CHAPTER 3 - REVIEW OF CORROSION

3.1 Introduction

A distinction is drawn between pinhole formation and corrosion. Corrosion is generally taken to be a large scale loss of metal while pinhole is highly localized, small diameter hole that goes through the pipe wall. Nevertheless, because the underlying causal mechanism is the same, in this chapter, a review of corrosion is presented. Recent handbook on corrosion by Roberge (2000) contains comprehensive details.

First, general types of corrosion are introduced. Details regarding corrosion specific to copper pipe namely, uniform, pitting, and erosion corrosion are explained in a later section. Corrosion indices for determining the corrosiveness of water are also introduced.

Second, the crucial concepts, thermodynamics and electrode kinetics are introduced. In addition, various kinds of corrosion rate measurement methods and techniques currently used are given. Most of the contents in this chapter are the summary of the currently available corrosion references focusing on the corrosion of home plumbing copper pipe.

Table 3.1 contains the distribution of the copper pipe failure types that occurred during 1980’s (Copper Development Association, 1983).

Table 3.1 Types of Failures in Copper Pipe ((Original source: Statistics from US Copper Development Association and (CDA))

Cause of failure	Frequency (%) U.S.A. (1983)
Pitting Corrosion	58
Erosion Corrosion	24
Faulty Workmanship*	5
Outside Corrosion	7
Fatigue	2
Other	4

3.2 General types of corrosion

Various forms of general corrosion that not only can take place in water distribution system but also in the atmosphere are described. Usually, corrosion is classified as uniform, galvanic, crevice, pitting, inter-granular, erosion, and stress corrosion. These are identified visually or with the aid of inspection tools and classified according to their characteristics and mechanisms.

3.2.1 Uniform Corrosion

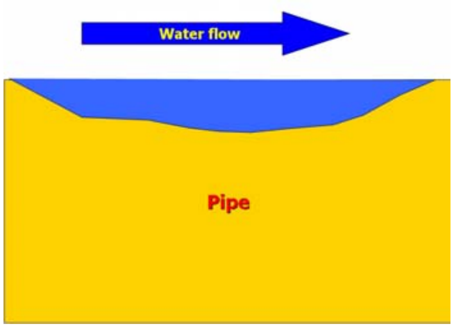

Figure 3.1 Uniform Corrosion

Uniform corrosion is the most frequent form in corrosion. Electrochemical reaction proceeds uniformly over the surface. From Figure 3.1, it is seen that general thinning of metal leads to failure. Uniform corrosion accounts for the greatest loss of metal. But from engineering considerations, this is not critically important as they rarely result in leaks or failures of infrastructure even though they lead to the shortage of design life and/or loss of efficiency of the infrastructure.

3.2.2 Erosion Corrosion

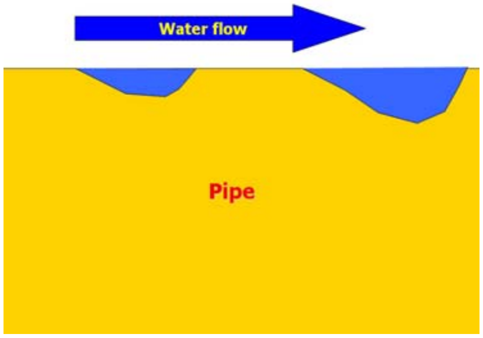

Figure 3.2 Erosion Corrosion

By definition, “erosion corrosion is the cumulative damage induced by electrochemical corrosion reactions and mechanical effects from relative motion between the electrolyte and the corroding surface or accelerated degradation in the presence of this relative motion caused by high velocity, with mechanical wear and abrasion effects”(Roberge, 2000). Pipe bends, elbows, joints, valves, pumps, nozzles, heat exchangers, and turbine blades are the most frequent places where the erosion corrosion takes place. Figure 3.2 shows the mechanism schematically.

3.2.3 Pitting Corrosion

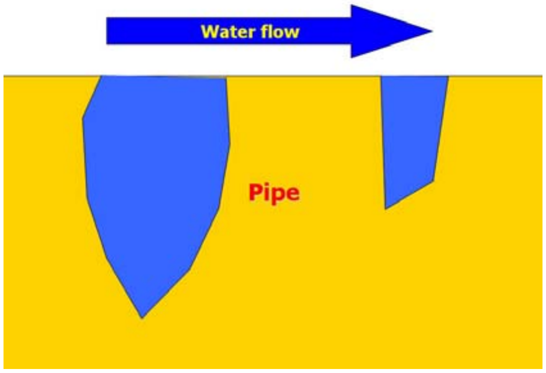

Figure 3.3 Pitting Corrosion

Pitting is considered to be one of the most dangerous and destructive forms of corrosion. Even though the weight loss of the material is very small compared to the other forms corrosion, it causes the system fail easily. From Figure 3.3, it is shown that pitting corrosion does little harm in weight loss, but it deteriorates the system locally. From an engineering viewpoint, pitting corrosion is significant as their occurrence is dominant as shown in Table 3.1. The size of the pitting corrosion on metal is so small that it’s very difficult to detect and to measure the variable depth and number of pits.

