

Introduction to Atmospheric Corrosion

Causes, Effects, and Prevention

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Introduction to Atmospheric Corrosion

- Thermodynamics & Definitions of Corrosion
- Chemistry of Corrosion
- Forms of Atmospheric Corrosion
- Mitigation of Corrosion

What Is Corrosion?

Corrosion is the force driving a material towards its natural, lowest-energy state.*

Corrosion is *an electrochemical process that returns refined metals to their natural oxide states*

**European Coil Coating Association*

What Is *Atmospheric Corrosion*?

Atmospheric Corrosion is a process that takes place in a film of moisture on the metal surface. The moisture film may be so thin that it is invisible to the naked eye.

ISO 9223

Corrosion and Thermodynamics

Corrosion is a **thermodynamic** process by which systems are driven towards their lowest-energy state

To begin to understand it, it's useful to recall the Second Law of Thermodynamics

Second Law of Thermodynamics

“The total **entropy** of an isolated system can never decrease over time.”

- “Entropy” can be thought of as “disorder”
- The natural tendency of any isolated system is to degenerate into a more disordered state (higher entropy)
- An **increase** in Entropy results in a **decrease** in total Energy



Thermodynamics & Corrosion

- Nearly all metals in nature exist as oxides because this is the **lowest-energy** state
- Refining metals requires heat energy to break apart the oxide molecule
- Once exposed to nature, refined metals begin reverting back to lower-energy states, some form of metal oxide or a salt



Corrosion Examples



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Corrosion of Metals

Thermodynamically, **corrosion** of metals is a return of refined metals to low-energy oxide and hydroxide states

This involves both **electrochemistry** (REDOX) and **acid/base** (Lewis) chemistry

Corrosion Chemistry of Iron

- The corrosion chemistry presented in this section is general to any metal
- Iron (Fe) is used throughout as an example because it is used widely, corrodes readily, and displays complex corrosion behavior



Ions of Iron



Iron(II)

Ferrous ion



Iron(III)

Ferric ion

Ferrous ion freely donates an electron to oxygen to become a ferric ion, so ferric oxides and hydroxides are most common.

Iron Occurs Naturally in Different States

Oxides (dry or *anhydrous*)

Hematite	Fe_2O_3	Iron(III) oxide
Magnetite	Fe_3O_4	Iron(II,III) oxide ($\text{FeO}\cdot\text{Fe}_2\text{O}_3$)
Wuestite	FeO	Iron(II) oxide (rare near Earth's surface)

Hydrated oxides and oxide-hydroxides

Goethite	$\text{FeO}(\text{OH})$	Iron(III) oxide-hydroxide
Limonite	$\text{FeO}(\text{OH})\cdot n\text{H}_2\text{O}$	(hydrated form)

Iron minerals have crystalline and amorphous forms.

Hydrated compounds include water molecules within the crystal structure.

Electrochemistry of Corrosion

Corrosion is a multi-step process initiated by two types of reactions:

Oxidation *Loss of an electron*

Reduction *Gain of an electron*

mnemonic device: "OIL RIG"

Oxidation of Metals



where n is the valence of the metal ion and the number of electrons lost through oxidation

Examples of Metal Oxidation Reactions

Oxidation of Metals



These *anodic* reactions initiate corrosion of steel, aluminum, and zinc

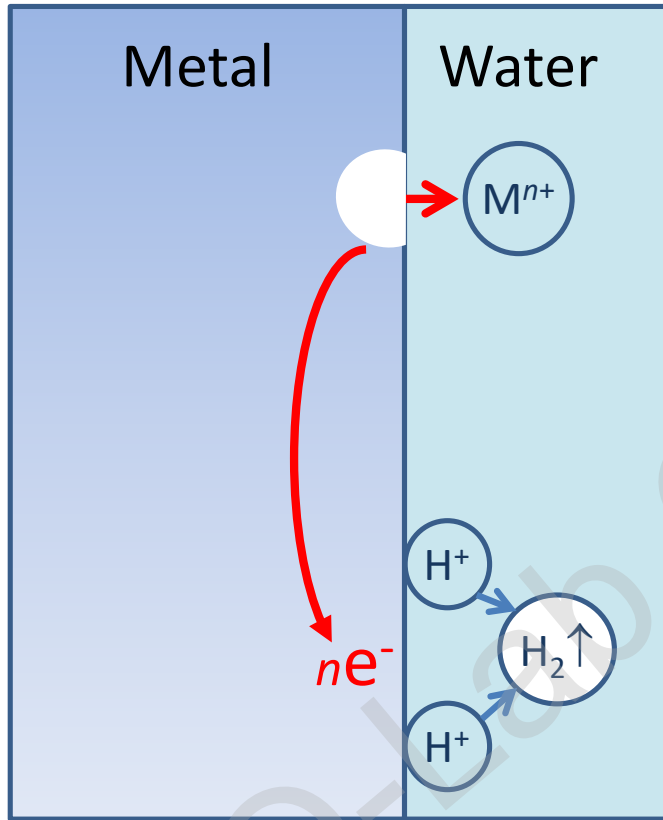
Examples of Reduction Reactions

	Reduction
Hydrogen “evolution”	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
Oxygen reduction	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4(\text{OH}^-)$
Oxygen reduction	$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$

