Mat E 272

Lecture 26: Oxidation and Corrosion

December 11, 2001

Introduction:

Environmental degradation of materials is one of the most costly failure modes, accounting for over 5 percent of the total gross national product in most industrialized nations. In many cases, these degradation modes become the primary limitation to engineering applications for metals. The two most important degradation modes are oxidation and corrosion. <u>Oxidation</u> is a chemical reaction between a metal and atmospheric oxygen, resulting in the formation of metal-oxide compounds by way of electron transfer from the metal atoms. While these oxides are frequently destructive, they can also play a beneficial role, in the case of a stable protective oxide film which protects the metal from more serious attack. <u>Corrosion</u> is the dissolution of a metal in an aqueous environment, also due to electron transfer. At one time, automotive corrosion was one of the leading causes for vehicle replacement, especially in northern climates. However, due to improved materials and better engineering design of components, most new cars come with a 100,000 mile rust-through warranty. Still, corrosion is a major problem and to understand how do deal with it, we must understand the underlying chemical reactions and environments.

Oxidation

Oxidation:

Most metals form stable oxide compounds when exposed to air

- **oxides are usually more stable than pure metals**

"Oxidation" refers to the general class of reactions involving an electron transfer, and is really two separate "half-reactions," ***oxidation*** **+** ***reduction*.**

Specifically,

<u>Oxidation</u>: a loss of one (or more) valence electron , viz.

$M \dashrightarrow M^{(n+)} + (n)e^-$ (this occurs at the metal-scale interface)

<u>Reduction</u>: a gain of one (or more) valence electron ***from the metal atoms*****, (usually to form an anion)**

$\frac{1}{2}O_2 + (n)e^- \dashrightarrow O^{(n)-}$ (this occurs at the scale-gas interface)

In words: ***a material is oxidized if its atoms lose electrons and is reduced if its atoms gain electrons*****. Thus, it is not necessary for oxygen to be explicitly involved; in fact, "oxidation" describes a broad range of reactions such as that between iron and sulfur or chlorine, either of which accept electrons from the iron atoms.**

Unprotective scale formation

Types of oxidation:

1) Unprotective ("bad" oxidation)

A <u>porous</u> oxide film (like a sponge) forms on the surface of a metal, and because of the porosity, molecular oxygen penetrates to the metal surface. There, it reacts with the metal to form more oxide, the process continuing until all of the original metal is consumed.

Rate equation: oxygen (gas) is available (and consumed) at a <u>constant rate</u>, therefore, we can write

$$\frac{dy}{dt} = c_1$$

where dy/dt is the rate at which the oxide thickness is increasing with time. Integrating this, we obtain $y = c_1 t + c_2$ which relates the oxide thickness, y, to time, t. (c_2 is the initial thickness at t = 0) This is appropriately called a *linear growth rate law*.

Protective scale formation

Types of oxidation:

2) Protective ("good" oxidation)

A non-porous oxide film forms on the surface of a metal; because it is not porous, oxygen ions can only react with metal ions through *diffusion* (there is no direct penetration route). Hence, the growth rate decreases as the scale thickness increases[(1)]. If the rate of scale growth is inversely proportional to scale thickness, we can write

$$\frac{dy}{dt} = c_3 \frac{1}{y}$$

Integration of this equation gives the result: $y^2 = c_4 t + c_5$ **where $c_4 = 2c_3$ and c_5 is the square of the scale thickness at t = 0. This is called a *parabolic growth rate law*.**

There are actually 3 categories of protective oxidation:

1) **metal ions diffuse through the scale; react at scale-gas interface**
2) **oxygen ions diffuse through the scale; react at scale-metal interface**
3) **both ions diffuse through the scale; react within the scale**

(1) as the scale thickness increases, the attractive force between the negative oxygen ions at the scale-gas interface and the positive metal ions at the scale-metal interface decreases.

