

CORROSION –

EFFECTS ON METALS & ELECTRONIC EQUIPMENT, PROCESSES & PREVENTION

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ABSTRACT

Disaster-generated contaminants challenge operational integrity of electrical and mechanical equipment. Under “normal” conditions, equipment experiences environmental degradation as well as functional wear and tear. Corrosive contaminants that may emanate from a fire, water event, or certain fire extinguishing effluents (ABC dry chemical), compromise protective coatings on printed circuit boards (PCB’s) and deteriorate components/metal surfaces. This paper provides information and analysis on why certain metals corrode, the types of corrosion, protecting metals from natural degradation, effects of corrosion on PCB’s, ways to slow the rate of corrosion post-loss, passivation, and addressing surfaces with accelerated oxidation.

WHY DO CERTAIN METALS CORRODE?

Corrosion can be defined as a natural chemical attack on certain metals to mutate them to more chemically-stable forms such as oxides, hydroxides, chlorides, nitrates and sulfides. Minerals in those forms are the stable form of most metallic elements. It is actually rare to find iron alone. Because of the abundance in nature of iron and chemically active reactants, iron will be found combined with other elements. The same is true for ores or minerals such as hematite (Fe_2O_3), magnetite (Fe_3O_4), siderite (FeCO_3), pyrite (FeS_2), limonite ($\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$), limonite and goethite ($\text{FeO} \cdot \text{Fe}_3\text{O}_4 + \text{H}_2\text{O}$) and chromite ($\text{FeO} \cdot \text{Cr}_2\text{O}_3$).

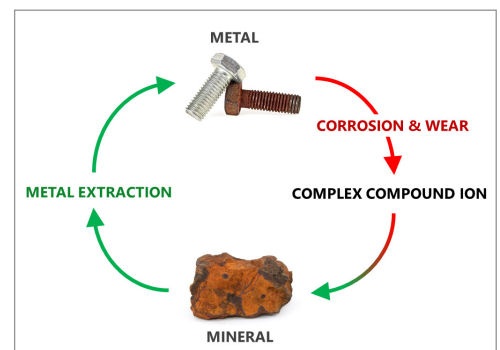


Figure 1.0 - The cycle of metals

Through the natural process of corrosion, a steel panel (chemically unstable and a non-natural material) is transformed into stable and natural compound such as iron chloride, iron oxides, iron, hydroxides, iron sulfide and iron sulfate (see Figure 1.0).



Figure 2.0 - Nature continuously attempts to transform the Eiffel tower, which is constructed from a non-natural material, steel, into its natural & stable form, an iron mineral, through corrosion. As a result, every structural steel component in the tower needs to be painted to create a protective barrier between the surface and the corrosive atmosphere (water, oxygen, combustion byproducts). Figure 2.1 - An iron ore mine.

It is also rare to find copper alone. Copper will be found in nature combined with other elements. The same is true for chalcocite (Cu_2S), chalcocite (CuFeS_2), covellite (CuFeS_2), bornite (Cu_5FeS_4) and enargite (CuAsS_4).

Through corrosion, a copper wire (an unstable and a non-natural material) is transformed into a stable and natural compound such as copper chloride, copper oxide, copper hydroxide, copper sulfide and copper sulfate (see Figures 3.0 - 3.3).



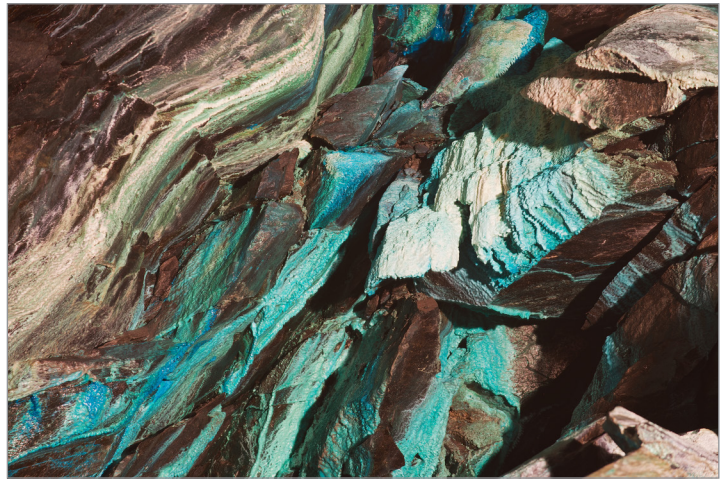
Face reproduction of the Statue of Liberty



Green patina on the statue due to corrosion



Minneapolis Hennepin county courthouse copper roof



Copper mineral deposits with green patina characteristics

Figures 3.0 through 3.3 - Copper corrosion formation

WHEN DOES CORROSION START?