Cathodic reactions consume the electrons lost by the metal

Oxidation & Reduction always balance in terms of electrical charge (electrons are conserved)

Oxidation & Reduction of a Metal



Oxidation

Metal atoms lose electrons and dissolve in a layer of water

Reduction

Electrons are consumed by an acceptor

Conditions for Corrosion to Occur

Anode	Source of electron in an oxidation reaction (where corrosion occurs)
Cathode	Where electrons are consumed in a reduction reaction
Electrolyte	Solution of ions in water, which provides a return path for negatively charged ions flowing to the anode
Electron flow	Conductive pathway for electron flow is a given for corrosion of metals

Acidity & Corrosion

- pH of a solution refers to concentration of hydrogen ions (H^+) in a water-based solution
 - Equilibrium reaction: $H_2O \leftrightarrow H^+ + OH^-$
 - $pH = -\log_{10}(H^+)$
 - pH of 7 is considered a “neutral” pH (pure water)
 - pH < 7 is **acidic**
 - pH > 7 is **basic**
- **Excess hydrogen ions are available to absorb electrons lost by metals when they are oxidized**

pH of Water in the Environment

- Carbon Dioxide (CO_2) exists in equilibrium with the atmosphere and water in the environment
- In water, it reacts to form carbonic acid:

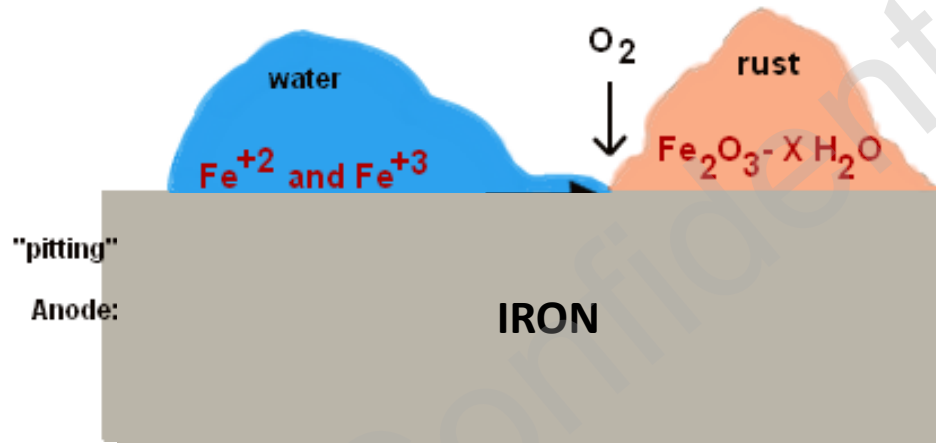


- Carbonic acid may lose one or two protons in water (*reduction*):



pH of rain water is about 5.6 (weak acid) because of this equilibrium, even without pollutants

Iron Corrosion Cell



Anodic Reactions (Oxidation)	Cathodic Reactions (Reduction)
$Fe^0 \rightarrow Fe^{2+} + 2e^-$	<i>Neutral or Alkaline Water</i>
$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$	$O_2 + 2H_2O + 4e^- \rightarrow 4(OH^-)$
$Fe^{2+} \rightarrow Fe^{3+} + e^-$	<i>Acidic Water</i>
	$2H^+ + 2e^- \rightarrow H_2$ $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Reaction Rate-Limiting Factors

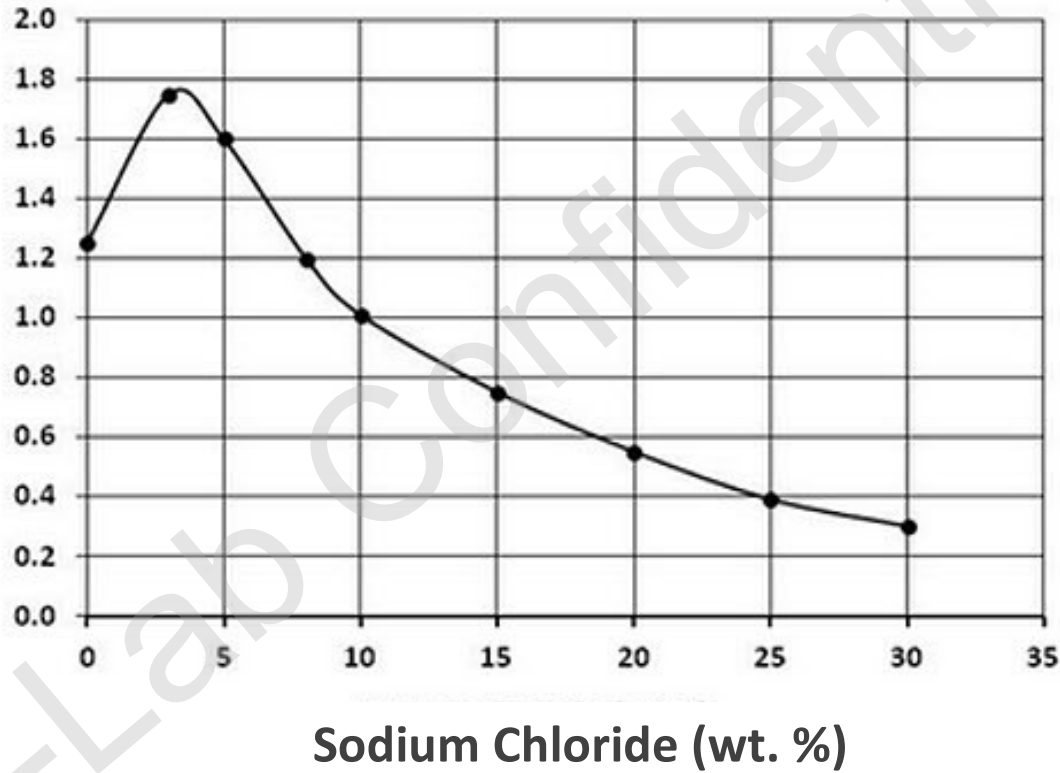
- Oxidation & Reduction must always balance
- Corrosion slows down when either one of these is limited
- This can be caused by:
 - decreased concentration of dissolved oxygen (O_2)
 - decreased concentration of hydrogen ions (H^+) and/or increased hydroxyl (OH^-) ion concentration
- *Increased ion concentrations drive out dissolved oxygen.
However ...*

