CHEMISTRY
Module 2
Corrosion

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TERMINAL OBJECTIVE

1.0 Without references, **DESCRIBE** the causes and effects of corrosion on metals and the type of chemistry used in a plant to minimize corrosion.

ENABLING OBJECTIVES

1.1 **DEFINE** the following terms:

a. Ionization
b. Conductivity
c. Corrosion
d. Electrolysis
e. General corrosion

1.2 **DESCRIBE** an electrochemical cell with respect to the corrosion of metals.

1.3 **STATE** what happens to a metal during the oxidation step of the oxidation-reduction process.

1.4 **STATE** what happens to a metal during the reduction step of the oxidation-reduction process.

1.5 **DEFINE** the following terms:

a. Passivity
b. Polarization

1.6 **DESCRIBE** the affects of passivity and polarization on the corrosion process.

1.7 **LIST** the two conditions that contribute to general corrosion.

1.8 **DESCRIBE** how the rate of corrosion occurring in the plant is affected by the following:

a. Temperature
b. Water velocity
c. Oxygen
d. pH
e. Condition and composition of the metal surface

ENABLING OBJECTIVES (Cont.)

1.9 **LIST** the three products that are formed from the general corrosion of iron.

1.10 **IDENTIFY** the action taken for initial fill of a reactor system to limit general corrosion.

1.11 **STATE** the four methods used to chemically control general plant corrosion.

1.12 **LIST** the six water chemistry conditions that limit corrosion of aluminum.

1.13 **DEFINE** the following terms:

a. Crud
b. Scale
c. Galvanic corrosion

1.14 **IDENTIFY** the five problems associated with the presence or release of crud into reactor coolant.

1.15 **STATE** the four causes of crud bursts.

1.16 **STATE** the two conditions that can cause galvanic corrosion.

1.17 **EXPLAIN** the mechanism for galvanic corrosion.

1.18 **IDENTIFY** the two locations that are susceptible to galvanic corrosion.

1.19 **STATE** the five control measures used to minimize galvanic corrosion.

1.20 **DEFINE** the following terms:

a. Pitting corrosion
b. Crevice corrosion
c. Stress corrosion cracking

1.21 **STATE** the two conditions necessary for pitting corrosion to occur.

1.22 **STATE** the particular hazard associated with pitting corrosion.

1.23 **STATE** the four controls used to minimize pitting corrosion.

ENABLING OBJECTIVES (Cont.)

1.24 **IDENTIFY** the three conditions necessary for stress corrosion cracking to occur.

1.25 **DEFINE** the term chemisorption.

1.26 **STATE** the hazard of stress corrosion cracking.

1.27 **STATE** the three controls used to prevent stress corrosion cracking.

1.28 **DESCRIBE** the two types of stress corrosion cracking that are of major concern to nuclear facilities including:

a. Conditions for occurrence
b. Method(s) used to minimize the probability of occurrence

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CORROSION THEORY

Uncontrolled corrosion in DOE facilities can cause many serious problems. Corrosion occurs continuously, and every metal in every facility is subject to some type of corrosion. Even though corrosion cannot be eliminated, it can be controlled.

EO 1.1 DEFINE the following terms:

a. Ionization
b. Conductivity
c. Corrosion
d. Electrolysis
e. General corrosion

EO 1.2 DESCRIBE an electrochemical cell with respect to the corrosion of metals.

EO 1.3 STATE what happens to a metal during the oxidation step of the oxidation-reduction process.

EO 1.4 STATE what happens to a metal during the reduction step of the oxidation-reduction process.

EO 1.5 DEFINE the following terms:

a. Passivity
b. Polarization

EO 1.6 DESCRIBE the affects of passivity and polarization on the corrosion process.

Corrosion

In DOE facilities, especially reactor plants, many precautions are taken to control the corrosion of metals used in the various primary and secondary systems. Uncontrolled corrosion of the reactor systems is detrimental for the following reasons.

- Rapid localized corrosion may lead to penetration of the metal containing the coolant. Radioactive coolant would then leak from the system and jeopardize safe operation.

- Corrosion of the nuclear fuel cladding may cause the cladding to become brittle and less ductile. The swelling from the generation of fission gases within the fuel may then cause the cladding to crack or blister, and highly radioactive fission products may then be released to the coolant.

- Some of the metallic oxide corrosion products released to the coolant may be deposited on surfaces in the reactor core. The neutron flux in the core produces nuclear reactions in the corrosion products, and they become highly radioactive. Subsequently, these activated corrosion products may be released from the core and redeposited on surfaces outside the core region. The radiation fields resulting from this redeposited material may then significantly increase radiation levels, thereby complicating maintenance and access capabilities. The corrosion product oxides may also result in fouling of heat transfer surfaces and in the accelerated wear of moving parts by corrosion products trapped in or between them.

Current is the flow of electrons through a medium. An electric current can flow through a metal conductor, and the metal will not show any obvious chemical changes. This type of conduction of electricity is called metallic conduction.

Ionization is the process of adding electrons to or removing electrons from atoms or molecules, creating ions. High temperatures, electrical discharges, and nuclear radiation can cause ionization. Many metals have a tendency to lose electrons to atoms or ions that have a tendency to gain electrons. Current can be conducted by the movement of these ions. The compounds that conduct electric current by ion movement are called electrolytes, and this ionic motion is call electrolytic conduction. *Conductivity* is a measure of the ability of a substance to allow electron flow. In the context of corrosion, conductivity indicates the amount of ions in solution, which relates directly to the potential of corrosion taking place.

Corrosion is the deterioration of a material due to interaction with its environment. Corrosion can have many forms, both wet and dry. *Electrolysis* is the decomposition by electric current (in the context of corrosion the use of electrical current to bring about chemical change). This chapter will concentrate on the corrosion of metals in water-based environments (electrolytes). An electrolyte is defined as an electricity-conducting fluid; that is, it has positive and negative ions that can move and constitute an electrical current. Pure water has a limited number of dissociated H^+ and OH^- ions and is a relatively poor conductor of electricity. Addition of acids, bases, or salts that dissociate into ions increases the current-carrying capability of the water (electrolyte).

Electrochemical Cells

Corrosion is electrochemical in nature because the corrosive chemical reactions involve transfer of charge. Figure 1 shows the transfer of charge when iron is in contact with water or an acidic water solution.

Iron goes into solution as Fe^{++} ions. As these ions go into solution, the metal becomes negatively charged (by the electrons left behind) with respect to the electrolyte. A potential difference (voltage) is produced between the electrolyte and the metal. The process in which electrons are given up and positive metal ions are formed is called oxidation. The sites at which the oxidation takes place on the surface of the metal become electrochemical cells made up of micro-electrodes of the two different substances; the metal and the electrolyte.

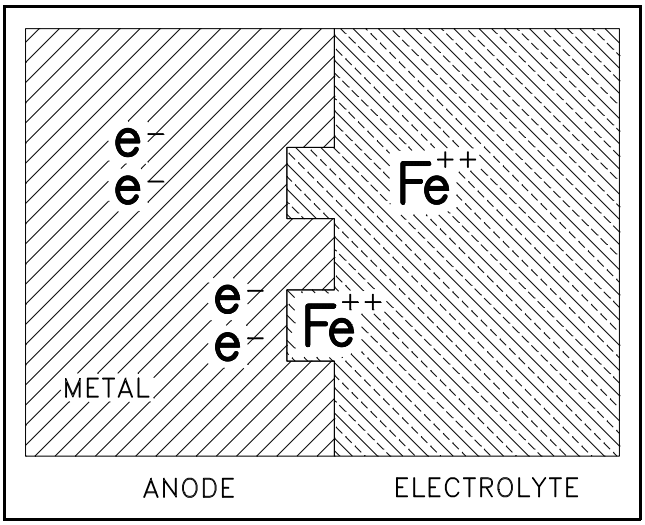

Figure 1 Formation of Ferrous (Fe^{++}) Ions in the Corrosion of Iron

These micro-electrodes set up many micro-cells connected through the bulk of the metal. If a different metal is used, it will go into solution to a greater (or lesser) extent producing a larger (or smaller) potential difference between the metal and electrolyte than was the case for iron. For example, magnesium and zinc go into solution to a greater extent than iron, and these metals will be more negative with respect to the electrolyte than iron. Nickel, lead, and copper go into solution less readily and produce a smaller potential difference. Table 1 lists the potential differences for various metals in water. The order of the series can change for different electrolytes (for example, different pH, ions in solution).

Electrochemical cells and oxidation potentials are very important in understanding most corrosion processes. Examples of electrochemical cells include galvanic cells (cells made up of electrodes of two different substances) and concentration cells (cells containing electrodes of the same substance under different conditions of concentration).

TABLE 1
Electromotive - Force Series (77°F)

Element	Electrode Reaction	Standard Electrode Potential, v
Sodium	$Na \rightarrow Na^{+} + e$	-2.712
Magnesium	$Mg \rightarrow Mg^{++} + 2e$	-2.34
Beryllium	$Be \rightarrow Be^{++} + 2e$	-1.70
Aluminum	$Al \rightarrow Al^{+++} + 3e$	-1.67
Manganese	$Mn \rightarrow Mn^{++} + 2e$	-1.05
Zinc	$Zn \rightarrow Zn^{++} + 2e$	-0.762
Chromium	$Cr \rightarrow Cr^{+++} + 3e$	-0.71
Iron	$Fe \rightarrow Fe^{+++} + 3e$	-0.44
Cadmium	$Cd \rightarrow Cd^{++} + 2e$	-0.402
Cobalt	$Co \rightarrow Co^{++} + 2e$	-0.277
Nickel	$Ni \rightarrow Ni^{++} + 2e$	-2.250
Tin	$Sn \rightarrow Sn^{++} + 2e$	-0.136
Lead	$Pb \rightarrow Pb^{++} + 2e$	-0.126
Hydrogen	$H \rightarrow 2H^{+} + 2e$	0.000 (reference)
Copper	$Cu \rightarrow Cu^{++} + 2e$	+0.345
Copper	$Cu \rightarrow Cu^{+} + e$	+0.522
Silver	$Ag \rightarrow Ag^{+} + e$	+0.800
Platinum	$Pt \rightarrow Pt^{++} + 2e$	+1.2
Gold	$Au \rightarrow Au^{+++} + 3e$	+1.42

The surface of any metal is a composite of a very large number of micro-electrodes, as illustrated in Figure 2. In order for corrosion to occur, the micro-cells must also be connected through some conducting path external to the metal. Usually the external connection is provided by water or an aqueous solution and the cells produce a current, allowing the chemical reactions responsible for corrosion to proceed.

Consider iron in water again. If the surface of the iron and the water solution were uniform, iron would go into solution as Fe^{++} ions until the difference in potential between the positively-charged solution and the negatively-charged metal stopped the iron ions from leaving the surface. In practice, though, impurities and imperfections (for example, oxide coatings) lead to preferential removal of metal from certain parts of the surface, and potential differences arise as in the two metal system. The corrosion cells, changing as surface and solution differences change, cause general overall corrosion. If the cells do not shift, pitting results.

