Cathodic Delamination of Marine Hardware: Causes and Mitigation Strategies

Thomas Ramotowski
NAVSEA Warfare Center Newport
Sensors and Sonar Systems Department (Code 15)
1176 Howell Street, Newport, RI, 02841
ramotowskits@npt.nuwc.navy.mil

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    - Nanocomposite barrier coatings

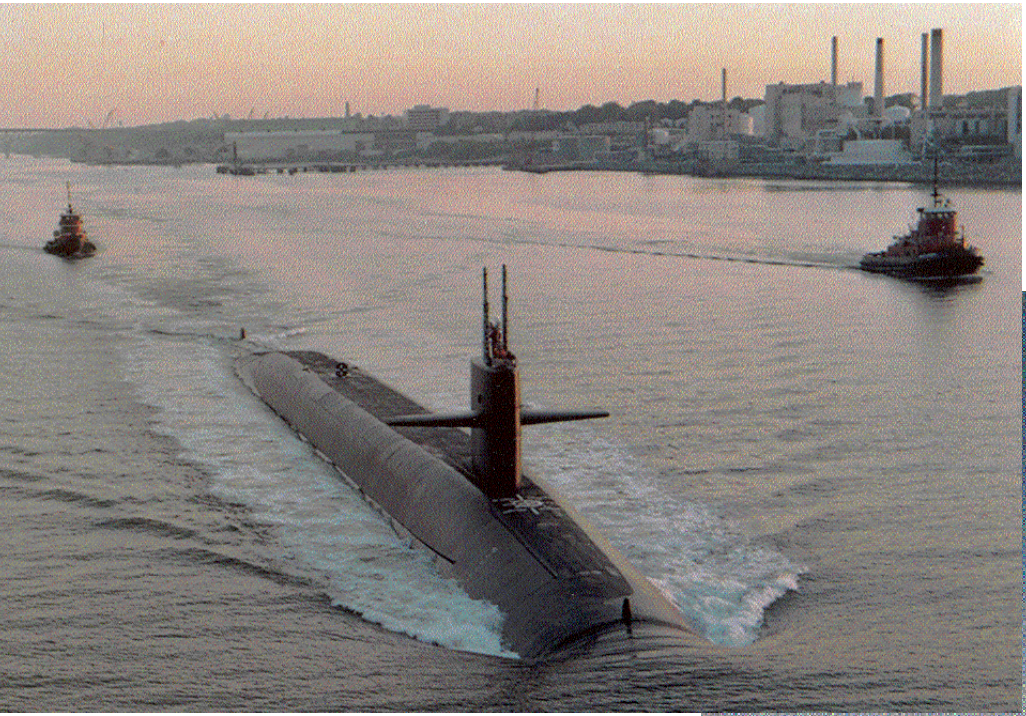
- Summary

NUWC Division Newport Location

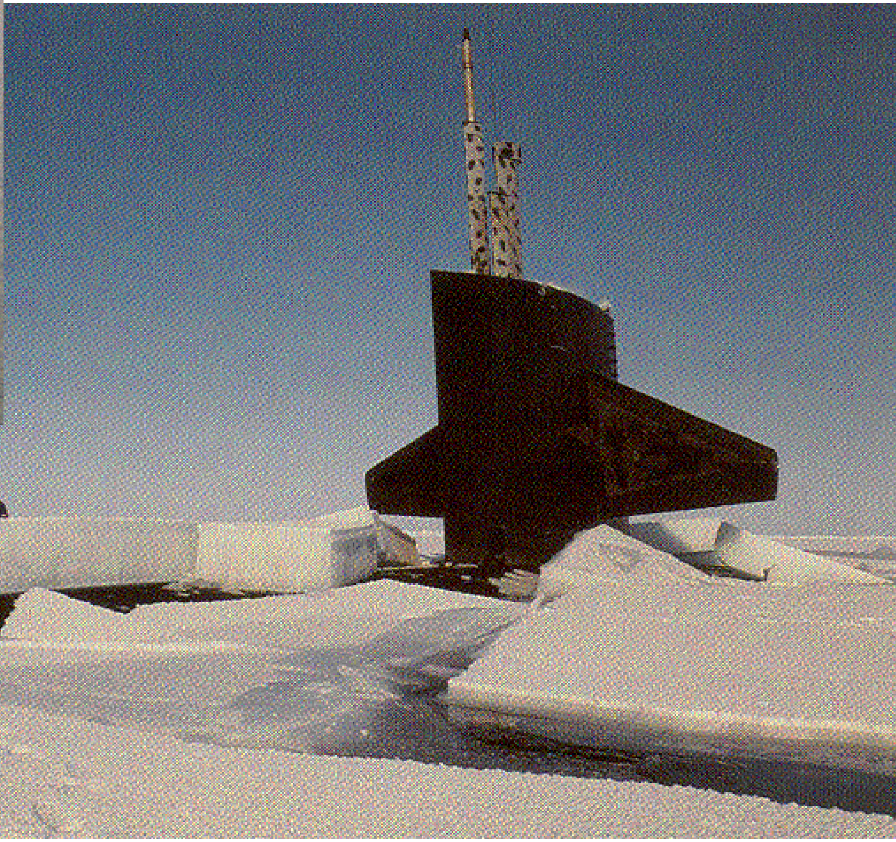
NAVSEA
WARFARE CENTERS
NEWPORT

NAVSEA Undersea Warfare Center (NUWC) Division Newport

NUWC’s Mission:



R&D, T&E, and Fleet support for submarines and submarine related systems.

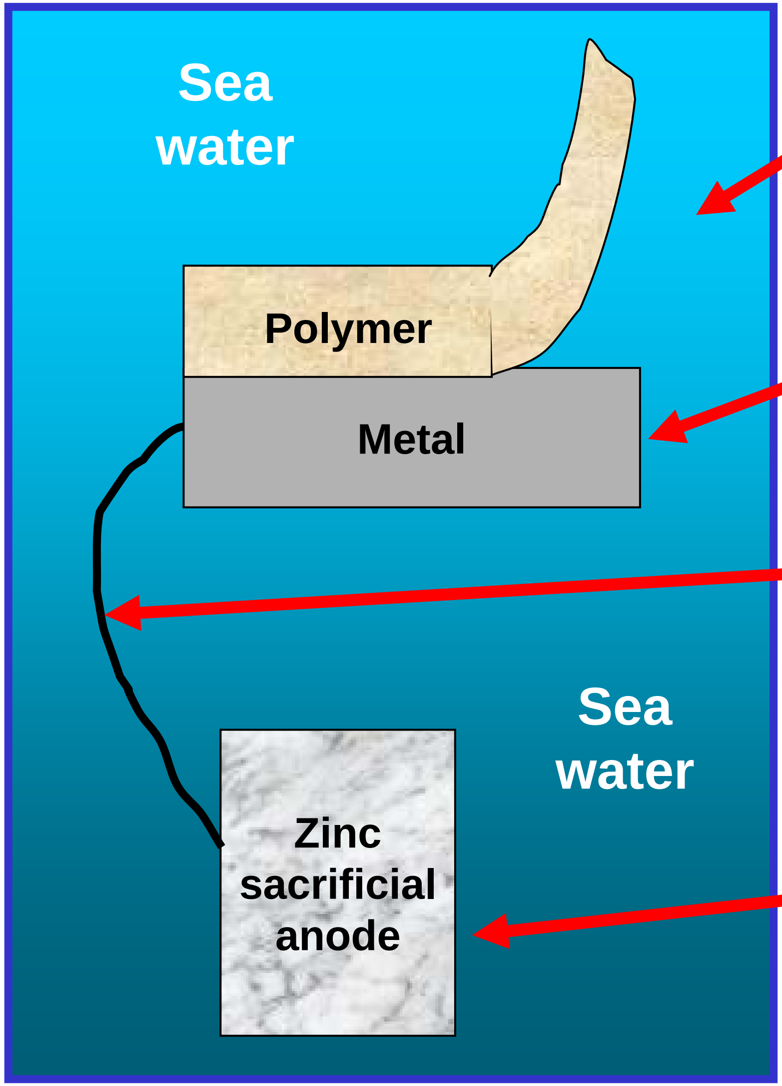


sonar and sensors,
periscopes, antennae,
torpedoes, UUVs,
sub-launched weapons,
systems integration.

Chemistry Lab: R&D projects of naval interest and fleet support work

Cathodic Delamination: Description and Mechanism

The Four Requirements for Corrosion:



- **Electrolyte**

  (Seawater)

- **Cathode**

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

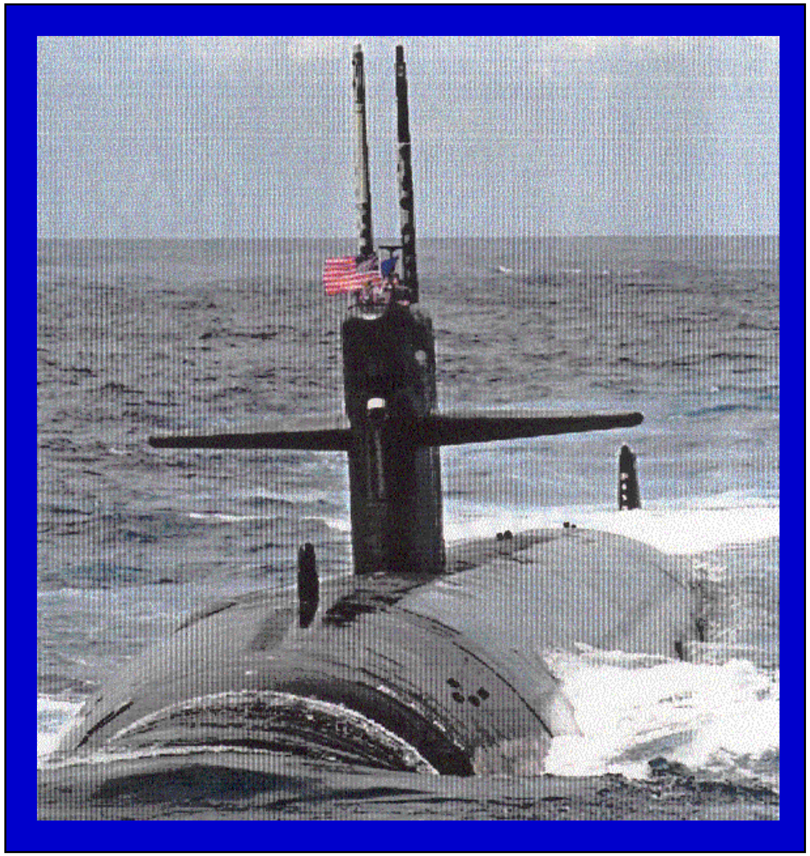
- **Electron Path**

  (Direct contact between metals)

- **Anode**

  ($Zn \rightarrow Zn^{2+} + 2e^-$)

Why Do We Cathodically Polarize Metals in Seawater?