Chlorides, Sulfates, and Corrosion

- Chlorine and sulfate ions in solution facilitate charge transfer between anode and cathode, accelerating corrosion
- Corrosion products include:
 - FeCl_2
 - FeCl_3
 - $\text{Fe}(\text{SO}_4)$
 - $\text{Fe}(\text{SO}_4)\text{OH}$
 - *Many more*

Corrosion of Steel vs. Salt Concentration

Corrosion Rate
(mm/yr)



Corrosion acid/base chemistry

- Electrochemistry doesn't fully describe corrosion product formation
- **Lewis acid-base** concept is an additional chemistry that completes it

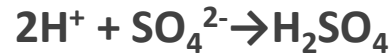
Lewis Acids & Bases

- **Lewis acids** accept electron pairs
- **Lewis bases** donate electron pairs
- Resulting molecule includes a covalent bond (sharing of an electron pair)
- *These reactions, combined with electrochemistry, describe corrosion*

Lewis Acid/Base Pairs

Hardness	Lewis Acid (e- receptors)	Lewis Base (e- donors)
Soft	Cu ⁺ Ag ⁺	H ₂ S HS ⁻
Intermediate	Fe ²⁺ Ni ²⁺ Cu ²⁺ Zn ²⁺ Pb ²⁺	SO ₃ ²⁻ NO ₂ ⁻ Cl ⁻ NH ₃
Hard	H ⁺ Na ⁺ Mn ²⁺ Al ³⁺ Cr ³⁺ Fe ³⁺ Ti ⁴⁺	H ₂ O OH ⁻ O ₂ ⁻ SO ₄ ²⁻ NO ₃ CO ₃ ²⁻

Electron sharing occurs between species with similar electron valences (“hard” or “soft”). Examples:



Acid/Base Reactions in Iron Corrosion



- Oxidation products are formed in these reactions
 - *No oxidation/reduction is taking place*

Oxidation/Reduction vs. Acid/Base

- **Oxidation/Reduction** electrochemical reactions are not spontaneously reversible (they need energy to be reversed)
- Lewis **Acid/Base** chemical reactions exist as an equilibrium (they are reversible)
- Both processes take place in **Atmospheric Corrosion**

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Corrosion varieties

Cosmetic corrosion

- Paint Protection
- High Moisture
- Road Splash Effect



Structural Corrosion

- No UV
- Parts may not be coated



General or “Free” Corrosion



- Relatively uniform corrosion, occurs at a decreasing rate over time
- Measured in $\text{mg}/\text{m}^2/\text{year}$ (mass) or $\mu\text{m}/\text{year}$ (thickness)
- Typically a corrosion rate is designed into the system

General Corrosion



Galvanic Series (ASTM G82)

Magnesium
Zinc
Aluminum
Cast Iron/low carbon steel
Steel (low alloy)
Brass
Copper
Nickel
Stainless Steel
Silver
Gold
Platinum

Active (Anode)

Negative

Corrosivity

Electrochemical
Potential

Noble (Cathode)

Positive

Galvanic Corrosion



Galvanic Series may change depending on environment

ASTM G82 describes a galvanic series for seawater and how to develop & use series for other environments