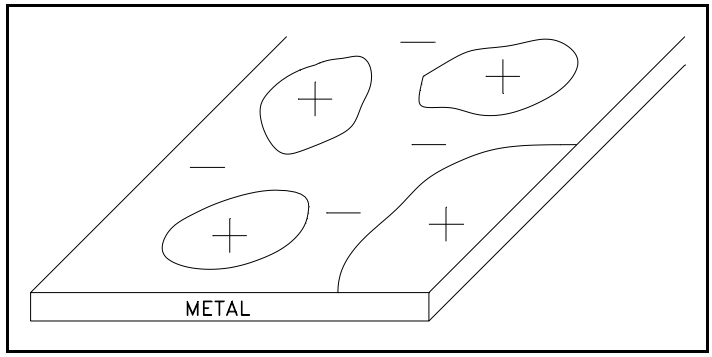

Figure 2 Metal Surface Showing Arrangement of Micro-cells

Oxidation-Reduction Reactions

The corrosion of a metal (that is, the chemical transformation that is recognized as destructive to the metal) is the oxidation step of the overall oxidation-reduction process. Oxidation is the process of losing electrons; reduction is the process of gaining electrons. The metal atoms release electrons (are oxidized) and become positive ions. The site at which this occurs is known as the anode. Typical oxidation half-reactions include the following.

$$Zn \rightarrow Zn^{+2} + 2e^{-} \tag{2-1}$$

$$Al \rightarrow Al^{+3} + 3e^{-} \tag{2-2}$$

$$Fe \rightarrow Fe^{+2} + 2e^{-} \tag{2-3}$$

The cations (positive ions) may then go into solution, or they may combine with any available anions (negative ions) or water to form ionic compounds. The exact fate of the cations is important to subsequent processes, but the primary effect is that atoms leave the metallic state, and the metal deteriorates.

An oxidation process cannot take place without a simultaneous reduction (gain of electrons) process. The nature of the reduction step in corrosion sometimes varies with the metal and the environment to which it is exposed. For most metals in an aqueous environment, the important reduction half-reaction is the reduction of hydronium ions (a hydronium ion is simply a hydrogen ion attached to a water molecule).

$$H_3O^{+} + e^{-} \rightarrow H + H_2O \tag{2-4}$$

Small concentration variations within a solution in contact with the metal may also affect the rate and nature of corrosion reactions. Therefore, it is often impossible to predict the exact nature of corrosion reactions. It is generally found, however, that for most metals exposed to an aqueous environment the half-reactions involved in corrosion are the reduction reaction of Equation (2-4) and an oxidation half-reaction of the type shown in Equations (2-1) through (2-3).

General corrosion is the process whereby the surface of a metal undergoes a slow, relatively uniform; removal of material. This occurs on the surface of a single metal rather than dissimilar metals. In general corrosion, a nearly infinite number of micro-cells are established on the metal surface. Oxidation occurs at anodic areas and reduction at cathodic areas. The micro-cells are uniformly distributed over the metallic surface, and as the reaction proceeds the cells may migrate, or disappear and re-form. That is, any particular micro-region may be alternately anodic and cathodic. The result is a uniform attack on the metal surface.

Under some conditions, relatively large regions become anodic or cathodic. Such regions have less tendency to migrate and may remain operative for long periods of time. In this case, there will be severe attack of the metal at the anodic (oxidation) region. The result may be a visible pit in the metal surface.

Iron and steel are resistant to rapid corrosion in water despite the tendency of iron to oxidize as indicated by its standard electrode potential listed in Table 1. The reasons for this resistance are the passivating effect of the oxide film and cathodic polarization due to atomic hydrogen that absorbs on the oxide surface, both of which are explained in the next section.

Passivity and Polarization of Metal

Metals that normally fall victim to corrosion will sometimes exhibit a passivity to corrosion. *Passivity* is the characteristic of a metal exhibited when that metal does not become active in the corrosion reaction. Passivity is caused by the buildup of a stable, tenacious layer of metal oxide on the surface of the metal. This oxide layer is formed by corrosion on a clean metal surface, where the corrosion products are insoluble in the particular environment to which the metal is exposed. Once the layer, or film, is formed, it acts as a barrier separating the metal surface from the environment. For further corrosion to occur, the reactants must diffuse through the oxide film. Such diffusion is very slow or nonexistent, thus corrosion either decreases markedly or stops.

Metals such as zirconium, chromium, aluminum, and the stainless steels form thin, tenacious oxide films when exposed to the atmosphere or to pure water at room temperature. In some cases, the film is extremely thin and may be invisible to the unaided eye, but it is still very effective in giving these metals a marked passivity.

If there is a net conversion of reactants to products in a system, the system will be chemically unstable, and the reaction will continue until a stable state is attained. This stable state is known as equilibrium.

An active electrochemical cell (oxidation-reduction reaction) is an unstable chemical system. The potential associated with a galvanic cell, for example, steadily decreases as current flows and the oxidation-reduction reaction proceeds. Eventually, the potential falls to zero, the cell no longer supplies electrical energy, and no further net reaction takes place. At this point the system is at equilibrium. In electrochemical cells, the decrease in cell potential caused by the operation of the cell (current flow) is called *polarization*.

This change in cell potential can be determined. Consider the zinc-copper galvanic cell shown in Figure 3. As the reaction takes place, Zn^{+2} ions (produced by the oxidation of zinc metal) pass into solution. The Cu^{+2} ions in solution are reduced as the copper metal plates out. Thus, the concentration of Zn^{+2} in solution increases and the concentration of Cu^{+2} decreases according to the following overall reaction.

$$\mathbf{Zn + Cu^{+2} \rightarrow Zn^{+2} + Cu} \qquad (2\text{-}5)$$

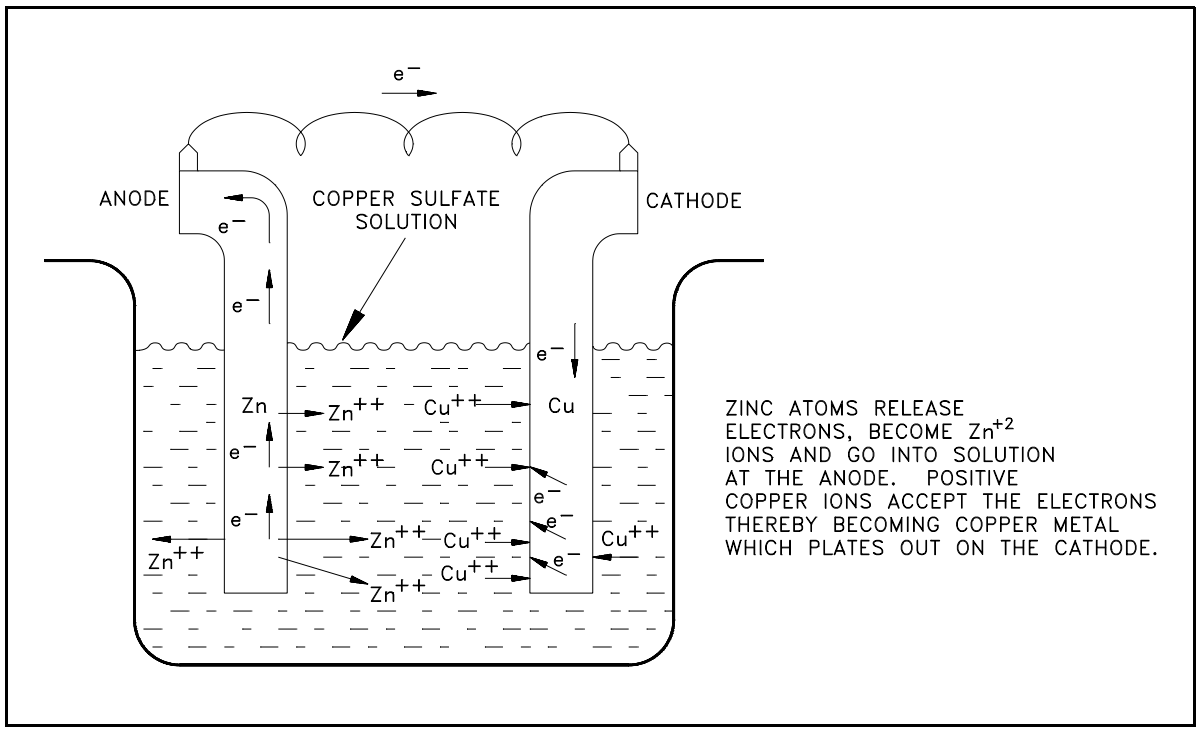

Figure 3 A Galvanic Cell

As Zn^{+2} increases and Cu^{+2} decreases, the electrical potential decreases. This decrease in cell potential, which results from changes in concentrations, is one form of polarization called concentration polarization.

Now consider a galvanic cell with zinc and platinum electrodes, such as that shown in Figure 4. The half-reactions in the cell are as follows.

$$Zn \rightarrow Zn^{+2} + 2e^{-}$$
$$H_3O^{+} + e^{-} \rightarrow H + H_2O \qquad (2\text{-}4)$$

Again, as the cell operates, the cell potential drops. The decrease is partially due to the increase in Zn^{+2} concentration and the decrease in H_3O^{+} concentration, but another type of polarization also occurs in this cell. This second type is associated with the reduction half-reaction.

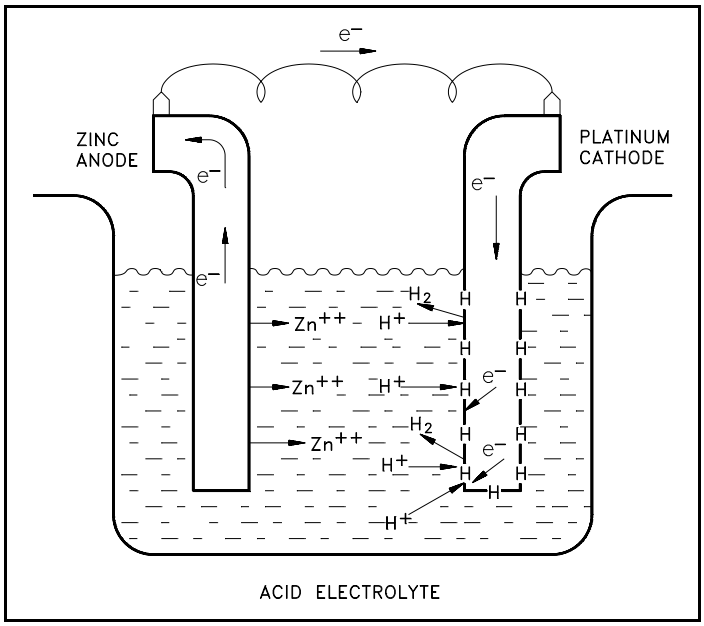

Figure 4 A Galvanic Cell Showing Absorbed Hydrogen Atoms on a Cathode

The hydrogen atoms formed by the reaction of Equation (2-4) absorb on the surface of the metal and remain there until removed by one of two processes: combination of two hydrogen atoms to form molecular hydrogen, which is then released as a gas or reaction with dissolved oxygen to form water. In the absence of oxygen (deaerated solutions), the first process applies.

$$2H \rightarrow H_2 \qquad (2\text{-}6)$$

Combining Equation (2-6) with Equation (2-4), the net reduction half-reaction is obtained.

$$2(H_3O^{+} + e^{-} \rightarrow H + H_2O)$$

$$2H \rightarrow H_2 \qquad (2\text{-}6)$$

$$2H_3O^{+} + 2e^{-} \rightarrow H_2 + 2H_2O \qquad (2\text{-}7)$$

Until the absorbed hydrogen atoms are removed from the metal surface, they effectively block the sites at which the reaction of Equation (2-4) can occur. At low temperatures the reaction of Equation (2-6) is slow relative to the reaction of Equation (2-4) because, although the reaction is energetically favored, the combination of two hydrogen atoms requires a large activation energy. Equation (2-6) shows the rate-controlling step of the net reduction half-reaction. Because the oxidation half-reaction can occur no faster than the reduction half-reaction, the rate of the overall oxidation-reduction reaction is controlled by the reaction of Equation (2-6).

