

# CORROSION BASICS

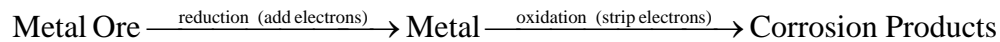
(from Swain (1996) and Schultz (1997))

## What is corrosion?

- Webster's Dictionary - corrode (v.) To eat away or be eaten away gradually, especially by chemical action.
- NACE Corrosion Basics - corrosion may be defined as the deterioration of a material (usually a metal) because of a reaction with the environment.

## Why do metals corrode?

Most metals are found in nature as ores. The manufacturing process of converting these ores into metals involves the input of energy. During the corrosion reaction the energy added in manufacturing is released, and the metal is returned to its oxide state.



In the marine environment, the corrosion process generally takes place in aqueous solutions and is therefore electrochemical in nature.

## Corrosion consequences

*Economic* - corrosion results in the loss of \$8 - \$126 billion annually in the U.S. alone. This impact is primarily the result of:

1. Downtime
2. Product Loss
3. Efficiency Loss
4. Contamination
5. Overdesign

### *Safety / Loss of Life*

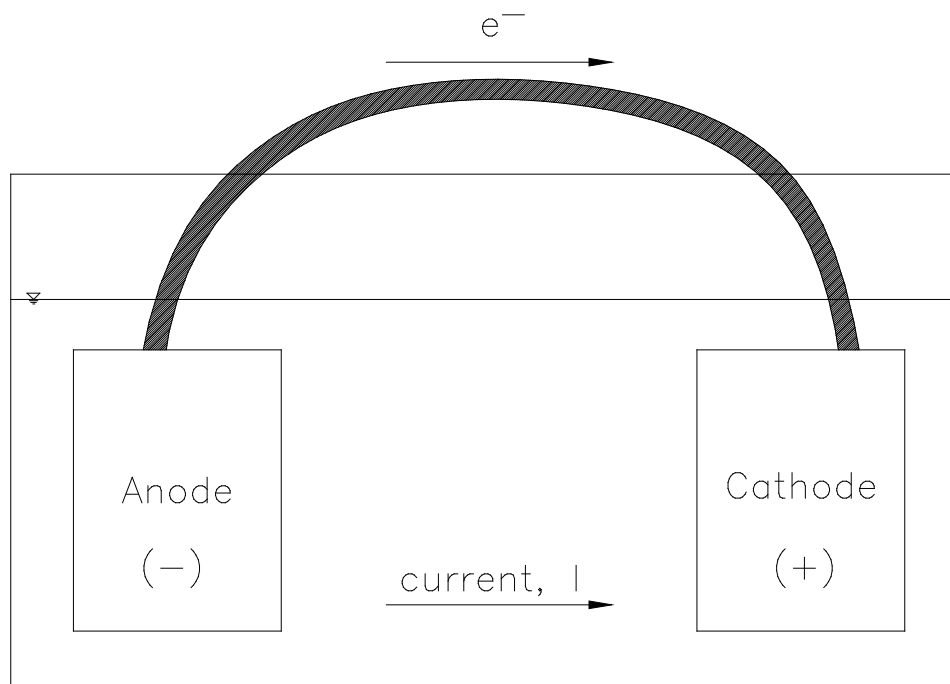
Corrosion can lead to catastrophic system failures which endanger human life and health.

Examples include a 1967 bridge collapse in West Virginia which killed 46. The collapse was attributed to stress corrosion cracking (SCC). In another example, the fuselage of an airliner in Hawaii ripped open due to the combined action of stress and atmospheric corrosion.

## Corrosion cell

Corrosion occurs due to the formation of electrochemical cells. In order for the corrosion reaction to occur five things are necessary. If any of these factors are eliminated, galvanic corrosion will not occur. **THIS IS THE KEY TO CORROSION CONTROL!** The necessary factors for corrosion to proceed are:

1. ANODE - the metal or site on the metal where oxidation occurs (loss of electrons). The anode has a more negative potential with respect to (wrt) the cathode and is termed less noble wrt the cathode.
2. CATHODE - the metal or site on the metal where reduction occurs (gain of electrons). The cathode has a more positive potential wrt the anode and is termed more noble wrt the anode.
3. ELECTROLYTE - the electrically conductive medium in which the anode and cathode reside.
4. ELECTRICAL CONNECTION - the anode and the cathode must be electrically connected.
5. POTENTIAL DIFFERENCE - a voltage difference must exist between the anode and the cathode.



Schematic of the corrosion cell

The electrochemical cell is driven by the potential difference between the anode and the cathode. This causes a current to flow, the magnitude of which will be determined by the resistance of the electrochemical circuit (i.e. Ohm's Law,  $I=V/R$ ). The three main types of electrochemical cells are:

- Concentration Cells - this is where the anode and the cathode are the same material, but concentrations of reactants and therefore potential differ at the electrodes. These can be oxygen concentration or metal ion concentration cells.
- Bimetallic Cells - where the anode and cathode are different materials.
- Thermo-galvanic Cells - where the anode and the cathode are of the same material and the composition of the electrolyte is the same but the temperature at the electrodes are different.