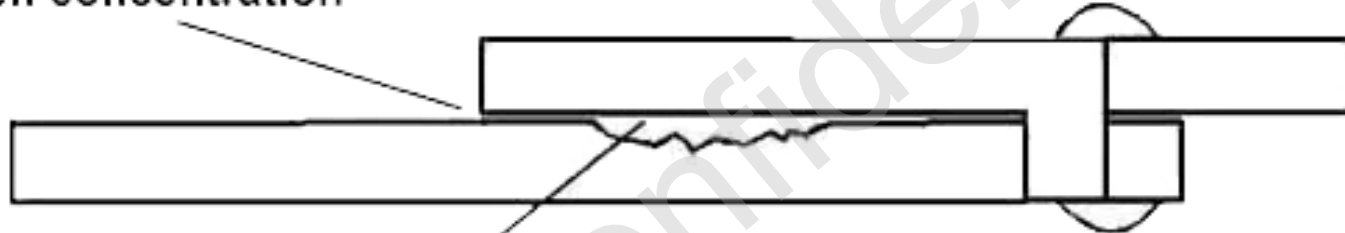
Crevice Corrosion



Localized corrosion in areas with limited access to oxygen relative to adjoining areas

Crevice Corrosion

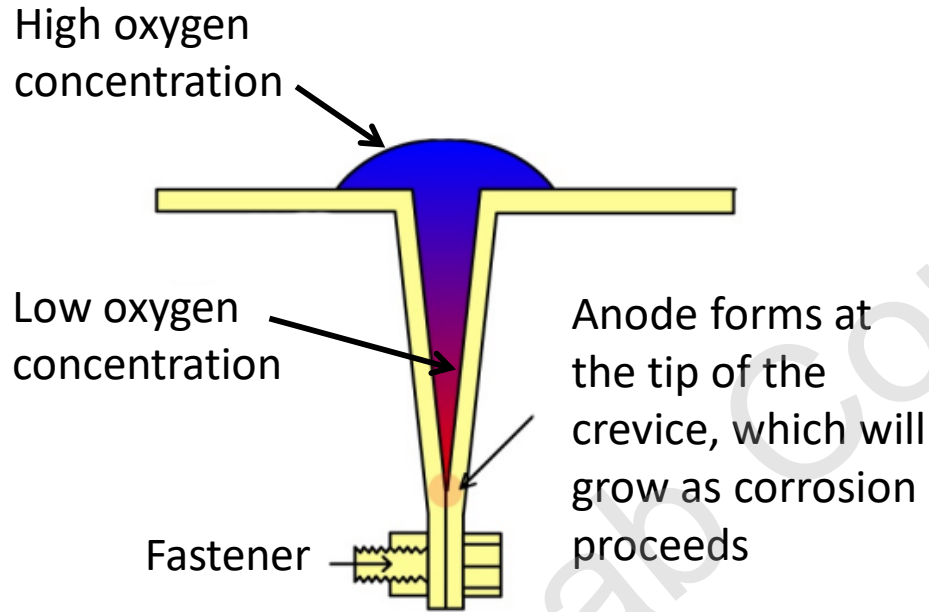
Relatively higher oxygen concentration



Low oxygen concentration area

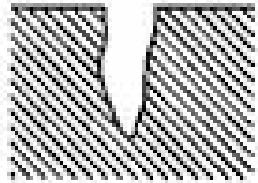
The driver of this corrosion is called an **oxygen concentration cell**; less oxygen is available for reduction, making the site anodic relative to the area with higher oxygen concentration

Crevice Corrosion

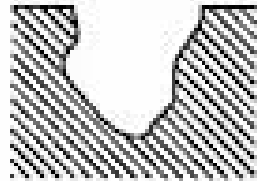


- Crevice corrosion is a good example of why testing **assemblies** rather than materials is often a good idea
- This diagram shows how crevice corrosion is related to the next type, pitting

