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# UNIT 10 DEGRADATION OF MATERIALS

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## 10.1 INTRODUCTION

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Many people identify corrosion with rusting. Rust is a by-product of corrosion but a general meaning of corrosion is the deterioration of a material and its properties due to the reaction with the environment. Any design engineer needs to consider the service life of the product, he is designing, and corrosion may be the limiting factor in determining the service life of the product under design. Depending on the user environment, the effect of corrosion will vary. A reactor in a chemical factory will obviously be subjected to more serious deterioration than a system in a clean atmosphere-controlled indoor environment. Hence, the design engineer is required to know the user environment, the possible deterioration due to environment and provide allowances for such degradations and/or provide design features which include protection of the product. The scope of this chapter is to introduce corrosion and protection to the engineer.

### Objectives

After completing this unit, you will be in a position to understand

- what is corrosion,
- the corrosion processes which limit the life of the components,
- the effect of mechanical stress on such degradation processes, and
- general corrosion protection techniques by surface coatings/treatments.

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## 10.2 CORROSION OF METALS

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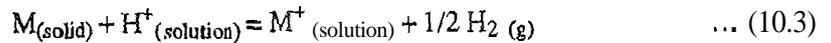
The way sugar dissolves in water and the way a metal dissolves in an acid are different. In the case of a metal, dissolution occurs through electrochemical reactions. When sugar goes into solution there is no involvement of electrons and ions. When a metal goes into solution, it forms the corresponding metal ion. Let us try to balance the equation which represent the dissolution.



Here, the metal ion goes into the solution. What happens to the electron? The electron can move to another part of the metal (remember the metals are good conductors of electricity) and at that place, the electron may be involved in another reaction such as the one below:



The hydrogen ion is in the aqueous medium which is in contact with the metal. This ion consumes the electron and forms half a molecule of hydrogen gas. The gas may build up in the form of a bubble and get released. Here, the reactions (10.1) and (10.2) together cause the dissolution of the metal or its corrosion. Each of these reactions is half the chemical reaction as given below

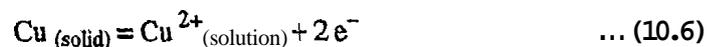


The overall corrosion reaction is the dissolution of metal and the consequent displacement of hydrogen from the solution. In a common chemical reaction, all the participants of the reaction, namely, the reactants and products are in the same location, in space. However, in an electrochemical reaction, the two half reactions may take place at two different locations in space and this warrants the movement of electrons from one place to another through an electronic conductor. Since we deal with metallic corrosion, it is easy for us to see the role of the metal as the conductor. The metal is converted into its ion (oxidised) at a given location (anode) and the released electron goes through the metal to another site in the metal (cathode) where a reduction reaction takes place associated with the consumption of electrons. The evolution of hydrogen, as given in reaction (10.2) is not necessary for corrosion to take place. All that is needed is that the electron generated during the anodic reaction (metallic dissolution as per reaction (10.1)) should be associated with a reaction that consumes the electron. Let us look at other possibilities:



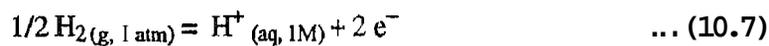
The alternatives to reaction (10.2) as given by (10.4) and (10.5) has constraints different from those for reaction (10.2). While (10.2), requires presence of hydrogen ions in the medium, reaction (10.5) requires oxygen. You may even note that the reaction (10.5) is not associated with the evolution of hydrogen. Hence the medium determines the way the metal corrodes. All these reactions require water (aqueous corrosion).