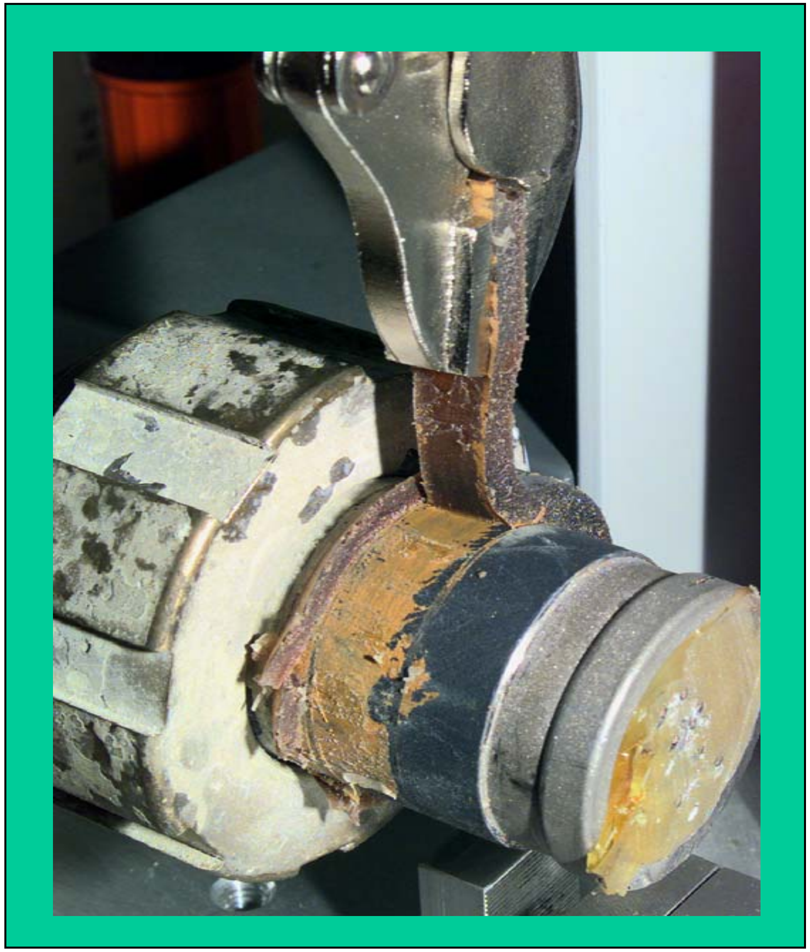
> In a corrosion cell, the cathode does not mass waste or dissolve

> Steel and many other metals are not electrochemically stable in seawater (they behave like anodes)

> Sacrificial anodes or impressed currents protect vulnerable metals by making them behave as cathodes.

Coupling two dissimilar metals together and submerging them in seawater will produce an anode/cathode couple that will cause the more active metal to dissolve (galvanic corrosion).

What Is “Cathodic Delamination”



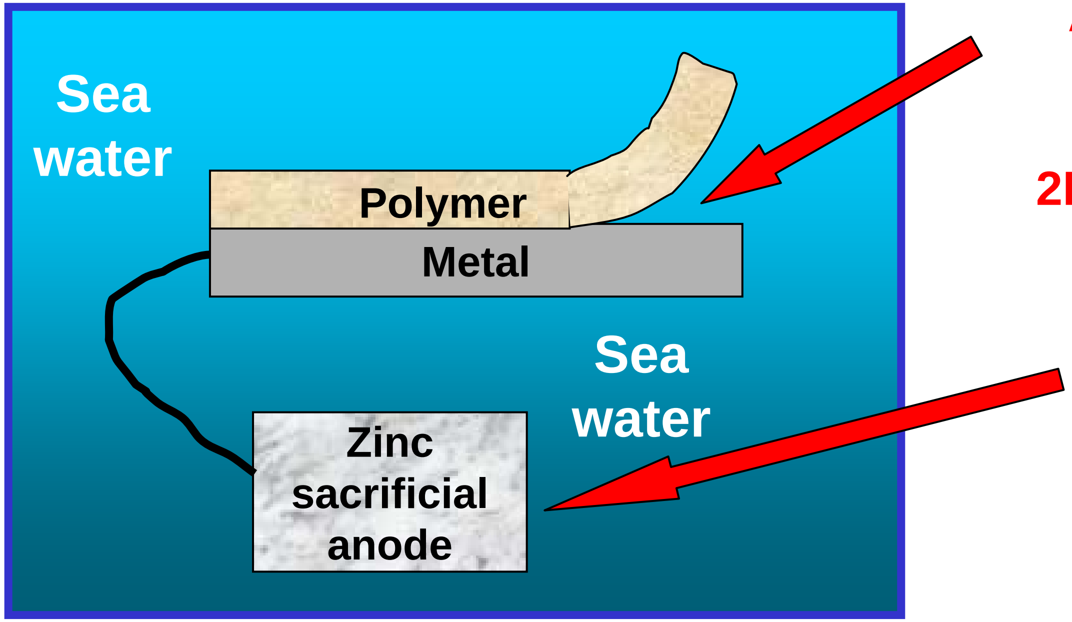
“<u>Cathodic Delamination</u>” is a corrosion reaction that occurs spontaneously in seawater.

It occurs on cathodically polarized surfaces (usually metal, but not always!).

The reaction produces a very high pH environment at the interface between the cathodically polarized surface and the material directly above it.

The high pH conditions directly or indirectly cause the overlying material to delaminate from the cathodically polarized substrate.

Polymer-Metal Bonding Failures: Cathodic Delamination



At the polymer-metal interface:

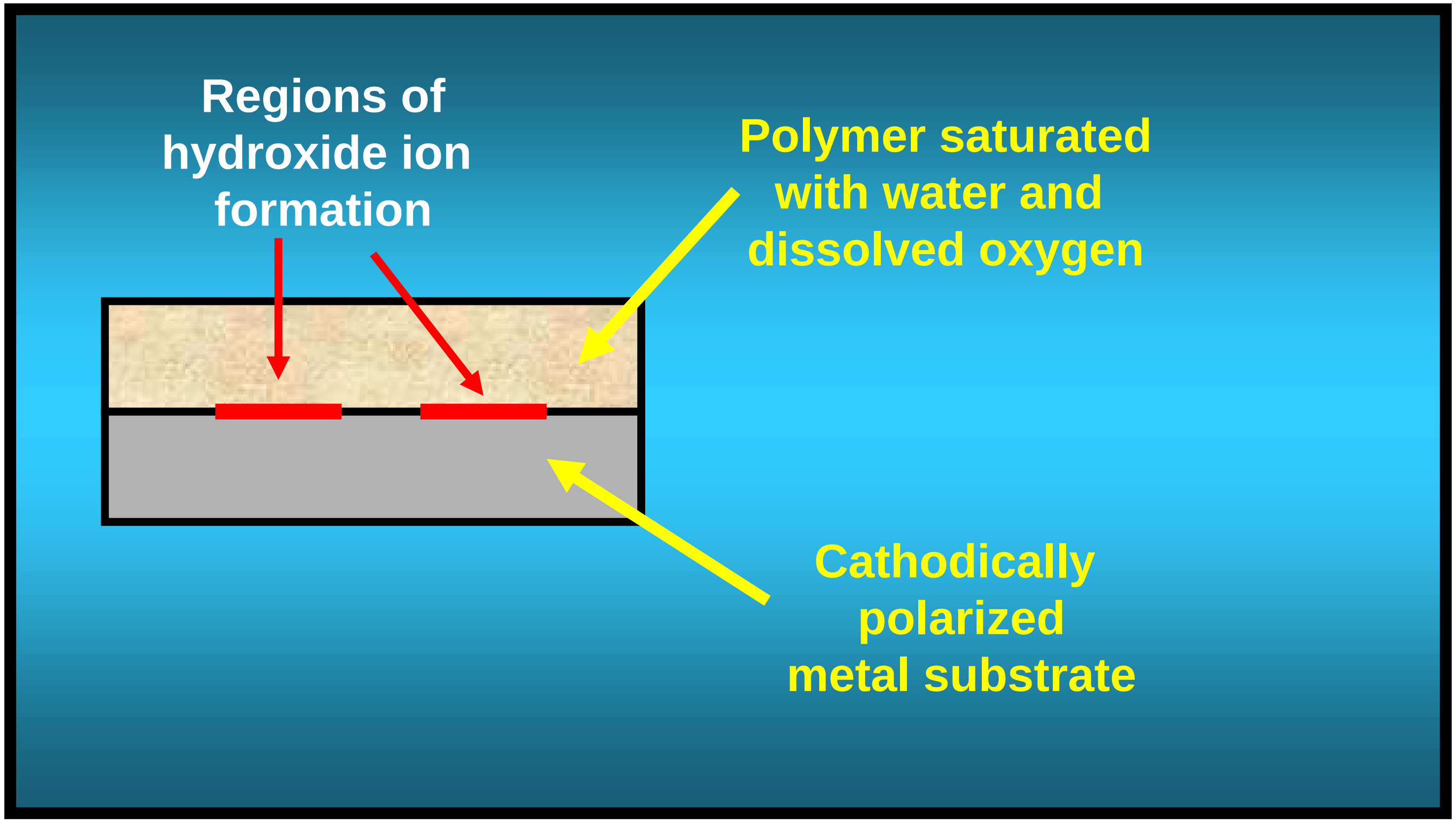
$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$

At the zinc-seawater interface:

$Zn \rightarrow Zn^{2+} + 2e^-$

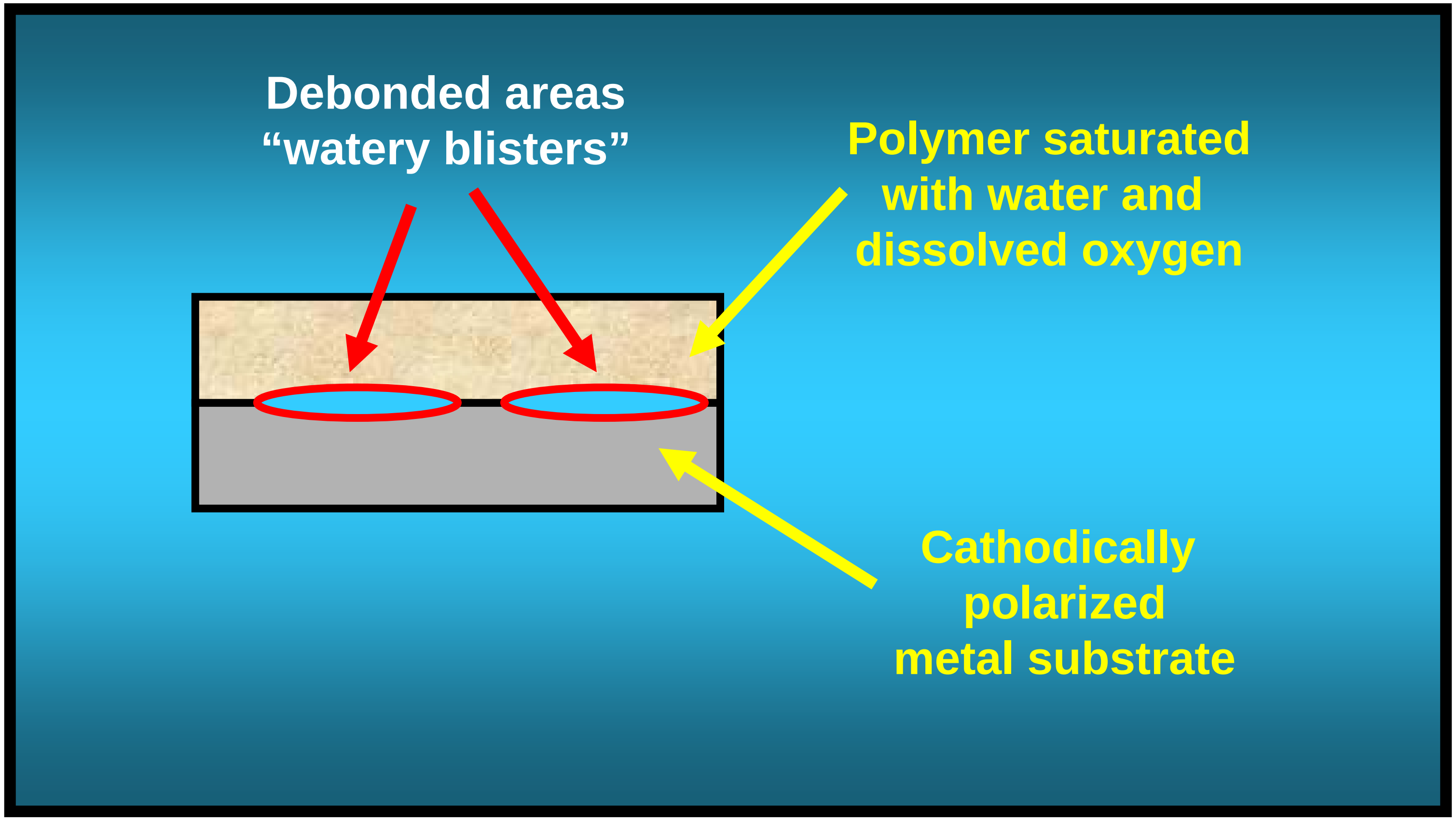
The most common failure mechanism for metal-polymer bonds in a marine environment is "cathodic delamination". Sacrificial zinc anodes on the hull cathodically polarize metal surfaces. Caustic hydroxide ions (OH^-) are generated on the metal surface; this reaction weakens/destroys metal-polymer bonds.