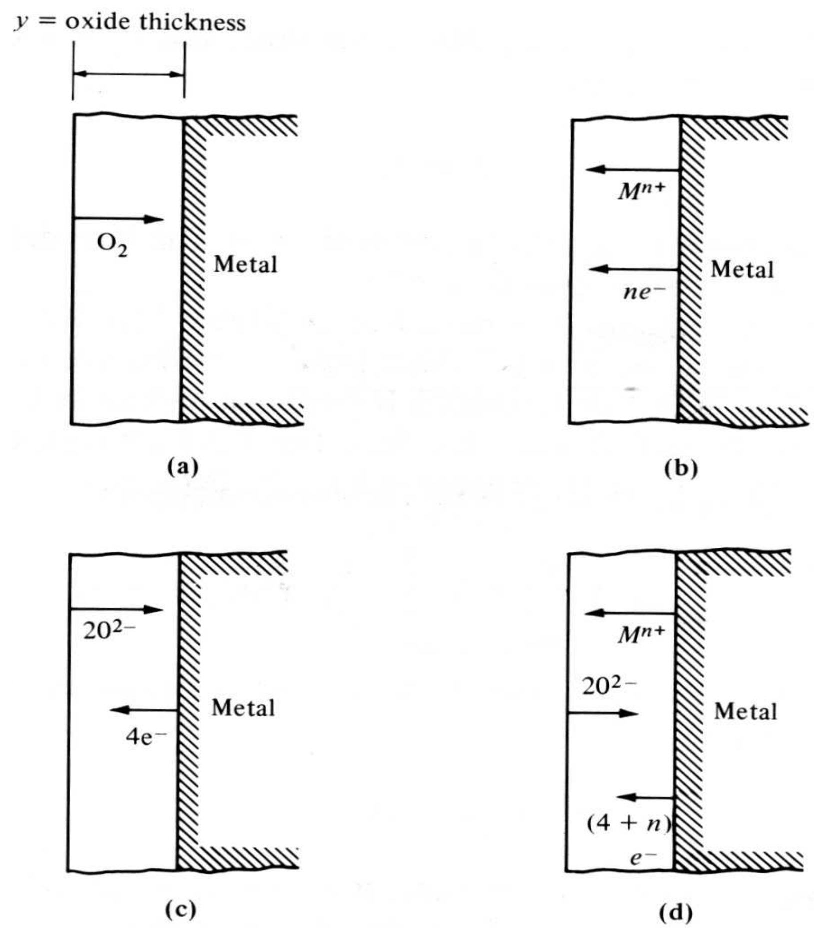
Oxidation models

Types of oxidation:

The four primary oxidation modes are shown in the figure.

(a) corresponds to a porous, non-protective oxide; (molecular oxygen comes in direct contact with the metal surface)

(b), (c), and (d) correspond to dense, protective oxide films (or *scales*). In each case, transport of metal and/or oxygen ions is by diffusion through the scale.

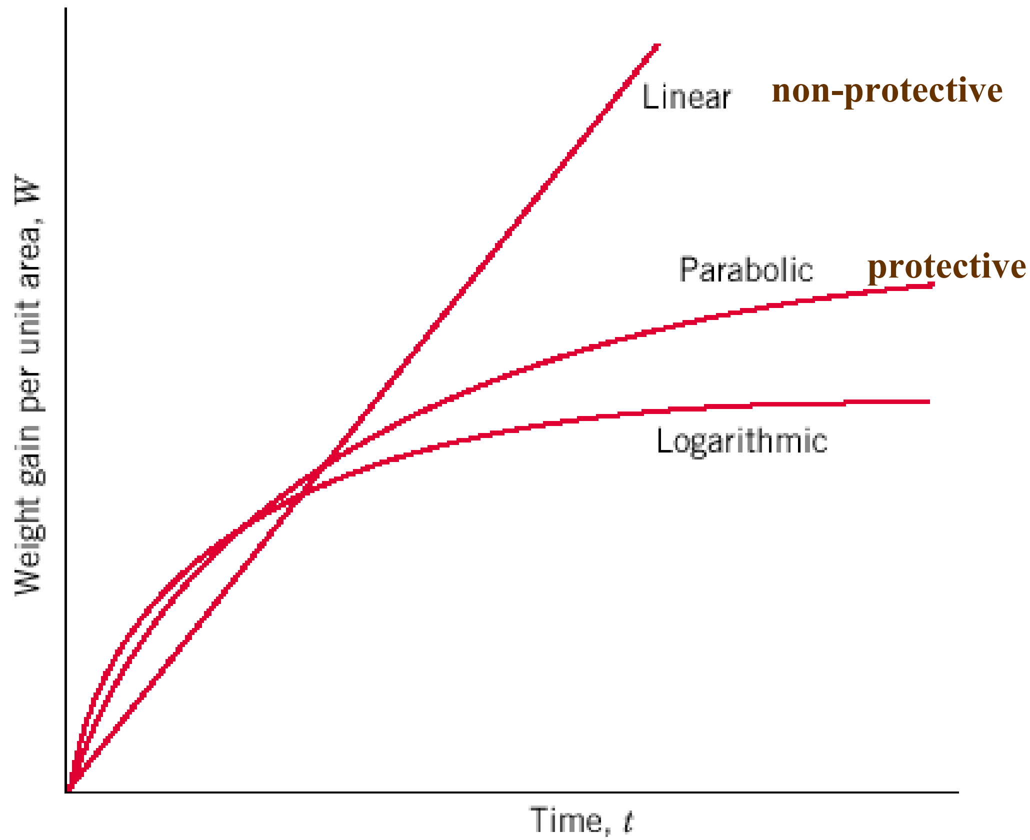


In (b), the metal cations are the primary diffusing species; in (c), the oxygen anions are the primary diffusing species, and in (d), both cations and anions diffuse more or less equally.

