Corrosion

Corrosion 2
Principle and Mechanism of Corrosion 2
Forms of corrosion: 3
Chemical Corrosion 4
Electrochemical Corrosion 5
Electrode Potential 8
Electromotive Force Series 8
Nernst Equations 10
Evan’s Diagram 12
Rate of Corrosion or Plating 14
Mechanism of Oxidation 14
Corrosion Prevention Methods 15
Corrosion Testing 18
Quasi-Crystals 19
    Applications 19

Corrosion

Corrosion is an unintentional gradual destruction of metals by chemical of electrochemical reaction with its environment, which involves removal of the metals or its conversion to an oxide or other compounds such as oxide, chloride, nitrate, sulphate etc. depending upon the environment. The environment may be solid, liquid or gaseous.

The processes of corrosion are

a) Combination of metals with non-metals in the absence of water

$$2Fe + O_2 \rightarrow 2FeO$$
$$2FeO \rightarrow Fe_2O_3$$

b) Combination of metals with oxygen in the presence of water

$$Fe + ½\,O_2 + H_2O \rightarrow Fe(OH)_2$$

c) Displacement of hydrogen from an acid by metal

$$2Ag + H_2S \rightarrow Ag_2S + H_2$$

d) Displacement of metals from its salt by another metal

$$2Na + FeSO_4 \rightarrow Na_2SO_2 + Fe$$

Principle and Mechanism of Corrosion

There are three mechanisms of corrosion:

a) Direct chemical attack (dry corrosion)

Reactive chemicals can attack metals directly with a chemical reaction. This is called direct chemical attack.

b) Electrochemical attack (wet corrosion)

Electrochemical attack is a different type of mechanism where there is current flow that drives corrosion. Electrochemical attack is the most important mechanism characterized by the establishment of an anode and a cathode areas separated by finite distance in the metal causing a flow of current between these areas. Depending upn the conditions either i) galvanic cell of ii) concentration cells setup. Sometimes both kinds of cells may exists simultaneously. There are other cells as well, iii) composition cell, iv) stress cell etc. Here cell means the active corrosion area on a work piece.

c) Physical mechanism (erosion, galling, wear, tear etc.)

Erosion is the action of surface processes (such as water flow or wind) that removes soil, rock, or dissolved material from one location on the Earth's crust, and then transports it to another location (not to be confused with weathering which involves no movement). **Galling** is a form of wear caused by adhesion between sliding surfaces. When a material galls, some of it is pulled with the contacting surface, especially if there is a large amount of force compressing the surfaces together. **Wear** and **tear** is damage that naturally and inevitably occurs as a result of normal wear or aging. It is used in a legal context for such areas as warranty contracts from manufacturers, which usually stipulate that damage from wear and tear will not be covered.

Forms of corrosion:

i) Dry Corrosion

Involved chemical reaction with non-electrolyte gas or liquid.

Example: corrosion of steel with SO_2, CO_2, O_2 etc.

ii) Wet corrosion

Corrosion in contact with electrolyte such as aqueous solution of salt, alkalies and acids

Example: Corrosion of steel in see water, acid and alkalies.

iii) Uniform Corrosion

Uniform attack of electrochemical or chemical reaction over the entire surface.

Example: Steel immersed in dilute sulphuric acid.

iv) Pitting Corrosion

Localized attack in the form of pit (hole, split)

Example: Stainless steel, aluminum alloy Cu-alloy and mixed alloys immersed in chloride solution.

v) Galvanic Corrosion

Dissimilar metals immersed in a corrosive medium and connected electrically.

Example: zinc and iron salt solution

vi) Crevice Corrosion

Intense localized corrosion in shallow holes.

Example: the crevice under bolt and rivet heads

vii) Intergranular Corrosion

Corrosion occurring in the vicinity of the grain boundaries.

Example: weldmelt of stainless steel.

viii) Stress Corrosion

Cracking caused by simultaneous presence of tensile stress and particular corrosion medium.

Example: Seasonal cracking of brass and caustic embrittlement of steel

ix) High Temperature Oxidation

Oxidation or reaction with the product of fuel combustion

Ex.: Corrosion with steel with combustion product such as CO_2, SO_2, O_2 etc.

x) Erosion Corrosion

Acceleration of corrosion because of relative movement between corrosive fluid and the metal.

Ex. Corrosion in pumping equipment, corrosion in the area between bearing and shaft.

xi) Corrosion Fatigue

Combined action of corrosive media and stress.

Ex.: Heat exchange tube of chemical equipment.

Chemical Corrosion

In **chemical corrosion**, or direct dissolution, a material dissolves in a corrosive liquid medium. The material continues to dissolve until either it is consumed or the liquid is saturated. An example is the development of a green patina on the surface of copper-based alloys. This is due to the formation of copper carbonate and copper hydroxides and is why, for example, the Statue of Liberty looks greenish. The chemical corrosion of copper, tantalum, silicon, silicon dioxide, and other materials can be achieved under extremely well-controlled conditions. In the processing of silicon wafers, for example, a process known as chemical mechanical polishing uses a corrosive silica-based slurry to provide mechanical erosion. This process creates extremely flat surfaces that are suitable for the processing of silicon wafers. Chemical corrosion also occurs in nature. For example, the chemical corrosion of rocks by carbonic acid (H_2CO_3) and the mechanical erosion of wind and water play an important role in the formation of canyons and caverns.

Liquid Metal Attack

Liquid metals first attack a solid at high-energy locations such as grain boundaries. If these regions continue to be attacked preferentially, cracks eventually grow (Figure 23-1). Often this form of corrosion is complicated by the presence of fluxes that accelerate the attack or by electrochemical corrosion. Aggressive metals such as liquid lithium can also attack ceramics.

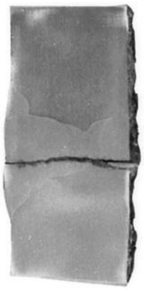


Figure 1: Molten lead is held in thick steel pots during refining. In this case, the molten lead has attacked a weld in a steel plate, and cracks have developed. Eventually, the cracks propagate through the steel, and molten lead leaks from the pot.

Selective Leaching

One particular element in an alloy may be selectively dissolved, or leached, from the solid. **Dezincification** occurs in brass containing more than 15% Zn. Both copper and zinc are dissolved by aqueous solutions at elevated temperatures; the zinc ions remain in solution while the copper ions are re-plated onto the brass (Figure 2). Eventually, the brass becomes porous and weak. **Graphitic corrosion** of gray cast iron occurs when iron is selectively dissolved in water or soil, leaving behind interconnected graphite flakes and a corrosion product. Localized graphitic corrosion often causes leakage or failure of buried gray iron gas lines, sometimes leading to explosions.

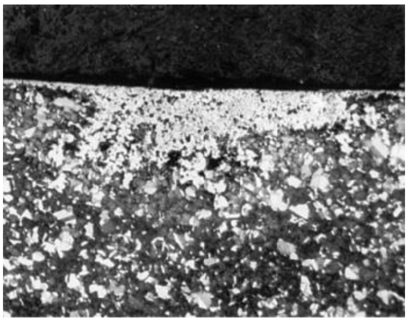


Figure 2: Micrograph of a copper deposit in brass, showing the effect of dezincification.

