Period #6 Notes: Steel Corrosion and Connections

A. CORROSION OF STEEL

1. Overview

Iron exists naturally in oxide forms [magnetite (Fe_3O_4), hematite (Fe_2O_3), limonite ($Fe_2O_3 + H_2O$), and siderite ($FeCO_3$).]. Even after iron is refined and processed to form steel, it has a strong tendency for it to return to these oxidized forms. We see this return of steel (or its primary component iron) to oxidized form as **corrosion**. While structural steel has many truly excellent mechanical properties that make it a great structural material (high stiffness & strength, high ductility, etc.) one of the key problems with steel is that it corrodes.

We will discuss here **dry corrosion**, and **wet corrosion** of metals.

After discussion of wet and dry corrosion, methods for inhibiting corrosion of steel and prolonging its service life are discussed.

2. Dry Corrosion

The dry oxidation of a metal follows a relatively simple process: $M + O \rightarrow MO$

This simple reaction occurs at the interface of the metal and oxygen, and the metallic oxide is produced and deposited at this interface.

If the metallic oxide layer adheres well to the parent metal, then it may serve as a barrier that inhibits further reaction.

However, if the oxide layer tends to peel away from the parent metal, the dry corrosion process will continue.
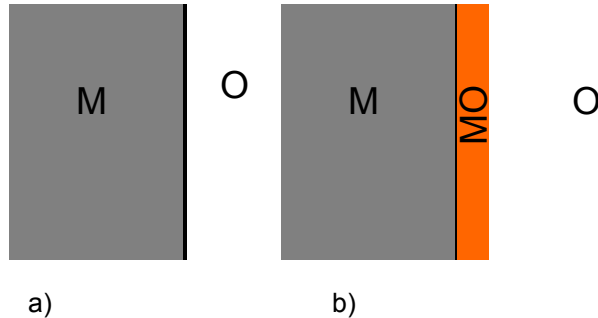
a)   b)

Fig. 6.1. a) Dry corrosion takes place at the oxygen-metal interface; b) If the metallic-oxide layer adheres well to the parent metal, it forms a barrier separating the metal and oxygen, and inhibits further corrosion.

When the MO's mass density matches that of the parent metal, and its surface energy with the metal is relatively low, it forms a good protective barrier against further corrosion.

When the MO's mass density differs significantly from that of the parent metal, and the surface energy between the M and MO is high, then the MO layer will peel or spall off.

Aluminum, chromium, and nickel are metals whose oxides tend to form a good protective layer that inhibits further corrosion.

Generally, iron oxides have a much lower mass density than that of iron. Hence, they do not adhere well to steel/iron.

3. Wet Corrosion

Frequently, corrosion of metals takes place much more rapidly in water than in a dry environment.

An understanding of wet corrosion can be understood by looking at two common prototypical examples: (a) the galvanic cell; and (b) the bi-metallic couple.

The elements necessary for wet corrosion to occur are: (1) an electrolytic solution; and (2) the functional equivalent of a battery to drive electronic current associated with corrosion.
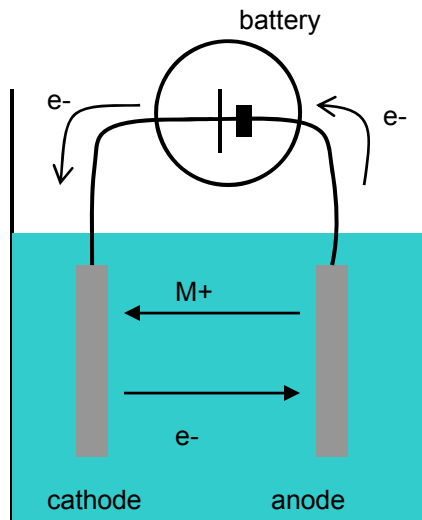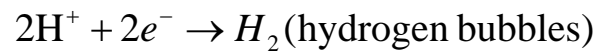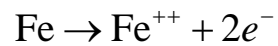
a. The Galvanic Cell

Fig. 6.2. A battery with two electrodes submersed in an electrolytic solution forms a galvanic cell. The battery drives electron current from the cathode to the anode, and the metallic current from the anode to the cathode. In this case, the metal of the anode deposits itself on the cathode. Hence, the anode corrodes.

If the two electrodes in this example were iron, the following reactions would take place:

At the anode :

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

$$H_2O \rightarrow H^+ + (OH)^-$$

$$2H^+ + 2e^- \rightarrow H_2 \text{(hydrogen bubbles)}$$

At the cathode :

$$Fe^{++} + 2(OH)^- \rightarrow Fe(OH)_2 \text{ (slimy orange film)}$$

b. The Bi-Metallic Couple

It is known from experience, that the battery is not absolutely necessary to drive the corrosion process.

