

# LECTURE NOTES ON CHE 431

## COURSE TITLE: Corrosion of Metals and Alloys

CREDIT UNITS: 3 units

### Module 1

Corrosion is the gradual destruction of materials, (usually metals), by chemical reaction with its environment.

**Rusting**, the formation of iron oxides, is a well-known example of electrochemical corrosion

In the most common use of the word, this means electrochemical oxidation of metals in reaction with an oxidant such as oxygen. Rusting, the formation of iron oxides, is a well-known example of electrochemical corrosion. This type of damage typically produces oxide(s) or salt(s) of the original metal.

**1.0 Corrosion** is the deterioration or destruction of metals and alloys in the presence of an environment by chemical or electrochemical means. In simple terminology, corrosion processes involve reaction of metals with environmental species. **Corrosion** is the gradual destruction of materials, (usually metals), by chemical reaction with its environment. This means electrochemical oxidation of metals in reaction with an oxidant such as oxygen.

Rusting, the formation of iron oxides, is a well-known example of electrochemical corrosion.

**This type of damage typically produces oxide(s) or salt(s) of the original metal. Corrosion can also occur in materials other than metals, such as ceramics or polymers, although in this context, the term degradation is more common.** Corrosion degrades the useful properties of materials and structures including strength, appearance and permeability to liquids and gases. Many structural alloys corrode merely from exposure to moisture in air, but the process can be strongly affected by exposure to certain substances. Corrosion can be concentrated locally to form a pit or crack, or it can extend across a wide area more or less uniformly corroding the surface. **Because corrosion is a diffusion-controlled process, it occurs on exposed surfaces.** As a result, methods to reduce the activity of the exposed surface, such as passivation and

**chromate conversion**, can increase a material's corrosion resistance. However, some corrosion mechanisms are less visible and less predictable.

However Engineering materials are majorly divided into 4. These are::

1. metals, non-metals and alloy;
2. Glass and ceramics,
3. Polymers and lastly: 4. Composite

#### **Corrosion depends on:**

- 1. Chemicals present
- 2. Type of material (metal, ceramic, polymer)
- 3. Temperature
- 4. Exposure time and 5. Stress

#### **Corrosion classification**

Corrosion occurs in several widely different forms. Classification is usually based on one of the three factors:

1. Nature of the corroding: corrosion can be classified as wet or dry. A LIQUID / MOISTURE is necessary for wet corrosion while dry corrosion usually involves the reaction with high temperature gases
2. Mechanism of corrosion : this involves either electrochemical or direct chemical reactions
3. Appearance of the corroded metal: Corrosion is either **uniform**: here the metal corrodes at the same rate over the entire surface or it is **localised** in which case only small areas are affected.

Classification by appearance which is particularly useful in failure analysis is based on identifying forms of corrosion by visual observation with either naked eyes or magnification. The morphology of attack is the basis for classification.

Corrosion: The process of slowly eating away of the metal due to attack of air, water, etc. on the surface of the metal is called corrosion.

The rusting of iron can be prevented by painting, oiling, greasing, galvanising, chrome plating, anodising or making alloys.

Galvanisation is a method of protecting steel and iron from rusting by coating them with a thin layer of zinc. The galvanised article is protected against rusting even if the zinc coating is broken.

**Alloys:** An alloy is a homogeneous mixture of two or more metals, or a metal and a non-metal.

**Alloys and their constituents:**

<b>Alloy</b>	<b>Constituents</b>
Brass	Copper, zinc
Bronze	Copper, tin
Steel	Iron, carbon
Stainless steel	Iron, nickel, chromium
Solder	Lead, tin

**Corrosion Protection of Al Alloys**

Aluminium and its alloys have excellent durability and corrosion resistance, but, like most materials, their behaviour can be influenced by the way in which they are used. (Although pure **Aluminium lacks mechanical strength but has higher resistance to corrosion than its alloys**). Aluminium is commercially important metal and its alloys are widely used in many industries such as reaction vessels, pipes, machinery and chemical batteries because of their advantages. Aluminium is a well-known sacrificial anode if couple with more passive metal as it is most reliable and cost effective anode. Aluminium sacrificial anode has been used in major project all over the world. It is used in offshore application including structures, platforms, pipelines, jetties and power plants. Aluminium anode is also used for ship-hull and ballast tank protection.