Oxide scale growth kinetics

Protective vs. non-protective growth kinetics:

Weight gain is an equivalent parameter to thickness for uniform films, and often easier to measure. This can be done in real time using an instrument called a thermogravimetric analyzer (TGA).



Pilling-Bedworth ratio

Prediction of protective nature of oxide coating:

An indication of the degree to which an oxide coating is likely to be protective is given by the "Pilling-Bedworth" ratio:

$$R = \frac{\left(\dfrac{A_o}{d_o}\right)}{\left(\dfrac{A_m}{d_m}\right)} = \frac{A_o d_m}{A_m d_o}$$

where A_o and A_m are the atomic weights of the oxide and metal, respectively, and d_o and d_m correspond to the density of each. Physically, the P-B ratio gives the oxide volume produced per unit volume of metal consumed.

P-B < 1: porous and non-protective

1 < P-B < 2: protective

P-B > 2: non-porous but subject to large compressive stresses leading to *spalling*

Table 18.3 Pilling–Bedworth Ratios for a Number of Metals

Protective		*Nonprotective*	
Ce	1.16	K	0.45
Al	1.28	Li	0.57
Pb	1.40	Na	0.57
Ni	1.52	Cd	1.21
Be	1.59	Ag	1.59
Pd	1.60	Ti	1.95
Cu	1.68	Ta	2.33
Fe	1.77	Sb	2.35
Mn	1.79	Nb	2.61
Co	1.99	U	3.05
Cr	1.99	Mo	3.40
Si	2.27	W	3.40

Note: these P-B ratios are for metal oxides

Oxidation protection

Best way: addition of an element that will form a dense, coherent oxide layer in which the mobility of both ions and electrons is low.

Examples:

1) addition of <u>Cr to steel.</u> Typically, *stainless steels* contain from 11 to 25 wt. % Cr; the Cr forms a Cr_2O_3 oxide scale which protects the bulk of the steel from subsequent oxidation.

2) addition of B to Mo_5Si_3. Mo_5Si_3 is a refractory material possessing excellent high temperature creep resistance but intrinsically poor high temperature oxidation resistance. Addition of boron (1 - 3 wt. %) produces a dense, protective borosilicate glass oxide scale.

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Fe	1.77	Sb	2.35
Mn	1.79	Nb	2.61
Co	1.99	U	3.05
Cr	1.99	Mo	3.40
Si	2.27	W	3.40

for metal oxides

Corrosion

Definition: **Corrosion is the dissolution of a metal into an aqueous environment**

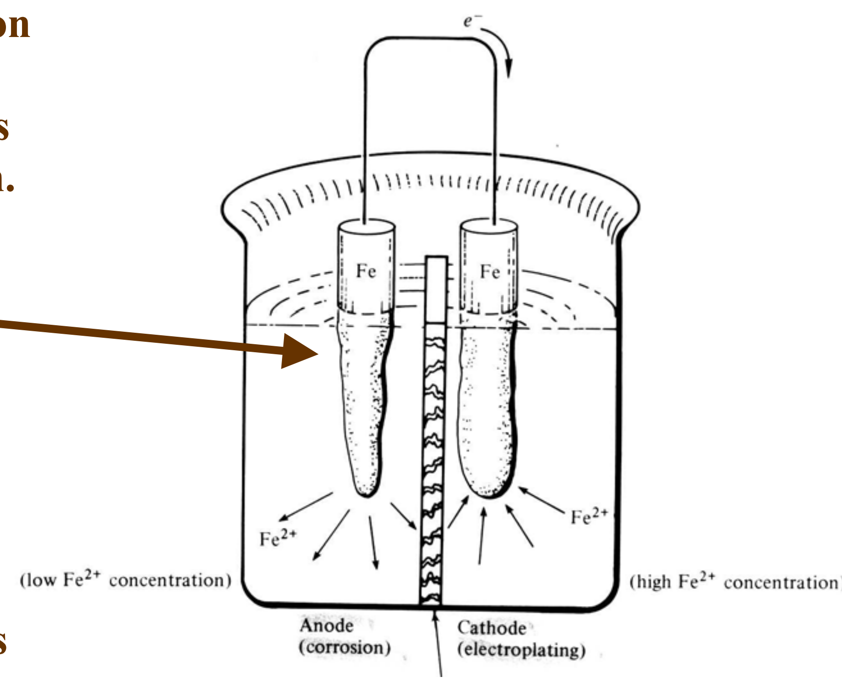
Consider the model for aqueous corrosion of <u>iron</u> shown at right: The difference between the two halves of the chamber is the concentration of Fe^{2+} ions in solution.

