محاضرات – رابعة كيمياء خاص – corrosion

### FORMS OF CORROSION

This introductory section includes basic definitions related to chemical and electrochemical reactions in the forward (f) and reverse (r) directions. The word **Corrosion** stands for material or metal deterioration or surface damage in an aggressive environment. Corrosion is a chemical or electrochemical oxidation process, in which the metal transfers electrons to the environment and undergoes a valence change from zero to a positive value z, The environment may be a liquid, gas or hybrid soil-liquid. These environments are called electrolytes since they have their own conductivity for electron transfer.

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An electrolyte is analogous to a conductive solution, which contains positively and negatively charged ions called cations and anions, respectively. An ion is an atom that has lost or gained one or more outer electron (s) and carries an electrical charge. Thus, the corrosion process which can be chemical in nature or electrochemical due to a current flow, requires at least two reactions that must occur in a particular corrosive environment. These reactions are classified as anodic and cathodic reactions and are defined below for a metal M immersed in sulfuric acid  $H_2SO_4$ solution as an example. Hence, metal oxidation occurs through an anodic reaction and reduction is through a cathodic reaction as shown below.

$$M \rightarrow M^{+z} + ze^{-} \qquad (Anodic \equiv Oxidation) \ (1.1a)$$

$$zH^{+} + zSO_{4}^{-} + ze^{-} \rightarrow \frac{z}{2}H_{2}SO_{4} \qquad (Cathodic \equiv Reduction)(1.1b)$$

$$M + zH + zSO_{4}^{-} \rightarrow M^{+z} + \frac{z}{2}H_{2}SO_{4} \qquad (Overall \equiv Redox) \ (1.1c)$$
where
$$M = \text{Metal} \qquad M^{+z} = \text{Metal cation}$$

$$H^{+} = \text{Hydrogen cation} \qquad SO_{4}^{-} = \text{Sulfate anion}$$

$$Z = \text{Valence or oxidation state}$$

The interpretation of the above equations indicate that an anodic reaction, which is equivalent to what is known as oxidation, loses  $Ze^{-}$  metal electrons and the cathodic reaction accepts or gains  $Ze^{-}$ electrons for reducing pertinent ions. Consequently, both anodic and cathodic reactions are coupled in a corrosion process. Adding eq. (1.1a) and (1.1b) yields eq. (1.1c). Thus, REDOX (RED = reduction and OX = oxidation) is the resultant reaction equation, eq. (1.1c), and represents the overall reaction at equilibrium where the anodic and cathodic reaction rates are equal. Observe that the anodic reaction is also referred to as an oxidation reaction since it has lost  $Ze^-$  electrons, which has been gained by the cathodic reaction for producing sulfuric acid  $H_2SO_4$  Thus, a cathodic reaction is equivalent to a reduction reaction. Furthermore, The arrows in eq. (1.1) indicate the reaction directions as written and they represent irreversible reactions. On the other hand, a reversible reaction is represented with an equal sign. Thus, the metal reaction can proceed to the right for oxidation or to the left for reduction as indicated by eq. (1.2)

$$M = M^{+z} + ze^{-} \tag{1.2}$$

This expression means that the reaction proceeds from left to right or vice versa under specific chemical or electrochemical conditions. The concepts of metal oxidation and metal reduction or electrode position are schematically shown in Figure 1.1. The dark thick line on the metal electrode is a representation of metal deposition as a result of metal ion reduction and metal oxidation is shown on the left-hand side of the electrode.



Figure 2.1 Schematic electrochemical cell.

# **Classification of Corrosion**

There is not a unique classification of the types of corrosion, but the following classification is adapted hereafter.

## **1- General Corrosion (or Uniform Corrosion)**

This is the case when the exposed metal/alloy surface area is entirely corroded in an environment such as a liquid electrolyte (chemical solution, liquid metal), gaseous electrolyte (air,  $CO_2$ ,  $SO_2^$ etc.), or a hybrid electrolyte (solid and water, biological organisms, etc.). Some types of general corrosion and their description are given below.

- **a- Atmospheric Corrosion** on steel tanks, steel containers, *Zn* parts, *Al* plates, etc..
- **b-Galvanic Corrosion** between dissimilar metal/alloys or microstructural phases (pearlitic steels,  $\alpha \beta$  copper alloys,  $\alpha \beta$  lead alloys).
- **c- High-Temperature Corrosion** on carburized steels that forms a porous scale of several iron oxide phases.
- **d- Liquid-Metal Corrosion** on stainless steel exposed to a sodium chloride (*NaCl*) environment.
- e- Molten-Salt Corrosion on stainless steels due to molten fluorides, LiF and  $BeF_2$ , etc.).
- **f- Biological Corrosion** on steel, Cu-alloys, Zn-alloys in seawater.
- g- Stray-Current Corrosion on a pipeline near a railroad.

Now we will dissected one by one

**a**-<u>Atmospheric Corrosion</u>: This is a uniform and general attack, in which the entire metal surface area exposed to the corrosive environment is converted into its oxide form, provided that the metallic material has a uniform microstructure.