3.2.4 Galvanic Corrosion

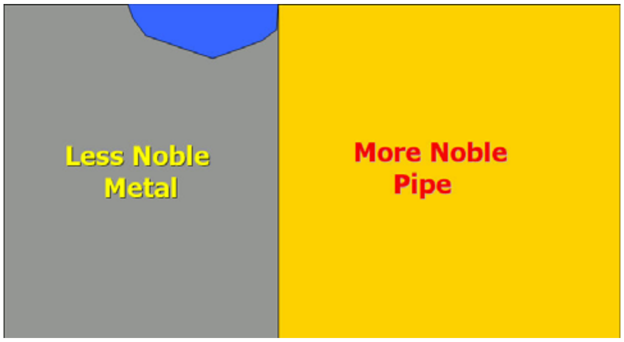

Figure 3.4 Galvanic Corrosion

When two adjacent and dissimilar metals are immersed in corrosive or conductive solution, as shown in Figure 3.4, cathodic and anodic areas are determined. As there exists potential difference between the different metals, electrochemical reaction occurs. This is called galvanic corrosion. In this process, less noble metal will corrode becoming anodic (negative electrode) and more noble metal becomes cathodic (positive electrode). In Table 3.2, the galvanic series is shown. The more noble metals (non-corrosive) are listed towards the bottom of the table; the upper part of the table has the less noble metals which are more easily corroded. For example, if gold and steel are immersed in a conductive solution, gold will remain un-corroded and steel corrodes according to the galvanic series table. As shown in Table 3.2, copper is nobler than any of the materials that are commonly used in water distribution systems. The galvanic series shown in Table 3.2 provides the basis for assessing corrosion tendencies (Fontana, 1986). The farther apart in the series, the greater is the potential difference and the possibility for galvanic corrosion.

Table 3.2 Galvanic series

Corroded End (Anodic, or Least Noble)

Magnesium
Magnesium Alloy
Zinc
Aluminum
Cadmium
Steel or Iron
Cast Iron
Iron alloys
Lead-tin solders
Lead
Tin
Nickel
Brasses
Copper
Bronzes
Titanium
Monel
Silver solder
Silver
Carbon (graphite)
Gold

Non-corroded end (cathodic, or most noble)

3.2.5 Crevice Corrosion

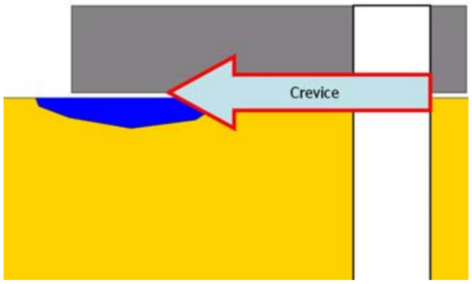

Figure 3.5 Crevice Corrosion

As shown in Figure 3.5, in some locations such as crevices, oxygen may be depleted during corrosion reaction. So, the oxygen reduction reaction cannot be continued and this results in the anodic characteristic. This specific area can be highly corrosive. The characteristics of the metal and the concentration of the aqueous solution which is involved in the reaction are the most crucial factors that determine the potential of the corrosion. Corrosion reaction is due to the concentration differences and this reaction can be said to be the equalizing potential process. For estimating the potential, Nernst equation can be used. (explained in a later section). Crevice corrosion forms under gaskets, washers, lap joints, and crevices.

3.2.6 Inter-granular corrosion

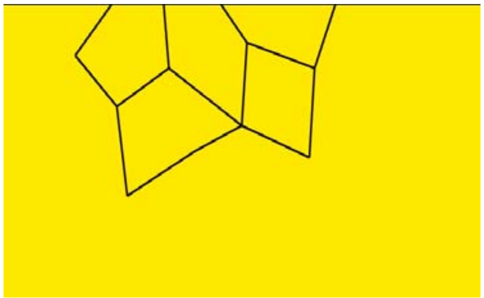

Figure 3.6 Inter-granular Corrosion

Microstructure of the metals or alloys is called as grain. And grain boundary separates the grain. When there’s localized attack along the grain boundaries or adjacent to the grain boundaries, it is called inter-granular corrosion as shown in Figure 3.6. So, the metal disintegrates and loses its strength. Impurities at the grain boundaries or diminution, enrichment of one of alloys in the boundary of the grain may result in inter-granular corrosion.

3.2.7 Stress Corrosion Cracking (SCC)

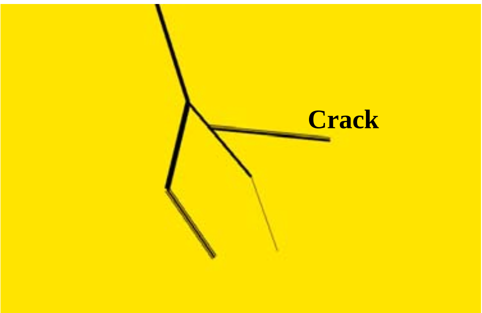

Figure 3.7 Stress Corrosion Cracking

Tensile stress in corrosive medium can create cracking in metals and this is called the Stress corrosion cracking (SCC). Unlike other forms of corrosion, it is only identifiable with microscopic examination. Usually the fine cracks occur into the material but not on the surface as shown in Figure 3.7. It’s hard to find location of the fine cracks, and prediction of the damage is not easy.