Corrosion will occur in an electrolyte, in the absence of a battery as long as the two electrodes are of different metals (Fig. 6.3).

Each metal has what is called an electrode potential (see Table 6.1).

A metal that has a high electrode potential tends to function as a cathode, and a metal with a lower potential will function as an anode and thus corrode.

e-

e-

M+

e-

cathode
(larger
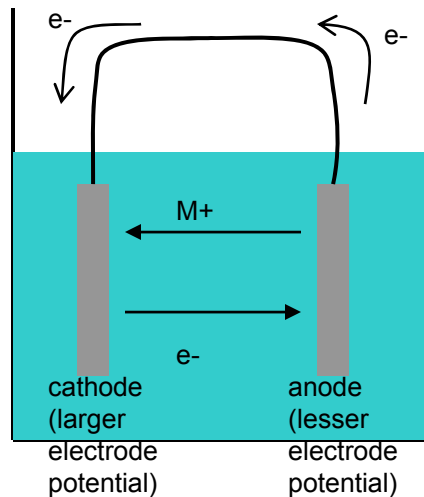electrode
potential)

anode
(lesser
electrode
potential)

Fig. 6.3. A bi-metallic galvanic cell in which two different metals are immersed in an electrolyte. The difference in electrode potential between the two metals drives electron current from the cathode to the anode, and the metallic current from the anode to the cathode. In this case, the metal of the anode deposits itself on the cathode. Hence, the anode corrodes.

Table 6.1. Standard Electrode Potentials of Different Elements

Metal	Reaction	Electrode Potential (V)
Li	$Li \leftrightarrow Li^+ + e^-$	-2.96
K	$K \leftrightarrow K^+ + e^-$	-2.92
Na	$Na \leftrightarrow Na^+ + e^-$	-2.71
Mg	$Mg \leftrightarrow Mg^{++} + 2e^-$	-2.40
Al	$Al \leftrightarrow Al^{+++} + 3e^-$	-1.70
Zn	$Zn \leftrightarrow Zn^{++} + 2e^-$	-0.76
Cr	$Cr \leftrightarrow Cr^{3+} + 3e^-$	-0.74
Fe	$Fe \leftrightarrow Fe^{++} + 2e^-$	-0.44
Cd	$Cd \leftrightarrow Cd^{++} + 2e^-$	-0.40
Ni	$Ni \leftrightarrow Ni^{++} + 2e^-$	-0.22
Sn	$Sn \leftrightarrow Sn^{++} + 2e^-$	-0.13
Pb	$Pb \leftrightarrow Pb^{++} + 2e^-$	-0.12
H_2		0.00
Cu	$Cu \leftrightarrow Cu^{++} + 2e^-$	+0.34
Ag	$Ag \leftrightarrow Ag^+ + e^-$	+0.80
Hg	$Hg \leftrightarrow Hg^{++} + 2e^-$	+0.86
Cl	$2Cl^- \leftrightarrow Cl_2 + 2e^-$	+1.36
Au	$Au \leftrightarrow Au^+ + e^-$	+1.50

More likely to corrode

Less likely to corrode

c. Practical Aspects:

In civil engineering practice, it is important to be aware of the difference in electrode potentials between various metals. If two dissimilar metals are fielded in a wet environment (underwater, near a waterline, or underground) the metal having the lower electrode potential will corrode onto the one having the higher potential. The rate of corrosion increases with the difference in electrode potentials of the metals.

Example 6.1: If an aluminum pipe with steel fittings were placed underground in a wet region, what do you expect might happen?

Answer: Since iron has an electrode potential of (-.44V) and aluminum a potential of (-1.70V) we would expect the aluminum pipe to corrode onto the steel fittings.

Example 6.2: If zinc and iron were placed underground in a wet environment what would be expected?

Answer: Since zinc has a lower potential (-0.76V) than iron (-0.44V), the zinc would be expected to corrode onto the iron.

When iron or steel parts are placed underground as part of civil infrastructure they are very susceptible to wet corrosion. There are a variety of strategies that can be used to inhibit corrosion of the steel and thus prolong the service life of the infrastructure.

1._Anodic protection_: A sacrificial metal of lower electrode potential (such as zinc, or magnesium) can be placed alongside the steel. This sacrificial metal will corrode onto the steel and thus extend the service life of the steel. This protection is not permanent, and once the sacrificial metal has completely corroded, the level of protection provided begins to drop off.

