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BASICS OF CORROSION

Class content material

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BASICS OF CORROSION

Fundamental concepts, atmospheric corrosion and industrial metals

Teaching chapter "CORROSION SHENG" by Julia Claudia Mirza-Rosca

Learning objectives

After studying this chapter, students should be able to define corrosion; distinguish corrosion environments, forms and mechanisms; explain the basic electrochemical reactions involved in aqueous and atmospheric corrosion; identify the main atmospheric contaminants and environmental variables; describe the corrosion products commonly associated with zinc, copper, aluminium and steel; and select general approaches for reducing corrosion damage.

1. Introduction and definition

Corrosion is the deterioration of a metal or alloy as a result of physicochemical interaction with its environment. The definition used in the source presentation emphasizes the destruction of a metal under the influence of physicochemical environmental factors. In practical terms, corrosion is the gradual conversion of a metallic material into more chemically stable compounds, such as oxides, hydroxides, sulfides or salts. The process can reduce the thickness of a component, damage its surface, alter its mechanical properties, contaminate a product or cause a complete loss of function.

Corrosion is important because metals are used in buildings, bridges, transport systems, pipelines, marine structures, energy systems, industrial equipment and biomedical devices. The presentation notes that more than 30% of world production of metals and alloys corrodes. This figure is best understood as an indication of the scale of the problem rather than a universal constant: actual losses depend on the material, environment, service life and how corrosion is measured. Even when corrosion is expected, the aim of engineering is to manage it so that components remain safe and economically useful.

Corrosion is not always visible as uniform rust. A surface may appear almost unchanged while deep pits develop at a few locations, or a crack may grow under the combined effects of corrosion and stress. Therefore, appearance alone is not a reliable measure of remaining integrity. A proper assessment considers the metal, its microstructure, the environment, the geometry of the component, the exposure time and the consequences of failure.

2. Classification of corrosion

2.1 Classification by environment

The source presentation groups corrosion environments into soil, air and water. These categories provide a useful first description, although real service conditions may combine them.

- Soil corrosion: buried components such as water pipes, tanks, foundations and cables may be exposed to moisture, dissolved salts, variable oxygen availability, microorganisms and differences in soil resistivity. Soil composition and drainage strongly affect corrosion.
- Atmospheric corrosion: metals exposed to air are usually covered by a thin film of moisture, even when no visible water is present. Oxygen, airborne salts, industrial gases and deposited dust can dissolve in or modify this film.
- Water corrosion: components in fresh water, seawater, process solutions or other aqueous media may corrode because water acts as an electrolyte. Dissolved oxygen, pH, temperature, conductivity, flow and chemical species influence the rate and form of attack.

A single component may experience more than one environment. For example, a steel structure can be exposed to air above a waterline, continuously immersed below itand buried in soil at its supports. Each zone may require a different corrosion-control strategy.

2.2 Classification by form

Figure 2. Schematic forms of corrosion (illustrative, not to scale)

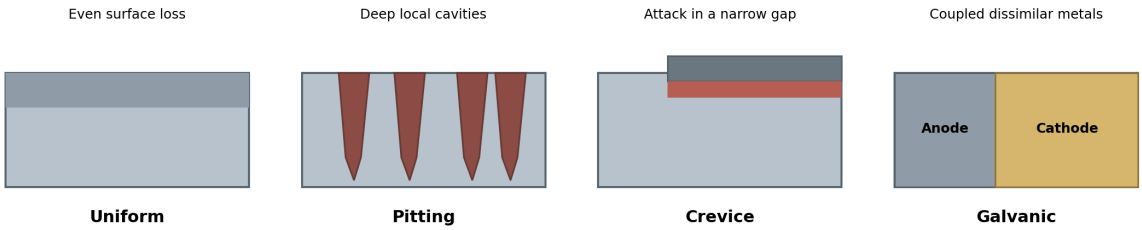

Figure 2. Schematic forms of corrosion. Diagrams are conceptual and not to scale.