The <u>anode</u> is the metal that dissolves, or corrodes (by giving up electrons) in an *anodic reaction*:

$$Fe \rightarrow Fe^{2+} + 2e^- \qquad (1)$$

The <u>cathode</u> is the metals that accepts electrons from the anode and neutralizes the cations in a *cathodic reaction*:

$$Fe^{2+} + 2e^- \rightarrow Fe \qquad (2)$$



An electrochemical cell, initially containing different concentrations of the Fe^{2+} ion in each half, separated by a permeable membrane.

reaction (1) is called "oxidation," while reaction (2) is called "reduction"

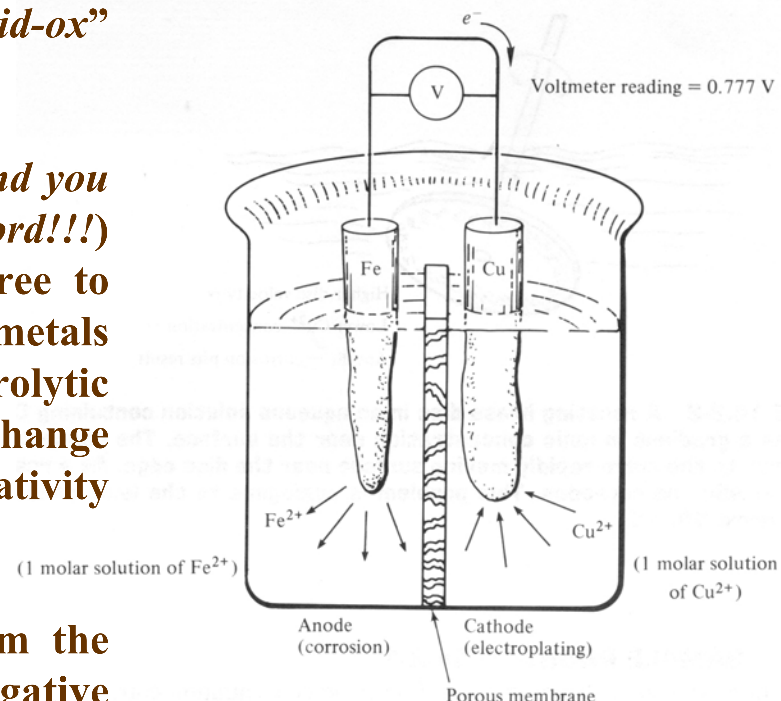
Corrosion

Galvanic two-metal corrosion:

The driving force for the oxidation and reduction reactions shown on the previous slide is the system's attempt to equalize the ion concentration in both halves of the electrochemical cell (initially at different Fe^{2+} ion concentrations).

There can be other driving forces for "*rid-ox*" reactions as well.

Recall the concept of <u>electronegativity</u>? (*And you thought you had heard the last of that word!!!*) Electronegativity is a measure of the degree to which an atom attracts a free electron. If 2 metals are in contact (either by way of an electrolytic solution or by a wire), they will exchange electrons, according to their electronegativity difference.



There will be a net flow of electrons from the more electropositive (anode) to the electronegative (cathode) metal:

Corrosion

Galvanic two-metal corrosion:

In this example, the *anodic* reaction is

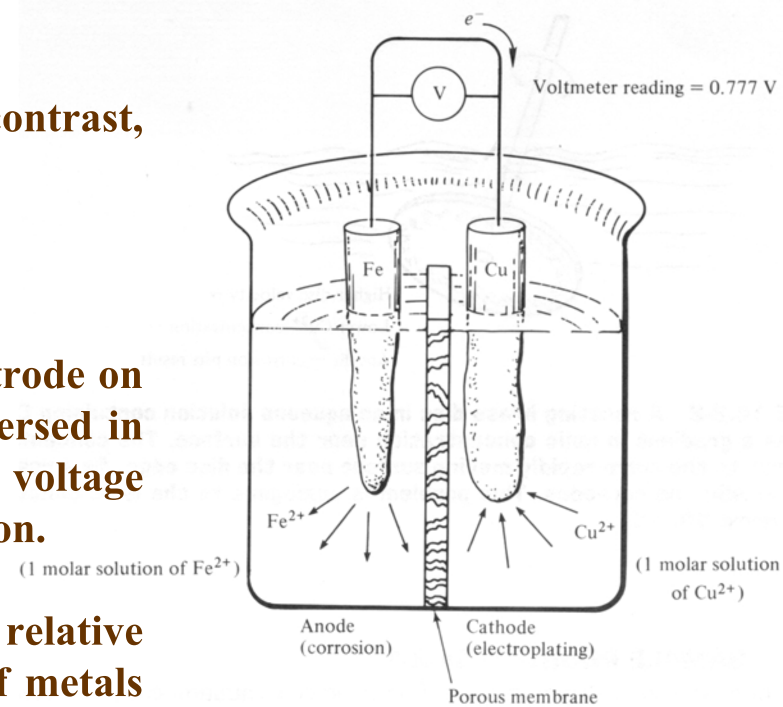
$$Fe \rightarrow Fe^{2+} + 2e-$$

which occurs at the electrode on the left. In contrast, the *cathodic* reaction is

$$Cu^{2+} + 2e- \rightarrow Cu$$

and we say that copper "plates out" at the electrode on the right. (Remember, the electrodes are immersed in solutions containing their respective cations.) A voltage difference of 0.78V is associated with this reaction.

Tables have been constructed listing the relative tendency for electron transfer between pairs of metals in their respective electrolytic solutions, and the respective voltages. This is called the standard EMF series...



Corrosion

Galvanic two-metal corrosion:

These emf values are listed relative to a standard hydrogen reference half-cell.

To find the net emf for any given pair of electrodes, simply take the difference between the values listed.

Table 18.1 The Standard emf Series

	Electrode Reaction	Standard Electrode Potential, V^0 (V)
Increasingly inert (cathodic) ↑	$Au^{3+} + 3e^- \longrightarrow Au$	+1.420
	$O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$	+1.229
	$Pt^{2+} + 2e^- \longrightarrow Pt$	~+1.2
	$Ag^+ + e^- \longrightarrow Ag$	+0.800
	$Fe^{3+} + e^- \longrightarrow Fe^{2+}$	+0.771
	$O_2 + 2H_2O + 4e^- \longrightarrow 4(OH^-)$	+0.401
	$Cu^{2+} + 2e^- \longrightarrow Cu$	+0.340
	$2H^+ + 2e^- \longrightarrow H_2$	0.000
	$Pb^{2+} + 2e^- \longrightarrow Pb$	−0.126
	$Sn^{2+} + 2e^- \longrightarrow Sn$	−0.136
	$Ni^{2+} + 2e^- \longrightarrow Ni$	−0.250
	$Co^{2+} + 2e^- \longrightarrow Co$	−0.277
	$Cd^{2+} + 2e^- \longrightarrow Cd$	−0.403
	$Fe^{2+} + 2e^- \longrightarrow Fe$	−0.440
Increasingly active (anodic) ↓	$Cr^{3+} + 3e^- \longrightarrow Cr$	−0.744
	$Zn^{2+} + 2e^- \longrightarrow Zn$	−0.763
	$Al^{3+} + 3e^- \longrightarrow Al$	−1.662
	$Mg^{2+} + 2e^- \longrightarrow Mg$	−2.363
	$Na^+ + e^- \longrightarrow Na$	−2.714
	$K^+ + e^- \longrightarrow K$	−2.924

For any given metal, say Fe^{2+}, anything above it on the table would act as a *cathode* relative to the iron and cause it to corrode. Similarly, anything listed below iron would act as an *anode* relative to iron and cause it to plate out. Remember, it's all relative!

Corrosion

Relative corrosion potential:

Since the preceding table was constructed under highly idealized conditions, it is sometimes more useful to rank the metals according to their general tendency to corrode in *seawater*.

Metals near the top are highly cathodic (meaning that they resist corrosion and accept electrons), whereas metals near the bottom corrode rather easily and act as a source of electrons.