Aqueous corrosion of iron (*Fe*) in  $H_2SO_4$  solution and of *Zn* in diluted  $H_2SO_4$  solution are examples of uniform attack since *Fe* and *Zn* can dissolve (oxidize) at a uniform rate according to the following anodic and cathodic reactions, respectively.

$$Fe \rightarrow Fe^{+2} + 2e^{-}$$
 (1.3a)

$$2H^+ + 2e^- \rightarrow H_2 \uparrow \tag{1.3b}$$

$$Fe + 2H^+ \rightarrow Fe^{+2} + H_2 \uparrow$$
 (1.3c)

$$Z \rightarrow Z^{+2} + 2e^{-} \tag{1.4a}$$

$$2H^+ + 2e^- \rightarrow H_2 \uparrow$$
 (1.4b)

$$Z + 2H^+ \rightarrow Z^{+2} + H_2 \uparrow \qquad (1.4c)$$

where  $H_2 \uparrow$  is hydrogen gas. The cathodic reaction is the common hydrogen evolution process. In fact, the aggressiveness of a solution to cause a metal to oxidize can be altered by additions of water, which is an amphitheatric compound because it can act as an acid or base due to its dissociation as indicated below

$$H_2 O \to H^+ + O H^- \tag{1.5}$$

Atmospheric corrosion of a steel structure is also a common example of uniform corrosion, which is manifested as a brown-color corrosion layer on the exposed steel surface. This layer is a ferric hydroxide compound known as **Rust**. The formation of **Brown Rust** is as follows

$$(Fe \rightarrow Fe^{+2} + 2e^{-})(x2)$$
 (1.6a)

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{1.6b}$$

$$2Fe + O_2 + 2H_2O \rightarrow 2Fe^{+2} + 4OH^- \rightarrow 2Fe(OH)_2 \downarrow (1.6c)$$

$$2Fe(OH)_2 + \frac{1}{2}O_2 + H_2O \quad \rightarrow \quad 2Fe(OH)_3 \downarrow \equiv Fe_2O_3 \cdot 3H_2O \downarrow \quad (1.7)$$

where (x2) = Multiplying factor for balancing the number of electrons  $2Fe(OH)_2 =$  Ferrous hydroxide (unstable compound)  $2Fe(OH)_3 =$  Ferric hydroxide (with  $Fe^{+3}$  cations)  $Fe_2O_3 \cdot 3H_2O =$  Hydrated Ferric hydroxide  $\downarrow =$ The compound precipitates as a solid

In addition, Zn can uniformly corrode forming a White Rust according to the following reactions

$$(Zn \rightarrow Zn^{+2} + 2e^{-})x^2$$
 (1.8a)

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{1.8b}$$

$$2Zn + O_2 + 2H_2O \rightarrow 2Zn^{+2} + 4OH^-$$
 (1.8c)

$$2Zn^{+2} + 4OH^{-} \rightarrow 2Zn(OH)_{2} \downarrow \qquad (1.8d)$$

$$2Zn(OH)_2 + CO_2 + O_2 + H_2O \rightarrow Zn_4CO_3 \cdot (OH)_6 \downarrow \qquad (1.9)$$

In fact, the compound or is zinc carbonate  $Zn_4CO_3.(OH)_6$  or  $ZnCO_3 3Zn(OH)_2$  or white rust or wet-storage stain (porous). Atmospheric corrosion of aluminum is due to a passive oxide film formation instead of a porous layer. The gray/black-color film may form as follows

$$(Al \rightarrow Al^{+3} + 3e^{-})x2 \qquad (1.10a)$$

$$\frac{3}{2}O_2 + 3H_2O + 6e^- \to 6OH^-$$
(1.10b)

$$2Al + \frac{3}{2}O_2 + 3H_2O \rightarrow 2Al^{+3} + 6OH^- \rightarrow Al_2O_3 \cdot 3H_2O \downarrow \quad (1.11)$$

In general, the oxidation process can be deduced using a proper Pourbaix diagram, as schematically shown in Figure 1.2. This diagram is a plot of electric potential of a metal as a function of pH of water at  $25^{\circ}C$ 

This type of diagram indicates the possible electrochemical process on a metal surface if the potential and the pH of the electrochemical systems are known or estimated. In fact, corrosion rates can not be determined from a Pourbaix diagrams. The diagram includes regions identified as corrosion where a metal oxidizes, passive region where a metal is protected by a stable oxide film being adhered on the metal surface, and immunity where corrosion or passivation are suppressed.



Figure 2.2 Schematic Purbaix diagram for a hypothetical metal.

Furthermore, the **prevention of uniform corrosion** can be accomplished by selecting an adequate 1) material having a uniform microstructure, 2) coating or paint, 3) inhibitor(s) for retarding or suppressing corrosion. These are classified as adsorption-type hydrogen-evolution poisons, scavengers, oxidizers, and vapor-phas,

and 4) cathodic protection, which is an electrochemical process for suppressing corrosion in large steel structures. Figures 1.3 and 1.4 show atmospheric uniform corrosion on typical structures. Both the steel bridge structures and the pipeline were exposed to air by the ocean. Notice how the steel structures were subjected to chemical reactions, which proceeded uniformly over the exposed metal surface area.



