Introduction to Atmospheric Corrosion
Causes, Effects, and Prevention
大气腐蚀概论：成因，影响以及防护

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Introduction to Atmospheric Corrosion
大气腐蚀概论

- Thermodynamics & Definitions of Corrosion

腐蚀的定义（热力学解释）

- Chemistry of Corrosion

腐蚀的化学理论

- Forms of Atmospheric Corrosion

大气腐蚀的形态

- Mitigation of Corrosion

腐蚀的减缓

What Is Corrosion?
什么是腐蚀

Corrosion is the force driving a material towards its natural, lowest-energy state.*
腐蚀是将材料推向其自然、最低能量状态的一种力

Corrosion is *an electrochemical process that returns refined metals to their natural oxide states*
腐蚀是一种电化学过程，它使精炼金属恢复到它们的天然氧化状态

**European Coil Coating Association*

What Is *Atmospheric* Corrosion?
什么是大气腐蚀

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.

大气腐蚀发生在金属表面的那层水膜中。湿膜可能很薄，以至于肉眼看不到

-ISO 9223

Corrosion and Thermodynamics
腐蚀的热力学解释

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

腐蚀是一个热力学过程，通过这个过程系统被驱动到它们的最低能量状态

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

我们来回顾下热力学第二定律以更好地理解腐蚀

Second Law of Thermodynamics
热力学第二定律

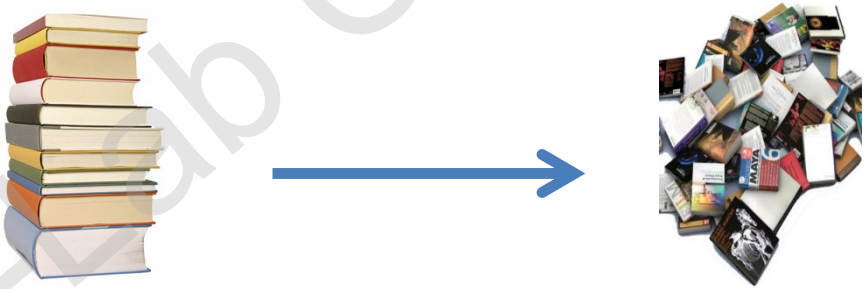
"The total **entropy** of an isolated system can never decrease over time."
孤立系统的总熵永远不会随着时间而减少

- "Entropy" can be thought of as "disorder"

熵可以被认为是一种无序

- The natural tendency of any isolated system is to degenerate into a more disordered state (higher entropy)

任何孤立系统的自然倾向是到一个更无序的状态(更高的熵)



Thermodynamics & Corrosion
腐蚀的热力学解释

- Nearly all metals in nature exist as oxides because this is the **lowest-energy** state

自然界中几乎所有的金属都以氧化物的形式存在，因为氧化物是能量最低的状态

- Refining metals requires heat energy to break apart the oxide molecule

精炼金属需要热能来分解氧化物分子

- Once exposed to nature, refined metals begin reverting back to lower-energy states, some form of metal oxide or a salt

一旦暴露在大自然中，精炼的金属就会恢复到低能状态，变成某种形式的金属氧化物或盐

Corrosion Examples

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Corrosion of Metals
金属的腐蚀

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

热力学上，金属的腐蚀是精炼金属向低能量状态的氧化物和氢氧化物状态的回归

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

涉及到电化学腐蚀和酸碱理论

Corrosion Chemistry of Iron
铁的腐蚀

- The corrosion chemistry presented in this section is general to any metal

本节介绍的腐蚀化学对任何金属都是通用的

- Iron (Fe) is used throughout as an example because it is used widely, corrodes readily, and displays complex corrosion behavior

本课件以铁(Fe)作为一个例子，因为它使用广泛，容易腐蚀，并表现出复杂的腐蚀行为

Ions of Iron
铁离子

Fe^{2+}	Iron(II)	Ferrous ion亚铁离子
Fe^{3+}	Iron(III)	Ferric ion 铁离子

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

亚铁离子自由地给氧一个电子变成一个铁离子，所以氧化铁和氢氧化物是最常见的

Iron Occurs Naturally in Different States
铁自然存在的不同形式

Oxides (dry or *anhydrous*) 氧化物

Hematite 赤铁矿	Fe_2O_3	Iron(III) oxide
Magnetite 磁铁矿	Fe_3O_4	Iron(II,III) oxide ($FeO \cdot Fe_2O_3$)
Wuestite 方铁矿	FeO	Iron(II) oxide (rare near Earth's surface)

Hydrated oxides and oxide-hydroxides 水合氧化物和氧化氢氧化物

Goethite 针铁矿	FeO(OH)	Iron(III) oxide-hydroxide
Limonite 褐铁矿	$FeO(OH) \cdot nH_2O$	(hydrated form)

Iron minerals have crystalline and amorphous forms.
Hydrated compounds include water molecules within the crystal structure.
铁矿物有结晶和非晶形态。水合化合物在晶体结构中含有水分子

Electrochemistry of Corrosion
腐蚀电化学

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

腐蚀是一个多步骤的过程，由两种反应引起

Oxidation 氧化反应 *Loss* of an electron 失去电子

Reduction 还原反应 *Gain* of an electron 得到电子

*mnemonic device: "**OIL RIG**"*

Oxidation of Metals
金属的氧化

$$M^0 \rightarrow M^{n+} + ne^-$$

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

n是金属离子的价或是在氧化过程中失去的电子数

Examples of Metal Oxidation Reactions
金属氧化

Oxidation of Metals
$Fe^0 \rightarrow Fe^{2+} + 2e^-$
$Fe^0 \rightarrow Fe^{3+} + 3e^-$
$Fe^{2+} \rightarrow Fe^{3+} + e^-$
$Al^0 \rightarrow Al^{3+} + 3e^-$
$Zn^0 \rightarrow Zn^{2+} + 2e^-$

