

PROTECTING METAL SURFACES FROM CORROSION: THE ROLE OF HIGH PERFORMANCE COATINGS

1

Corrosion Defined

Corrosion can be defined as the deterioration of metallic surfaces, such as carbon steel. Corrosion is a natural process, the propensity or tendency of materials to “give up” energy and return to their natural state. While it takes tremendous amounts of energy to convert materials found in nature into usable materials for construction (like carbon steel), these materials will release that energy and convert back to their original state unless the process is stopped or slowed down.



Corrosion in Process

The Role of Protective Coatings in Preventing/Slowing Corrosion

The most widely used method to prevent corrosion today, particularly on carbon steel, is the application of high performance, protective coatings. High performance coatings protect thousands of structures, including: off-shore drilling rigs, ships, storage tanks, sewage systems, power plants, shipping containers, pipelines, railway cars, refineries, and commercial buildings.



Industrial protective coatings have been around since the 1930s, but the industry was given a boost during World War II. The need to keep ships out to sea longer and in dry dock less, led first to the development of the epoxy resin, and next to the polyamide epoxy, which had better adhesion, some flexibility, and an increased resistance to water. As the demand for the materials of war increased, the demand for improvements to industrial coatings grew with it. Better adhesion, faster cures, and better resistance to abrasion were some of the driving forces, but the need to keep materials from corroding remained the primary motivation for improvements to coatings.

The Fundamentals of Corrosion

This discussion about corrosion fundamentals will focus on metals. Corrosion of metals is a natural process involving a chemical reaction – actually an electrochemical reaction, meaning that electric current is produced during the process. Corrosion will occur when four required elements are all present (note that it is assumed that oxygen is always present). If any one of the elements is missing, the corrosion process will not proceed. The required elements, which compose a “corrosion cell,” are:

1. Anode
2. Cathode
3. Metallic pathway (connecting the anode and cathode)
4. Electrolyte

The surface of carbon steel already contains three of the four elements: the anode, cathode, and metallic pathway; only the electrolyte is missing. An electrolyte is a liquid that contains ions or “charged particles.” All salts (e.g., sodium or calcium chloride) form ions when dissolved in water. Once the electrolyte is present, the process of corrosion will proceed.

To analyze how the four elements of a corrosion cell work together to produce the process of corrosion, we can use the example of a common household battery.



*Dry Cell Battery - Example of Galvanic
(Electrochemical) Corrosion*

A corrosion cell is essentially a natural battery. The anode and its counterpart, the cathode, represent negative and positive terminals of the “battery.” During the chemical reaction process, electrical current (or electrons) flows from the anode to the cathode via the metallic pathway or connection. The electrolyte carries ions from the cathode to the anode to complete the electrical circuit. The anode (negative terminal) decays during this process while the cathode (positive terminal) remains intact or “protected.” The only difference between a corrosion cell and a manufactured battery is that the reaction process is designed to produce an electrical current for a productive use in the manufactured battery. A natural corrosion cell, however, is generally destructive since the reaction process depletes or decays the anode.

When the anode is depleted in a manufactured battery, the reaction will stop and the battery will “die” since it can’t produce more energy. When a corrosion cell is formed on a metal surface, some areas of the metal act as the anode and other adjacent areas the cathode. The corrosion reaction will not stop so easily since the anode may have a near endless supply as corrosion (and the anode) spreads across the surface of the steel.

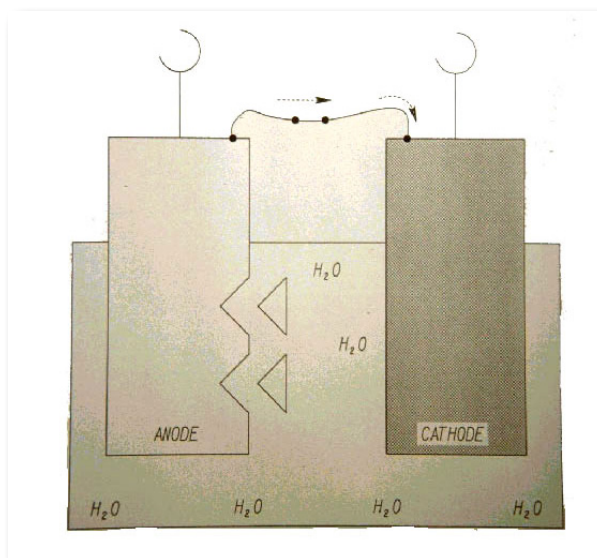


Illustration of Corrosion Cell - Current Flows from Anode to Cathode, Anode Decays in Electrolyte Solution

