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CHEMISTRY II

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CORROSION: MECHANISMS AND CONTROL

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Contents

Introduction
Definitions
Chemical and Electrochemical Corrosion

Corrosion: Electrochemical Considerations
Anodic and Cathodic Processes
The Electrode Potential in Electrochemical Cells

Corrosion Kinetics
Corrosion Rates
Examples

Forms of Corrosion
Uniform Attack; Galvanic Corrosion; Crevice Corrosion; Pitting; Stress Corrosion

Passivity
Passivity: General Considerations

Corrosion Prevention
Protection against Electrochemical Corrosion
Inhibitors; Cathodic Protection; Coatings

Corrosion

***Corrosion** is the spontaneous destruction of metals and alloys caused by chemical, biochemical, and electrochemical interaction between metals and alloys and the environment.*

Corrosive environments include moisture, oxygen, inorganic and organic acids, high pressure, temperature, and chlorides.

Chemical and Electrochemical 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.*

***Electrochemical corrosion**: deterioration of metals by an electrochemical process. 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.*

Why does the Statue of Liberty look greenish?

Chemical corrosion of copper. Formation of copper carbonate and copper hydroxides on the surface of copper based alloys.

The layer of copper $CuCO_3$ which is a Green substance is also called patina.

Anodic and Cathodic Processes

Anode reaction

The anode which is a metal, undergoes an oxidation reaction by which metal atoms are ionized:

$$\boxed{M \longrightarrow M^{n+} + n\,e^{-}}$$

The anode **corrodes** or **oxidizes**.

Cathode reaction in **Electroplating**

In electroplating, a cathodic reduction reaction occurs:

$$\boxed{M^{n+} + n\,e^{-} \longrightarrow M}$$

The **metal then plates out** and covers the cathode surface.

Cathode reaction in **Corrosion**

1. The hydrogen electrode: In oxygen-free liquids (HCl), H_2 (g) may be envolved at the cathode:

$$2\,H^+ + 2\,e^- \longrightarrow H_2\,(g)$$

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

$$Zn \longrightarrow Zn^{2+} + 2e^- \quad \text{(Anode reaction)}$$

$$2H^+ + 2e^- \longrightarrow H_2\,(g) \quad \text{(Cathode reaction)}$$

$$Zn + 2\,H^+ \longrightarrow Zn^{2+} + H_2\,(g) \quad \text{(Overall reaction)}$$

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 hydroxide ions ions form:

$$\tfrac{1}{2}\,O_2 + H_2O + 2\,e^- \longrightarrow 2\,OH^-$$

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 :

$$Fe \longrightarrow Fe^{2+} + 2\,e^- \quad \text{(Anode reaction)}$$

$$\left.\begin{array}{l} \tfrac{1}{2}\,O_2 + H_2O + 2\,e^- \longrightarrow 2\,OH^- \\ Fe^{2+} + 2\,OH^- \longrightarrow Fe(OH)_2 \end{array}\right\} \text{(Cathode reaction)}$$

$$Fe + \tfrac{1}{2}\,O_2 + H_2O \longrightarrow Fe(OH)_2 \quad \text{(Overall reaction)}$$

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

$$2\,Fe(OH)_2 + \tfrac{1}{2}\,O_2 + H_2O \longrightarrow 2\,Fe(OH)_3$$

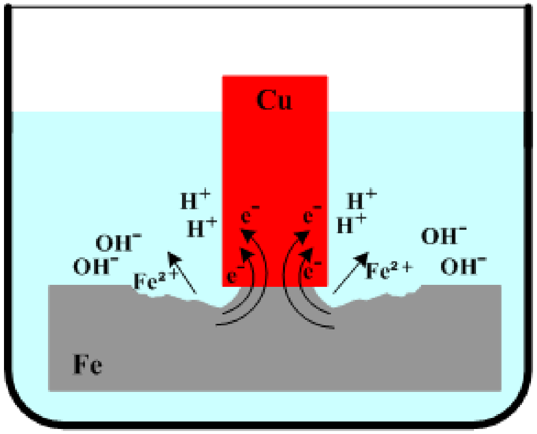
3. The water electrode: In oxidizing acids, the cathode reaction produces water as a byproduct:

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

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.

