Objective

The primary objective of this experiment is to introduce the students to the corrosion phenomena as occurs in engineering materials. Some commonly used techniques for measuring and preventing corrosion will be studied. Accordingly, the following will be investigated:

1. Measurement of the electrode potentials of the metals/alloys.

2. Demonstration of the principles of the electroplating process.

3. Demonstration of the principles of electrolyses plating and passivation.

4. Corrosion prevention by cathodic protection.

5. Corrosion mitigation by the addition of inhibitors.

Background

Corrosion can be defined as the degradation of a material when it comes in contact with the environment. The dissolving of a material by a corrosive liquid is called chemical corrosion. The material continues to dissolve until either it is consumed or the liquid is saturated. A simple example is salt dissolving in water. The removing of metal atoms from a solid material as the result of an electric circuit is called electrochemical corrosion. In this form of corrosion, metal atoms lose electrons and become ions thus forming a byproduct. Electrochemical corrosion occurs most frequently in aqueous mediums, in which ions are present in water or moist air. In this process, an electric circuit is created and the system is called an electrochemical cell. Corrosion of a steel pipe or a steel automobile panel, creating holes in the steel and rust as the byproduct, are examples of this reaction.

Protection Against Electrochemical Corrosion

A number of techniques are used to combat corrosion, including design, coating, inhibitors, cathodic protection, passivation, and material selection.

1. **Coatings**

Coatings are used to isolate the anode and the cathode regions. The category of coatings includes oil and paint type applications as well as electroplating. The electroplating process consists of immersing a part to be coated in a solution of the metal to be coated and passing direct current between the part (cathode) and another electrode (anode). The final composition and the nature of the plating depends on various factors like temperature, current density, time and composition of the bath. A majority of metals like copper, chromium, zinc, nickel, cadmium, etc. can be applied by using this process.
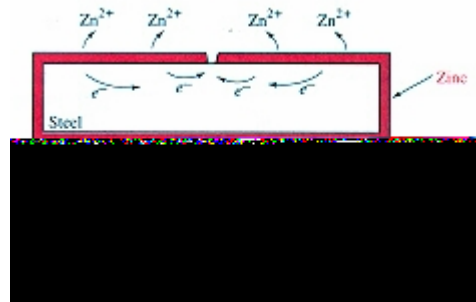

Figure 1 - Zinc-plated Steel and Tin plated Steel are protected differently. Zinc protects steel even when the coating is scratched, since Zinc is anodic to steel. Tin does not protect Steel when the coating is disrupted, since Steel is anodic with respect to Tin. [Askeland, 1994]

2. Inhibitors

An inhibitor is a substance which when added in small quantities to a corrosive fluid decreases the corrosion rate by several orders of magnitude. An inhibitor can be regarded as a retarding catalyst. They can be classified into several groups according to the mechanisms by which they function.

   a. The Absorption Type get absorbed on the surface of the metal that corrodes and suppress the metal dislocation and reduction reactions. (ex. organic amines)

   b. Scavengers are a special type of inhibitors which remove the corrosion causing reagents from the environment. (ex. sodium sulfite, hydrazine)

   c. Vapor Phase Inhibitors are similar to the adsorption type and possess a high vapor pressure. They can be placed in the environment without any contact with the metal. They form a thin adsorbed layer on the metal by sublimation followed by condensation on the surface

   d. Oxidizers are the substances which are effectively used to inhibit the corrosion of metals that demonstrate active-passive transitions like iron, titanium etc. (ex. chromate, nitrate)

   e. Hydrogen Evolution Inhibitors, such as antimony, retard the hydrogen reduction reaction.

3. Cathodic Protection

Cathodic Protection is a common method of corrosion prevention employed in pipelines where the metal behaves entirely as a cathode and hence corrosion is averted. This can be achieved in two ways:

   a. Impressed Voltage: As shown in the figure 1a, an external dc power supply is connected to the metal to be protected. The negative terminal of the power supply is connected to the metal and the positive terminal to an inert anode like graphite. The process can be described as the passage of a suitable electric current in an opposite direction at an equal or a greater rate than it was flowing when the metal was not protected.