Dissolution and Oxidation of Ceramics

Ceramic refractories used to contain molten metal during melting or refining may be dissolved by the slags that are produced on the metal surface. For example, an acid (high SiO_2) refractory is rapidly attacked by a basic (high CaO or MgO) slag. A glass produced from SiO_2 and Na_2O is rapidly attacked by water; CaO must be added to the glass to minimize this attack. Nitric acid may selectively leach iron or silica from some ceramics, reducing their strength and density. As noted in Chapters 7 and 15, the strength of silicate glasses depends on flaws that are often created by corrosive interactions with water.

Chemical Attack on Polymers

Compared to metals and oxide ceramics, plastics are considered corrosion resistant. Teflon^{TM} and Viton^{TM} are some of the most corrosion-resistant materials and are used in many applications, including the chemical processing industry. These and other polymeric materials can withstand the presence of many acids, bases, and organic liquids. Aggressive solvents do, however, often diffuse into low molecular- weight thermoplastic polymers. As the solvent is incorporated into the polymer, the smaller solvent molecules force apart the chains, causing swelling. The strength of the bonds between the chains decreases. This leads to softer, lower-strength polymers with low glass-transition temperatures. In extreme cases, the swelling leads to stress cracking. Thermoplastics may also be dissolved in a solvent. Prolonged exposure causes a loss of material and weakening of the polymer part. This process occurs most easily when the temperature is high and when the polymer has a low molecular weight, is highly branched and amorphous, and is not cross-linked. The structure of the monomer is also important; the CH_3 groups on the polymer chain in polypropylene are more easily removed from the chain than are chloride or fluoride ions in polyvinyl chloride (PVC) or polytetrafluoroethylene (Teflon^{TM}). Teflon has exceptional resistance to chemical attack by almost all solvents.

Electrochemical Corrosion

Electrochemical corrosion, the most common form of attack of metals, occurs when metal atoms lose electrons and become ions. As the metal is gradually consumed by this process, a byproduct of the corrosion process is typically formed. Electrochemical corrosion occurs most frequently in an aqueous medium, in which ions are present in water, soil, or moist air. In this process, an electric circuit is created, and the system is called an **electrochemical cell**. Corrosion of a steel pipe or a steel automobile panel, creating holes in the steel and rust as the byproduct, are examples of this reaction. Although responsible for corrosion, electrochemical cells may also be useful. By deliberately creating an electric circuit, we can *electroplate* protective or decorative coatings onto materials. In some cases, electrochemical corrosion is even desired. For example, in etching a polished metal surface with an appropriate acid, various features in the microstructure are selectively attacked, permitting them to be observed. In fact, most of the photographs of metal and alloy microstructures in this text were obtained in this way, thus enabling, for example, the observation of pearlite in steel or grain boundaries in copper.

Components of an Electrochemical Cell

There are four components of an electrochemical cell (Figure 3):

1. The **anode** gives up electrons to the circuit and corrodes.

2. The **cathode** receives electrons from the circuit by means of a chemical, or cathode, reaction. Ions that combine with the electrons produce a byproduct at the cathode.

3. The anode and cathode must be electrically connected, usually by physical contact, to permit the electrons to flow from the anode to the cathode and continue the reaction.

4. A liquid **electrolyte** must be in contact with both the anode and the cathode. The electrolyte is conductive, thus completing the circuit. It provides the means by which metallic ions leave the anode surface and move to the cathode to accept the electrons.

This description of an electrochemical cell defines electrochemical corrosion. If metal ions are deposited onto the cathode, electroplating occurs.

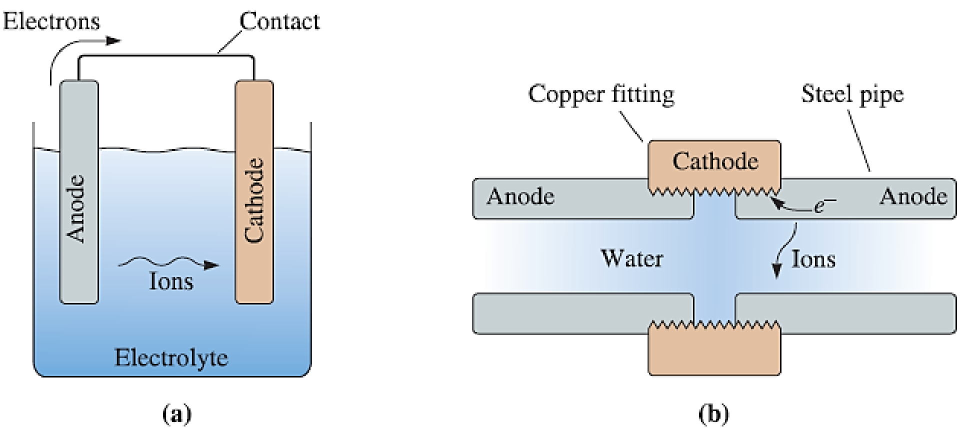


Figure 3: The components in an electrochemical cell: (a) a simple electrochemical cell and (b) a corrosion cell between a steel water pipe and a copper fitting.

Anode Reaction

The anode, which is a metal, undergoes an **oxidation reaction** by which metal atoms are ionized. The metal ions enter the electrolytic solution, while the electrons leave the anode through the electrical connection:

$$\mathrm{M} \rightarrow M^{n+} + n^{e-}$$

Because metal ions leave the anode, the anode corrodes, or oxidizes.

Cathode Reaction in Electroplating

In electroplating, a cathodic **reduction reaction,** which is the reverse of the anode reaction, occurs at the cathode:

$$M^{n+} + n^{e-} \rightarrow \mathrm{M}$$

The metal ions, either intentionally added to the electrolyte or formed by the anode reaction,combine with electrons at the cathode. The metal then plates out and covers the cathode surface.

Cathode Reactions in Corrosion

Except in unusual conditions, plating of a metal does not occur during electrochemical corrosion. Instead, the reduction reaction forms a gas, solid, or liquid byproduct at the cathode (Figure 4).

1. ***The hydrogen electrode*:** In oxygen-free liquids, such as hydrochloric acid (HCl) or stagnant water, hydrogen gas may be evolved at the cathode:

$$2\mathrm{H}^+ + 2e^- \longrightarrow \mathrm{H}_2 \uparrow \text{(gas)}$$

If zinc were placed in such an environment, we would find that the overall reaction is

$$\mathrm{Zn} \longrightarrow \mathrm{Zn}^{2+} + 2e^- \text{ (anode reaction)}$$
$$2\mathrm{H}^+ + 2e^- \longrightarrow \mathrm{H}_2 \uparrow \text{(cathode reaction)}$$
$$\mathrm{Zn} + 2\mathrm{H}^+ \longrightarrow \mathrm{Zn}^{2+} + \mathrm{H}_2 \uparrow \text{(overall reaction)}$$

The zinc anode gradually dissolves, and hydrogen bubbles continue to evolve at the cathode.

