CHAPTER 2

CORROSION AND ELECTROMOTIVE POTENTIAL

(from Swain (1996), Schultz (1997) and Dawson (2003))
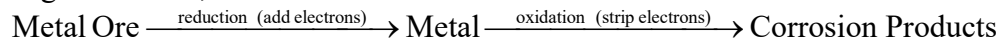
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What is corrosion?
- Webster's Dictionary - corrode (v.) To eat away or be eaten away gradually, especially by chemical action.
- NACE Corrosion Basics - corrosion may be defined as the deterioration of a material (usually a metal) because of a reaction 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.

$$\text{Metal Ore} \xrightarrow{\text{reduction (add electrons)}} \text{Metal} \xrightarrow{\text{oxidation (strip electrons)}} \text{Corrosion Products}$$

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.

2.1 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.
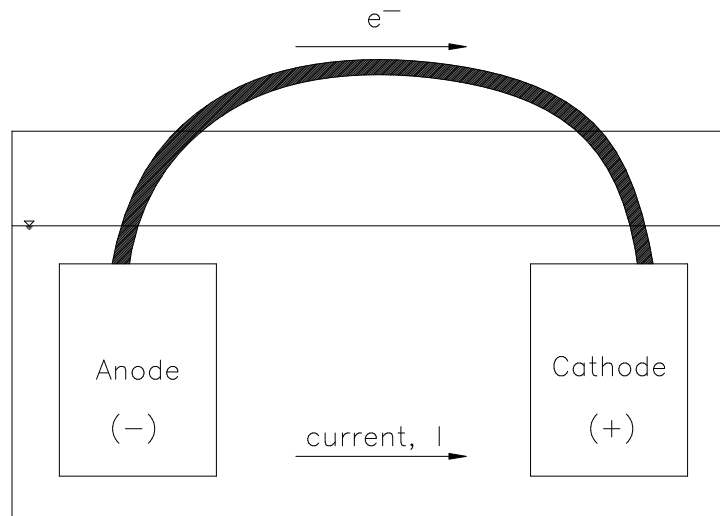


Schematic of the corrosion cell

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.

Anode half-cell reaction
Oxidation of the metal at the anode may be expressed by the following half-cell reaction:
$$M \rightarrow M^{n+} + ne^-$$
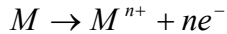
Cathode half-cell reaction
The reduction half-cell reaction at the cathode depends mainly on environmental conditions. The following six reactions represent common cathodic reactions along with the conditions in which they generally occur:

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
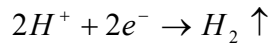5. $M^{n+} + e^- \rightarrow M^{(n-1)+}$ metal reduction

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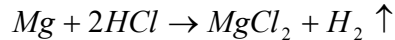
Solution:

Anodic $Mg \rightarrow Mg^{2+} + 2e^-$

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

Overall reaction $Mg + 2HCl \rightarrow MgCl_2 + H_2 \uparrow$

2.2 Specific Examples of Electrochemical Reactions

Keeping in mind the definition of corrosion as a destructive electrochemical process, resulting in material wastage, we examine here the basic concept of a corrosion cell and its associated reactions.

Iron Bar in Hydrochloric Acid
To begin, we consider a simple idealized case where a perfectly homogeneous bar of iron (every part the same as every other part) is placed in a container of hydrochloric acid (Hcl). On placing the bar in the acid, some of the iron will initially tend to go into solution as ferrous iron (Fe $^{++}$) as a result of attractive forces exerted by the ionized acid solution. Such a situation will, however, leave the departure points on the bar with electrons, causing negative charge so the tendency for ion formation is thus counteracted by local electrostatic attraction from these fixed electrons, i.e. the reaction stops. If the bar is perfectly homogeneous, as assumed, there will accordingly be no loss of metal to the solution and therefore no corrosion of the bar.

