



Corrosion Classification, Rate And Corrosion Product Type: A Review

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1. Introduction

Corrosion is a slow process that occurs primarily on metal surfaces, but the corrosion related losses are of high order. When considering only the loss of metal, the damages cannot be measured. Except for the least active noble metals, corrosion occurs with all metals. The indirect losses are much higher. Consideration must also be given to the cost of fabrication and cost of preventing corrosion. Indirect losses are higher than the direct losses. When a structure such as building or bridge collapsed due to problems with corrosion the damage often involves the loss of human life and property and the cost of subsequent reconstruction and alternative solution. Corrosion is quite noticeable in some types of corrosion and is only seen when an accident occurs.

1.1 Definition

Corrosion is “the destruction of material or consequent loss of metals through chemical or electrochemical attack by the environment. Process of corrosion is the transformation of pure metal in to its undesired metallic compound. Corrosion can be fast or slow process depending upon the metal and environment which it is undergo corrosion”.

1.2 Why do metals undergo corrosion?

Some metal are obtained in nature and forming a compound. Metal extracted from ores by reduction. Extraction of metal from the ores energy will be supplied in the form of heat/ electrical energy and they are natural tendency to return back to their combined state. Ores are lesser energy compared to pure metal. Metals are used in various ways; they combine with environment and converted to compound. Corrosion of metal is taking in to reverse of extractive metallurgy.

1.3 Losses caused due to corrosion

Every year, every country in the world is faces with large amount of economic losses due to corrosion.

- Loss of valuable products: - There is no particular concern about the loss of sulfuric acid to the drain, as it is a cheap product. Slightly losses of uranium compound or solution are harmful and can be very costly. In such situations, it is well justified to use more costly construction and better building materials.
- Price of repair of corroded products and equipment including labor cost.
- Shutdown of machinery due to failure of the corrosion. Sometimes these shutdowns are caused by corrosion that does not impact process conditions, yet sometimes this is induced by improvement in operating process that are incorrectly through capable of raising the extent of corrosion.
- Contamination of the product: - In many cases, the product's market value is directly linked to its purity and quality. In certain cases, very slight amounts of corrosion that brings other metal ion into the solution may cause a product catalytic decay, example in the manufacture and transport of concentrated hydrogen peroxide or hydrazine.
- Damage to equipment adjacent to the damage caused by corrosion. For example, in aircraft and other applications, chemical machining/ chemical milling are commonly used. Unmasked areas exposed to acid

when there is oxidation of excess metal. This procedure is implemented, when it is extra cost effective/ when the components are difficult to manufacture using more conventional methods.

1.4 Reasons to study corrosion

- Corrosion poses an enormous economic loss and much can be done to reduce it.
- Corrosion of Bridge is a major problem, costing billions when they age and require replacement.
- The petroleum industry is investing a million dollars a day securing underground pipelines.
- It is estimated from the paper industry that corrosion raises paper costs.
- The conversion of coal to gas and oil requires high temperatures, erosive particles and corrosive gases, resulting in problems that need to be solved.

To overcome all the above challenges there is need to study the various preventive measures against corrosion.

1.5 Classification of corrosion

Corrosion can be considered in distinct techniques; one technique is corrosion at lesser temperature and greater temperature. Another one is direct chemical corrosion and electrochemical corrosion.

1.5.1 Direct chemical corrosion/ Dry corrosion

Metal will be along with corrosive environment and no conducting medium, corrosive medium will directly attack the metal. When liquid phase is absent dry corrosion will be occur. Vapor and gas is also source of corrode. Since dry corrosion involves direct contact so it is called direct corrosion. Here chemical interaction takes place so it is called chemical corrosion. Example is sodium metal corroding Cd rods in nuclear power point.

