

VELAGAPUDI RAMAKRISHNA SIDDHARTHA ENGINEERING COLLEGE (AUTONOMOUS), VIJAYAWADA DEPARTMENT OF CHEMISTRY LIST OF SECOND ASSIGNMENT QUESTIONS, 2020-21			
Q. No.	Question	CO	Cog. Level
1.	Illustrate with suitable diagram the mechanism of corrosion of iron in alkaline environment.	3	K2
2.	Make use of suitable chemical equations and diagram to explain the principle and process of corrosion control by using electroplating.	3	K3
3.	Make use of suitable chemical equations and diagram to explain the principle and process of corrosion control by using electrolessplating.	3	K3
4.	Illustrate the mechanism of electrochemical corrosion of iron in acidic environment with suitable chemical equations.	3	K2
5.	Discuss cathodic protection using i) Sacrificial anode method ii) Impressed current method. With suitable examples.	3	K2
6.	Discuss anodic protection method with suitable example.	3	K2
7.	Define corrosion inhibitors. Explain the mechanism of corrosion inhibition by anodic inhibitors and cathodic inhibitors.	3	K2
8.	Identify any one practical example of differential aeration corrosion and explain with mechanism.	3	K3

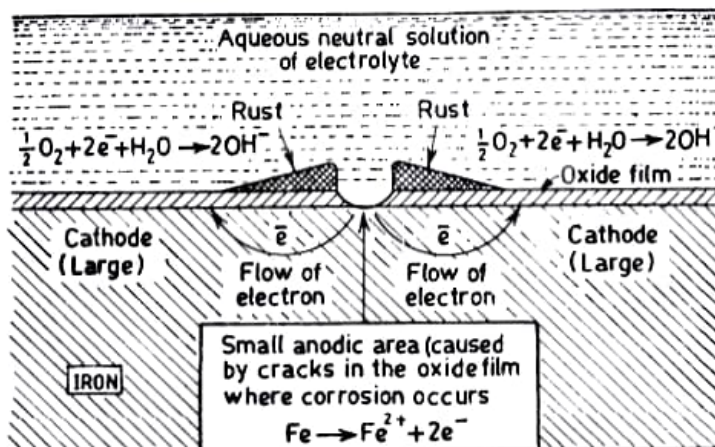
CO3: Evaluate corrosion processes as well as protection methods..
Cognitive Levels: K1-Remember; K2-Understand; K3-Apply; K4-Analyze; K5-Evaluate;

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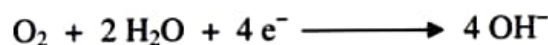
b) *Oxygen absorption corrosion*: This type of corrosion occurs when the corrosive environment is either neutral or alkaline in nature. Rusting of iron in such media is an example of this type of corrosion. Usually, there will be an oxide film on iron due to initial corrosion. But when some cracks are formed in the oxide layer, they become anodic areas leaving behind the remaining areas as cathodic. Thus, the anodic areas are smaller when compared with cathodic areas.



At anodic areas, iron dissolves as ferrous ions with liberation of electrons.



The liberated electrons flow from anodic to cathodic areas through iron metal where electrons are consumed by dissolved oxygen as follows:

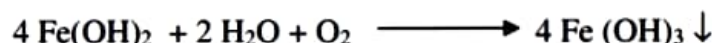


The Fe^{2+} ions at anodic areas and OH^- at the cathodic areas diffuse and when they meet, they precipitate as ferrous hydroxide:



The two reactants Fe^{2+} and OH^- originate from the anode and cathode respectively, but their combination occurs, more commonly at cathode because of the fast diffusion of Fe^{2+} ions than hydroxide ions (due to smaller size of ferrous ion). Hence, corrosion product is deposited at the cathode.

If enough oxygen is present in the medium, ferrous hydroxide is easily oxidized to ferric hydroxide.



This product is called yellow rust.

If the supply of oxygen is limited, the corrosion product may be even black anhydrous magnetite, Fe_3O_4 .