Iron and Copper in Hydrochloric Acid
Suppose, however, that we now place a second metal bar, say a copper, in the acid and connect a wire between them as indicated in the figure below:
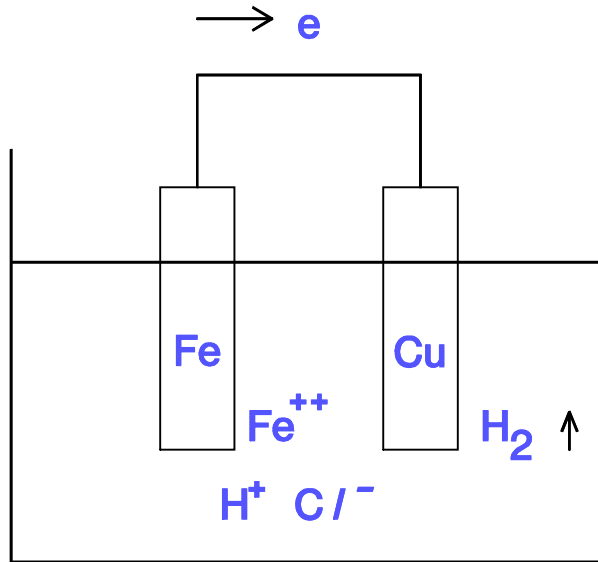
Iron and Copper in Hydrochloric Acid

In this case, we have what is called a corrosion, or galvanic cell. Again, there is a tendency for the iron to be drawn into solution as ferrous ions and leave behind electrons. But now, these electrons will no longer be fixed in place at the departure sites of the ions. They will, in fact, be drawn through the iron bar and connecting wire by the natural potential difference existing between the two metals. In this way, the iron ions are thus fully drawn into solution because the freed electrons are drained away rather than remain at the departure sites to attract the ions back to the metal. Of course, <u>when the electrons reach the copper bar, they must be used in some way if the process is to continue</u>. This happens because the electrons can combine with the hydrogen (H^+) ions in solution to form hydrogen (H_2) gas on the surface of the bar which then bubbles off. In addition, the Fe^{++} ions can combine with the Cl^- ion in solution to form ferrous chloride. Thus, as long as the above conditions exist, corrosion of the iron bar will continue.

In the above example, oxidation occurs at the anode according to the reaction:

$$Fe \rightarrow Fe^{++} + 2e^-$$
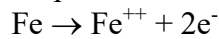
Reduction occurs at the cathode according to the reaction:

$$2H^+ + 2e^- \rightarrow H_2\uparrow(gas)$$
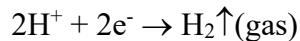
A compound also forms as described by:

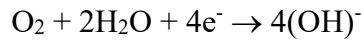$$Fe^{++} + 2Cl^- \rightarrow FeCl_2$$

Which is ferrous chloride. (Note how the reaction is balanced, so <u>remember your chemistry</u>).

<u>Iron and Copper in Water</u>
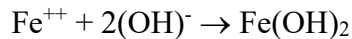Suppose now that we place the iron and copper bars in water rather than HCl. In this case, the anode reaction is still:
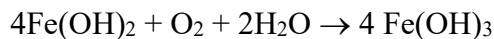
$$Fe \rightarrow Fe^{++} + 2e^-$$

The cathode reaction is, however, now mainly

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

that is the production of hydroxide ions. The additional reaction in the electrolyte is

$$Fe^{++} + 2(OH)^- \rightarrow Fe(OH)_2$$

which is ferrous hydroxide. This compound in the presence of oxygen is converted to ferric hydroxide according to the reaction

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4\ Fe(OH)_3$$

Ferric hydroxide is orange to red-brown in color and compromises <u>most of ordinary rust</u>.

<u>Non-Perfect Bar</u>
The above discussion assumed a homogeneous iron bar such that if placed alone in an electrolyte, no corrosion would occur. In reality, though, no bar is perfectly homogeneous, and when placed alone in an electrolyte, a part of it will act as an anode and a part as a cathode, thus giving rise to a <u>local corrosion cell</u> as indicated in the figure below
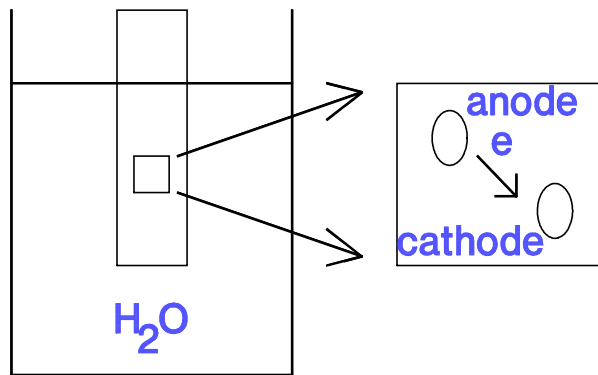
Local Anodes and Cathodes
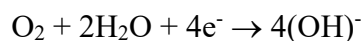
As corrosion proceeds, the location of the anode and cathode regions will shift around on the bar and the bar will corrode more or less uniformly. This is the basis for the uniform corrosion (rusting) of an iron bar immersed in water. At the anode region, the reaction as before is