2. *Barrier coatings*: The steel can be coated so that it is not directly exposed to the electrolyte (water). There are a range of different types of barrier coatings that can be employed:

    a. *Metallic coatings:* Generally, a metal of lower electrode potential is used to coat steel, with zinc being most commonly used. Hence the zinc functions as the anode and steel as the cathode. Zinc galvanization of steel is discussed quite extensively in the materials provided by the American Galvanizers Association. Hot-dip zinc galvanization actually forms a multi-layered zinc-iron alloy protective barrier on the steel. While the outer zinc layer itself is fairly soft, some of the zinc-iron allows in the barrier are harder than the steel itself and thus less vulnerable to abrading. (Please consult the reference materials provided.)

    Metals other than zinc can be used to coat steel. For example, chrome-plating of steel can be performed to provide a protective metallic coating.

    b. *Inorganic coatings*: Ceramic coatings such as porcelain and glass are sometimes used to protect steel.

    c. *Organic coatings*:   Most paint type coatings are polymer-based, and are relatively simple and inexpensive to apply. Care must be taken in preparing the metal surface before painting to get proper adherence. If the paint coat is scratched, chipped or degraded due to UV radiation, its effectiveness as a protectant is negated.

3. *Cathodic Protection:* By using impressed direct currents, the oxidation of iron in a wet underground environment can be prevented. This essentially involves setting up a galvanic cell with a battery similar to that shown in Fig. 6.2 wherein the steel is established as the cathode, and a sacrificial metal is utilized as an anode. Such a system requires some maintenance to insure that the battery remains charged and that anode has not completely corroded.

While many measures can be taken to prevent and slow corrosion of steel, the steel will eventually corrode. Therefore, the initial dimensions of the steel parts should be specified larger than is necessary to allow for reductions due to corrosion.

d.   Stainless steels

A particularly corrosion resistant class of steel alloys are the "stainless steel" alloys which have a minimum of 10% chromium by weight. Compared to most structural steels that have chromium contents of 0.3%-0.4%, stainless steels have much higher corrosion resistance as indicated by Fig. 6.4 below which gives the galvanic series of various metals and alloys in seawater.
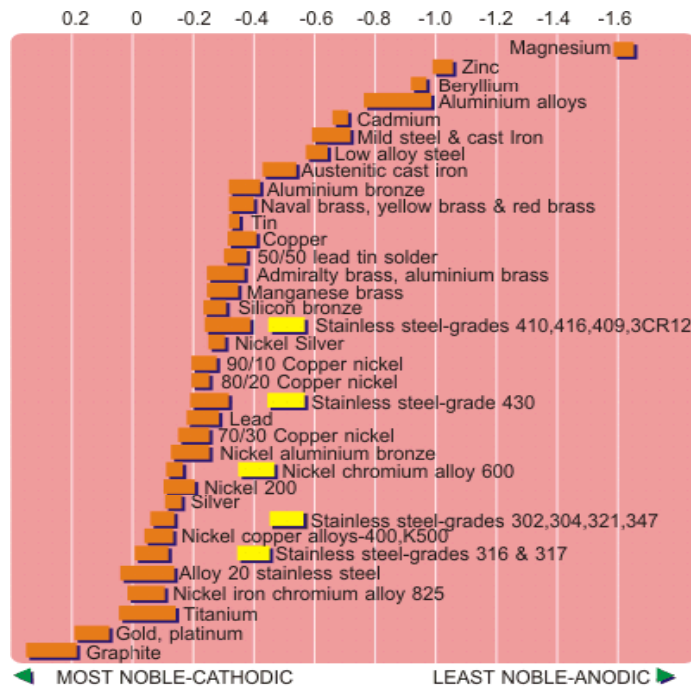

Fig. 6.4. Galvanic series of metals (including AISI grades of stainless steel) in seawater. (Provided by azom.com)

There are many different types and grades of stainless steels depending upon their heat treatments and alloying compositions. Their strength properties and corrosion resistance properties can vary greatly. Stainless steels are frequently classified into those having *ferritic, austenitic,* and *martinsitic* structures.   A few of the noteworthy grades of potential interest for civil infrastructure applications are briefly described below:

Grade 410: This is a high-strength *martensitic* stainless steel alloy (12.5% Cr) produced by quenching and tempering that is relatively inexpensive due to its low nickel content. Its strength properties are strongly dependent on the temperature at which it is tempered. (see Table 6.2) The corrosion resistance of grade 410 stainless steels is not the highest.

Table 6.2 Properties of 410 stainless steel with tempering temperature.