Energy Required to Convert Ores into Metals

Most metals are not found in their pure state in nature, but rather as ores where they are combined with oxygen and other elements. The relative reactivity of metals is directly proportional to the amount of energy required for their conversion from ore. The chart below indicates how much energy is required to convert common metals to their pure form. Note that there are some metals that do exist in their pure form in nature such as gold, silver and copper; these metals are at the stable end of the chart.

Common Metals	Most Energy to Convert (Less Stable)
Zinc	
Aluminum	
Cast Iron	
Carbon Steel	
Stainless Steel, Type 430, active	
Stainless Steel, Type 304, active	
Stainless Steel, Type 410, active	
Copper	
Brass	
Bronze	
Stainless Steel, Type 430, passive	
Nickel	
Stainless Steel, Type 410, passive	
Silver	
Titanium	
Stainless Steel, Type 304, passive	
Stainless Steel, Type 316, passive	
Zirconium	
Platinum	
Gold	
	Least Energy to Convert (More Stable)

Dissimilar Metals

A corrosion cell can also be formed when two dissimilar metals are in contact with one another. When two dissimilar metals are connected, the metal that is higher in the chart – i.e., requires more energy to convert to a pure metal – is the one that becomes the anode and corrodes, while the other metal acts as the cathode. The physical connection between the metals serves as a metallic pathway and water or moisture typically serves as the electrolyte needed to complete the cell. The metal that acts as the anode will decay while the other “cathodic” metal remains intact. The anodic metal thereby provides “cathodic protection” to the other metal.

Corrosion Versus Oxidation

The corrosion of some metals does not necessarily create a problem. For example, aluminum will quickly oxidize (corrode) forming a layer of aluminum oxide on the metal surface. But the aluminum oxide layer essentially seals the metal surface and becomes protective because it stays tightly adhered and is not porous. Copper is another example of a metal that forms a protective oxide layer – in this case the characteristic green color that forms as copper weathers (known as “Patina”).

For many metals, however, corrosion is a problem because the oxidation of the metal surface does not stop after an initial layer is formed. In the case of iron (and steel), a porous layer of iron oxide is formed which is loosely held to the surface. The porosity allows corrosion to continue into the iron.



Oxidation

What is Steel?

When considering the corrosion of common carbon steel, we can look at iron since it is the primary component of the steel that corrodes. Steel is primarily composed of iron at concentrations from 95 to 99 percent by weight. The difference between ordinary steel and pure iron is the addition of carbon (typically up to 2 percent) and other elements. The carbon increases strength and adds other desirable properties to the metal. A variety of steel alloys can be produced by adding elements such as copper, chromium, nickel, or phosphorus (and others). Some of these additions can produce a significant reduction in the corrosion rate for particular steel alloys. One such alloy is known as “weathering steel.”

Weathering Steel

Weathering steels, also called high-strength, low-alloy steels (or CORTEN, a US Steel trademark), provide greater resistance to atmospheric corrosion than conventional carbon steels. In the corrosion of weathering steel, the iron oxide layer becomes protective, similar to other metals like aluminum or copper. The oxide layer of weathering steel forms differently than for ordinary steel and its appearance changes from the typical red-orange color of rust to a dark purple as the weathering process proceeds. Weathering steel is designed to remain uncoated but can be coated for additional protection. Weathering steel is not recommended for certain environments including severe industrial exposures, locations subjected to salt-water spray, or continuous submergence in water.

How Coatings Protect the Substrate from Corrosion

Corrosion of metals really cannot be completely stopped. Slowing down the process as much as possible is the only option to preserve the metal and this is where protective coatings play a crucial role. Coatings are considered to function as a protective layer in three different ways: by providing barrier, sacrificial or inhibitive protection.