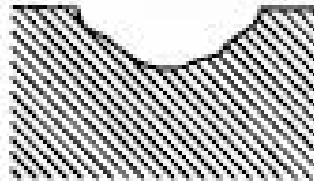
Pitting Corrosion



Narrow, Deep



Elliptical



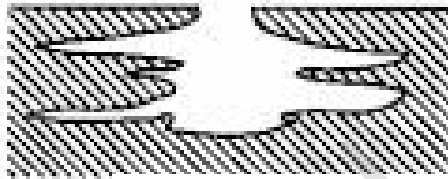
Wide, Shallow



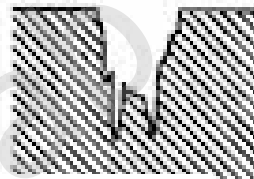
Subsurface



Undercutting



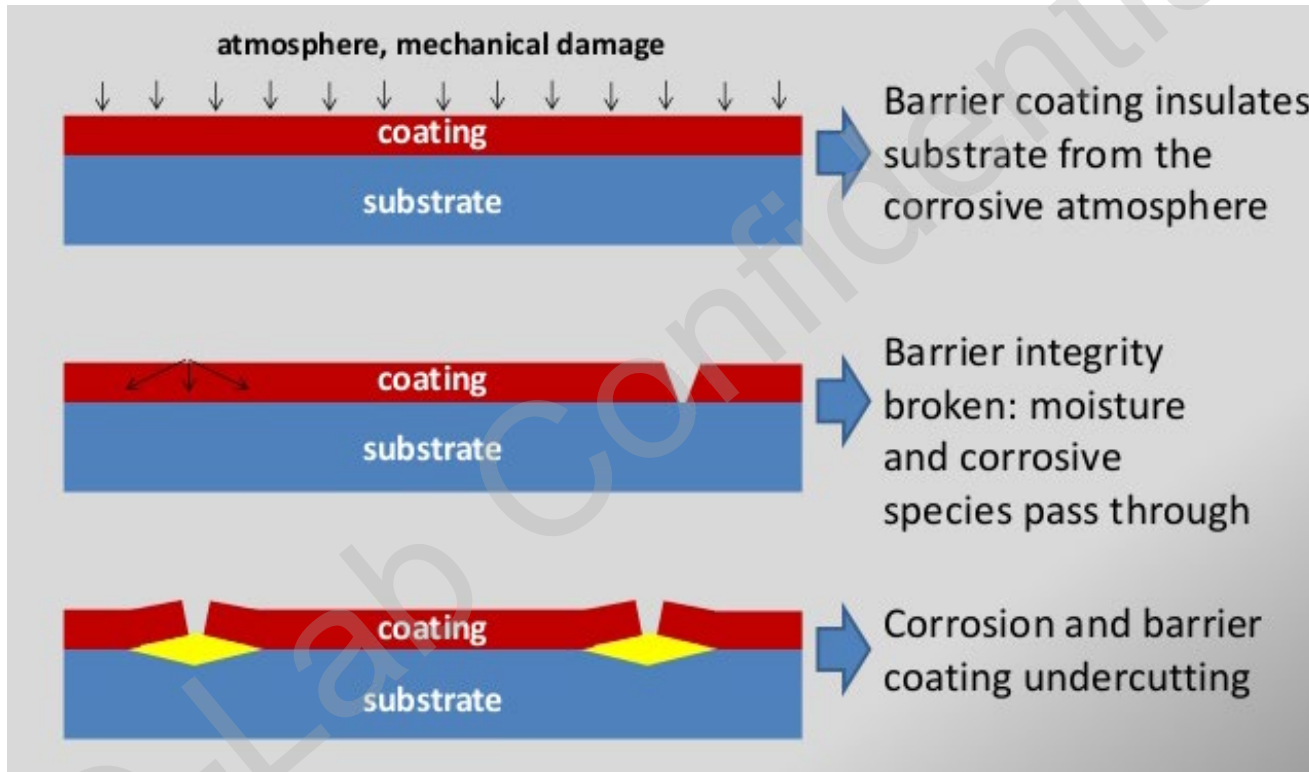
Horizontal



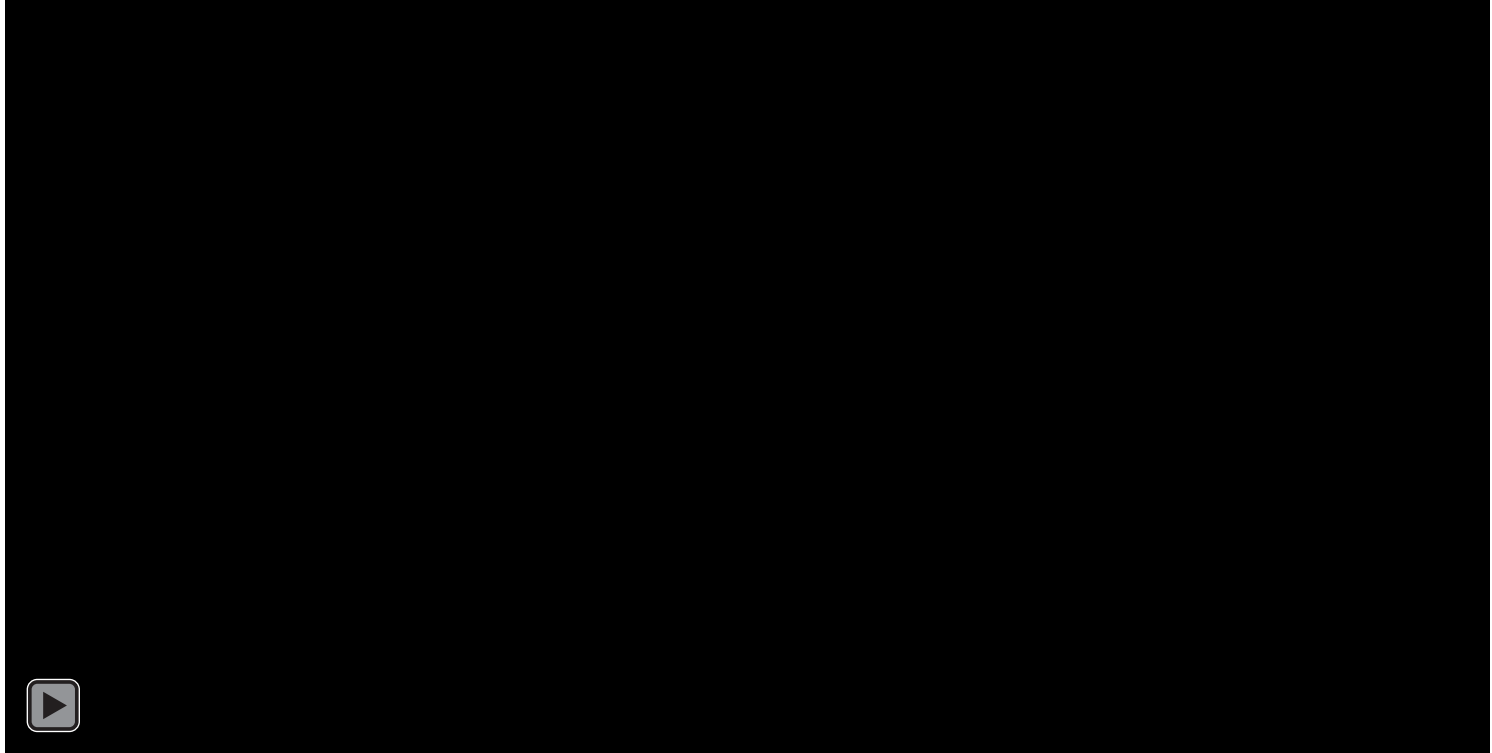
Vertical

- Localized corrosion that typically occurs in passivated or coated metals
- Oxygen-deprived areas create acids (a type of crevice corrosion)

Underfilm corrosion mechanics



Pitting Corrosion



Pitting Corrosion

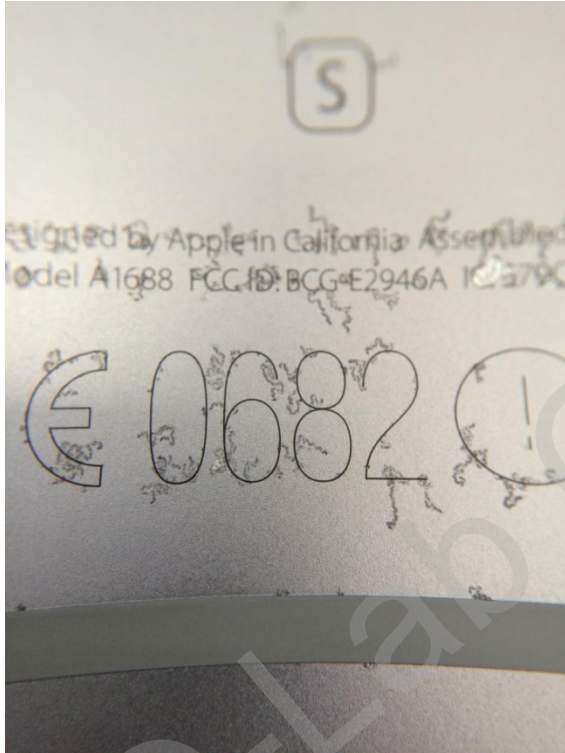