3.3 Corrosion rate measurement

There are several ways to assess the rate of corrosion. Before assessing the rate measurement methods, corrosion rate expression is presented. A commonly used expression for corrosion (Fontana, 1986) is

$$\text{Mils per year (mpy)} = \frac{534 \cdot W}{D \cdot A \cdot T} \tag{3-1}$$

Where; W = weight loss, (mg)

D = density of specimen, (g/cm^3)

A = area of specimen, (cm^2)

T = exposure time, (hr)

$\text{Mil} = \text{milli inch} = \frac{1}{1000}$ inch

Also, corrosion rate can be expressed in terms of current density.

Faraday's law for charge passed through a conductor, Q is given by (Jones, 1996)

$$Q = \int_0^t I dt = \frac{mnF}{a} \tag{3-2}$$

in which; I = current in amperes,

F = Faraday's constant = 96,500 coulombs/ mole of electrons,

n = number of moles of electrons,

a= atomic mass of the anode material,

m = mass of anode lost,

t = time duration (seconds)

Dividing both the sides of Eq. (3.2) by (tA) where A = surface area, we obtain

$$\frac{Q}{tA} = \frac{I}{A} = i = \frac{m}{At}\left(\frac{nF}{a}\right) = r\left(\frac{nF}{a}\right) \tag{3-3}$$

where; $r = \frac{m}{At}$ = rate of corrosion in depth units and

$$r = \frac{ia}{nF} \tag{3-4}$$

3.4 Corrosion and scale formation index

A method of corrosion prevention is to have the correct amount of $CaCO_3$ scale to form within a pipe providing a protective coating. The Langelier and Ryznar indices are widely used (Tchobanoglous and Schroeder, 1985). The Langelier index (LI) is given by

$$\mathrm{LI} = \mathrm{pH}_{\mathrm{measured}} - \mathrm{pH}_{\mathrm{sat}} \qquad (3\text{-}5)$$

in which; $\mathrm{pH}_{\mathrm{measured}}$ = actual pH value measured in the water

$\mathrm{pH}_{\mathrm{sat}}$ = pH of the water in equilibrium with solid $CaCO_3$ (Saturated pH)

LI > 0 water is scale forming (supersaturated with respect to calcite $CaCO_3$)

LI = 0 neutral

LI < 0 water is corrosive (unsaturated with respect to $CaCO_3$)

The Ryznar index (RI) is given by

$$\mathrm{RI} = 2\mathrm{pH}_{\mathrm{sat}} - \mathrm{pH}_{\mathrm{measured}} \qquad (3\text{-}6)$$

with RI < 5.5 heavy scale will form

5.5 < RI < 6.2 scale will form

6.2 < RI < 6.8 no difficulties

6.8 < RI < 8.5 water is corrosive

RI > 8.5 water is very corrosive

The value of $\mathrm{pH}_{\mathrm{sat}}$ is obtained from

$$\mathrm{pH}_{\mathrm{sat}} = -\log_{10}\left[\frac{\mathrm{K}_2\gamma_{\mathrm{Ca}^{+2}}[\mathrm{Ca}^{2+}]\gamma_{\mathrm{HCO}_3^-}[\mathrm{HCO}_3^-]}{\mathrm{K}_{\mathrm{sp}}}\right] \qquad (3\text{-}7)$$

in which; $\gamma_{(\cdot)}$ = activity coefficient

$$\log_{10}\gamma_{\mathrm{i}} = -\frac{0.5(\mathrm{z_i})^2\mu^{\frac{1}{2}}}{1+\mu^{\frac{1}{2}}} \text{ for } \mu < 0.1 \qquad (3\text{-}8)$$

where; γ_{i} = activity coefficient for ionic species i

z_i = charge of ionic species i

μ = ionic strength of solution = $\frac{1}{2}\sum_i c_i z_i^2$

c_i = concentration of ionic species i (moles/ liter)

K_2 = second dissociation constant of carbonic acid from bicarbonate to carbonate

$$= \frac{[H^+][CO_3^{-2}]}{[HCO_3^-]}$$

and K_{sp} = solubility product constant = $[Ca^{+2}][CO_3^{-2}]$

$[\cdot]$ = concentration in moles/ liter (molar concentration)

an estimate for $\mu = 2.5\ (10^{-5})$ TDS g/m^3

and TDS = Total dissolved solids

3.5 Copper corrosion

3.5.1 Electrochemistry of copper-water pipes

The term corrosion is exclusively used for metals (Basalo, 1992). Electrochemistry is the inter-conversion of electrical energy and chemical energy (Chang, Raymond,: Chemistry, Mcgraw Hill, New York, 1998). Electrochemical processes are redox [oxidation (giving up electrons) – reduction (accepting electrons)] reactions. In redox reactions pertaining to metals carrying water, the metal gives up electrons and therefore corrodes forming the anode- negative electrode- positive node for the external flow of electrons. The cations from the metal flow internally through the solution to the cathode-positive electrode – negative node for the current; the anions from the solution move toward the anode. The following discussion is based on Basalo (1992). A metal atom can be oxidized as