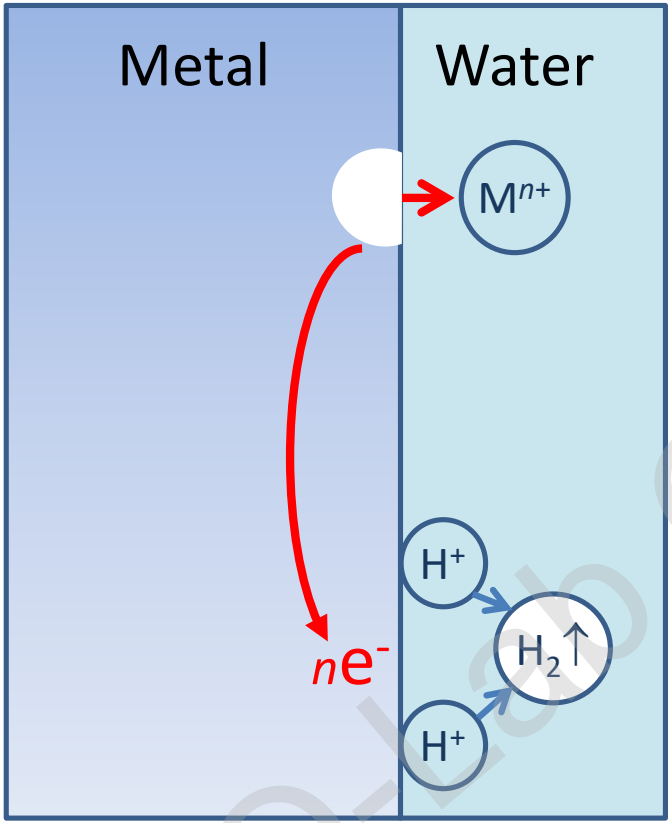
These *anodic* reactions initiate corrosion of steel, aluminum, and zinc
这些阳极反应引起钢、铝和锌的腐蚀

Examples of Reduction Reactions
还原反应

Reduction	
Hydrogen “evolution” 析氢	$2H^+ + 2e^- \rightarrow H_2$
Oxygen reduction 吸氧	$O_2 + 2H_2O + 4e^- \rightarrow 4(OH^-)$
Oxygen reduction 氧还原	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Cathodic reactions consume the electrons lost by the metal
阴极反应消耗金属失去的电子
Oxidation & Reduction always balance in terms of electrical charge (electrons are conserved)
氧化和还原总是在电荷方面保持平衡(电子守恒)

Oxidation & Reduction of a Metal



Oxidation 氧化反应

Metal atoms lose electrons and dissolve in a layer of water

金属原子失去电子，溶解在一层水里

Reduction 还原反应

Electrons are consumed by an acceptor

电子被受体消耗

Conditions for Corrosion to Occur
发生腐蚀的条件

Anode 阳极	Source of electron in an oxidation reaction (where corrosion occurs) 氧化反应中的电子来源(在发生腐蚀的地方)
Cathode 阴极	Where electrons are consumed in a reduction reaction 还原反应中电子被消耗
Electrolyte 电解质	Solution of ions in water, which provides a return path for negatively charged ions flowing to the anode 离子在水中，为带负电荷的离子流动到阳极提供了路径
Electron flow 电子流	Conductive pathway for electron flow is a given for corrosion of metals 电子流动的导电通道是金属腐蚀的必经之路

Acidity & Corrosion
酸和腐蚀

- pH of a solution refers to concentration of hydrogen ions (H^+) in a water-based solution

pH是指水溶液中氢离子(H+)的浓度

  - Equilibrium reaction: $\mathbf{H_2O \leftrightarrow H^+ + OH^-}$
  - $pH = -\log_{10}(H^+)$
    - 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**

多余的氢离子可以吸收金属氧化时失去的电子

pH of Water in the Environment
环境中水的pH值

- Carbon Dioxide (CO_2) exists in equilibrium with the atmosphere and water in the environment

二氧化碳(CO2)与大气和环境中的水处于平衡状态

- In water, it reacts to form carbonic acid: 在水中，它会发生反应生成碳酸

$$CO_{2\ (aq)} + H_2O \leftrightarrow H_2CO_{3\ (aq)}$$

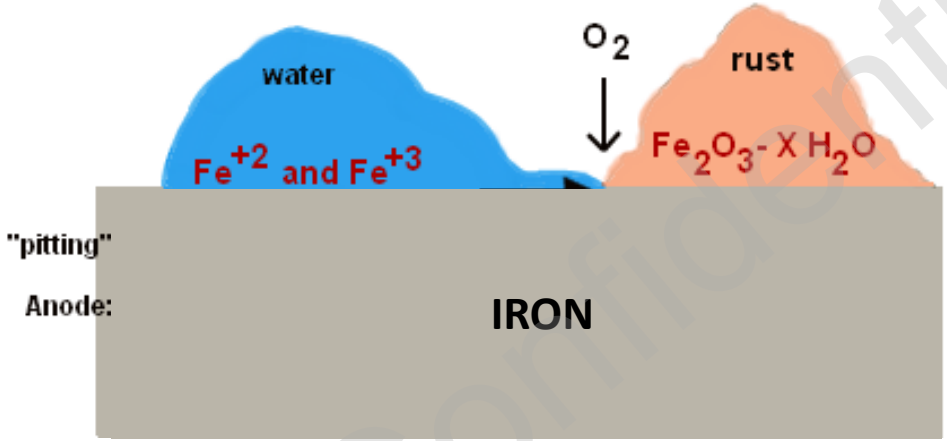
- Carbonic acid may lose one or two protons in water *(reduction):*碳酸在水中会失去一到两个质子(还原)

$$H_2CO_{3\ (aq)} \leftrightarrow H^+_{\ (aq)} + HCO_3^-{}_{\ (aq)}$$
$$HCO_3^-{}_{\ (aq)} \leftrightarrow H^+_{\ (aq)} + CO_3^{2-}{}_{\ (aq)}$$