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

At the cathode region

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

As discussed above, ferric hydroxide is formed from the Fe^{++} and OH^- ions and this compound (rust) precipitates out of solution. Of course, if a non-perfect bar of iron is connected to a copper bar, as described earlier, the cathodic behavior of the copper bar will generally override that of any regions of the iron bar itself, and the entire iron bar will act as an anode.

When two bars are placed in an electrolyte and connected, the question of which one acts like the anode and which like the cathode is determined by the potential difference existing between them. The same is also true regarding regions of a non-perfect bar.

2.3 Measurement of Potential

Consider again the iron and copper bars discussed earlier. To fix ideas, we now suppose the iron to be immersed in a solution of iron ions (Fe^{++}) with a concentration of 1 mole/liter. Similarly, we suppose the copper is immersed in a solution of copper ions (Cu^{++}) with a concentration of 1 mole/liter. We also suppose a voltmeter connected between the two bars as indicated in the figure below:
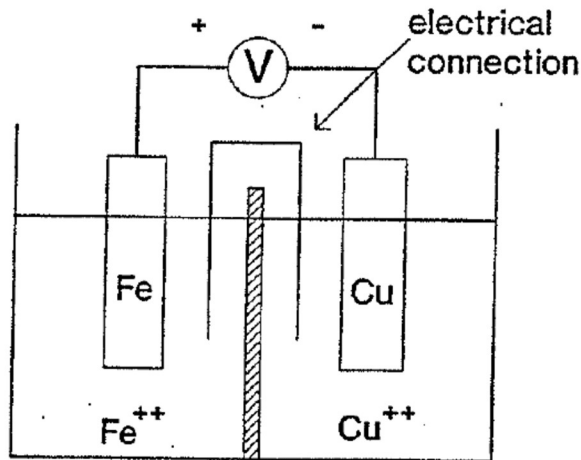
Iron and Copper Bars with a Voltmeter Connection

If we measure the potential difference when no current exists, we find with the voltmeter hook-up indicated that

$$\Delta V = V_{Fe} - V_{Cu} = -0.789 \text{ volts}$$

Since this shows the potential of the copper to be greater (i.e. less negative), the direction of the current, externally will be from the copper to the iron when the (open circuit) voltmeter is replaced by a connecting wire. By convention, <u>the current direction is opposite to the flow of electrons</u>. The electrons would therefore flow from the iron to the copper through the connecting wire and the iron would thus act as the anode and corrode and the copper would act as the cathode and would not corrode. This, of course, is consistent with what we assumed earlier when discussing the iron and copper bars.

Standard Hydrogen Electrode

It is useful to use a standard hydrogen electrode to measure the potentials of the various metals for comparative purposes. The hydrogen electrode consists of a platinum tube immersed in a 1 mole/liter solution of H^+ ions through which hydrogen gas is bubbled, as shown below:
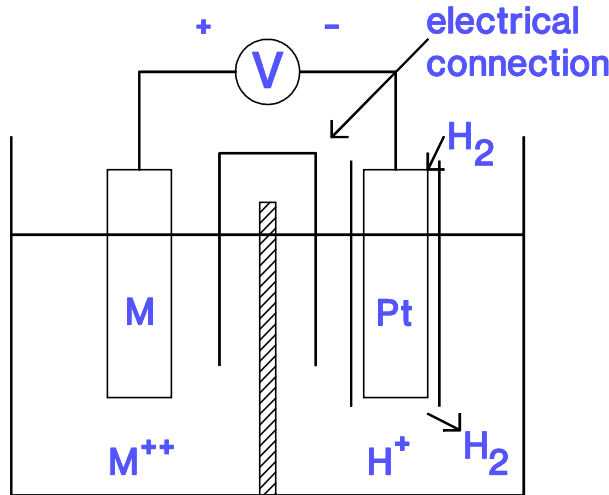
Hydrogen Half-Cell Electrode, As connected to Measure Potential

Note: With the wire in place, it is equivalent to not having a barrier between the 1 mole/liter ion solutions. The potential reaction of the hydrogen half-cell is

$$1/2\ H_2 \leftrightarrow H^+ + e^-$$

the potential reaction being to the right when the half-cell is anodic to the sample and to the left when it is cathodic.