Filiform Corrosion

- Thread-like corrosion cell underneath a coating
- Difficult to re-create in the laboratory
- Often just a cosmetic problem, but sometimes...
- May lead to more significant coating delamination

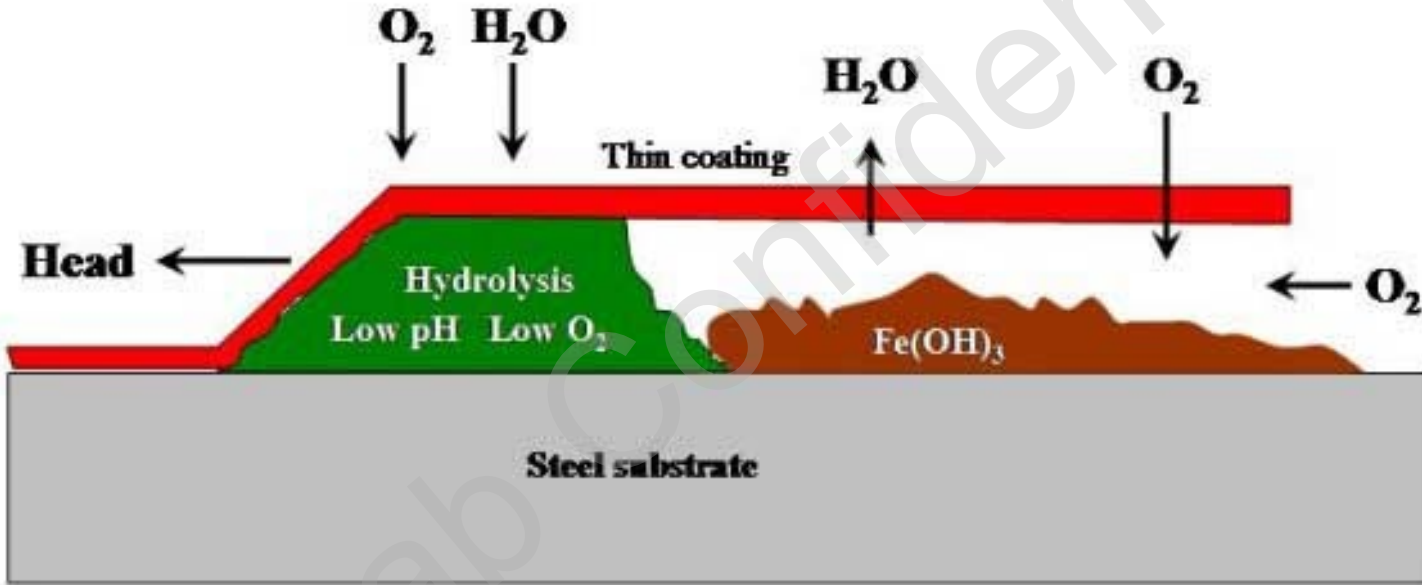


Filiform Corrosion



Filiform corrosion on the aluminum body of a smartphone

Filiform Corrosion on Steel



Cross sectional view of a corrosion filament on a steel substrate

Filiform/Underfilm Corrosion



Underfilm corrosion on a car (steel) and



Filiform corrosion on a helicopter (aluminum)