In the corrosion cell, metal ions formed from metal oxidation (cations) migrate from the anode to the cathode through the electrolyte. The electrons given off by this oxidation reaction move from the anode to the cathode through the electrical connection. Current flows from cathode to the anode through the electrical connection and from the anode to the cathode in the electrolyte.

### **Surface potential**

The surface potential of a metal is a measure of its activity. When a metal is immersed in an aqueous environment, both oxidation and reduction reactions occur until some equilibrium is reached. These reactions tend to create an electrical double layer at the surface which establish an electrical potential. The more positive metals are said to be more noble and less reactive, while the more negative metals are called base metals and are highly reactive. The standard potential of metals are given in the following table termed the standard electromotive force series. It should be made clear however that a metal's actual potential can be greatly altered by its environment.

Standard EMF Series Table [from Jones (1996)]

	Reaction	Standard Potential, $e^\circ$ (volts vs. SHE)
Noble	$\text{Au}^{3+} + 3e^- = \text{Au}$	+1.498
	$\text{Cl}_2 + 2e^- = 2\text{Cl}^-$	+1.358
	$\text{O}_2 + 4\text{H}^+ + 4e^- = 2\text{H}_2\text{O}$ (pH 0)	+1.229
	$\text{Pt}^{2+} + 3e^- = \text{Pt}$	+1.118
	$\text{NO}_3^- + 4\text{H}^+ + 3e^- = \text{NO} + 2\text{H}_2\text{O}$	+0.957
	$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- = 4\text{OH}^-$ (pH 7) <sup>a</sup>	+0.82
	$\text{Ag}^+ + e^- = \text{Ag}$	+0.799
	$\text{Hg}_2^{2+} + 2e^- = 2\text{Hg}$	+0.799
	$\text{Fe}^{3+} + e^- = \text{Fe}^{2+}$	+0.771
	$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- = 4\text{OH}^-$ (pH 14)	+0.401
	$\text{Cu}^{2+} + 2e^- = \text{Cu}$	+0.342
	$\text{Sn}^{4+} + 2e^- = \text{Sn}^{2+}$	+0.15
	$2\text{H}^+ + 2e^- = \text{H}_2$	0.000
	$\text{Pb}^{2+} + 2e^- = \text{Pb}$	-0.126
	$\text{Sn}^{2+} + 2e^- = \text{Sn}$	-0.138
	$\text{Ni}^{2+} + 2e^- = \text{Ni}$	-0.250
	$\text{Co}^{2+} + 2e^- = \text{Co}$	-0.277
	$\text{Cd}^{2+} + 2e^- = \text{Cd}$	-0.403
	$2\text{H}_2\text{O} + 2e^- = \text{H}_2 + 2\text{OH}^-$ (pH 7) <sup>a</sup>	-0.413
	$\text{Fe}^{2+} + 2e^- = \text{Fe}$	-0.447
$\text{Cr}^{3+} + 3e^- = \text{Cr}$	-0.744	
$\text{Zn}^{2+} + 2e^- = \text{Zn}$	-0.762	
$2\text{H}_2\text{O} + 2e^- = \text{H}_2 + 2\text{OH}^-$ (pH 14)	-0.828	
$\text{Al}^{3+} + 3e^- = \text{Al}$	-1.662	
$\text{Mg}^{2+} + 2e^- = \text{Mg}$	-2.372	
$\text{Na}^+ + e^- = \text{Na}$	-2.71	
$\text{K}^+ + e^- = \text{K}$	-2.931	
Active		

### Anode half-cell reaction

Oxidation of the metal at the anode may be expressed by the following half-cell reaction:

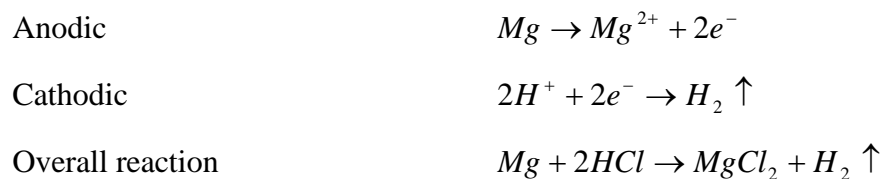


### Cathode half-cell reaction

The reduction half-cell reaction at the cathode depends mainly on environmental conditions. The following six reactions represent common cathodic reactions along with the conditions in which they generally occur:

1.  $O_2 + 2H_2O + 4e^{-} \rightarrow 4OH^{-}$  aerated neutral to alkaline water
2.  $O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O$  aerated acidic solutions
3.  $2H^{+} + 2e^{-} \rightarrow H_2 \uparrow$  hydrogen evolution (in acids)
4.  $M^{n+} + ne^{-} \rightarrow M$  metal deposition
5.  $M^{n+} + e^{-} \rightarrow M^{(n-1)+}$  metal reduction

**Example:** Magnesium is submerged into a bath of HCl. What would the predominate anodic and cathodic reactions be?



## Corrosion thermodynamics

As we have observed, corrosion reactions inevitably involve electron transfer. For this reason, the reactions may be considered electrochemical in nature. Thermodynamics can provide a basis for the understanding of the energy changes associated with the corrosion reaction. It can, in general, predict when corrosion is possible. Thermodynamics cannot predict corrosion rates. The rate at which the reaction proceeds is governed by kinetics.

The Gibb's free energy, given by the following equation, provides us a tool with which to predict if a corrosion reaction is thermodynamically possible:

$$\Delta G = -nFE$$

where :  $\Delta G$  = Gibb's free energy (Joules)

$n$  = electrons transferred in oxidation reaction ( $\text{mol e}^-$ )

$F$  = Faraday's constant ( $96,500 \text{ J/v} \cdot \text{mol e}^-$ )

$E$  = Standard emf potential =  $E_{\text{ox}}^{\circ} + E_{\text{red}}^{\circ}$  (volts)

$E_{\text{red}}^{\circ}$  = Standard potential for cathode half cell (volts)

$E_{\text{ox}}^{\circ}$  = Standard potential for anode half cell (volts)

If  $\Delta G$  is positive, the reaction will not proceed. If  $\Delta G$  is negative, the reaction is possible.

**Example:** Steel is placed in aerated seawater with a neutral pH. Is corrosion of the steel possible, why? (Assume valence of 2)

Anodic  $Fe \rightarrow Fe^{2+} + 2e^-$   $E_{\text{ox}}^{\circ} = 0.447 \text{ v}$

Cathodic  $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$   $E_{\text{red}}^{\circ} = 0.820 \text{ v}$

Overall reaction  $2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2$

$$E = E_{\text{ox}}^{\circ} + E_{\text{red}}^{\circ}$$

$$E = 1.267 \text{ v}$$

$$\Delta G = -nFE$$

$$\Delta G = -(2 \text{ mol e}^-)(96,500 \text{ J/v} \cdot \text{mol e}^-)(1.267 \text{ v})$$

$$\Delta G = - 244,531 \text{ J}$$

negative sign indicates corrosion reaction, as written, is possible

It should be stated that potential values of a metal are modified by the environment. Concentrations of anodic and cathodic reactants will alter the balance between the oxidation and reduction reactions. The Nernst equation allows us to calculate metal potentials under differing metal ion or oxidation/reduction conditions. The Nernst equation may be stated as follows:

$$E_{cell} = E^{\circ} + 2.3 \frac{RT}{nF} \log_{10} \frac{[oxid.]}{[red.]}$$

where :  $E_{cell}$  = Cell potential under environmental conditions (volts)

$E^{\circ}$  = Standard reduction potential @ 25<sup>o</sup> C and unit activity (volts)

$R$  = Universal gas constant (8.3143 J/mol °K)

$T$  = Absolute temperature (degrees Kelvin)

$n$  = electrons transferred in the reaction (mol e<sup>-</sup>)

$F$  = Faraday's constant (96,500 coulombs/mol e<sup>-</sup>)

[*oxid.*] = activity of oxidized species (M)

[*red.*] = activity of reduced species (M)

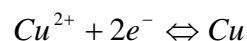
At standard temperature and pressure (25°C and 760mm Hg) this may be simplified to the following:

$$E_{cell} = E^{\circ} + \frac{0.059}{n} \log_{10} \frac{[oxid.]}{[red.]}$$

The Nernst equation can also be written for each half cell as is shown in the following metal ion concentration cell example.

**Example:** A circular copper coupon is rotated in seawater. A gradient in the metal ion concentration is set up on the disk surface. On periphery of the disk copper ion concentration is 0.001 M. Near the center of the disk the copper ion concentration is 10 M. What are the potentials of anodic and cathodic sites on copper? Where will the metal loss occur? Assume STP.