Electroplating (Electrodeposition)

Principle: Electroplating or electrodeposition is the process by which the coating metal is deposited on the base metal by passing a direct current through an electrolytic solution, containing the soluble salt of the coating metal.

Process: In case of copper electroplating on iron article, copper metal bar is to be taken as anode and iron article as cathode. When these two electrodes are dipped in an electrolytic solution containing copper ions and connected to a d.c. source, the following reactions will occur at the electrodes:

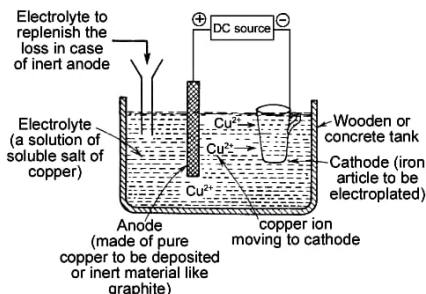
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At anode : $\text{Cu} \longrightarrow \text{Cu}^{2+} + 2\text{e}^-$

At cathode: $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$

The deposited copper on the iron article produces as a thin layer to protect the base metal iron. The thickness of the copper deposit depends on the concentration of the electrolyte, power provided to the electrodes, current density, time of plating, etc.



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Conditions for electroplating of copper:

Plating bath composition (per Litre): 200 – 250 g of Copper sulphate, 50-75 g of sulphuric acid and the balance water, Anode: P contained rolled Copper

Additives: Gelatin or dextrin, sulphur-containing brightener, sulphonic acid.

Temperature ($^{\circ}\text{C}$): 20 – 40, **Current density (mA.cm^{-2}):** 20 – 50, **Current efficiency (%):** 95 – 98 and

Throwing power: low

Surface preparation: In order to ensure the effective electroplating, proper cleaning of the surface to be plated is a very important step. Surface preparation can be done by the following methods:

- Solvent cleaning:** It is used to remove oils, greases and fatty substances. This process involves cleaning the surfaces by the application of organic solvents like naphtha, chlorinated hydrocarbons like CCl_4 , toluene, xylene or acetone.
- Alkali cleaning:** It is used for the removal of old paint coating from metal surfaces. Alkali cleaning agents are trisodium phosphate along with soaps and wetting agents like caustic soda. An alkali treatment is always to be followed by a very thorough rinsing with water and then immersion in a slightly acid solution of 0.1 % chromic acid (or sodium or potassium chromate) to remove the last traces of alkalis.
- Mechanical cleaning:** It removes loose rust and other impurities from the surface. This is generally done by using bristle brush and some abrasive like sand paper and detergent like soap. Impact tools like dull chisels, knife scrapers, wire brushes, grinding wheels and cutters are also used for removing strongly adhering scales, etc.

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- Sand-blasting:** It is used for removing oxide scales, particularly when a slightly roughened surface is desired. This method is especially suitable for large steel surfaces. The process consists in introducing the sand into an air stream under pressure of 25 to 100 atmospheres.
- Pickling:** Acid pickling is more convenient method of scale removal in many cases than mechanical cleaning or sand-blasting. It is usually accomplished by immersing the metal in an acid pickling solution. In case of aluminium, pickling is done in alkaline solution.

Electroless plating: Deposition of a metal from its salt solution on a catalytically activated surface

Electroless plating: *Deposition of a metal from its salt solution on a catalytically activated surface by a suitable reducing agent without the aid of electrical energy is known as electroless plating.* Metal ions are reduced to the metal with the help of reducing agents. Once the metal atoms are formed, they get plated over a catalytic surface.

Metal ions + Reducing agent \longrightarrow Metal plated on a catalyst surface + Oxidized products

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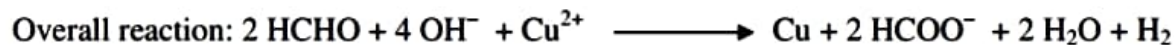
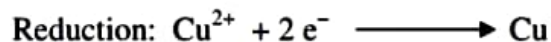
The following techniques are used for the preparation of the surface of the object so that an active surface is obtained.