Tempering Temp (°C)	Tensile strength (MPa) and (ksi)	Yield strength (MPa) and (ksi)	Elongation at failure (%)
204	1310 (188)	1000 (143)	16
316	1240 (177)	960 (138)	14
427	1405 (202)	950 (136)	16
538	985 (141)	730 (105)	16
650	755 (108)	575 (82)	23
Annealed	480 (69)	275 (39)	25

Grade 304: Is a 19% Cr, 10%Ni, .08%C annealed *austenitic* steel alloy that is often used in chemical and food-processing equipment because of its high hardness. Its typical yield strength is 42 ksi (290 MPa) and tensile strength is 84 ksi (580 MPa). The elongation of this grade is typically about 55% at failure.

Grade 304L: Is a low-carbon (.03%C) variant of Grade 304 that has similar mechanical properties but is better for welding.

Grade 316: is the standard molybdenum-bearing grade, second in importance to 304 amongst the *austenitic* stainless steels. The molybdenum gives 316 better overall corrosion resistance properties than Grade 304, particularly higher resistance to pitting and crevice corrosion in chloride environments. It has excellent forming and welding characteristics. Its characteristic yield strength is 29 ksi (205 MPa), tensile strength is 74 ksi (515 MPa), and elongation is 40% at failure.

Grade 430 (17%Cr, 0.75%Ni) is an annealed ferritic stainless steel alloy. Characteristic yield strength values are 50 ksi (345 MPa) while tensile strengths are 75 ksi (517 MPa). Elongation at failure is typically about 25%.

Grade 446 (25%Cr) is an annealed ferritic stainless steel alloy generally used for high-temperature applications. Characteristics yield strength values are 50 ksi (345 MPa) while tensile strengths are 80 ksi (552 MPa).

Grade 2205 (22%Cr, 5%Ni) is often called a duplex stainless steel because its microstructures consist of a mixture of *austenite* and *ferrite* phases. As a result, duplex stainless steels display properties characteristic of both *austenitic* and ferritic stainless steels. Duplex stainless steels are in most cases, tougher than *ferritic* stainless steels (grades 430 and 446). The yield strength of 2205 is 65 ksi (450 MPa) while the tensile strength is 89 ksi (620 MPa). The elongation at failure is 25%.

The corrosion resistance of grade 2205 is greater than that of the most commonly used grades of stainless steels, i.e. 304 and 316.

Relative Costs of Stainless Steel Products:
Current U.S. market prices (as of February 2006) for steel are as follows:
- Hot-rolled steel sheet $540/ton
- Hot-dipped zinc galvanized sheet steel $665/ton
- Cold-rolled steel plate $774/ton
- Cold-rolled or hot-rolled 304 stainless steel $2700/ton
- Cold-rolled or hot-rolled 316 stainless steel $4800/ton

Thus, the cost of stainless steel grades can be as much as 9 times those of carbon or alloy steels!

B. CONNECTIONS OF STEEL

Steel parts must inevitably be joined or connected to form structural systems. There are clearly a number of options on how steel members can be joined or connected. The primary classification of connection options are: (1) bolting and riveting, and (2) welding and brazing/soldering.

1. Bolting and Riveting of Steel:

Currently, bolting of steel members is much more commonly used than riveting, which was used quite extensively in the past. One of the reasons that bolting is used extensively today is that in the design process, arrays of bolt holes can be specified and then achieved precisely and automatically during computer-controlled fabrication.

The grades of steel used in bolts are usually very strong, since bolts are generally subject to both tension and transverse shear.

Care must be taken in bolting steel members together to use bolts, nuts, and washers that have similar electrode potential to each other and to the steel parts being joined.   If there is a significant difference in electrode potentials of any of these metals, galvanic corrosion can result.

2. Welding of Steel

Welding of metals involves melting of the material being joined thereby placing it in the liquid state, and allowing the molten metal to form a continuous joint. Upon cooling, a continuous joint is realized.

Welding differs from brazing and soldering in that it involves melting of the parent metal parts being joined. In brazing and soldering, a second lower temperature metal is melted to form the joint, and the parent metal is not melted. Since they involve lower temperature metals, brazed/soldered joints do not achieve the high quality (strength) that can be achieved with welded steel joints.