The presentation distinguishes general corrosion from localized corrosion. General, or uniform, corrosion removes material over a comparatively broad surface. If the average penetration rate is known, the remaining thickness can often be estimated with reasonable confidence. Localized corrosion affects limited areas and may penetrate deeply while most of the surface remains intact.

- Uniform corrosion: broadly distributed attack, often producing an approximately even reduction in thickness.
- Pitting corrosion: small cavities form at particular points. Pits can be difficult to detect and may perforate a thin wall before substantial average mass loss occurs.
- Crevice corrosion: attack develops in narrow gaps, beneath deposits, washers, gaskets or overlapping surfaces where the local chemistry differs from that of the surrounding environment.
- Galvanic corrosion: electrically connected dissimilar metals experience different electrochemical potentials in a common electrolyte. The less noble metal generally corrodes preferentially, especially when a small anode is coupled to a large cathode.
- Intergranular corrosion: attack follows grain boundaries when local chemistry or microstructure makes these regions susceptible.

- Erosion-corrosion: material loss is accelerated by the combined action of corrosion and moving fluid or entrained particles.

These forms are not mutually exclusive. A component may exhibit general corrosion together with pitting, or localized attack at a galvanic joint. Identifying the morphology is a key step in diagnosing the mechanism.

2.3 Classification by mechanism

The source presentation lists chemical, electrochemical and microbiological mechanisms. Chemical corrosion can occur through direct chemical reaction between a metal and a gas or other environment without a conventional aqueous electrochemical cell. Electrochemical corrosion involves coupled anodic and cathodic reactions and is particularly important when a conductive liquid film is present. Microbiologically influenced corrosion (MIC) occurs when microorganisms or their metabolic products alter local chemistry, deposits, electrochemical conditions or protective films. Microorganisms do not need to consume the metal directly to influence corrosion.

3. Fundamental electrochemistry of corrosion

Figure 1. Simplified electrochemical corrosion cell

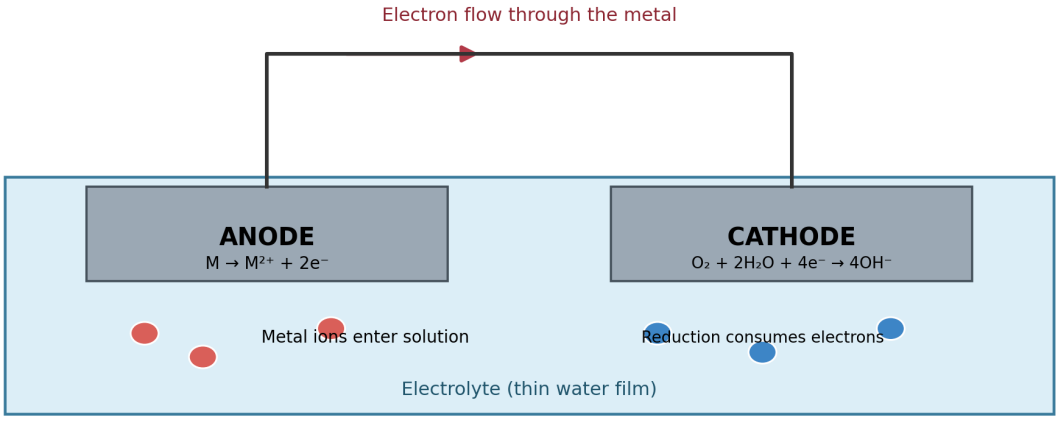

Figure 1. Simplified electrochemical corrosion cell: anodic dissolution, electron flow and cathodic reduction.

Many common corrosion processes are electrochemical. Different areas of a metallic surface can behave as anodes and cathodes. At the anode, metal atoms lose electrons and enter the environment as ions. At the cathode, a reduction reaction consumes the electrons. The metal conducts electrons between these regions, while an electrolyte-such as a thin film of water containing dissolved ions-supports ionic transport.

3.1 The anodic reaction

For a divalent metal M, a simplified anodic reaction is:

$$\mathbf{M \rightarrow M^{2+} + 2e^-}$$

This reaction represents metal oxidation and is the direct step in which metallic material is lost. The exact ion charge and reaction products depend on the metal and the environment. The electrons remain in the metal and are consumed by a cathodic reaction elsewhere on the surface.