2.4 Standard Electromotive Force (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)]
(Note, these potentials are in a solution of 1 mole/liter of their own ions, measured against a standard hydrogen electrode)

	Reaction	Standard Potential, $e°$ (volts vs. SHE)
Noble	$Au^{3+} + 3e^- = Au$	+1.498
	$Cl_2 + 2e^- = 2Cl^-$	+1.358
	$O_2 + 4H^+ + 4e^- = 2H_2O$ (pH 0)	+1.229
	$Pt^{2+} + 2e^- = Pt$	+1.118
	$NO_3^- + 4H^+ + 3e^- = NO + 2H_2O$	+0.957
	$O_2 + 2H_2O + 4e^- = 4OH^-$ (pH 7)a	+0.82
	$Ag^+ + e^- = Ag$	+0.799
	$Hg_2^{2+} + 2e^- = 2Hg$	+0.799
	$Fe^{3+} + e^- = Fe^{2+}$	+0.771
	$O_2 + 2H_2O + 4e^- = 4OH^-$ (pH 14)	+0.401
	$Cu^{2+} + 2e^- = Cu$	+0.342
	$Sn^{4+} + 2e^- = Sn^{2+}$	+0.15
	$2H^+ + 2e^- = H_2$	0.000
	$Pb^{2+} + 2e^- = Pb$	−0.126
	$Sn^{2+} + 2e^- = Sn$	−0.138
	$Ni^{2+} + 2e^- = Ni$	−0.250
	$Co^{2+} + 2e^- = Co$	−0.277
	$Cd^{2+} + 2e^- = Cd$	−0.403
	$2H_2O + 2e^- = H_2 + 2OH^-$ (pH 7)[a]	−0.413
	$Fe^{2+} + 2e^- = Fe$	−0.447
	$Cr^{3+} + 3e^- = Cr$	−0.744
	$Zn^{2+} + 2e^- = Zn$	−0.762
	$2H_2O + 2e^- = H_2 + 2OH^-$ (pH 14)	−0.828
	$Al^{3+} + 3e^- = Al$	−1.662
	$Mg^{2+} + 2e^- = Mg$	−2.372
	$Na^+ + e^- = Na$	−2.71
	$K^+ + e^- = K$	−2.931
Active		

Consider the potential difference between iron and copper. We have

$$\Delta V = V_{Fe} - V_{Cu} = -0.447 \ - 0.342 = - 0.789 \text{ volts}$$

as before. The iron would thus act as an anode in a corrosion hook-up and corrode.

Next consider potential difference between iron and zinc.

$$\Delta V = V_{Fe} - V_{Zn} = -0.447 - (-0.762) = +0.315 \text{ volts}$$

Hence, in this case the zinc would act as the anode and corrode while the iron would act as the cathode in a corrosion hookup. If we put the (+) probe on the iron and the (-) probe on the zinc, we would read +0.323 volts on the voltmeter. This means that the current would be from the iron to the zinc and hence that the electrons would flow from the zinc to the iron in accordance with our previous discussion.

It should be noted that any metal listed in the electromotive series table will act as an anode when connected to one above it in the series and hence will corrode.

For example, if tin (Sn) and zinc (Zn) are connected in a corrosive cell, the tin will act as the cathode and be protected and the zinc will act as the anode and corrode. Similarly, if iron is placed in a solution of nickel ions, the iron will corrode and the nickel will plate out at the local cathode regions. This is known as a DALIC process. The nickel plating of steel is a common process for the restoration of dimensions on shafts and the mating surfaces of press fittings. It is also important to note that given time, as ΔV increases, the rate of reaction also increases.