Etching (acid treatment) and treatment of surface with stannous chloride and palladium chloride alternately for non-conducting surfaces such as plastics and printed circuit boards.

Electroless plating of copper:

The surface to be treated is degreased and etched in acid. On gold, silver, platinum, palladium, rhodium, iron, cobalt and nickel, electroless copper gets deposited spontaneously in presence of reducing agents. But insulators like plastics, printed circuit boards and glass are activated by dipping first in stannous chloride and then in palladium chloride.

A solution of copper sulphate (12 g/L), formaldehyde (8 g/L) as reducing agent, sodium hydroxide (15 g/L) and Rochelle salt (14 g/L) as buffer, EDTA as complexing agent (20 g/L) acts as plating bath solution for copper plating. For an effective plating of copper, the pH and temperature to be maintained are 11.0 and 25 °C respectively. The following reactions occur during plating:



Cupric ions and formaldehyde consumed during plating are replenished periodically.

Advantages of electroless plating:

1. Use of electrical contacts or electrical power is eliminated.
2. Throwing power of electroless bath is better so intricate parts with irregular shapes can be uniformly coated.
3. Plastics and other insulators and semiconductors can also be plated by electroless plating.
4. Resulting deposits have unique chemical, mechanical and magnetic properties.

Electrochemical corrosion: Corrosion of a metal in an aqueous solution is an electrochemical phenomenon involving flow of electrons between the anodic and cathodic areas. The anodic reaction involves in dissolution of metal as corresponding metallic ions with the liberation of free electrons.

i.e., at anodic areas: $M \longrightarrow M^{n+} + n e^{-}$

Electrons released in this reaction are consumed at cathodic areas by some reduction reaction. Several cathodic reactions are possible during wet corrosion based on the nature of the environment.

There are two important cathodic reactions that frequently occur during electrochemical corrosion.

With reference to these reactions, mechanism of electrochemical corrosion is discussed as follows.

a) Hydrogen evolution corrosion: This type of corrosion occurs in acidic environments like industrial wastewaters and solutions of non-oxidizing acids like HCl. Consider a metal like Fe in the acidic environment. Suppose that a portion of the metal surface possesses high concentration of hydrogen ions relative to the rest of the surface. This portion becomes cathodic area and the rest of the surface anodic.

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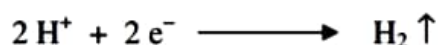
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At anodic areas, the reaction is



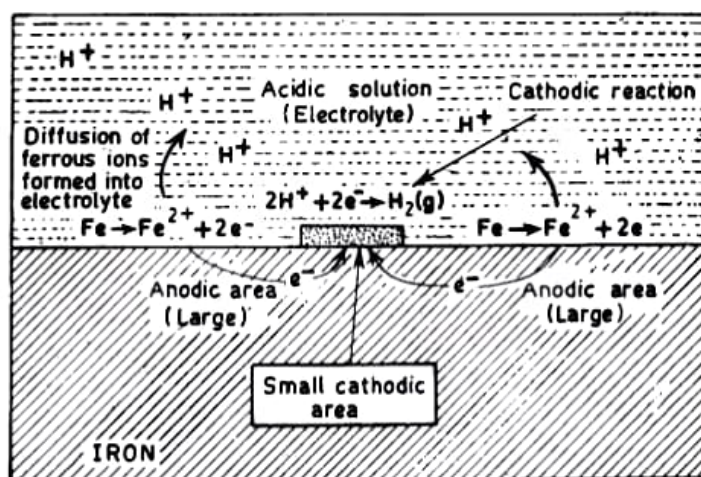
These electrons flow through the metal from anode to cathode.

At cathode, H^{+} ions of the acidic medium undergo reduction to evolve as hydrogen gas.