Figure 2.3 Uniform corrosion (atmospheric attack) of a steel bridge.



Figure 2.4 Uniform corrosion (atmospheric attack) of a pipeline located on a concrete pier above the ocean water.

**b-** <u>Galvanic Corrosion</u>: Galvanic corrosion is either a chemical or an electrochemical corrosion. The latter is due to a potential difference between two different metals connected through a circuit

for current flow to occur from more active metal (more negative potential) to the more noble metal (more positive potential).

Galvanic coupling is a galvanic cell in which the anode is the less corrosion resistant metal than the cathode. Figure 1.5 shows atmospheric galvanic corrosion of a steel bolt-hexagonal nut holding a coated steel plate and. Both corroded bolt-nut and the steel box are the anodes having very small surface areas, while the coated steel plate and the steel post have very large cathodic surface areas. Corrosion rate can be defined in terms of current density, such as i = I/A where I is the current and A is the surface area. Therefore, the smaller A the larger i. This is an area effect on galvanic coupling. Thus, the driving force for corrosion or current flow is the potential (voltage) E between the anode and cathode. Subsequently, Ohm's law, E = IR = iAR, is applicable. Here, R is the galvanic cell resistance.



Figure 2.5 Galvanic corrosion (atmospheric attack) of a a) steel bolt/nut and b) steel sheet box attached to a painted steel electrical post.

In addition, galvanic corrosion can be predicted by using the electromotive force (emf) or standard potential series for metal reduction listed in Table 2.1. These reactions are reversible. The standard metal potential is measured against the standard hydrogen

electrode (*SHE*), which is a reference electrode having an arbitrary standard potential equals to zero.

In selecting two metals or two alloys for a galvanic coupling, both metals should have similar potentials or be close to each other in the series in order to suppress galvanic corrosion. For example, Fe-Cr, Cu-Sn or (bronze) couplings develop a very small potential differences since they are close to each other in their respective standard potential series. The given data in Table 2.1 is very appealing in designing against galvanic corrosion of pure metals. The closer the standard potentials of two metals the weaker the galvanic effect; otherwise, the galvanic effect is enhanced.

Eventually, galvanic coupling can be used for cathodic protection purposes. In fact, in coupling two different metals the metal with the lowest standard potential acts as the anode and its standard potential sign is changed. Figure 1.6 shows two galvanic coupling cases, in which copper and zinc can be in the form of sheets or electroplated coatings. Recall that iron (*Fe*) is the base metal for steel; therefore, *Fe* is to be protected against corrosion. Therefore, *Fe* is the anode for *Cu* and the cathode for *Zn* couplings. In the latter case, Zn becomes a sacrificial anode, which is the principle of coupling for galvanized steel sheets and pipes. On the other hand, if Cu coating breaks down, steel is then exposed to an electrolyte and becomes the anode, and therefore, it oxidizes. These two cases are schematically shown in Figure 2.6.

Other types of galvanic coupling are batteries and fuel cells. Both are electrochemical power sources in which chemical energy is converted into electrochemical energy through controlled redox electrochemical reactions. Subsequently, these electrochemical devices represent the beneficial application of galvanic corrosion. Among the reactions that occur in batteries, high hydrogen evolution is desirable, includes details of several types of batteries and fuel cells which are briefly described below.



Figure 2.6 Schematic galvanic couplings [5].

## i) Lithium Ambient-Temperature Batteries (LAMBS):

These are high energy density devices, in which the  $Li^+$  anode is passivated. The solid cathode can be made of LiCuO,  $LiMnO_2$ ,  $LiV_2O_5$  or  $LiBi_2Pb_2O_5$  Some LAMBS use liquid cathodes, such as For negative cathodes made of carbon (graphite or coke) in lithiumion batteries, the reaction on this electrode is

$$C_6 + xLi^+ + xe^- \quad \xleftarrow{Charge}{Discharge} = Li_xC_6 \tag{1.12}$$

The reduction reaction is for charging and the oxidation is for discharging processes of the lithium-ion cells.

ii) <u>Lead-Acid Battery</u>: The basic operation of a lead-acid  $Pb-H_2SO_4$  battery is based on groups of positive and negative plates immersed in an electrolyte that consists of diluted sulfuric acid and water. Hence, the mechanism of this type of battery is based on the electron-balanced anodic (-)

cathodic (+) reactions. Hence, the ideal electrode reactions are reversed and during charging  $\xrightarrow{c}$  and discharging  $\xleftarrow{d}$  uy

Cathode (+) : 
$$PbSO_4 + 2H_2O \stackrel{\sim}{\underset{d}{\leftarrow}} PbO_2 + 3H^+ + HSO_4^- + 2e$$
 (a)

Anode (-) : 
$$PbSO_4 + H^+ + 2e \xrightarrow{Charge}_{Discharge} Pb + HSO_4^-$$
 (b)

The redox reaction in lead-acid batteries is the sum of the above half-cell reaction