Cathodic Delamination Theory Part I



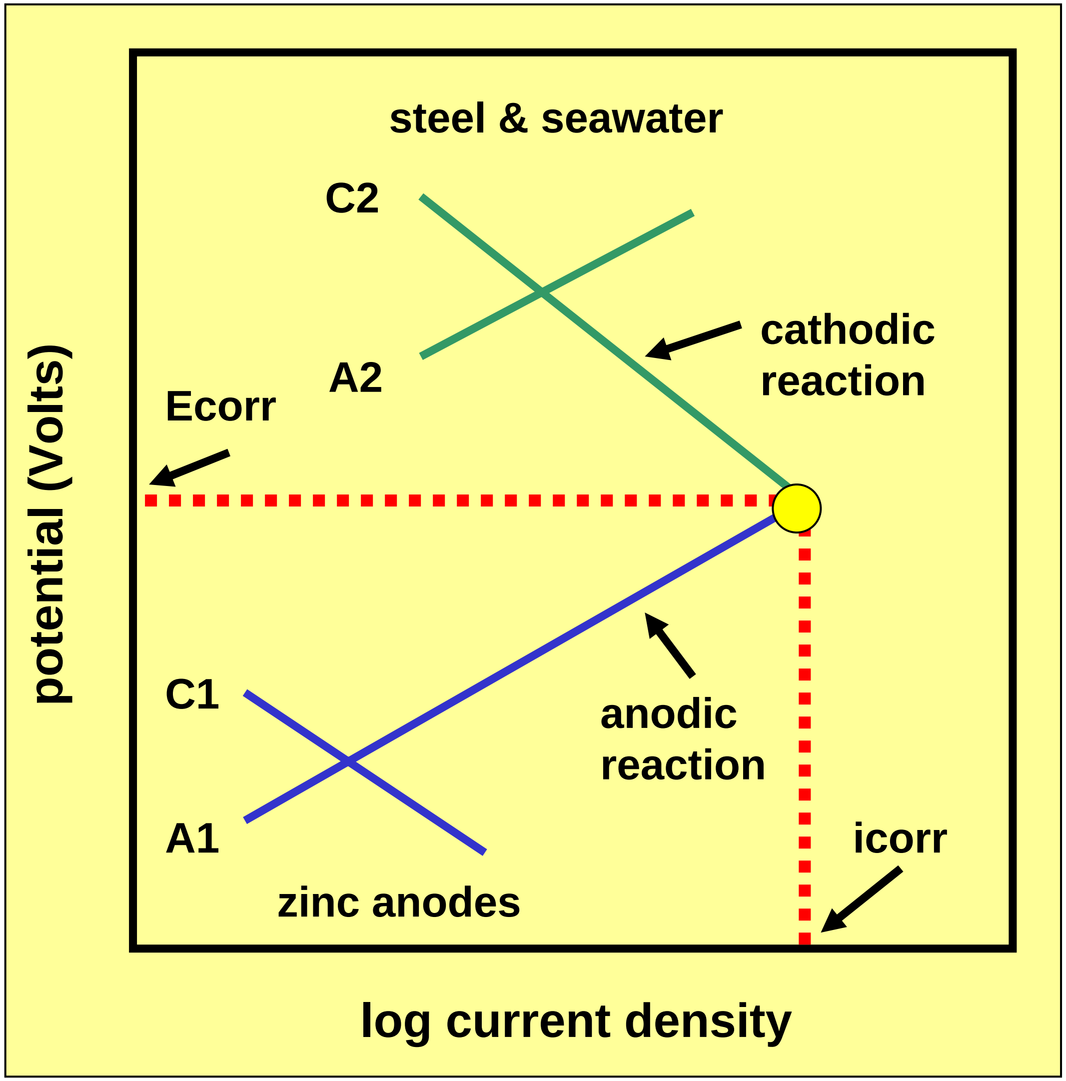
Once the polymer is saturated with water and dissolved oxygen, hydroxide (OH^-) ions are formed at the metal/polymer interface due to a cathodic corrosion reaction.

Cathodic Delamination Theory Part II:



As hydroxide (OH^-) ions are formed at the metal/polymer interface, osmotic pressure leads to the formation of high-pressure water “blisters” at the bondline. Blister growth is governed by the permeability of the polymer.

Evans Diagram for Sacrificial Anodes

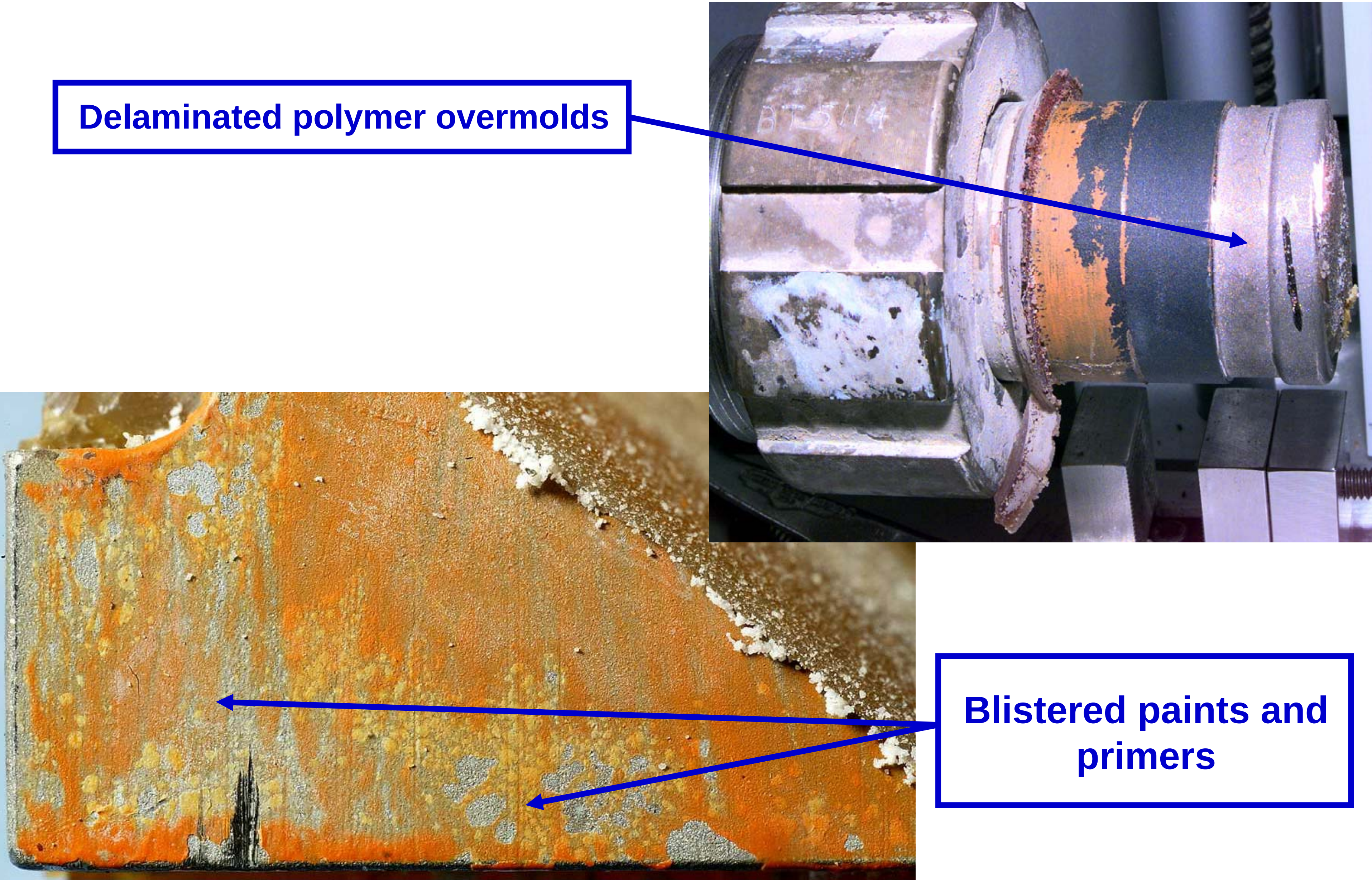


In a two electrode system (e.g., steel hulls and sacrificial zinc anodes) the natural corrosion potential (Ecorr) will be between the E values for the two electrodes, and the natural corrosion current (icorr) will be greater than either electrode's original current value. The combined system wants to be at Ecorr and icorr.

In all cases, the Tafel lines must be followed!

Current density is directly proportional to the reaction rate!

Results of Cathodic Delamination:



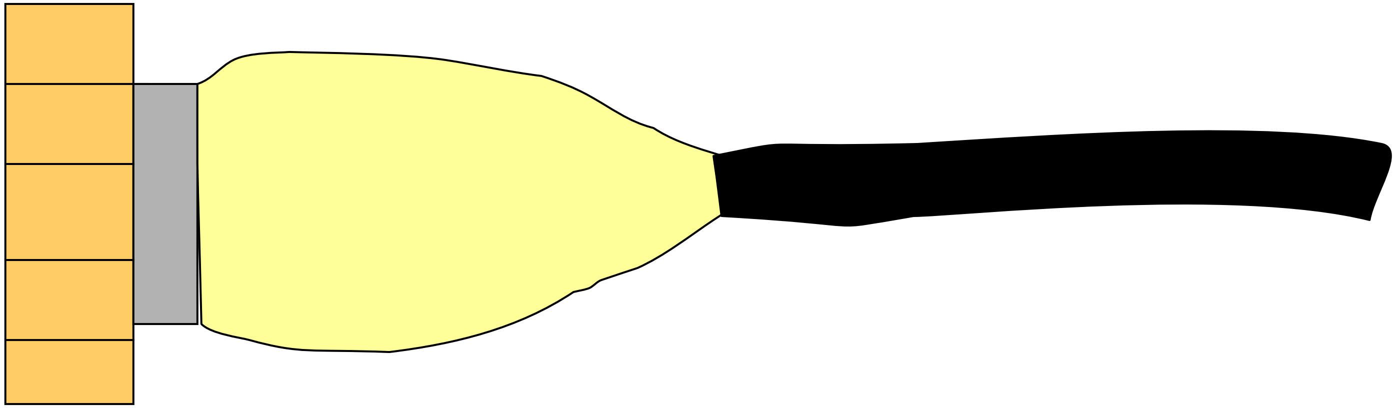
Delaminated polymer overmolds

Blistered paints and primers

Accelerated Life Testing:
Theory and Practical Considerations

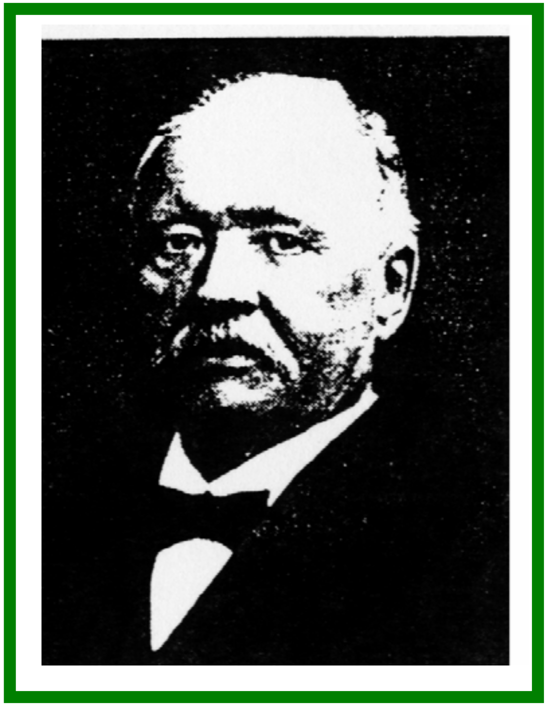
What is Accelerated Life Testing?