The Electrode Potential in Electrochemical Cells

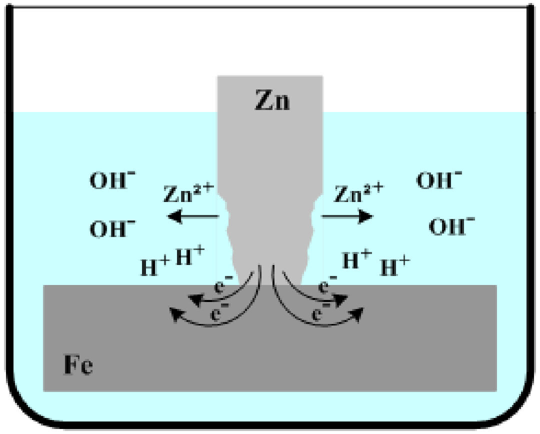
Galvanic couple: two metals electrically connected in a liquid electrolyte wherein one metal becomes an anode and corrodes, while the other acts as a cathode



An electrochemical cell consisting of iron and copper electrodes, each of which is immersed in a 1 M solution of its ion. ***Iron corrodes while copper electrodeposits****.*

$$Cu^{2+} + Fe \longrightarrow Cu + Fe^{2+}$$

$$E^\circ = 0.780\ V$$



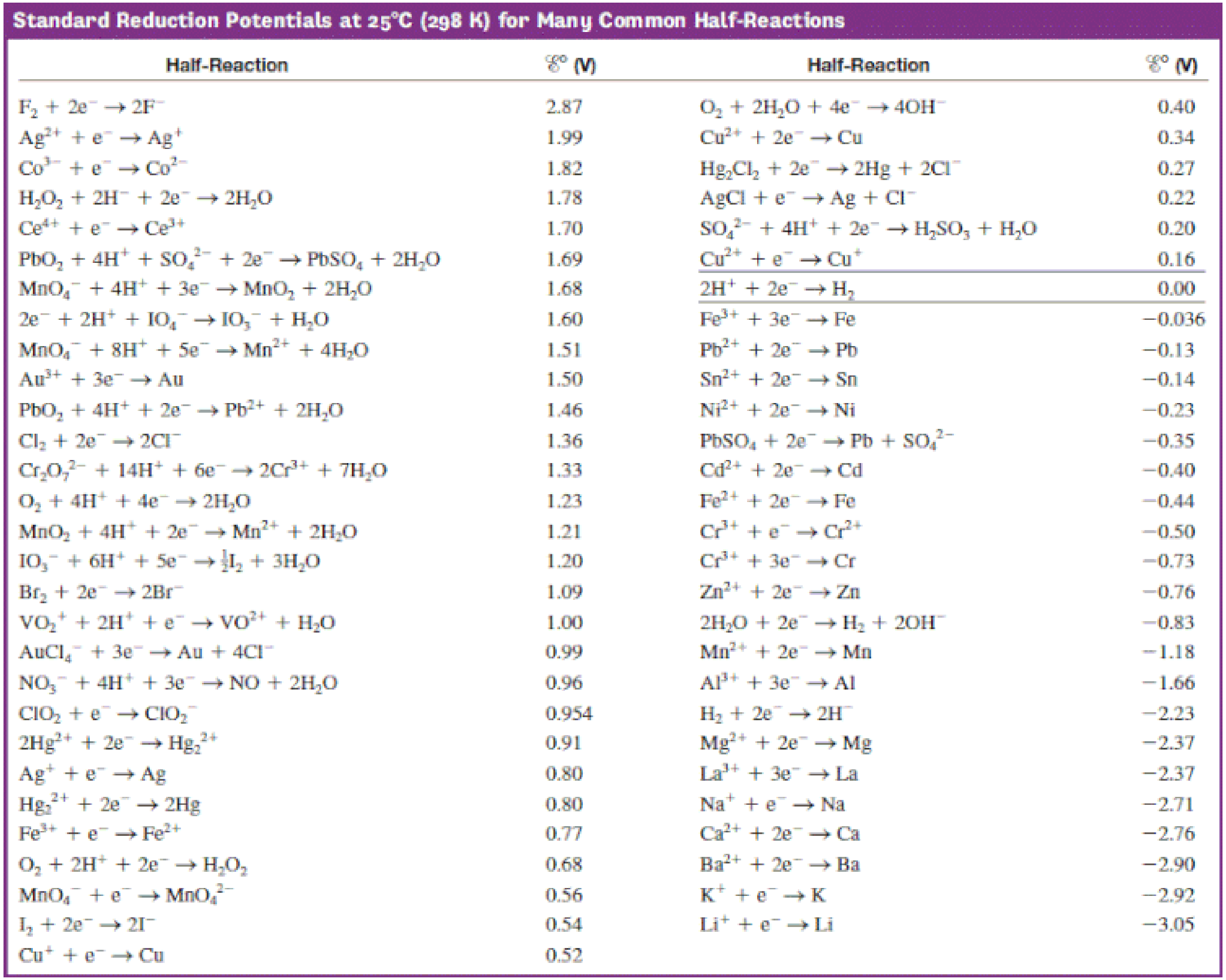
An electrochemical cell consisting of iron and zinc electrodes, each of which is immersed in a 1 M solution of its ion. ***The iron electrodeposits while the zinc corrodes****.*

$$Fe^{2+} + Zn \longrightarrow Fe + Zn^{2+}$$

$$E^{\circ} = 0.323\ V$$

The Standard efm Series

Increasingly inert (cathodic)



