

Corrosion

Basics

Lecture 1



What is Corrosion

- With a few exceptions, most of metals are unstable and they react with surrounding environment.
- As the surrounding environment gives these metals, opportunity to combine chemically and return to their original stable level as they were found in nature (e.g. oxide, hydroxide, or sulphide etc.)
- **Corrosion** is a natural process which converts refined active metal into a more chemically stable material.
- It is the gradual destruction of materials by chemical or electrochemical reaction.



What is Corrosion

- The most common well known example is Iron rusting. Where it forms oxides / hydroxide by reacting with oxygen and water.
- This reaction damages iron surface . The product is distinctive red/ orange colour.
- Other type of corrosions take place due to corrosive gases or liquid available in environment or dissolved in water like CO_2 , H_2S , NH_3 , organic acids etc.
- In absolute terms no metal is corrosion resistant. These may be having an insignificant reaction, undetectable with eye.
- Stainless steel, Monel , Inconel also can get corroded in specific environments.

Consequences of Corrosion

1. Corrosion degrades properties of materials, like strength, appearance, permeability to liquids etc.
2. Degradation makes it weak due to a loss of material and reduction in metal strength e.g. Hydrogen embrittlement, Sulphide stress cracking, Chloride attacks etc.
3. This may result in plant safety , loss of life, financial losses etc.

Some examples :

- Reduced value of product due to surface marks or mixture with rust contamination.
- Leakage from vessels and pipes making plant unsafe.
- Loss of property of component e.g. roller bearing, heat transfer across corroded tubes.
- Damage to valves, pumps, boiler or pressure vessel.

Consequences of Corrosion

Few examples:

1. A tube to tube sheet joint may leak and damage the exchanger performance.
2. A tank or pressure vessel may leak.
3. Distillation trays or tower internals may fail, and impact column performance.



Finding out Corrosion rate and corrosion allowance

- Corrosion rates can be expressed in a variety of ways such as :
 - Percent weight loss,
 - Milligrams per square centimetre per day
 - Milligrams per square inch per hour.
- However above values do not express corrosion resistance of any particular metal.
- An engineer's outlook is always the equipment or plant design life.
- The most desirable way of expressing corrosion rates is mils per year (mpy) .

Finding out Corrosion rate and corrosion allowance

- Corrosion rates are established by placing sample coupon in the environment for a fixed time and checking loss of weight with respect to time.
- Accordingly the additional thickness is added to component based on the design life of item.
- This additional thickness which takes care of future reduction of thickness is called Corrosion Allowance. Applied to all process wet areas.
- Normally in process industry the designed life of an equipment is taken as 20 years.

Finding out Corrosion rate and corrosion allowance

- Periodic inspection and thickness measurements of equipment is carried out to decide balance life.
- Normally for process equipment made of CS a corrosion allowance of 3mm is a common practice.
- It may go as high as 4.5 or 6mm for CS.
- Some times a corrosion allowance is also specified on stainless or other corrosion resistant steels (1 or 2 mm)
- Trays and tower internals of CS are normally given $\frac{1}{2}$ the CA provided for vessels. Applied to both side wetted surface.
- Normally no corrosion allowance is specified on exchanger tubes.

Classification of Corrosion

Corrosion can be classified in different ways, such as

- I. Chemical and electrochemical
- II. High temperature corrosion
- III. Wet corrosion
- IV. Dry corrosion.

Dry corrosion occurs in the absence of aqueous environment, usually in the presence of corrosive gases / vapours mainly at high temperatures.