Corrosion starts the very moment a non-natural metallic material is created. For example, during the formation of a steel ingot, corrosion starts when oxygen and water in the atmosphere encounter the bare steel surfaces. Without any protective coatings, electrochemical corrosion begins in an effort to transform this non-natural metallic material into oxides and hydroxides (natural and stable compounds). In an effort to protect steel objects from atmospheric deterioration, painted coatings are applied or a metallic coating such as nickel, chromium or zinc.



Figure 4.0 - Steel plates minutes after manufacturing. The arrows showcase scale (iron oxides) produced by dry corrosion. This is a natural process that transforms the “non-natural” material (steel) back to a mineral.

TYPES OF CORROSION

There are two general types of corrosion:

1. Dry corrosion
2. Wet or electrochemical corrosion

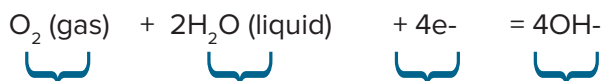
DRY CORROSION

Dry corrosion appears at high temperatures, when oxygen in the air reacts with a metal without the presence of a liquid. Higher temperatures coupled with contaminated environments (those that may contain sulfur, nitrogen and chloride compounds), increase the surface oxidation rate which accelerates damage to the metallic material. The rate of oxidation will vary depending on the type of metal.

ELECTROCHEMICAL CORROSION

Rust observed on steels in cars, bridges, cables, tanks and pipes occurs as a result of electrochemical (wet) corrosion. This type of corrosion develops when an electrochemical cell is produced. Electrochemical cells consist of an anodic area, cathodic area and an electrolyte. The anode is the susceptible metal. The cathode is some other conducting matter (such as a dissimilar conductive material). During the reaction between the anode and the cathode, the cathode will gain electrons and is protected from corrosion. The electrolyte is the conductor through which the electrons travel such as elevated humidity or direct water exposure.

Cathodic Area – Cathodic Reaction



oxygen (gas) + water (liquid) + 4 electrons = hydroxide ion

Cathodic reactions occur every time oxygen in humid air, or oxygen in water, come in contact with an untreated (unpainted or uncoated) bare metallic surface such as iron, steel copper and aluminum.

Anodic Area – Anodic Reactions

Fe (Iron solid) - 2e⁻ → Fe⁺⁺ (ionic specie)

Cu (Copper solid) - 2e⁻ → Cu⁺⁺ (ionic specie)

Zn (Zinc solid) - 2e⁻ → Zn⁺⁺ (ionic specie)

Al (Aluminum solid) - 3e⁻ → Al⁺⁺⁺ (ionic specie)

Metal (solid) - n (number of) electrons = Metallic ions forming salts, oxides, hydroxides, sulfides (corrosion products).

FACTORS THAT INFLUENCE ATMOSPHERIC ELECTROCHEMICAL CORROSION ON CARBON STEELS

The atmospheric electrochemical corrosion rate of carbon steels depends on the following:

1. Relative humidity
2. Airborne particles (salts)
3. Pollutants or contaminants (gases)
4. Rain
5. Temperature

RELATIVE HUMIDITY

The most important factor in atmospheric corrosion, overriding pollution, is moisture. Moisture in the form of rain, dew, condensation or high relative humidity. In the absence of moisture, most contaminants would have little or no corrosive effect.

Electrochemical corrosion in “clean” atmospheres (without airborne particles or contaminants), develops on carbon steels at relative humidity values higher than 70 percent. The higher the humidity level in the atmosphere, the faster the corrosion rate.

AIRBORNE PARTICLES (SALTS)

Airborne particles such as marine salts (chlorides and sulfates), industrial dust and soot, increase the atmospheric corrosion rate of carbon steels. Airborne marine salts that dissolve in the water are carried by the local atmosphere and can condense as visible water or moisture on the surface of bare carbon steels. These deposited salts, in turn, increase the electrical conductivity of the aqueous environment, making it much more corrosive. The higher the salinity, the saltiness of a body of water, the faster the electrochemical corrosion rate.

By extension, the faster the electrochemical corrosion rate, the higher the possibility of failures related to corrosion such as loss of material thickness, pitting, cracking and fracturing. Faster rates of corrosion result in the need for more surface maintenance in the form of cleaning and repainting. Among the most susceptible to electrochemical corrosion in marine environments include offshore oil platforms, ships, ports, bridges, buildings, electrical substations, power transmission towers, etc.

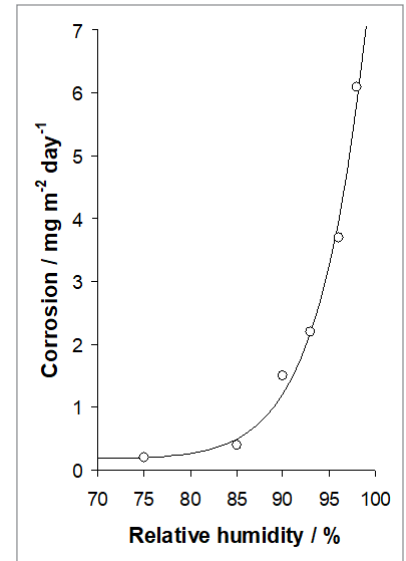


Figure 6.0 - Corrosion rate versus relative humidity.