**Aluminium is an active metal and its resistance to corrosion depends on the formation of the protective oxide film.** There are several methods to protect the aluminium and its alloys from corrosion such as coatings (Metallic, Inorganic, conversion and organic coatings), control of environment (operating variable i.e. pH, dissolved oxygen, temperature) and corrosion inhibitors (organic and inorganic additives).

Aluminium can be alloyed with different elements like zinc, magnesium, silicon, copper, manganese, as well as lithium. As a result, it can be used for different applications like manufacturing of aluminium foil covering, food packaging industry, food and chemical industry, vehicle panelling, mine cages, air frames, chemical plants, pressure vessels, road tankers, transportation of ammonium nitrate, irrigation pipes and window frames.

*Some industrial applications for aluminium alloy are listed below:*

1. Aluminium alloys are highly resistant to non-heat treatments. They are good conductors of heat and electricity and that is why they are being used in different chemical industries for preparation of aluminium products.
2. Aluminium alloys get hardened during the process of reactions. That is why they are highly favourable alloys for the factor of weld ability as well as formability. Also, they are superior for the cryogenic uses even in the condition of annealed treatments.
3. Aluminium alloys is its high resistance to corrosion. They deter it from different harsh chemical treatments and help in retaining its lustre and strength. It also has high resistance to sea and ocean water. Therefore, it can be used for different air cages without any hassles.
4. Aluminium alloys can be converted into any form as they are ductile in nature. Be it sheets or wires, they can be drawn into various shapes without any inconvenience.
5. Aluminium alloy also used as sacrificial anode for the cathodic protection system (pipeline cathodic protection, oil tank, ship hull aluminium cp anode,

### ***Corrosion in nonmetals***

Most ceramic materials are almost entirely immune to corrosion. The strong chemical bonds that hold them together leave very little free chemical energy in the structure; they can be thought of as already corroded. When corrosion does occur, it is almost always a simple dissolution of the material or chemical reaction, rather than an electrochemical process. A common example of **corrosion protection in ceramics is the lime added to soda-lime glass to reduce its solubility in water; though it is not nearly as soluble as pure sodium silicate, normal glass does form**

**sub-microscopic flaws when exposed to moisture.** Due to its brittleness, such flaws cause a dramatic reduction in the strength of a glass object during its first few hours at room temperature.

**Corrosion of glasses:** Glass disease is the corrosion of silicate glasses in aqueous solutions. It is governed by two mechanisms: diffusion-controlled leaching (ion exchange) and hydrolytic dissolution of the glass network. Both mechanisms strongly depend on the pH of contacting solution: the rate of ion exchange decreases with pH as  $10^{-0.5\text{pH}}$  whereas the rate of hydrolytic dissolution increases with pH as  $10^{0.5\text{pH}}$ .

## **1.2 Effects of corrosion with respect to appearance, performance, safety and cost**

The effect of corrosion in our daily lives are both direct and indirect because it affects the useful service lives of our possessions and indirect in that producers and suppliers incur corrosion cost which they pass on to consumers. At home corrosion is readily recognized on automobile body panels, outdoor furniture and metal tools.

The corrosion of steel reinforcing bar result in failure of a section highway, the collapse of electrical towers and damage to buildings, parking structures and bridges.