Redox:  $2PbSO_4 + 2H_2O \xrightarrow{Charge}_{Discharge} PbO_2 + 32H^+ + 2HSO_4^- + Pb$  (1.13) According to the above half-cells, the anode is pure lead Pb and the cathode is lead dioxide  $(PbO_2)$  In addition, both electrodes dissolve electrolyte during discharge, forming lead the in sulfate  $(PbSO_4)$  However, when the battery is charged, reverse reactions occur. Thus, this reversible electrochemical cycle can last for a prolong time, but in practice batteries have a finite lifetime due to the lead sulfate build-up acting as an insulation barrier. Most automotive batteries have lead-calcium grids for maintenance-free and have a life time from 1 to 5 years; however, longer battery life is possible. Generally, a lead-acid battery is used as a 12 - voltelectrochemical device, which consists of six 2 - volt cells connected in series. The average activity and density of the sulfuric acid

solution are in the order of  $4.5 \, mol/L = 4.5 \, x 10^{-3} \, mol/L$ =  $432 \, g/L$  and  $1.25 \, g/cm^3$  at 20°C, respectively. If the battery is overcharged, then electrolysis (dissociation) of water occurs leading to hydrogen evolution at the cathodes and oxygen evolution at the anodes. In general, batteries can store and supply energy because of the interactions between the electrodes submerged in the electrolyte.

**Dry-Cell Battery:** This is a common galvanic cell which contains a moist ammonium chloride electrolyte. An schematic battery is shown in Figure 2.7. The zinc casing and the solid carbon in contact with the electrolyte (electric conductor) develop a potential difference, which in turn, produces an electron flow when the zinc and carbon are electrically connected. Consequently, the zinc eventually corrodes galvanically since it provides the electrons to the electrolyte for generating reduction reactions. The electrolyte (moist paste) carries the current from the zinc anode to the carbon cathode.



Figure 2.7 Two-dimensional view of a schematic dry-cell battery

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**iii) Sintered Nickel Electrode in Alkaline Batteries:** These batteries are galvanic devices containing a porous *Ni* matrix that holds the active (anodic) materials. The following reaction is reversed upon discharging

$$Ni(OH)_2 + OH^- \xleftarrow{Charge}{Discharge} NiOOH + H_2O + e^-$$
 (1.15)

In addition, corrosion of the *Ni* electrode may occur under unfavorable conditions, leading to loss of electrical continuity due to the following reaction

$$2Ni + O_2 + 2H_2O \quad \xleftarrow{Charge}{Discharge} \quad 2Ni(OH)_2 \tag{1.16}$$

Other side reactions must be taken into account for characterizing nickel-hydrogen cells. The subject of galvanic corrosion is discussed in next chapter using polarization curves. For purpose of clarity, the driving force for current flow through a moist electrolyte and electrochemical corrosion is the potential (voltage) difference between the anode and the cathode electrodes. With this in mind, an example usually helps the reader to understand the simple mathematics and parameters involved in determining the magnitude of the available driving force needed to operate a simple battery for a time t in fact, a battery is simply an electrochemical device used as a energy storage. Thus, the reader is briefly introduced to the concepts of electric charge (Q), the Faraday's constant (F) and valence. **Example** : Calculate a) the mass and number of moles of the available of the mass and number of moles of the mass

manganese dioxide  $MnO_2$  in the electrolyte if the battery has a stored energy of 36kJ/V and a power of 3 Watts. c) Find the time it takes to consume the stored energy if the battery operates at a current of 2 A and the potential (voltage). The thickness of the cell is x = 1mm. Other dimensions, such as length (L) and radius r, are indicated below. The discharging reaction is

 $MnO_2 + H^+ + e \rightarrow MnOOH$ 



### **Solution :**

The stored energy needs to be converted into units of coulombs. Hence,  $Q = 36 \ kJ/V = 36,000 \ A.s = 36,000 \ Coulombs$ The area and volume are  $A_s = 2\pi Lr = (2\pi) (6 \ cm) (1.5 \ cm) = 56.55 \ cm^2$  $V = xA_s = (0.1 \ cm) (5.6549 \ cm^2) = 5.65 \ cm^3$ 

a) The mass and the moles of **Zn** are

$$m_{Zn} = V\rho = (5.65 \text{ cm}^3) (7.14 \text{ g/cm}^3) = 40.34 \text{ g}$$
  
$$X_{Zn} = \frac{m_{Zn}}{A_{w,Zn}} = \frac{40.34 \text{ g}}{65.37 \text{ g/mol}} = 0.62 \text{ mol}$$

b) The moles and the mass of MnO<sub>2</sub> are

$$\begin{array}{rcl} X_{MnO_2} &=& \displaystyle \frac{Q}{zF} = \frac{36,000 \ A.s}{(1) \ (96,500 \ A.s/mol)} \\ X_{MnO_2} &=& 0.37 \ mol \\ M_{MnO_2} &=& \displaystyle X_{MnO_2}A_{w,MnO_2} = (0.37 \ mol) \ (86.94 \ g/mol) \\ M_{MnO_2} &=& \displaystyle 32.17 \ g \end{array}$$