If metal "A" falls below metal "B" on this list, "A" will most likely corrode and eventually disintegrate when electrically connected to "B"

Table 18.2 The Galvanic Series

	Platinum
	Gold
	Graphite
	Titanium
	Silver
	316 Stainless steel (passive)
	304 Stainless steel (passive)
↑	Inconel (80Ni–13Cr–7Fe) (passive)
	Nickel (passive)
	Monel (70Ni–30Cu)
Increasingly inert (cathodic)	Copper–nickel alloys
	Bronzes (Cu–Sn alloys)
	Copper
	Brasses (Cu–Zn alloys)
	Inconel (active)
	Nickel (active)
	Tin
	Lead
Increasingly active (anodic)	316 Stainless steel (active)
	304 Stainless steel (active)
	Cast iron
↓	Iron and steel
	Aluminum alloys
	Cadmium
	Commercially pure aluminum
	Zinc
	Magnesium and magnesium alloys

Corrosion

So where does "rust" come from?

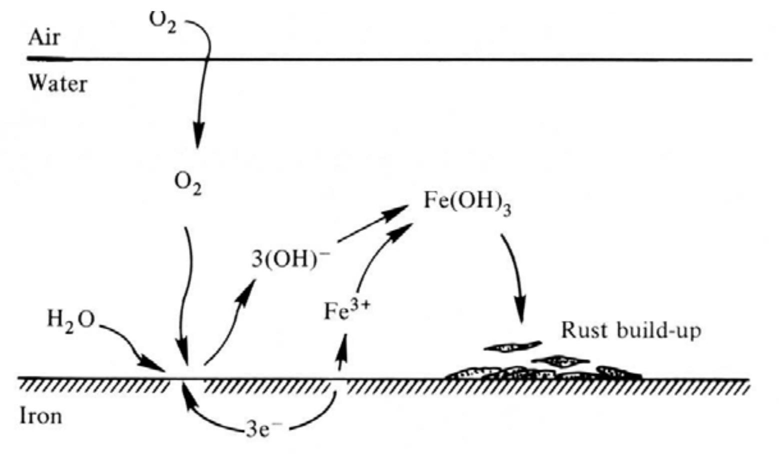
Recall the two-metal Cu - Fe electrolytic cell shown earlier. We said that the anodic reaction was $Fe \rightarrow Fe^{2+} + 2e-$; what happens to the iron cations?

If dissolved oxygen is present in an aqueous solution, then the cathodic reaction becomes:

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

In other words, electrons from the anode combine with water and dissolved oxygen to form hydroxyl ions.

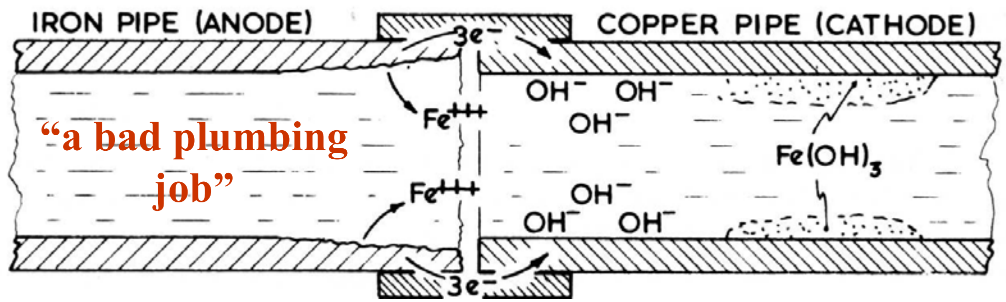
The hydroxyl ions react with the iron cations to form *ferric hydroxide*, $Fe(OH)_3$ a.k.a. RUST, which becomes an insoluble product and usually falls from the cathode to the bottom of the cell. The process of rusting is illustrated at right:



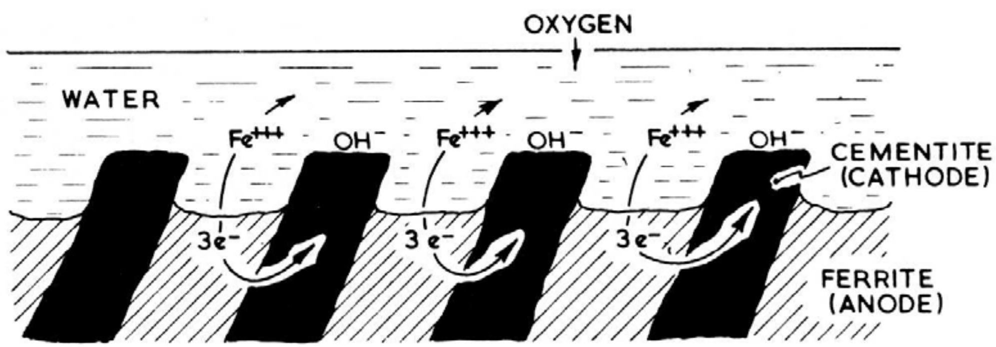
Corrosion protection/minimization

Methods of reducing or avoiding the effects of corrosion:

1) Avoid galvanic couples such as zinc and iron pipe connections:



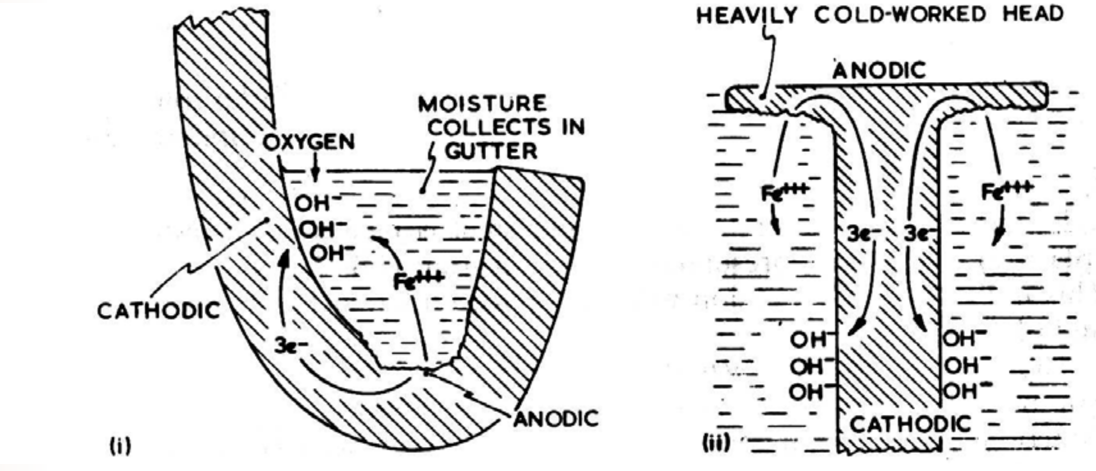
2) Avoid "duplex" microstructures (when possible)
dissimilar metals can exhibit galvanic effects (corrosion). This can also happen on a microscopic scale, within a material. Consider pearlite, for example:



Corrosion protection/minimization

Methods of reducing or avoiding the effects of corrosion:

3) **Avoid heavily cold-worked regions where localized stress regions become anodic (differential cold-work)**



Examples of oxidation-reduction reactions due to localized stress (cold work); rim of an automobile 'wing' (left), a cold-forged iron nail head (right).

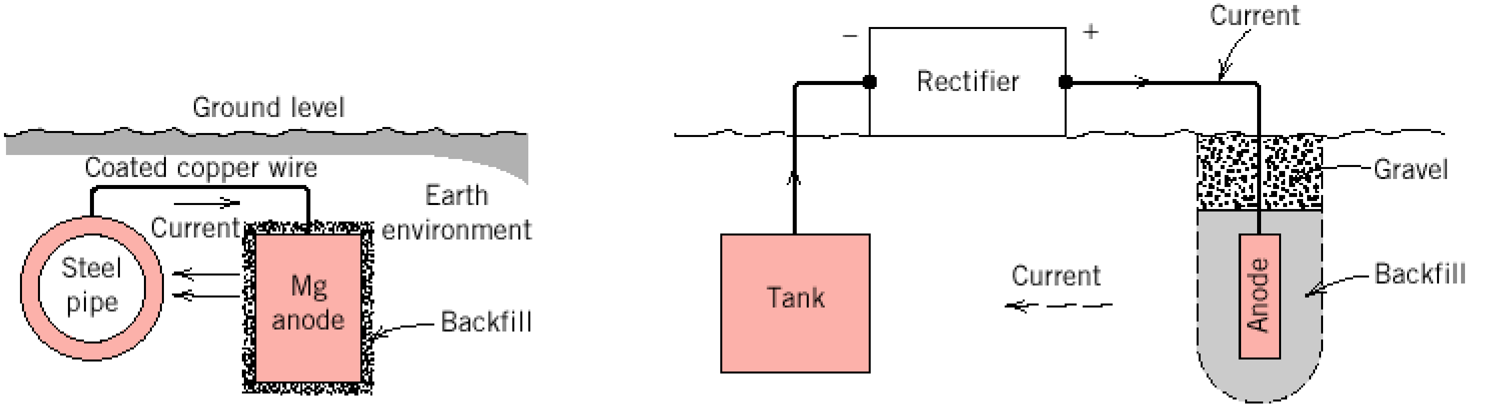
Any cold-worked region of a metal will be anodic relative to stress-free regions in a potentially corrosive environment.