In this case we find the standard EMF for the following equation:



$$E^{\circ} = 0.342 \text{ volts}$$

$$E_{outside} = E^{\circ} + \frac{0.059}{n} \log_{10} \left( \frac{[10^{-3}]}{[1]} \right)$$

$$E_{center} = E^{\circ} + \frac{0.059}{n} \log_{10} \left( \frac{[10^1]}{[1]} \right)$$

$$E_{outside} = 0.342\text{v} + \frac{0.059}{2 \text{ mol e}^{-}} \log_{10} (10^{-3}) = 0.2535\text{v}$$

$$E_{center} = 0.342\text{v} + \frac{0.059}{2 \text{ mol e}^{-}} \log_{10} (10^1) = 0.3715\text{v}$$

Metal will be lost from the outside of the disk (it is more negative)

$$E_{overall} = E_{center} - E_{outside} = 0.118\text{v}$$

### Electrochemical kinetics of corrosion

We now have a tool to predict if the corrosion reaction is possible, but it would also be handy to predict how fast the reaction will proceed. In theory, Faraday's law can be used do this. Faraday's law may be stated as follows.

$$m = Izt$$

where :  $m$  = mass of metal lost to corrosion (grams)

$I$  = corrosion current (amps)

$z$  = electrochemical equivalent =  $\frac{a}{nF}$  (g/A - s)

$a$  = atomic weight of corroding metal (grams)

$n$  = electrons transfered in oxidation reaction (mol e<sup>-</sup>)

$F$  = Faraday's constant (96,500 A - s/mol e<sup>-</sup>)

$t$  = time of reaction (seconds)



**Example:** A steel coupon with an anode surface area of 1000 cm<sup>2</sup> is placed in an electrolyte. The corrosion current is measured to be 1 mA. What mass of steel will be lost in 6 hours? What is the corrosion rate in μg/cm<sup>2</sup>/day? In mpy? Assume valence of 2.

$$m = Izt$$

$$I = 0.001\text{A}$$

$$z = \frac{a}{nF} = \frac{55.847\text{g}}{(2 \text{ mol e}^-)(96,500 \text{ A} \cdot \text{s/mol e}^-)} = 2.89 \times 10^{-4} \text{ g/A} \cdot \text{s}$$

$$t = (6 \text{ hr}) \left( \frac{60 \text{ min}}{1 \text{ hr}} \right) \left( \frac{60 \text{ s}}{1 \text{ min}} \right) = 21,600 \text{ s}$$

$$m = (0.001\text{A})(2.89 \times 10^{-4} \text{ g/A} \cdot \text{s})(21,600\text{s})$$

$$m = 6.255 \times 10^{-3} \text{ g}$$

To find the corrosion rate in μg/cm<sup>2</sup>/day, first divide by anode area and time.

$$\text{rate} = \frac{m}{At} = \frac{6.255 \times 10^{-3} \text{ g}}{(1000 \text{ cm}^2)(21,600 \text{ s})} \left( \frac{10^6 \mu\text{g}}{1 \text{ g}} \right) \left( \frac{3600 \text{ s}}{1 \text{ hr}} \right) \left( \frac{24 \text{ hr}}{1 \text{ day}} \right) = 25.02 \mu\text{g/cm}^2/\text{day}$$

To find the corrosion rate in mpy, divide by the metal density.

$$\text{rate} = \frac{25.02 \mu\text{g/cm}^2/\text{day}}{\rho} = \frac{25.02 \mu\text{g/cm}^2/\text{day}}{7.20 \times 10^6 \mu\text{g/cm}^3} \left( \frac{365 \text{ days}}{\text{yr}} \right) \left( \frac{1 \text{ mil}}{2.54 \times 10^{-3} \text{ cm}} \right)$$

$$\text{rate} = 0.499 \text{ mpy}$$

The following table gives density, atomic mass, valence, and corrosion rate for various metals.

Corrosion data for various metals [from Swain Classnotes (1996)].

Element	Atomic Mass (g/mole)	Valence	Electrochemical Equivalent (g/coulomb)	Corr. rate equivalent to 1 $\mu\text{A}/\text{cm}^2$ (mm/yr)	Density ( $\text{g}/\text{cm}^3$ )
Magnesium	24.31	2	1.26E-04	0.023	1.74
Zinc	65.38	2	3.39E-04	0.015	7.13
Aluminum	26.98	3	9.30E-05	0.011	2.72
Iron	55.85	2	2.89E-04	0.013	7.20
Iron	55.85	3	1.93E-04	0.087	7.20
Copper	63.54	1	6.58E-04	0.023	8.94
Copper	63.54	2	3.29E-04	0.012	8.94
Nickel	58.71	2	3.04E-04	0.011	8.89