Standard Reduction Potentials at 25°C (298 K) for Many Common Half-Reactions

Half-Reaction	$\mathscr{E}^\circ$ (V)	Half-Reaction	$\mathscr{E}^\circ$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$2e^- + 2H^+ + IO_4^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	−2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	−2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	−2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	−3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

Increasingly active (anodic)

Corrosion Rates

Corrosion Rate*: rate of material removal as a consequence of the chemical action.*

Corrosion Penetration Rate (CPR)*:* thickness loss of material per unit of time.

$$CPR = \frac{KW}{\rho At} \quad (mm/year)$$

K	Constant (its magnitude depends on the system of units used) K = 534 (CPR in mpy) K = 87.6 (CPR in mm/yr)
W	Weight loss after exposure time *t* (mg)
ρ	Density (g/cm^3)
A	Exposed specimen area (inch^2 when CPR is mpy and cm^2 when CPR is in mm/yr)
t	Exposure time (h)

Corrosion Rate (r) *as a function of the* current density.

$$r = \frac{i}{nF} \quad (mol/m^2 s)$$

i	Current density (A/m^2)
n	Number of electrons associated with the ionization of each metal atom
F	Faraday constant (C/mol)

Forms of corrosion: Metallic corrosion

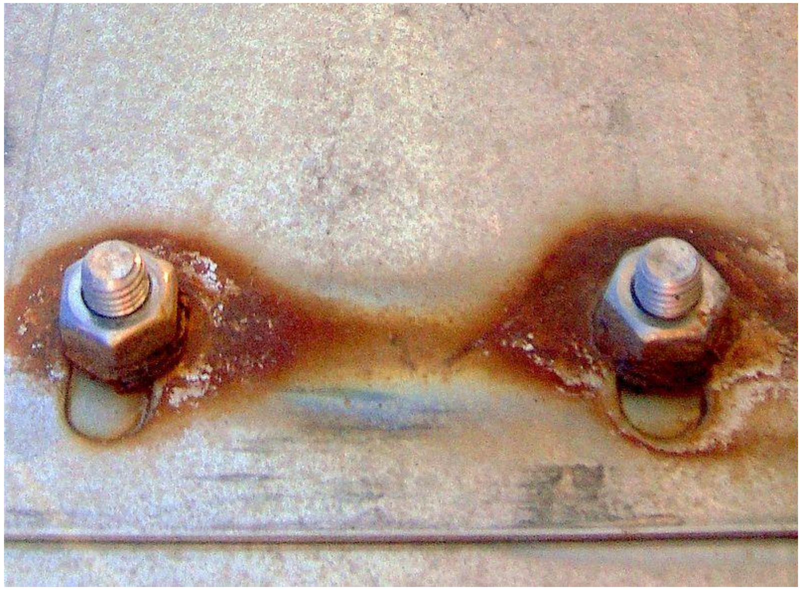
Classification of corrosion according to the manner in which it is manifest.

Uniform Attack

Uniform Attack*: is the most common form of corrosion. It is normally characterized by a chemical or electrochemical reaction which proceeds uniformly over the entire exposed surface or over a large area.*

Galvanic corrosion

***Galvanic corrosion**: occurs when two metals or alloys having different compositions are electrically coupled while exposed to an electrolyte.* The less noble or more reactive metal in the particular environment will experience corrosion.



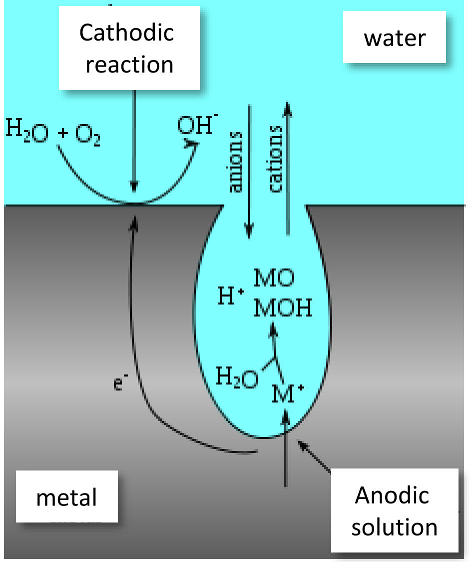
Photograph showing galvanic corrosion. Corrosion occurred between a mild steel that was cast around a stainless steel core.