Barrier Protection

Barrier protection is the simplest way a coating functions as a protective layer and refers to the physical barrier that is formed on the substrate surface by any coating. This physical barrier prevents air and water, which are necessary for corrosion, from reaching the substrate. All coatings provide barrier protection, although some coatings have characteristics that enhance the barrier function of the coating. For example, coatings that contain micaceous iron oxide (MIO) or aluminum flakes in their formulation form plate-like layers (called lamellar pigments) in the coating film. Water or air cannot penetrate the “plates” and must take a longer path to eventually reach the substrate.

Sacrificial or Cathodic Protection

Coatings also may protect a substrate by providing sacrificial or cathodic protection. This occurs when the coating layer contains a metal that will act as the anode in the corrosion process, thereby protecting the metal substrate (or cathode). Sacrificial coatings are generally used as primers since the sacrificial metal must be in direct contact with the metal substrate. Zinc is the most common sacrificial metal used to protect iron-based steel materials. The best example of this is with zinc-rich primers where zinc dust is added to the coating formulation in amounts up to 90% by weight. A zinc layer can also be formed on a steel substrate by metallizing or galvanizing – both of which essentially deposit a solid zinc layer on the substrate. Metallizing is accomplished by melting the zinc (and/or aluminum) and spraying it onto the substrate surface using flame spray, electric arc or plasma arc processes. Metallizing can be performed in the shop or field at a project site. Galvanizing is completed by dipping steel parts in a molten zinc bath. The galvanizing process generally provides superior protection to metallizing for comparable zinc thicknesses, with the obvious limitation that it can only be done in a factory or shop setting for new steel before erection.

Inhibitive Protection

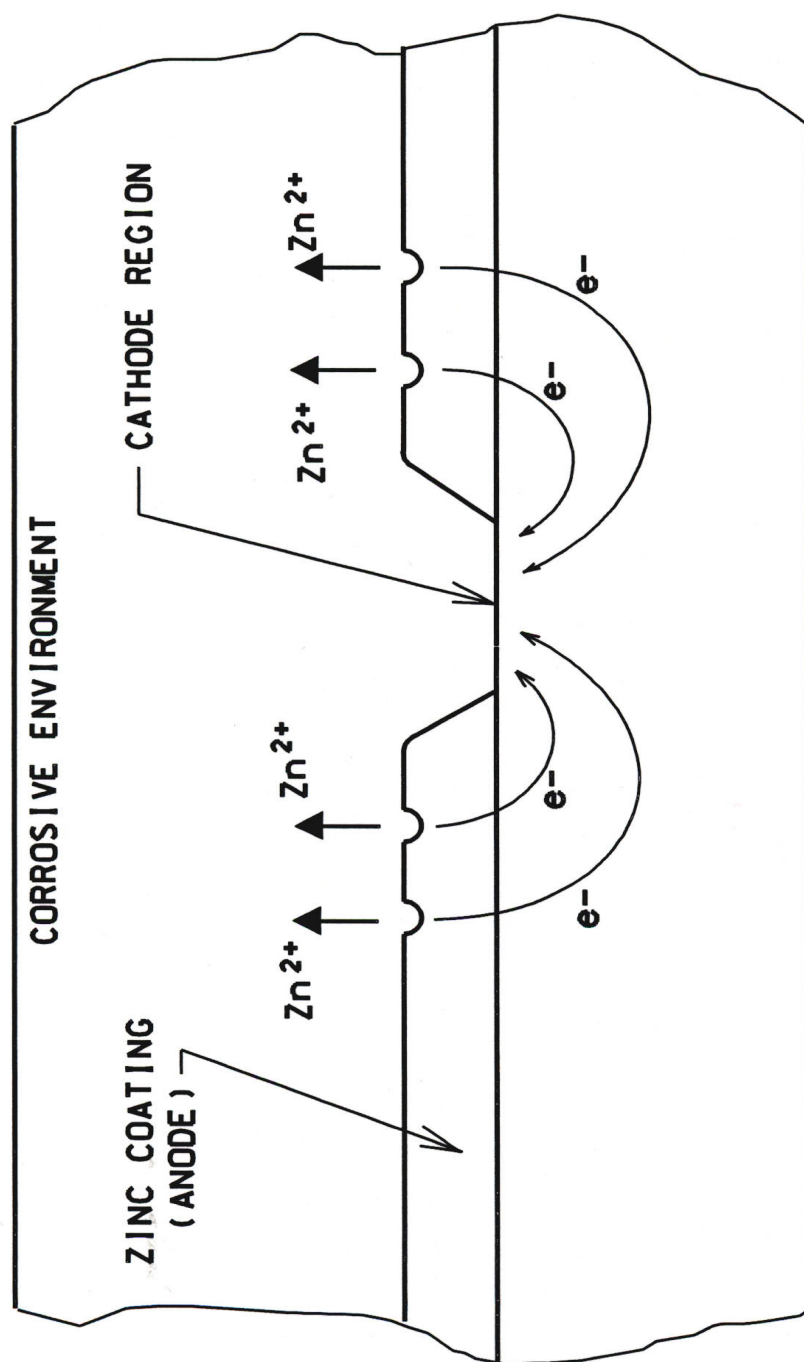
Some coatings also provide protection by containing inhibitive pigments that disrupt or prevent typical corrosion reactions from occurring. The mechanism by which inhibitors work is not always clear, but the common theory is that the inhibitive materials react or bind with water to prevent it from further penetrating the coating film, or produce compounds that inhibit corrosion reactions. A good example of an inhibitor is lead, which is no longer widely used in coatings since it is a health and environmental hazard. Other inhibitive pigments may include borates, chromates (which are restricted like lead), phosphates or molybdates.