2. ***The oxygen electrode:*** In aerated water, oxygen is available to the cathode, and hydroxyl, or $(OH)^-$, ions form:

$$\frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$$

The oxygen electrode enriches the electrolyte in $(OH)^-$ ions. These ions react with positively charged metallic ions and produce a solid product. In the case of rusting of iron:

$$Fe \rightarrow Fe^{2+} + 2e^- \text{ (anode reaction)}$$

$$\left.\begin{array}{l} \frac{1}{2}O_2 + H_2O + 2e^- \rightarrow 2(OH)^- \\ Fe^{2+} + 2(OH)^- \rightarrow Fe(OH)_2 \end{array}\right\} \text{(cathode reactions)}$$

$$Fe + \frac{1}{2}O_2 + H_2O \rightarrow Fe(OH)_2 \text{ (overall reaction)}$$

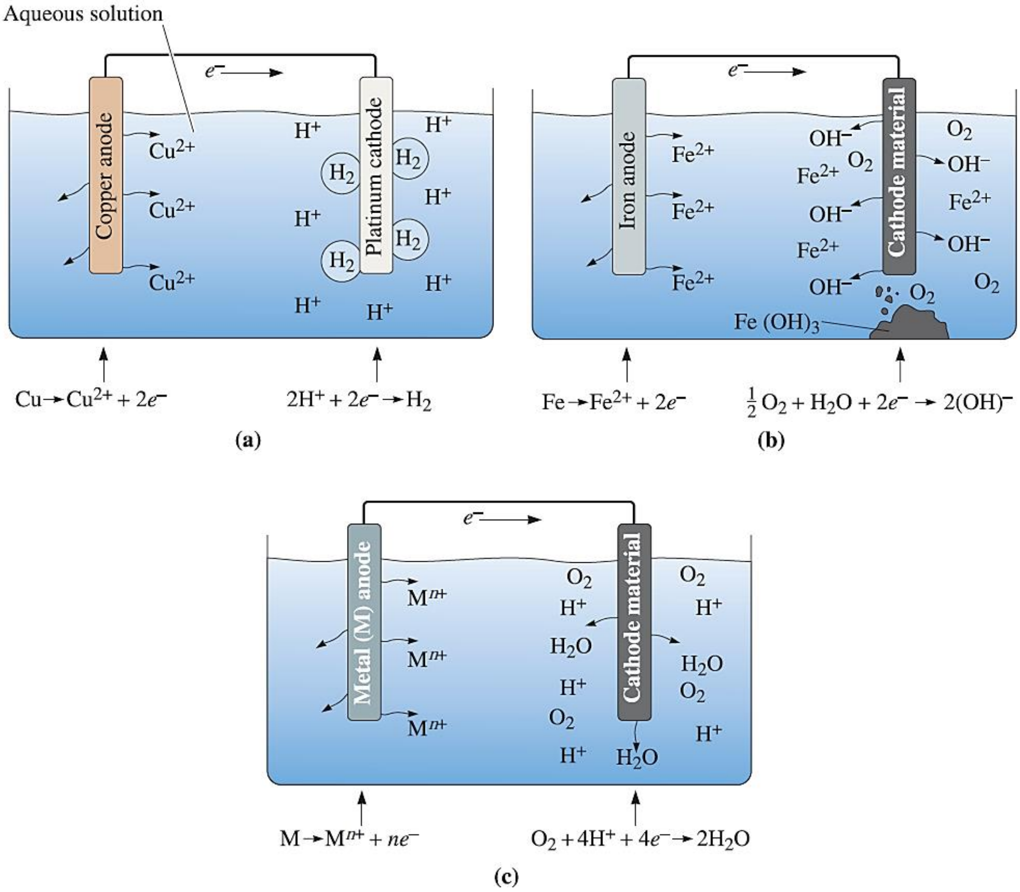


Figure 4: The anode and cathode reactions in typical electrolytic corrosion cells: (a) the hydrogen electrode, (b) the oxygen electrode, and (c) the water electrode.

The reaction continues as the $Fe(OH)_2$ reacts with more oxygen and water:

$$2Fe(OH)_2 + \frac{1}{2}O_2 + H_2O \rightarrow 2Fe(OH)_3$$

$Fe(OH)_3$ is commonly known as rust.

3. ***The water electrode:*** In oxidizing acids, the cathode reaction produces water as a byproduct:

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

If a continuous supply of both oxygen and hydrogen is available, the water electrode produces neither a buildup of solid rust nor a high concentration or dilution of ions at the cathode.

Electrode Potential

When a pure metal is placed in an electrolyte, an **electrode potential** develops that is related to the tendency of the material to give up its electrons; however, the driving force for the oxidation reaction is offset by an equal but opposite driving force for the reduction reaction. No net corrosion occurs. Consequently, we cannot measure the electrode potential for a single electrode material.

Electromotive Force Series

To determine the tendency of a metal to give up its electrons, we measure the potential difference between the metal and a standard electrode using a half-cell (Figure 5). The metal electrode to be tested is placed in a 1 molar (M) solution of its ions. A reference electrode is also placed in a 1 M solution of ions. The reference electrode is typically an inert metal that conducts electrons but does not react with the electrolyte. The use of a 1 M solution of hydrogen (H^+) ions with the reference electrode is common. The reaction that occurs at this hydrogen electrode is $2H^+ + 2e^- = H_2$. H_2 gas is supplied to the hydrogen electrode. An electrochemical cell such as this is known as a standard cell when the measurements are made at 25°C and atmospheric pressure with 1 M electrolyte concentrations. The two electrolytes are in electrical contact but are not permitted to mix with one another. Each electrode establishes its own electrode potential. By measuring the voltage between the two electrodes when the circuit is open, we obtain the potential difference. The potential of the hydrogen electrode is arbitrarily set equal to zero volts. If the metal has a greater tendency to give up electrons than the hydrogen electrode, then the potential of the metal is negative—the metal is anodic with respect to the hydrogen electrode. If the potential of the metal is positive, the metal is cathodic with respect to the hydrogen electrode. The electromotive force (or emf) series shown in Table 1 compares the standard electrode potential E_0 for each metal with that of the hydrogen electrode under standard conditions of 25°C and a 1 M solution of ions in the electrolyte. Note that the measurement of the potential is made when the electric circuit is open. The voltage difference begins to change as soon as the circuit is closed.