Crevice corrosion

***Crevice corrosion**: Electrochemical corrosion may also occur as a consequence of concentration differences of ions or dissolved gases in the electrolyte solution, and between two regions of the same metal piece. For such a **concentration cell**, corrosion occurs in the locale that has the lower concentration. This type of corrosion occurs in crevices.*

A

B



A) Crevice corrosion

B) Mechanism of crevice corrosion

Pitting

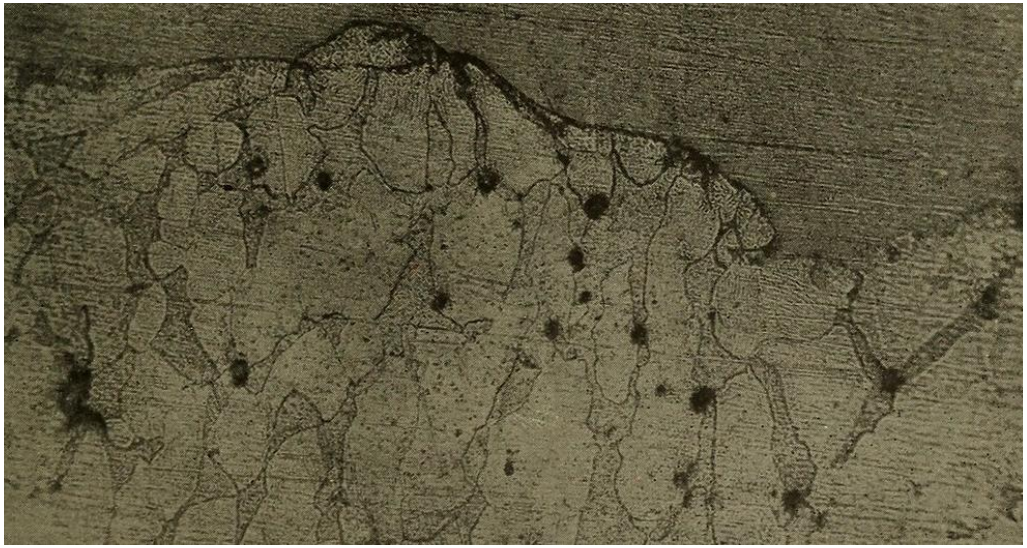
***Pitting**: is another form of very localized corrosion attack in which small pits or holes form. They ordinarily penetrate from the top of a horizontal surface downward in a nearly vertical direction. It is an extremely insidious type of corrosion, often going undetected and with very little material loss until failure occurs.*

The pitting of aluminium plate

Stress Corrosion

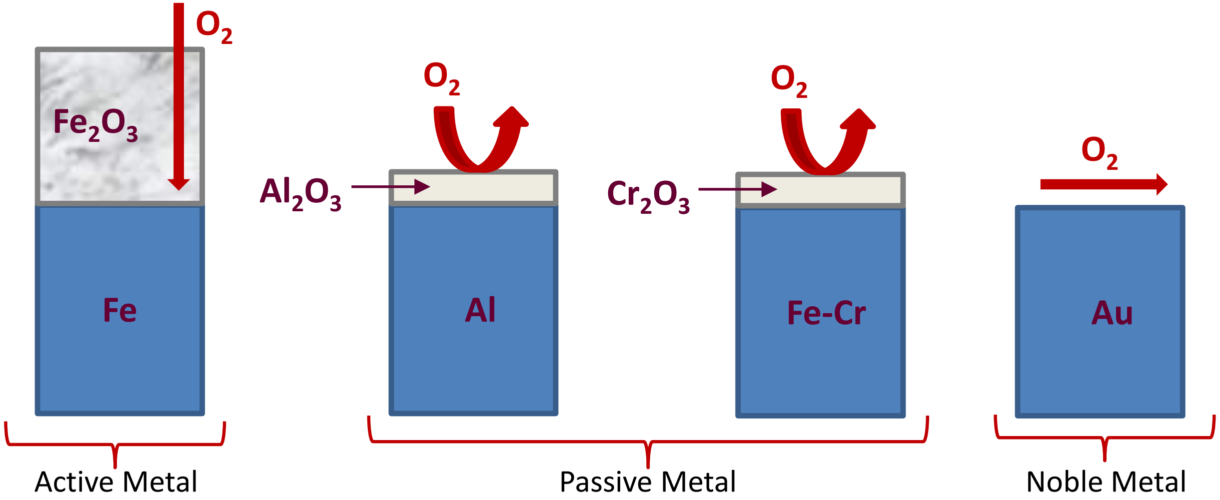
***Stress corrosion (Stress corrosion cracking)**: results from the combined action of an applied tensile stress and a corrosive environment. Small cracks form and then propagate in a direction perpendicular to the stress with the result that failure may eventually occur.*