Additional Cathodic Protection

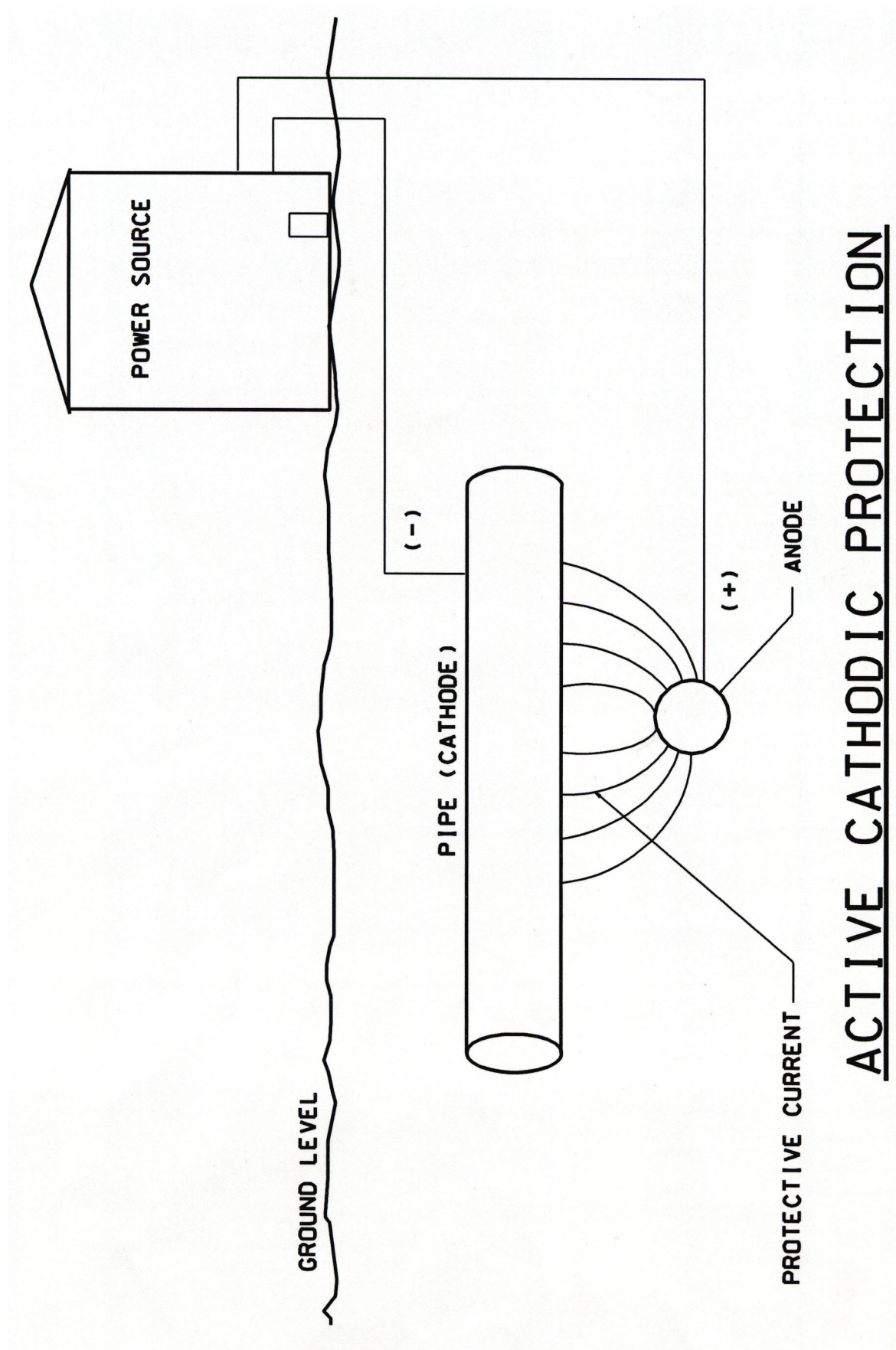
As previously described, coatings provide cathodic protection when a component of the coating acts as a sacrificial metal to the substrate (e.g., zinc coatings on steel). But additional cathodic protection can be provided by passive or active means. Passive cathodic protection