**Rusting**, the formation of **iron** oxides is a well-known example of electrochemical corrosion. Rust is one of the most common causes of bridge accidents. As rust has a much higher volume than the originating mass of iron, its build-up can also cause failure by forcing apart adjacent parts. Similarly, corrosion of concrete-covered steel and iron can cause the concrete to spall, creating severe structural problems. It is one of the most common failure modes of reinforced concrete bridges. Measuring instruments based on the half-cell potential can detect the potential corrosion spots before total failure of the concrete structure is reached.

Until 20–30 years ago; galvanized steel pipe was used extensively in the potable water systems for single and multi-family residents as well as commercial and public construction. Today, these systems have long ago consumed the protective zinc and are corroding internally resulting in poor water quality and pipe failures. The economic impact on homeowners, condo dwellers, and the public infrastructure is estimated at 22 billion dollars as insurance industry braces for a wave of claims due to pipe failures.

**Elements can be broadly divided into two categories:** metals and non-metals. They differ both in physical and chemical properties.

### *Metal Properties*

Metals are malleable.

They Ductilily can be beaten into thin sheets. They are also ductile and can be drawn into wire (except a few metals like Na, K etc.)

Metallic Lusture All the metals show metallic lusture.;

Hardness Metals are generally hard

Physical state: They exist in solid and liquid states.

Sonorous Metals are sonorous and produce characteristic metallic sound when struck (e.g school bell)

Density: High density and lastly: Electrical conductivity Good conductor of electricity.

### *Non-metals Properties*

Mercury is the only metal and bromine is the only non-metal which exist in liquid state at room temperature.

Graphite and iodine possess metallic lusture though they are non-metals.

Sodium metal is soft like wax and it can be cut with a knife.

Gallium metal would melt if kept on our palm

Gold and silver are the most malleable and ductile metals.

Diamond is a better conductor of heat than copper but poor conductor of electricity.

Graphite is the only non-metal which is a good conductor of electricity but poor conductor of heat.

Gold, silver, platinum and copper are found in the free state. This is because of their poor reactivity as compared to other metals.

### **Electrochemical theory of wet corrosion: fundamentals**

The corrosion of metals by reaction with air and water to form metal hydroxides is a very important wet corrosion process, especially in the construction industries.

As with dry corrosion wet corrosion reactions are only possible if the free energy of the products of reaction is lower than the free energy of the reactants. This is the case however for the reaction of nearly all metals with water and oxygen to give metal hydroxides:

In addition, and unfortunately, the *rate* of wet corrosion may often be very high compared with dry corrosion on the same metal at the same temperature. There are two underlying reasons for this:

- \_ the dipolar water molecule stabilizes the free (dissociated) metal ions in solution;
- \_ the metallic structure and water in contact with it can both conduct electric current.

### **Passivation**

It refers to the spontaneous formation of an ultrathin film of corrosion products known as passive film, on the metals surface that act as a barrier to further oxidation. The chemical composition and microstructure of a passive film are different from the underlying metal. Typical passive film thickness on aluminium, stainless steels and alloys are within 10 nanometers. The passive film is different from oxide layers that are formed upon heating and are in the micrometer thickness range – the passive film recovers if removed or damaged whereas the oxide layer does not. Metals such as: Zirconium, chromium, Aluminum and stainless steel form oxide films when exposed to the atmosphere or to water. The films is invisible to the naked eyes mostly, however it is still very effective.

**Passivity may be stable or unstable.** A stable passivity depends on sufficient availability of an oxidizer. Passivation in natural environments such as air, water and soil at moderate pH is seen in such materials as aluminum, stainless steel, titanium, and silicon.

Passivation is primarily determined by metallurgical and environmental factors. The effect of pH is summarized using Pourbaix diagrams, but many other factors are influential.

### **Pourbaix diagram**

**It is** also known as a **potential/pH diagram**,  **$E_H$ -pH diagram** or a **pE/pH diagram**, maps out possible stable (equilibrium) phases of an aqueous electrochemical system. Predominant ion boundaries are represented by lines. As such a Pourbaix diagram can be read much like a standard phase diagram with a different set of axes. But like phase diagrams, they do not allow for reaction rate or kinetic effects.