3.2 Cathodic reactions

In aerated, approximately neutral water, oxygen reduction is often an important cathodic reaction:

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

In acidic solutions, hydrogen-ion reduction may occur:

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

The dominant cathodic reaction depends on pH, oxygen availability, potential and solution chemistry. Oxygen is not itself a pollutant, as stressed in the presentation, but dissolved oxygen can strongly support corrosion by accepting electrons. In a wet atmospheric film, the amount of oxygen reaching the metal and the time for which the film remains conductive can therefore be decisive.

3.3 The role of the electrolyte and corrosion potential

An electrolyte contains mobile ions that carry charge. Pure water has relatively low conductivity, whereas water containing chlorides, sulfates or other dissolved salts can conduct more readily. A corrosion cell can develop when anodic and cathodic areas are electrically connected through the metal and ionically connected through the electrolyte. Differences in oxygen concentration, composition, temperature, stress or microstructure can create local electrochemical differences.

The electrode potential describes the tendency of an electrode reaction to occur under specified conditions. The electrochemical series compares standard potentials, but it does not by itself predict the actual corrosion rate in service. Real corrosion also depends on passive films, kinetics, mass transport, solution chemistry and the ratio of anodic to cathodic areas. A metal that is thermodynamically reactive may corrode slowly if a stable protective film forms; a metal that appears resistant may suffer rapid localized attack under particular conditions.

3.4 Passivity and protective films

Some metals form a thin, adherent film that slows further reaction with the environment. This condition is called passivity. The film may be an oxide or a hydrated oxide and is often too thin to be seen clearly. Aluminium and stainless steels are familiar examples of materials that rely on passive films. Protection is not absolute: chlorides, mechanical damage, deposits or unfavorable pH may locally destabilize the film and initiate pitting or crevice corrosion.

Corrosion products should therefore not automatically be considered protective. A compact, adherent and chemically stable layer may slow corrosion, whereas a porous, cracked, soluble or easily detached deposit may offer little protection. The behaviour of zinc and copper in the atmosphere, discussed later, illustrates this difference.

4. Atmospheric corrosion

Atmospheric corrosion is the degradation of metal exposed to air and its contaminants. The presentation describes it as the oldest known form of corrosion. Although air may appear dry, a surface can adsorb water vapour or develop a thin electrolyte film through condensation, rain, sea spray or hygroscopic deposits. When a conductive film forms, electrochemical reactions can proceed. Atmospheric corrosion is consequently controlled not only by the composition of the air but also by surface wetness and the duration of wet periods.

4.1 Clean and contaminated atmospheres

In relatively clean atmospheres, many metals corrode slowly at room temperature. Some form passive or patina layers that limit further attack. In industrial or marine atmospheres, however, contaminants can change the conductivity and acidity of surface moisture, damage protective films or create deposits that retain water. The presentation emphasizes that industrial metals are exposed to contaminant-driven corrosion; in practice, the rate varies substantially between alloys and exposure conditions.

4.2 Major atmospheric contaminants

Chlorides

The presentation identifies chlorides as the most aggressive contaminants. Chloride ions are especially important in marine environments and areas affected by sea spray or de-icing salts. They can increase the conductivity of surface moisture and destabilize passive films on susceptible alloys. Chloride deposits may remain on a surface after visible water has evaporated and then absorb moisture again when humidity rises. On aluminium and stainless steels, this can promote pitting or crevice corrosion; on other metals, chloride-containing corrosion products may also be damaging.

Sulfur dioxide (SO_2)

Sulfur dioxide can originate from combustion of sulfur-containing fuels and other industrial activities. It may be absorbed by moisture on a metal surface and undergo oxidation and hydration reactions that produce acidic species, including sulfuric acid under suitable conditions. Acidic surface films can dissolve corrosion products and increase metal dissolution. The presentation notes that, in the presence of SO_2, corrosion products may be removed, including by rainwater, exposing fresh metal to further attack.