*c) The time for discharging the stored energy and the potential are* 

$$t = \frac{Q}{I} = \frac{36,000 \text{ A.s}}{2 \text{ A}} = 5 \text{ hours}$$
  
$$E = P/I = (3 \text{ V.A}) / (2 \text{ A}) = 1.5 \text{ V}$$

#### MICROSTRUCTURAL EFFECTS

A mechanically deformed metal or alloy can experience galvanic corrosion due to differences in atomic plane distortion and a high dislocation density. In general, dislocations are line defects in crystals. Figure 2.8a shows a mechanically worked steel nail indicating localized anodes. The tip and the head of the nail act as stress cells for oxidation of iron to take place, provided that the nail is exposed to an aggressive environment. These two parts of the nail are examples of strain hardening, but are susceptible to corrode galvanically due to the localized crystal defects and the presence of mainly compressive residual stresses induced by the mechanical deformation process. Furthermore, the nail shank act as the cathode and the tip/head-shank form galvanic cells in a corrosive environment.

In addition, improper heat treatment can cause non-uniform microstructure and therefore, galvanic-phase corrosion is enhanced in corrosive media. In a crystalline metal, galvanic coupling can occur between grains and grain boundaries. Figure 1.8b shows a schematic microstructure of a metal subjected to corrosion along the grain boundaries, as in the case of a typical polished and etched microstructure. This type of corrosion can be referred to as grainboundary corrosion because the grain boundaries act as anodes due to their atomic mismatch and possible segregation of impurities.



Figure 1.8 Localized galvanic cells. a) Stress cells and b) microcells.

Galvanic corrosion can occur in a polycrystalline alloys, such as pearlitic steels, due to differences in microstructural phases. This leads to galvanic-phase coupling or galvanic microcells between ferrite  $(\alpha - Fe)$  and cementite  $(Fe_3C)$  since each phase has different electrode potentials and atomic structure. Therefore, distinct localized anodic and cathodic microstructural areas develop due to microstructural inhomogeneities, which act as microelectrochemical cells in the presence of a corrosive medium (electrolyte). This is an electrochemical action known as galvanic corrosion, which is mainly a metallic surface deterioration.

This form of corrosion is not always detrimental or fatal to metals. For instance, revealing the microstructure of pearlitic steels with a mild acid can be accomplished due to the formation of galvanic microcells. In this case, pearlitic consists of ferrite and cementite and when it is etched with a mild acid, which is the electrolyte, galvanic microcells between ferrite (*cathode*) and cementite (*anode*) are generated. Consequently, pearlitic is revealed as dark cementite and white ferrite.

In addition, if a zinc is immersed in hydrochloric acid HCl (reagent) at room temperature and it spontaneously reacts in this strong corrosive environment. Figure 2.9 shows a galvanized steel nail was immersed in such as solution. Notice that nail is covered with hydrogen bubbles. This is an example of hydrogen evolution that occurs in acid solutions. Thus, HCl acid solution acts as an oxidizer and the corrosion rate of zinc is increased very rapidly. The initial chemical reactions for the case shown in Figure 2.9 are similar to eq. (2.14) with the exception of the source of the hydrogen ions. In general, the following reactions take place on the surface of the galvanized steel nail surface during oxidation

$$Zn \longrightarrow Zn^{+2} + 2e^{-}$$
 (1.16)

$$HCl \longrightarrow H^+ + Cl^-$$
 (1.17)

$$2H^+ + 2e^- \longrightarrow H_2 \uparrow \tag{1.18}$$

 $Zn + HCl \longrightarrow Zn^{+2} + H_2 \uparrow + Cl^-$  (1.19)



Figure 1.9 A galvanized steel nail reacting in concentrated HCl acid solution.

Furthermore, solid surfaces, such as automobile underbody parts, in contact with a mixture of mud, soil and salt can deteriorate due to galvanic corrosion. In this case, the mixture is an stagnant electrolyte that causes the least galvanic action when compared with agitated electrolytes. In fact, agitation and temperature gradients can accelerate the galvanic action due to a higher current density and consequently, galvanic corrosion is manifested as metal dissolution. If the corroding metal part is under the influence of a tensile stress, then it may become weak and may fail due to reduction in cross-sectional area.

Furthermore, the microstructure of crystalline solids is composed of grains, which are surrounded by grain boundaries. A single grain is composed of a regular and repeated array of atoms, which in turn, form the atomic structure. The most common crystal lattices in engineering materials are the body-centered cubic (BCC), facecentered cubic (FCC) and hexagonal close-packed (HCP). For instance, Figure 1.10. shows the BCC crystal structure encountered in engineering metallic materials, such as chromium, iron, carbon steels, molybdenum and the like. On the other hand, brass and the 300-series stainless steels have an FCC crystal structure. Other crystal structures can be found in any book on Physical Metallurgy and Materials Science. The closed-packed spheres in Figure 1.10 represent an atomic arrangement having unit cells, which repeat themselves forming the lattice crystal structure. Each atom is bounded to its neighbors and each atom has its nucleus surrounded by electrons. The outer atoms forming the electrode surface exposed to a corrosive medium become electron-deficient and are detached from the lattice and form part of the medium, such as an aqueous electrolyte or react with atoms from the medium to form a surface corrosion product. The corrosion rate in terms of current density or penetration per time is the kinetic parameter that must be determined experimentally.