Deterioration of Muntz (variety of brass) metal



Passivity: General Considerations

Passivity: *phenomenon through some normally active metals and alloys, under particular environmental conditions, lose their chemical reactivity and become extremely inert. It is displayed by chromium, iron, nickel, titanium, and many of their alloys. This passive behavior results from the formation of a* <u>*highly adherent and very thin oxide film*</u> *on the metal surface, which serves as a protective barrier to further corrosion.*



Protection against Electrochemical Corrosion

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

- Selection of **materials**: It is not always economically feasible to employ the material that provides the optimum corrosion resistance.
- Character of the **environment**: Lowering the fluid temperature and/or velocity usually produces a reduction in the rate at which corrosion occurs.

Inhibitors

***Inhibitors**: are substances that, when added in relatively low concentrations to the environment, decrease its corrosiveness.*

Some inhibitors react with and virtually eliminate a chemically active species in the solution (such as dissolved oxygen).

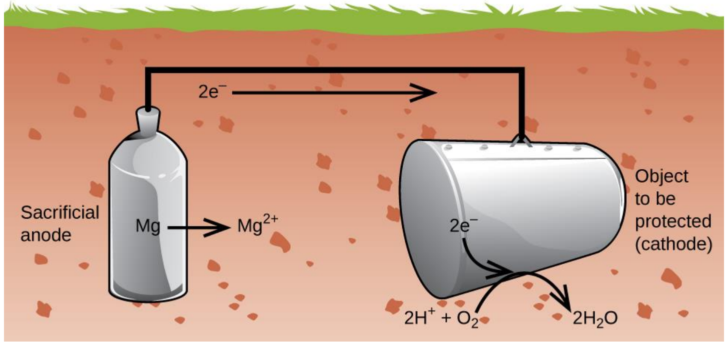
A variety of chromates, phosphates, molybdates, and nitrites produce protective films on anodes or cathodes in power plants and heat exchangers, thus stifling the electrochemical cell.

Prestone AMAM 5050 with Superiority Claim works from the action of inhibitors.

Cathodic Protection

Cathodic protection simply involves supplying, from an external source, electrons to **the metal to be protected, making it a cathode**. The reaction above is thus forced in the reverse (or reduction) direction. One cathodic protection technique employs a galvanic couple: **the metal to be protected is electrically connected to another metal that is more reactive** in the particular environment.

Sacrificial Anode



Sacrificial Anode *Steel pipeline*

Cathodic protection of a buried steel pipeline. A sacrificial magnesium anode ensures that the galvanic cell makes the pipeline the cathode.

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.

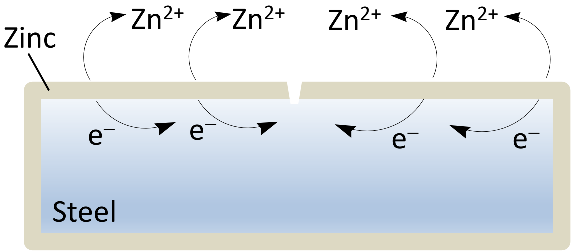
Impressed voltage

Cathodic protection of a buried steel pipeline. An impressed voltage between a scrap iron auxiliary anode and the pipeline ensures that the pipeline is the cathode.

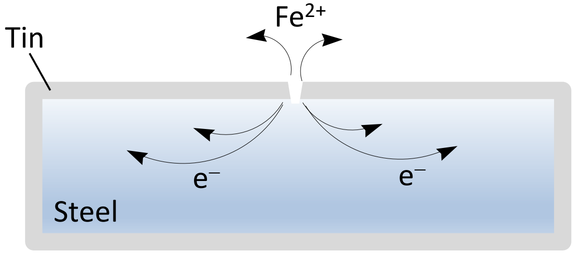
An impressed voltage is obtained from a direct current source connected between an auxiliary anode and the metal to be protected. Essentially, we have connected a battery so that electrons flow to the metal, causing the metal to be the cathode. The auxiliary anode, such as scrap iron, corrodes.

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.



Zinc-plated steel and tin-plated steel are protected differently. <u>Zinc protects steel</u> even when the coating is scratched since zinc is anodic to steel.



<u>Tin does not protect steel</u> when the coating is disrupted since steel is anodic with respect to tin.

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