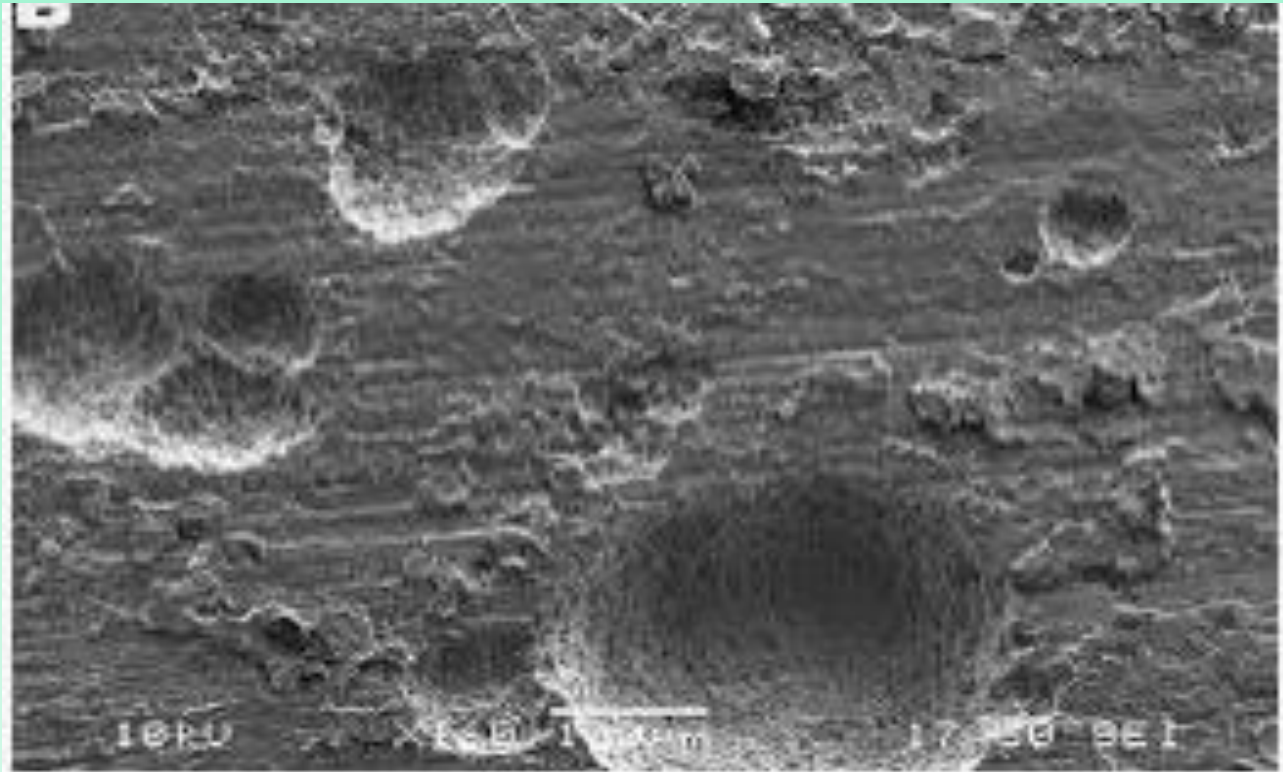
Acid theory of corrosion

- Corrosion is a complex electrochemical phenomenon.
- It starts at a particular spot on the surface of metal.
- The electrons released at this anodic spot move through the metal and combine with OH^- to form Hydroxides.
- Rusting of iron makes hydrated oxide, $\text{Fe}(\text{OH})_3$, $\text{FeO}(\text{OH})$, $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. The process needs presence of water, oxygen and an electrolyte.
- Water is normally acidic which is believed to be available from carbonic acid (H_2CO_3) formed due to dissolved CO_2 in water in moist air condition of atmosphere.

Chemical formula for rust

- The chemical formula for rust is Fe_2O_3 and is commonly known as ferric oxide or iron oxide.
- The final product is below
$$4\text{Fe} + 3\text{O}_2 + 6\text{H}_2\text{O} \rightarrow 4\text{Fe}(\text{OH})_3.$$
- The rusting process requires both oxygen and water. The process is accelerated by presence of acids, strains in the iron or rust itself.
- The loose porous rust $\text{Fe}(\text{OH})_3$ slowly transforms into $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, which is the familiar red-brown stuff
- Air with RH over 50% provides the necessary amount of water good to initiate corrosion. RH above 80% corrosion is worse.

Surface Pitting Corrosion



Pitting corrosion

- Pitting is among the most common and damaging forms of corrosion in passivated alloys.
- In the worst case, almost all of the surface will remain protected, but tiny local flaws degrade the oxide film.
- Corrosion at these points is amplified, and forms a small pit.
- While the corrosion pits only nucleate under fairly extreme circumstances, they can continue to grow even when conditions return to normal.
- Since the interior of a pit is naturally deprived of oxygen and locally the pH decreases to very low values and the corrosion rate increases.

Pitting corrosion

- A thin film with a small hole on the surface can hide a thumb sized pit below. This corrosion is often difficult to detect due to the fact that it is usually relatively small in size at the surface.
- Pitting results when a small hole, or cavity, forms in the metal, usually as a result of depassivation of a small area.
- This area becomes anodic, while part of the remaining metal becomes cathodic, producing a localized galvanic reaction.
- The deterioration of this small area penetrates the metal and can lead to failure.