   b. Sacrificial Anode or Galvanic: As shown in figure 1b, a metal which has a higher tendency to corrode, anodic from the emf series, is coupled with the metal to be protected. The sacrificial anode corrodes, supplies electrons to the metal, and thereby prevents an anode reaction at the metal. The sacrificial anode is consumed and must eventually be replaced.
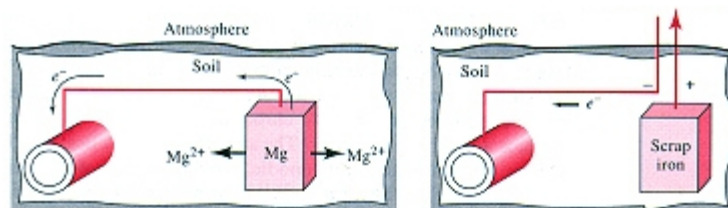

Figure 2: Cathodic Protection of a buried steel pipeline; (a) A sacrificial Mg anode assures that the galvanic cell makes the pipeline the cathode. (b) An impressed voltage between a scrap Iron auxiliary anode and the pipe line assures that the pipeline is the cathode. [Askeland, 1994]

4. Passivation

Certain metals protect themselves by forming an ultra thin (<100A thick) surface layer of an oxide which forms a shield to oxygen penetration, e.g. stainless steel forms a thin layer approximately 20A of chromium oxide. The metal is said to passivate itself in these cases. Passive films can be formed on brasses, aluminum alloys etc. by the use of oxidizers added to solution. For example, chromate and nitrate salts are passivators.

Components of an Electrochemical Cell

Anode: The anode gives up electrons to the circuit and corrodes.

Cathode: The cathode receives electrons from the circuit by means of a chemical reaction. Ions that combine with the electrons produce a byproduct at the cathode.

Contact: The anode and cathode must be electrically connected permitting electron flow.

Electrolyte: The electrolyte is the liquid or gas in contact with both the anode and cathode. It provides the means by which the metallic ions leave the anode surface and assures that ions move to the cathode to accept the electrons.
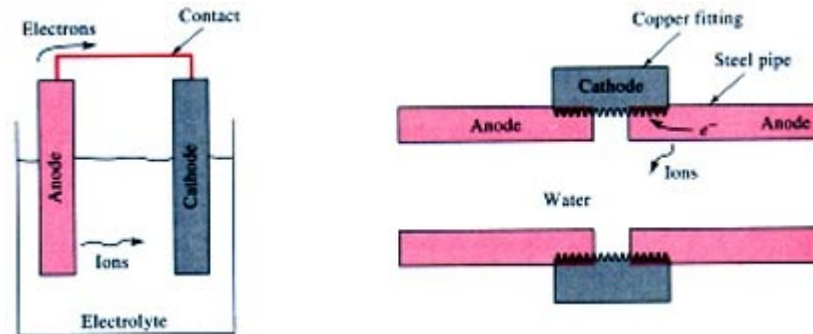

Figure1: The components in an electrochemical cell: (a) a simple electrochemical cell and (b) a corrosion cell between a steel water pipe and a copper fitting. [Askeland, 1994]

Reactions of an Electrochemical Cell

Oxidation

Oxidation is a metal anode reaction by which metal atoms are ionized. The metal ions enter the electrolytic solution while the electrons leave the anode through the electrical connection:

$$M \rightarrow M^{n+} + ne^-$$

Because metal ions leave the anode, the anode corrodes.

Reduction

1. The Electroplating Reaction: Reduction reactions are the reverse of the anode reactions - Electroplating:
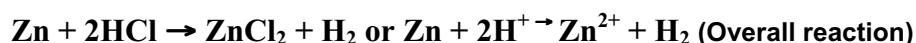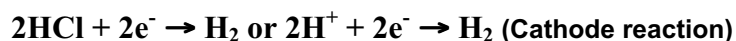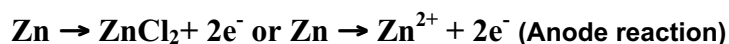
$$M^{n+} + ne^- \rightarrow M$$

The metal ions, either intentionally added to the electrolyte or formed by the anode reaction, combine with electrons at the cathode. The metal then plates out and covers the cathode surface. In many cases plating does not actually occur; a byproduct is formed at the cathode instead.