We had discussed the common reactions occurring during aqueous corrosion. What is the driving force behind corrosion? One may seek an answer in thermodynamics. We had learnt earlier that a spontaneous reaction is associated with the lowering of the free energy of the system. The overall reaction such as (10.3) should be associated with the lowering of free energy or the free energy change associated with the reaction should be negative. Consider reaction (10.1). The metal has a tendency to go into solution to form the metal ion, with the electron left in the metal. Simultaneously, the metal ion in the solution has a tendency to pick up an electron from the metal, depositing the metal atom on the surface of the metal. These two tendencies oppose each other. Hence, the driving force for the reaction (10.1) should be a net result of these two opposing tendencies. One can see the tendency of the metal ion in solution to deposit on the metal (reverse of reaction (10.1)) should depend on how many metal ions are there in solution. In other words, the concentration of the metal ions in the solution should affect the overall free energy change for the reaction (10.1). Further, the metal may not be pure and the form in which the metal exists will change the tendency of the metal to go into solution. Taking all these into consideration, the free energy change for the process of the metal going into solution determines whether the process is spontaneous or not. Now, let us limit our discussion to the metal in its pure and stable form. Let us consider the example of pure copper dipped in a solution of an aqueous solution of copper sulphate. Let the quantity of copper sulphate be 1 mole per litre of the solution. (Do you remember what is the unit for such a solution? Recall your memory from your first chemistry course.) The reaction is



The free energy change for the above at the standard temperature (298 K) be  $\Delta G^{\circ}_{298}$ . The superscript on G indicates that we had chosen a set of standard conditions for reaction (10.6). The A symbol indicates that it is the free energy change for the chosen (10.6) reaction. Further, as the above reaction proceeds, as we already mentioned, there is charge separation. The negative charge that resides on the metal and the copper ion that enters the solution are attracted by coulombic forces. Such a separation of charges cannot go on indefinitely. While the tendency of the metal to go into solution, allows the separation of charges, the coulombic attraction will prevent such a process. Eventually, the two competing driving forces balance each other and the process should stop. Under such a situation, a potential difference exists between the solution and the metal. The tendency to

dissolve will depend on the concentration of the metal ion already present in the solution and it should depend on the nature of the metal ion and how it gets stabilised in the solution form. If we can measure such a potential difference at a fixed concentration of metal ion in solution, then, this difference in potential should represent the intrinsic tendency of the metal to go into solution, and this intrinsic tendency will vary with different metals. This should create a potential difference between the solution and the metal. Let us call it "Single electrode potential". This difference in potential should be related to the tendency of the metal to go into solution. We may arrange the different metals in decreasing order of such potential differences and this order should give the difference in tendencies among different metals to go into solution. But, how do we measure this potential difference? We need a pair of metallic conductors to connect to the potential measuring device. We need another metal electrode to make contact to the solution. Again, that metal may have some tendency to go into solution and create its potential and what we measure will actually be the difference between the single electrode potentials of copper and the metal electrode which we use. While we can measure the differences between the single electrode potentials, we cannot derive the single electrode potential of copper (for that matter my metal) from it, unless we know at least one of the single electrode potentials. As we noted already, it is not possible. However, if we are not interested in the absolute tendencies of metals to undergo dissolution and if we are interested in the relative tendencies only, then we may have to assume one of the single electrode potentials. This assumption should be universal. This universal assumption states that for the reaction



the single electrode potential is zero. The subscripts indicate that hydrogen gas is at one atmospheric pressure at 298 K; hydrogen ion in aqueous medium is at 1 M concentration. Since we cannot make electrical contact to hydrogen, we use an electrode, a plainised platinum wire in contact with hydrogen and hydrogen ion and use it as an electrical lead. This is called a standard hydrogen electrode. Now that we have a reference point, we may use this electrode to measure the single electrode potentials of any metal. The measured values will be offset by the absolute value of the standard hydrogen electrode, but we may still use these to find the relative tendencies of metals to go into solution. Table 10.1 gives the single electrode potentials of various metals.

Table 10.1 Single Electrode Potentials

Metal-Metal ion at Unit Concentration	Single Electrode Potential (vs. Standard Hydrogen Electrode) at 25 °C (V)
Au, Au <sup>3+</sup>	+ 1.48
Pt, Pt <sup>2+</sup>	+ 1.2
Pd, Pd <sup>2+</sup>	+ 0.987
Ag, Ag <sup>+</sup>	+ 0.799
Cu, Cu <sup>2+</sup>	+ 0.337
H <sub>2</sub> , H <sup>+</sup>	0.00
Sn, Sn <sup>2+</sup>	- 0.136
Ni, Ni <sup>2+</sup>	- 0.250
Fe, Fe <sup>2+</sup>	- 0.440
Zn, Zn <sup>2+</sup>	- 0.763
Al, Al <sup>3+</sup>	- 1.662
Mg, Mg <sup>2+</sup>	- 2.363
K, K <sup>+</sup>	- 2.925

The metals which are above hydrogen in the above table are copper, silver and gold and these are noble. They have less tendency to get corroded under the standard conditions (of unit concentrations and 25 °C). Those metals which are below hydrogen have more tendency to get dissolved. A piece of potassium reacts violently to get dissolved in water, where one takes special steps to dissolve gold.