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Passivation

- Corrosion products, usually oxides, of some metals are relatively stable and corrosion-resistant
- A thin oxide layer, sometimes invisible, is corroded onto the surface and provides protection against additional corrosion
- This is called **passivation** and can occur either spontaneously in the atmosphere or artificially

Corrosion Evolution Over Time

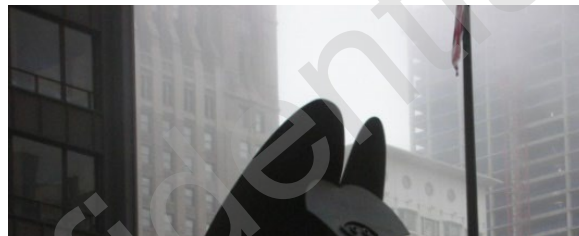
- Fully-evolved corrosion products, called **patinas**, offer some protection of remaining metal
- Protection can be significant, depending on corrosion product properties:
 - Crystalline structure & porosity
 - Electrical conductivity
- Creating artificial patinas is one example of passivation



Passivation

Protective oxides occur spontaneously on the following:

- Aluminum
- Titanium
- Zinc
- Stainless steel
- “Weathering steel”



Conversion Coatings

Protective oxides can also be intentionally created using acid baths to convert surface layers of metal to protective oxides:

- Removing free iron from stainless steel surface
- Phosphating of iron, zinc
- Chromating (steel, Al, Zn, Cu, Mg, Sn)
- Anodizing (Al, Ti, Mg, Zr)
- Black oxide on steel (including “bluing”)

Passivation



Stainless steel and other metals can be immersed in an acid bath to maximize the protective oxide film after machining operations

Paint 😊



Paint ☹️

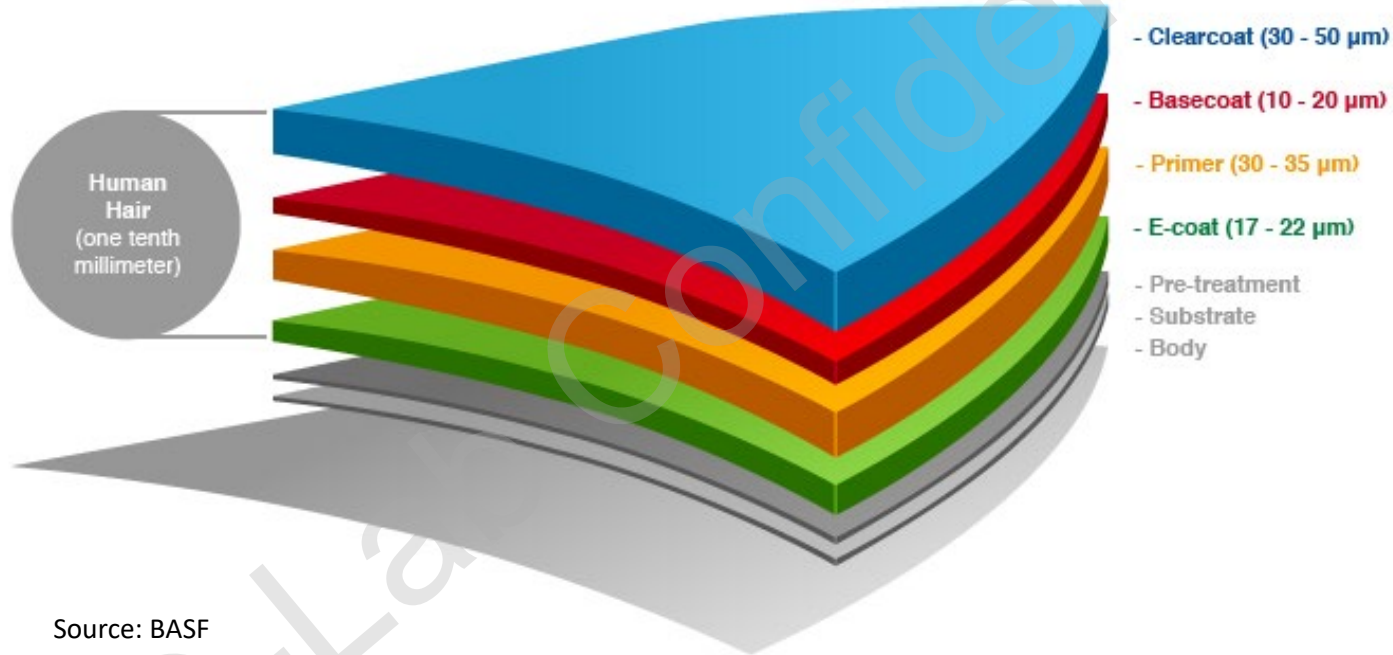


Organic Coatings (Paint)