The layer of absorbed atomic hydrogen is said to polarize the cell. This type of polarization is called activation polarization and is sometimes referred to as hydrogen polarization, or cathodic polarization, because the polarizing reaction occurs at the cathode.

Both concentration and activation polarization decrease the net oxidation-reduction reaction rate. In corrosion processes, activation polarization usually has the greater effect.

Summary

The important information in this chapter is summarized below.

Corrosion Theory Summary

- Ionization is the process of adding electrons to or removing electrons from atoms or molecules which creates ions.
- Conductivity is a measure of the ability of a substance to allow electron flow.
- Corrosion is the deterioration of a material due to interaction with its environment.
- Electrolysis is the decomposition by electric current.
- General corrosion is the process whereby the surface of a metal undergoes a slow, relatively uniform, removal of material.
- Corrosion is electrochemical in nature because the corrosive chemical reactions involve a transfer of charge. The metal ions go into solution causing the metal to become negatively charged with respect to the electrolyte. The difference in the charge causes a potential to develop and produces a voltage between the electrolyte and the metal.
- The oxidation step of the oxidation-reduction process is where an atom (in this case a metal atom) releases electron(s) and becomes a positively-charged ion. The areas where oxidation takes place become electrochemical cells made up of two different substances. The oxidation step results in a chemical transformation that is destructive to the metal. The positive metal ions may go into solution, or they may combine with any available negative ions or water to form ionic compounds. An example of the oxidation step is:

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

Corrosion Theory Summary (Continued)

- The reduction step of the oxidation-reduction process is where a positively-charged ion gains electron(s). The reduction step for most metals, in an aqueous environment, is the reduction of hydronium ions. An example of the reduction step is:

$$H_3O^+ + e^- \rightarrow H + H_2O$$

- Passivity is the buildup of a stable, tenacious layer of metal oxide on the surface of the metal that acts as a barrier separating the metal surface from the environment. Passivity decreases or stops the corrosion process because of the formation of the layer.

- Polarization is the decrease in cell potential caused by the operation of the electrochemical cell. Polarization can be in two forms; concentration or activation. Concentration polarization is associated with the concentration of ions in solution which shields the metal, thereby causing a decrease in the electrical potential of the cell. Activation polarization is the formation of a layer containing absorbed hydrogen atoms that block the metal's surface from the corrosion process.

GENERAL CORROSION

This chapter describes the general corrosion processes of iron and carbon steel (not stainless steels) in aqueous environments. Of particular interest is the formation of the oxide film and the effects of system variables on the corrosion process.

EO 1.7 **LIST the two conditions that contribute to general corrosion.**

EO 1.8 **DESCRIBE how the rate of corrosion occurring in the plant is effected by the following:**

a. Temperature
b. Water velocity
c. Oxygen
d. pH
e. Condition and composition of the metal surface
f. Dissolved solids

EO 1.9 **LIST the three products that are formed from the general corrosion of iron.**

EO 1.10 **IDENTIFY the action taken for initial fill of a reactor system to limit general corrosion.**

EO 1.11 **STATE the four methods used to chemically control general plant corrosion.**

EO 1.12 **LIST the six water chemistry conditions that limit corrosion of aluminum.**

Conditions Contributing to General Corrosion

General corrosion is the process whereby the surface of a metal undergoes a slow, relatively uniform, removal of material. The two conditions typically required for a metal to undergo general corrosion are: 1) metal and water in the same environment, and 2) a chemical reaction between the metal and water that forms an oxide.

Corrosion of Iron

Unless noted otherwise, the following discussion applies to deaerated water at room temperature and approximately neutral pH. The affects of temperature, oxygen, and pH are discussed later in this chapter.

The oxidation and reduction half-reactions in the corrosion of iron are as follows.

$$Fe \rightarrow Fe^{+2} + 2e^{-} \quad \text{(oxidation)} \tag{2-3}$$

$$H_3O^{+} + e^{-} \rightarrow H + H_2O \quad \text{(reduction)} \tag{2-4}$$

The overall reaction is the sum of these half-reactions.

$$Fe + 2H_3O^{+} \rightarrow Fe^{+2} + 2H + 2H_2O \tag{2-8}$$

The Fe^{+2} ions readily combine with OH^{-} ions at the metal surface, first forming $Fe(OH)_2$, which decomposes to FeO.

$$Fe^{+2} + 2OH^{-} \rightarrow Fe(OH)_2 \rightarrow FeO + H_2O \tag{2-9}$$

Ferrous oxide (FeO) then forms a layer on the surface of the metal. Below about 1000°F, however, FeO is unstable and undergoes further oxidation.

$$2FeO + H_2O \rightarrow Fe_2O_3 + 2H \tag{2-10}$$

Atomic hydrogen then reacts to form molecular hydrogen, as described previously, and a layer of ferric oxide (Fe_2O_3) builds up on the FeO layer. Between these two layers is another layer that has the apparent composition Fe_3O_4. It is believed that Fe_3O_4 is a distinct crystalline state composed of O^{-2}, Fe^{+2}, and Fe^{+3} in proportions so that the apparent composition is Fe_3O_4. These three layers are illustrated in Figure 5.

Once the oxide film begins to form, the metal surface is no longer in direct contact with the aqueous environment. For further corrosion to occur, the reactants must diffuse through the oxide barrier. It is believed that the oxidation step, Equation (2-3), occurs at the metal-oxide interface. The Fe^{+2} ions and electrons then diffuse through the oxide layer toward the oxide-water interface. Eventually, Fe^{+2} ions encounter OH^{-} ions and form FeO. The electrons participate in the reduction reaction with hydronium ions. These latter reactions are believed to take place predominately at the oxide-water interface, but some reaction may occur within the oxide layer by the diffusion of H^{+}, OH^{-}, and H_2O into the layer.

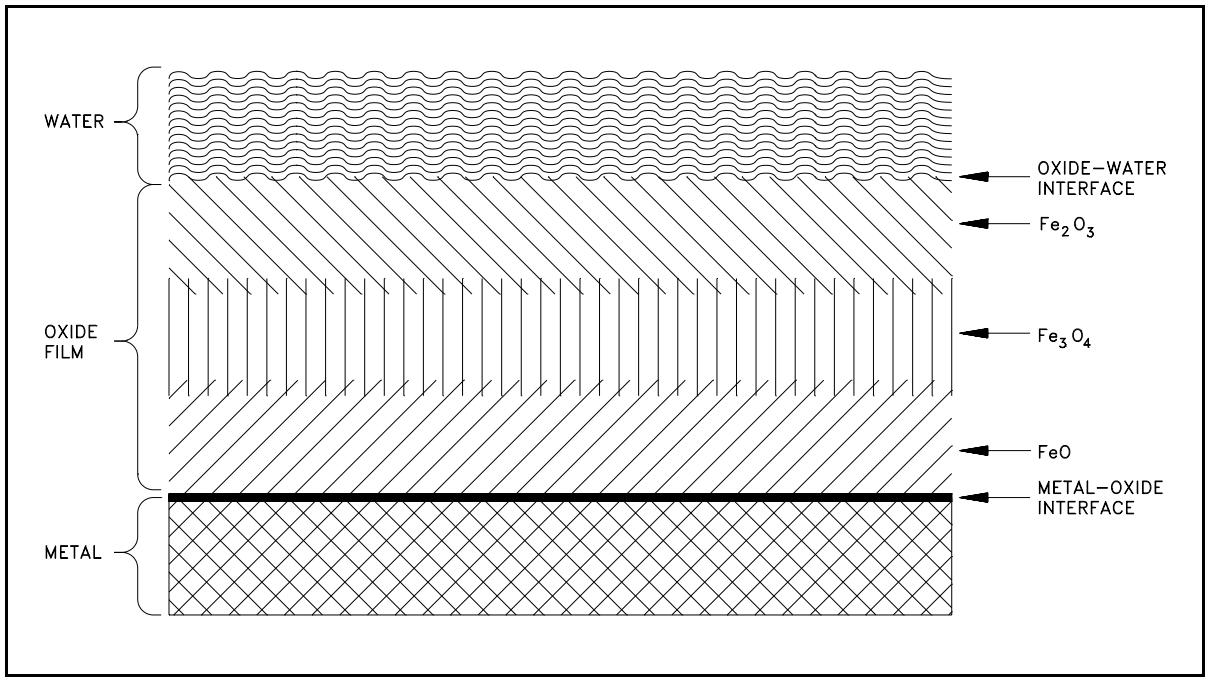

Figure 5 Simplified Schematic Diagram of Oxide Corrosion Film on the Surface of a Metal

Regardless of the exact diffusion mechanism, the oxide layer represents a barrier to continued corrosion and tends to slow the corrosion rate. The exact effect of this layer on the corrosion rate depends on the uniformity and tenacity of the film. If the film is loosely attached, develops defects, or is removed, the metal surface is again exposed to the environment and corrosion occurs more readily.

Factors Affecting General Corrosion Rate

Like most other chemical reactions, corrosion rates increase as temperature increases. Temperature and pressure of the medium govern the solubilities of the corrosive species in the fluid, such as oxygen (O_2), carbon dioxide (CO_2), chlorides, and hydroxides. A rule of thumb is that the reaction rate doubles with a 20°F to 50°F temperature rise. This linear increase with temperature does not continue indefinitely due, in part, to a change in the oxide film.

When water velocity is extremely high, the impact of the water tends to remove the protective oxide layer and some of the metal under it (erosion), thus, exposing more metal to corrosion. Water velocities of 30 to 40 ft per second are usually considered to cause erosion.

The presence of oxygen in water to which iron is exposed increases the corrosion rate. The reason for this increase is the rapid reaction between oxygen and the polarizing layer of atomic hydrogen absorbed on the oxide layer. The following reaction rapidly removes the polarizing layer.

$$O_2 + 4H \rightarrow 2H_2O \qquad (2\text{-}11)$$

The overall reaction can be obtained by combining Equations (2-4) and (2-11).

$$O_2 + 4H_3O^+ + 4e^- \leftrightarrows 6H_2O$$

The controlling step is believed to be diffusion of O_2 to the metal surface where it can react directly with iron or with FeO.

$$2Fe + O_2 \rightarrow 2FeO \qquad (2\text{-}12)$$

$$4FeO + O_2 \rightarrow 2Fe_2O_3 \qquad (2\text{-}13)$$

Oxygen, therefore, has two effects: it removes the polarizing layer of atomic hydrogen, and it can react directly with the metal or metal oxide; thus, the corrosion rate increases. Substances, such as O_2 in this case, that remove the absorbed atomic hydrogen are called depolarizers. The depolarizing effect of O_2 is illustrated in Figure 6.