2. The Hydrogen Electrode: In oxygen-free liquids, such as HCl or stagnant water, hydrogen gas may be evolved at the cathode:
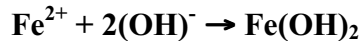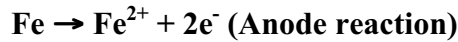
$$2H^+ + 2e^- \rightarrow H_2$$

A classic example of this is the attack on zinc by hydrochloric acid. When zinc is placed in hydrochloric acid it dissolves forming zinc chloride with the release of hydrogen gas. During metallic corrosion, the rate of oxidation equals the rate of reduction in terms of electron production and consumption.
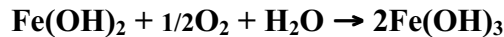
$$Zn \rightarrow ZnCl_2 + 2e^- \text{ or } Zn \rightarrow Zn^{2+} + 2e^- \text{ (Anode reaction)}$$

$$2HCl + 2e^- \rightarrow H_2 \text{ or } 2H^+ + 2e^- \rightarrow H_2 \text{ (Cathode reaction)}$$

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2 \text{ or } Zn + 2H^+ \rightarrow Zn^{2+} + H_2 \text{ (Overall reaction)}$$

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3. The Oxygen Electrode: In aerated water oxygen is available to the cathode and hydroxyl ions form:

$$1/2O_2 + H_2O + 2e^- \rightarrow 2(OH)^-$$
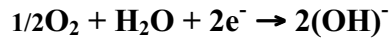
The oxygen electrode enriches the electrolyte in OH- ions. These ions react with positively charged metallic ions and produce a solid product. In the case of the rusting of iron:

$$Fe \rightarrow Fe^{2+} + 2e^- \text{ (Anode reaction)}$$

$$1/2O_2 + H_2O + 2e^- \rightarrow 2(OH)^- \text{ (Cathode reactions)}$$

$$Fe^{2+} + 2(OH)^- \rightarrow Fe(OH)_2$$

$$Fe + 1/2O_2 + H_2O \rightarrow Fe(OH)_2 \text{ (Overall reaction)}$$

The reaction continues to produce rust.

$$Fe(OH)_2 + 1/2O_2 + H_2O \rightarrow 2Fe(OH)_3$$

4. The Water Electrode: In oxidizing acids the cathode reaction produces water as a byproduct:

$$-O_2 + 4H^+ + 4e^- \rightarrow 2 H_2O$$
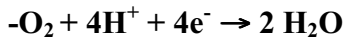
If a continuous supply of both oxygen and hydrogen is available, the water electrode produces neither a buildup of rust nor a high concentration or dilution of ions at the cathode.
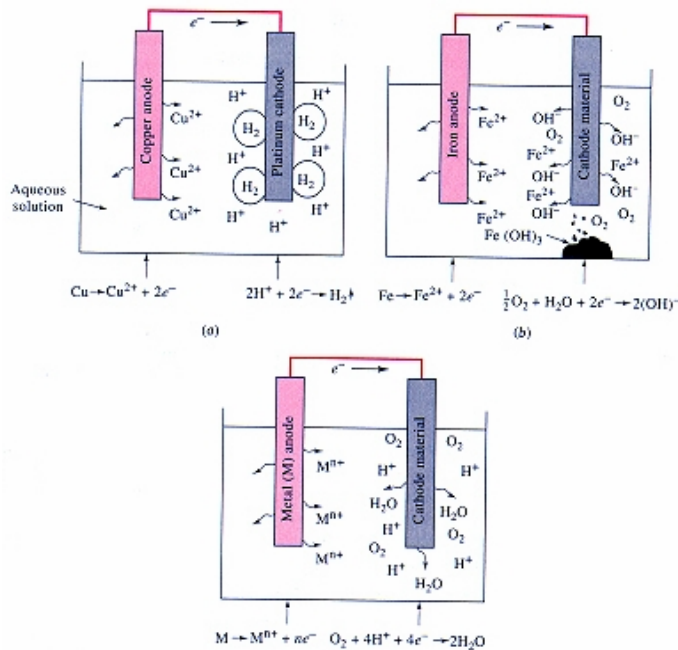

Figure 2 - The anode and cathode reactions in typical electrolytic corrosion cells: (a) the hydrogen electrode, (b) the oxygen electrode, and (c) the water electrode. [Askeland, 1994]

When a metal is exposed to an aqueous environment it develops an electric potential called a half-cell potential that is characteristic of the metal and the environment. This potential can be measured by using a reference electrode. Table 1 lists the half-cell potentials under standard conditions, frequently called emf series, of several

metals against a hydrogen reference electrode. If two dissimilar metals are connected an electron flow occurs due to their potential difference. The metal with lower potential is the anode and dissolves to produce ions and electrons while the metal/alloy with a higher potential is the cathode, which accepts electrons via metal circuit. Note that electrons do not flow through liquid solutions. Table 2 presents the galvanic series of some of the commercial materials and alloys in seawater. This series has been constructed since the emf series provides us with the potentials of pure metals whereas alloys are very commonly used in practical applications.