Nitrogen-containing compounds

Nitrogen compounds can arise from natural processes, including lightningand from human activities such as the use of ammonia-based fertilizers. Their effects depend on the particular species and conditions. Some nitrogen oxides can form acidic products in atmospheric moisture, while ammonia may alter local solution chemistry. The source presentation groups these contaminants as nitrogen compounds; their individual effects should not be treated as identical.

Hydrogen sulfide (H_2S)

Hydrogen sulfide can be produced during decomposition of sulfur-containing organic matter and by sulfate-reducing bacteria (SRB) in suitable environments. It is relevant to industrial systems, wastewater, deposits and some microbial environments. Depending on the metal and conditions, sulfide-containing products may

form and may be protective or damaging. H_2S can also contribute to specific forms of degradation in susceptible steels, so exposure requires attention to material selection and service conditions.

Oxygen

Oxygen is a normal atmospheric constituent rather than a pollutant, but it plays a central role in many corrosion cells. It dissolves in the moisture layer and can be reduced at cathodic areas. Differences in oxygen access can produce differential-aeration cells: a region with less oxygen may become anodic relative to a better-aerated region. Oxygen availability also affects the formation and transformation of corrosion products.

Dust and deposited particles

Dust adheres to surfaces and can absorb water or acidic species. Deposits may contain salts, industrial contaminants or particles that retain moisture, making the metal wet for longer than an exposed clean surface. Under a deposit, oxygen availability may differ from that at the surrounding surface, encouraging localized attack. Cleaning and deposit control can therefore be important even when the underlying metal appears intact.

5. Atmospheric variables controlling corrosion

Figure 3. Environmental factors controlling atmospheric corrosion

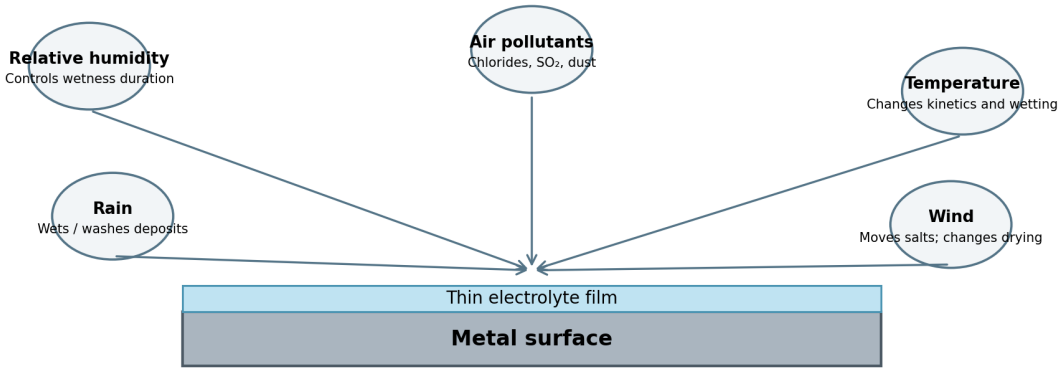

Figure 3. Relative humidity, pollutants, temperature, rain and wind interact to control atmospheric corrosion.

5.1 Relative humidity and time of wetness

Relative humidity is the ratio, expressed as a percentage, between the water-vapour pressure in air and the saturation vapour pressure at the same temperature. As humidity increases, water adsorption and condensation become more likely. Hygroscopic salts can retain moisture even below the humidity at which pure water would condense. Once a continuous electrolyte film is present, electrochemical corrosion can proceed; the longer the surface remains wet, the longer the reactions may continue.

The presentation introduces the concept of critical relative humidity and gives approximate values of 60% for iron and 50–70% for copper, nickel and zinc. These values should be treated as indicative rather than universal thresholds: the critical humidity depends on the contaminant, surface condition, temperature and

measurement method. A salt-contaminated surface can remain wet at a lower relative humidity than a clean surface.