The effect of the pH of water to which iron or steel is exposed is influenced by temperature in the following manner. The potential of hydrogen or symbol (pH) is defined as the negative logarithm of the hydrogen concentration, represented as $[H^+]$ in moles/liter.

$$pH = -\log [H^+]$$

The pH value is used to represent the acidity of a solution.

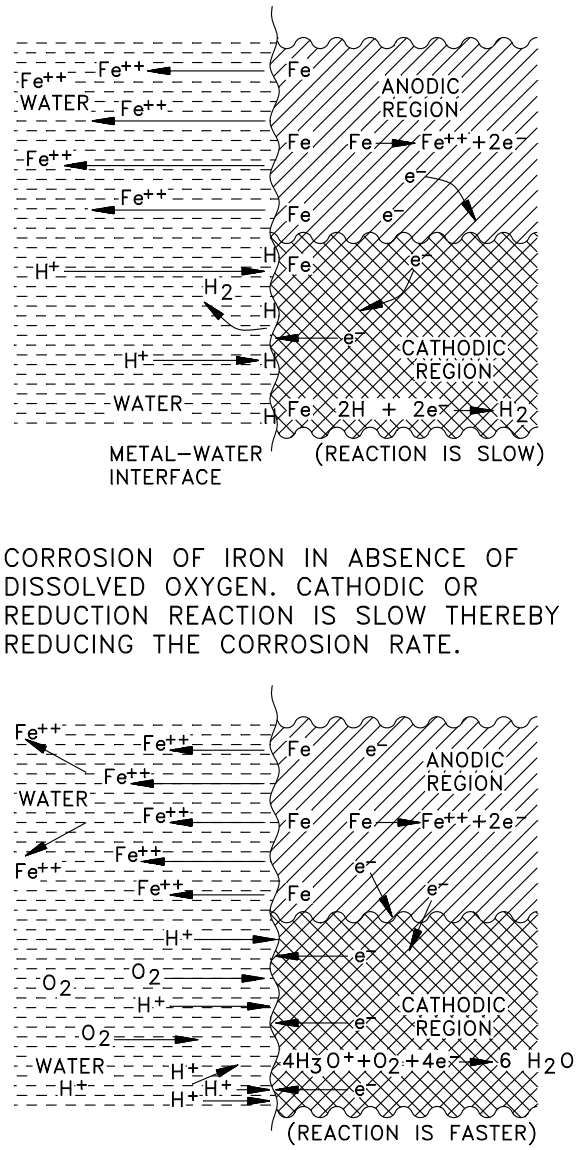

Figure 6 Representation of Cathodic Depolarization by Oxygen

First, consider the exposure of iron to aerated water at room temperature (aerated water will contain dissolved oxygen). The corrosion rate for iron as a function of pH is illustrated in Figure 7. In the range of pH 4 to pH 10, the corrosion rate of iron is relatively independent of the pH of the solution. In this pH range, the corrosion rate is governed largely by the rate at which oxygen reacts with absorbed atomic hydrogen, thereby depolarizing the surface and allowing the reduction reaction to continue. For pH values below 4.0, ferrous oxide (FeO) is soluble. Thus, the oxide dissolves as it is formed rather than depositing on the metal surface to form a film. In the absence of the protective oxide film, the metal surface is in direct contact with the acid solution, and the corrosion reaction proceeds at a greater rate than it does at higher pH values. It is also observed that hydrogen is produced in acid solutions below a pH of 4, indicating that the corrosion rate no longer depends entirely on depolarization by oxygen, but on a combination of the two factors (hydrogen evolution and depolarization). For pH values above about pH 10, the corrosion rate is observed to fall as pH is increased. This is believed to be due to an increase in the rate of the reaction of oxygen with $Fe(OH)_2$ (hydrated FeO) in the oxide layer to form the more protective Fe_2O_3 (note that this effect is not observed in deaerated water at high temperatures).

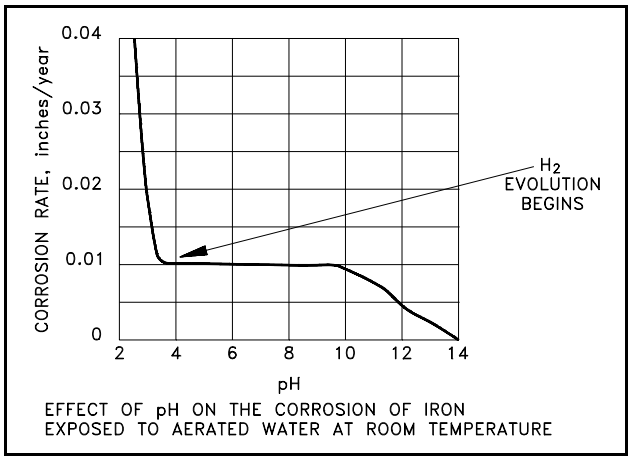

Figure 7 Effect of pH on the Corrosion Rate of Iron in Water

A plot of the relative corrosion rate for iron at various pH values in 590°F, oxygen-free water is presented as Figure 8. The curve illustrates that the corrosion rate of iron in high temperature water is lower in the pH range of 7 to 12 than it is at either lower or higher pH values (at very high pH values, greater than pH 13.0, the oxide film becomes increasingly more soluble because of increased formation of soluble FeO_2 at high temperatures, and corrosion rates increase). As a result of the data plotted in Figure 8 and other similar measurements, it is general practice to maintain high temperature water in the alkaline condition (but below very high pH values) to minimize the corrosion of iron and the steels exposed to the high temperature water.

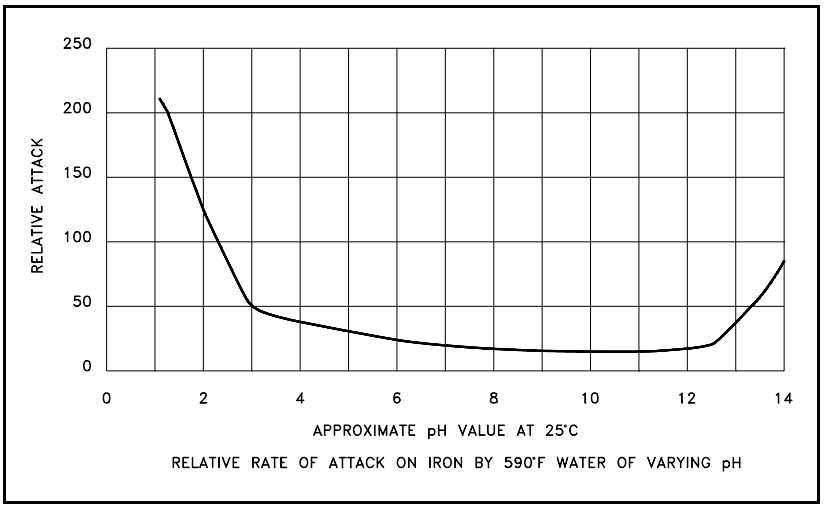

Figure 8 Effect of pH on the Relative Attack Rate of Iron in Water

The hydrogen normally dissolved in reactor coolant does not have any detectable direct effect upon the corrosion rate of the iron and steels exposed to reactor coolant. It does, however, have an important indirect effect by preventing the accumulation of dissolved oxygen in reactor coolant, which would accelerate corrosion. Dissolved oxygen reacts with the protective hydrogen gas layer at the cathode to form water.

The condition and composition of the metal surfaces affects the corrosion rate. Deposits, scale, or irregular surfaces create areas on the metal where local corrosion can initiate and proceed at a faster rate than normal. Certain alloys of metals have higher corrosion resistance than others, as discussed in the Material Science Handbook.

When iron or steel is exposed to high temperature water, the rate of corrosion of the metal is observed to decrease with exposure time during the early period of exposure. After a few thousand hours, the corrosion rate becomes relatively constant at a low value. During the early period of exposure, while the corrosion rate is decreasing, the oxide film on the surface of the metal grows in thickness. However, the rate at which the film grows decreases with time. The thickness of the oxide film soon reaches a relatively constant value, and thereafter film thickness does not change appreciably with further exposure. As might be expected, a relatively constant corrosion rate and oxide film thickness are attained at about the same time. Because a tightly adhering corrosion film inhibits further corrosion, great care is taken during the initial fill of reactor plants to promote formation of the best possible corrosion film. This process, referred to as pretreatment, or pickling, involves careful control of reactor coolant water chemistry and temperature during the pretreatment period.

Prevention Chemistry Control

Plant chemistry is used to control corrosion. The type of corrosion determines the method used for preventing or minimizing the corrosion rate.

Passivators and Inhibitors

Passivation is the condition where a naturally active metal corrodes at a very low rate, probably due to an oxide coating or an absorbed layer of oxygen. Some chemical substances, called passivators or inhibitors, if added to water, can provide this type of passivation by undergoing reduction at the metal surface. A common inhibitor is potassium chromate.

Cathodic Protection

The use of cathodic protection, supplying an external electric current to the iron so that it acts as a cathode and has no anodic areas, is another method of preventative chemical control. This can be accomplished by the use of an external voltage source or by the use of a sacrificial anode (e.g., zinc) which will corrode and provide the current.

Removing Corrosive Agents

Chemistry control in the form of removal of corrosive agents from a system is a widely used method. One method is using deaerators to remove dissolved oxygen and to a lesser extent carbon dioxide. Treating the water by softening and demineralization removes the dissolved solids and reduces the conductivity.

Chemical Addition

Chemical additions to a system that alter the chemical reaction or tie up a particular corrodant is a common method of control. Filming amines (organic compounds that are derivatives of ammonia) accomplish protection by forming adhering organic films on metal surfaces to prevent contact between corrosive species in the condensate and the metal surface. Phosphates and sodium hydroxide are used to adjust the system pH and remove hardness.

Corrosion of Aluminum

The corrosion of aluminum is dependent upon a vast number of variables. These variables include environment, temperature, alloy in question, flow velocities, impurities present in the environment, and chemistry conditions to which it is exposed. An additional factor that affects corrosion is pretreatment.

Many of the factors are controlled by design and construction, such as alloy type, temperature, and flow velocities. Pretreatment, soluble and solid impurities, and chemistry are within the control of the operator and will be discussed in this text.

Experiments have shown that prefilming limits corrosion on aluminum-clad fuel assemblies. In the tests conducted, the ratios of oxide film thickness for nonprefilmed and prefilmed elements were on the order of 2 to 3 and in some cases even greater.

Impurities are major contributors to the corrosion of aluminum. In most cases studied, the major source of contaminants has been makeup water systems. Corrosion products from other plant materials also contribute to the overall inventory of ionic and solid impurities. Finally, organic impurities from the resin used in ion exchangers have been detected. These occur in some installations because of the type of resin used and the particle filters normally installed on the ion exchanger effluents. This problem has been reduced by improved resins and installing filters capable of removing smaller particles.

Chemistry controls, including pH, dissolved oxygen, and conductivity, greatly influence the formation and propagation of the oxide film on aluminum surfaces. Dissolved oxygen is controlled for essentially the same reasons as for the corrosion of iron. Conductivity is a quantitative indication of the impurities present in the system, and pH theoretically dictates the value of conductivity.