Image courtesy of the Swedish International Development Cooperation Agency.

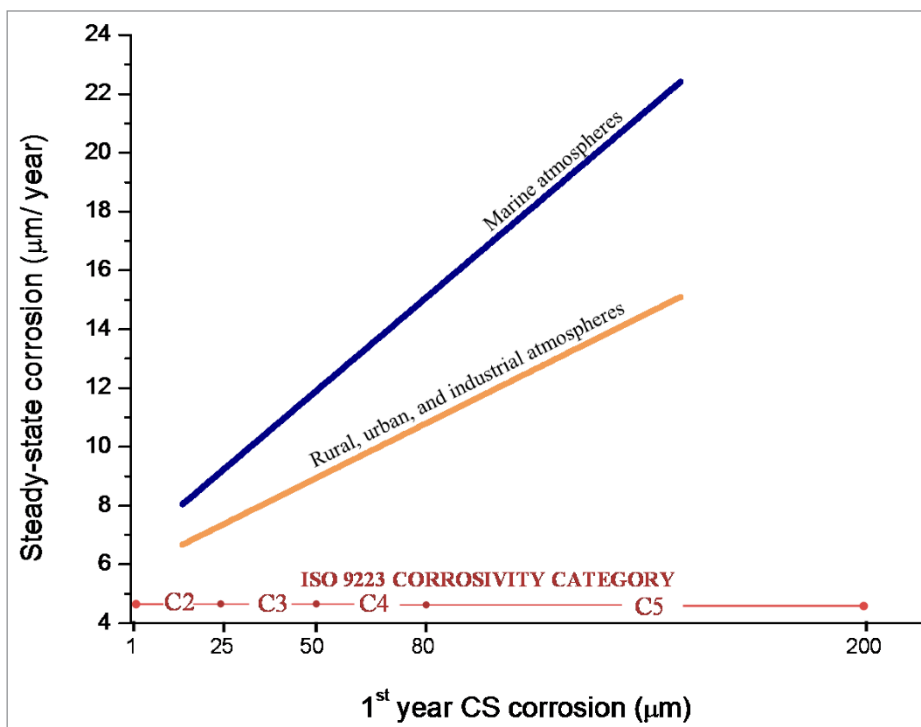


Figure 7.0 - Relationship between steady-state corrosion rate of carbon steel and atmospheric corrosivity category according to ISO 9223 for different types of atmospheres.

Image courtesy of the National Centre for Metallurgical Research.

POLLUTANTS OR CONTAMINANTS (GASES) & RAIN

Many gases and solid particles are present in the atmosphere, as well as solid airborne particles that are man-made. Sulfur and nitrogen compounds are found among these gases, which together with moisture form sulfuric and nitric acids. Such acids increase the atmospheric corrosion rate of steels when exposed to acid rain. Rain that is not contaminated may actually benefit equipment as it washes away atmospheric pollutants that settled on exposed surfaces.

SOURCES OF NATURAL POLLUTANTS	
<p>Primary Volcanic action</p> <p>Biological respiration Animal waste Vegetation Soil microbes Sea spray Soil (earth) from the ground Natural (forest) fires</p> <p>Secondary Oxidation of SO₂ Reaction of NH₃ + SO₄²⁻ Reaction of sea-spray with SO₃</p> <p>Oxidation of N₂ during lightning Atmospheric photochemistry Plant hydrocarbons + O₃</p>	<p>Primary SO₂, H₂S, HCl, Cl₂ – gaseous; Volcanic ash - particulate CO₂ – gaseous NH₃, organic sulphides – gaseous Hydrocarbons – gaseous N₂O – gaseous Cl⁻, SO₄²⁻ – particulate aerosol Inorganic dusts - particulate CO₂ – gaseous Ash and smoke - particulates</p> <p>Secondary SO₃ – gaseous SO₄²⁻ – particulate aerosol (NH₄)₂SO₄ – particulate aerosol HCl – gaseous NO/NO₂ (NO_x) – gaseous O₃ (ozone) – gaseous Hydrocarbon peroxides and radicals ("Blue mountains of Virginia") – gaseous</p>
SOURCES OF MAN-MADE POLLUTION	
<p>Primary General combustion (all fuels)</p> <p>Fossil fuel combustion (oil, coal, gas) Incineration (waste, plastics, coal) Transport (vehicle exhaust)</p> <p>Chemical processing Sewage treatment Farming (domesticated animals) Farming (growing crops)</p> <p>Secondary Oxidation of SO₂ by O₃ Reaction of NH₃ + SO₄²⁻ Oxidation of NO_x by O₃ Hydrocarbons + O₃</p>	<p>Primary CO, CO₂ – gaseous "Fly-ash", carbon (smoke) – particulate SO₂, NO_x – gaseous HCl, Cl₂ – gaseous NO_x, CO, hydrocarbons – gaseous carbon (smoke) – particulate Hydrocarbons, sulphides, NH₃ – gaseous Sulphides, NH₃ – gaseous CH₄, NH₃, sulphides – gaseous Hydrocarbons (CH₄) – gaseous</p> <p>Secondary SO₃ – gaseous SO₄²⁻ – particulate aerosol (NH₄)₂SO₄ – particulate aerosol H₂SO₄ – "acid rain" NO₃⁻ - particulate aerosol HNO₃ – "acid rain" Hydrocarbon peroxides and radicals ("Photochemical smog") – gaseous</p>