The above ideas can be reworded as follows:

- 1) Under conditions of equilibrium between a metal and a solution of its ions an electrical potential step exists at the interface between the metal and the solution.

- 2) The magnitude of this potential depends on the metal, its state as an alloy and the concentration of the metal ion in the solution. (You may note that the concentration of a given metal ion, when varied independently, it is done along with a counter ion of negative charge).
- 3) The relative values of these potentials under a set of conditions indicate the tendency of the metal to undergo dissolution.

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### 10.3 ELECTROCHEMICAL CELL

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Let us consider a system containing two copper rods dipped in a solution of 1 M copper sulphate. Both rods have equal tendency to go into solution and if we measure the potential difference between the rods, we find it to be zero. Naturally, no current flows between the rods. Next let us take a container with two compartments separated by a porous membrane. In the compartments let us take 1 M solution of ferrous sulphate and 1 M solution of copper sulphate. Let us dip an iron and a copper rods respectively in their solutions as shown in Figure 10.1.

There is a potential difference which is equal to 0.777 V if you do not allow the current to flow by using a high impedance bridge. In other words, we are measuring the difference

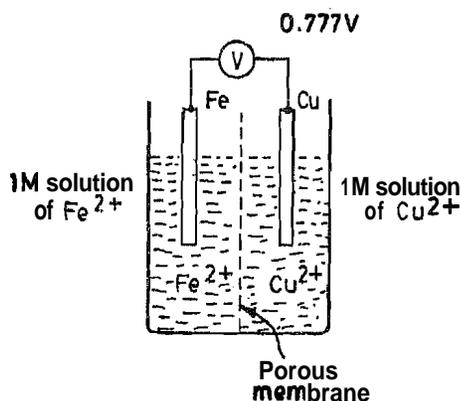


Figure 10.1 : A Galvanic Cell Formed by Two Different Metals

under equilibrium conditions. What we have is an electrochemical cell. It is also known as a Galvanic Cell after the Italian scientist Galvani. The potential difference, thus measured is called the emf (electro motive force) of the cell. Copper is positive as the tendency of copper ions to be in the metallic state is more than that of ferrous ions.

#### SAQ 1

Find the emf of the cell comprising of iron and zinc electrodes dipped in their solutions with a concentration of 1 M at 25 °C. Identify the polarity of the electrodes.

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### 10.4 KINETIC ASPECTS OF CORROSION

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The equilibria described in the above section is dynamic and the forward and the reverse reactions occur simultaneously with no net realisable reaction. These reactions should be happening at the same rate so that the net reaction at any instant of time is zero. Since these reactions occur with the release and consumption of electrons, we can see it as two currents of equal magnitude flowing in opposite directions (exchange currents,  $i_e$ ). The opposing reactions or currents do not happen without any barrier. We have already seen the coulombic forces to be a barrier for charge separation. Though the barriers exist, thermal activation helps in overcoming the barriers on either side and result in these exchange currents. These activation processes are governed by Arrhenius rate equations. The rates of the oxidation and the reduction reactions are equal and are given by