5.2 Temperature

Temperature affects corrosion in more than one way. Increasing temperature often accelerates electrochemical reaction kinetics and diffusion, but it can also reduce the solubility of oxygen in water, change evaporation and condensation, alter the stability of corrosion products and modify the duration of surface wetness. Consequently, the source presentation's notation that the rate may increase or decrease with temperature is appropriate: the net effect must be determined for the particular material and environment.

5.3 Rain

Rain can wash soluble contaminants and loose corrosion products from a surface, which may reduce the accumulation of aggressive deposits. However, rain also wets the metal and can extend the time of wetness. Acidic rain or rainwater containing dissolved industrial pollutants may be more corrosive than clean water. Geometry matters: sheltered surfaces may not be washed by rain and can accumulate salts and dust, whereas exposed surfaces may undergo repeated wetting and drying.

5.4 Wind and air movement

Wind influences the transport of airborne contaminants, the deposition of sea salt and dust, drying rate and the supply of oxygen. Strong air movement may dry a clean surface quickly, but it can also deliver aggressive particles or contribute to erosion of fragile films. Wind-driven rain and salt spray can increase exposure on coastal structures. Its effect is therefore context-dependent rather than uniformly beneficial or harmful.

5.5 Combined environmental effects

Atmospheric corrosion is governed by interacting variables. For example, a chloride deposit may be relatively inactive while dry, become conductive when humidity risesand produce localized attack during a prolonged wet period. Rain may remove some deposits but also renew wetness. Temperature changes may produce condensation on a surface colder than the surrounding air. Corrosion assessment should therefore consider exposure cycles, not just a single reading of temperature or humidity.

6. Corrosion behaviour of industrially important metals

Figure 4. Simplified comparison of atmospheric corrosion products

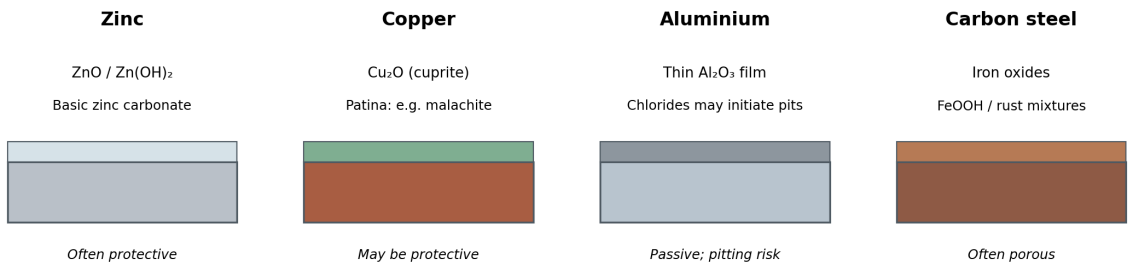

Figure 4. Indicative corrosion-product layers for zinc, copper, aluminium and carbon steel; actual phases depend on exposure conditions.

6.1 Zinc

Zinc is widely used as a protective coating on steel, notably in galvanized products. In the atmosphere, zinc can form zinc oxide (ZnO), zinc hydroxide [$Zn(OH)_2$] and in the presence of carbon dioxide, basic zinc carbonate products. Under suitable conditions, these layers are relatively protective and slow further metal consumption. This helps explain the practical value of zinc coatings: they provide a physical barrier and can also offer sacrificial protection to exposed steel at small coating defects.

The source presentation also highlights that sulfur-containing atmospheric contaminants can lead to zinc sulfate ($ZnSO_4$) and that some corrosion products are soluble and may be removed by rain. The key distinction is between a stable, adherent patina and soluble or poorly adherent products. If the protective layer is repeatedly dissolved or washed away, fresh zinc is exposed and corrosion continues. Zinc performance therefore depends on atmospheric chemistry, wetness, pollutant levels and coating thickness.

6.2 Copper

Copper can develop cuprite (Cu_2O), a red-brown oxide, during atmospheric exposure. With time, moisture, carbon dioxide and other environmental constituents can contribute to the formation of a more complex patina. One familiar green corrosion product is malachite, $Cu_2CO_3(OH)_2$, a basic copper carbonate. Such patinas are often relatively adherent and can slow further corrosion, although their protective performance depends on the environment.