Figures 8.0 & 8.1 - Sources of natural and man-made pollution.

Tables published by the Institute of Corrosion.

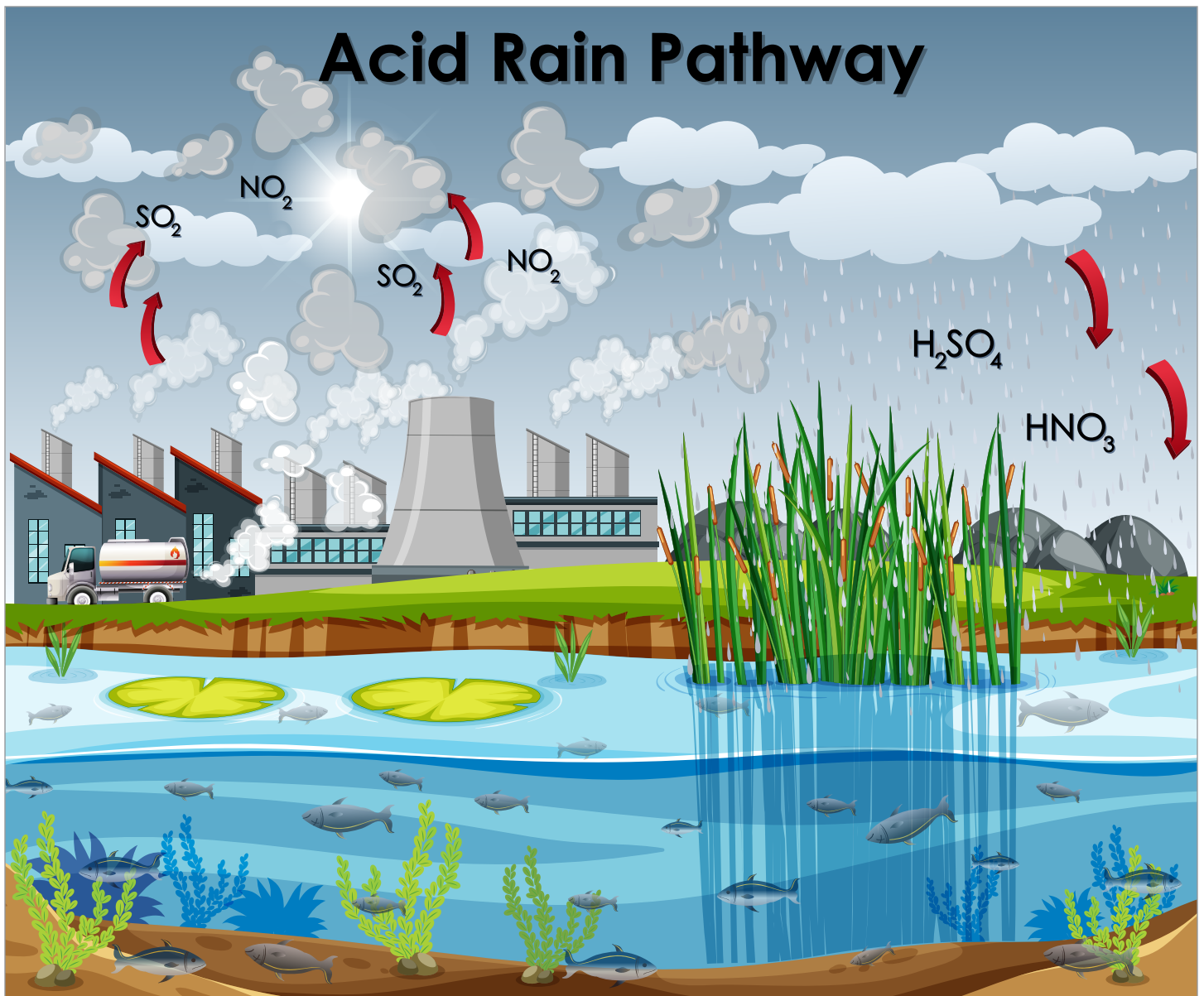


Figure 9.0 - How acid rain is formed

TEMPERATURE

Temperature plays an important role in two ways when considering atmospheric corrosion. Chemical reactions occur more rapidly at higher temperatures. An often quoted rule of thumb based on the Arrhenius equation, is that a rise in 10 degrees Celsius (18 degrees Fahrenheit) results in around double the reaction rate. Atmospheric corrosion during cold months is negligible.