Thus the overall reaction is $Fe + 2 H^{+} \longrightarrow Fe^{2+} + H_2 \uparrow$

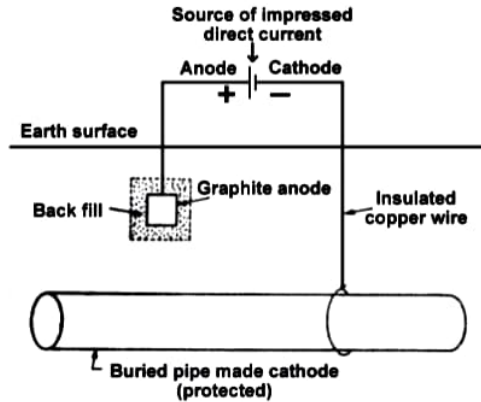
This type of corrosion occurs in case of the metals present above hydrogen in the electrochemical series.



b) Oxygen absorption corrosion: This type of corrosion occurs when the corrosive environment is

Cathodic Protection: Cathodic protection involves forcing the metal to be protected to behave like a cathode so that corrosion does not occur. This is based on the principle that during electrochemical corrosion, cathodic areas are not affected by corrosion. The base metal can be forced to behave as cathode by using two methods.

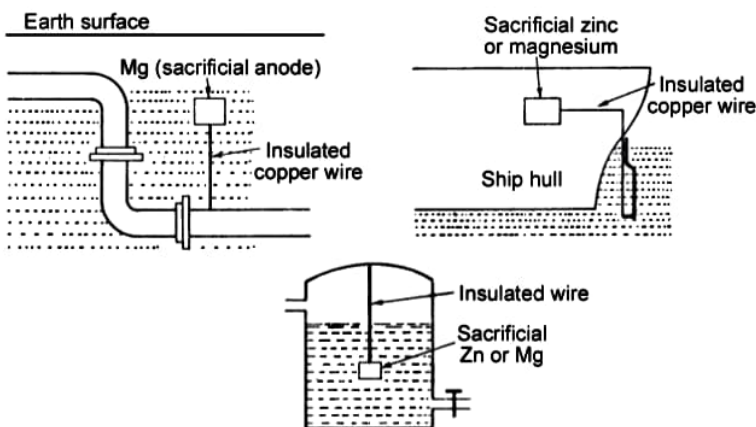
i) *Impressed current method:* In this method, an impressed current is applied in opposite direction to nullify the corrosion current, and convert the corroding metal from anode to cathode. Impressed current can be derived from a DC source with an insoluble anode like graphite, high silica iron, scrap iron, stainless steel or platinum.



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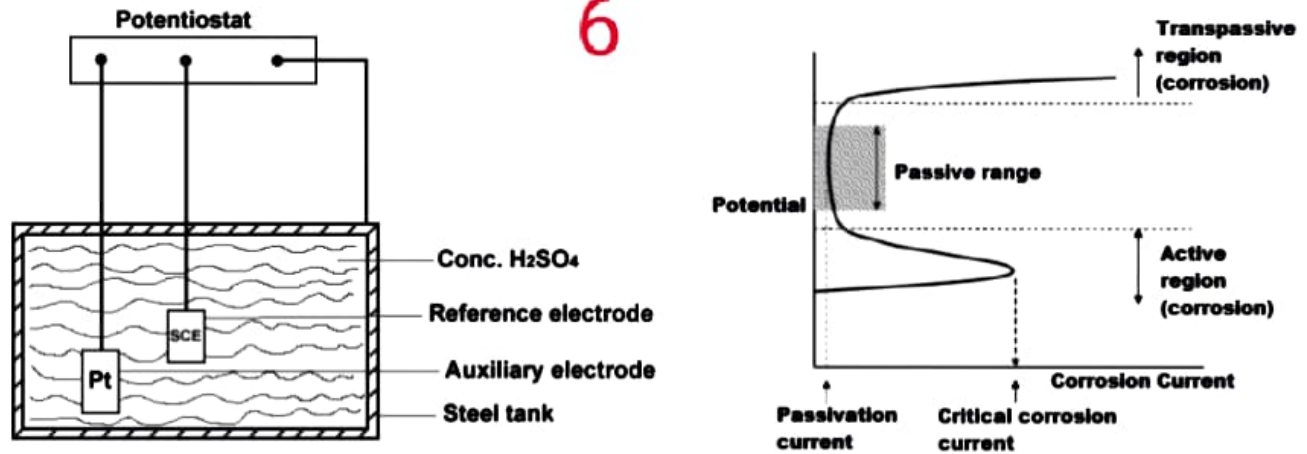
Usually, a sufficient D. C. current is applied to an insoluble anode, buried in the soil (or immersed in the corroding medium) and connected to the metallic structure to be protected. The anode is usually in backfill (composed of coke breeze or gypsum) so as to increase the electrical contact with the surrounding soil. This method has been applied to water tanks, buried oil or water pipes, condensers, transmission line towers, marine piers, laid-up ships, etc. This kind of protection technique is particularly useful for large structures for long-term operation.