For those reactor plants in which aluminum is used for cladding and other structural components, pH is controlled in an acidic condition because of the corrosion properties of aluminum. Plant pH has a marked effect on the rate of chemical reaction between the coolant water and aluminum. In the area of the cladding, the corrosion reduces the thickness and forms an oxide film that is a thermal barrier. Extensive tests carried out in support of DOE test reactors have revealed that minimum aluminum corrosion results with a pH of 5.0 at normal operating temperatures. Additionally, studies have shown that the aluminum corrosion products also exhibit a minimum solubility at a pH near 5.5 at 25°C. The aluminum corrosion products tend to reduce the substrate (base) aluminum metal corrosion rates. Because it is desirable to maintain dissolved aluminum in the reactor coolant at the lowest practicable level, it is desirable to maintain the system pH level in the range of minimum oxide solubility. Figure 9 shows the effect of pH on aluminum oxide solubilities for various forms of oxide, and the effect of pH on corrosion rates. It should be noted that the values at which minimum corrosion and solubility are found shift to a lower pH as the temperature is increased. For example, at 300°C, the value for minimum aluminum corrosion is near pH 3.0. Therefore, the optimum pH for operation is determined by the operating temperature.

The conditions that have proven to be most effective in limiting corrosion of aluminum are as follows.

- Maintaining pH slightly acidic with the value of the pH depending largely upon operating temperature
- Elimination of dissolved oxygen
- Elimination of soluble and solid impurities
- Prevention of the introduction of organic impurities
- Pretreatment (or pickling)
- Maintaining water purity

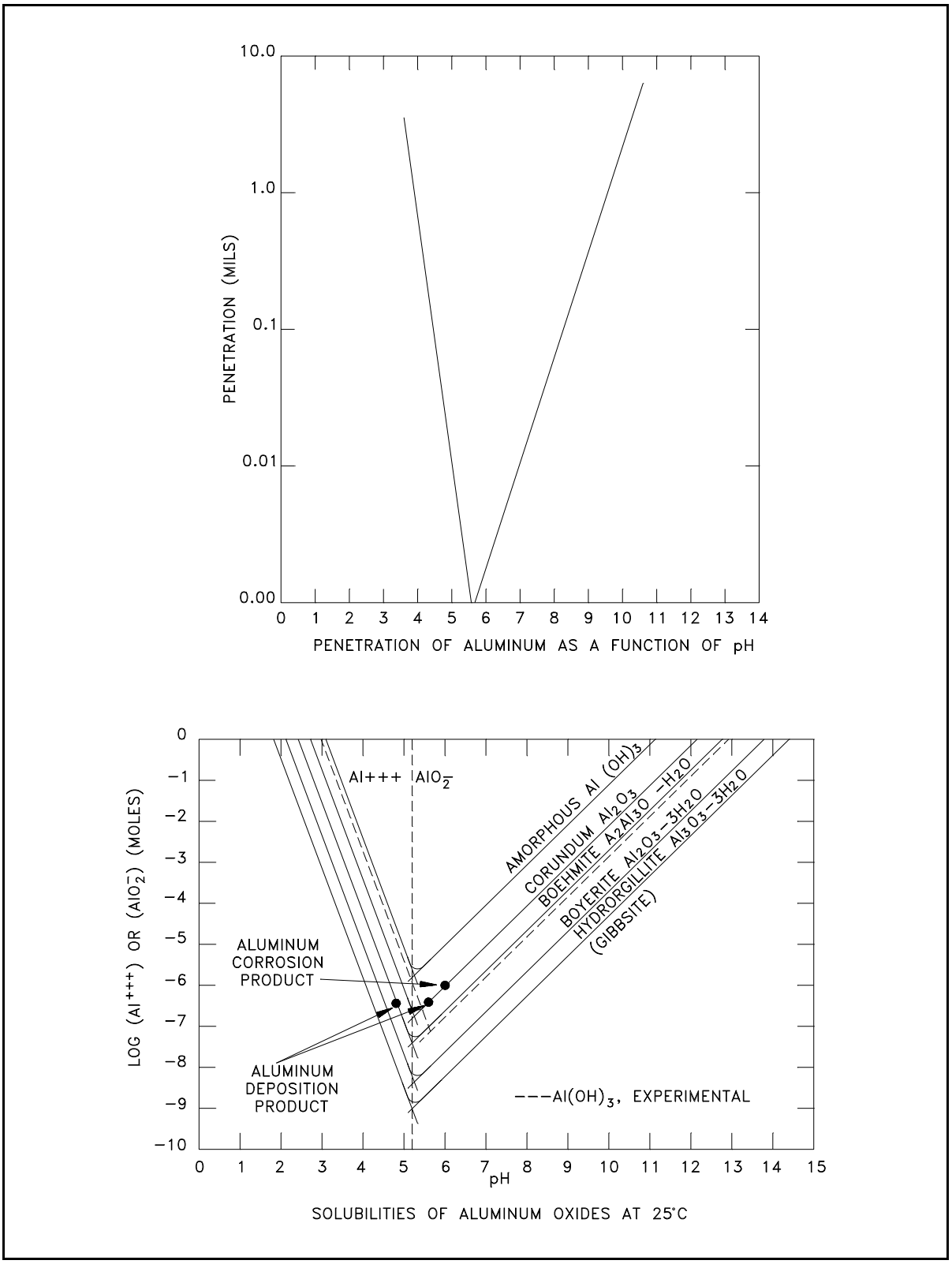

Figure 9 Effect of pH on Aluminum Corrosion and Oxide Solubility

Summary

The major points of this chapter are summarized below.

General Corrosion Summary

- The two conditions that contribute to general corrosion are:

  Metal and water in the same environment
  Chemical reaction between the metal and water to form an oxide

- The corrosion rate is affected by the following:

  A temperature rise in the range of 20°F to 50°F doubles the corrosion rate until the formation of the protective oxide film is complete.

  An extremely high water velocity, 30 to 40 ft per second, tends to remove the oxide film allowing the corrosion rate to increase.

  The presence of oxygen in water to which iron is exposed increases the corrosion rate. The reason for the corrosion rate increase is due to the rapid reaction between the oxygen and the polarizing layer of hydrogen absorbed on the oxide layer.

  A pH between 4 and 10 results in minimal corrosion rate. If the pH falls below or above this range, the corrosion will normally increase.

  The condition and composition of the metal surfaces affects the corrosion rate. Deposits, scale, or irregular surfaces create areas on the metal where local corrosion can initiate and proceed at a faster rate than normal.

  Dissolved solids tend to make it easier for current to flow, which results in a higher corrosion rate.

- The three products formed from general corrosion of iron are FeO, Fe_2O_3, and Fe_3O_4.

General Corrosion Summary (Cont.)

- During the initial fill of a reactor system, great care is taken to promote the formation of the best possible protective corrosion film. The protective film acts as a barrier and stops further uncontrolled corrosion from taking place. This process, called pretreatment or pickling, involves careful control of reactor coolant water chemistry and temperature during the pretreatment period.

- Four methods used to chemically control general plant corrosion are:

  Passivators (inhibitors) consist of a naturally active metal that corrodes at a very low rate. A common passivator is potassium chromate.

  Cathodic protection is the external application of an external electric current to the iron so that it acts as a cathode and has no anodic areas. This is accomplished by using either an external electrical source or the use of a sacrificial anode to provide the electrical current.

  Removing corrodants to reduce the dissolved oxygen and lesser extent carbon dioxide. Treating the water in this manner reduces the dissolved solids and reduces the conductivity.

  Chemical addition to alter the chemical reaction or tie up a particular corrodant. Filming amines, phosphates, and sodium hydroxide are used to provide organic films and adjust the system pH.

- The six water chemistry conditions that limit corrosion of aluminum are:

  Maintaining pH slightly acidic with the value of the pH depending largely on operating temperature.

  Elimination of dissolved oxygen

  Elimination of soluble and solid impurities

  Prevention of the introduction of organic impurities

  Pretreatment (or pickling)

  Maintaining water purity

CRUD AND GALVANIC CORROSION

A major potential problem is crud. Crud can cause an increase in background radiation levels. When two dissimilar metals are in close vicinity, the opportunity for ion transfer is high. The result is a perfect environment for galvanic corrosion. Because of the numerous types of materials used in nuclear facilities, galvanic corrosion is a major concern.

EO 1.13 DEFINE the following terms:

a. Crud
b. Scale
c. Galvanic corrosion

EO 1.14 IDENTIFY the five problems associated with the presence or release of crud into reactor coolant.

EO 1.15 STATE the four causes of crud bursts.

EO 1.16 STATE the two conditions that can cause galvanic corrosion.

EO 1.17 EXPLAIN the mechanism for galvanic corrosion.

EO 1.18 IDENTIFY the two locations that are susceptible to galvanic corrosion.

EO 1.19 STATE the five control measures used to minimize galvanic corrosion.

Crud

In addition to the corrosion film, corrosion products in the form of finely divided, insoluble oxide particles called *crud* become suspended in the reactor coolant or loosely adhere to metal surfaces. Crud has several undesirable characteristics. It can be transported throughout the reactor coolant system. As a result, it can accumulate and foul heat-transfer surfaces or clog flow passages. The most undesirable characteristic of crud, however, is that it becomes activated when exposed to radiation. Because crud can be transported throughout the reactor coolant system, it can collect outside the reactor core, causing radiation hot spots that increase ambient radiation levels. Hot spots caused by collections of crud may occur at the entrance to the purification heat exchanger and other areas of low flow velocity. Crud that is loosely adhered to metal surfaces can suddenly become suspended in the reactor coolant.

The crud release can result from an increased oxygen concentration, a reduced (or significantly changed) pH, a large temperature change (heatup or cooldown), or a physical shock to the system. Physical shocks include starting, stopping, or changing pump speeds, or other evolutions like a reactor scram or a relief valve lift. The result is a sudden increase in reactor coolant activity. The release of crud in this fashion is termed a crud burst. Crud bursts often lead to the removal of protective corrosion films and make the freshly exposed metal more susceptible to additional corrosion. In addition to the corrosion film and crud, some of the corrosion products are soluble and are easily transported throughout the system.

High crud concentrations in the system can also complicate disposal of primary coolant. Many of the corrosion products have relatively long half-lives and represent significant biological hazards. If, therefore, primary coolant is drained or leaks from the plant shortly after a crud burst, additional procedures may need to be utilized to minimize the effects of this condition.

Therefore, if the conditions mentioned previously (O_2, pH) are changed, the solubility of these corrosion products will change, and they can then be transported to and deposited anywhere in the reactor coolant system.

Another corrosion byproduct is *scale*, which is made up of deposits on surfaces from the formation of insoluble compounds from normally soluble salts. Most common are calcium or magnesium carbonates ($CaCO_3$ or $MgCO_3$).

Galvanic Corrosion

Galvanic corrosion is the corrosion that results when two dissimilar metals with different potentials are placed in electrical contact in an electrolyte.