Question: How long will a given cable/connector function in the marine environment?



Answer: Use accelerated life testing techniques to “speed up” the aging process - samples can be aged rapidly in the laboratory to determine the service life of a variety of hardware components

The Theoretical Basis for Accelerated Life Testing



Svante Arrhenius
(1859 - 1927)

Winner of the Nobel Prize for Chemistry in 1903

The Arrhenius Equation

$$K = Ae^{-E/kT}$$

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

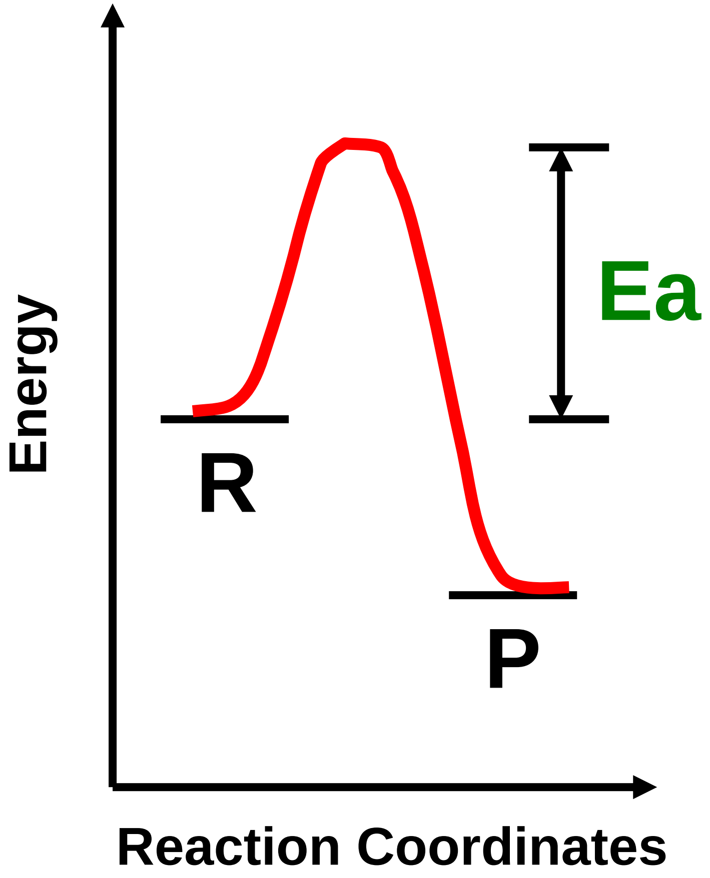
The Arrhenius equation is a mathematical expression that describes the effect of temperature on the velocity of a chemical reaction.

The Meaning of Activation Energy (Ea)

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).

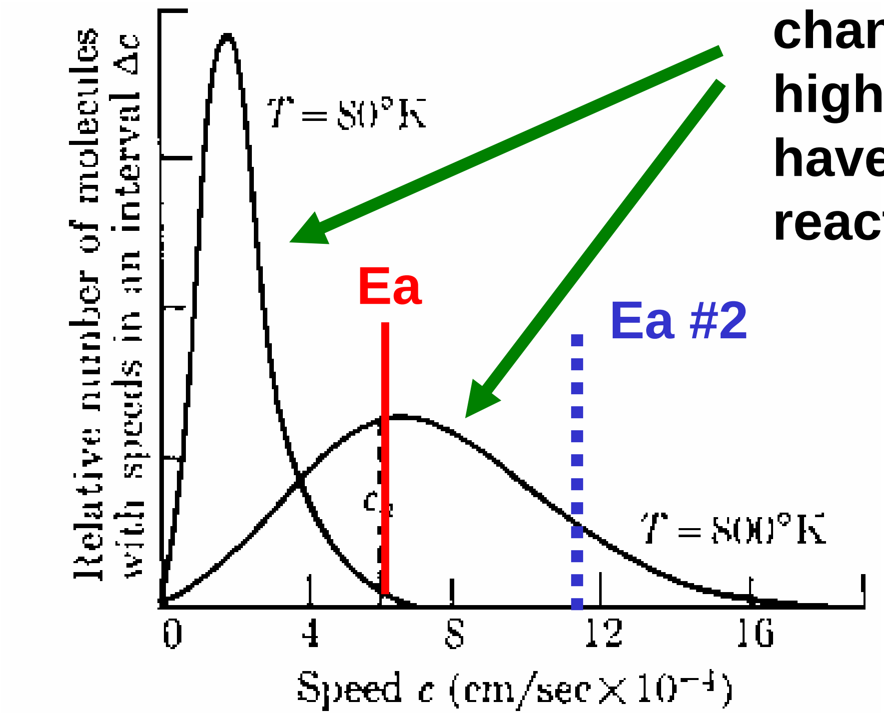
For most reactions, the Activation Energy must be determined by experimentation. There are few published values in the literature



The Time-Temperature Relationship

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

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:

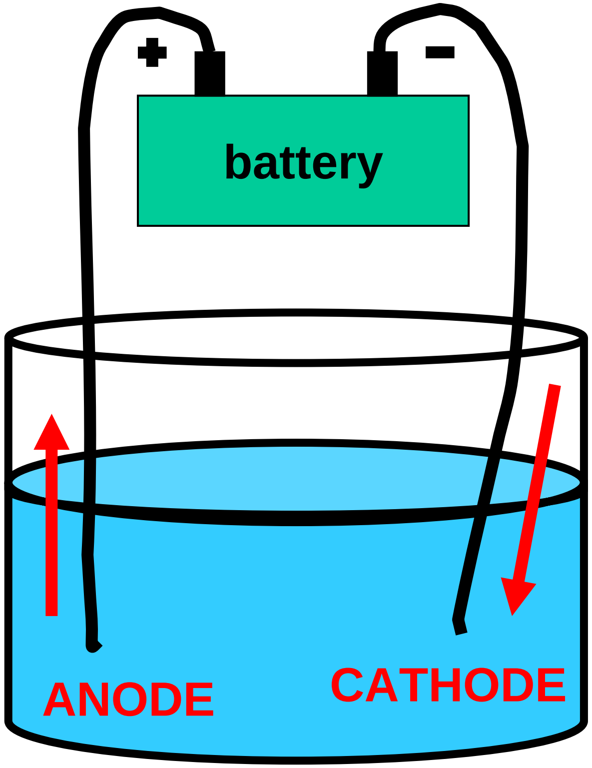
$$\boxed{\frac{TF_1}{TF_2} = RAF = e^{\frac{-E\left(T_2 - T_1\right)}{R\left(T_1 T_2\right)}}}$$

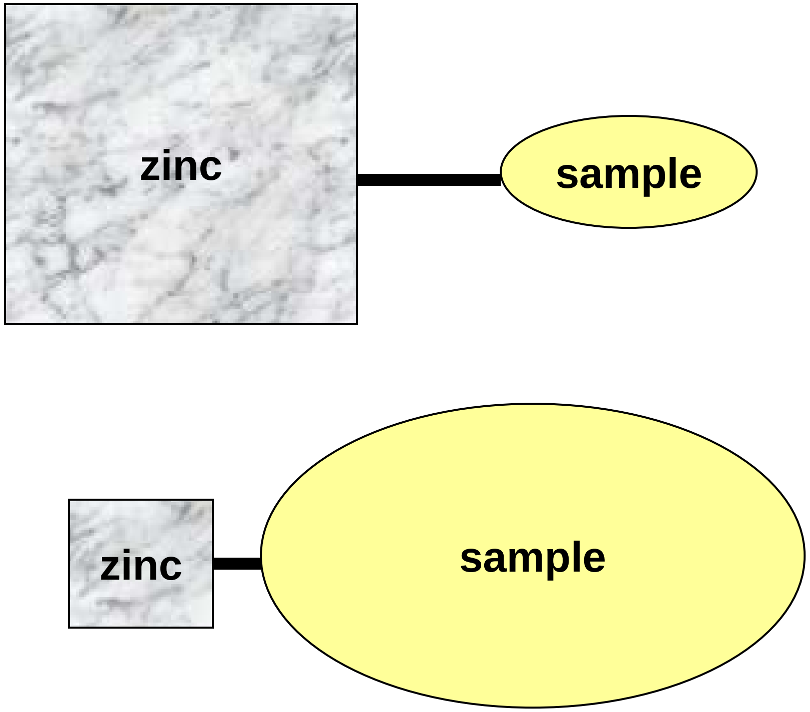
E = activation energy
R = gas constant
T_1= normal operating temperature of the item
T_2= temperature at which the ALT is run
e = base of natural logarithm system
TF_1 = time to failure at temperature T_1
TF_2 = time to failure at temperature T_2

The RAF indicates how much faster a given process will occur in the ALT

Proper Cathodic Delamination
ALT Voltage:

If a sacrificial zinc anode is used, the voltage will be correct.
If a battery is used, a reference electrode must be used (chemical equations are typically versus SCE), the polarization must be correct, and the "throw weight" of the zinc electrode must be factored into the set-up.





Voltages and Current Density

Certain voltages and current densities are required for the proper functioning of a cathodic delamination ALT.

If the voltage is not correct, the desired reactions may not occur, and other undesired reactions may occur.

If the current density is not correct, then the desired reaction may be accelerated/decelerated. This will compromise a temperature-based ALT.

WHY?