ii) *Sacrificial anode method:*



In this method, the metallic structure to be protected, is connected to a more anodic (active) metal so that entire corrosion is concentrated on this more-active metal. The more active metal itself gets corroded, while the parent structure (which becomes cathode) is protected. The more-active metal so-employed is called sacrificial anode. The corroded sacrificial anode block is replaced by a fresh one, when consumed completely. Metals commonly employed as sacrificial anodes are magnesium, zinc, aluminium and their alloys. Important applications of sacrificial anodic method include protection of buried pipeline, underground cables, marine structures, ship-hulls, water-tanks, etc.

Anodic protection (Anodization): This method is based on the formation of protective film on metals by externally applied anodic currents. This method is useful for active-passive metals like Cr, Fe, Ni, Ti and their alloys.



If carefully controlled anodic currents are applied to these metals, they get passivated and the rate of material dissolution decreases. For this purpose, a device called potentiostat is used. It is an electronic device, which maintains a metal at a constant potential w.r.t. the reference electrode. It has three terminals, one connected to the base metal (eg. steel tank), other to the reference electrode (Calomel electrode) and the third to an auxiliary electrode (platinum). This method is based on the principle that a protective oxide surface film is formed on metal/alloy by the application of anodic current on the appliance in a suitable oxidizing environment. From electrochemical measurements, the optimum potential is determined for protection. The required potential for protecting the metal can be obtained from its 'potential-current curve'.

When the potential of the base metal is gradually increased, corrosion current increases from A to B reaching a maximum, I_{crit} (critical current). Above this potential (E_{crit}), current decreases drastically and suddenly and maintains at I_p (passivation current), due to attainment of passive state. The corresponding potential required is called passivation potential. Until this minimum current, I_p is maintained by the potential, E_p , the object will be in its passive state. This method is mainly used for stainless steel containers used for storing or transporting corrosive chemicals like concentrated acids by maintaining the structures at their passivation current. This method is applicable to only those metals/alloys that exhibit passivity and are present in the oxidizing environment.

Corrosion inhibitors: A corrosion inhibitor is a substance which when added in small quantities to the aqueous corrosive environment, effectively decreases the rate of corrosion. They get dissolved in the corroding medium, but are capable of forming a protective layer either at anode or at cathode.

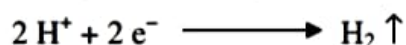
a) *Anodic inhibitors:* (Chromates, phosphates, tungstates and other transition metal compounds possessing high content of oxygen): These inhibitors control the corrosion process by controlling the following reaction taking place at anodic areas.



These inhibitors are soluble in the corrosive medium. The anions of the inhibitor are migrated towards anode and combine with the metal ions produced at anode due to initial corrosion and form insoluble/sparingly soluble metal compound, which forms as a protective film by adsorption and reduces corrosion rate. Although these inhibitors are effective, they are dangerous, if used in inadequate quantities. If certain areas are unprotected by the depletion of inhibitor layer, severe localized corrosion occurs.

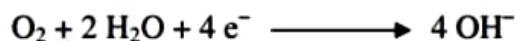
b) *Cathodic inhibitors:*

(i) *In acidic solutions:* The predominating cathodic reaction in acidic media is



Rate of this reaction can be reduced by controlling the diffusion of H^{+} ions to the cathodic sites. This can be achieved by organic inhibitors like amines, ureas, thioureas, mercaptans, heterocyclic nitrogen compounds, which adsorb at the metal surface. In order to control the above reaction, antimony and arsenic oxides can be used. They get deposited as metallic antimony or arsenic in the form of adherent film thereby increasing hydrogen over voltage.