(as with coatings) can be accomplished by attaching a dissimilar metal directly to a metal substrate to act as a sacrificial anode. Of course the other metal must be more reactive than the substrate to act as the anode and become sacrificial. To protect steel substrates or structures, zinc or aluminum are often the other (dissimilar) metals used. An example of passive cathodic protection is when sections of zinc or aluminum are attached to the underwater hull of a ship. The sections (anodes) will corrode instead of the steel thereby protecting the ship's hull in the vicinity of the attachment points – note that multiple sacrificial anodes are typically attached over the hull's surface. This protection is considered passive since corrosion (and cathodic protection) occurs spontaneously via the natural process.

For some structures, however, the potential for corrosion can be so great that passive cathodic protection may not provide adequate protection. Such environments might include offshore platforms or buried pipeline. In these cases, active cathodic protection can be provided by applying or “impressing” an electrical current to the structure (while also using a dissimilar metal to act as the anode). In effect, the impressed current prevents the spontaneous reaction that would normally take place in a natural corrosion cell from occurring in the first place. An impressed current system requires an external power source and must be specifically designed for the structure and environment if it is to function properly. Maintenance and monitoring of the system is required.



SACRIFICIAL PROTECTION



Summary

One definition of corrosion is the deterioration of metal surfaces. Corrosion is a natural process, the tendency of materials to “give-up” energy and return to their natural state. While it takes tremendous amounts of energy to convert materials found in nature into usable materials for construction, those same materials will readily release that energy and convert back to their original state unless the process is stopped or slowed down.

Corrosion is a natural process, which involves an electrochemical reaction. In addition to oxygen, only four elements are needed for corrosion to occur: an anode, a cathode, a metallic pathway, and an electrolyte. These four elements in combination are referred to as a corrosion cell. The surface of carbon steel contains three out of the four elements; only the electrolyte is missing. Once the electrolyte connects with the surface of carbon steel, the process of corrosion will proceed.

When all four elements are present, corrosion occurs at the anode, while the cathode remains intact or protected. This principle is used to create products that can protect the steel substrate (cathodic or sacrificial protection).

Most metals used in construction are not found in their pure state in nature. They exist first as ores where they are combined with oxygen and other elements. The more energy used to convert these metals to usable materials, the greater the tendency to give that “energy up” and return to a natural state (ore). Carbon steel has a strong tendency to corrode, since it is “less stable” than metals like gold, platinum, and silver. The addition of certain elements during the process of creating steel can produce steel alloys with a significantly lower corrosion rate. One such steel alloy is called weathering steel or CORTEN.