	Metal	Electrode Potential E_o (V)
Anodic	$Li \rightarrow Li^+ + e^-$	−3.05
	$Mg \rightarrow Mg^{2+} + 2e^-$	−2.37
	$Al \rightarrow Al^{3+} + 3e^-$	−1.66
	$Ti \rightarrow Ti^{2+} + 2e^-$	−1.63
	$Mn \rightarrow Mn^{2+} + 2e^-$	−1.63
	$Zn \rightarrow Zn^{2+} + 2e^-$	−0.76
	$Cr \rightarrow Cr^{3+} + 3e^-$	−0.74
	$Fe \rightarrow Fe^{2+} + 2e^-$	−0.44
	$Ni \rightarrow Ni^{2+} + 2e^-$	−0.25
	$Sn \rightarrow Sn^{2+} + 2e^-$	−0.14
	$Pb \rightarrow Pb^{2+} + 2e^-$	−0.13
	$H_2 \rightarrow 2H^+ + 2e^-$	0.00
	$Cu \rightarrow Cu^{2+} + 2e^-$	+0.34
	$4(OH)^- \rightarrow O_2 + 2H_2O + 4e^-$	+0.40
	$Ag \rightarrow Ag^+ + e^-$	+0.80
	$Pt \rightarrow Pt^{6+} + 4e^-$	+1.20
	$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	+1.23
Cathodic	$Au \rightarrow Au^{3+} + 3e^-$	+1.50

Table 1 - The electromotive force (emf) series for selected elements. [Askeland, 1994]
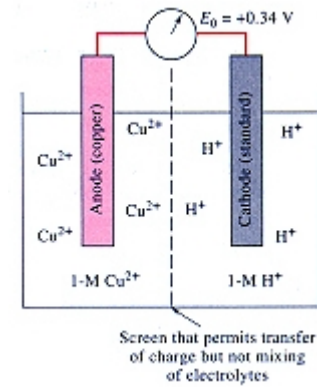
Figure 3 - The half-cell used to measure the electrode potential of copper under standard conditions. The electrode potential of copper is the potential difference between it and the standard hydrogen electrode in an open circuit. Since Eo is greater than zero, copper is cathodic compared with the hydrogen electrode. [Askeland, 1994]

Table 2: The galvanic series in seawater. [Askeland, 1994]

Anodic	Magnesium and Mg alloys	Anodic	Lead
	Zinc		Tin
	Galvanized steel		Cu-40% Zn brass
	5052 aluminum		Nickel-base alloys (active)
	3003 aluminum		Copper
	1100 aluminum		Cu-30% Ni alloy
	Alclad		Nickel-base alloys (passive)
	Cadmium		Stainless steels (passive)
	2024 aluminum		Silver
	Low-carbon steel		Titanium
	Cast iron		Graphite
	50% Pb-50% Sn solder		Gold
	316 stainless steel (active)	Cathodic	Platinum

After *ASM Metals Handbook*, Vol. 10, 8th Ed., 1975.

Procedure & Lab Requirements

Part A: Measurement

1. Half-Cell Potentials: In this part of the experiment, the electrode potentials of a number of metals and alloys will be measured and a galvanic series will be constructed. The electrolyte used is 3.5wt% NaCl. Clean and depolarize the materials (see table below) by buffing them with emery paper followed by dipping them momentarily in diluted HCl and a final rinse in water. All specimens should be cleaned before a new test is performed. The half-cell potentials will be measured with respect to the reference electrode by using a potentiostat. Construct the galvanic series for the following materials:

Material	Electrode Potential

Reference Electrode	
Brass	
1090 steel	
Aluminum alloy	
Zinc	
Titanium alloy	
Ni alloy	
Stainless steel	

2. <u>Potential Difference</u>: Two different metals/alloys are connected and the potential difference between the two is measured with a voltmeter. The measured potential difference should be theoretically equal to the difference between the half-cell potentials measured for the metals/alloys individually. Calculate the expected potential difference between the two metals using the formula:

    Potential Difference = $E_{cathode} - E_{anode}$

    Where $E_{cathode}$ = the half cell potential of the cathodic material; and

    E_{anode} = the half cell potential of the anodic material.