In chloride-containing atmospheres, copper may form basic copper chloride products such as paratacamite. The source slide gives a simplified formula for this compound; in practice, the precise phase and composition depend on conditions and may require analytical confirmation. Copper patina colour alone does not establish whether corrosion is active or protective. Deposits, pollutant exposure, moisture retention and the stability of the corrosion layer must also be considered.

6.3 Aluminium

Aluminium rapidly forms a thin oxide film when exposed to air. This film is the main reason aluminium often exhibits good atmospheric corrosion resistance. However, the source presentation specifically draws attention to pitting corrosion. Chloride ions can locally disrupt the passive film, creating small anodic sites surrounded by a larger cathodic surface. The resulting pits may penetrate deeply even when the overall mass loss is low.

Alloy composition, heat treatment, surface finish, crevices and deposits influence susceptibility. Design should avoid stagnant chloride-containing solutions and narrow moisture-retaining gaps where possible. Appropriate alloy selection, cleaning, coatings and inspection are useful controls, particularly in marine environments.

6.4 Steels and iron corrosion products

Steel corrosion in atmospheric moisture commonly produces a sequence of iron oxides and oxyhydroxides. The source presentation represents the progression schematically from hydrated iron-containing products to magnetite and hematite and also identifies goethite (FeOOH). The exact sequence is not universal: it depends on oxygen supply, wet–dry cycling, pollutants, pH and time. Rust is generally a mixture rather than a single pure compound.

Magnetite (Fe_3O_4) is a mixed-valence iron oxide, while hematite (Fe_2O_3) is an iron(III) oxide. Goethite (α-FeOOH) is an iron oxyhydroxide commonly found in atmospheric rust. Rust layers on ordinary carbon steel are often porous, cracked and insufficiently adherent to stop corrosion, unlike the more protective passive films on some other metals. Corrosion may continue beneath the visible rust.

The presentation notes that the passive layer can be disrupted by wind erosion, rain, defects and impurities. More generally, mechanical damage, inclusions, surface heterogeneity and repeated wetting can expose fresh metal or create local electrochemical differences. Unlike stainless steel, ordinary carbon steel usually does not rely on a stable, self-healing chromium-rich passive film. Protective paints, metallic coatings, suitable design and maintenance are therefore common means of controlling its atmospheric corrosion.

7. Factors affecting corrosion rate and practical assessment

Corrosion rate is not determined by a single property. It reflects the coupled effects of material composition and microstructure, surface condition, electrolyte chemistry, temperature, oxygen supply, geometry, flow and exposure time. The same alloy may perform well in one environment and poorly in another. Likewise, two samples exposed to the same atmosphere may behave differently if one retains deposits or contains a crevice.

For uniform corrosion, rate may be expressed as penetration per unit time, for example millimetres per year (mm/y), or as mass loss per area per time. Weight-loss measurements require a defined exposure period and careful removal of corrosion products without excessive removal of the base metal. Localized corrosion requires additional descriptors such as maximum pit depth, pit density or the depth distribution, because average mass loss can conceal dangerous penetration.

Electrochemical methods can help assess corrosion behaviour. Open-circuit potential (OCP) records the potential of a specimen relative to a reference electrode when no externally imposed current is applied. Potentiodynamic polarization measures current as potential is varied and can help estimate corrosion parameters, provided the experimental assumptions are appropriate. Electrochemical impedance spectroscopy (EIS) applies a small alternating perturbation over a range of frequencies to examine the response of the metal–electrolyte interface. These methods complement, rather than automatically replace, exposure tests and physical inspection.

A sound corrosion investigation should record the alloy and surface preparation, solution composition, temperature, exposed area, test duration, reference electrode, replicate count and data-analysis method. Results from different tests should only be compared when the conditions and calculation procedures are sufficiently similar.