$$M \rightarrow M^{n+} + ne^{-} \qquad (3\text{-}9)$$

Specifically for copper we have

$$Cu \rightarrow Cu^{2+} + 2e^{-} \qquad (3\text{-}10)$$

The scheme is shown in Figure 3.8. The loss of electrons from the metal indicates that the metal serves as a micro-anode. The related electrons are captured by several mechanisms resulting in the respective micro-cathodes within the water carrying pipe. If the solution is lacking dissolved oxygen, the available H^+ ions in the water react with the released electrons to form the hydrogen gas by

$$2H^{+} + 2e^{-} \Leftrightarrow H_2 \qquad (3\text{-}11)$$

The location at which the mechanism takes place is called the hydrogen electrode. If the solution has sufficient dissolved oxygen, we have

$$O_2 + 2H_2O + 4e^{-} \Leftrightarrow 4OH^{-} \qquad (3\text{-}12)$$

forming an oxygen electrode along with hydroxide ions. If the solution contains the disinfectant chlorine in the form of chlorine gas Cl_2, two reactions occur - hydrolysis and ionization (Tchobanoglous and Schroeder, 1987). In the hydrolysis reaction, hypochlorite, HOCl is formed; the chlorite ion OCl^- is formed in the ionization reaction. The two reactions and the corresponding equilibrium constants are given by

$$Cl_2 + H_2O \Leftrightarrow HOCl + H^+ + Cl^- \text{ and} \tag{3-13}$$

$$K_1 = \frac{[HOCl][H^+][Cl^-]}{[Cl_2]} = 4.5(10^{-4}) \text{ at } 25^oC \tag{3-14}$$

With $[H_2O] = \frac{1000g}{18.02g/mol} = 55.5$ moles and the concentration of water, $[H_2O]$ is mol/l or 55.5 M (in molarity). This is a large value and compared to the other concentrations in the expression, it is generally taken that $[H_2O]$ does not change. This constant $[H_2O]$ is absorbed into the reported equilibrium constant values. The ionization reaction is given by

$$HOCl \Leftrightarrow H^+ + OCl^- \tag{3-15}$$

$$K_2 = \frac{[H^+][OCl^-]}{[HOCl]} = 3.7(10^{-8}) \text{ at } 25^oC \tag{3-16}$$

For pH less than 7.5, the preponderant residual component is HOCl and the corresponding reduction equation is

$$HOCl + H^+ + 2e^- \rightarrow Cl^- + H_2O \tag{3-17}$$

For pH greater than 7.5, the preponderant residual component is OCl^- ion and

$$OCl^- + 2H^+ + 2e^- \rightarrow Cl^- + H_2O \tag{3-18}$$

The standard electromotive force (emf) of a cell, E_{cell} is given by

$$E^o_{cell} = E^o_{cathode} - E^o_{anode} = E^o_{red} + E^o_{oxid} \tag{3-19}$$

in which E^o_{anode} must be used as a reduction potential from the reduction potential table. For the anode reduction of $Cu \rightarrow Cu^{++} + 2e^-$ from the standard reduction potentials we have (Chang, 1998)

$$E^o_{Cu/Cu^{++}} = -E^o_{Cu^{++}/Cu} = -0.34V = E^o_{oxid} \tag{3-20}$$

For the cathode reactions from Eq. (3-11)

$$E^o_{H^+/H_2} = 0V \tag{3-21}$$

$$\text{From Eq. (3-12) } E^o_{red} = 0.40 \tag{3-22}$$

$$\text{and from Eq.(3-13) } E^o_{red} = 1.482 \tag{3-23}$$

Therefore, the reactions of HOCl or OCl^- are more significant in copper corrosion.

Nernst equation (3-24) given by

$$E = E_o - \frac{RT}{nF}\ln Q \qquad (3\text{-}24)$$

enables the calculation of E when the reaction quotient, Q, is not equal to the equilibrium constant K; further in Eq.(3-24) R = universal gas constant ($J/^oK \;\; Kg \cdot mol$), T= absolute temperature (^{o}K), n= number of moles of electrons that pass through the circuit (mol), F= Faraday's constant (J/V kg mol).

It is pointed out that Eq. (3-24) provides only the potential. It does not provide the current or rate of reaction. It is also pointed out that the Faraday's law simply states that if the amount of charge transmitted over certain time is available, only then with the aid of Eq. (3-24) one can obtain estimates of the rate of corrosion. Therefore, the above so called thermodynamic analysis does not provide information on the rate of corrosion or the corrosion current. A positive E from Eq.(3-24) when plugged into

$$\Delta G = \text{free energy change} = -nFE \qquad (3\text{-}25)$$

yields a negative value for ΔG which indicates that the reaction is spontaneous or will occur; but does not say at what rate. Following Jones (1996), consider

$$3Pb + 2Al^{3+} = 3Pb^{2+} + 2Al \qquad (3\text{-}26)$$

with the two half-cells

$$Pb^{2+} + 2e^- = Pb \qquad (3\text{-}27)$$

$$\text{and } Al^{3+} + 3e^- = Al \qquad (3\text{-}28)$$

From the standard reduction potential table

$$E_{pb/pb}{}^{2+} = +0.126 \text{ V} = E_{oxid} \qquad (3\text{-}29)$$

$$\text{and } E_{Al^{3+}/Al} = -1.662V = E_{red} \qquad (3\text{-}30)$$

Assuming that the reaction (3-26) proceeds from the left to the right

$$E_{cell} = -1.662 - (-0.126) = -1.532V \qquad (3\text{-}31)$$

which will yield from Eq. (3-25), a positive free energy change, $\Delta G > 0$. It indicates that the left to right equation is not possible and the reaction must proceed in the opposite direction with