- Probably most laboratory corrosion tests are performed on organic coatings
- Sunlight exposure can be an issue – may want to combine corrosion test with weathering testing
- Many types of paint are used

Organic Protective Coatings

Typical automotive coating system



Source: BASF

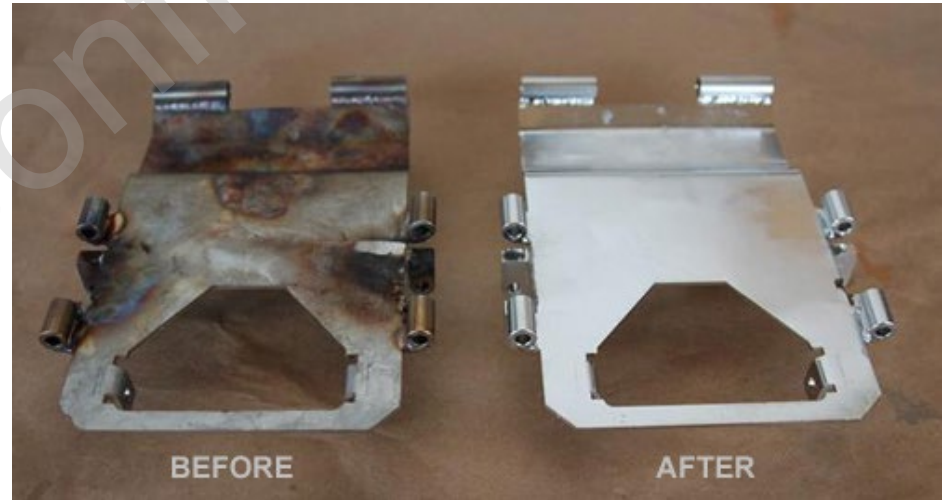
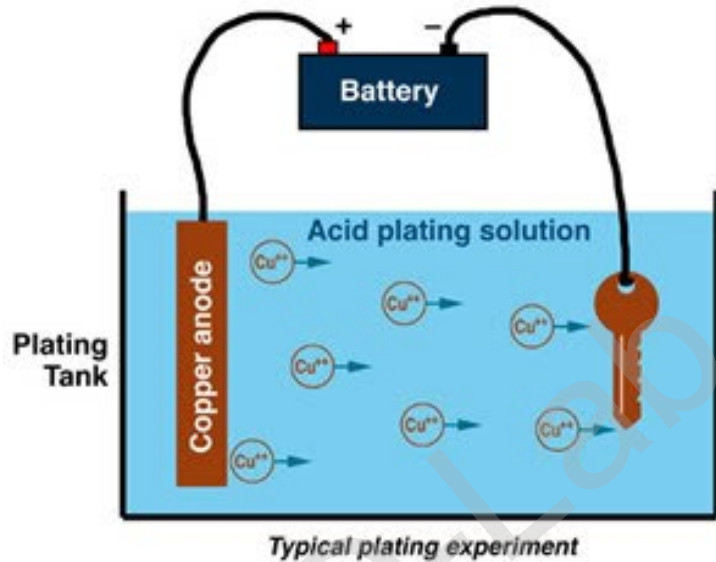
Sacrificial (anodic) Coatings

Galvanizing – Zinc plated onto steel via hot dip or electroplating process serves as the anode in a steel/zinc couple



Noble Metal Coatings

Electroplating - Galvanic cell acting in reverse, created by applying current to the metal intended to be plated onto another.



Conclusions

Atmospheric Corrosion: Chemistry

Corrosion of metals always involves two types of chemistry:

- **Oxidation/Reduction** (REDOX) electrochemistry
- **Lewis Acid/Base** chemistry

Atmospheric Corrosion: Key Factors

Corrosion is affected by:

- Acidity (pH) of solutions
- Availability & diffusion of oxygen
- Concentration & diffusion of other oxidizing agents
- Geometry of construction

Atmospheric Corrosion: Types

Atmospheric Corrosion can take many forms:

- General or “free” corrosion
- Galvanic
- Crevice
- Pitting
- Intergranular
- Exfoliation
- Filiform
- Stress

Atmospheric Corrosion: Mitigation

Atmospheric Corrosion can be mitigated a number of ways:

- Passivation
- Conversion Coatings (pretreatments)
- Organic Coatings (Paint)
- Sacrificial Coatings (galvanizing)
- Metal (Noble) Coatings
- Mechanical Design

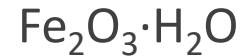
Atmospheric Corrosion: Complexity

Corrosion of steel under atmospheric exposure

- Each metal has unique corrosion properties and pathways; very difficult to predict.
- Understanding atmospheric corrosion requires multiple scientific disciplines



Ingredients:



secret spices

Questions?



info@q-lab.com