2.5 Correction for Solution Concentration: Nernst Equation

The potential values listed in the electromotive series table are for a unit concentration (1 mole/liter) of the metal ions in solution. For other concentrations, we may calculate the potential using the Nernst equation, which simplifies to:

$$E = E_o + (0.0592/Z) \log_{10}(c)$$

where E_o is the potential at unit concentration, Z is the valence of the ion (Z = 2 for iron, 3 for aluminum, etc.) and c is the concentration (moles/liter).

Example: As an example, we may calculate the electrode potential of iron in contact with a solution of 10^{-3} moles/liter of Fe^{++} ions. We have from Table 1, E_o = -0.440 V and

$$E = -0.440 + (0.0592/2)\log_{10}(10^{-3})$$

or

$$E = -0.529 \ V$$

2.6 Reference electrodes

Half-cell reference electrodes are used in corrosion measurements to determine the potentials of specific metals in selected aqueous environments. The hydrogen half-cell provides the basic standard, but in practice is awkward to use. For this reason, several other types of 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

The following sub-sections present more details on the construction of Saturated Calomel, Saturated Copper-Copper Sulfate and Silver-Silver Chloride half cells.

Saturated Calomel Reference Electrode
In establishing the galvanic series of metals and alloys in seawater, use is generally made of the saturated calomel half-cell, which derives its name of calomel from one of its ingredients, mercurous chloride (Hg_2Cl_2). The potential reaction is

$$2Hg + 2Cl^- \leftrightarrow Hg_2Cl_2 + 2e^-$$
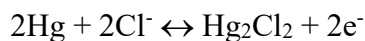
The potential of the saturated calomel half-cell relative to the hydrogen half-cell is + 0.246V. The cell is illustrated below.
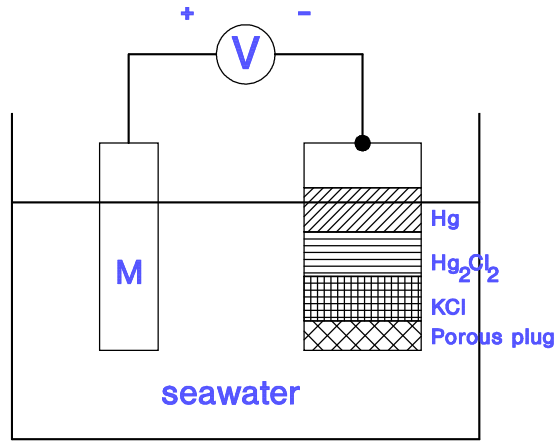
Figure: Saturated Calomel Reference Electrode

Saturated Copper-Copper Sulfate Reference Electrode

The saturated copper-copper sulfate half-cell is an equally useful cell for corrosion measurements. A sketch of the cell is illustrated below. When used, it is immersed in seawater where the porous plug makes the connection to the cell. The half-cell potential reaction is $Cu \leftrightarrow Cu^{++} + 2e^-$ and its reverse. The potential of the copper-copper sulfate half-cell, relative to the hydrogen electrode is +0.316 V
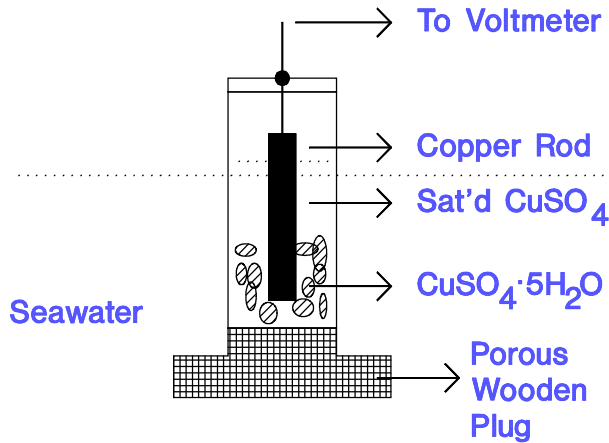
Silver-Silver Chloride Half-Cell