### Reference electrodes

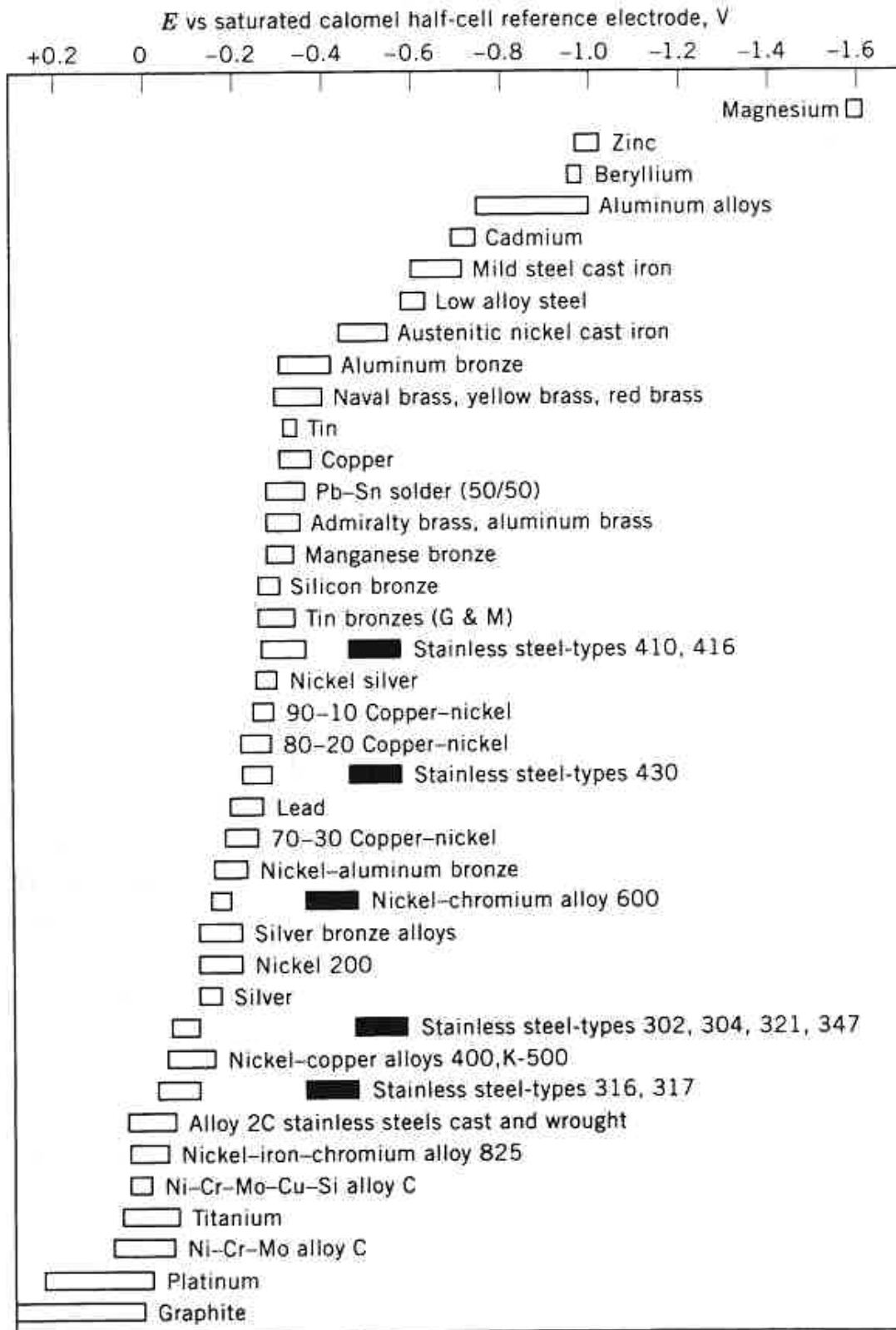
The reaction potential is measured with reference to a standard half-cell or electrode. The hydrogen half-cell provides the basic standard, but in practice is awkward to use. For this reason, several other reference half-cells have been developed. Some of these reference cells are listed in the following table along with their potential with respect to the hydrogen half-cell and location of use.

Commonly used half-cells [from Swain Classnotes (1996)].

Half-Cell	Potential Ref. SHE (v)	Environment
Copper : Copper Sulfate	+0.3160	Soil
Tenth Normal Calomel	+0.3337	Laboratory
Normal Calomel	+0.2800	Laboratory
Saturated Calomel	+0.2415	Laboratory
Silver : Silver Chloride (0.1M KCl)	+0.2880	Seawater
Silver : Silver Chloride (Seawater)	+0.2222	Seawater
Silver : Silver Chloride (3.8M KCl)	+0.1990	Seawater
Hydrogen	0	Laboratory
Zinc	-0.7600	Seawater

## **Galvanic series**

The electrochemical series presented earlier can only be applied to oxide free surfaces at ion concentrations for which the standard potentials are valid. When metals are exposed in a more complex electrolyte such as seawater, the galvanic series may be used to help predict if corrosion of a metal is possible. The galvanic series for many commonly used metals is given in the table on the next page. It should be noted that for some metals, such as the stainless steels, there are significant differences in the potential they are likely to exhibit. These differences are generally owed to the condition of the metal surface. For example, 316 stainless steel has a potential of about -0.1v ref saturated calomel when it is passive (protected by a thin oxide film). If the oxide layer is compromised, the potential may shift to -0.4v and corrode. In service, severe localized attack may occur at active sites.



Galvanic Series [from Fontana (1986)].