Pourbaix diagrams have several uses, for example in corrosion studies, geology and in environmental studies.

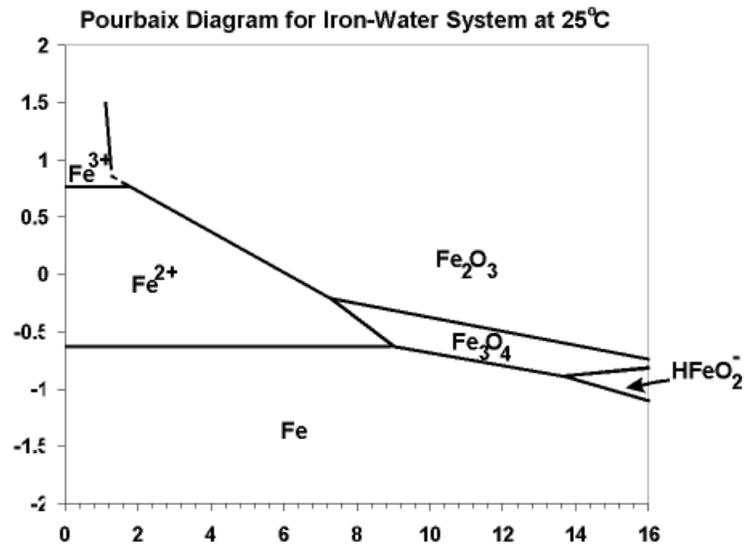
Objectives of Pourbaix diagram:

1. To show directions of the various reactions at given pH and potential.
2. To make a basis for estimation of the corrosion product compositions at various pH and potential combinations.
3. To show which environmental pH and potential changes will reduce or prevent corrosion.

**In environmental chemistry:** Pourbaix diagrams are widely used to describe the chemical behaviour of chemical species in the hydrosphere

***Pourbaix diagram of iron***

These widely used diagrams show how corrosion behaviour depends on electrical potential  $E$  and pH. A simplified Pourbaix diagram for iron is shown here.



Pourbaix diagram for iron, showing regions of active corrosion, passivity and immunity.

When evaluating the stability of the corrosion state, the distance to the passivity region in the Pourbaix diagram along the pH axis should be taken into account, because the reactions lead to pH changes close to the metal surface

**Polarization:** This refers to condition when reaction rate is controlled by the **slowest** step in the process. *I.e. there is an energy barrier related to this slowest step.* This may be affected by the composition of the metal,. In polarization, metal with low potential will corrode if 2 metals are connecting.

*An introduction to the electrochemical series and corrosion of metals: The potential difference between an anode and a cathode can be measured by a voltage measuring device. The absolute potential of the anode and cathode cannot be measured directly. Defining a standard electrode, all other potential measurements can be made against this standard electrode. If the standard electrode potential is set to zero, the potential difference measured can be considered as the absolute potential.*

**Standard Hydrogen Electrode:** is the half-cell in which the hydrogen reaction takes place is called the Standard Hydrogen Electrode - SHE

**Standard Electrode Potential:** is the potential difference measured between metal M, and the Standard Hydrogen Electrode - SHE

The electrochemical series (electro-motive series) consists of a list of metals which have been arranged in order of their standard potentials to hydrogen electrode.

<b>Element</b>	<b>Electrode Potential (Volts)</b>
Lithium	-3.04
Rubidium	-2.92
Potassium	-2.92
Calcium	-2.87
Barium	-2.80
Sodium	-2.71
Magnesium	-2.37
Beryllium	-1.85
Aluminum	-1.67
Manganese	-1.19
Nickel	-0.24
Tin	-0.14
Lead	-0.13
Hydrogen	+0.00
Antimony	+0.10
Copper	+0.34

Iodine	+0.54
Silver	+0.80
Mercury	+0.85
Bromine	+1.07
Platinum	+1.20
Chlorine	+1.36
Gold	+1.50
Fluorine	+2.87

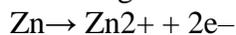
**IMPORTANT!** Metals which are higher in the electrochemical series displace metals which are lower in the sequence, which means when connecting two metals, the metal with lowest potential will corrode.