This electrode consists of silver chloride covering a silver plated platinum wire sealed in a glass tube, as indicated below. When the electrode is immersed in a chloride solution (such as seawater), the potential reaction is:

$$Ag + Cl^- \leftrightarrow AgCl + e^-$$

The potential of the silver-silver chloride electrode relative to the hydrogen half-cell is +0.266V.
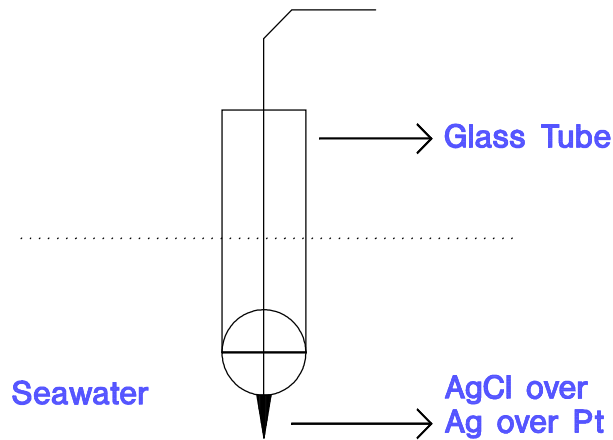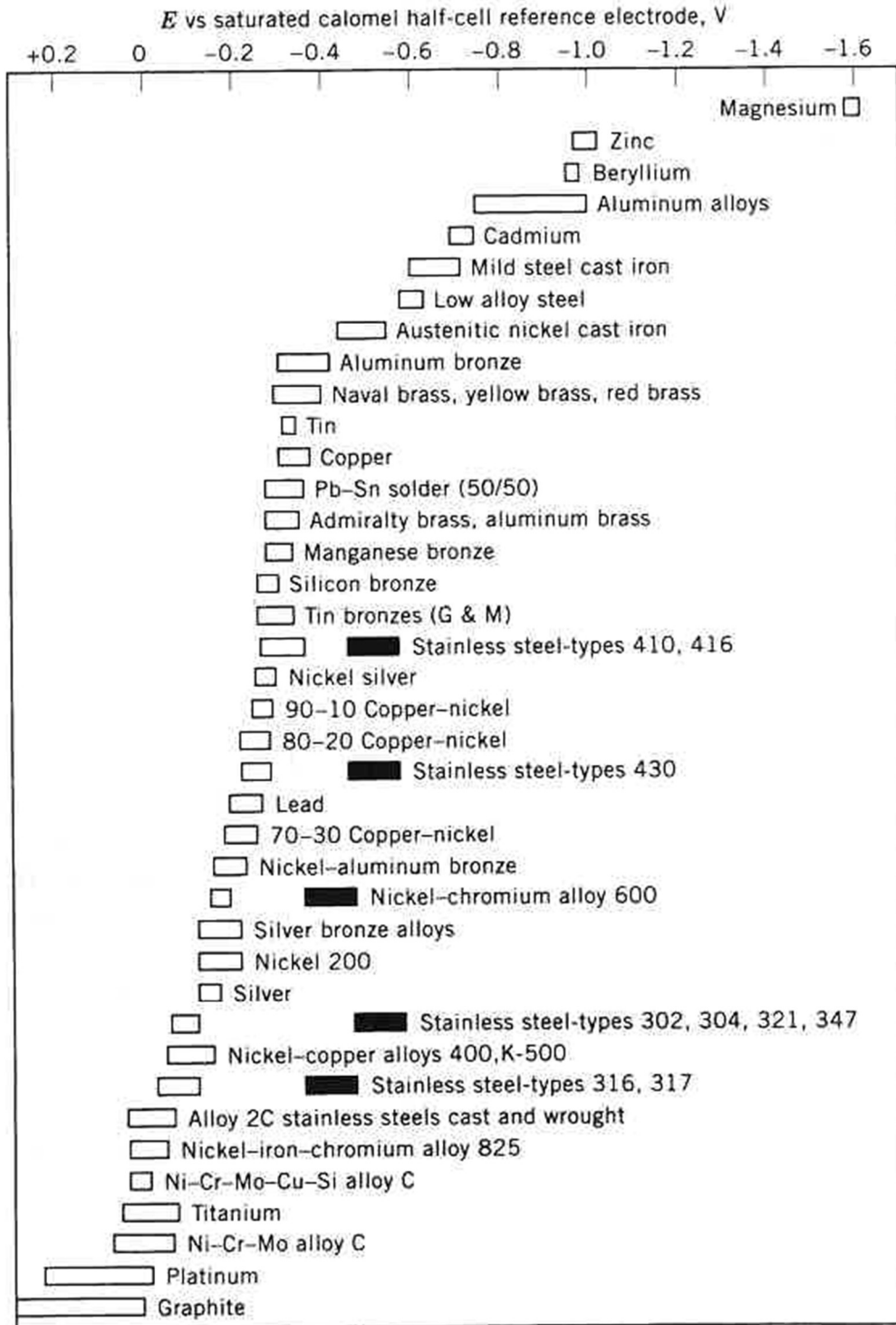
Figure: Silver-Chloride Half Cell

2.7 Galvanic series

In marine applications, we are obviously not so much interested in the potential of a metal immersed in a solution of its own ions as we are in the relative potentials of metals placed in seawater. Such a ranking is known as the **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.