$$R_o = R_1 \exp\left(\frac{-E_o}{kT}\right) \text{ and}$$

$$R_r = R_2 \exp\left(\frac{-E_r}{kT}\right), \text{ respectively.}$$

Here,  $E_o$  and  $E_r$  are the activation energies for the oxidation and reduction reactions, respectively. With each of the two reactions (dissolution of copper and the deposition of copper) there is a current,  $i_e$  and this current is a measure of the rate of the reaction. In case, you apply an additional potential on the metal in solution from an external source, what will you observe? The added driving force will induce a flow of current in the direction indicated by the potential. We do need two electrodes to apply a potential. Let us assume two copper rods dipped in a solution of copper sulphate, over which we apply the potential, then one which is positive will have a tendency to give out copper ions (dissolution) and the other (negative electrode) will pick up copper ions and copper is deposited on the electrode. Now, the current flows, there is no equilibrium and the net reaction is the transfer of copper from the first electrode (anode) to the second electrode (cathode). Now look at each electrode separately. In each electrode both the oxidation and reduction were going on at zero potential. With the superimposed potential, in one electrode, say cathode, reduction occurs at a faster rate than the oxidation. The net reaction at anode being reduction. The added potential has altered the barrier which existed under equilibrium conditions. Let us call the excess potential applied as over potential,  $\eta$ . The extra barrier for the electron to go through because of this is  $\eta_e$ , where  $e$  is the charge on the electron. If one considers the reduction reaction on one electrode

$$R_r = R_2 \exp\left(\frac{-E_r + ne\eta}{kT}\right) = i_e \exp\left(\frac{ne\eta}{kT}\right) \quad \dots (10.8)$$

and when the oxidation is considered, the rate is changed to

$$R_o = R_1 \exp\left(-E_o - \frac{ne\eta}{kT}\right) = i_e \exp\left(\frac{-ne\eta}{kT}\right) \quad \dots (10.9)$$

Here 'n' is the number of electrons on the ion. The value 'n' for copper ion is two. These two currents passing through the chosen electrode are opposing and are no more equal. Then, the net current is the difference

$$i = i_e \left[ \exp\left(\frac{ne\eta}{kT}\right) - \exp\left(\frac{-ne\eta}{kT}\right) \right] \quad \dots (10.10)$$

## SAQ 2

Can you write what happens to the anode? What is the value of the net current?

You may know that the value of  $kT$  is 0.025 eV at room temperature and is too small compared to the numerator inside the exponent. So even a small over potential makes the current increase as

$$I \approx i_e \exp\left(\frac{ne\eta}{kT}\right) \quad \dots (10.11)$$

Taking logarithms,

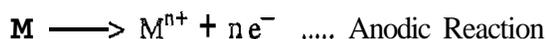
$$\log i \approx \log i_e + \frac{ne\eta}{kT} \quad \dots (10.12)$$

$$\eta \propto \log i - \log i_e$$

We see a linear variation of over potential versus the current across the electrode solution interface by this model. This model is too simple a model and other factors such as the

mobility of the ion in solution do affect. Let us not go into the details of such effects. Let us compare how the current varies for different metals. In this attempt, we try to combine the thermodynamic (equilibrium) considerations with the kinetic considerations. In a plot of potential vs log (i), they are above or below in the potential axis depending on their single electrode potentials. The y-axis is marked zero at the standard hydrogen electrode potential. These are called Tafel plots (see Figure 8.2).

While a general plot of potential versus log (i) is called the polarisation curve, the plot with a linear variation of log (i) with potential is known as Tafel plot. The rate at which the current increases in Tafel plot (the slope), is equal to the charge on the ion. At equilibrium, there is no net current flow and we should have the single electrode potential. As the current increases, the over potential term is added to the equilibrium potential. We need to fix the direction of current and that of the potential difference. We cannot be arbitrary. Anodic reactions (oxidations) require a positive potential, and the current-potential curve slope up. Similarly, the cathodic reactions slope down. We can use these diagrams to find which of the several possible reactions will occur in the chosen medium. We have different reactions possible in a given medium which consume electrons or release electrons. Let us look at the first instance a simple pair of anodic and cathodic reactions. Let us consider our already known example of a metal dipped in an acidic solution of concentration 1M. The possible reactions are



and

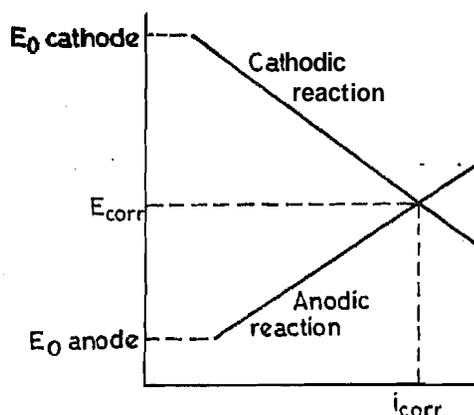
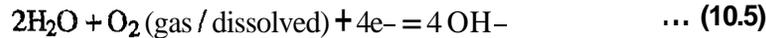