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

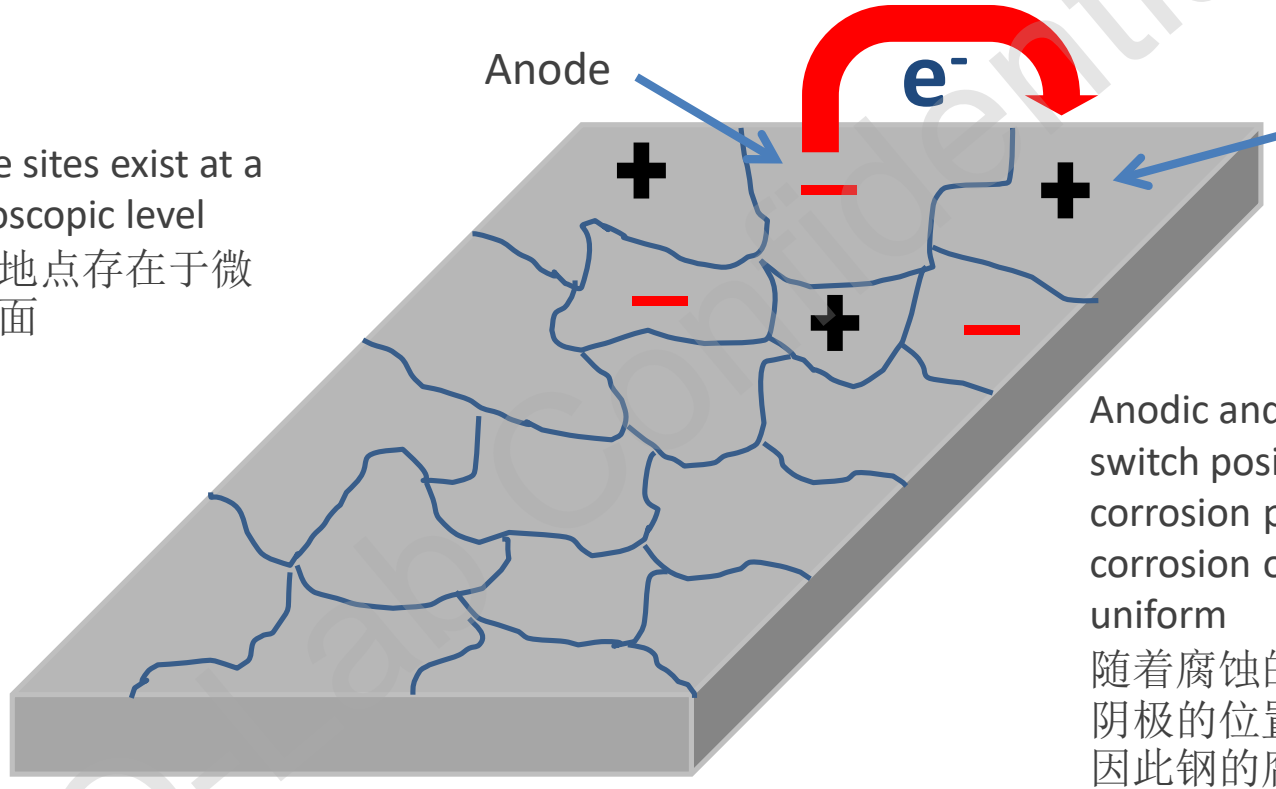
由于这种平衡，雨水的pH值约为5.6(弱酸)，即使没有污染物

Iron Corrosion Cell



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

Alternating Anodic / Cathodic Surface Sites



These sites exist at a microscopic level
这些地点存在于微观层面

Anodic and Cathodic sites switch positions as corrosion proceeds, so corrosion of steel appears uniform
随着腐蚀的进行，阳极和阴极的位置会发生切换，因此钢的腐蚀呈现均匀性

Reaction Rate-Limiting Factors

- Oxidation & Reduction must always balance

氧化和还原必须始终保持平衡

- Corrosion slows down when either one of these is limited

当这两者中的任何一种受到限制时，腐蚀就会减慢

- This can be caused by:
  - decreased concentration of dissolved oxygen (O_2) 溶解氧(O2)浓度降低
  - decreased concentration of hydrogen ions (H^+) and/or increased hydroxyl (OH^-) ion concentration
    氢离子(H+)浓度降低或氢氧根离子(OH-)浓度升高

- *Increased ion concentrations drive out dissolved oxygen. However …*

离子浓度增加会驱逐溶解氧

Chlorides, Sulfates, and Corrosion
氯化物，硫酸盐和腐蚀

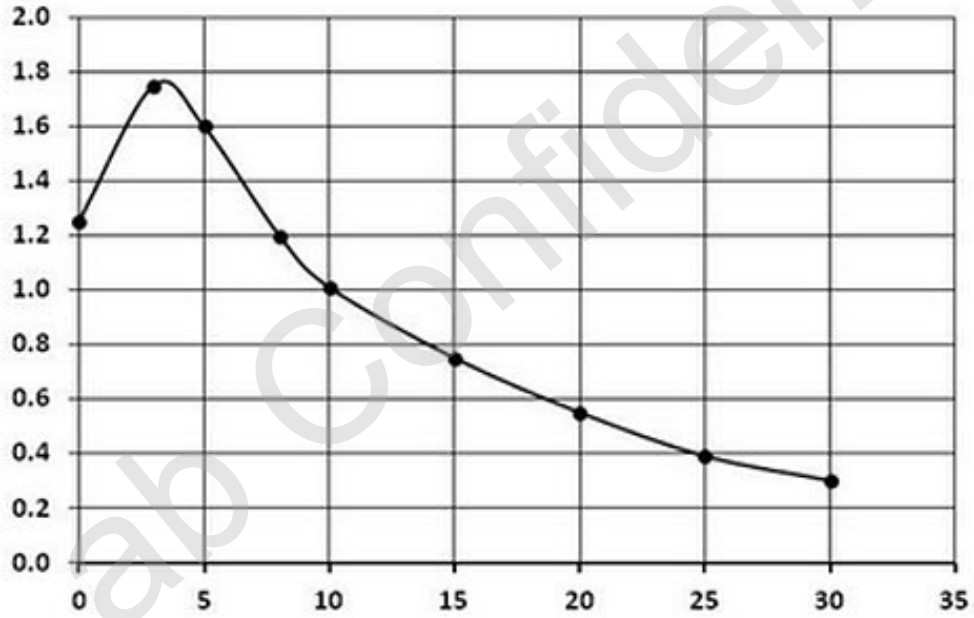
- Chlorine and sulfate ions in solution facilitate charge transfer between anode and cathode, accelerating corrosion

溶液中的氯离子和硫酸盐离子有助于阳极和阴极之间的电荷转移，加速腐蚀

- Corrosion products include:
  - $FeCl_2$
  - $FeCl_3$
  - $Fe(SO_4)$
  - $Fe(SO_4)OH$
  - *Many more*

Corrosion of Steel vs. Salt Concentration
钢的腐蚀与盐浓度的关系

Corrosion Rate (mm/yr)



Sodium Chloride (wt. %)

Corrosion acid/base chemistry
酸碱理论

- Electrochemistry doesn't fully describe corrosion product formation

电化学不能完全描述腐蚀产物的形成

- **Lewis acid-base** concept is an additional chemistry that completes it

路易斯酸碱理论是对它的补充

Lewis Acids & Bases
路易斯酸碱理论

- **Lewis acids** accept electron pairs

路易斯酸接受电子对

- **Lewis bases** donate electron pairs

路易斯碱提供电子对

- Resulting molecule includes a covalent bond (sharing of an electron pair)

得到的分子包含一个共价键(共享一对电子)

- ***These reactions, combined with electrochemistry, describe corrosion***

这些反应，加上电化学，完整描述了腐蚀

Lewis Acid/Base Pairs

Hardness	Lewis Acid (e- receptors)	Lewis Base (e- donors)
Soft	Cu^{+} Ag^{+}	H_2S 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_2O OH^{-} O_2^{-} SO_4^{2-} NO_3 CO_3^{2-}