The most widely used method to prevent corrosion, particularly on carbon steel, is the application of high performance, protective coatings. Coatings protect metal surfaces from corrosion using three methods: barrier protection, sacrificial or cathodic protection, and inhibitive protection. All coatings provide some type of barrier protection, forming a physical barrier that prevents air and water from reaching the substrate. Sacrificial or cathodic protection is provided when a coating contains a metal which will become the anode in the corrosion process, thereby protecting the metal substrate (or cathode). Zinc is the most common sacrificial metal and is often added to primers, where the zinc can come into direct contact with the steel substrate. Pure zinc can also be melted and used to coat steel parts. The metallizing process melts zinc and uses flame spray, electric arc, or plasma arc to spray the zinc onto the substrate. Galvanizing is completed by dipping steel parts into a molten zinc bath.

An additional method to provide passive cathodic protection (which is also provided by sacrificial coatings) can be accomplished by attaching a dissimilar metal directly to a metal substrate to act as a sacrificial anode (usually pieces of zinc or aluminum). The sacrificial anode will corrode instead of the steel.

For some structures, including offshore platforms and buried pipeline, passive cathodic protection may not provide adequate protection. By applying (impressing) an electric current to the structure, while using a dissimilar metal to act as the anode, the current prevents the spontaneous reaction (corrosion) from occurring in the first place.

	Module One
	Protecting Metal Surfaces from Corrosion: The Role of High Performance Coatings

	Module One Learning Outcomes
	Comprehension of Module One will enable the participant to: ➢ Identify the elements of a corrosion cell ➢ Describe the corrosion of metals ➢ Explain how industrial coatings control corrosion ➢ Describe alternative methods used to protect carbon steel from corrosion

	Corrosion Defined
■ Corrosion is: ➢ A natural process ➢ Deterioration of metallic surfaces ■ Metals “give up energy” and return to their original state	

	Corrosion Defined, con't.
■ Carbon Steel: ➢ Takes enormous energy to form ➢ Will release energy ■ Process must be stopped or slowed down	

	The Role of Protective Coatings
■ Coatings are used: ➢ To prevent/slow onset of corrosion ➢ To improve aesthetics ➢ As safety indicators ➢ As process aids (e.g., material flow) ➢ To protect the environment	

	Use of Protective Coatings
■ Coatings Protect: ➢ Off-shore rigs/platforms ➢ Ships ➢ Pipelines ➢ Tanks ➢ Sewage systems ➢ Commercial buildings ➢ Transmission towers	■ Coatings Protect: ➢ Bridges ➢ Exhaust stacks ➢ Stadiums ➢ Refineries ➢ Railway cars ➢ Cranes ➢ Other structures/facilities

Push for Better Protective Coatings

- Industrial protective coatings:
 - Around since the 1930's
 - Industry given a boost during World War II (ships needed to stay out to sea longer)
 - Development of the epoxy resin, then the polyamide epoxy



Fundamentals of Corrosion

- Focus on metals
- Natural process
- Involves a chemical or electrochemical reaction
- Electric current is produced

Fundamentals of Corrosion

- Elements Required for Corrosion to Occur (oxygen assumed)
 1. Anode
 2. Cathode
 3. Metallic Pathway
 4. Electrolyte



Analogy: Dry Cell Battery

Fundamentals of Corrosion

- The Anode
 - Negative sites on steel surface
 - *Deteriorates* in corrosion process
- The Cathode
 - Positive sites on steel surface
 - *Remains intact* or protected

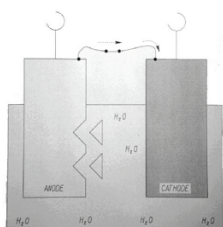
Fundamentals of Corrosion

- The Metallic Pathway
 - Electrons (or the electrical current) flow from the anode to the cathode via the metallic pathway
- The Electrolyte
 - A liquid that contains ions or "charged particles"

Fundamentals of Corrosion

- Three out of four elements are present on the surface of carbon steel
 - Anode
 - Cathode
 - Metallic Pathway
- If electrolyte is isolated, corrosion is stopped

Current Flows from Anode to Cathode



Energy Required to Convert Ores into Metals

- Most metals are not found in their pure state in nature
- Ores are combined with oxygen and other elements

- (less stable)
- Zinc
 - Aluminum
 - Cast Iron
 - Carbon Steel
 - Stainless Steel (430 series-active)
 - Stainless Steel (410 series-active)
 - Bronze
 - Nickel
 - Stainless Steel (410 series-passive)
 - Silver
 - Titanium
 - Stainless Steel (304 series-passive)
 - Stainless Steel (316 series-passive)
 - Platinum
 - Gold (more stable)

Dissimilar Metals

- Corrosion cell can be formed when two dissimilar metals are in contact with one another

Dissimilar Metals, con't.