$$3Pb^{2+} + 2Al \rightarrow 3Pb + 2Al^{3+} \tag{3-32}$$

Corrosion rate

The following discussion is based on Fontana (1986). He points out that the standard reduction potentials are measured when the metal and the metal ions in the solution are in equilibrium. However, during corrosion this ideal condition does not exist. There will be initially current flow between the anode and the cathode. To satisfy the charge conservation hypothesis, the process has to seek the condition of the total rate of oxidation must equal the total rate of reduction. The current density corresponding to this point is called corrosion current density i_{corr} since it represents the rate of metal dissolution. To obtain the exact amount of metal loss i_{corr} should be used in place of i in Faraday's law. The corrosion current should be calculated as follows. (Callister, W.D, Material Science and Engineering, John Wiley, New York, NY, 2000). The reduction potential is obtained as

$$E_{red,corr} = E_{corr} = E^0_{red} + \beta_{red}\log(\frac{i_{corr}}{i_{0,red}}) \tag{3-33}$$

Similarly the oxidation potential is given by

$$E_{oxid,corr} = E_{corr} = E^0_{oxid} + \beta_{oxid}\log(\frac{i_{corr}}{i_{0,oxid}}) \tag{3-34}$$

in which: E^0 = standard potential, red = reduction, oxid = oxidation, β = Tafel coefficient, and E = potential. By setting $E_{red, corr} = E_{oxid, corr}$, we obtain i_{corr}.

For zinc corroding in an acid solution we can use (Callister, 2000)

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2 \tag{3-35}$$

with E^0_{red} = - 0.763V, E^0_{oxid} = 0 V, $i_{0,red} = 10^{-7}$ A/cm^2, $i_{0,oxid} = 10^{-10}$ A/cm^2,

β_{red} = + 0.09 and β_{oxid} = - 0.08. We are interested in calculating the corrosion rate of zinc. By setting

$$-0.763 + 0.09\log[\frac{i_{corr}}{10^{-7}}] = 0 - 0.08\log[\frac{i_{corr}}{10^{-10}}] \tag{3-36}$$

we have $i_{corr} = 1.19(10^{-4})$ A/cm^2

From Fraday's law (Jones, 1996) corrosion rate, r, in mpy (milli inches per year) $r = \frac{0.129ai}{nD}$

in which: r (mpy), i = current density ($\mu\mathrm{A/cm^2}$), D = density ($\mathrm{g/cm^3}$), n = number of moles, a = gram atomic mass

$$\mathrm{r} = \frac{(0.129)(65.37)119}{2(7.14)} = 70.3\mathrm{mpy} \qquad (3\text{-}37)$$

For copper corroding in an acid solution we can use (Callister, 2000)

$$\mathrm{Cu} + 2\mathrm{H}^+ \rightarrow \mathrm{Cu}^{2+} + \mathrm{H}_2 \qquad (3\text{-}38)$$

with $\mathrm{E^0_{red}}$ = 0.337 V, $\mathrm{E^0_{oxid}}$ = 0 V, $i_{0,red}$ = 2* 10^{-7} $\mathrm{A/cm^2}$, $i_{0,oxid}$ = 10^{-10} $\mathrm{A/cm^2}$,

For β_{red} =+0.09, +0.10, +0.11, +0.12, +0.13, +0.14, and +0.15, β_{oxid} = - 0.08. We are interested in calculating the corrosion rate of copper. By setting

$$0.337 + \underline{0.09} \cdot \log(\frac{i_{corr}}{2*10^{-7}}) = 0 - 0.08\log(\frac{i_{corr}}{10^{-10}}) \qquad (3\text{-}39)$$

we have i_{corr} = 5.8244* (10^{-11}) $\mathrm{A/cm^2}$ when β_{red} is +0.09,

in the same way, i_{corr} =9.1555* (10^{-11}) $\mathrm{A/cm^2}$ when β_{red} is +0.10,

i_{corr} = 1.3722 * (10^{-10}) $\mathrm{A/cm^2}$ when β_{red} is +0.11,

i_{corr}= 1.9752 * (10^{-10}) $\mathrm{A/cm^2}$ when β_{red} is +0.12,

i_{corr}= 2.7462 * (10^{-10}) $\mathrm{A/cm^2}$ when β_{red} is +0.13,

i_{corr}= 3.7054 * (10^{-10}) $\mathrm{A/cm^2}$ when β_{red} is +0.14,

i_{corr}= 4.8711 * (10^{-10})$\mathrm{A/cm^2}$ when β_{red} is +0.15.