CORROSION VERSUS RUST

Often used interchangeably, corrosion and rust are a result of oxidation reactions. Oxidation describes a reaction in which an element combines with oxygen. The reaction between magnesium metal and oxygen, to form magnesium oxide, involves oxidation of magnesium. Corrosion impacts a wide range of objects, while rust only impacts iron and its alloys, such as steel. Therefore, rust is a form of corrosion, although it specifically refers to oxidation of metals containing iron.

The chart below describes the various differences between corrosion and rust.

CORROSION VS. RUST	
CORROSION	RUST
Corrosion includes rust.	Rust is a type of corrosion.
Corrosion is the process by which certain materials, metals and non-metals, deteriorate as a result of oxidation.	Rusting is oxidation of iron in the presence of air and moisture.
Corrosion can occur on materials such as ceramics or polymers.	Rusting occurs on surfaces of iron and its alloys.
Corrosion requires surface exposure to air or chemicals.	Rusting requires surface exposure to both air and moisture.
Depending on the material, corrosion can emerge in different colors such as blue and green.	Rust has an orange brown color.

PROTECTING METALS FROM NATURAL DETERIORATION

According to Latem Industries (Latem), there are practical ways to prevent corrosion on metal parts. Latem notes that engineers can incorporate corrosion control into the design process and manufacturers and equipment restoration professionals can apply protective corrosion barriers. Finally, the people who use the parts can take preventative steps to prolong their life.

DESIGN

Corrosion control begins at the engineering stage. If the part is for use in an environment where it is susceptible to corrosion, manufacturers should design the part with that in mind.

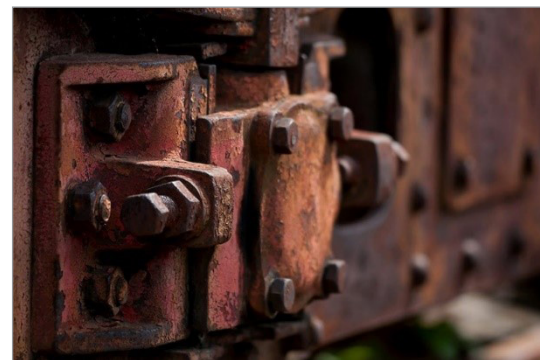


Figure 10.0 - Electrochemical corrosion

Image courtesy of Latem Industries

For example, parts exposed to the elements should allow water and debris to drain off instead of collecting on the surface. To reduce crevice corrosion, designers should eliminate narrow gaps that allow air or fluid to enter and become stagnant. For corrosive environments, such as those with exposure to saltwater, it is wise to engineer for a degree of corrosion allowance.

PROTECTIVE COATINGS

Coatings can provide a layer of protection against corrosion by acting as a physical barrier between the metal parts and oxidizing elements in the environment. One common method is galvanization, in which manufacturers coat the part with a thin layer of zinc.

Powder coatings are another effective way to prevent corrosion in metal parts. With proper application, a powder coating can seal the surface of the part away from the environment to guard against corrosion.

The application of a paint coating is a cost-effective way of preventing corrosion. Paint coatings act as a barrier to prevent the transfer of electrochemical charge from the corrosive solution to the metal underneath. While

inexpensive, paint coatings wear faster, requiring the surface to be repainted on a regular basis to maintain the same level of protection as powder coating or galvanization.

Rust prevention lubricants are used to coat untreated metal surfaces and protect parts from oxidation. The lubricants act as a corrosion inhibitor by forming a barrier film on the surface. The lubricants consist of polar molecules possessing water-repellent properties. The barrier film protects the parts from the attack of oxygen, water and other chemically active substances.

Rust inhibiting lubricants also contain surfactants (wetting agents), which form a strong bond with the metal part and provide efficient spreading of the inhibitor molecules over the surface. Such lubricants provide the shortest protection period and require frequent applications.

ENVIRONMENTAL CONTROL

Many environmental factors impact the likelihood of corrosion. It helps to keep metal parts in a clean dry place when not in use. If the intent is to store them for a long time, consider using methods to control the level of sulfur, chloride, or oxygen in the surrounding environment.

CATHODIC PROTECTION

It is possible to prevent some types of corrosion by applying an opposing electrical current to the metal's surface. One method of cathodic protection is an impressed current, which uses an outside source of electrical current to overpower a corrosive current in the part.