- The metal that requires the most energy to convert becomes the anode and corrodes
- The other metal acts as the cathode
- A form of cathodic protection

Corrosion Verses Oxidation

- Some metals oxidize (or corrode) without consequence
 - Aluminum
 - Copper
- "Patina" is formed, which seals the surface

	Corrosion of Iron and Carbon Steel
	■ Oxidation or corrosion forms a porous layer of iron oxide ■ Iron oxide loosely held to the surface ■ Porosity allows corrosion to continue into the iron

	What is Steel?
	■ Composed of iron at concentrations from 95 to 99% by weight ■ Addition of carbon (about 2%) to the iron to produce steel ■ Carbon gives steel strength ■ Iron is the primary component of steel that corrodes

	The Addition of Alloys to Carbon Steel
	■ Steel alloys produced by adding copper, chromium, nickel, or phosphorus and other elements ■ Some additives (e.g., copper) produce alloys with a significant reduction in the corrosion rate ➢ "Weathering steel" (ASTM A588)

	The Addition of Alloys to Carbon Steel
	■ Weathering Steel: ➢ A high-strength, low alloy steel ➢ CORTEN (a US Steel trademark) ➢ The iron oxide (corrosion) layer becomes protective (like aluminum or copper) and turns dark purple/brown ■ Not recommended for: ➢ Severe industrial exposures ➢ Locations with salt water spray ➢ Continuous submergence in water

	Corrosion Protection
	■ Coatings protect the substrate from corrosion by: ➢ Barrier protection ➢ Sacrificial or cathodic protection ➢ Inhibitive protection

	Corrosion Protection
	■ Barrier Protection ➢ Coating provides a physical barrier ➢ Prevents air and water (electrolyte) from reaching the substrate ➢ All coatings provide some level of "barrier protection"

Corrosion Protection

■ Barrier Protection, continued

- Lamellar pigments
 - Form plate-like layers in the coating film
 - Water and air take longer pathway to reach the substrate
 - Examples:
 - Micaceous iron oxide (MIO)
 - Leafing aluminum

Corrosion Protection

■ Sacrificial or Cathodic Protection

- Coating contains a metal that becomes the anode in the corrosion process
- Protects the metal substrate (or cathode)
- Generally used as primers (e.g. zinc-rich)
- Sacrificial metal must be in direct contact with the substrate

Corrosion Protection

■ Sacrificial or Cathodic Protection, continued

- Thermal Spray Coatings (TSC)
 - Metals (e.g., zinc, aluminum, other alloys) are melted and sprayed onto the substrate surface (metallizing)
- Galvanizing (zinc)
 - Hot-dip, mechanical, electro-deposited
 - New steel only

Corrosion Protection

■ Inhibitive Protection

- The addition of inhibitive pigments to the coating to interfere with corrosion process
 - Lead*
 - Chromate*
 - Phosphate
 - Iron oxide
 - Others

**no longer widely used*

Corrosion Protection

■ Cathodic Protection (CP)

- Used in conjunction with coatings
- Sacrificial Anode CP
 - Attach a dissimilar metal directly to a metal substrate
 - The dissimilar metal acts as a sacrificial anode
- Impressed Current CP
 - For extremely corrosive environments
 - Use a dissimilar metal to act as the anode
 - Impress an electrical current (mV) to the structure
 - Must be designed for the structure and the environment to function properly

Module 1 Summary

- Corrosion is the deterioration of metals
- Coatings retard the corrosion process and improve aesthetics
- Elements of a corrosion cell:
 - Anode
 - Cathode
 - Metallic pathway
 - Electrolyte
- Coatings prevent electrolyte from contacting the steel
- Addition of copper alloy improves corrosion resistance (weathering steel)
- Coatings protect by barrier, inhibitive and sacrificial means
- Cathodic protection can be used in conjunction with coatings for severe environments