## Anodic and Cathodic Reactions

While the Pourbaix diagram shows a qualitative picture of what can happen at a given pH and potential, we also need knowledge about the electrode kinetics to predict:

- which values the potential and the local pH can attain, and
- the reaction rates for the actual pH–potential combinations.

To begin with we look at the Zn–H cell again. We have previously considered this as a reversible cell (equilibrium at the electrodes, large resistance in the voltmeter, so that the current through the meter is close to zero). If instead of the voltmeter we only have a conductor that short-circuits the cell, electrons will flow through the conductor from the negative Zn electrode to the Pt plate. The Zn electrode and the Zn reaction are moved away from equilibrium by this removal of negative charges from the Zn plate. In an attempt to re-establish the equilibrium, positive ions are released from the Zn plate to the liquid. Thus, Zn is dissolved at the same rate as electrons are transported to the Pt plate, where they are consumed in the hydrogen reaction. Thus the following reactions occur at the electrodes:



The same cell process can be totally obtained on a Zn plate submerged in a solution containing hydrogen ions and Zn ions. The reactions are accompanied by the same changes in free enthalpy and have the same equilibrium potentials as before. There is, however, a higher resistance against the hydrogen reaction on the Zn plate than on Pt, and thus the reaction rate will be lower on the Zn surface. Here we have a typical corrosion process, with an anodic reaction = oxidation ( $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ ) on those parts of the surface that constitute the anode, and a cathodic reaction = reduction ( $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ ) on the areas that constitute the cathode. The

anode and cathode areas may change positions, such that a given surface area element is alternately the site for the Zn reaction and for the hydrogen reaction. If there is no such alternation or if it occurs very slowly, different forms of localized corrosion may be the result. This depends on whether there are homogeneous or inhomogeneous conditions along the surface. Inhomogeneous conditions cause permanent anodes and cathodes, while under homogeneous conditions arbitrary variations in the liquid may determine if a given area element is anode or cathode at a certain moment.

## **THE CONSEQUENCES OF CORROSION**

The consequences of corrosion are many and varied and the effects of these on the safe, reliable and efficient operation of equipment or structures are often more serious than the loss of a mass of metal. Failures of various kinds and the need for expensive replacements may occur even though the amount of metal destroyed is quite small.

**Some of the major harmful effects of corrosion can be summarised as follows:**

1. Reduction of metal thickness leading to loss of mechanical strength and structural failure or breakdown. When the metal is lost in localised zones so as to give a crack like structure, very considerable weakening may result from quite a small amount of metal loss.
2. Hazards or injuries to people arising from structural failure or breakdown (e.g. bridges, cars, aircraft).
3. Loss of time in availability of profile-making industrial equipment.
4. Reduced value of goods due to deterioration of appearance.
5. Contamination of fluids in vessels and pipes (e.g. beer goes cloudy when small quantities of heavy metals are released by corrosion).
6. Perforation of vessels and pipes allowing escape of their contents and possible harm to the surroundings. For example a leaky domestic radiator can cause expensive damage to carpets and decorations, while corrosive sea water may enter the boilers of a power station if the condenser tubes perforate.
7. Loss of technically important surface properties of a metallic component. These could include frictional and bearing properties, ease of fluid flow over a pipe surface, electrical conductivity of contacts, surface reflectivity or heat transfer across a surface.
8. Mechanical damage to valves, pumps, etc, or blockage of pipes by solid corrosion products.

9. Added complexity and expense of equipment which needs to be designed to withstand a certain amount of corrosion, and to allow corroded components to be conveniently replaced.