Cathodic Delamination: Reactions and Voltages

At voltages lower than -0.5 V SCE:

$O_2 + 2H_2O + 2e^- \rightarrow HOOH + 2OH^-$

At voltages between -0.7 V and -1.2 V SCE:

$HOOH + 2e^- \rightarrow 2OH^-$

If hydrogen peroxide is not stable on metal surface:

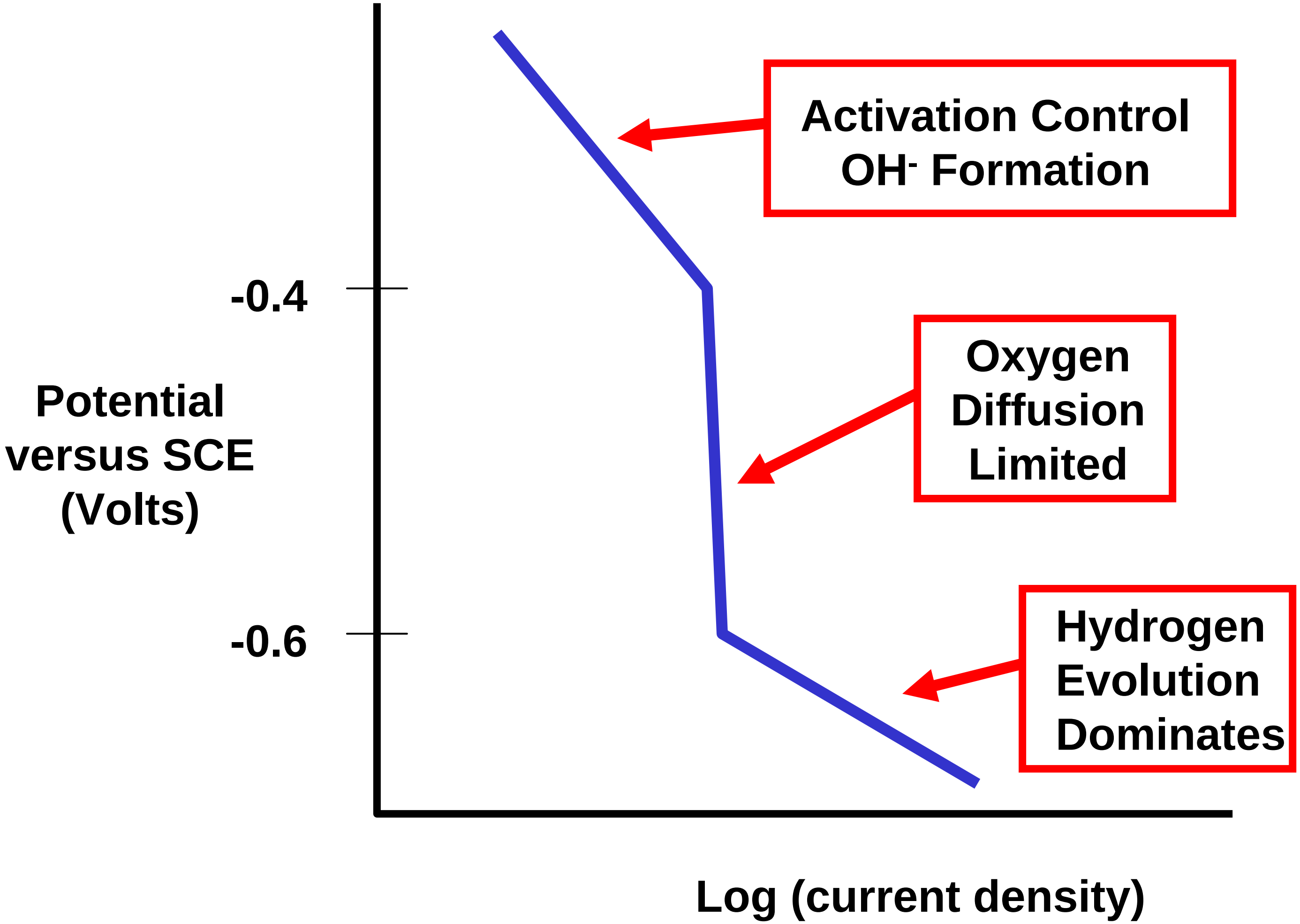
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

At voltages above -0.6 V SCE:

$2H^+ + 2e^- \rightarrow 2H \rightarrow H_2$

All of these reactions increase the pH of the solution in contact with the surface of the metal

Effect of Potential on Reaction Rate



Changes in potential may change the current (and hence, the rate) of the cathodic delamination reaction.

Chemical Equilibrium & Le Chatelier's Principle

$Zn \rightarrow Zn^{2+} + 2e^-$

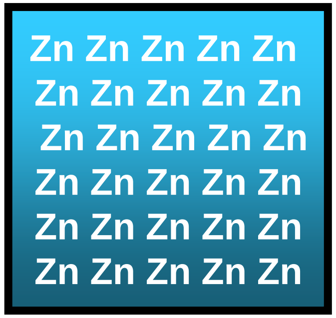
Anode

$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$

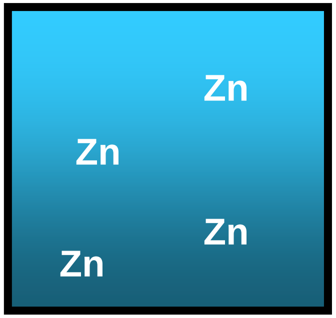
Cathode

Zinc ions will build up over time in the ALT tank water. If they are not removed from time to time, the anodic reaction will slow down and perhaps even reverse!

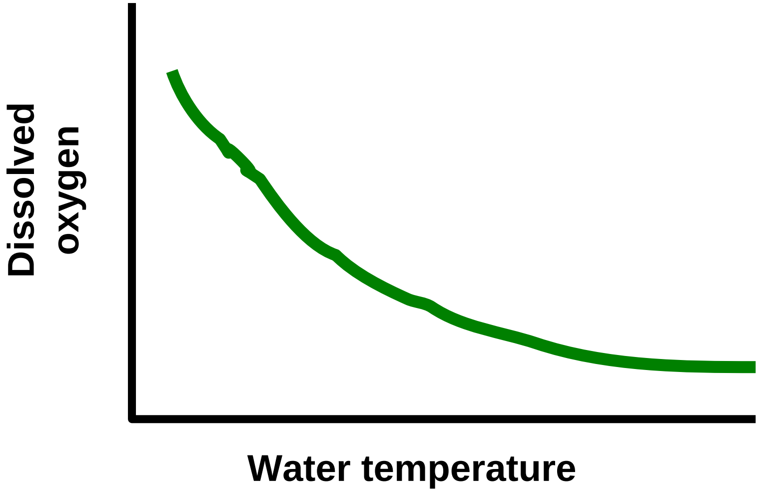
The solubility of oxygen drops as the temperature of water increases. The lower concentration of dissolved oxygen in hot water may slow down the cathodic reaction.



Slower



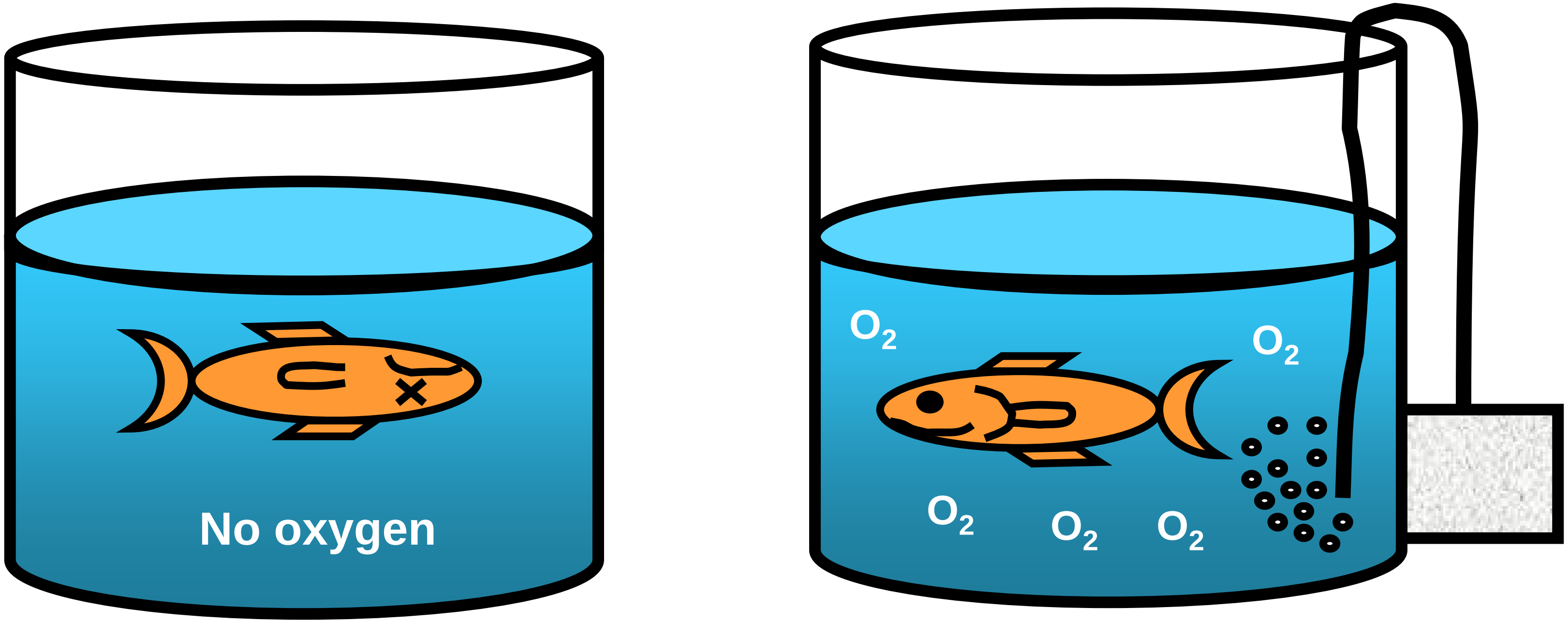
Faster



The Importance of Dissolved Oxygen

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$

The cathodic delamination reaction consumes oxygen. In an ALT test tank, oxygen must be continually replenished or the reaction will stop.



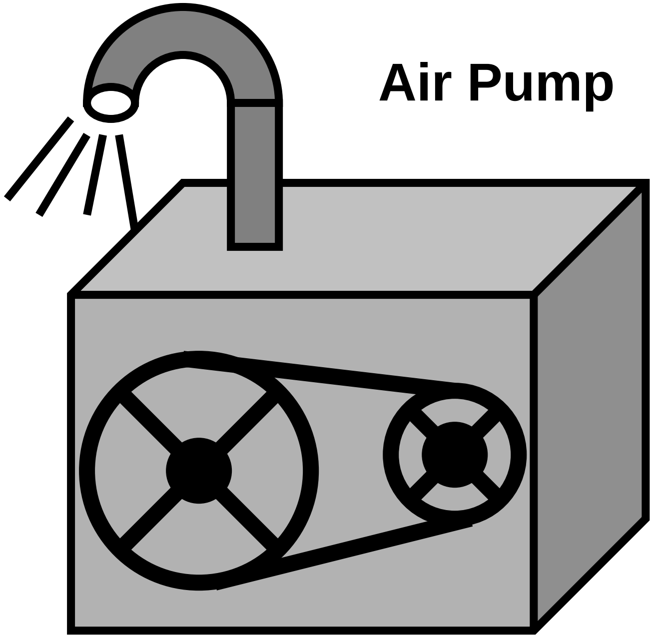
Maintaining Dissolved Oxygen

Bubbling pure oxygen through the ALT tank water is the best way to maintain dissolved oxygen levels. Pumping laboratory air may be more convenient, but carbon dioxide in the air can react with water to form carbonic acid and lower the pH of the ALT tank water:

$$CO_2 + H_2O \rightarrow H_2CO_3$$

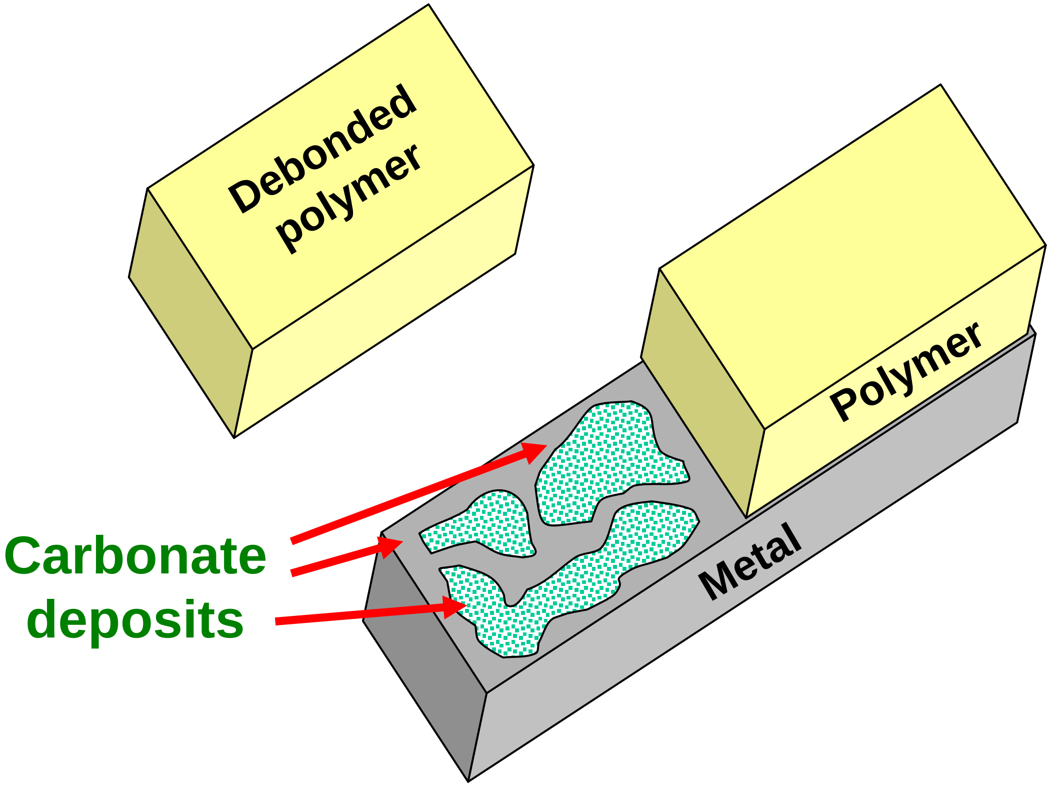
Carbonic Acid

Water can hold much more dissolved carbon dioxide than dissolved oxygen



Carbonate Precipitation

At high pH values, various carbonate minerals can precipitate from seawater. As they precipitate, these carbonates form non-conductive coatings that may interfere with the primary cathodic delamination reaction.

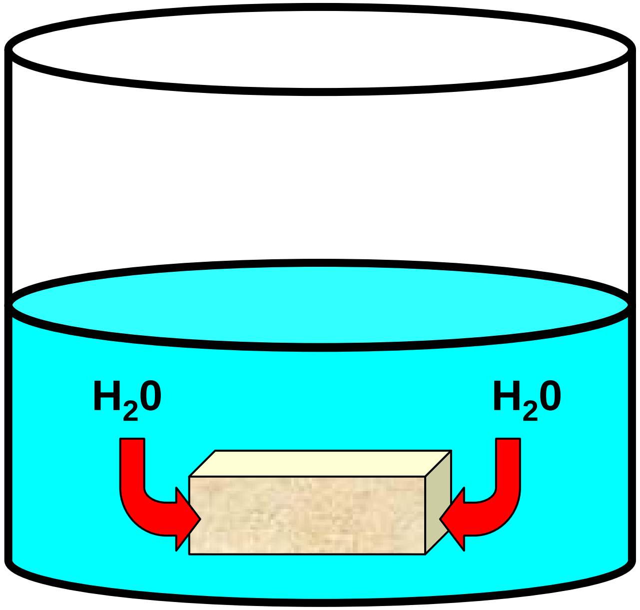


Carbonates only precipitate at high pH. Cathodically polarized metal surfaces generate hydroxide ions in ALTs. "Smoking-gun" evidence for cathodic delamination?

Calcium, zinc and iron carbonates have been found on ALT samples

Activation Energy:
The Critical Parameter

What is actually being accelerated in a standard ALT experiment?



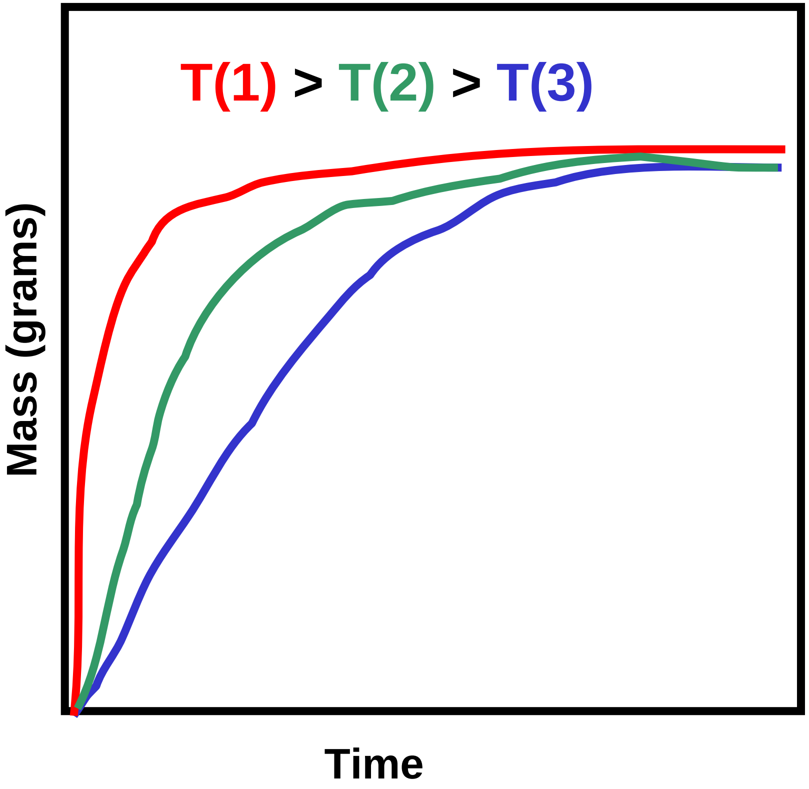
The permeation of water into and through the polymeric overmolding compound is considered to be the rate-limiting step in the cathodic delamination process. Water is needed to make hydroxide ions and to form the blisters that cause debonding.

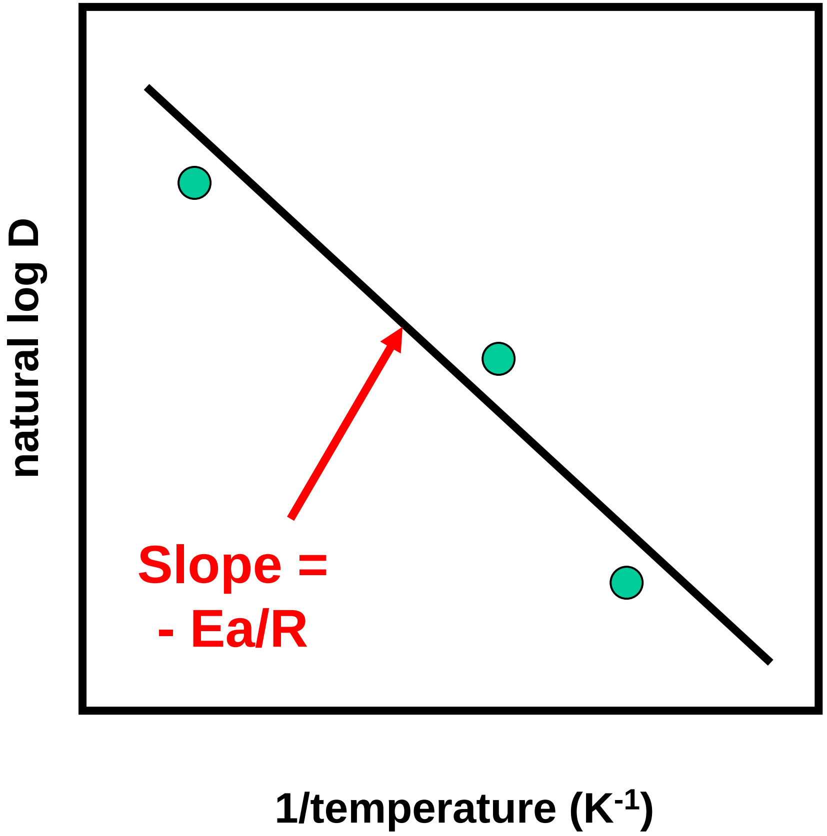
The activation energy used for standard ALTs is that for the permeation of water into the polymeric overmolding compound

Determination of Ea for Water Diffusion into Polymers

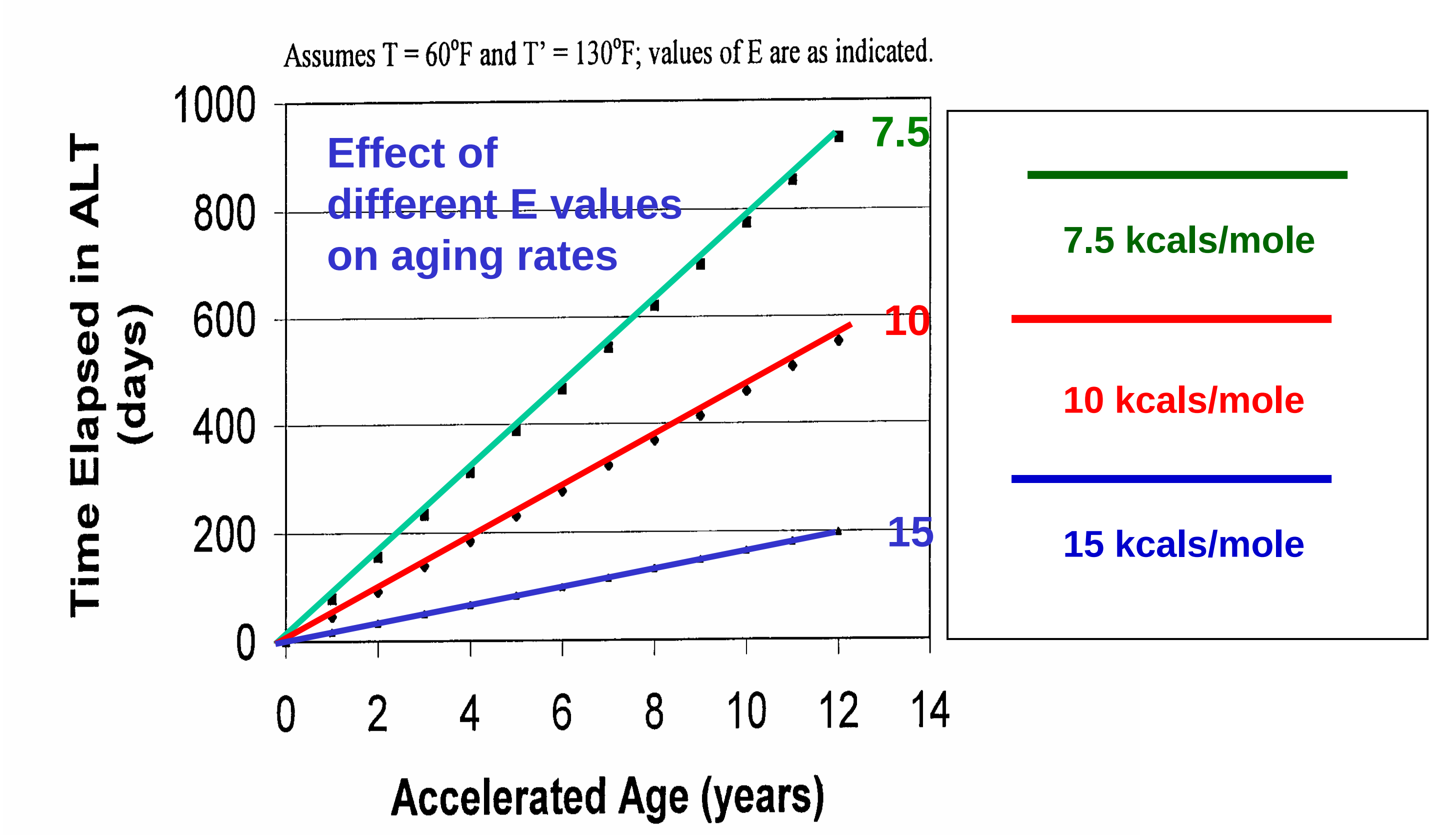
Calculate diffusion constants (D) at three different temperatures