A less-complex method of cathodic corrosion protection is the use of sacrificial anodes. This involves attaching a small reactive metal to the part that needs to be protected. The sacrificial anode consists an alloy (zinc, aluminum and magnesium) with a higher electrode potential that is attached (by bolting or welding) to the metallic material being protected (steel of hulls, pipes and tanks, as examples). Electrons will flow from the reactive metal to the less active part, reducing corrosion at the expense of the sacrificial part.

MAINTENANCE

Protective coatings, environmental control, and cathodic protection are effective ways of preventing corrosion in metal parts. However, these measures are not maximized without ongoing maintenance and monitoring. Coatings can degrade over time; even small nicks and scratches can lead to corrosion. Parts need to be kept clean and additional protection should be applied as necessary.

EFFECTS OF CORROSION ON PCB's

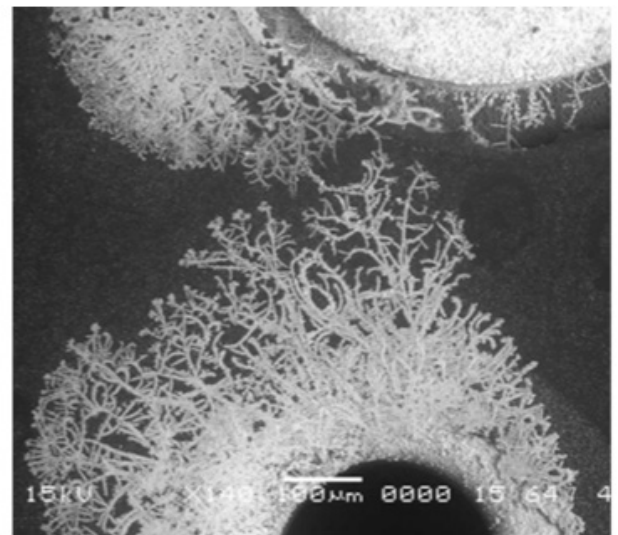
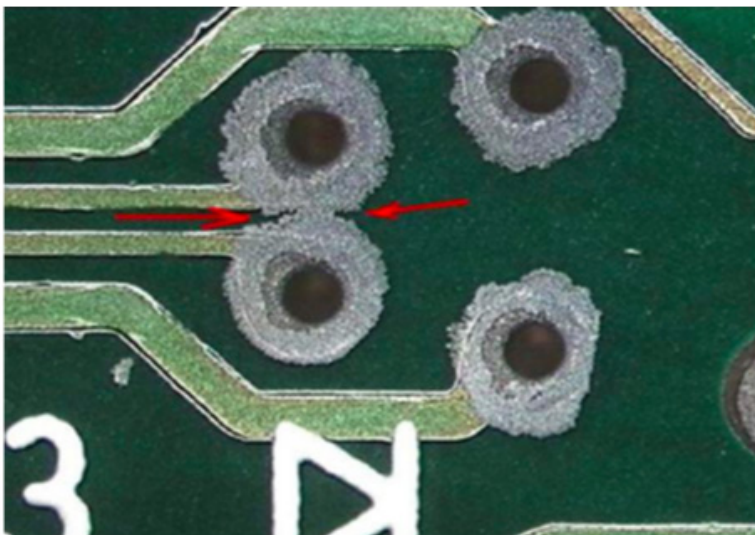
Sandia Laboratories prepared a study for the U.S. Nuclear Regulatory Commission titled, "Circuit Bridging of Components by Smoke". The study advises that when advanced electronic circuits are considered, a potential does exist for short-term corrosive attack to compromise circuit performance and represents a significant contributor to plant fire risk. For example, circuit miniaturization efforts are resulting in smaller circuit path traces being used in the fabrication of printed circuit boards. For these small circuit traces, even a relatively limited and short-term corrosive attack, particularly if the attack is in the form of "pitting" corrosion rather than general surface corrosion, may result in short-term loss of circuit functionality. Hence, for advanced circuit board-based devices, direct corrosive attack is of potential concern.

Experience in the telecommunications industry has shown that interactions of the acidic smoke from a cable fire with the galvanized surfaces of common air handling ductwork, can introduce galvanic salts into the smoke stream. These galvanic salts readily deposit onto component surfaces, resulting in direct and aggressive corrosive attack.

In his book, “Disaster & Recovery Planning”, Joseph Gustin notes that cables and wiring, printed and integrated circuitry, transistors, as well as various insulators are combustible. When plastics burn, the vapors that are emitted may combine with oxygen and moisture, causing electronic circuitry to corrode. The corrosion may be exacerbated by increased temperatures at the source of the fire.