From Faraday's law (Jones, 1996) corrosion rate, r, in mpy (milli inches per year) $\mathrm{r} = \frac{0.129\mathrm{ai}}{\mathrm{nD}}$

in which: r (mpy), i = current density ($\mu\mathrm{A/cm^2}$), D = density ($\mathrm{g/cm^3}$), n = number of moles, a = gram atomic mass

$$r = \frac{(0.129)\cdot(63.55)\cdot(i_{corr})}{2\cdot(8.92)} \qquad (3\text{-}40)$$

For different tafel coefficient, r can be calculated as,

$r_1 = 2.67647 * (10^{-5})$ mpy, (when β_{red} : 0.09)

$r_2 = 4.20721 * (10^{-5})$ mpy, (when β_{red} : 0.10)

$r_3 = 6.30593 * (10^{-5})$ mpy, (when β_{red} : 0.11)

$r_4 = 9.07671 * (10^{-5})$ mpy, (when β_{red} : 0.12)

$r_5 = 0.0001262$ mpy, (when β_{red} : 0.13)

$r_6 = 0.0001703$ mpy, (when β_{red} : 0.14)

$r_7 = 0.0002238$ mpy, (when β_{red} : 0.15)

For the maximum values of corrosion rate for copper, $i_{0,red} = 2 * 10^{-7}$ A/cm^2 can be plugged in Eq. (3) instead of i_{corr}. Then, r is <u>0.091905 mpy</u>.

If we convert it, 0.091905 mpy = 0.091905 * 10^{-3} inch/ year = $0.091905 * 10^{-3} * \frac{\text{inch}}{\text{year}} * \frac{25.4(\text{mm})}{1(\text{inch})}$ = 0.002334 mm/ year. From this, we can infer that penetrating a hole through 2 mm thickness of plumbing pipe takes (2/0.0233 = 856.76) about <u>857 years</u>.

Compared to the corrosion rate of zinc (70.3 mpy), the corrosion rate of copper is much slower than that of the zinc.

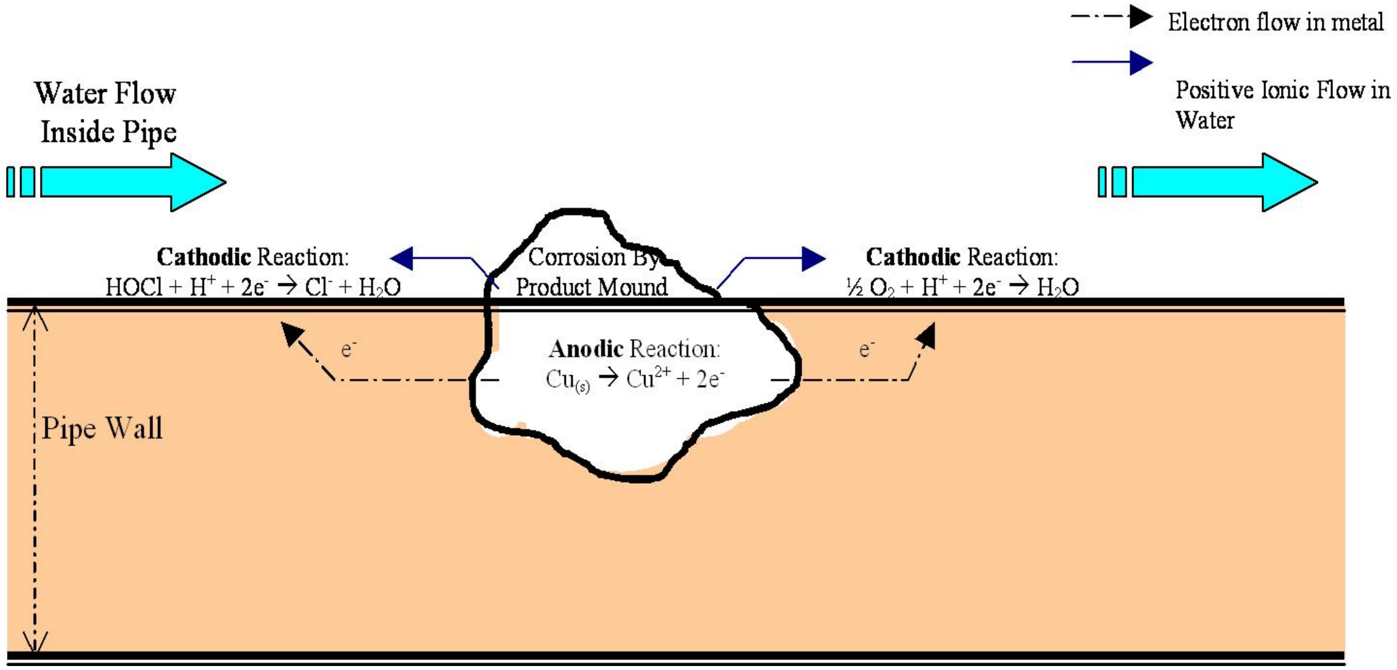

Figure 3.8 Pitting corrosion scheme (From Edwards, 2002 MUSES seminar)

3.5.2 Copper Chemistry

When copper corrodes, it is oxidized to Cu (I) (cuprous) and Cu (II) (cupric) states. They form insoluble precipitates and soluble complexes. They can form scale but often found as suspensions. The soluble complexes influence the solubility of passivating solids and contribute to copper concentration in drinking water. Oxidation of Cu (m) forms Cu^+ as the initial product followed by precipitation of cuprite (Cu_2O).