Figure 10.2 : Tafel Plots for a Simple Set of Reactions

The two reactions should occur simultaneously and the electrons generated in the first reaction should be consumed in the second reaction. That means in the polarisation curve, the point of intersection of the two curves representing the two reactions is the one which gives the rate of reaction or  $I_{corr}$ . The value of  $I_{corr}$  is a representation of the rate of corrosion of the metal in the chosen medium. While we equate the current in the anodic and cathodic reactions, the potential should also be the same as we have a common point (of intersection). This is obvious from the fact that the metal is a conductor and we cannot have a potential drop between the two places where the two reactions occur. The common potential is corrosion potential,  $E_{corr}$ . The difference between the equilibrium potential (when no reaction occurs) and the  $E_{corr}$  is the over potential. While it is positive for the anodic reaction, it is negative for the cathodic reaction. (Remember that the shifting of the potential are in opposite directions.) Figure 8.2 shows the Tafel plot for the said system. The value of  $E_{corr}$  is different from the single electrode potentials by an amount equal to the over potential. The rates of reaction as measured by anode and cathode currents must be equal,  $i_{corr}$ . When you want to reduce the corrosion, you have to reduce the  $i_{corr}$ , the corrosion current. This we can achieve by shifting the  $I_{corr}$  the point of intersection of the anodic and cathodic current-potential lines. We may do this by shifting the reference point (equilibrium potential). Since these values are fixed for a metal system at the standard conditions, we may change the conditions away from the standard conditions. In other

words, the concentrations of the ions in the aqueous medium is changed, the  $E_{O\text{cathode}}$  or the anode is changed as a consequence, the  $I_{\text{corr}}$  shifts.

We may look at another case wherein the aqueous medium is aerated. The presence of oxygen allows the possibility of another reaction competing with the hydrogen evolution.



Let us superimpose this over the polarisation diagram 10.2. The new diagram is shown in Figure 10.3. The lines for the two cathodic reactions intersect the anodic reaction line at two different points. The electrons generated in the anodic reaction has to be consumed by the possible two cathodic reaction (one with oxygen and the other without oxygen). The former takes place at a higher rate than the later and that will be the major cathodic reaction. The potential of the system ( $E_{\text{corr}}$ ) will also be fixed by that point of intersection.

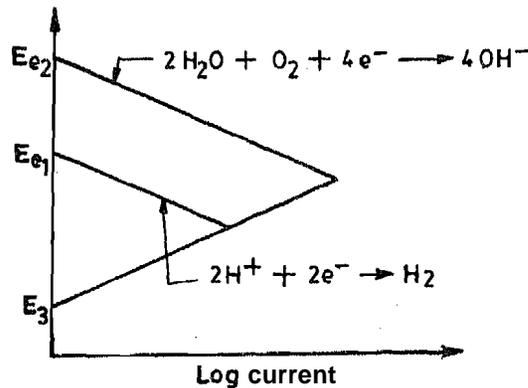


Figure 10.3: Tafel Plot for a Metal Reduction (Anodic Reaction) and Two Possible Cathodic Reactions

Here the oxygenated medium has enhanced the corrosion of the metal by choosing an alternate cathodic reaction.

We may change the slope of the lines so that  $I_{\text{corr}}$  is shifted. Though we had said the slope is related to the number of electrons on the ion, we had also indicated that the slope is affected by other factors which affect the activation energy or barrier. This could be by the formation of a layer on the metal which acts as a barrier for the transport of electrons / ions across. This could be achieved by an application of paints containing oxides acting as barriers. You may already know that a coat of red oxide primer is commonly used to prevent corrosion on steel structures. An oxide layer formed adherently will reduce the corrosion. Aluminium forms an adherent oxide on its surface which prevents corrosion. In fact, the metal is deliberately allowed to corrode or form an oxide on the surface which once formed acts as a corrosion protection mechanism. The oxide layer is called a passivating layer and the process is called passivation. In stainless steel, iron when alloyed with significant quantities of chromium, the chromium form an oxide on the surface which acts as a barrier to corrosion. Of course, if the metal is more noble, there is no reaction (the curves do not have a common point).