Corrosion protection/minimization

Methods of reducing or avoiding the effects of corrosion:

4) Use cathodic protection methods

If an external source of electrons is supplied, the metal can be made cathodic which forces the reverse reaction. Since the material becomes electrically cathodic, it will not corrode:



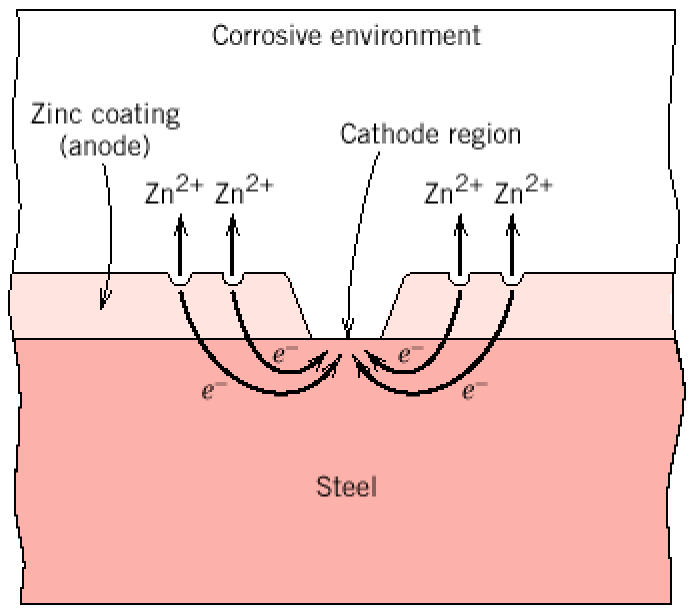
Connection of a steel pipe to a Mg anode (left) forces the steel to become the cathode, thereby preventing its corrosion. An external supply of current, properly biased (right), will serve the same function; the tank will be protected against corrosion.

Corrosion protection/minimization

Methods of reducing or avoiding the effects of corrosion:

4) Galvanic protection (sacrificial anode)

A coating of a more reactive metal is applied, such as zinc on steel (galvanized steel). If a breach in the protective Zn coating occurs, it becomes the anode leaving the steel to become the cathode. Zn is thus corroded (sacrificially) but the underlying steel is protected.

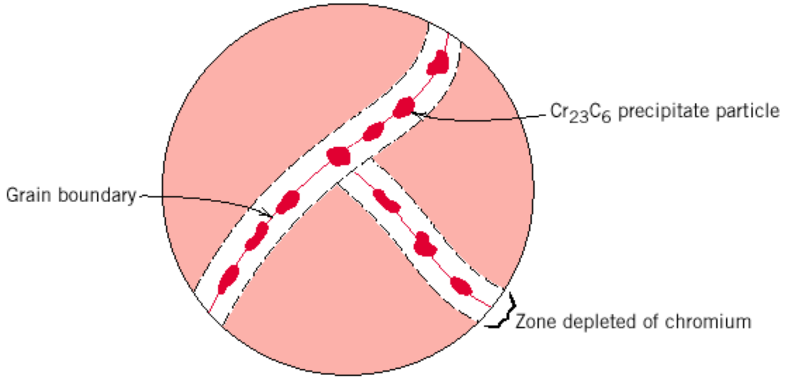


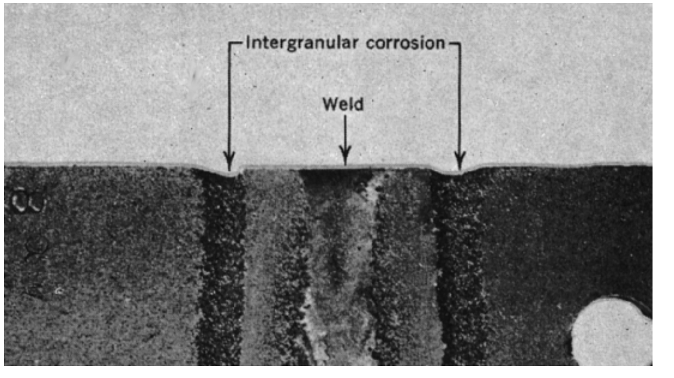
Corrosion protection/minimization

Methods of reducing or avoiding the effects of corrosion:

5) Be aware of microstructural changes resulting from welding (weld decay)

When a metal is welded, localized compositional changes can occur. For example, in stainless steels, the Cr and C react with each other at high temperatures to form the intermetallic C_6Cr_{23} within the grain boundary regions, which causes depletion of protective Cr from adjacent regions. Since the regions near the grain boundaries become depleted in Cr, they are subject to preferential corrosion, which weakens the material:





One solution is to heat treat the material after welding, which has the effect of re-depositing the components back into solution.