$$Cu(m) \rightarrow Cu^+ + e^- \tag{3-41}$$

$$2Cu^+ + H_2O \rightarrow Cu_2O_{(S)} + 2H^+ \tag{3-42}$$

Cuprite may be further oxidized to Cu (II) that can precipitate as tenorite (CuO).

$$\frac{1}{2} \cdot Cu_2O_{(s)} + \frac{1}{2} \cdot H_2O \rightarrow Cu^{2+} + OH^- + e^- \tag{3-43}$$

$$Cu^{2+} + H_2O \rightarrow CuO_{(s)} + 2H^+ \tag{3-44}$$

It is widely known that dissolved oxygen (DO) or residual chlorine can act as electron acceptors, and significantly affect copper oxidation and corrosion rates. The various copper solids that may form in water distribution systems are given below.

$$Cu^{+} + Cl^{-} \rightarrow CuCl \text{ (Cuprous chloride: Nantokite)} \qquad (3\text{-}45)$$

$$\mathrm{Cu}^{+} + \mathrm{H}_2 0 - \mathrm{H}^{+} \rightarrow \mathrm{CuOH} \text{ (Cuprous hydroxide)} \qquad (3\text{-}46)$$

$$Cu^{+} + CO_3^{-2} \rightarrow Cu_2CO_3 \text{ (Cuprous carbonate)} \qquad (3\text{-}47)$$

$$2Cu^{+} + SO_4^{2-} \rightarrow Cu_2SO_4 \text{ (Cuprous Sulfate)} \qquad (3\text{-}48)$$

$$2Cu^{2+} + 2H_2O \rightarrow Cu(OH)_2 + 2H^{+} \text{ (Cupric hydroxide)} \qquad (3\text{-}49)$$

3.5.3 Uniform corrosion

Copper is much more resistant to uniform attack than other metals. Evans (1982) showed that the corrosion rate of copper is the slowest as compared to that of iron and zinc. As pH value drops below 6, copper corrosion rate increases in uniform corrosion. This kind of uniform corrosion will shorten the life cycle of the material. The uniform corrosion is typically the result of copper oxidation. According to AWWA (1996), however, at high pH levels, the usual form of corrosion is non-uniform corrosion. The amount of copper corrosion is inversely proportional to the pH. As the pH of the water increases, the corrosion release decreases.

Calcium carbonate scale formation protects copper pipe. It is known that chloride, sulfate, and bicarbonate concentrations have much influence on copper release and corrosion. In addition, water velocity and temperature have significant role in copper corrosion. Velocity influences erosion corrosion. High velocity water can impact the scale and the rate of attack is proportional to temperature and affects the hot water system. In Figure 3.9, it is seen that as the temperature increases, corrosion rate increases and the velocity affects the corrosion rate.

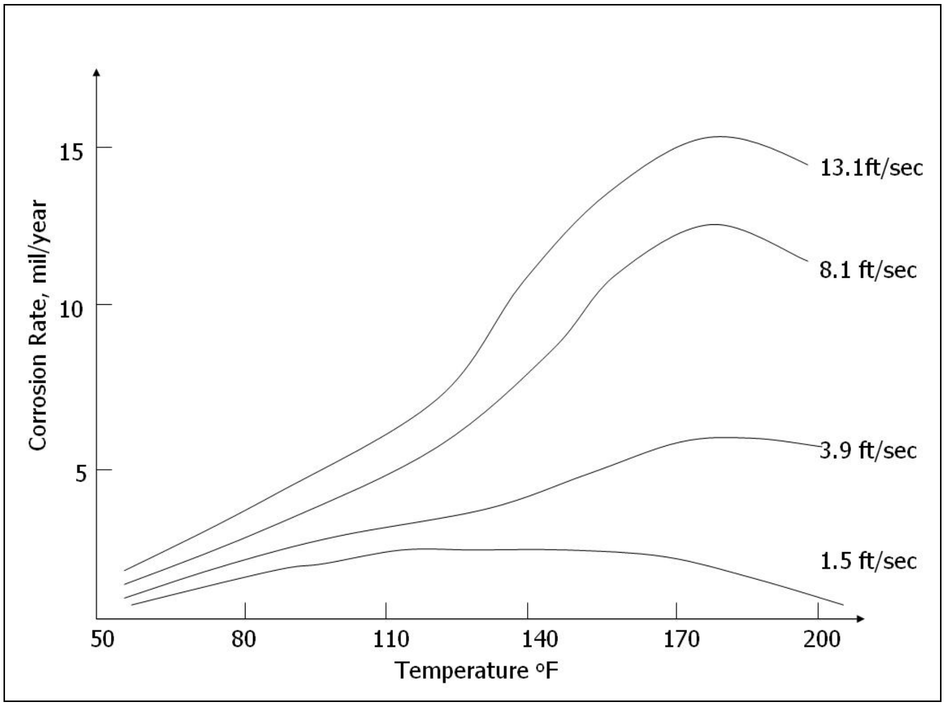

Figure 3.9 Corrosion Rate vs. Temperature (Source: Internal Corrosion of Water Distribution Systems by AWWA, 1996)

3.5.4 Pitting corrosion

When specific areas are targeted, pitting corrosion occurs. Pitting corrosion of copper is occurring at a significant rate across the US. The combination of high residual aluminum, relatively high total chlorine residuals, and pH above 8.2 are observed when pitting is associated with aluminum deposits.