While we had been talking about a single metal degrading by the process of corrosion, we come across many systems when more than one metal is involved in a system. A combination of two metals can be in the form of an alloy or two components in contact in a system. We had already seen the case of chromium protecting steel in an alloy form (stainless steel). Let us look at the structure containing two metals in contact. If we construct a structure made of copper and we use bolts made of copper. What will happen? The system will form an electrochemical cell. With moisture in atmosphere, the electrochemical cell will be formed. Iron bolt will be corroded in no time and the structure will fall apart. Look at the example we had seen in the section on electrochemical cell for details. The corrosion which is enhanced by the formation of electrochemical cells can be seen even in components, Let us consider brass which is an alloy of copper and zinc, While employed in an acidic environment, the electrochemical cell is formed and zinc is preferentially corroded. As a result, we may get a porous component wherein the zinc is removed and the component that has pits in them. As a consequence, the component loses its mechanical strength for which it was designed. The process is called dezincification or

in general it is called parting. **Parting** is observed in Copper-silicon and Copper-aluminium alloys as well. A similar problem arises in **white cast iron**, which contains **carbon** as cementite ( $\text{Fe}_3\text{C}$ ) or as a solution in iron. This is produced by a fast quenching of molten pig iron. However, if **cooled** slowly, it produces graphite precipitates in cast iron. **These** graphite particles are noble and form a cell with iron and the **corrosion** of iron is **enhanced**. This is commonly observed in cast iron pipes leading to failures. This is called **graphitisation**. Microscopic reasons as above cause corrosion even in stainless steels which are subjected to high temperature treatments ( $400\text{--}900^\circ\text{C}$ ). Under **these** high temperatures, **carbon** present in the steel diffuses towards grain **boundaries**. **There** they react with **chromium** to form chromium carbide ( $\text{Cr}_{23}\text{C}_6$ ) and **precipitates** at the grain boundaries. Once the chromium is depleted near grain boundaries, the iron in that zone becomes more susceptible to corrosion. Now we have a portion which is more active and another (without depletion of chromium) which is less active. These portions can **form** a cell leading to enhanced corrosion. During welding, the material is subjected to high **temperatures** near the weldment and these become the **focus** for the **corrosion**. This is known as **intergranular** corrosion as the attack is at the grain boundaries. Use of low carbon **alloys** can alleviate this problem

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## 10.5 EFFECT OF MECHANICAL STRESSES ON CORROSION

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Mechanical stresses can accelerate **failure** by corrosion. **Whenever** there are points of stresses in a given component along with regions of low or no stress, corrosion is enhanced. This is because, high stress regions are more active compared to low stress regions. These two regions form a stress cell and cause corrosion similar to a Galvanic cell. An iron rod left in aerated water corrodes more at the bent portion due to this effect.

There are other **forms** of corrosion, which a design engineer should remember. Consider stainless steel pipeline carrying a fluid at high velocities. Let us **look** at a portion which is bent. While, **the chromium** oxide on the surface allows the protection of the tube in oxidising media, reducing media cause damage by a process called **erosion-corrosion**. The relative movement of the **metal** and the media result in this.