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

$$Fe^{2+} + 2Cl^{-} \rightarrow FeCl_2 \qquad 2H^{+} + SO_4^{2-} \rightarrow H_2SO_4$$

Acid/Base Reactions in Iron Corrosion
铁腐蚀中的酸碱反应

$$Fe^{3+} + 3H_2O \leftrightarrow \boxed{Fe(OH)_3} + 3H^+$$

$$2Fe(OH)_3 \leftrightarrow \boxed{Fe_2O_3} + 3H_2O$$

$$Fe^{2+} + H_2SO_4 \leftrightarrow \boxed{FeSO_4} + H_2$$

$$Fe^{3+} + H_2SO_4 + OH^- \leftrightarrow \boxed{Fe(SO_4)(OH)} + H_2$$

- Oxidation products are formed in these reactions氧化产物在这些反应中形成
- *No oxidation/reduction is taking place 没有发生氧化还原反应*

Oxidation/Reduction vs. Acid/Base
氧化还原反应 vs. 酸碱理论

- **Oxidation/Reduction** electrochemical reactions are not spontaneously reversible (they need energy to be reversed)

氧化还原电化学反应不是自发可逆的(它们需要能量才能被可逆)

- Lewis **Acid/Base** chemical reactions exist as an equilibrium (they are reversible)

路易斯酸碱化学反应以平衡状态存在(它们是可逆的)

- Both processes take place in **Atmospheric Corrosion**

这两个过程都发生在大气腐蚀中

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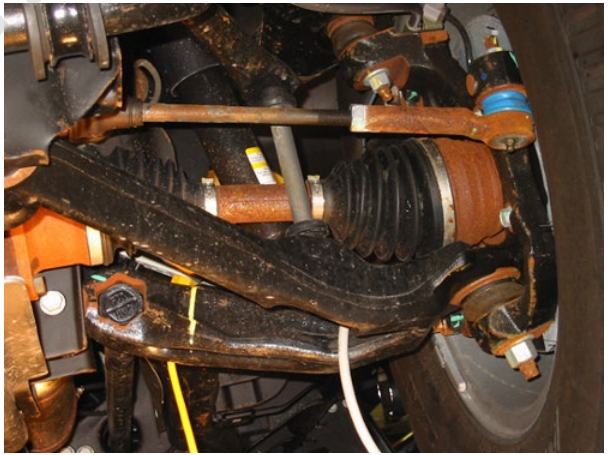
Corrosion varieties

Cosmetic corrosion 表面腐蚀

- Paint Protection 保护漆
- High Moisture 高湿
- Road Splash Effect 路面飞溅

Structural Corrosion 结构腐蚀

- No UV 没有紫外直接曝晒
- Parts may not be coated 可能没有涂层



General or “Free” Corrosion
全面腐蚀

- Relatively uniform corrosion, occurs at a decreasing rate over time

相对均匀的腐蚀，发生的速度随着时间的推移而降低

- Measured in $mg/m^2/year$ (mass) or µm/year (thickness)

以年腐蚀质量/厚度计算

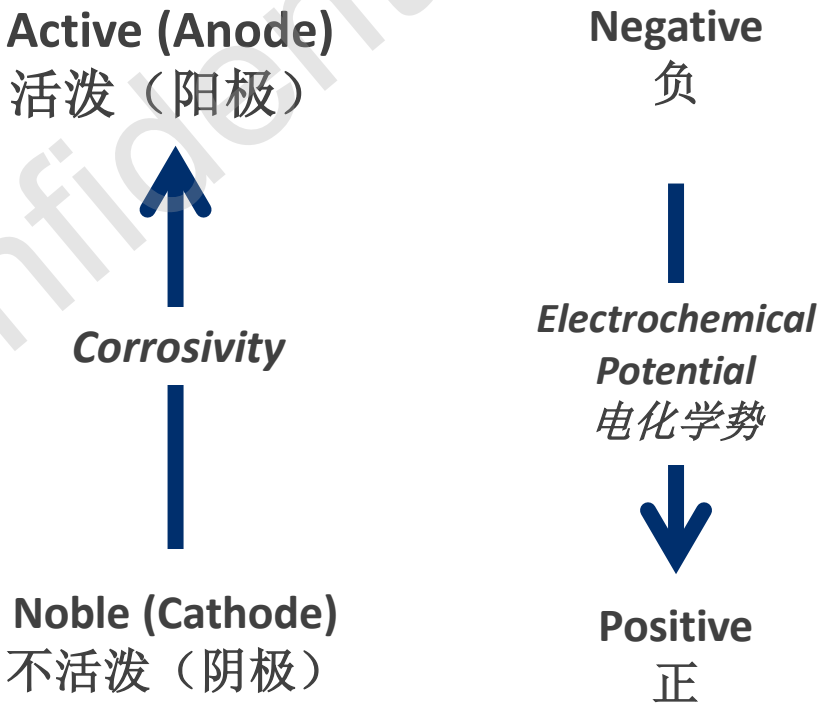
- Typically a corrosion rate is designed into the system

通常情况下，腐蚀速率被设计到系统中

General Corrosion

Galvanic Series (ASTM G82)
电位序

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



Galvanic Corrosion
电偶腐蚀

Galvanic Series may change depending on environment
电偶序可根据环境变化而变化

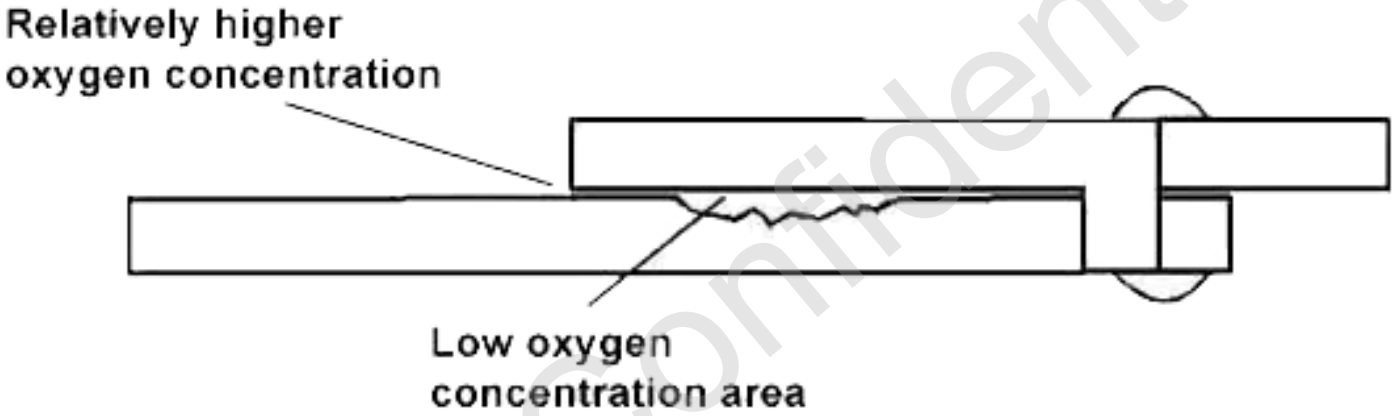
ASTM G82 describes a galvanic series for seawater and how to develop & use series for other environments
ASTM G82描述了用于海水的电偶序，以及如何开发和使用用于其他环境的电偶序