Plot ln(D) versus 1/T. The slope of the resulting line is -Ea/R



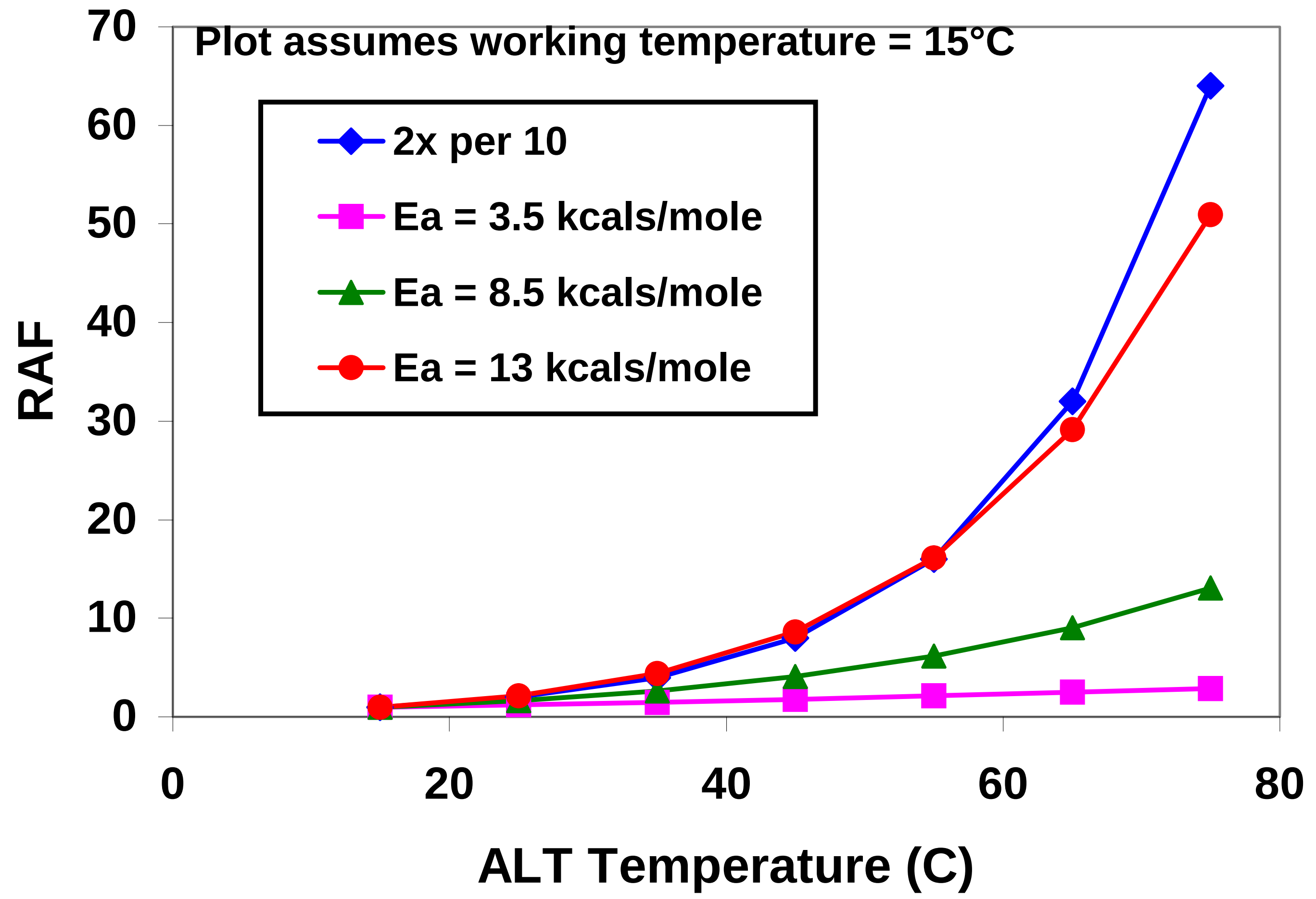


The Effect of Ea Values on an ALT



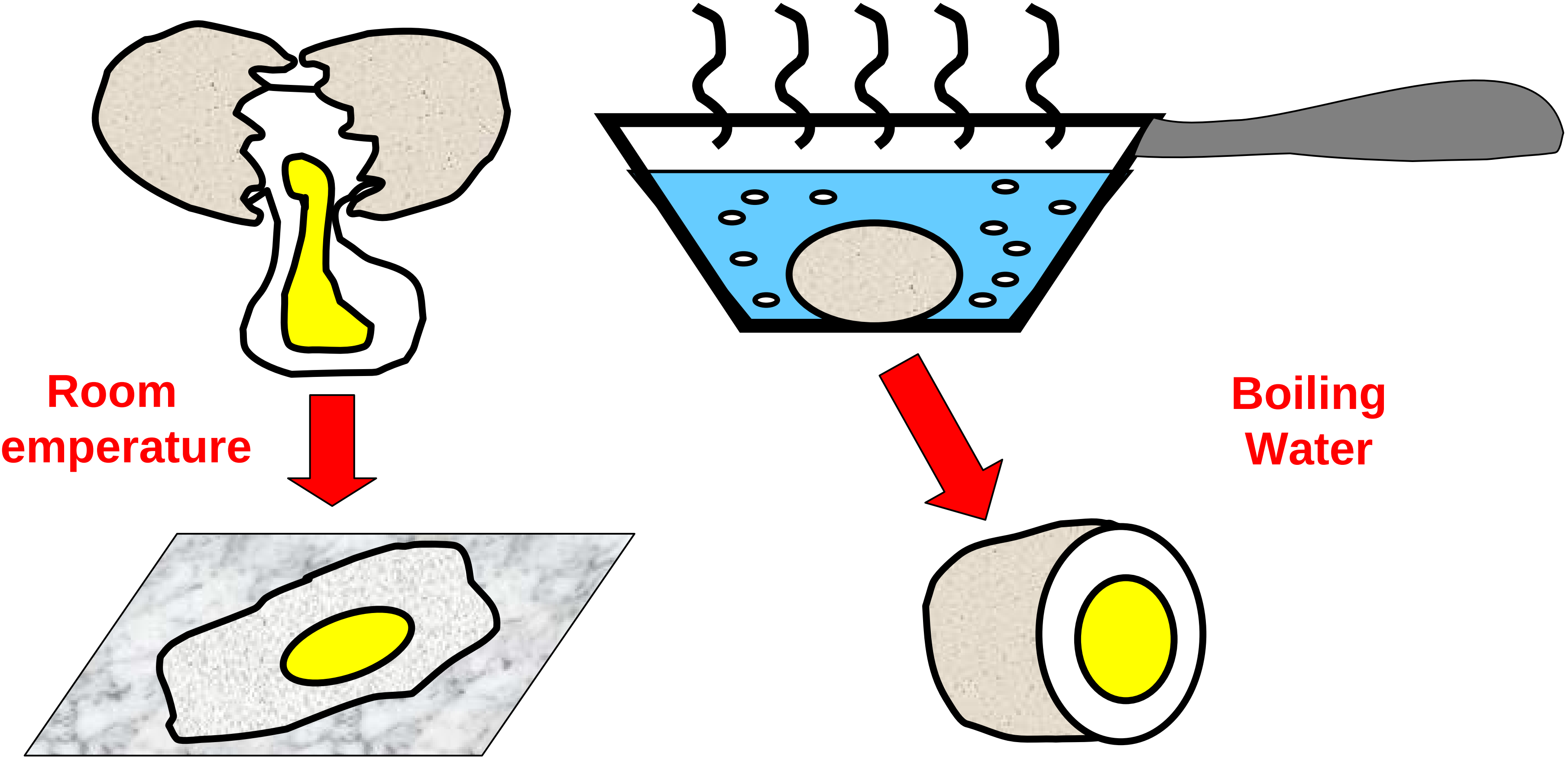
Because the Arrhenius Equation is exponential, small changes in Ea can have large effects on the RAF!

An ALT Myth: The 10°C = 2x Increase in the RAF for all Systems



The RAF in an ALT depends upon <u>both</u> the temperature difference and the activation energy (Ea). 10°C = 2x RAF only works for an Ea ≈ 13 kcals/mole! It does not work well for other Ea values.

ALT Temperature Limitations



Room Temperature

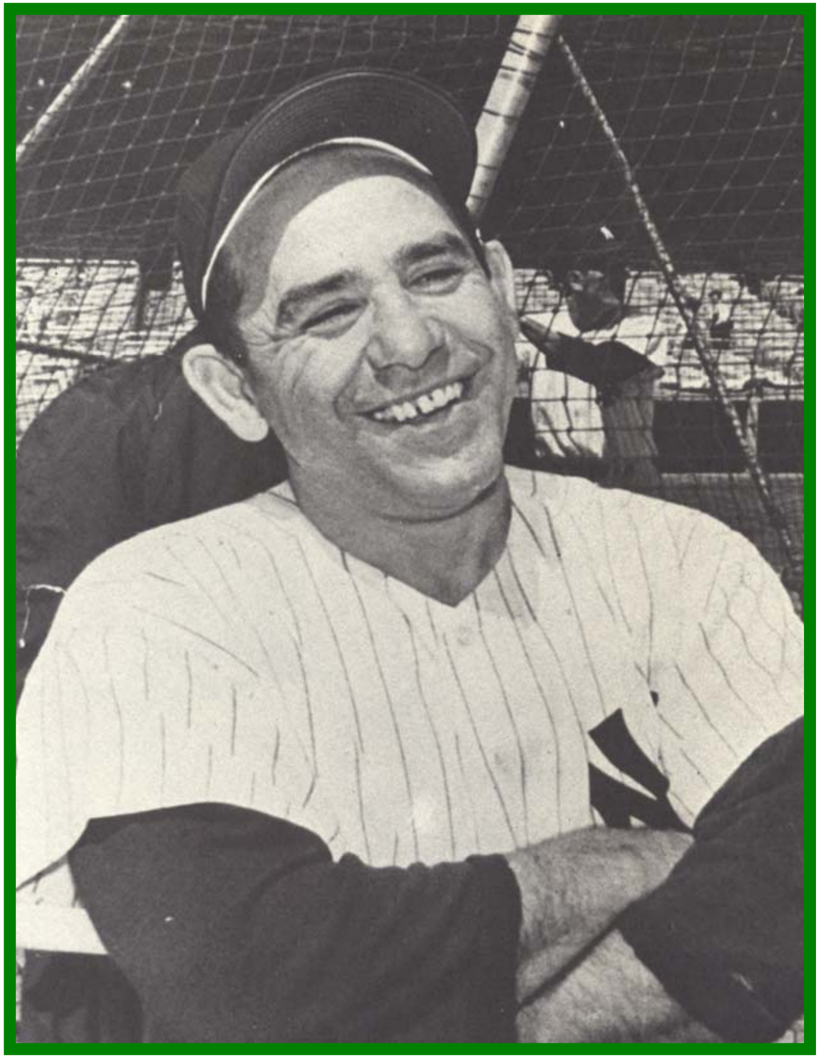
A mess!