In a paper titled “Creep Corrosion of Electronic Assemblies in Harsh Environments”, DfR Solutions advises that corrosion occurs in electronic assemblies and it is reminiscent to electromigration. Creep corrosion does not require an electrical field to drive the reaction, but corrosive elements and moisture must be present for creep corrosion to occur. Sulfur is the most prominent element to cause creep corrosion and it is readily available in environments such as paper mills, rubber manufacturing, mining (smelting), cement/asphalt manufacturing as well as waste water treatment facilities. It is often also found in companies and locations nearby such industries. The increasing usage of electronics in such environments makes creep corrosion a growing risk.

Analysis of creep failures revealed the corrosion product to be fairly resistive. Bridging of two conductors does not cause immediate failure. As the corrosion product increases in thickness, the resistance decreases until functional shorting occurs. For this reason, there are a multitude of symptoms that can take place as a result of creep corrosion (depending on which two conductors are the first to bridge). Additionally, it was found that many corrosion failures passed electrical testing upon arrival from the field (termed CND - cannot duplicate). Upon exposure to high humidity, the failure symptom would reoccur. Resistance measurements showed that when exposed to high humidity, the resistance of the corrosion product dropped from over 10 MΩ to below 1 MΩ. Due to the nature of this failure mechanism, it is difficult to identify corrosion failures without close inspection of each board.



Figures 11.0 & 11.1 - Creep corrosion on vertical interconnected access (VIA) pads (left) and magnified (right)

Image courtesy of National Instruments Corp.

WAYS TO SLOW THE RATE OF CORROSION

Immediately following a loss, the composition of settled particulate is unknown. Corrosive contaminants compromise susceptible metal surfaces, which accelerate the natural deterioration process. Slowing the oxidation or completely preventing it, ensures that recovery processes can be employed before metals start to pit. Pitting is the formation of cavities or holes within the metal that are irreversible.

Rust inhibiting coatings such as those manufactured by LPS, CRC, Corrosionx, Sprayon, Blaster, Rustlick and ZEP, form the barrier film discussed above between iron or steel and moisture/oxygen. Depending on the rust inhibiting solution, the metal can be immersed, sprayed, wiped or brushed.

Corrosion is also slowed significantly when the relative humidity is brought below 40 percent, which may be accomplished through the use of dehumidifiers, silica desiccants, or other means. Increasing the metal's surface temperature will control condensation.

WHAT IS PASSIVATION?

Best Technology describes passivation as a metal finishing process that prevents corrosion. In stainless steel, the passivation process uses nitric acid or citric acid to remove free iron from the surface. The chemical treatment leads to a protective oxide layer that is less likely to chemically react with air and cause corrosion.

HOW DOES PASSIVATION WORK?

Stainless steel is an iron-based alloy, typically composed of iron, nickel and chromium. Stainless steel derives its corrosion-resistant properties from the chromium content. Chromium, when exposed to oxygen (air), forms a thin film of chromium oxide that covers the stainless steel surface and protects the underlying iron from rusting. The purpose of passivation is to augment and optimize formation of the chromium oxide layer.

Immersion of stainless steel in an acid bath dissolves free iron from the surface while leaving the chromium intact. The acid chemically removes the free iron, leaving behind a uniform surface with a higher proportion of chromium than the underlying material.

Upon exposure to oxygen in the air after the bath, the stainless steel forms the chromic oxide layer over a period of 24 to 48 hours. The higher proportion of chromium at the surface allows for the formation of a thicker, more protective chromium oxide layer. Removal of free iron from the surface removes opportunities for corrosion to start. The resulting passive layer provides a chemically non-reactive surface that protects against rust.

PITTING

WebCorr, a provider of corrosion modeling, notes that pitting is the localized corrosion of a metal surface confined to a point or small area, which takes the form of cavities. Pitting is one of the most damaging forms of corrosion.

Pitting is usually found on passive metals such as aluminum, nickel and chromium alloys, as well as stainless steels when their ultra-thin passive film (oxide-film) is chemically damaged and does not immediately re-passivate. The resulting pits can become wide and shallow or narrow and deep, which can perforate the wall thickness of a metal.