Crevice Corrosion
缝隙腐蚀

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

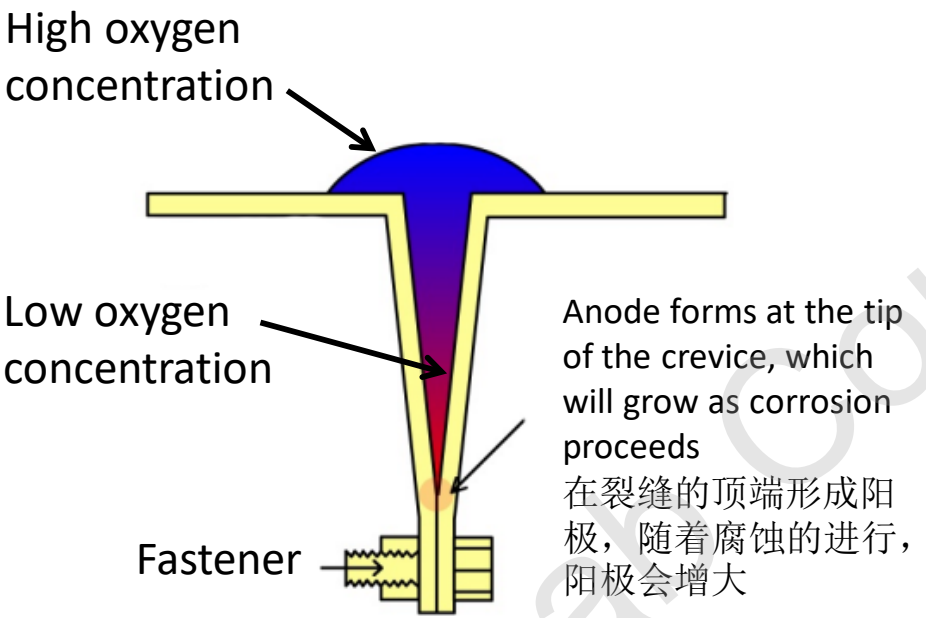
与邻近区域相比，接触氧气有限的区域出现局部腐蚀

Crevice Corrosion
缝隙腐蚀



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
这种腐蚀的驱动叫做氧浓度电池;可用于还原的氧气较少，该区域相对于氧浓度较高的区域会呈现为阳极

Crevice Corrosion
缝隙腐蚀



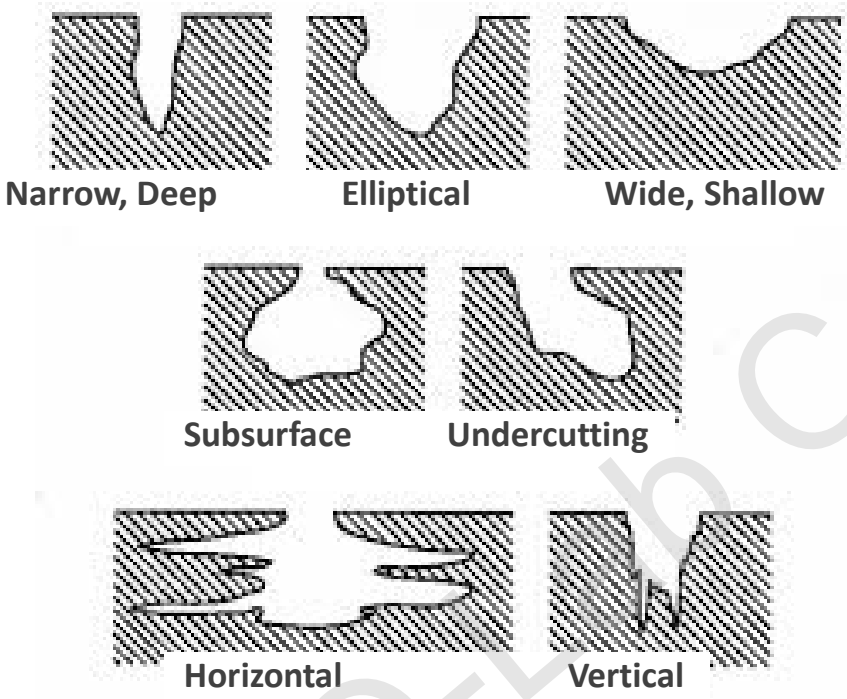
- Crevice corrosion is a good example of why testing **assemblies** rather than materials is often a good idea

裂缝腐蚀是一个很好的例子，说明为什么测试组件而不是材料通常是一个好主意

- This diagram shows how crevice corrosion is related to the next type, pitting

这张图显示了裂缝腐蚀与下一种类型点蚀的关系

Pitting Corrosion
点蚀



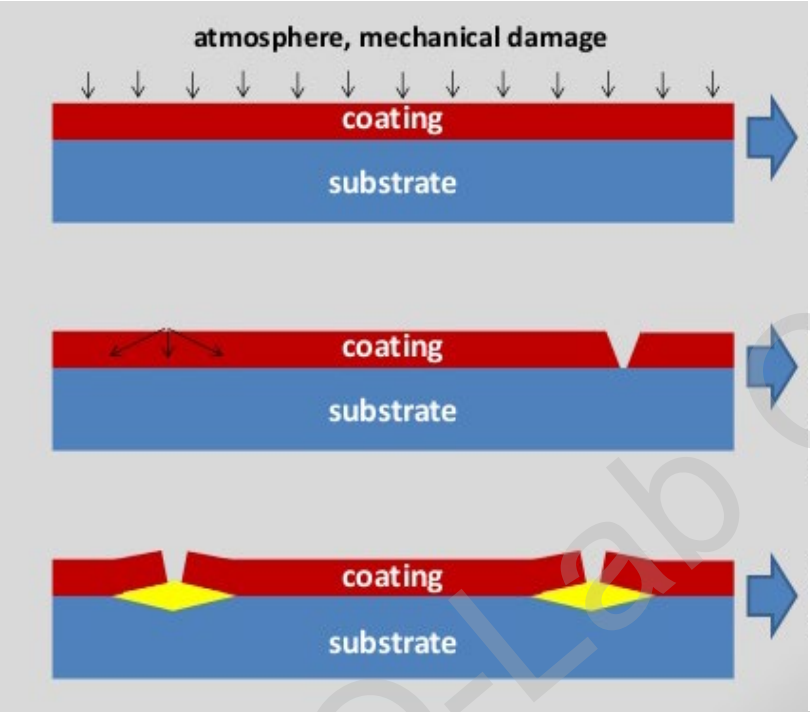
- Localized corrosion that typically occurs in passivated or coated metals