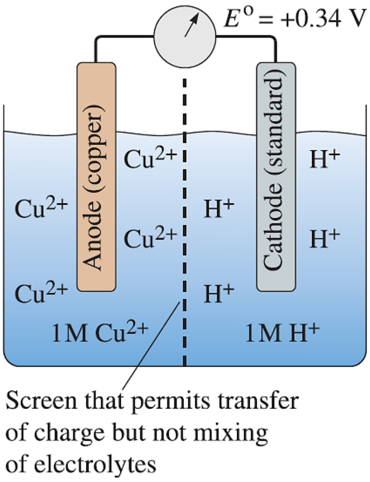
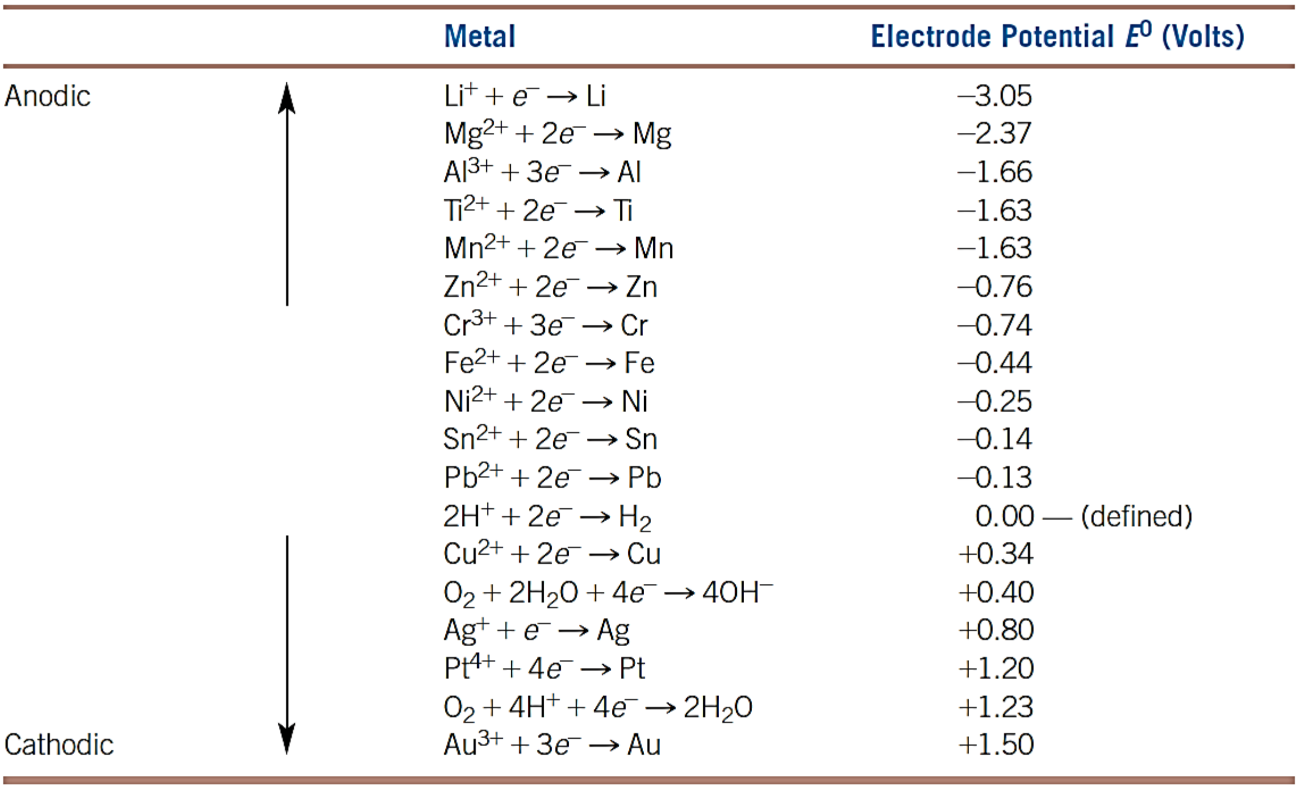


Figure 5: The half-cell used to measure the electrode potential of copper under standard conditions. The electrode potential of copper is the potential difference between it and the standard hydrogen electrode in an open circuit. Since E_0 is greater than zero, copper is cathodic compared to the hydrogen electrode.

TABLE 1 ■ The standard reduction potentials for selected elements and reactions



	Metal	Electrode Potential E^0 (Volts)
Anodic ↑	$Li^+ + e^- \rightarrow Li$	−3.05
	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
	$Ti^{2+} + 2e^- \rightarrow Ti$	−1.63
	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.63
	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.74
	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.25
	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
	$2H^+ + 2e^- \rightarrow H_2$	0.00 — (defined)
	$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34
	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	+0.40
	$Ag^+ + e^- \rightarrow Ag$	+0.80
	$Pt^{4+} + 4e^- \rightarrow Pt$	+1.20
	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.23
Cathodic ↓	$Au^{3+} + 3e^- \rightarrow Au$	+1.50

The more negative the value of potential for the oxidation of metal, the more electropositive is the metal; this means the metal will have a higher tendency to undergo an oxidation reaction. For example, alkali and alkaline earth metals (e.g., Li, K, Ba, Sr, and Mg) are so reactive that they have to be kept under conditions that prevent any contact with oxygen. On the other hand, metals that are toward the bottom of the chart (e.g., Ag, Au, and Pt) will not tend to react with oxygen. This is why we call them “noble metals.” Metals such as Fe, Cu, and Ni have intermediate reactivities; however, this is not the only consideration. Aluminum, for example, has a strongly negative standard electrode potential and does react easily with oxygen to form aluminum oxide; it also reacts easily with fluoride to form aluminum fluoride. Both of these compounds form a tenacious and impervious layer that helps stop further corrosion. Titanium also reacts readily with oxygen. The quickly formed titanium oxide creates a barrier that prevents the further diffusion of species and, thus, avoids further oxidation. This is why both aluminum and titanium are highly reactive, but can resist corrosion exceptionally well. Note that the emf series tells us about the thermodynamic feasibility and driving force, it does not tell us about the kinetics of the reaction.

Effect of Concentration on the Electrode Potential

The electrode potential depends on the concentration of the electrolyte. At 25 °C, the **Nernst equation** gives the electrode potential in nonstandard solutions:

$$E = E^0 + \frac{0.0592}{n} \log (C_{\text{ion}})$$

Where E is the electrode potential in a solution containing a concentration C_{ion} of the metal in molar units, n is the charge on the metallic ion, and E_0 is the standard electrode potential in a 1 M solution. Note that when $C_{ion} = 1$, $E = E_0$. The example that follows illustrates the calculation of the electrode potential.

Nernst Equations

The potential of a cell can be expressed as

$$E = E_{reduction} - E_{oxidation} \tag{1}$$

The tendency of a metal to corrode can be expressed in terms of the electromotive force (emf) of the corrosion cell as

$$\Delta G = -nEF \tag{2}$$

Where, n is the no of electron transfer in the reaction (no of chemical equivalent), F is the Faraday number (9600 coulomb/mole) and E is the potential difference between the electrodes.

Under standard condition, equation 2 can be written as,

$$\Delta G^0 = -nE^0F \tag{3}$$

Gibbs free energy released under non-standard condition can be related to Gibbs energy under standard condition by the relation,

$$\Delta G = \Delta G^0 + RT \ln K \tag{4}$$

Where K is the reaction quotient (ratio of concentration of products to the concentration of reactants).