Three types of dry corrosion are

- ❖ **Corrosion by oxygen:** - It involves the oxygen attack on the metal surface at either high or low temperature. At low temperature, alkali and alkali earth metals are oxidized, but most of them undergo a high temperature oxygen attack. The expected corrosion product is metal oxide film. If this oxide film is sufficiently stable, then prevent further oxygen attack on the metal. The oxide layer is found to be volatile in some cases and thus provides a fresh metal layer for corrosion at all times. If the layer is porous, then oxygen can easily attack the metal to convert more to corresponding oxides. In aluminium, the initial oxide layer formed is not stable in highly acidic and basic medium. Hence it undergoes further corrosion.
- ❖ **Corrosion by Hydrogen:** - It can occur by embrittling with hydrogen and decarburizing. In hydrogen, embrittlement metal loses its ductility and hence cracks. When we have metal in the hydrogen environment, it spread through the voids. Once exposed to the hydrogen environment, steel undergoes decarburization. Carbon gives extra strength to steel, but when exposed to hydrogen, carbon becomes methane. Thus the carbon content of steel gradually reduces and the formation of methane gas produces a cracks. Hence steel is totally destroyed.
- ❖ **Liquid metal corrosion:** - This occurs when the metal in liquid state flows at higher temperature over the solid metal. This either cause solid metal dissolution in the liquid metal or penetrate the solid metal. An example is the embrittlement of zinc in the presence of mercury. (Brasunas, 1953, Manly, 1956)

1.5.2 Electrochemical corrosion/Wet corrosion

“Wet corrosion is an electrochemical in nature, which takes place by the electrochemical attack on the metal in the presence of moisture or a conducting medium”. It is also known as electrochemical or indirect corrosion. When liquid phase is present wet corrosion will be occur, usually involved aqueous solution and electrolyte. Example is corrosion of steel by water.

The two types of wet corrosion are as follows

- ❖ **Differential metal corrosion:** - It is commonly referred to as bimetallic corrosion. Electrochemical reaction takes place when two different metals are electrically contact in the presence of an electrolyte. Metal having lower electrode potential act as anode, and greater electrode potential act as cathode. However, the potential difference between the metal plays a main role in determining the rate of differential metal corrosion. As increasing the potential difference between the metals, the corrosion rate at anode is also increases. Iron is contact with zinc, the zinc is having lower potential undergoes corrosion. (Iverson, 1987)

❖ **Concentration cell:** - This is a common form of corrosion found in our daily life. It occurred when the metal surface exposed to varying electrolyte concentration or aeration. Both anodic and cathodic region are formed on a single metal component. We can usually think that difference in the extent of aeration experienced, which creates a potential difference. The poor oxygenated region acts as an anode and corrodes. (Lynes, 1956)

1.6 Types of corrosion

1.6.1 Uniform corrosion

“The most common type of corrosion is uniform corrosion. It is generally considered a chemical reaction/ electrochemical reaction that occur uniformly over the whole surface”.



Figure 1. Uniform corrosion

The metal parts are become tinned and the portion of metal eventually fails by the method of corrosion. Suitable materials include coatings, inhibitors and cathodic protection can prevent or reduce uniform corrosion. (Crolet, 1993)

1.6.2 Galvanic corrosion

Potential difference is exist between when two dissimilar metals are in physical contact in aqueous electrolyte or they must be connected by an external metal path. When two metals are connected potential difference produced makes the flow of electron between them. (Zhang, 2011)



Figure 2. Galvanic corrosion

The minimum contact between the metals causes reduced corrosion resistance and the value is found to increase with increase in the contact area. This corrosion needs the presence of two metals of varying electrode potential. The more resistance metal is cathodic and less resistance metal becomes anodic. Corrosion of cathode metal is very little in the presence of electric current and two dissimilar metals, this kind of corrosion is also known as “two- metal corrosion”.

1.6.3 Crevice corrosion

This type of corrosion is an intensive localized corrosion. Some shielded area exposed to corrosives on metal surfaces. Corrosion site should be permitting the liquid entry but sufficiently.



Figure 3. Crevice corrosion

For example corrosion taking place around sides of nuts and bolts. Best example for this corrosion is gasket stainless steel interface. Contact between metal and nonmetallic surface, as in the case of gasket, can cause crevice corrosion. Some examples of material they cause crevice corrosion wood, glass, plastics, fabrics etc. (Betts and Boulton, 1993)

1.6.4 Pitting corrosion

“Pitting is an extremely localized form of attack which causes holes in the metal”. These holes are smaller than the diameter and larger in depth. It is called as pits. Sometimes pits are isolated and they see like rough surface because these are closed together. This form of corrosion is one of the most damaging. Pit is a structure that has diameter very lesser than its length. It has very lesser area. It is act as anode result in accelerated corrosion. The pits formed cannot be easily detected. The quantity of pits cannot be measured easily. Pits are covered with corrosion products so they have very small size. This causes small percent of weight loss in the entire structure. They are too dangerous since they can destroy the whole article without any clues because it is localized and intense form of corrosion. (Frankel, 2003)