Figure 1.10 Closed packed body-centered cubic crystal structure

The grain boundaries in crystalline solids represent high-energy areas due to the atomic mismatch and therefore, they are considered microstructural defects, which corrode more rapidly than the grain surfaces. Figure 2.11 illustrates two microstructures of AISI 304 stainless steel being annealed at 1000°C for 0.5 hours and 24 hours 1100°C consolidated for a rapidly solidified and at  $Ni_{53}Mo_{35}B_9Fe_2$  alloy (RSA). Figure 2.12a shows the grain boundaries as dark lines because of the severe chemical attack using an Aqua Regia etching solution (80% HCl + 20% HNO<sub>3</sub>). Figure 1.12b shows crystalline particles embedded in an Ni-Mo matrix after being etched with Marble's reagent. Denote that the RSA alloy does not have visible grain boundaries, but it is clear that the severe chemical attack occurred along the matrix-particle interfaces due to

localized galvanic cells. These interfaces appear as bright areas due to optical effects.



Figure 2.11 Photomicrograph revealing the microstructure of annealed a) AISI stainless steel 304 at 200x and b) rapidly solidified alloy (RSA)  $Ni_{53}Mo_{35}B_9Fe_2$  at 5,000x [19]

Another metallurgical aspect to consider is the dislocation network encounter in plastically deformed alloys. In general, dislocations are linear defect, which can act as high energy lines and consequently, they are susceptible to corrode as rapidly as grain boundaries in an corrosive medium. Figure 2.12 illustrates dislocation networks in an AISI 304 stainless steel and in RSA  $Ni_{53}Mo_{35}B_9Fe_2$  The relevant pretreatment conditions can be found elsewhere. as rapidly as grain boundaries in an corrosive medium. Figure 2.12 illustrates

With respect to Figure 2.12b, there is a clear grain boundary shown as a dark horizontal line across the upper part of the TEM photomicrograph. The small white areas surrounded by dislocations are called sub-grains, which are crystal having an FCC structure for both alloys.

- A number of measures may be taken to significantly reduce the effects of galvanic corrosion:
- 1. Avoiding galvanic couples, especially if these metals are further apart in the galvanic series.

- 2. If coupling of dissimilar metals is necessary, metals that are close together in the galvanic series should be chosen and the cathodic/anodic area ratio must below.
- 3. During the design, easier replacement of the anodic material must be predicted and planned, or the thickness of the anodic material must be increased.
- 4. Connections between metals must be insulated with insulated flanges, and metal surfaces must be insulated with paints or coatings.
- 5. A third, more anodic metal can be electrically connected to the other two, leading to a form of cathodic protection.
- 6. If the system is a closed system, inhibitors should be used.

## c-Corrosion in Water

**i.** <u>**Corrosion in Seawater**</u>: In the seawater, salt concentration varies from 32 g/L up to 36 g/L in tropical waters and away from the coasts. Of this 36 g, roughly around 20 g is Cl, 11 g is Na, 3 g is S04,1 g is Mg, 0.5 g is Ca, 0.5 g is K, and the rest is bicarbonates, bromides, and strontium. Salt concentration (S) of sea is calculated by multiplying a constant with chloride percentage by weight:

Salt Concentration 
$$(g/kg) = 1.80655 \times wt.of chlorides$$
  
per liter of seawater $(g/kg)$  (4)

Dissolved oxygen concentration decreases with salt concentration, and it is 11.0 mg/L at 0°C for 36g/L chloride concentration, compared to 14.6 mg/L in fresh water. There are differences in terms of aeration and thus in terms of dissolved oxygen concentration reaching different parts of a steel structure embedded in the sea. The part of the steel structure over the sea water is exposed to atmospheric corrosion, which is like a marine environment with high chloride concentrations. The part at the sea level is always wetted with the waves and is also called the "splash zone," and the corrosion deposits are constantly washed away and cannot form a protective layer on the metal surface. The corrosion rate is the highest at this level. Right below the sea level, structure gets wet and dry, a protective layer can form promptly, and thus the corrosion rate is relatively low. Inside the sea in the regions near the sea surface, corrosion rate is also high, since the structure is always wet and dissolved oxygen concentration is high. At the lowest level of the structure in the deeper sea level, the dissolved oxygen concentration is the lowest, and thus the corrosion rate is the lowest as well.

Sea water's pH is 8 on average; however, it is higher near the surface of the sea since the plants that live at the surface of the sea get sunlight and use dissolved carbon dioxide for photosynthesis, thus reducing the pH. At deep waters, due to formation of carbon dioxide and hydrogen sulfide originating from rotting dead bodies of living organisms, pH is around 7.5.

High conductivity of seawater causes formation of macro corrosion cells in addition to the microcells. Low ohmic resistance of the electrolyte results in the large ratio of the cathodic area to anodic area leading to severe pitting corrosion. Secondly, high chloride concentrations prevent reformation of passive films on the surfaces of metals that can normally passivate, e.g., aluminum and iron, making them susceptible to corrosion in the seawater. Calcium and magnesium ions present in the seawater can precipitate on the metal surface, which is accelerated with the formation of hydroxide ions at the cathode, and especially when cathodic protection is applied. Therefore, while the required current for cathodic protection is high during the first several days, less is needed after the formation of the protective layer, which consists of 57% calcium carbonate, 19% iron oxides and hydroxides, 8% silicates, and 16% magnesium hydroxide, calcium sulfate, and others.