通常发生在钝化或涂层金属中的局部腐蚀

- Oxygen-deprived areas create acids (a type of crevice corrosion)

缺氧区域会产生酸(一种缝隙腐蚀)

Underfilm corrosion mechanics
膜下腐蚀



- Barrier coating insulates substrate from the corrosive atmosphere

障壁涂层使基材与腐蚀环境绝缘

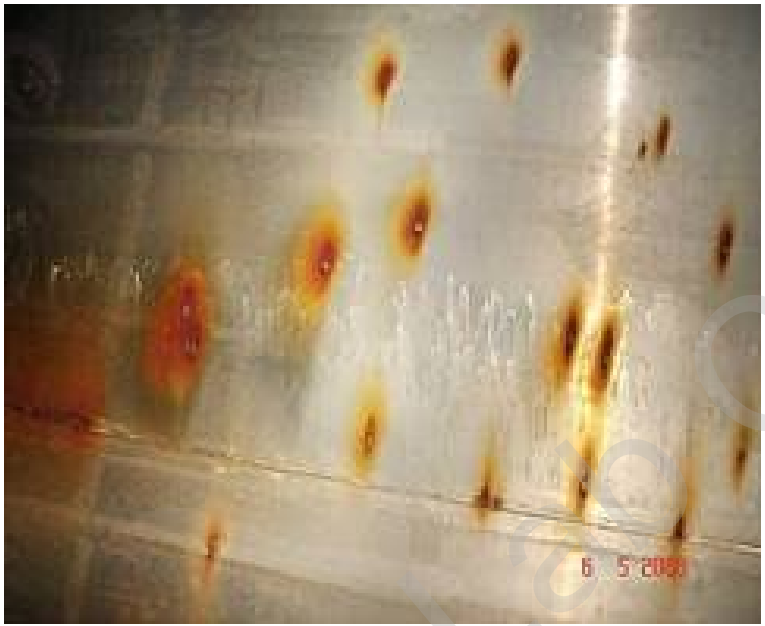
- Barrier integrity broken: moisture and corrosive species pass through

屏障完整性被破坏:水分和腐蚀性物质通过

- Corrosion and barrier coating undercutting

腐蚀和涂层破坏

Pitting Corrosion
点蚀



Pitting Corrosion
点蚀

Filiform Corrosion
丝状腐蚀

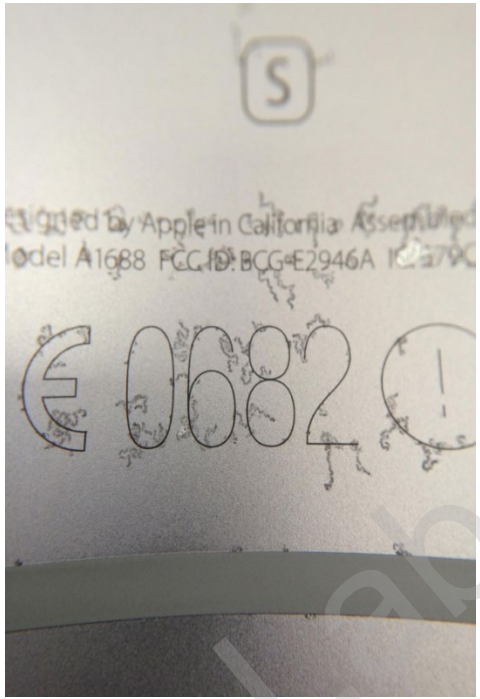
- Thread-like corrosion cell underneath a coating
涂层下的线状腐蚀