## Corrosion rates

The rate of corrosion (or current density) is determined by the potential difference between the anode and the cathode and the resistance of the corrosion cell. The corrosion current is therefore:

$$I = \frac{V}{R}$$

The resistance of the cell may be as a result of electrical resistance or electrode polarization. The greater the resistance the lower the corrosion current and from Faraday's law the lower the mass loss. A high resistance within the corrosion cell is beneficial for control. This resistance may result from one or more of the following factors:

- Resistance of the electrical connection between anode and cathode.
- Resistance of the electrolyte.
- High concentration of anode metal ions in solution.
- Reactant build-up at the cathode.
- Lack of reactants at the cathode.

The action of these resistances may be expressed in a polarization diagram. These diagrams plot potential difference versus current (or log current). The slope of the curve represents the resistance.

## Polarization

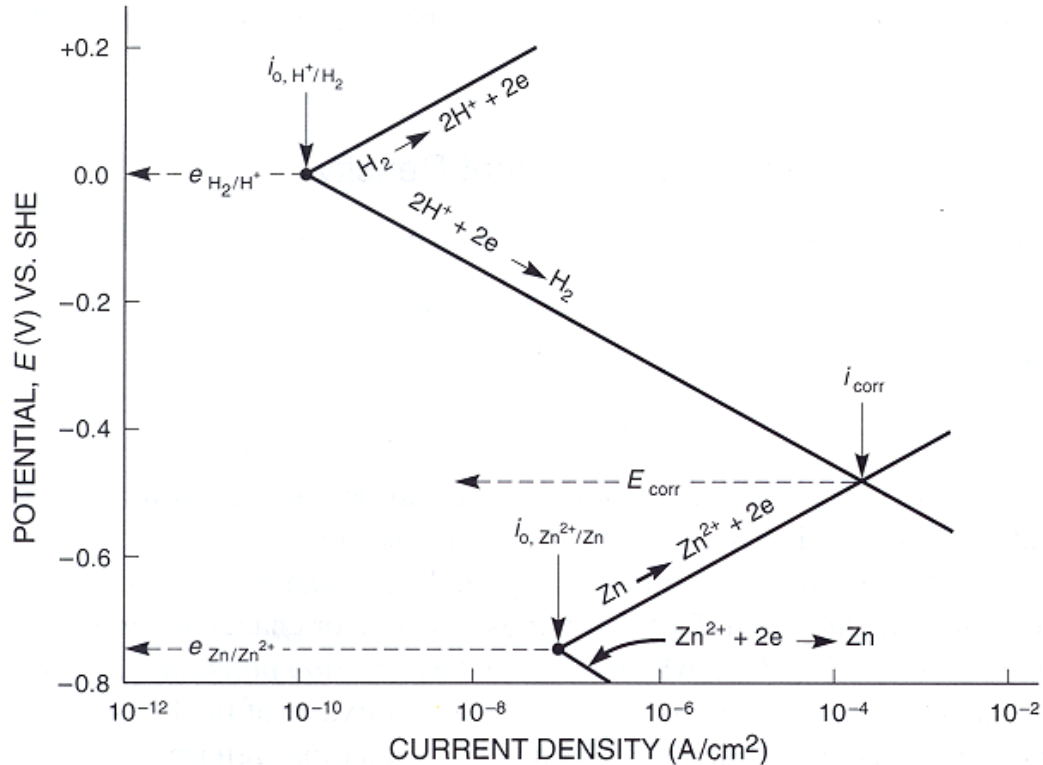
Polarization may be defined the shift in electrode potential which results from the effects of current flow w.r.t. the zero current flow potential. All corrosion reactions involve current flow and will alter the potential of the metal surfaces involved. The degree of polarization will be determined by the resistance of the corrosion cell. The higher the cell resistance, the larger the shift in potential.

$$V = IR$$

The two types of polarization that may be encountered at the electrode surface are:

Activation polarization - this is the energy required to overcome the exchange current density to allow the electrode reaction to proceed.

Concentration polarization - this is the shift in potential due to concentration changes in the environment adjacent to the electrode surface.

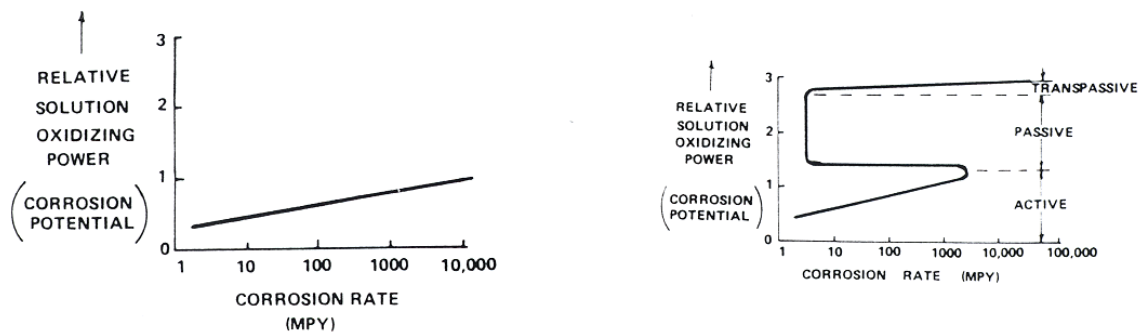


Polarization diagram [from Jones (1996)].