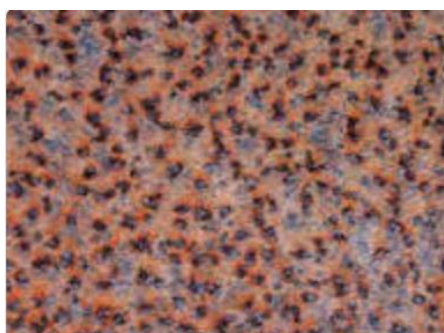


Figure 4. Pitting corrosion

Pits usually grow in the direction of gravity that is vertically downwards. Formation of pits require a very long time. This may be caused due to undercut surfaces, presence of corrosion media as a spot on the surface. Once pit is formed it grows in very increased rate. This is then supported by undesired area effect also.

Pitting may be an intermediate stage between number of corrosion and uniform corrosion. It was seen that at cold condition of dil. FeCl_3 medium stainless steel showed no corrosion but as the temperature was increased and concentration was raised pitting started and at very high temperature and concentration uniform corrosion was seen. (Burstein et al., 2003)

1.6.5 Stress corrosion

Construction process of metal has got highly stressed position like joints or bends and if corrosive medium is present then the corrosion that occurs in the stress points is called stress corrosion. Result is breaking of the material at the joint or bend. Hence it is also stress corrosion cracking. (Sieradzki and Newman, 1987)

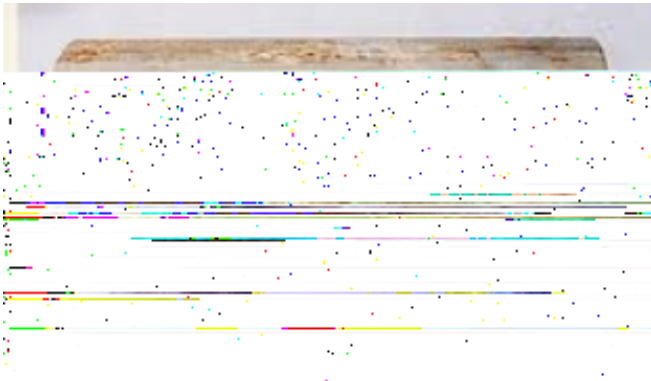


Figure 5. Stress corrosion

Two major examples that can be given below:

- ❖ **Seasonal cracking:** - This occurs particularly in a season. For example, brass cartridge cases had cracks during heavy rainfall in monsoon season. It was later found that ammonia, which was resulting from decomposed organic matter, caused this cracking.
- ❖ **Caustic embrittlement:** - This happens in steel boilers usually boilers are used to generate steam by boiling water at high temperature. Basically sodium carbonate is added to soften the hard water which is used to produce steam. Calculated amount of sodium carbonate must be added. If there is excess of sodium carbonate it undergoes hydrolysis and produces NaOH. It makes the water alkaline and this water enters the moment cracks that may be present in the inner walls of container. An amount of NaOH inside the cracks increases as more and more alkaline water enters the cracks. It results in development of stress in the region which finally causes setting up of a concentration cell in boiler. The NaOH in the stressed region reacts with higher concentration of NaOH present and form sodium ferrate. This further reacts with water to give still more amount of NaOH to the stress region. Thus more and more NaOH gets finally deposited in the stress regions which finally cause the container to break. To make caustic embrittlement minimum we can use external process to soften the hard water.

1.6.6 Intergranular corrosion

“Localized attack at and adjacent to grain boundaries with relatively little corrosion of the grains, is Intergranular corrosion”. They caused impurities in the grain boundary. For examples, aluminium having small amount of iron, iron solubility is low so they separated grain boundaries, causes Intergranular corrosion. Chromium in a grain boundary region of stainless steel, they cause Intergranular corrosion.

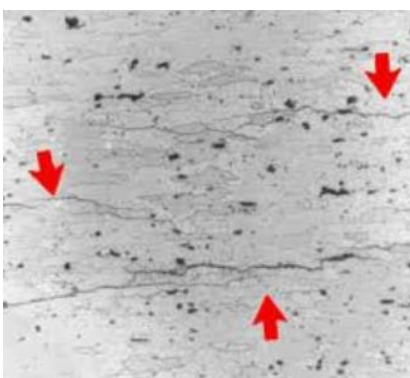


Figure 6. Intergranular corrosion

In case of stainless steel, steel contain about 0.0.2% of carbon and about 18% chromium. Stainless steel not undergoes corrosion easily because of chromium forming protective layer. When steel is heated in high temperature about 950⁰ to 1450⁰ F, steel becomes sensitive. In this temperature protective layer broken and it react with carbon to form Cr₂₃C₆. Takes out carbide precipitates, then decreases chromium content are that is adjacent to the grain boundaries. Hence corrosives easily attacked the boundary part because chromium exhausted region present in the grain boundary, those point exposed iron well and they do not have sufficient corrosion resistance means chromium is lost. (Phull, 2003, Matula et al., 2003)