- Difficult to re-create in the laboratory
很难在实验室里重现

- Often just a cosmetic problem, but sometimes…
通常只是表面问题，但有时…

- May lead to more significant coating delamination
可能导致更明显的涂层分层

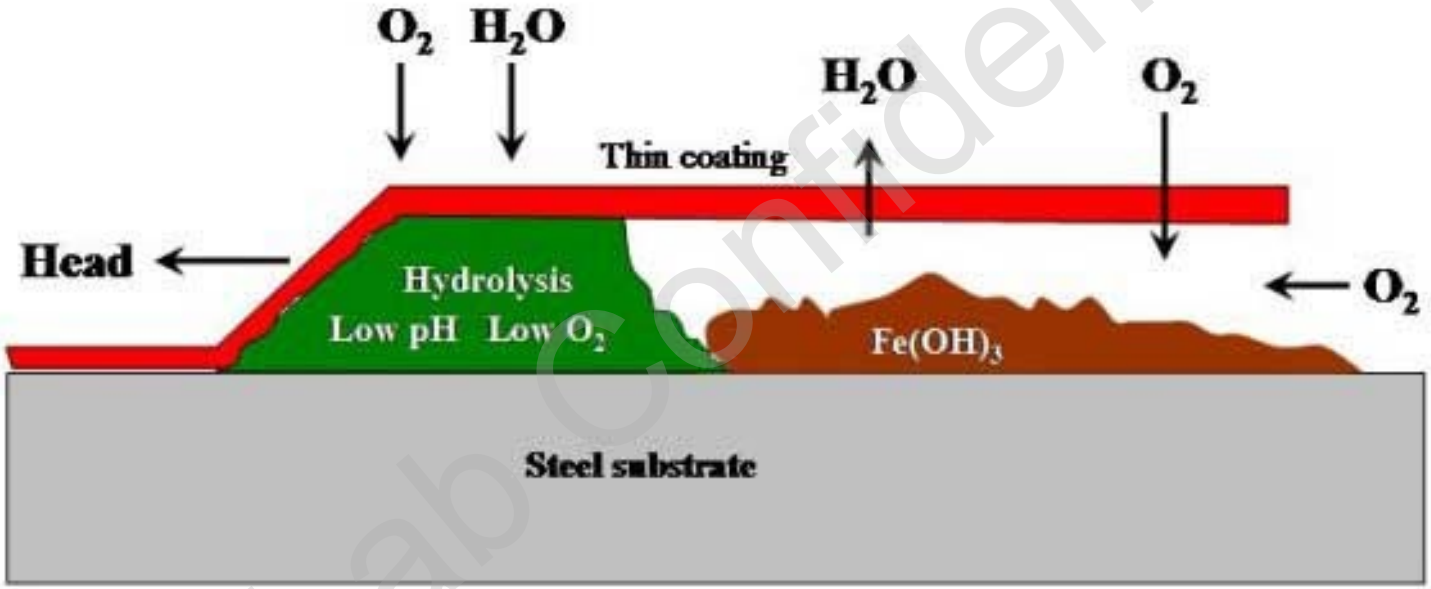
Filiform Corrosion
丝状腐蚀



Filiform corrosion on the aluminum body of a smartphone

智能手机铝制机身上的丝状腐蚀

Filiform Corrosion on Steel
钢铁上的丝状腐蚀



Cross sectional view of a corrosion filament on a steel substrate

Filiform/Underfilm Corrosion
丝状/膜下腐蚀

Underfilm corrosion on a car (steel) and

Filiform corrosion on a helicopter (aluminum)

汽车(钢)的膜下腐蚀和直升机(铝)的丝状腐蚀

Introduction to Atmospheric Corrosion
大气腐蚀概论

- Thermodynamics & Definitions of Corrosion

腐蚀的定义（热力学解释）

- Chemistry of Corrosion

腐蚀的化学理论

- Forms of Atmospheric Corrosion

大气腐蚀的形式

- Mitigation of Corrosion

腐蚀的减缓

Passivation
钝化

- Corrosion products, usually oxides, of some metals are relatively stable and corrosion-resistant

一些金属的腐蚀产物，通常是氧化物，是相对稳定的

- A thin oxide layer, sometimes invisible, is corroded onto the surface and provides protection against additional corrosion

一层薄的、有时看不见的氧化层被腐蚀在表面，并提供了防止进一步腐蚀

- This is called **passivation** and can occur either spontaneously in the atmosphere or artificially

这称为钝化，可以在大气中自发产生，也可以人为作用

Corrosion Evolution Over Time
腐蚀随时间的演变

- Fully-evolved corrosion products, called **patinas,** offer some protection of remaining metal

自发形成的铜绿，对金属提供一层保护

- Protection can be significant, depending on corrosion product properties:

可以很好起到保护，关键在于：

  - Crystalline structure & porosity 晶体结构和孔隙度
  - Electrical conductivity 导电性

- Creating artificial patinas is one example of passivation

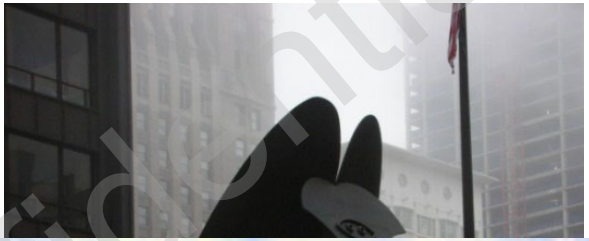
人造绿锈是钝化的一个例子

Passivation

Protective oxides occur spontaneously on the following:

保护性的氧化物会自发地在以下金属上发生

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



Conversion Coatings
转化膜

Protective oxides can also be intentionally created using acid baths to convert surface layers of metal to protective oxides:
保护性氧化物也可以人为使用酸浴将金属表层转化为保护性氧化物

- Removing free iron from stainless steel surface
去除不锈钢表面游离铁
- Phosphating of iron, zinc
铁、锌的磷化
- Chromating (steel, Al, Zn, Cu, Mg, Sn)
铬化处理
- Anodizing (Al, Ti, Mg, Zi)
阳极氧化
- Black oxide on steel (including “bluing”)
发蓝发黑处理

Passivation
钝化

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

不锈钢和其他金属可以浸在酸液中，以最大限度地提高加工后的氧化保护膜

Paint ☺

Paint ☹

Organic Coatings (Paint)
有机涂层

- Probably most laboratory corrosion tests are performed on organic coatings

可能大多数的实验室腐蚀试验都是在有机涂层上进行的

- Sunlight exposure can be an issue – may want to combine corrosion test with weathering testing