## Passivating films

Passivity can be defined as the loss of chemical reactivity exhibited by certain metals under specific environmental conditions. In some cases, oxide films which form on the surface of a metal exposed in an electrolyte can have a marked effect on its corrosion behavior. This is notable with metals near the top of the electromotive series. Aluminum, for example, would corrode rapidly in seawater if it were not protected by a thin oxide surface film.

Alloys containing chromium, iron, nickel, and titanium can become “passive” in strong oxidizing solutions when they form protective surface films. In this state, they may have a resistance to corrosion which is orders of magnitude greater than the unfilmed or “active” metal surface. The stainless steels can often exhibit this behavior. The passivating film is usually of the order of only 3 nm in thickness, however. This means that the film can be quite delicate. The ability of the surface film to adhere or self heal if compromised by turbulence or mechanical effects can be the determining factor in their corrosion rate. It is in cases which the surface film does not remain intact that stainless steels can undergo severe localized attack.



Nonpassivating (left)/ passivating metal (right) [from Corrosion Basics (1984)].

## Concentration Cells

As stated previously, the electrochemical cell may be the result of differing concentrations of reactants on a metal surface. This can be in the form of either oxygen or metal ion concentrations. In both the case of the oxygen concentration cell and the metal ion concentration cell, the surface potential is lowered at the site of lower concentration. Our earlier example of the rotating copper disk was a metal ion concentration cell. In this case the higher velocity on the periphery of the disk led to a turbulent boundary layer. This is much more diffusive than its laminar counterpart. The metal ions produced at the surface move more rapidly from the surface on the periphery. A lower ion concentration at the metal surface is established, and corrosion occurs on the outer part of the disk. Copper and its alloys are the most susceptible to setting up a metal ion concentration cell.

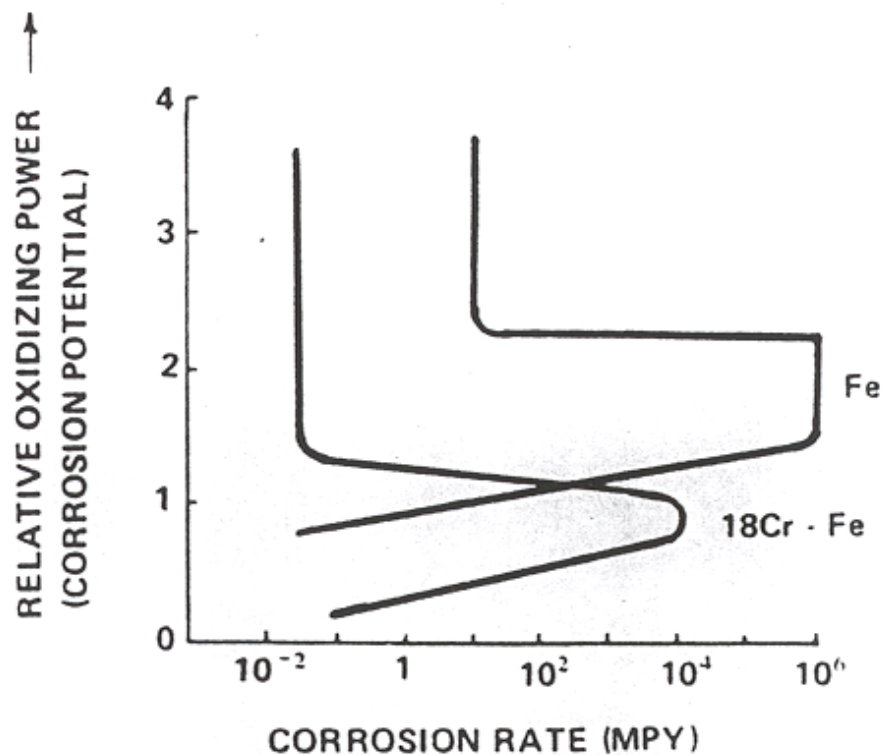
If we this time look at a rotating iron disk placed in aerated seawater, it is observed that the corrosion attack occurs near the center of the disk. Why is this? In this case, an oxygen concentration cell is established on the iron surface. The oxygen on the metal surface is able to reach a higher concentration at the periphery of the disk, where turbulent flow allows higher diffusion. At the center, oxygen concentrations at the metal surface are lower. This causes attack at the center of the iron disk. Iron and its alloys are the most susceptible to forming an oxygen concentration cell.