Pitting corrosion

- When corrosion starts on a metal surface at certain small spot becomes an initiation point.
- The pit becomes deeper so its bottom has low oxygen which makes it more anodic.
- The outside pit surface area has higher oxygen concentration, hence become cathodic.
- Pitting is more severe in sea water. It can take place even in Stainless Steel.



A pitted flange face

Dry corrosion due to gases

1. Dry corrosion or oxidation occurs when oxygen in the air reacts with metal without the presence of a water or liquid.
2. Dry corrosion is sensitive to high temperature.
3. Dry corrosion is classified into three types:
 - a. Oxidation,
 - b. Molten-salt corrosion
 - c. Hydrogen attack.

Dry corrosion due to gases

1. Gases responsible for dry corrosion are:
 - H_2
 - SO_2
 - CO_2
 - Cl_2
 - etc.
2. Here corrosive effect depends mainly on the chemical affinity between the metal and the gas involved.
3. Degree of attack depends on type of protective or non protective films formed on the surface.
4. If volume of corrosion film formed is strong and non-porous, it does not allow further gas penetration.
e.g. $Ag + Cl_2 \rightarrow 2AgCl$ (protective film)

Dry corrosion due to gases

5. If lower thickness of protective layer forms pores/cracks and allow the penetration of corrosive gases ,
6. It leads to further corrosion of the underlying metal

Example :

H₂ gas at high temperature reacts with carbon at boundary on the layer of Iron structure converting it to Methane.

This is called Hydrogen attack, where metal develops cracks and blistering.

Passivation of surface

Passivity

1. Passivity occurs when an oxide layer forms a continuous film on a metal surface which prevents further oxidation (corrosion).
2. Metals which build layer of metal oxide on surface, exhibit passivity.
3. The metal oxide acts as a barrier by separating the metal surface from its environment and prevents corrosion.

Passivity

4. In order to provide passivity, this oxide layer must be both stable and firm.
5. Products of corrosion must be strong and insoluble in the environment.
6. Metals like Zirconium, Chromium, Aluminium and stainless steel form oxide films when exposed to the atmosphere or to water.
7. The film is so thin that it's invisible to the naked eye but very effective in giving these metals passivity and thus corrosion resistance.

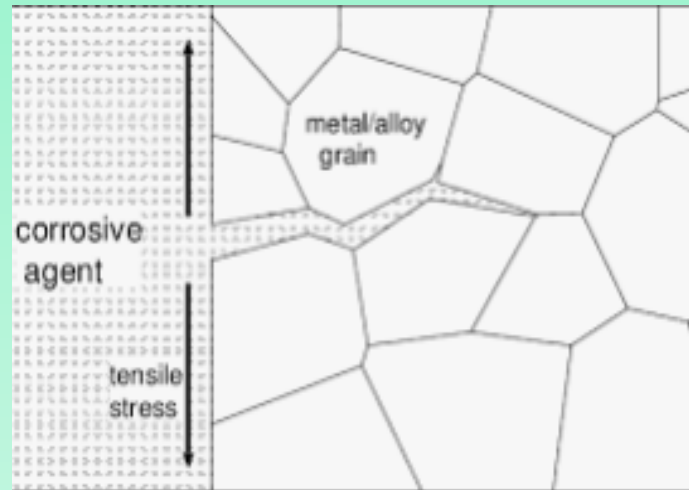
Why Stainless steel does not
corrode

Why Stainless steel does not corrode

- Stainless steel contains a minimum Cr content of 10.5%. The chromium reacts with the oxygen in the air and forms a protective layer that makes stainless steel highly resistant to corrosion and rust.
- Even with these impressive features, stainless steel can also rust .
- Some types of stainless steel are more prone to corrosion than others, depending on the chromium content.
- The higher the chromium content, the less likely the metal will rust.
- But, over time if not maintained correctly or in high Chloride environment it can also corrode.

Other type of Corrosion (next lectures)

1. Crevice corrosion
2. Hydrogen attack
3. Inter-granular corrosion
4. Chloride attack
5. Sulphide Stress corrosion cracking
6. Sulphur attack
7. Mercury attack
8. Molten salt corrosion
9. Caustic corrosion
10. Microbes corrosion



Thank you