Of all the different types of corrosion, galvanic corrosion corresponds most closely to the electrochemical cells described previously in this module because galvanic corrosion occurs when two electrochemically dissimilar metals are joined together (in electrical contact) in a conducting medium (electrolyte). It may also take place with one metal with heterogeneities (dissimilarities) (for example, impurity inclusions, grains of different sizes, difference in composition of grains, differences in mechanical stress); abnormal levels of pH; and high temperatures. A difference in electrical potential exists between the different metals and serves as the driving force for electrical current flow through the corrodant or electrolyte. This current results in corrosion of one of the metals. The larger the potential difference, the greater the probability of galvanic corrosion. Galvanic corrosion only causes deterioration of one of the metals. The less resistant, active metal becomes the anodic corrosion site. The stronger, more noble metal is cathodic and protected. If there were no electrical contact, the two metals would be uniformly attacked by the corrosive medium as if the other metal were absent. Two locations susceptible to galvanic corrosion is a piping transition from one metal to another and a sacrificial anode (such as zinc).

Figure 10 illustrates that galvanic corrosion occurs when two different metals are in contact and exposed to an electrolyte.

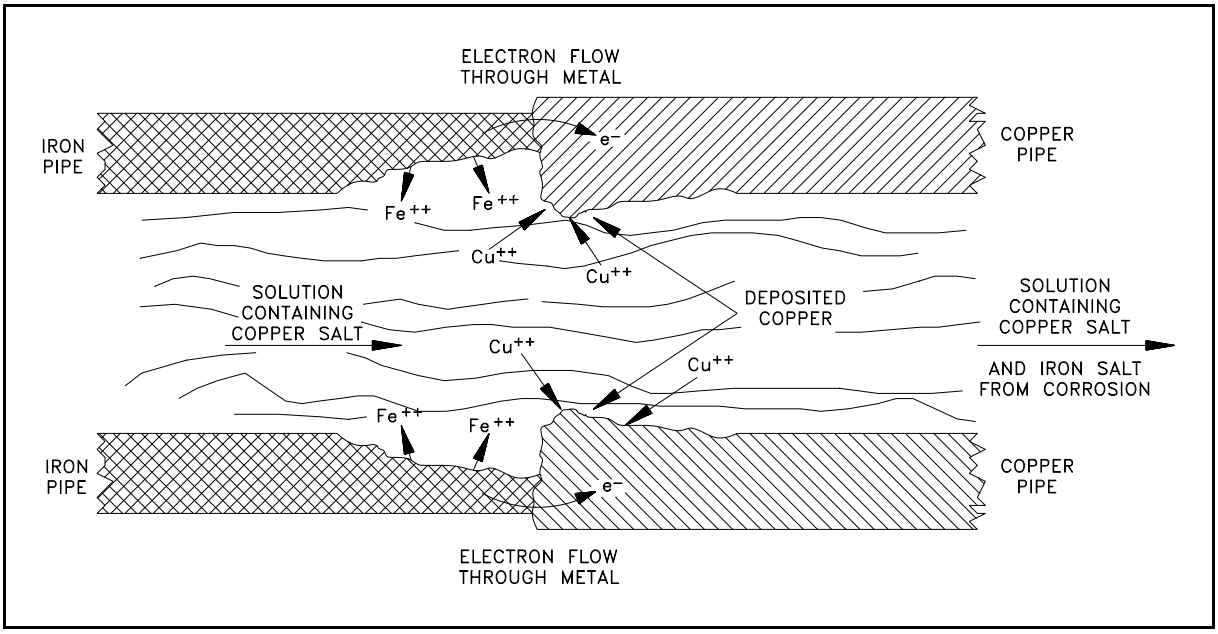

Figure 10 Galvanic Corrosion at Iron-Copper Pipe Junction

Figure 10 shows the junction of iron and copper pipes containing a solution of a copper salt. The oxidation potential of iron is sufficiently greater than that of copper so that iron is capable of reducing Cu^{+2} ions to copper metal. In this case, iron corrodes near the junction, and additional copper builds up on the copper pipe near the junction.

The solution to which the metal junction is exposed need not contain a salt of one of the metals for galvanic corrosion to occur. If the iron-copper junction were exposed to water without Cu^{+2} ions, the reduction reaction would be as shown in Equation (2-4).

$$H_3O^+ + e^- \rightarrow H + H_2O \qquad (2\text{-}4)$$

Again, iron would corrode near the junction, but in this case hydrogen would be formed on the surface of the copper.

Prevention of Galvanic Corrosion

A method called cathodic protection, discussed previously in this module, is often used to retard or eliminate galvanic corrosion. One of several ways of accomplishing this is to attach a third metal to the metals to be protected. This metal must have an oxidation potential even greater than that of the metal to be protected. The most active metal then tends to corrode in place of the protected metal. The metal that corrodes to protect another metal is called a sacrificial anode. This method is applied in the original design of structural materials. Zinc is a common sacrificial anode and is often used in cooling water systems that contain seawater.

Galvanic corrosion can also be limited by: 1) using only metals that are close on the activity series (discussed in the chapter on *Corrosion Theory*), 2) electrical insulation of dissimilar metals, and 3) using poorly-conducting electrolytes (very pure water).

The relative surface areas of the two metals are also important. A much larger surface area of the non-active metal, compared to the active metal, will accelerate the attack. It has been determined that the relative surface area is the determining factor in the corrosion rates.
The required electrical current for galvanic corrosion will be stopped if the dissimilar metals are:

- separated by a non-conducting junction,
- separated from a conductive environment, and
- located in a poorly conducting electrolyte (pure water).

Summary

The important information of this chapter is summarized below.

Crud and Galvanic Corrosion Summary

- Crud is corrosion products in the form of finely divided, insoluble oxide particles suspended in the reactor coolant or loosely adhered to metal surfaces or activated corrosion and wear products.

- Scale is the deposition on the surfaces of the piping from the formation of insoluble compounds from normally soluble salts. Most common are calcium or magnesium carbonates.

- Galvanic corrosion is the corrosion that results when two dissimilar metals with different potentials are placed in electrical contact in an electrolyte.

- The problems of crud in reactor plants are:

  Fouling of coolant flow paths
  Fouling of heat transfer surfaces
  High general background (ambient) radiation levels
  Radiation hot spots
  Radioactive waste disposal

Crud and Galvanic Corrosion Summary (Cont.)

- The causes of a crud burst in the reactor coolant are:

  Increased oxygen concentration
  Reduced (or significantly changed) pH
  Large temperature change
  Physical shock (for example, starting and stopping pumps, changing speeds of pumps, reactor scram, or relief valve lift)

- Galvanic corrosion functions on the principle of the electrochemical cell, and occurs when two electrochemically dissimilar metals are joined together in a conducting medium. The two dissimilar metals generate an electrical potential, and this electrical potential serves as the driving force for the electrical current flow through the corrodant or electrolyte. The less resistant metal, called the active metal, becomes anodic. The other metal, called the noble metal, becomes cathodic.

- The two locations susceptible to galvanic corrosion are piping transitions between two dissimilar metals and at sacrificial anodes.

- Measures used to control galvanic corrosion include:

  Cathodic protection by introducing a third metal (sacrificial anode, normally zinc) to the metals being protected or using only metals that are close on the activity series.

  Choosing relative surface areas such that the material to be protected has a larger surface area than the active metal.

  Separating dissimilar metals with a non-conducting material

  Separating the metals from a conductive environment

  Use of poorly conducting electrolytes (pure water)

SPECIALIZED CORROSION

The environment in which a metal exists has direct bearing on the corrosion rate of that metal. Because of the unique environment possible in the nuclear industry, there are a few specialized types of corrosion that must be considered.

EO 1.20 DEFINE the following terms:

a. Pitting corrosion
b. Crevice corrosion
c. Stress corrosion cracking

EO 1.21 STATE the two conditions necessary for pitting corrosion to occur.

EO 1.22 STATE the particular hazard associated with pitting corrosion.

EO 1.23 STATE the four controls used to minimize pitting corrosion.

EO 1.24 IDENTIFY the three conditions necessary for stress corrosion cracking to occur.

EO 1.25 DEFINE the term chemisorption.

EO 1.26 STATE the hazard of stress corrosion cracking.

EO 1.27 STATE the three controls used to prevent stress corrosion cracking.

EO 1.28 DESCRIBE the two types of stress corrosion cracking that are of major concern to nuclear facilities including:

a. Conditions for occurrence
b. Method(s) used to minimize the probability of occurrence

Pitting and Crevice Corrosion

Another possible effect of dissolved oxygen is accelerated localized attack. This is especially likely in areas of limited circulation. The resulting corrosion is called pitting corrosion.

Pitting corrosion occurs where the anodic site becomes fixed in a small area and the formation of holes (deep attack) in an otherwise unaffected area takes place. *Crevice corrosion* is a type of pitting corrosion that occurs specifically within the low flow region of a crevice.

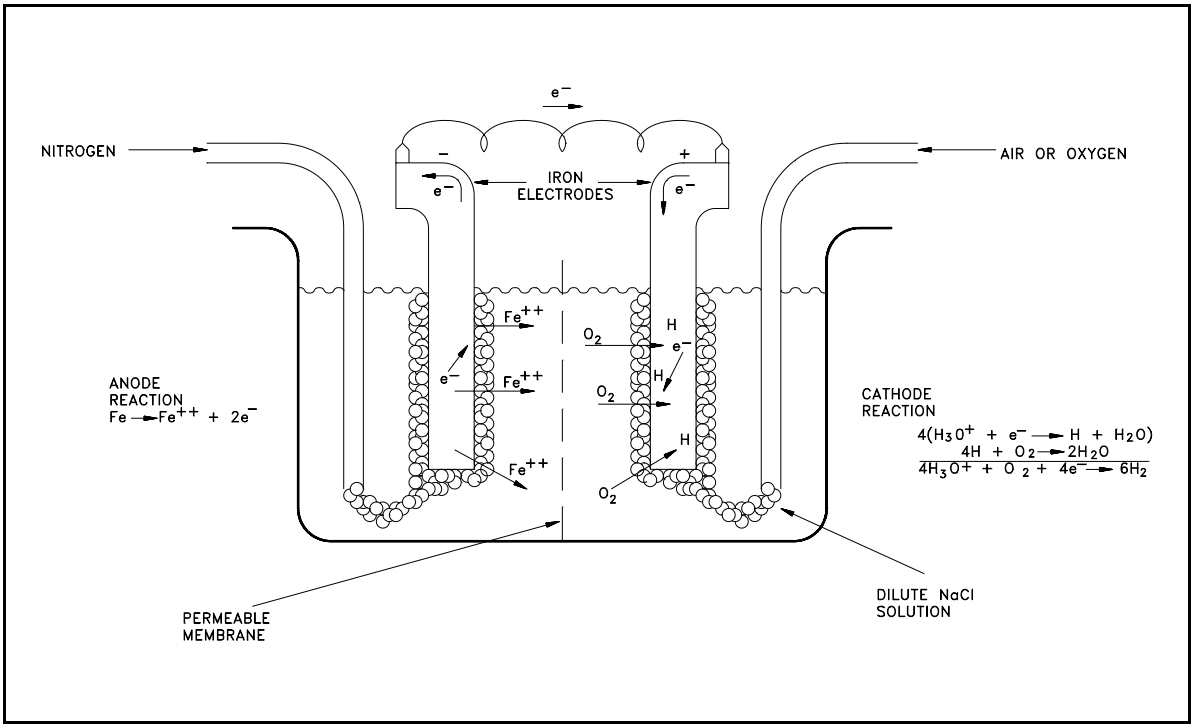

Figure 11 Differential Aeration Cell

To illustrate pitting attack, consider a special type of galvanic cell called a differential aeration cell such as the one illustrated in Figure 11. This particular differential aeration cell is showing current flow as a result of depolarization of one electrode (cathode) by oxygen. In this type of cell, two iron electrodes are exposed to a dilute solution of an electrolyte (NaCl, for example). Air (or oxygen) is bubbled around one electrode, and nitrogen is bubbled around the other. A current flows through the wire connecting the two electrodes. The difference in potential is a result of the difference in oxygen concentration at the two electrode surfaces. At the electrode exposed to nitrogen, electrons are given up by the iron as it is oxidized. These electrons readily flow through the external circuit to the electrode exposed to oxygen. At this depolarized electrode they can participate in a reduction reaction. As a result, oxidation occurs at the electrode exposed to nitrogen and reduction occurs at the aerated electrode. Oxidation at one electrode and reduction at the other creates a potential and a flow of current through the connecting wire. Note that loss of metal occurs at the electrode that is deficient in oxygen.