(ii) *In neutral or alkaline solutions:* The predominating cathodic reaction in these media is



The rate of this reaction can be reduced in two ways:

1. By eliminating oxygen from the medium by deaeration or deactivation (hydrazine, etc.).
2. By retarding the diffusion of oxygen to cathodic areas. This can be achieved by adding salts of Mg, Zn or Ni. They release corresponding metal ions into the medium, which diffuse to cathodic sites and react with hydroxide ions produced during the above reaction to form insoluble metal hydroxides. These hydroxides deposit on cathodic sites as protective film.

Electroplating (Electrodeposition)

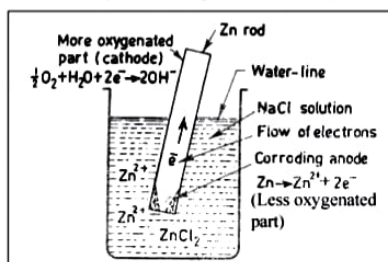
Concentration Cell Corrosion: The electrochemical attack on the metal surface exposed to an electrolyte of varying concentrations or of varying aeration is called concentration cell corrosion. It may be due to local difference in ion concentration or inadequate agitation or slow diffusion of metal ions produced by corrosion.

Differential aeration corrosion: It is the most common type of concentration cell corrosion. It is also called oxygen concentration cell corrosion. It occurs due to exposure of different parts of a metal to different concentrations of oxygen. It causes difference in potential between differently aerated areas. Poor-oxygenated parts are anodic, while more-oxygenated parts are cathodic. It causes a flow of electrons from poor-oxygenated parts to more-oxygenated parts. *Waterline corrosion* is an example of differential aeration corrosion. Here corrosion of metal takes place just below the waterline, when the metal is partially immersed in a solution.



If a metal (say zinc) is partially immersed in a dilute solution of a neutral salt (say NaCl) and the solution is not agitated properly, then the part above and closely adjacent to the waterline are more aerated and it becomes cathodic. The part of the metal immersed to greater depth, which has less access to oxygen, becomes anodic. Hence, difference of potential is created, which causes a flow of current between the two differently-aerated areas of the same metal.

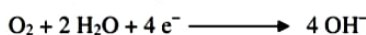
Then, oxidation of zinc takes place at anodic areas,



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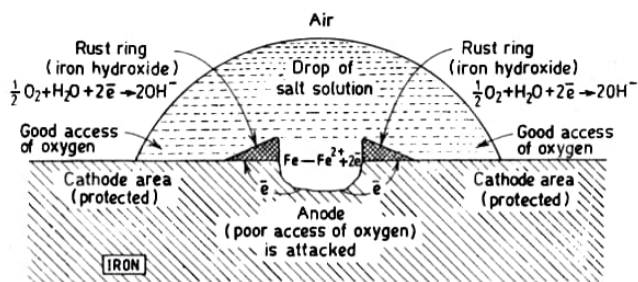
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and reduction of oxygen takes place at cathodic areas,



The flow of electrons takes place through the metal and migration of ions takes place through the electrolyte.

Another example of differential aeration corrosion is the corrosion of iron under the drops of water (or salt solution). Here, areas covered by droplets are less-oxygenated parts and become anodic, while the surrounding parts are more-oxygenated and become cathodic. The corrosion starts at the metal under the droplet. Similarly, corrosion is accelerated at the places where the access to oxygen is less. The oxygen-deficient parts serve as anodes and hence cracks and crevices are formed at those places.



Practical examples for differential aeration corrosion:

- 1) Part of nail inside the wall
- 2) Window rods inside the frame
- 3) Paper pins inside the paper
- 4) Partially buried pipelines in soil

Corrosion due to dissimilar metals (Galvanic corrosion or bimetallic corrosion): When two