Boiling Water

A boiled egg!

ALT temperatures cannot be raised indefinitely. At some point, the temperature becomes high enough for “unrealistic” reactions to occur.

Some ALT Words of Wisdom



Lawrence "Yogi" Berra
Catcher, NY Yankees and
World-Renowed Philosopher

"Prediction is difficult… especially about the future"

and

"If you don't know where you are going, you'll wind up somewhere else."

Cathodic Delamination: Mitigation Strategies

Deoxygenate the Surrounding Water

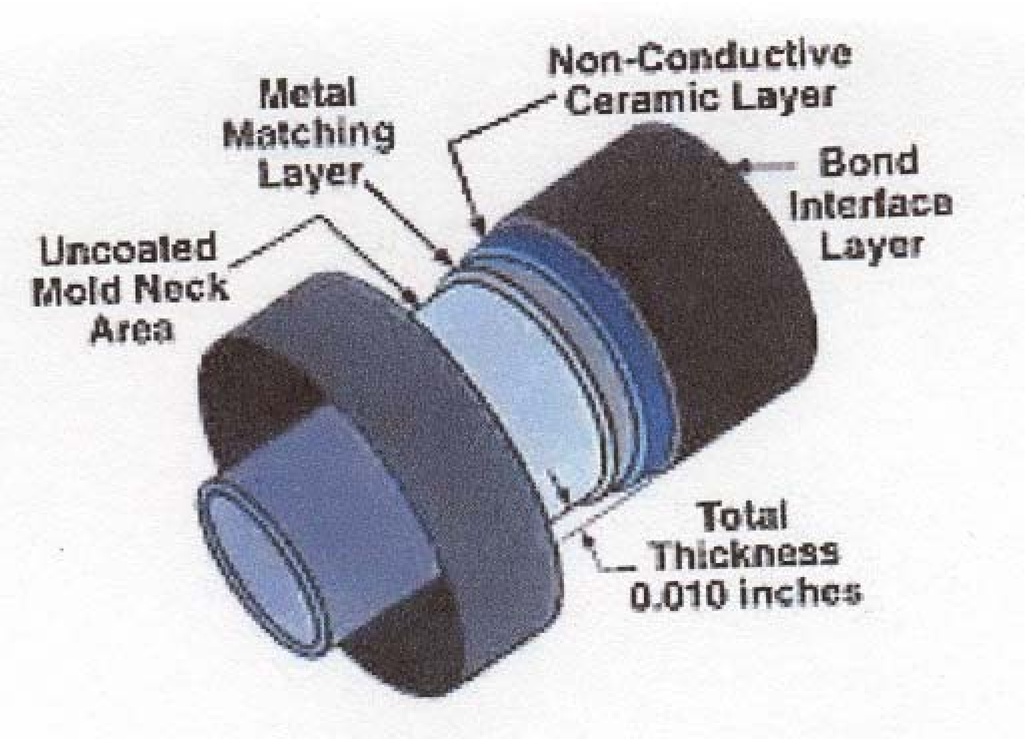
Dissolved oxygen is a critical requirement of the cathodic delamination Process. Cut off the DO, and the reaction stops!

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$$

- Certain chemical species can be added to water to remove (consume) DO.
- Only viable if the hardware is located such that its immediate environment can be isolated from the rest of the marine environment.

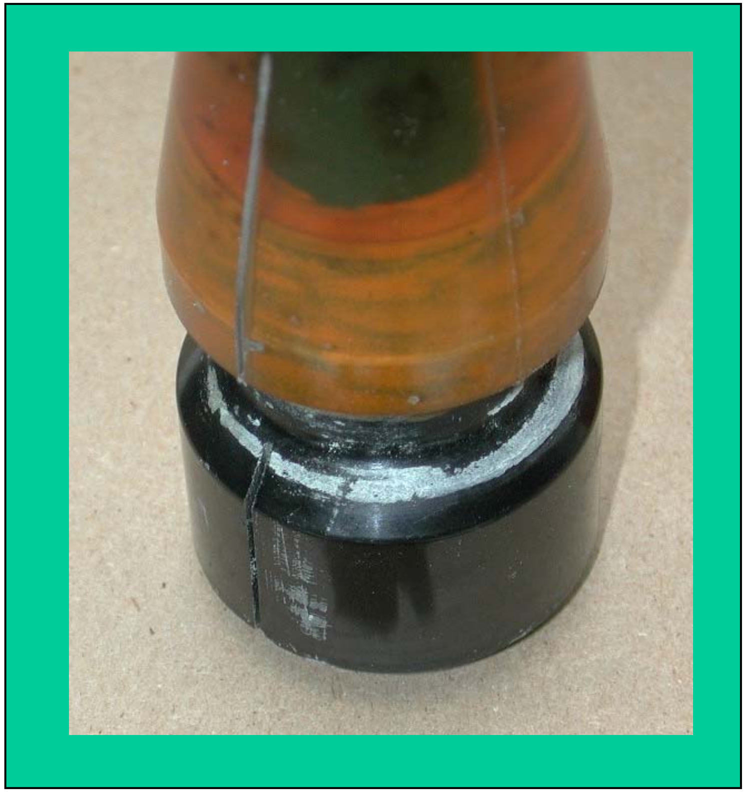
Non-Conductive Ceramic (NCC) Coatings

- **Plasma-sprayed ceramic coatings (≈ 10 microns thick)**
- **Prevents electrons from reaching the metal/polymer interface**
- **Used on connector backshells; other uses under consideration**
- **Porosity of NCC coating can be problematic for some applications**



before **after**
NCC coating

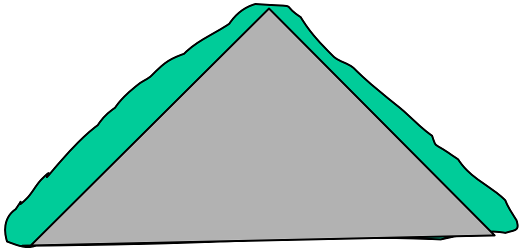
GRE-Coated Connector Backshells



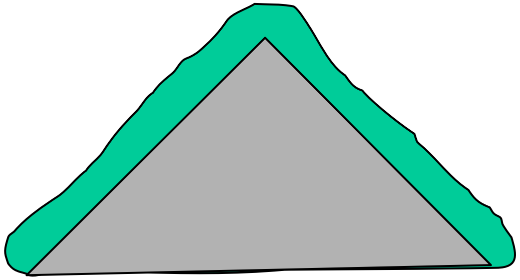
- Similar to NCC coatings, but material is glass re-enforced epoxy (GRE)
- Prevents electrons from reaching the polymer-metal interface
- Held in place mechanically (cure-shrinkage induced constriction and circumferential grooves
- Can be cracked/damaged if connector nut is overtightened
- Application limited to cylindrical hardware (need for constriction).

Thick, Quick-Drying Paints

Normal paint produces thinnest coating over sharp angles

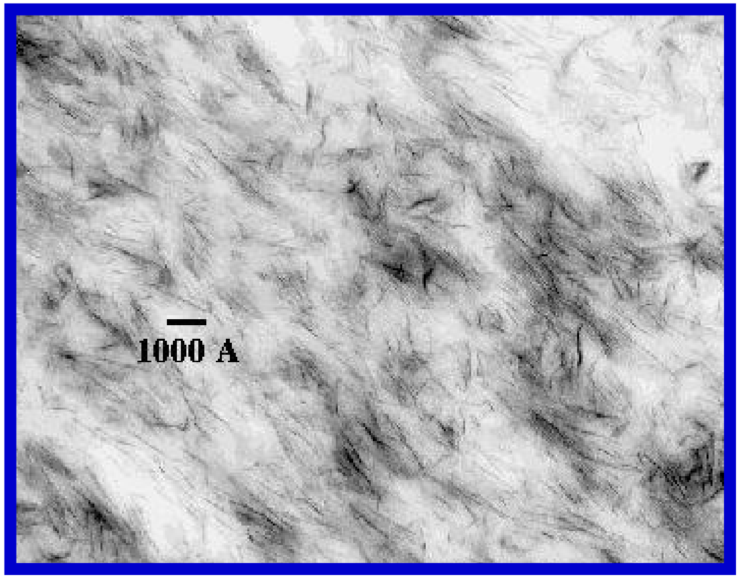


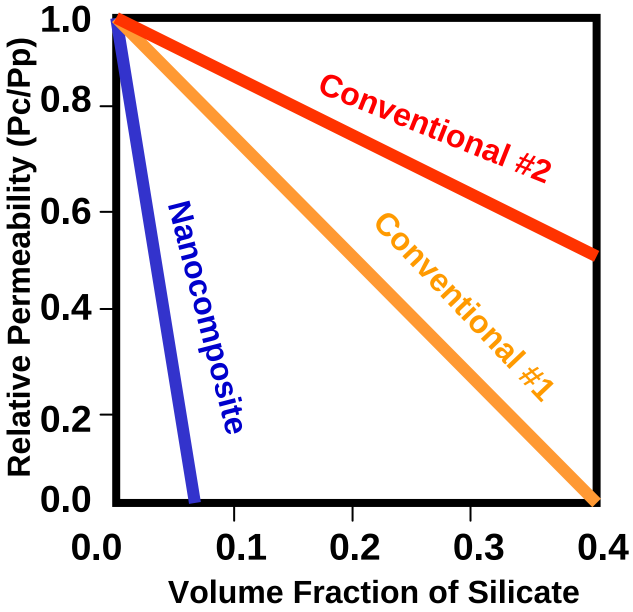
Thick, quick-drying paints produce even thickness coatings



- Most paints produce thinner coatings around sharp corners
- Thinner coatings increase the flux of permeating species and thereby speed up the cathodic delamination process
- U.S. Navy study revealed that cathodic delamination of paint invariably begins at sharp corners
- Paints that are designed to dry “instantly” do not flow away from sharp corners and coat them more uniformly.
- Delays but does not prevent the cathodic delamination process

Nanocomposite Barrier Coatings





- Polymer-clay nanocomposites with intercalated particulate geometry can exhibit orders of magnitude better barrier properties than the polymer alone

- Greatly reduces the permeation of water and dissolved oxygen

- Can be added to paints and encapsulates

- Low cost and low volume fractions

Summary:

- Cathodic delamination is a corrosion reaction responsible for a significant portion of the metal-to-polymer bond failures that occur in the marine environment.

- Accelerated life testing techniques can be used to speed up cathodic delamination in laboratory experiments to allow researchers to predict how long hardware can be expected to survive in the ocean.

- ALT tanks must maintain the proper chemical environment and electrical potentials for cathodic delamination to occur.

- Use of the proper activation energy values in the ALT age calculations is critical.

- Several techniques now exist for protecting hardware from cathodic delamination – more research is needed in this area!