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## 10.6 ATMOSPHERIC DEGRADATION

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Atmospheric corrosion of steel is one of the most commonly **known** degradation. **This** degradation is known to **mankind** for ages and **man** has been trying to win over this process as long. Most **materials** degrade in the ambient. The surface subjected to radiation, moisture, erosive flows, heat and temperature cycles, microorganisms, chemicals present in **the** atmosphere as pollutants undergo degradation. Cycling of temperature induces stresses and develops cracks which subsequently grow. The aging of **materials** with time can be due to the formation of such cracks, or may be due to grain growth, or polymerisation / **depolymerisation** caused by the environment. Metals exposed to **air** may **tarnish** which is a result of reactions with the components of air. There is a threshold level of humidity below which corrosion is negligible and above a critical level, the corrosion shows a **sharp** increase. **At** room **temperature**, the threshold humidity for iron is about 55% and it shoots up above 75%. **At** high levels of **humidity** there is even condensation **and** condensation accelerates corrosion. You **might** have observed that steel frames of windows corrode more easily in Bombay **compared** to those in **Delhi** where humidity levels **are** low. The rate of corrosion varies between seasons as well as humidity levels vary over a large range with **changing** seasons. Pollutants enhance **corrosion**. Generally the pollutants in **air** are oxides of sulphur, of nitrogen **and** of carbon, which are generated during combustion of fuels. In places close to chemical industries, other pollutants such as **ammonia** are **more**. **This** causes enhanced corrosion in highly industrial areas. In **marine** environment, **there** are electrolytes like sodium chloride add to the corrosive tendency of the ambient. While precious **materials** can be stored in controlled **atmospheres** to prevent environmental degradation, it is **not** possible for every system. We **need** to worry more about **atmospheric** degradation for **many building materials**. It is better to fight **corrosion** armed with better materials. It is better to use aluminium window **frames** rather than mild steel frames in Bombay if other considerations are **same**. Trace elements present in the alloys may make it resistant to corrosion. As an example, traces of technetium seems to

protect iron. Structures **which are** buried in soil undergo corrosion as soil **has** several ingredients. Apart from the possibility of electrochemical corrosion, due to concentration differences in the constituents **along the structure** (differential aeration, **difference in the constituents themselves**) some **microorganisms enhance** corrosion. These microorganisms as a result of some biochemical reactions generate **some** chemicals which **enhance** corrosion. **As an example**, in certain clays, steel is found to corrode rapidly even under anaerobic (de-aerated) conditions. Formation of ferrous sulphide was observed in such cases. This is mainly due to a sulphate reducing bacteria, *Desulfovibrio desulfuricans* present in the acidic sulphate containing soils. The corrosion reaction is suggested as follows :

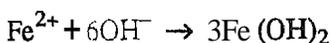
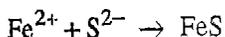
Anodic reactions



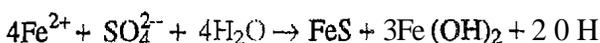
Cathodic reactions



bacteria



Overall reaction is



The cathodic reaction is **depolarised** by bacteria and hence, the corrosion rate does not decrease with time.

Soil particle size and distribution combined with moisture retention cause differences in aeration of the soil. In general well aerated soils are **less** corrosive than poorly aerated soils. **There is a difference in the electrode potential** when there is a difference in oxygen availability. And these differences give rise to galvanic corrosion. The top soil may be well aerated **and** the bottom may be poorly aerated and it can lead to electrochemical **cells** leading to corrosion of these structures.

Other causes are the stray currents induced in **structures** by any high voltage lines in the vicinity may lead to increased corrosion. In case of a high voltage overhead line in **the vicinity**, a **potential** difference is induced in the soil along a buried pipeline. This difference sets up **an electrochemical cell** leading to **increased** corrosion.

## 10.7 CORROSION OF STEEL IN CONCRETE

Corrosion of reinforcement steel leads to secondary failures which are more serious **than** the primary cause. When iron rusts, the **material** expands about ten fold **and** this expansion leads to stress in concrete, causing cracking and **spalling** of the concrete. Once the concrete **spalls** off, the reinforcement is directly exposed to atmosphere further accentuating the failure. Cement is essentially alkaline **and** corrosive since the constituents are lime, silicates and **sulphate** of magnesium. While a strong **alkaline** medium inhibits rust formation, while a strong alkaline medium is **corrosive**. If **concrete has any** excess free alkali present, then no serious damage is envisaged. Also, the solubilities of corrosive salts are **nearly** insoluble in water and do not cause **corrosion**. **In fact**, during the setting of cement, calcium hydroxide is **released** during setting of concrete and the steel is in a **passivated** state. However, any saline sand used in concrete will **induce** corrosion and related failures. Even if the sand is not saline, the permeability of moisture and air through hairline **cracks** can lead to corrosion of steel.