It's known that copper pitting is composed of 1) initiation of pitting, 2) propagation of pitting, and 3) revitalization of the pitting. Serious pitting requires these processes. Rushing (2002) asserts that in order to reduce the pitting corrosion pH should be reduced, add phosphate (PO_4), NOM should be present, and use ferric coagulants ($FeCl_3$). Main causes of pitting are water quality, hydraulics, and microbiology. Rather than just one factor, a combination of these factors influences pitting.

According to AWWA (1996), pH, pE (measure of redox potential), chloride, sulfate, and other organic/inorganic ions; hardness and other organic/inorganic cations; oxidant type and concentration; alkalinity should be considered.

3.5.5 Empirical models

J.R.Myers (1991, from Lane 1993) developed an equation for pit depth in copper tubing exposed to cold aggressive water using experiments.

$$P = 0.04\ t^{1/3} \tag{3-50}$$

Where; P = the pit depth in inches

t = time in years

The requirements are that pH of 7.0 ~ 7.7, DO $\geq$ 3mg/L, Carbon Dioxide $\geq$ 15mg / L, Chloride (Cl^-) $\geq$ 15 mg/ L, and SO_4^{2-} $\geq$ 15 mg/L.

And in hot water

$$P = 0.0148\ t^{0.5} \tag{3-51}$$

Where; P = the pit depth in inches

t = time in years

With a temperature greater than 130° F and containing > 0.1 mg/L aluminum, bicarbonate < 75mg/L, and pH < 7.6, and bicarbonate – sulfate ratio < 1.5.

Illinois State Water Survey (Neff, Sollo, and Lane 1975) determined the corrosion rate for copper pipe in cold water based on data from 21 different locations.

$$\begin{aligned}\text{Corrosion rate (mdd)} = 2.993 &- \{0.03084 * [\text{mg/L carbon dioxide (as } CO_2)]\} \\ &+ [0.001857 * (\text{mg/L TDS})] - [0.3268 * (\text{pH})]\end{aligned} \tag{3-52}$$

(mdd: milligrams per square decimeter per day, so if multiplied by 0.16, that would be exprssion in mils per year(mpy)).

The requirements are that TDS (Total Dissolved Solids) is 115 ~ 1,312 mg/L, CO_2 (as CO_2) is 0.0 ~ 27 mg/L, and pH is 7.1 ~ 9.7.

Edwards, Ferguson, and Reiber (1994) classified pitting corrosion into type I (cold water), type II (hot water), and type III (soft water). Their findings for copper corrosion are shown in Table 3.3.

Table 3.3 Pitting corrosion (Original from Edwards, 1994, summarized from AWWA)

	Effects	Water quality	Main causes	Reducing methods
Type I Pitting (Cold Water)	Failure of pipe	Cold water, pH above 7.	Deposits on pipe, Stagnation at early period, chlorine concentration, Aluminum coagulants	NOM/ increase bicarbonate and pH, orthophosphate
Type II Pitting (Hot water)	Failure of pipe	Hot water, pH below 7.2	High temp, chlorine residuals, Aluminum coagulation	Reduce temperature, pH.
Type III Pitting (Soft Water)	Blue water, release of voluminous by-product	Soft water, pH above 8.0	Stagnation, high pH values, Aluminum coagulation	NOM, avoid stagnation

It takes approximately three to four years, but sometimes within a few months for type I pitting to penetrate the pipe. Pitting is more frequent in Type I than Type II or III. Multiple pits are likely to lie along longitudinal lines. In addition, most pits and leaks are found in horizontally installed pipes. Some of the known conditions for initiation of pitting are associated with the condition of the metal before it is exposed to water and water quality has significant impact related to the propagating tendency. Type II is much slower in corroding than type I and rarely causes failures in a system. If failure happens, it occurs in water temperature greater than $60^{o}C$ and in soft water (water that has scale-forming impurities removed) areas.

3.5.6 Erosion corrosion

Copper is a soft metal and readily damaged than other metals. Copper pipe is susceptible to erosion corrosion. High velocity (greater than 4 ft/sec) and temperature are the main reasons for erosion corrosion. High velocity usually results from faulty workmanships. There are national standards that restrict the velocity. National Association of Corrosion Engineer's recommendation is 4fps for K copper pipe. Temperature is also an important factor for erosion corrosion. Majority of the erosion corrosion is reported from hot water tubing system. In this situation, the velocity should be less than 1.5fps by national recommendation (AWWA, 1996).

3.5.7 Microbiologically Induced Corrosion

It is known that in interior pipe surfaces, bacteria can be the cause of copper corrosion. Bacteria often grow in biofilms with scales and corrosion products. Experiments show that after disinfections, the rate of problems has decreased.

3.6 Summary

In this chapter, a general review of corrosion is presented. First, the various types of corrosion that can occur in water contacting metals are described. Corrosion rate is crucial in the decision making process. As the focus of the thesis is on drinking water copper pipe, corrosion of copper pipe contacting potable water is addressed in detail. Corrosion scale, copper chemistry, and frequent forms of corrosion in copper pipe are explained.