E vs saturated calomel half-cell reference electrode, V

+0.2   0   −0.2   −0.4   −0.6   −0.8   −1.0   −1.2   −1.4   −1.6

Magnesium
Zinc
Beryllium
Aluminum alloys
Cadmium
Mild steel cast iron
Low alloy steel
Austenitic nickel cast iron
Aluminum bronze
Naval brass, yellow brass, red brass
Tin
Copper
Pb–Sn solder (50/50)
Admiralty brass, aluminum brass
Manganese bronze
Silicon bronze
Tin bronzes (G & M)
Stainless steel-types 410, 416
Nickel silver
90–10 Copper–nickel
80–20 Copper–nickel
Stainless steel-types 430
Lead
70–30 Copper–nickel
Nickel–aluminum bronze
Nickel–chromium alloy 600
Silver bronze alloys
Nickel 200
Silver
Stainless steel-types 302, 304, 321, 347
Nickel–copper alloys 400,K-500
Stainless steel-types 316, 317
Alloy 2C stainless steels cast and wrought
Nickel–iron–chromium alloy 825
Ni–Cr–Mo–Cu–Si alloy C
Titanium
Ni–Cr–Mo alloy C
Platinum
Graphite

Galvanic Series [from Fontana (1986)].

2.8 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.
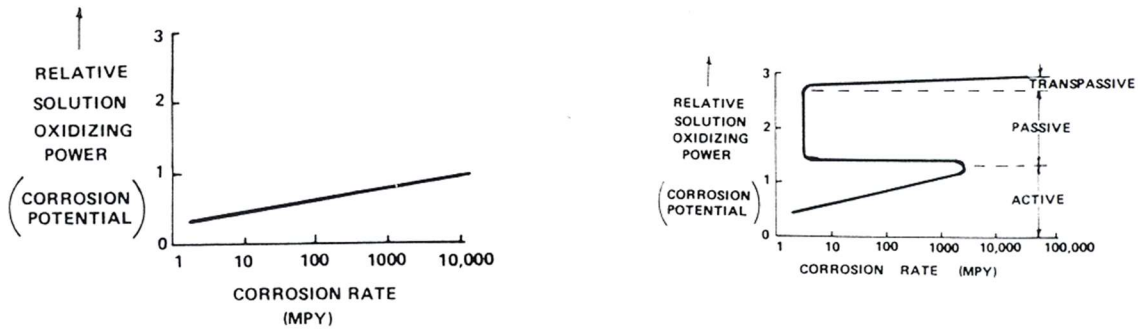
Nonpassivating (left)/ passivating metal (right) [from Corrosion Basics (1984)].

2.9 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.