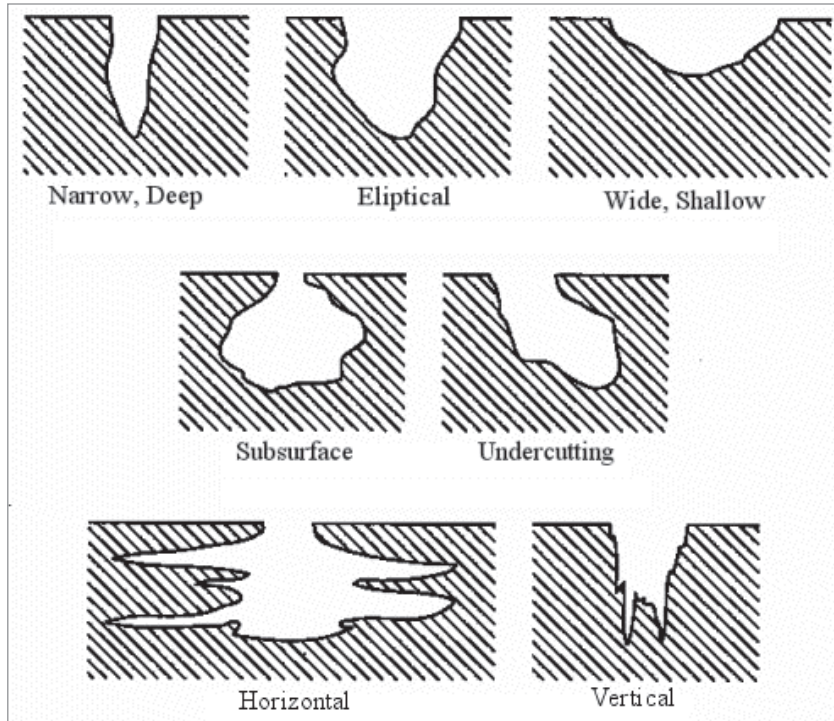


Figure 12.0 - ASTM-G46 chart for rating pitting corrosion

The shape of pitting can only be identified through metallography where a pitted sample is cross-sectioned and the pit shape, size and depth can be determined.

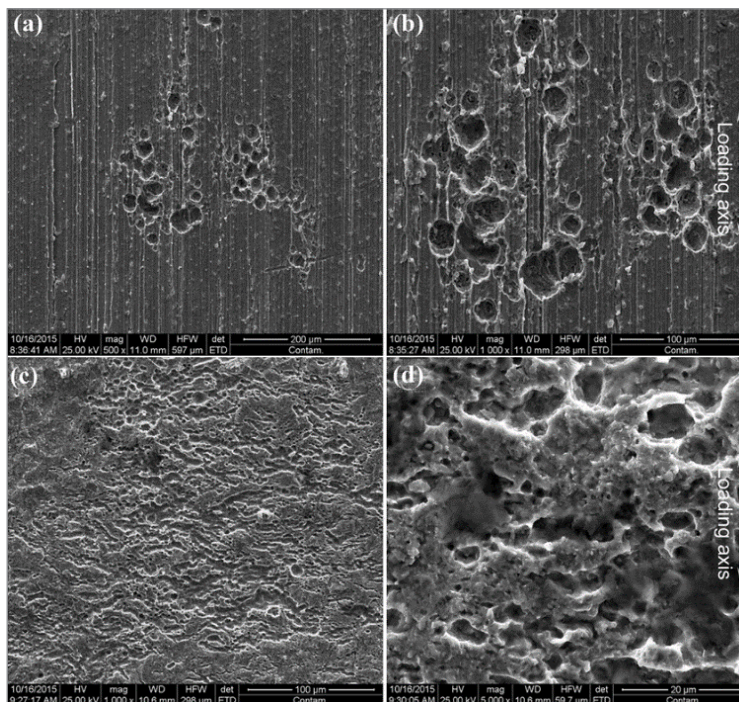


Figure 13.0 - Scanning electron microscope (SEM) morphologies of tensile specimens (a, b) 5 cm and (c, d) 25 cm away from the opening under a disbonded coating: Pitting damage is the dominant corrosion form for the tensile specimen 5 cm away from the opening (a, b); Some pits occur in clusters and coalesce with each other to form coalesced pitting (c, d).

Image courtesy of the Environmental Corrosion Center, Institute of Metal research

SUMMARY

Corrosion and rust result from oxidation reactions that are a natural process. Corrosion impacts a wide range of objects, while rust only impacts iron and its alloys, such as steel. Susceptible surfaces corrode unless they are continuously protected. When environments are compromised due to loss related contaminants or exposure to the elements, protection mechanisms that were safeguarding those susceptible metal and electronic surfaces are compromised. The newly introduced contaminants can be visible and benign, or blend in with pre-existing dust/debris and be highly corrosive. Three immediate actions should be employed in an effort to mitigate secondary damage.

1. The ionic makeup of contaminants should be quantified empirically. Since equipment staged in different parts of a facility is not uniformly contaminated, develop a triage plan based on items that are most prone to deterioration, coupled with analytical laboratory results that point to areas with elevated corrosive matter.
2. Control the environment. Lower the relative humidity to below 40 percent.
3. Preserve equipment with rust inhibiting solutions that are appropriate for the contaminated surface.

Post-loss, there are areas within a facility that require no action, while others require immediate mitigation measures to slow corrosive agents (both environmental and loss related) from corroding/rusting compromised surfaces. Consider professional decontamination experts that employ a scientific approach, in an effort to avoid addressing unaffected items, and ensure that recovery processes suitable for the equipment are utilized to safely restore metal surfaces and sensitive electronic modules.

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