry Potentiostat was used as a zero resistance ammeter in an environmental chamber to measure the current consumed by the zinc-monel 400 couple in a 3.5% NaCl solution as a function of temperature:

<table>
<thead>
<tr>
<th>Couple</th>
<th>Temperature</th>
<th>3.5% NaCl Solution Voltage (vs SCE)</th>
<th>3.5% NaCl Solution Current Density*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc/Monel</td>
<td>20° C</td>
<td>-1.03</td>
<td>48.0</td>
</tr>
<tr>
<td>Zinc/Monel</td>
<td>40° C</td>
<td>-1.07</td>
<td>74.4</td>
</tr>
<tr>
<td>Zinc/Monel</td>
<td>60° C</td>
<td>-1.09</td>
<td>130.5</td>
</tr>
</tbody>
</table>

* Units = 10⁻⁶ A/cm²

The current density changes significantly as a function of temperature whereas the voltage does not.

These data are being used to calculate an Ea for CD for the zinc/monel-400 couple. This Ea is independent of the coatings/primers/PUs used, but can only be used for the zinc/monel-400 couple.
The Future: Accelerated Life Testing for CD Without Using Heat

New ALT Techniques for the CD Process Using Dissolved Oxygen

Henry’s Law

\[ y_i P = x_i H_i \]

Effect of \( p(O_2) \) at 1.0 atm and 25\(^\circ\)C on the dissolved oxygen (DO) concentration in water

Increasing \( p(O_2) \) at 1.0 atm and 25\(^\circ\)C from 21\% to 100\% raises the concentration of DO in water from \(~8\) ppm to \(~40\) ppm (a 5x increase!). This effect can be extended by increasing the total pressure beyond 1.0 atm with \( p(O_2) = 100\% \).
ALT Protocol for CD without Heat: Possible or Impossible?

• First successful demonstration that cathodic delamination ALTs can be run at fixed temperature using changes in voltage and dissolved oxygen content to accelerate the rate of the reaction.

Potentiostat plot of voltage versus current density for three different partial pressures of oxygen gas. These data prove that in the voltage range of interest, the CD reaction can be accelerated by an increase in dissolved oxygen content at constant temperature.

No heat and known/fixed voltages means no unexpected/unanticipated reactions!

NUWC prototype pressurized oxygen cathodic delamination accelerated life test cell
Questions?