In general, temperature increases corrosion rate in seawater as well; however, since it also leads to quick formation of the protective layer and decreases the dissolved oxygen concentration, a peak of maximum corrosion is reached at around 80°C, and the corrosion rate reduces thereafter.

Some plants and animals that live in the sea adhere to the protective coating on the metal surface, leading to "fouling effect," which reduces the diffusion of oxygen to the metal surface and at the same time forms an acidic environment due to their rotten dead bodies, leading to increased corrosion as a result. These living organisms damage the paint coatings as well, unless the paint is poisonous.

Mobility of the metallic structures in the sea also affects the corrosion rate; for example, ships in seas with strong waves are more susceptible to corrosion, as it is clear in the case of application of cathodic protection, since the cathodic protection current need doubles when the ship is in motion, compared to being anchored at a port.

concentration is higher in fresh waters compared to the seawater since it decreases with increasing salt concentration, and thus it is very dangerous to use pipes made of steel and copper in cold water or cooling water systems, for instance. However, dissolved oxygen concentration is relatively very low in closed circulated hot water systems due to the decreasing dissolved oxygen concentration with increasing temperature; thus it is not appropriate to replace radiator waters, since it will cause the oxygen to be replenished, and so oxygen scavengers such as sulfites or hydrazine are used to totally remove the oxygen. The amount of dissolved oxygen in distilled water at  $0^{\circ}$ C is 14.6 mg/L, which decreases down to 2.8 mg/L 80°C. Therefore, although the corrosion rate doubles with every 10°C increase in temperature, due to the reduction in dissolved oxygen concentration, a peak is reached at around 80°C, as it is the case in seawater, and the corrosion rate reduces thereafter until the temperature reaches 100°C, at which points water evaporates, resulting in a dissolved oxygen amount of 0, and aqueous corrosion ceases.

Substantial corrosion takes place for pH values lower than 4 even in the absence of oxygen, since the primary cathodic reaction at that pH level will be hydrogen reduction.

Corrosion is impeded due to water hardness precipitating on metal surfaces in the form of calcium carbonate along with the other corrosion products present at the metal surface at pH values higher than the saturation pH (pHs):

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$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + H_2O + CO_2$$
 (Eq. 59)  
If pH is lower than pHs, then the existing calcium carbonate  
precipitates may also dissolve back into the solution in the form of  
bicarbonates. The difference between both pH values is called the  
Langelier index, which is used to determine whether a protective  
shell is formed or not:

$$Langelier index (L) = pH - pHs,$$
(5)

while for values of L > 0,  $CaCO_3$  precipitation occurs; for values of L < 0, it does not.

**d-** <u>High Temperature Corrosion</u> : High temperature corrosion is a type of dry corrosion. Oxidation of metals and alloys at high temperatures is one of the fundamental problems in energy production technology, as it is in gas turbines. As a result of oxidations at high temperatures, eutectic mixtures of low melting points can also form between the different oxides of the metals as they occur in the case of hot vapor turbines. Oxides generally are semiconductors. ZnO, for instance, is less protective when Zn<sup>+2</sup> ions are replaced with Al<sup>+3</sup>, since Al<sup>+3</sup> will donate the extra electron it has to the ZnO film, making it an ntype semiconductor, while it will be more protective when Zn<sup>+2</sup> ions are replaced with Li<sup>+</sup>. Spinel oxides have less conductivity, such as dark red FeO.Al<sub>2</sub>O, which has 18% Al and is used instead of chromium steels at low temperatures, because at high temperatures, less noble element in the alloy oxidizes at the surface, leaving the nobler metal behind, making the alloy rich in the nobler element. Thus, if nickel is alloyed with gold, for instance, gold forms a protective coating at the surface at high temperatures.

In petroleum refining, lighter products separate during the refining process, which leads to an increase in the concentration of sulfur and vanadium, creating problems that surface during energy production. Vanadium compounds that have low melting points lead most alloys to be able to be used only for a few months unless Co-Cr alloys are used as structural materials. Another prevention method is increasing the melting points of vanadium compounds with the addition of calcium and magnesium compounds. On the other hand, extracting vanadium from within the system is an expensive method. Sulfates and pyrosulfates also lead to the formation of low melting point compounds; however, calcium and magnesium compounds bind 90% of the sulfur.

Melted salts increase conductivity, and presence of oxidizing and reducing agents prevent polarization, which both accelerate corrosion at high temperature environments.

Nonmetals such as concrete easily break during freezing and melting, especially if there are salt and acidic anhydrides such as carbon dioxide and sulfur dioxide present in the environment. Acidic anhydrides become acids with rain waters and become even more concentrated due to the presence of bacteria, which are the primary cause of wooden materials to break apart. Polymers and plastics can also break due to UV light, ozone, solvents, and vapors. Use of carbon black pigment can prevent the UV damage, and it is used for that purpose in automobile tires.