In iron that is exposed to water, a similar action can occur if adjacent areas of the metal surface become exposed to solutions with different oxygen concentrations. For example, the solution in a crevice exchanges slowly with the bulk of the solution outside the crevice. Oxygen in the solution inside the crevice will be depleted initially by the corrosion reaction.

$$2Fe + O_2 \rightarrow 2FeO \qquad (2\text{-}12)$$

This reaction alone does not produce a protective film on the metal. Because of restricted flow into the crevice, replenishment of oxygen will be very slow; therefore, the solution inside the crevice will have a low oxygen concentration relative to that outside the crevice as shown in Figure 12. The two adjacent areas then establish a concentration cell with electrons flowing from the region of low oxygen concentration to the region of high concentration. Thus, metal goes into solution (oxidation) inside the crevice, and reduction occurs outside the crevice. Metal ions diffuse out of the crevice, more metal dissolves, and the process continues. This results in the formation of a pit inside the crevice.

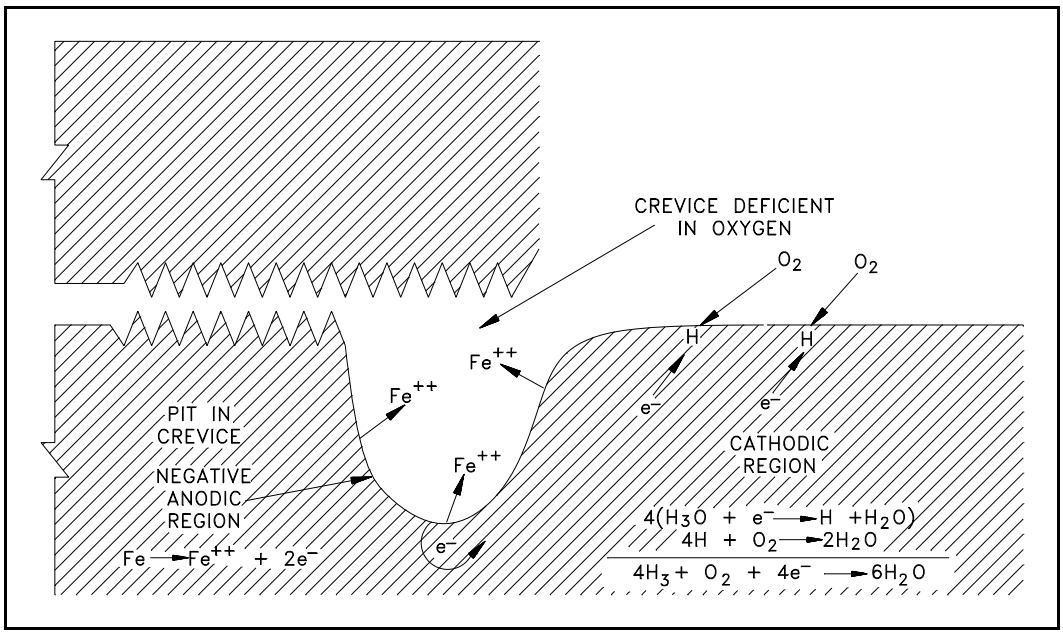

Figure 12 Representation of Crevice Pitting

The presence of oxygen can also promote pitting at areas on the metal surface that are initially anodic with respect to an adjacent area. For example, suppose that adjacent areas on a metal surface exhibit slightly different oxidation potentials. Oxidation, or loss of metal, proceeds at the region of higher potential. Corrosion in the region of higher potential leads to formation (at least initially) of a porous oxide film. The thickness of the film formed on the adjacent cathodic region will be much less. Oxygen in the bulk of solution can reach the cathodic surface (with the thin film) more readily than it can the nearby anodic surface region (with the thicker oxide film). Depolarization of the cathodic region (thin film) by oxygen tends to maintain this region cathodic, while a deficiency of oxygen under the thicker porous corrosion film assists in maintaining an anodic condition in this region. The overall result is corrosion, or wasting away, of the metal in the anodic region under the thicker film. Thus, a pit in the metal surface is formed under the mound of surface oxide, as illustrated in Figure 13. Pitting of this type is common in both low temperature and high temperature iron-water systems if precautions are not taken to remove the oxygen from the water within the system.

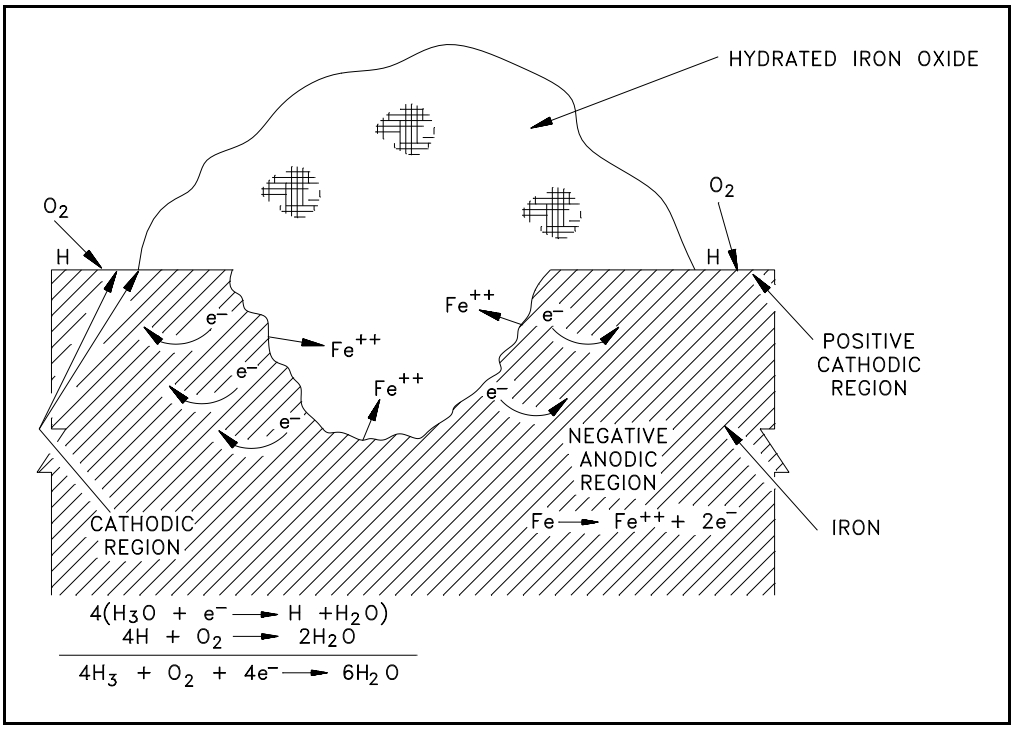

Figure 13 Pit in Metal Surface Promoted by Depolarization

It is also found that certain ions, notably chloride ions, cause pitting of iron and steel. The exact mechanism by which this occurs is not clear, but in some way chloride ions cause defects in the passivating oxide layer on the metal surface. The defects are highly localized and are surrounded by large passive areas that tend to be cathodic. Thus, a small anodic (oxidation) site is surrounded by a large cathodic (reduction) area. The current density will then be very large at the anodic site, and attack on the metal will be rapid. In some test cases, deep pits have been observed within a few hours.

Pitting and crevice corrosion are a major hazard to a nuclear facility because of the rapid penetration of the metal with little overall loss of mass. A nuclear facility minimizes pitting and crevice corrosion by the following actions.

- Avoiding stagnant or low flow conditions.
- Using metals and alloys that are less susceptible to the corrosion.
- Avoiding agents in the medium that cause pitting (for example, chlorides and oxygen).
- Designing the system and components such that no crevices are present.

Stress Corrosion Cracking

Stress corrosion cracking (SCC) is a type of intergranular attack corrosion that occurs at the grain boundaries under tensile stress. Grain boundaries are discussed in detail in the *Material Science* Handbook. SCC occurs in susceptible alloys when the alloy is exposed to a particular, specific environment if the alloy is in a stressed condition. Stress corrosion cracking appears to be relatively independent of general uniform corrosion processes. Thus, the extent of general corrosion can be essentially nil, and stress cracking can still occur. Most pure metals are immune to this type of attack.

According to the most widely accepted theory, stress corrosion cracking is caused by a process called chemisorption. Unlike relatively weak physical absorption, such as hydrogen gas on platinum metal, chemisorption may be thought of as the formation of a compound between the metal atoms on the surface as a monomolecular layer of the chemisorbed substance, such as Cl-, OH-, Br-, and some other ions. The formation of this chemisorbed layer greatly reduces the attraction between neighboring metal atoms. A defect initially present then grows as the metal atoms separate under stress, more chemisorption occurs, and the process continues. In very severe cases, the time required for this cracking to occur is only a matter of minutes.

Many stainless steels are susceptible to stress corrosion cracking. Stainless steels containing 18 percent chromium and 8 percent nickel are susceptible to cracking in environments containing chloride ions and in concentrated caustic environments (that is, in environments where the hydroxyl ion concentration is high). On the other hand, these types of stainless steels do not exhibit any tendency to crack when they are exposed to water environments containing nitrate (NO_3^-), sulfite (SO_3^{--}), and ammonium (NH_3^+) ions.

SCC is of great concern because it can readily crack metal of appreciable thickness. If the environment is severe enough, cracking can occur in a very short period of time. The crack can then lead to a serious failure of the component, or the system, and all the attendant results (for example, contamination, loss of coolant, and loss of pressure).

The most effective means for preventing SCC are proper design, reducing stress, removing critical environmental contributors (for example, hydroxides, chlorides, and oxygen), and avoiding stagnant areas and crevices in heat exchangers where chlorides and hydroxides might become concentrated. Low alloy steels are less susceptible than high alloy steels, but they are subject to SCC in water containing chloride ions. Nickel based alloys are not affected by chloride or hydroxide ions.

Two types of SCC are of major concern to a nuclear facility.