Different welding processes are generally used depending on the type of steel being joined. A nice summary of the welding processes used for different grades of steel is provided in the "Key to Steel" online database at http://www.key-to-steel.com/Articles/Art68.htm. A verbatim excerpt from this article is provided below and shows how the welding process and electrodes used in the welding process vary with the type of steel being welded:

Low-Carbon Steels and Low-alloy Steels

Low-carbon steels include those in the AISI series C-1008 to C-1025. Carbon ranges from 0.10 to 0.25%, manganese ranges from 0.25 to 1.5%, phosphorous is 0.4% maximum, and sulfur is 0.5% maximum. Steels in this range are most widely used for industrial fabrication and construction. These steels can be easily welded with any of the arc, gas, and resistance welding processes. The low-alloy high-strength steels represent the bulk of the remaining steels in the AISI designation system. These steels are welded with E-80XX, E-90XX, and E-100XX class of covered welding electrodes. It is also for these types of steels that the suffix to the electrode classification number is used. These steels include the low-manganese steels, the low-to-medium nickel steels, the low nickel-chromium steels, the molybdenum steels, the chromium-molybdenum steels, and the nickel-chromium-molybdenum steels.

These alloys are included in AISI series 2315, 2515, and 2517. Carbon ranges from 0.12-0.30%, manganese from 0.40-0.60%, silicon from 0.20-0.45% and nickel from 3.25-5.25%. If the carbon does not exceed 0.15% preheat is not necessary, except for extremely heavy sections. If the carbon exceeds 0.15% preheat of up to 260°C, depending on thickness is required. For the shielded metal arc welding process, attention was directed toward the selection of the class of covered electrodes based on their usability factors. All the electrodes described in AWS specification A5.1 are applicable to the mild and low-alloy steels. The E-60XX and E-70XX classes of electrodes provide sufficient strength to produce 100% weld joints in the steels. The yield strength of electrodes, in these classes, will overmatch the yield strength of the mild and low alloy steels. The E-60XX class should be used for steels having yield strength below 350 MPa and the E-70XX class should be used for welding steels having yield strength below 420 MPa. Low-hydrogen electrodes should be used and preheat is suggested when welding heavier materials, or restrained joints. The electrode that provides the desired operational features should be selected. When welding the low-alloy high-strength steels, the operating characteristics of the electrode are not considered since the E-80XX and higher-strength electrodes are all of the low-hydrogen type. There is one exception, which is the E-XX10 class. These are shown in the AWS specification for low-alloy steel-covered arc welding electrodes,

AWS 5.5. This specification is more complex than the one for mild steel electrodes, even though there are only two basic classes in each strength level. The lower strength level includes the E-8010, E-XX15, E-XX16, and the more popular E-XX18 classes. This new information now allows the selection of the covered electrode to match not only the mechanical properties of the base metal, but also to approximately match the composition of the base metal. From this reason, the base metal composition and the mechanical properties must be known in order to select the correct covered electrode to be used. The only E-80XX or higher-strength electrodes that do not have low-hydrogen coverings are the E-8010 type electrodes which are designed specifically for welding pipes. These high strength, cellulose-covered, electrodes are matched to specific alloy of the steel pipes. The deep penetrating characteristics of the cellulose-covered electrodes make them suitable for cross-country pipe welding. The theory and practice is that alloy steel pipe is relatively thin and it is welded with cellulose-covered electrodes at relatively high currents. In addition, each welding pass is very thin and the weld metal is aged for a considerable length of time prior to putting the pipeline into service. This allows for hydrogen, which might be absorbed, to escape from the metal and not adversely affect the service life of the pipeline.

Medium-Carbon Steels

The medium-carbon steels include those in the AISI series C-1020 to C-1050. The composition is similar to low-carbon steels, except that the carbon ranges from 0.25 to 0.50% and manganese from 0.60 to 1.65%. With higher carbon and manganese the low-hydrogen type electrodes are recommended, particularly in thicker sections. Preheating may be required and should range from 150-260°C. Postheating is often specified to relieve stress and help stress and help reduce hardness that may have been caused by rapid cooling. Medium-carbon steels are readily weldable provided the above precautions are observed. These steels can be welded with all of the processes mentioned above.

High-Carbon Steels

High-carbon steels include those in the AISI series from C-1050 to C-1095. The composition is similar to medium-carbon steels, except that carbon ranges from 0.30 to 1.00%. Special precautions must be taken when welding steels in these classes. The low-hydrogen electrodes must be employed and preheating of from 300-320°C is necessary, especially when heavier sections are welded. A postheat treatment, either stress relieving or annealing, is usually specified.

High-carbon steels can be welded with the same processes mentioned previously.

End of excerpt from article.

Whenever steel is joined through welding, it must be appreciated that the metal in the vicinity of the joint (or the Heat-Affected Zone [HAZ]) has been placed in the molten state and then cooled. Accordingly, any special effects from work-hardening or quenching and tempering of the steel cannot be guaranteed in the HAZ. Therefore, when considering the strength of the connection in analysis and design, considerable caution should be used in estimating the material properties in the HAZ.