Combining equation 2, 3 and 4 we get,

$$-nEF = -nE^0F + RT \ln K$$

$$E = E^0 - \frac{RT}{nF} \ln K \tag{5}$$

$$E = E^0 - \frac{2.303\, RT}{nF} \log K \tag{6}$$

Equation 5 and 6 are the Nernst equation. At standard temperature, T =298K, we can write

$$E = E^0 - \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log K$$

$$E = E^0 - \frac{0.0592}{n} \log K$$

This equation indicates that, cell potential gradually decreases until the reaction is at equilibrium at which $\Delta G = 0$. At equilibrium, reaction quotient K=K_{eq}, also at equilibrium $\Delta G^0 = -nFE^0$. Substituting these values, we get

$$0 = E^0 - \frac{RT}{nF} \ln K_{eq}$$

At T=298K it becomes,

$$0 = E^0 - \frac{0.0592}{n} \log K_{eq}$$

$$\log K_{eq} = \frac{nE^0}{0.0592} \tag{7}$$

This is the equilibrium constant at standard condition.

Problem 1: The emf of a cell is $E^0{}_{cell} = +1.10\ V$. For a redox reaction such as

$$Zn_{(s)} + Cu^{2+}_{(aq)} \leftrightharpoons Zn^{2+}_{(aq)} + Cu_{(s)}.$$

What is the equilibrium constant for this reaction? Given that [Cu^{2+}] = [Zn^{2+}] = 1 M, T = 298 K. Reaction proceed for 1 min then [Cu^{2+}] = 0.05 M, while [Zn^{2+}] = 1.95 M. Also find the cell emf

Solution:

We know, at standard condition, the Nernst eqn. can be written as

$$E = E^0 - \frac{0.0592}{n}\log K$$

$$E = 1.10 - \frac{0.0592}{2}\log\frac{1.95}{0.05} = 1.05\ V$$

Now the equilibrium constant is

$$\log K_{eq} = \frac{nE^0}{0.0592}$$

$$K_{eq} = Anti - \log\left[\frac{2 \times 1.10}{0.0592}\right] = 1.58 \times 10^{37}$$

Problem-2: The standard cell potential for the reaction

$$Fe_{(s)} + Zn^{2+}_{(aq)} \leftrightharpoons Fe^{2+}_{(aq)} + Zn_{(s)}.$$

is -0.353 V. If a piece of iron is placed in a 1M Zn^{2+} solution. What is the equilibrium concentration of Fe^{2+}?

Solution:

We know,

$$K_{eq} = Anti - \log\left[\frac{nE^0}{0.0592}\right]$$

$$K_{eq} = Anti - \log\left[\frac{2 \times (-0.353)}{0.0592}\right] = 1.18\ \times 10^{-12}$$

And also

$$K_{eq} = \frac{\left[Fe^{2+}_{(aq)}\right]}{\left[Zn^{2+}_{(aq)}\right]}$$

$$\left[Fe^{2+}_{(aq)}\right] = K_{eq}\left[Zn^{2+}_{(aq)}\right]$$

$$= 1.18\ \times 10^{-12} \times\ 1\text{M}$$

$$= 1.18\ \times 10^{-12}\ \ \text{M}$$

The Corrosion Current and Polarization

To protect metals from corrosion, we wish to make the current as small as possible. Unfortunately, the corrosion current is very difficult to measure, control, or predict. Part of this difficulty can be attributed to various changes that occur during operation of the corrosion cell. A change in the potential of an anode or cathode, which in turn affects the current in the cell, is called **polarization**.

There are three important kinds of polarization: (1) activation, (2) concentration, and (3) resistance polarization.

Activation Polarization

This kind of polarization is related to the energy required to cause the anode or cathode reactions to occur. If we can increase the degree of polarization, these reactions occur with greater difficulty, and the rate of corrosion is reduced. Small differences in composition and structure in the anode and cathode materials dramatically change the activation polarization. Segregation effects in the electrodes cause the activation polarization to vary from one location to another. These factors make it difficult to predict the corrosion current.

Concentration Polarization

After corrosion begins, the concentration of ions at the anode or cathode surface may change. For example, a higher concentration of metal ions may exist at the anode if the ions are unable to diffuse rapidly into the electrolyte. Hydrogen ions may be depleted at the cathode in a hydrogen electrode, or a high $(OH)^-$ concentration may develop at the cathode in an oxygen electrode. When this situation occurs, either the anode or cathode reaction is stifled because fewer electrons are released at the anode or accepted at the cathode. In any of these examples, the current density, and thus the rate of corrosion, decreases because of concentration polarization. Normally, the polarization is less pronounced when the electrolyte is highly concentrated, the temperature is increased, or the electrolyte is vigorously agitated. Each of these factors increases the current density and encourages electrochemical corrosion.

Resistance Polarization

This type of polarization is caused by the electrical resistivity of the electrolyte. If a greater resistance to the flow of the current is offered, the rate of corrosion is reduced. Again, the degree of resistance polarization may change as the composition of the electrolyte changes during the corrosion process.

Evan’s Diagram

An Evans diagram is a pictorial that depict the graphical representation between an electrode’s kinetic data (or current densities) and thermodynamics (or potential) in a corrosive process. An Evans diagram is also known as a mixed potential plot, where the mixed potential is the effective potential of a metallic surface in contact with an electrolyte that is driving electrochemical corrosion. Mixed potential theory explains metal corrosion as a reaction of two or more electrodes working simultaneously at the interface of the metal's surface and an electrolyte.

An Evans diagram is useful for understanding and determining the corrosion process.

An Evans diagrams may also be known as a polarization diagram, mixed potential diagram or mixed potential plot.

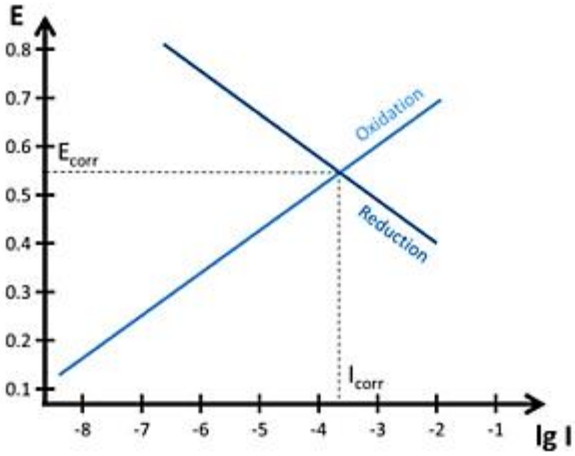


Figure 6: Evan’s Diagram

If these two reactions are responsible for the corrosion and no currents flow from or into the systems, all the electrons released by the oxidation must be accepted by the reduction. So the two reactions can only corrode at the potential where both reactions currents are the same i.e. the sum of anodic oxidation currents must equal the sum of cathodic reduction currents. This means the curves of the two reactions should intersect in the Evan’s Diagram.