## 10.8 SURFACE TREATMENTS FOR CORROSION PROTECTION

The best way to prevent corrosion is to choose **the material** that stands the service conditions. The **best** material **that** does not corrode is the most noble of the metals. However, the most noble metal is invariably the most expensive one too. As a practicing engineer, one might try to use the most economic design for his structure. How does one **make** the two ends meet. One way is to coat the **metal** chosen with an appropriate

overlayer that can stand the service conditions. These protective coatings act as a **barrier** between the **metal** and the **environment**. **Galvanised** steel is a classical **example** of such a system. The protection is **given** by a layer of **zinc** on steel. Zinc is **anodic** to iron **and** even if it **breaks** or has a pin hole, this **does not** lead to serious **localised** corrosion. In case a **more** noble **metal** such as tin is coated over steel, even a **small break in the** coating leads to a galvanic cell and the steel **that** is exposed is severely attacked. **Galvanisation** protects the steel by sacrificing the zinc. We had already seen how the incorporation of chromium in steel **makes** it stainless. It is just the chromium oxide on the **surface** which makes it stainless. A different class of surface treatment is by incorporating a small **quantity** of an organic substance in the **medium**. Such **substances** get adsorbed on the metal. The adsorbed **layer** prevents the corrosion by suppressing the gas **evolution**. These are called corrosion inhibitors.

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## 10.9 DEGRADATION OF POLYMERS

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At the time of conclusion you may **realise** that **this** unit almost entirely covers the degradation of **metallic** systems. Metals still are the **most** important structural material. We **may** also notice that other **materials** are increasingly being used in the place of metals. The reasons are **several**; it may be the cost or performance criteria or both. **The** most important **alternative** is polymer based composites. How do polymers **degrade**? The ultraviolet **component** of sunlight **comprises** energetic photons capable of breaking **chemical** bonds. The bonds when broken, lead to free **radicals** which are very reactive. In the presence of oxygen, the radicals react with oxygen. As a consequence, the polymer chains **may** be broken thus affecting the mechanical properties. The same free radicals may lead to bonding adjacent chains leading to cross linking. This results in a reduction in the elastic properties and **formation** of cracks. Another **damage** is to **the** transparency of polymers. **Polymers** which are transparent otherwise, become **translucent** and yellowish due to such degradation.

### SAQ 3

Explain **why** low molecular **mass** **LDPE** is more susceptible to photo-oxidation than high molecular-mass **HDPE**.

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## 10.10 SUMMARY

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Degradation of materials is one of the major considerations a design engineer has to bear in mind. **Different** metals degrade at different rates under a set of service conditions. The relative tendency of metals to get into a solution form is given by its single electrode potential. While this tendency is purely listed based on thermodynamic considerations, the moment the actual corrosion starts, the **kinetics** of the process take over from **that** point. The corrosion rates are **influenced** by **the** medium, the nature of the **metal**, its alloy form, mechanical stresses, and the temperature. One may protect the metal from corrosion by a suitable coating or by using inhibitors. Polymers degrade by the exposure to sunlight and oxygen.

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### 0 . 1 KEY WORDS

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**Single Electrode Potential** : The potential difference between a metal in a 1M solution of its ion and the solution at 25 °C measured **with** reference to a standard hydrogen electrode is called single electrode potential.

- Polarisation** : The shifting of electrode potential **away** from the equilibrium value as **the electrode reaction occurs** is called polarisation.
- Over Potential** : The difference between **the** equilibrium potential when no electrode **reaction** occurs and the potential as the electrode reaction proceeds is called over potential.

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## 10.12 ANSWERS TO SAQs

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### SAQ 1

0.323 V. **Note** that both iron and zinc are below hydrogen.

### SAQ 2

The net current is the **same** except **that** it is in the opposite direction.

### SAQ 3

It is easier to break the **bonds** near the head or tail of a polymer chain than in the middle. In **LDPE**, there are more such possibilities than in **HDPE**.

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