**e-** <u>Underground or Soil Corrosion</u>: Underground corrosion occurs for many reasons, such as galvanic effects, damaged coatings, different degrees of aeration and oxygen concentration, microorganisms present in the soil, differences in the nature and content of the soil, moisture content or humidity of the soil, electrolytes present in the soil and terrain's resistivity, redox potential of the terrain, acidity and pH of the soil, stray currents, and interference effects.

For aqueous, electrochemical, or wet corrosion to occur, a sufficient amount of dissolved oxygen is required, in addition to the electrolytic medium, which is regularly 8 ppm or 5.6 ml/L in water. Although it is easier for dissolved oxygen and water to reach the embedded metal structures in soils with large grains and gravels, it is difficult in soils with clay. Regions with less oxygen become the anode, and with more oxygen, become the cathode. As a result, in the case of buried pipelines and cables passing from one type of soil to another, the part of the pipeline that passes through the soil with clay, for instance, acts as the anode, while the part that passes through the soil with soil with sond or

sand with large grains and gravels, for instance, acts as the cathode due to differential aeration. When part of a pipeline is replaced with a new one, the new one becomes anode and the old one becomes the cathode, initiating corrosion due to potential difference between the two. Additionally, clay particles that adhere to pipelines cause potential difference and cause corrosion as well. Also, oxygen diffusion is greater in filled lands containing numerous air pockets than in natural ones, bringing about severe corrosion due to differential aeration. Another example is when there are different structures above the pipeline on the ground, e.g., asphalt vs. open ground, which results in the pipeline under the less permeable asphalt to become anode due to having less access to oxygen, and the surroundings become the cathode. Further, in wells, the region of the pipe embedded in water becomes the anode, since there is less oxygen in water and the part of the pipe right above the water that is in contact with air becomes the cathode.

In the presence of excess pesticides, germicides, or a large amount of organic matter, metals form soluble complexes, resulting in sufficient concentration difference of metal ions, resulting in several concentration cells, leading to severe soil corrosion. In water-logged areas, anaerobic bacteria becomes active, causing severe deterioration of soil in that area. Soils that have low resistivity have high corrosivity. Low resistivity of the soil is due to the presence of moisture and dissolved electrolytes. These two factors promote corrosion. Humidity is required for underground corrosion to occur, forming the electrolytic medium. In soils with mostly sand and gravel, water drains well, while in soils with clay, soil remains wet for long periods. Ground resistivity decreases with increasing soil humidity up to 20%-30% of the relative humidity, and remains constant afterwards. Ground resistivity decreases with temperature as well, while it increases substantially below 0°C. Ground resistivity also depends on the soil type, e.g., percentages of clay and silt, and on the dissolved ions present in the soil. Consequently, if ground resistivity is less than 1000 ohm cm, it is considered very conductive and corrosive; if between 1000 and 3000 ohm. cm, it is accepted as corrosive, if between 3000 and 10000 ohm. cm, it is medium corrosive, and if above 10000 ohm. cm, it is considered only slightly corrosive. Werner's four electrode method is a common way to measure the resistivity of soils at the surface of the earth. Regularly pH of soil is between 5 and 8, and does not have any effect on the corrosion leaving effect of the oxygen concentration as the primary determinant of corrosion. However, if pH of the soil is less than 5, which happens usually due to rotting organic materials or acid rains, numerous

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concentration cells cause corrosion, and protective coating of corrosion deposits or  $CaCO_3$  cannot form on the metal surface.

Redox potential also gives an idea about corrosion. Terrain potentials lower than 100 mV indicate severely corrosive environments, while potential values between 100-200 mV indicate corrosive environments, values between 200-400 mV indicate mildly corrosive environments, and values higher than 400 mV indicate only slightly corrosive environments. Redox potential is usually measured using platinum electrodes and a pH-meter A platinum electrode is placed in the environment and the potential difference with that of another reference electrode is measured and inserted into the following formula:

$$E_{redox} = E_{pt} + E_{ref} + 60 \ (pH-7) \tag{6}$$

 $E_{pt}$  is the potential of platinum electrode, and  $E_{ref}$  is the potential of reference electrode with respect to standard hydrogen electrode (SHE), e.g., for saturated Cu/CuSO<sub>4</sub> electrode (CSE), it is 316 mV compared to SHE.

Steel structures placed underground are usually expected to have a service life of 50 to 100 years; however, if environmental factors result in corrosive factors, this may lead the service life to be less than 50 years, and preventive measures have to be taken. If the anode and cathode are near one another and if the pH of the soil is higher than 5, the corrosion products are settled at the metal surface in the form of rust, leading to a reduction in the corrosion rate in time. However, especially in the case of pipelines buried underground, anode and cathode may be very far away from one another, and since the oxidized metal ions move towards the cathode, and hydroxide ions form at the cathode move towards the anode, rust forms somewhere in between, away from both the anode and the cathode, and thus the layer of corrosion products cannot protect the metal surface. It is usually not economical to change the properties of the soil to prevent corrosion; however, sometimes pipelines are embedded in clean sands covered with ditches or they are coated with protective coatings, but most commonly, cathodic protection is implemented.