This means, if the intersection in the Evan’s Diagram of the two reactions is known, then the corrosion potential and corrosion current are known.

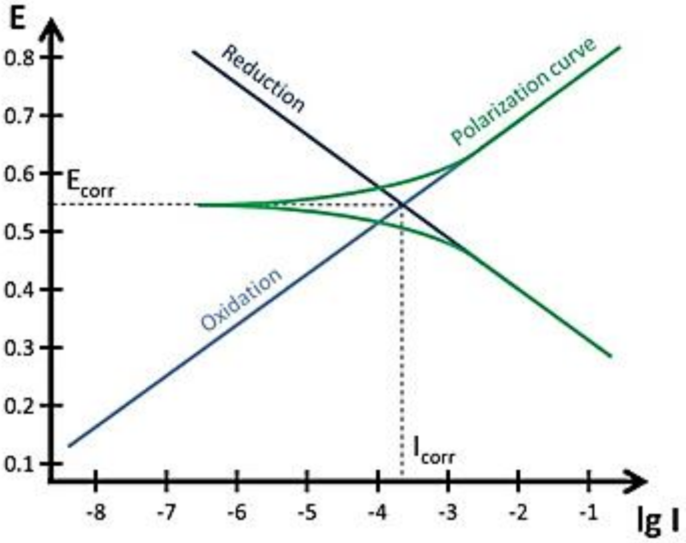


Figure 7: Polarization curve (green)
with Evan’s diagram (blue)

Evans diagrams and mixed potential plots are based on the mixed potential theory, where the x-axis of the plot is the current density and the y-axis is the potential. They consider a metal surface dipped in an electrolyte as being made up of two or more electrodes. These electrodes cause electrochemical corrosion with oxidation directly coupled to the reduction reaction of the depolarizer. The resulting potential of the electrodes is the mixed potential that drives the corrosion process. Cathodically polarizing the cathode reduces the corrosion current density, ultimately causing the corrosion rate to decrease.

Rate of Corrosion or Plating

The amount of metal plated on the cathode in electroplating, or removed from the anode by corrosion, can be determined from Faraday's equation,

$$w \propto Q$$

$$w = ZQ$$

$$w = \frac{ItM}{nF}$$

Where $Z = \frac{M}{nF}$ is the electrochemical equivalence, w is the weight plated or corroded (g), I is the current (A), M is the atomic mass of the metal, n is the charge on the metal ion, t is the time (s), and F is Faraday's constant (96,500 C). This law basically states that one gram equivalent of a metal will be deposited by 96,500 C of charge. Often the current is expressed in terms of current density, J = I/A, so above equation becomes

$$w = \frac{JAtM}{nF}$$

Where the area A (cm^2) is the surface area of the anode or cathode. Then the rate of corrosion is

$$\frac{w}{t} = \frac{JAM}{nF}$$

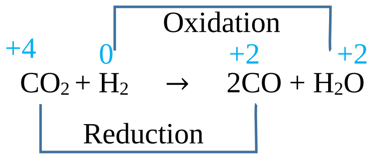
Mechanism of Oxidation

$2\,C + O_2 \rightarrow 2\,CO$	$2\,Mg + O_2 \rightarrow 2\,MgO$
$C + O_2 \rightarrow 2\,CO_2$	$2\,H + O_2 \rightarrow H_2O$
$C + 2\,F_2 \rightarrow CF_4$	$Fe + S \rightarrow FeS$

All of these reactions are oxidation reaction, in which elements combined with oxygen and termed as oxidation. The atom of metal is changed to a positive ion by passing the electron into the oxygen atom. So this process is of removal of electron. Metal have tendency to give up electrons. ($Zn \rightarrow Zn^{2+} + 2\,e^-$). This is called de-electronation. The electrode in which oxidation occurs is called anode.

The reduction process in nothing but taking up electron or adding electron to the atom. Metallic ores, usually oxides of metals, are reduced to the metals by removal of the oxygen or by some other combined with other element by providing another element which has higher affinity for the oxygen.

$$Al^{+++} + 3e^- \rightarrow Al \qquad \text{(from molten cryolite } Na_3AlF_6\text{)}$$



$$\overset{+4}{CO_2} + \overset{0}{H_2} \rightarrow \overset{+2}{2CO} + \overset{+2}{H_2O}$$

A spontaneous reaction is one that releases free energy, and so the sign of ΔG must be negative. Since both ΔH and ΔS can be either positive or negative, depending on the characteristics of the particular reaction, there are four different possible combinations. The outcomes for ΔG based on the signs of ΔH and ΔS are outlined in the table below. Recall that $-\Delta H$ indicates that the reaction is exothermic and a $+\Delta H$ means the reaction is endothermic. For entropy, $+\Delta S$ means the entropy is increasing and the system is becoming more disordered. A $-\Delta S$ means that entropy is decreasing and the system is becoming less disordered

$$\Delta G^{o} = \Delta H^{o} - T\Delta S^{o}$$

ΔH	ΔS	ΔG
negative	positive	always negative
positive	positive	negative at higher temperatures, positive at lower temperatures
negative	negative	negative at lower temperatures, positive at higher temperatures
positive	negative	always positive

Mg + H_2O → $Mg(OH)_2$; $\Delta G^0 = -142000\ cal$ [more forward (spontaneously)]

Cu + H_2O → $Cu(OH)_2$; $\Delta G^0 = -28000\ cal$ [forward (spontaneously)]

Au + H_2O → $Au(OH)_2$; $\Delta G^0 = +157000\ cal$ [does not occurred spontaneously]

Corrosion Prevention Methods

A number of techniques are used to combat corrosion, including proper design and materials selection and the use of coatings, inhibitors, cathodic protection, and passivation.

1. Design

Proper design of metal structures can slow or even avoid corrosion. Some of the steps that should be taken to combat corrosion are as follows:

a) Prevent the formation of galvanic cells. This can be achieved by using similar metals or alloys. For example, steel pipe is frequently connected to brass plumbing fixtures, producing a galvanic cell that causes the steel to corrode. By using intermediate plastic fittings to electrically insulate the steel and brass, this problem can be minimized.

b) Make the anode area much larger than the cathode area. For example, copper rivets can be used to fasten steel sheet. Because of the small area of the copper rivets, a limited cathode reaction occurs. The copper accepts few electrons, and the steel anode reaction proceeds slowly. If, on the other hand, steel rivets are used for joining copper sheet, the small steel anode area gives up many electrons, which are accepted by the large copper cathode area; corrosion of the steel rivets is then very rapid. This is illustrated in the following example.

c) Design components so that fluid systems are closed, rather than open, and so that stagnant pools of liquid do not collect. Partly filled tanks undergo waterline corrosion. Open systems continuously dissolve gas, providing ions that participate in the cathode reaction, and encourage concentration cells.

d) Avoid crevices between assembled or joined materials. Welding may be a better joining technique than brazing, soldering, or mechanical fastening. Galvanic cells develop in brazing or soldering since the filler metals have a different composition from the metal being joined. Mechanical fasteners produce crevices that lead to concentration cells. If the filler metal is closely matched to the base metal, welding may prevent these cells from developing.

e) In some cases, the rate of corrosion cannot be reduced to a level that will not interfere with the expected lifetime of the component. In such cases, the assembly should be designed in such a manner that the corroded part can be easily and economically replaced.