8. General principles of corrosion prevention and control

Corrosion control begins with understanding the environment and the consequences of failure. There is rarely one solution suitable for every case. Common strategies include:

- Material selection: choose a metal or alloy compatible with the environment, considering not only average corrosion rate but also pitting, crevice attack, stress-corrosion risks and galvanic compatibility.
- Protective coatings: paints, polymer layers, conversion coatings and metallic coatings separate the metal from the environment. Coating continuity, adhesion, edge coverage and maintenance are important.

- Cathodic protection: for suitable structures in conductive environments, the metal is polarized so that its corrosion is suppressed. This can be achieved using sacrificial anodes or an impressed-current system.
- Inhibitors: selected chemical species can reduce anodic dissolution, cathodic reactions or both. Their effectiveness depends on concentration, temperature, flow and environmental compatibility.
- Design: avoid water traps, inaccessible crevices and deposits; provide drainage and ventilation; make inspection and maintenance possible; and avoid unfavorable area ratios in dissimilar-metal joints.
- Environmental control: reduce contaminant deposition, manage humidity or temperature where feasible, control water chemistry and prevent stagnant zones.
- Inspection and maintenance: use visual examination, thickness measurements, electrochemical monitoring or other suitable methods to detect degradation before it threatens function.

For galvanic couples, electrical insulation between dissimilar metals or the use of compatible materials can reduce risk. If dissimilar metals must be connected, the relative exposed areas should be considered: a small anodic area connected to a large cathodic area can experience a high anodic current density. Coatings must be selected carefully, because coating only one member of a couple may alter the effective area ratio.

9. Summary

Corrosion is the deterioration of metals through interaction with their surroundings. It can be classified by environment (soil, air or water), by form (general or localized) and by mechanism (chemical, electrochemical or microbiologically influenced). In many practical situations, corrosion is electrochemical: metal dissolves at anodic sites while a reduction reaction, often involving dissolved oxygen, occurs at cathodic sites.

Atmospheric corrosion depends on the formation and persistence of a moisture film and on contaminants such as chlorides, sulfur dioxide, nitrogen compounds, hydrogen sulfide and dust. Relative humidity, temperature, rain and wind act together, so the effect of any one variable depends on the exposure conditions. Zinc may develop relatively protective carbonate-containing layers, copper may form cuprite and patinas such as malachite, aluminium is protected by a thin oxide film but can pit in chloride environments and ordinary steel commonly develops rust containing iron oxides and oxyhydroxides.

The engineering objective is not always to eliminate corrosion completely, which may be impractical, but to control its rate and form so that the component remains safe and functional throughout its intended service life. Effective control combines appropriate materials, design, coatings or electrochemical protection, environmental management and inspection.

Key terms

- **Anode:** The site of oxidation; metal dissolution commonly occurs here.
- **Cathode:** The site of reduction, such as oxygen reduction in aerated water.
- **Electrolyte:** An ion-conducting medium, including a thin moisture film on a metal.
- **Passivity:** A state in which a surface film markedly reduces the rate of metal dissolution.
- **Pitting:** Localized corrosion that forms small cavities or holes.
- **Patina:** A surface layer of corrosion products that may be protective, decorative or damaging depending on its properties.
- **Critical relative humidity:** An approximate humidity threshold above which a surface and its deposits retain sufficient moisture to support increased corrosion; it is system-dependent.

- **MIC:** Microbiologically influenced corrosion, in which microbial activity changes local conditions and affects corrosion.

Review questions

1. What is corrosion and why can visual inspection underestimate its severity?
2. Distinguish classification by environment, form and mechanism, giving an example of each.
3. Write a representative anodic metal-dissolution reaction and the oxygen-reduction reaction in neutral water.
4. Why is oxygen important to atmospheric corrosion even though it is not normally considered a pollutant?
5. Explain how chloride deposits and relative humidity can promote pitting.
6. How can rain both reduce and increase atmospheric corrosion?
7. Compare the atmospheric corrosion products and protective behaviour of zinc, copper, aluminium and carbon steel.
8. Why is a corrosion rate based on average mass loss insufficient for assessing pitting?
9. Name four general corrosion-control strategies and explain when each may be useful.

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