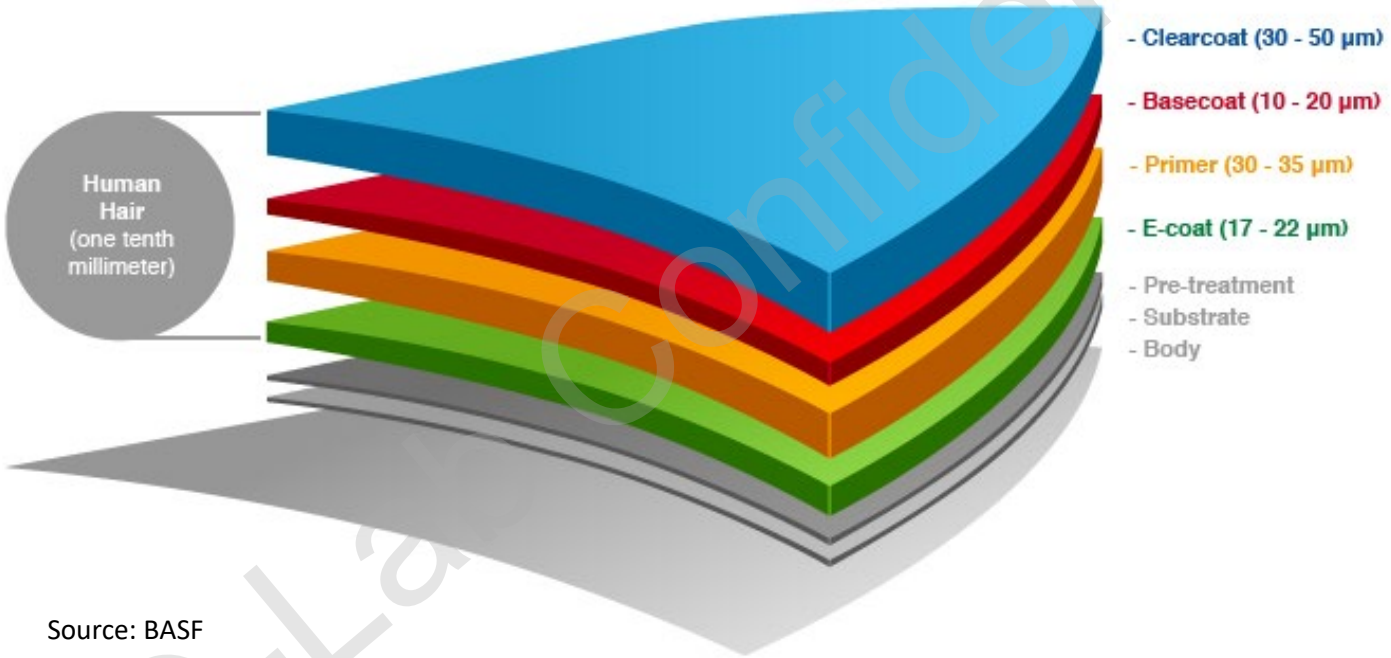
阳光照射可能是一个问题，可能需要结合腐蚀测试和紫外测试

- Many types of paint are used

使用多种类型的油漆

Organic Protective Coatings

Typical automotive coating system



Source: BASF

Sacrificial (anodic) Coatings
牺牲(阳极)涂料

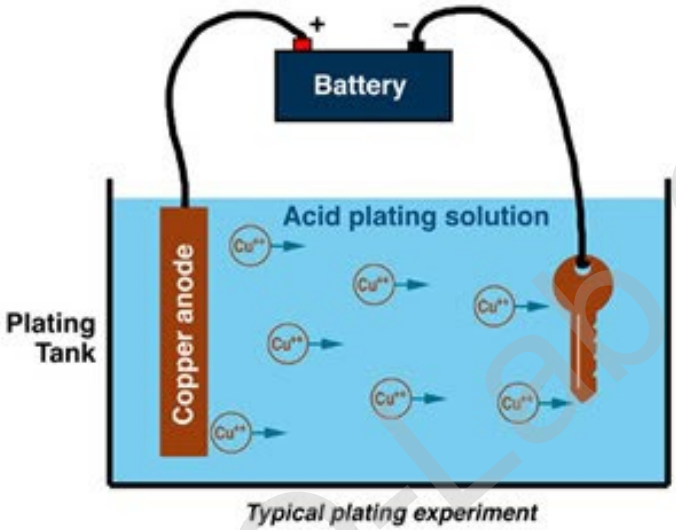
Galvanizing – Zinc plated onto steel via hot dip or electroplating process serves as the anode in a steel/zinc couple

镀锌- 通过热浸或电镀工艺将锌镀在钢上，锌作为钢锌电偶对的阳极

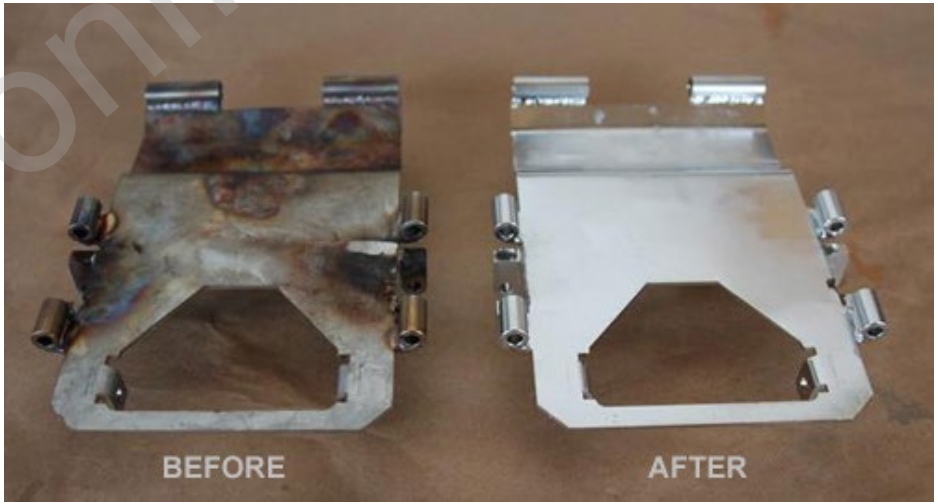
Noble Metal Coatings
金属涂层

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

电镀-原电池的反向作用，通过将电流施加到要电镀到另一金属上的金属而产生



Typical plating experiment



Conclusions

Atmospheric Corrosion: Chemistry
大气腐蚀:化学

Corrosion of metals always involves two types of chemistry:

金属的腐蚀总是涉及两种化学反应

- **Oxidation/Reduction** (REDOX) electrochemistry

氧化还原反应- 电化学

- **Lewis Acid/Base** chemistry

路易斯酸碱理论

Atmospheric Corrosion: Key Factors
大气腐蚀的关键因素

Corrosion is affected by:

腐蚀受如下因素：

- Acidity (pH) of solutions

溶液的PH值

- Availability & diffusion of oxygen

溶解氧的浓度和扩散

- Concentration & diffusion of other oxidizing agents

其他氧化剂的浓度和扩散

- Geometry of construction

物件的构造

Atmospheric Corrosion: Types
大气腐蚀的类型

Atmospheric Corrosion can take many forms:

- General or “free” corrosion

全面腐蚀

- Galvanic

电偶腐蚀

- Crevice

缝隙腐蚀

- Pitting

点蚀

- Intergranular

晶间腐蚀

- Exfoliation

剥离腐蚀

- Filiform

丝状腐蚀

- Stress

应力腐蚀

Atmospheric Corrosion: Mitigation
大气腐蚀的减缓

Atmospheric Corrosion can be mitigated a number of ways:
减缓大气腐蚀的方法有很多：

- Passivation
钝化
- Conversion Coatings (pretreatments)
转化膜
- Organic Coatings (Paint)
有机涂层
- Sacrificial Coatings (galvanizing)
镀锌
- Metal (Noble) Coatings
金属涂层
- Mechanical Design
结构设计

Atmospheric Corrosion: Complexity
大气腐蚀的复杂性

Corrosion of steel under atmospheric exposure

钢在大气暴露下的腐蚀

- Each metal has unique corrosion properties and pathways; very difficult to predict.

每种金属都有独特的腐蚀特性和腐蚀途径;很难预测

- Understanding atmospheric corrosion requires multiple scientific disciplines

了解大气腐蚀需要多种科学学科

Ingredients:

$Fe_2O_3 \cdot H_2O$

Fe_3O_4

$Fe(OH)_2$

$FeCl_2$

$FeCl_3$ $Fe(SO_4)(OH)$

$Fe(OH)_3$

secret spices

Questions?

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Q-Lab中国微信公众账号:
耐候腐蚀设备及测试专家

- ✓ 技术研讨会、网络研讨会信息
- ✓ 老化及腐蚀技术文章、最新测试标准解读等
- ✓ 相关技术问题，也可通过平台留言，我们会在24小时内和您联系

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