    Measure the potential difference for the following galvanic couples and indicate which is the anodic material:

Materials	Theoretical	Measured
Aluminum alloy – 1090 steel		
1090 steel – Zinc		
Brass –1090 steel		
Titanium alloy – Brass		
1090 steel – nickel alloy		

3. <u>Cathodic Protection</u>: Measure the weight and volume of each material sample listed below. Dip each in diluted acid solution (Must specify) and measure the loss of weight due to corrosion. Then, take a zinc piece, polish it, measure its weight and volume and couple it with another steel piece by means of a clip. Dip the coupled materials in the solution again and determine the weight loss of the material over the same time period. Write down your observation of the process.

Material	Initial weight	Final weight	Change in weight
Steel			
Zinc			
Steel & Zinc			

Part B: Demonstration

4. Describe the electroplating process as observed during the demonstration.

5. Describe the electroless plating process as observed during the demonstration.

Part C: Observation

6. Nail Observations: Nine test tubes containing a single low-carbon steel nail, each were cleaned at least two days ago. The steel nails were cleaned with 22-grit silicon carbide sandpaper and washed in methanol. This process removes any previous corrosion and any oil that may be on the nail. Describe your observations in terms of an electrochemical cell for each test tube.

    a. Is the galvanic cell operating?

    b. What acts as the anode, cathode, electrolyte, and contact?

    c. Using test tube 1 as a reference, what is the main difference in this test tube?

Test Tube Contents:

1. Tube 1: Clean steel nail covered in tap water.

2. Tube 2: Clean steel nail covered with tap water, boiled to drive off dissolved oxygen.

3. Tube 3: Clean steel nail covered with distilled water, boiled to drive off dissolved oxygen.

4. Tube 4: Steel nail, as received, covered with tap water.

5. Tube 5: Clean steel nail partially immersed in tap water.

6. Tube 6: Galvanized nail (zinc coated), one side ground flat, covered in tap water.

7. Tube 7: Clean steel nail, wrapped with copper wire or strip, covered with tap water.

8. Tube 8: Clean steel nail, wrapped with 60% tin 40% lead wire, covered with tap water.

9. Tube 9: Clean steel nail.

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Homework

1. Discuss a corrosion problem encountered in an engineering context and give three different methods for combating the problem.

2. What is cathodic protection? Discuss the mechanism involved.

3. What are inhibitors? Discuss in brief the mechanism of reducing the corrosion of metals by the addition of an inhibitor. Name an inhibitor for steel and state in what medium it is most effective.

4. Give some of the practical applications where the electroplating process is employed.
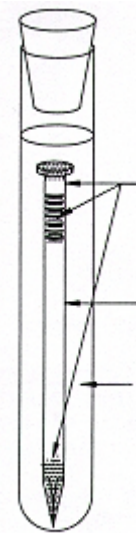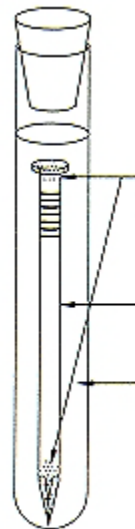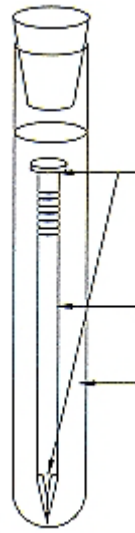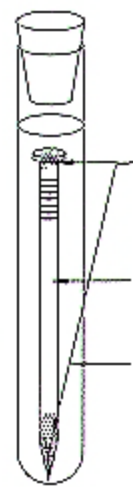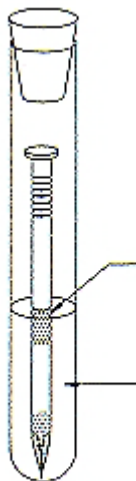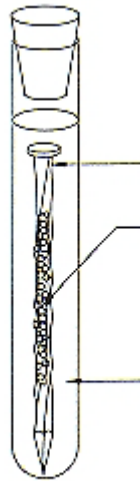
Tube 1   Tube 2   Tube 3   Tube 4

Tube 5   Tube 6   Tube 7   Tube 8   Tube 9