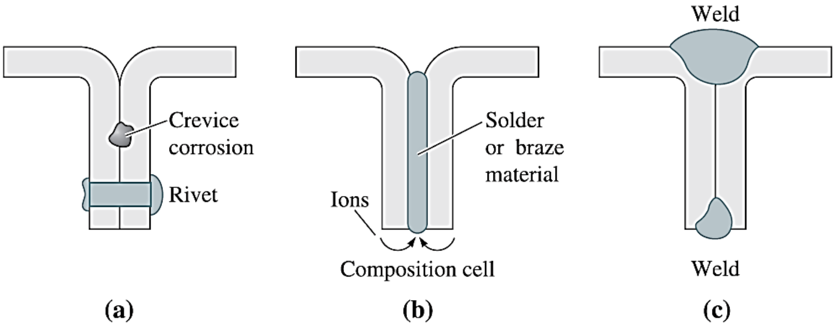


Fig. 8: Alternative methods for joining two pieces of steel: (a) Fasteners may produce a concentration cell, (b) brazing or soldering may produce a composition cell, and (c) welding with a filler metal that matches the base metal may avoid the formation of galvanic cells.

2. Coatings

Coatings are used to isolate the anode and cathode regions. Coatings also prevent diffusion of oxygen or water vapor that initiates corrosion or oxidation. Temporary coatings, such as grease or oil, provide some protection but are easily disrupted. Organic coatings, such as paint, or ceramic coatings, such as enamel or glass, provide better protection; however, if the coating is disrupted, a small anodic site is exposed that undergoes rapid, localized corrosion.

Metallic coatings include tin-plated and hot-dip galvanized (zinc-plated) steel (Figure 9). A continuous coating of either metal isolates the steel from the electrolyte; however, when the coating is scratched, exposing the underlying steel, the zinc continues to be effective, because zinc is anodic to steel. Since the area of the exposed steel cathode is small, the zinc coating corrodes at a very slow rate and the steel remains protected. In contrast, steel is anodic to tin, so a small steel anode is created when the tin is scratched, and rapid corrosion of the steel subsequently occurs.

Chemical conversion coatings are produced by a chemical reaction with the surface. Liquids such as zinc acid orthophosphate solutions form an adherent phosphate layer on the metal surface. The phosphate layer is, however, rather porous and is more often used to improve paint adherence. Stable, adherent, nonporous, non-conducting oxide layers form on the surface of aluminum, chromium, and stainless steel. These oxides exclude the electrolyte and prevent the formation of galvanic cells. Components such as reaction vessels can also be lined with corrosion-resistant Teflon^{TM} or other plastics.

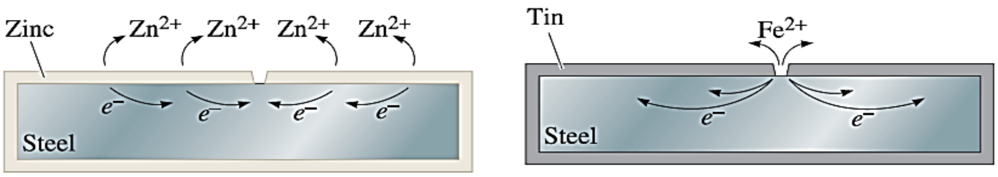


Fig. 9: Zinc-plated steel and tin-plated steel are protected differently. Zinc protects steel even when the coating is scratched since zinc is anodic to steel. Tin does not protect steel when the coating is disrupted since steel is anodic with respect to tin.

3. Inhibitors

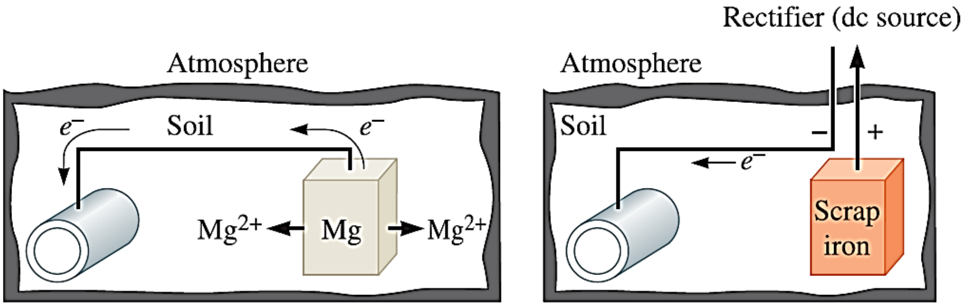
When added to the electrolyte, some chemicals migrate preferentially to the anode or cathode surface and produce concentration or resistance polarization— that is, they are **inhibitors**. Chromate salts perform this function in automobile radiators. A variety of chromates, phosphates, molybdates, and nitrites produce protective films on anodes or cathodes in power plants and heat exchangers, thus stifling the electrochemical cell. Although the exact contents and the mechanism by which it functions are not clear, the popular lubricant WD-40TM works from the action of inhibitors. The name “WD-40TM”was designated water displacement (WD) that worked on the fortieth experimental attempt!

4. Cathodic Protection

We can protect against corrosion by supplying the metal with electrons and forcing the metal to be a cathode (Figure 10). Cathodic protection can use a sacrificial anode or an impressed voltage.

A **sacrificial anode** is attached to the material to be protected, forming an electrochemical circuit. The sacrificial anode corrodes, supplies electrons to the metal, and thereby prevents an anode reaction at the metal. The sacrificial anode, typically zinc or magnesium, is consumed and must eventually be replaced. Applications include preventing the corrosion of buried pipelines, ships, off-shore drilling platforms, and water heaters. A magnesium rod is used in many water heaters. The Mg serves as an anode and undergoes dissolution, thus protecting the steel from corroding.

An impressed voltage is obtained from a direct current source connected between an auxiliary anode and the metal to be protected. Essentially, we have connected a battery so that electrons flow to the metal, causing the metal to be the cathode. The auxiliary anode, such as scrap iron, corrodes.