2.10 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.
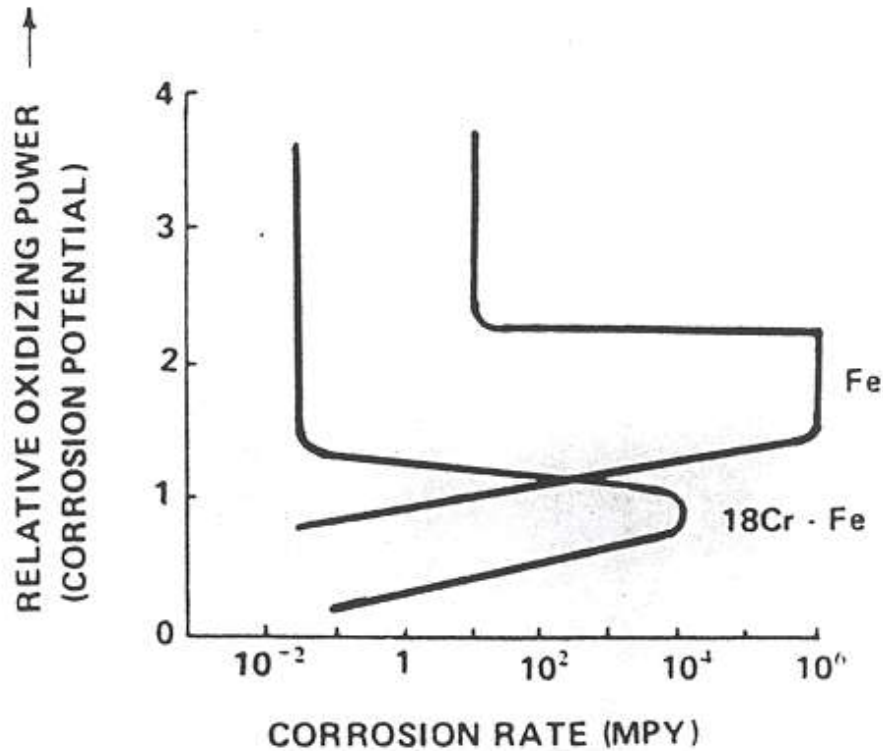
Effect of alloying on corrosion rate [from Corrosion Basics (1984)].

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.

2.11 Pourbaix, or pH 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.
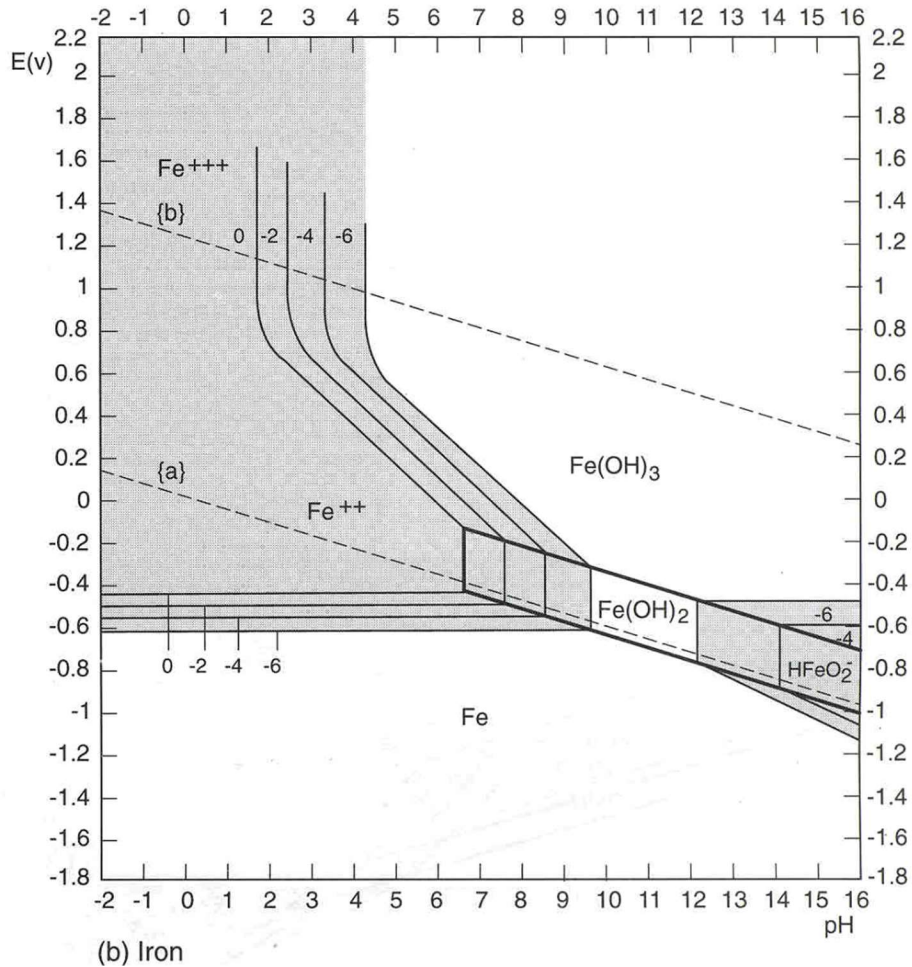
Pourbaix diagram for iron [from Jones (1996)].

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, and 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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