Chloride Stress Corrosion Cracking (Stainless Steels)

The three conditions that must be present for chloride stress corrosion to occur are as follows.

- Chloride ions are present in the environment
- Dissolved oxygen is present in the environment
- Metal is under tensile stress

Austenitic stainless steel is a non-magnetic alloy consisting of iron, chromium, and nickel, with a low carbon content. This alloy is highly corrosion resistant and has desirable mechanical properties. One type of corrosion which can attack austenitic stainless steel is chloride stress corrosion. Chloride stress corrosion is a type of intergranular corrosion.

Chloride stress corrosion involves selective attack of the metal along grain boundaries. In the formation of the steel, a chromium-rich carbide precipitates at the grain boundaries leaving these areas low in protective chromium, and thereby, susceptible to attack. It has been found that this is closely associated with certain heat treatments resulting from welding. This can be minimized considerably by proper annealing processes.

This form of corrosion is controlled by maintaining low chloride ion and oxygen content in the environment and the use of low carbon steels. Environments containing dissolved oxygen and chloride ions can readily be created in auxiliary water systems. Chloride ions can enter these systems via leaks in condensers or at other locations where auxiliary systems associated with the nuclear facility are cooled by unpurified cooling water. Dissolved oxygen can readily enter these systems with feed and makeup water. Thus, chloride stress corrosion cracking is of concern, and controls must be used to prevent its occurrence.

Figure 14 illustrates intergranular stress corrosion cracking. The pressure of a tensile stress opens up intergranular cracks and accelerates further corrosion. Chloride stress corrosion is a particularly significant problem in the operation of nuclear facilities because of the wide use of austenitic stainless steel, and the inherent presence of high tensile stresses associated with pressurization. Chloride stress corrosion cracks have been known to propagate in austenitic stainless steel at stresses of about one-fifth yield strength with chloride concentrations of less than 50 ppm. Yield strength is discussed in detail in the *Material Science* Handbook.

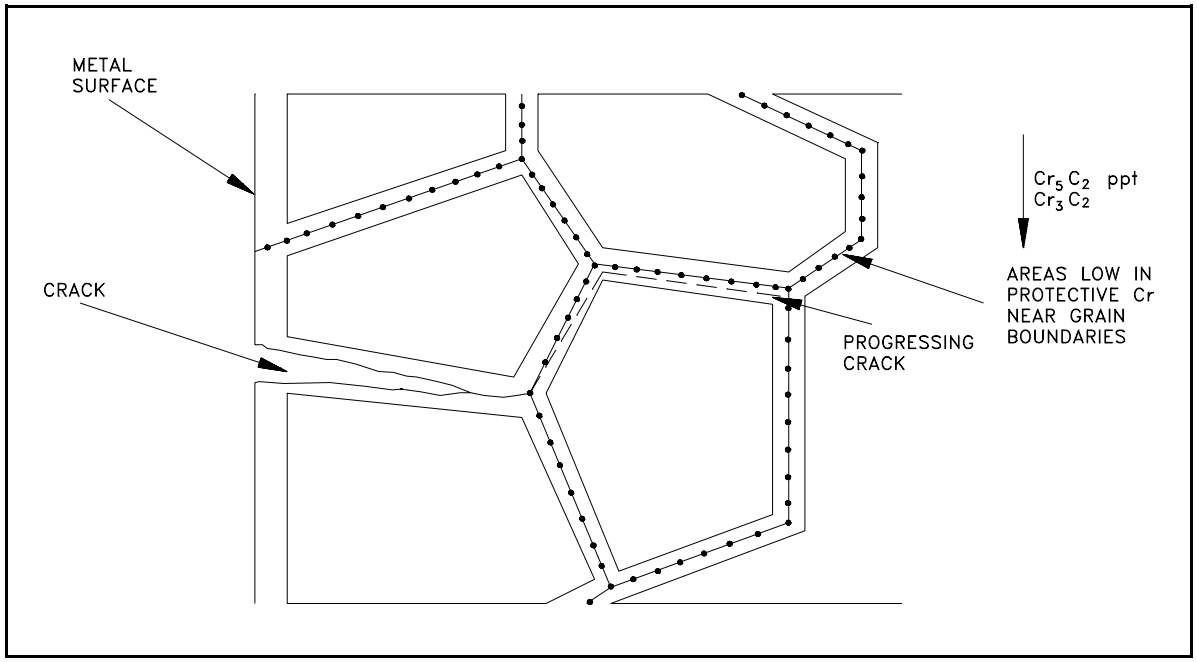

Figure 14 Intergranular Corrosion Cracking

Tests show that the 18-8 stainless steels are susceptible to chloride stress attack when both the chloride ion concentration and dissolved oxygen concentration are above certain values. The region of susceptibility for austenitic stainless steel is illustrated in Figure 15. Note that when dissolved oxygen is present at about 1 ppm, chloride stress corrosion cracking can be initiated at chloride ion concentrations near 1 ppm. However, when the concentration of dissolved oxygen is very low, susceptibility to chloride stress corrosion cracking is reduced.

High temperature tends to decrease the time required for chloride-induced cracking to occur, but there appears to be no practical temperature limit below which cracking will not occur, given sufficient time and severe conditions. The curve in Figure 15 is valid for temperatures in the range 470°F to 500°F.

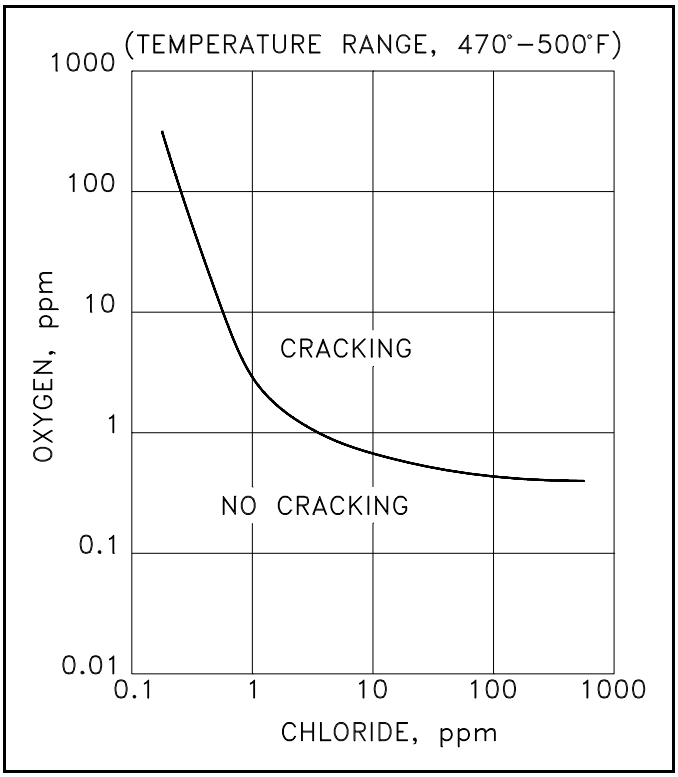

Figure 15 Austenitic Stainless Steel

Caustic Stress Corrosion Cracking

Caustic stress corrosion, or caustic embrittlement, is another form of intergranular corrosion cracking. The mechanism is similar to that of chloride stress corrosion. Mild steels (steels with low carbon and low alloy content) and stainless steels will crack if they are exposed to concentrated caustic (high pH) environments with the metal under a tensile stress. In stress cracking that is induced by a caustic environment, the presence of dissolved oxygen is not necessary for the cracking to occur.

Caustic stress corrosion cracking was first encountered in the operation of riveted steam boilers. These boilers were found to fail on occasion along riveted seams. Failure was attributed to caustic-induced cracking at the highly stressed regions near and under the rivets. Boiler water could easily flow into the crevices which existed under the rivets.

Radiative heating would cause the water in the crevices to boil. As steam was formed, it would escape from the crevice. More boiler water would then flow into the crevice, boil, and pass from the crevice as steam. The net result of this continuing process was concentration of caustic under the rivet. The combination of high stress and high caustic concentrations eventually led to destructive cracking of the boiler vessel.

Where the rate of steam generation (boiling) is high, it is more difficult to eliminate the problem of solute concentration in regions of the boiler. Caustic stress corrosion may concentrate in such regions as the water evaporates rapidly, but sufficient concentration of caustic by such a mechanism to induce stress cracking is considered unlikely.

Available data indicates that caustic concentrations greater than 10,000 ppm, and probably up to 50,000 ppm, are required to induce caustic stress cracking (40,000 ppm NaOH is equivalent to 40 grams per liter or 1 mole per liter). The pH of such a solution is on the order of 14. An alkaline environment is produced and controlled by use of a solution having some properties of a buffer, that is, one that tends to retard or slow a reaction or tends to force it in one direction or the other.

Summary

The important information of this chapter is summarized below.

Specialized Corrosion Summary

- Pitting corrosion occurs where the anodic site becomes fixed in a small area and the formation of holes in an otherwise unaffected area takes place.

- Crevice corrosion is a type of pitting corrosion that occurs specifically within the low flow region of a crevice.

- Stress corrosion cracking (SCC) is a type of intergranular attack corrosion that occurs at the grain boundaries under tensile stress.

- Pitting corrosion requires two conditions to occur, low flow and areas of both high and low oxygen concentration. When these conditions are met a differential aeration cell is established which produces an electron flow from the point of low oxygen concentration to the area of high oxygen concentration. The difference in oxygen concentration is usually due to a low flow condition.

- Pitting corrosion is a hazard due to the possible rapid penetration of the metal with little overall loss of mass. Pitting corrosion is minimized by:

  Avoiding stagnant conditions

  Using the correct metals and alloys that are less susceptible to the corrosion

  Avoiding agents in the medium that cause pitting

  Designing the system and components such that no crevices are present

- Stress corrosion cracking occurs when three conditions are met; the alloy is susceptible to stress corrosion cracking, the alloy is exposed to specific environment, and the alloy is in a stressed condition.

- Chemisorption is the formation of a monomolecular layer of a compound between the metal's surface atoms. This layer separates the metal's atoms thereby weakening the metal and allowing any existing defects to propagate when a stress is applied.

Specialized Corrosion Summary (Cont.)

- Stress corrosion cracking (SCC) is a great concern due to the hazard that it can readily crack metal of appreciable thickness. The crack can lead to a serious failure of the component, or system, and all the attendant results such as:

  Contamination
  Loss of coolant
  Loss of pressure

- SCC is prevented in reactor system by:

  Proper design

  Reducing stress levels

  Avoiding stagnant areas and crevices in heat exchangers, where chlorides and hydroxides might become concentrated.

- Chloride stress corrosion

  The three conditions that must be present for chloride stress corrosion to occur are:

  Chloride ions present
  Dissolved oxygen present
  Metal under tensile stress

  Chloride stress corrosion is controlled by maintaining low chloride ion and oxygen content in the environment and the use of low carbon steels.

- Caustic stress corrosion

  Caustic stress corrosion is similar to chloride stress corrosion. The metals involved are mild steels (steel with low carbon and low alloy content). The metals are exposed to concentrated caustic environments and under tensile stress. The presence of oxygen is not required for cracking to initiate. Concentration of greater than 10,000 ppm is required for cracking to initiate. The level may be higher for different caustic environments.