(a) **(b)**

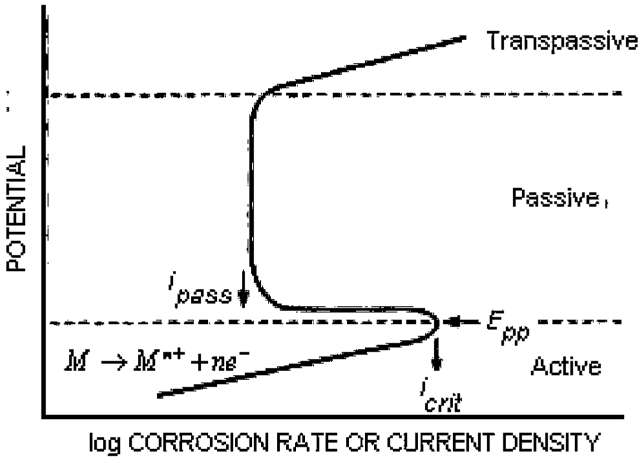
Fig. 10: Cathodic protection of a buried steel pipeline: (a) A sacrificial magnesium anode ensures that the galvanic cell makes the pipeline the cathode. (b) An impressed voltage between a scrap iron auxiliary anode and the pipeline ensures that the pipeline is the cathode.

5. Passivation or Anodic Protection

Metals near the anodic end of the galvanic series are active and serve as anodes in most electrolytic cells; however, if these metals are made passive or more cathodic, they corrode at slower rates than normal. **Passivation** is accomplished by producing strong anodic polarization, preventing the normal anode reaction; thus the term anodic protection.

We cause passivation by exposing the metal to highly concentrated oxidizing solutions. If iron is dipped in very concentrated nitric acid, the iron rapidly and uniformly corrodes to form a thin, protective iron hydroxide coating. The coating protects the iron from subsequent corrosion in nitric acid.

We can also cause passivation by increasing the potential on the anode above a critical level. A passive film forms on the metal surface, causing strong anodic polarization, and the current decreases to a very low level. Passivation of aluminum is called **anodizing**, and a thick oxide coating is produced. This oxide layer can be dyed to produce attractive colors. The Ta2O5 oxide layer formed on tantalum wires is used to make capacitors.



6. Materials Selection and Treatment

Corrosion can be prevented or minimized by selecting appropriate materials and heat treatments. In castings, for example, segregation causes tiny, localized galvanic cells that accelerate corrosion. We can improve corrosion resistance with a homogenization heat treatment. When metals are formed into finished shapes by bending, differences in the amount of cold work and residual stresses cause local stress cells. These may be minimized by a stress-relief anneal or a full recrystallization anneal.

Corrosion Testing

Salt Sprat test is a highly standardized test method which is used to measure the corrosion resistance strength of the coated sample when they are exposed to corrosive environment. To perform the salt spray test, different <strong>corrosion test chambers are used. These chambers are used to measure the strength, quality and working life of the metals by subjecting them to different environmental conditions

Salt Spray Chambers or Corrosion Test Chambers are widely used to perform the Salt Spray test where a sample is provided with a salty environment by spraying a salt solution on the material by means of a nozzle. This creates a corrosive environment for the products and helps to determine the quality of the material actual working life of the product. The test samples can be exposed to the highly appropriate volume of salt spray.

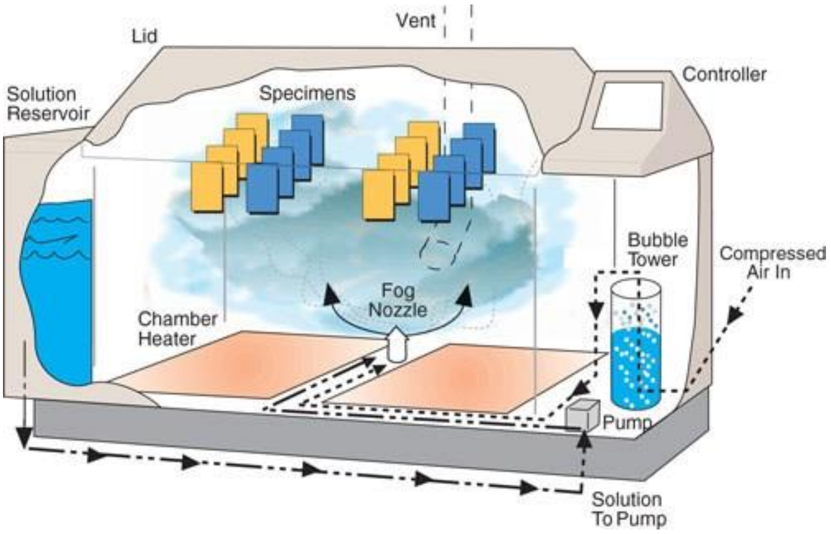


Fig. 11: Salt Spray test chamber.

Quasi-Crystals

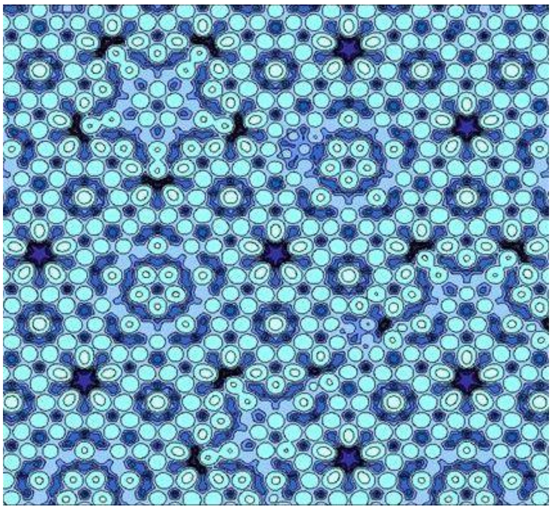
A quasiperiodic crystal, or **quasicrystal**, is a structure that is ordered but not periodic. A quasicrystalline pattern can continuously fill all available space, but it lacks translational symmetry. While crystals, according to the classical crystallographic restriction theorem, can possess only two, three, four, and six-fold rotational symmetries, the Bragg diffraction pattern of quasicrystals shows sharp peaks with other symmetry orders, for instance five-fold.

Applications

Quasicrystalline substances have potential applications in several forms.

Metallic quasicrystalline coatings can be applied by plasma-coating or magnetron sputtering.

An application was the use of low-friction Al-Cu-Fe-Cr quasicrystals as a coating for frying pans. Food did not stick to it as much as to stainless steel making the pan moderately non-stick and easy to clean; heat transfer and durability were better than PTFE non-stick cookware and the pan was free from perfluorooctanoic acid (PFOA); the surface was very hard, claimed to be ten times harder than stainless steel, and not harmed by metal utensils or cleaning in a dishwasher.



Quasicrystals were also being used to develop heat insulation, LEDs, diesel engines, and new materials that convert heat to electricity. Shechtman suggested new applications taking advantage of the low coefficient of friction and the hardness of some quasicrystalline materials, for example embedding particles in plastic to make strong, hard-wearing, low-friction plastic gears. The low heat conductivity of some quasicrystals makes them good for heat insulating coatings.[46]

Other potential applications include selective solar absorbers for power conversion, broad-wavelength reflectors, and bone repair and prostheses applications where biocompatibility, low friction and corrosion resistance are required. Magnetron sputtering can be readily applied to other stable quasicrystalline alloys such as Al-Pd-Mn.

Reference: The Science and Engineering of Materials, Sixth Edition by Donald R. Askeland.