Both the metal ion and oxygen concentration cell can also be established in metal crevices. In the case of the metal ion cell, corrosion occurs just outside the crevice. In the oxygen concentration cell, attack occurs in the crevice. In all these cases, if the concentrations are known, the driving potential can be predicted with the Nernst equation.



## Effect of Alloying

The graphs depicting the change in corrosion rate with increasing corrosion potential show how the amount of oxidizing agent in solution can have a great effect on the corrosion rate of a metal. Choosing proper alloying metals for a given metal can have a similar effect. Not only can alloying reduce the amount of oxidizer needed to make the metal go “passive”, but it can also reduce the corrosion rate of the metal while it is in the passive state. A good example would be adding 18% chromium to iron. This produces what is termed a ferritic stainless steel. The corrosion rates are shown in the following graph.



Effect of alloying on corrosion rate [from Corrosion Basics (1984)].

It can be seen that the stainless steel reaches passivity at a much lower corrosion potential and its corrosion rate in its passive state is much lower than that of iron.

## Pourbaix Diagrams

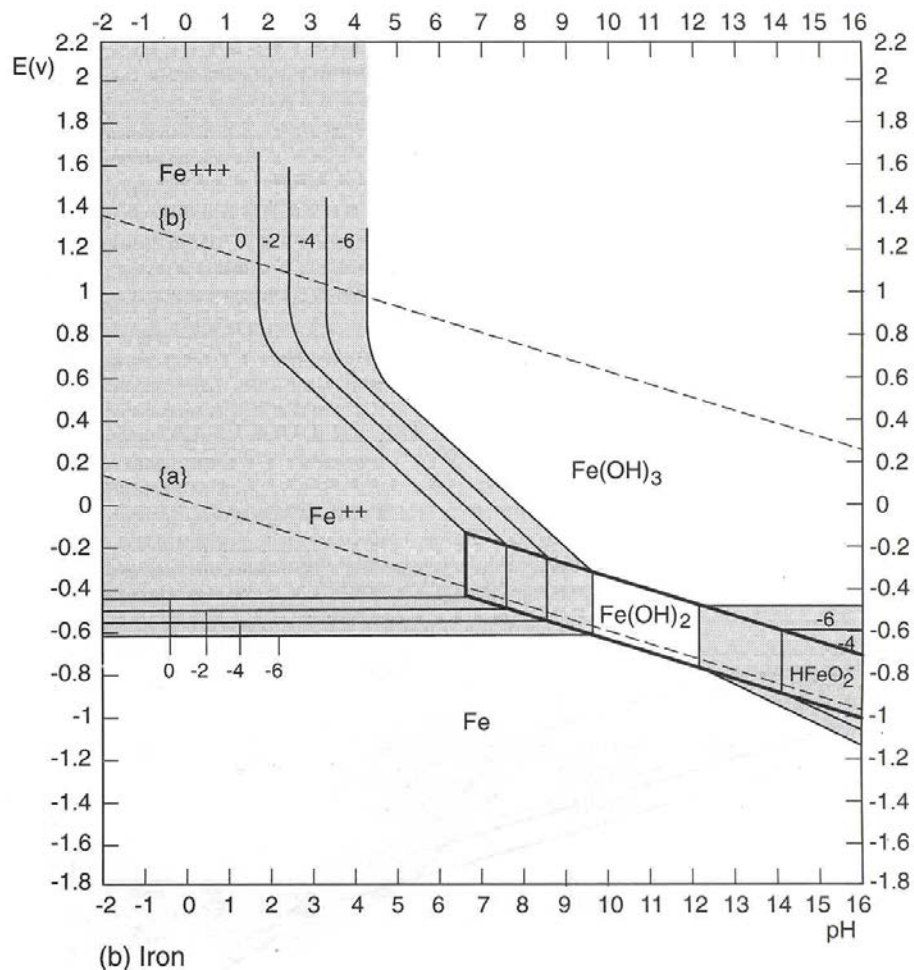
A plot for a given metal which expresses its potential versus pH, is termed a Pourbaix diagram.

The diagrams are generally constructed using equilibrium constants, solubility data, and a form of the Nernst equation which includes a pH term. These diagrams are some very important uses.

These include:

- Predicting if corrosion will occur.
- Finding what the corrosion products may be.
- Forecasting what effect environmental changes may have on corrosion.

The following is a Pourbaix diagram for iron immersed in water.



Pourbaix diagram for iron [from Jones (1996)].

Some interesting information can be gleaned from this diagram. The most striking thing is that if iron is kept at a potential of less than -1.2 v with respect to a hydrogen half cell, it should not corrode in a solution of any pH. To keep the iron protected, however, an external voltage would be required. This is the basis of cathodic protection, which we will discuss later in more detail. It can also be observed that in a potential range of about 0.7 v and -0.6 v and pH below 9, the corrosion product will be the ferrous ion. At more positive potentials, the ferric ion would be produced. In other cases, ferric or ferrous hydroxide and complex iron ions may be formed.

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