1.6.7 Selective leaching

“Removal of one element from a solid alloy by corrosion process this is known as selective leaching”. Best examples for selective leaching are dezincification of brass and graphitisation of iron alloys. (Li et al., 2018)



Figure 7. Selective leaching

Brass having Zn and Cu, Zn undergoes corrosion it is dezincification. Brass is yellow in colour but after dezincification it gets tarnished and become pinkish because more Cu will be present. Both Cu and Zn are going to the solution. But extent of Cu dissolution is less; Cu gets it deposited on the brass surface. Deposited Cu appears as pink patches.

In case iron alloy carbon alloy will be present. Carbon content increase when iron undergoes corrosion. This will be appears as black spots over the surface this is called as graphitisation.

1.6.8 Erosion corrosion

“Erosion corrosion is the acceleration or increase in rate of deterioration or attack on a metal because of relative movement between a corrosive fluid and the metal surface”. It is coaction of erosion-corrosion.



Figure 8. Erosion corrosion

This consists of the gradually loss of material from the solid surface due to corrosion and mechanical contact between surface and free flowing fluid. It involves the degradation of protective film in a turbulent fluid, where impingement corrosion of solid and liquid particle and cavitation of corrosion. Erosion corrosion largely depends upon the fluid critical velocity and density of gas-liquid mixture. (Bermudez, 2005)

1.6.9 Hydrogen Damage

“Hydrogen damage is refers to mechanical damage of a metal”. Usually in acidic medium, at cathode H^+ ions get reduced to vacant H. This vacant H can combine to give H_2 but sometimes the high energetic vacant hydrogen can percolate into the metal surface and cause damage. High temperature, moist environment, electrolysis are major sources of vacant hydrogen. (Djukic et al., 2015)



Figure 9. Hydrogen Damage

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There are four types of hydrogen damage;

- ❖ **Hydrogen blistering**:-The H atoms that went inside can combine inside the voids they form H₂ gas. It tries to come out by rupturing metal surfaces this is called blistering. Penetration of hydrogen with metal result is complete breaking of vessel wall.
- ❖ **Hydrogen embrittlement**:-In some other cases, the hydrogen gas formed inside the voids may react with metal and form metal hydride this is called as hydrogen embrittlement. It is loss of tensile strength and ductile because penetration of hydrogen with metal.
- ❖ **Decarburization**:-“For example carbon steel plate, the removal of carbon from steel is often produced by moist hydrogen at high temperature. Decarburization lowers the tensile strength of steel”.
- ❖ **Hydrogen attack**: - “The interaction between hydrogen and component of an alloy at high temperature. A usual example of hydrogen attack is the disintegration of oxygen containing copper in the presence of hydrogen”. (Esaklul, 2017)

1.7 Factors influencing the corrosion rate

Some of important factors which influencing the corrosion rate that is given below; factors mainly classified in to two types.

- ❖ Primary factor: - factor extremely dependent on metal
- ❖ Secondary factor: - factor dependent on corrosive environment

1.7.1 Primary factors

1.7.1.1 Nature of the metal

The lower electrode potential value of metal is more reactive and more susceptible of corrosion. Higher electrode potential value of metal is less reactive and less susceptible of corrosion. The tendency of metal undergoes corrosion less so more electrode potential. For example, active metal is lower electrode potential with higher susceptible of corrosion and noble metals are higher electrode potential with less susceptible of corrosion. Pure and homogeneous metal won't undergo corrosion. Since inhomogeneous or impure metals are accelerate corrosion.

1.7.1.2 Difference in potential between cathodic and anodic region

Large potential difference between the anodic and cathodic region in the corrosion cell result in more rate of corrosion because when more in potential difference they produced more corrosion current and decreased free energy. When two different types of metals are connecting with each other the more reactive metal undergoes corrosion easily.

1.7.1.3 Area effect

Anodic region is small and larger the cathodic region so corrosion is large and faster the corrosion rate at anodic region. When ratio decreases corrosion rate will be increases. In the anodic region oxidation occurs electrons are liberated and cathodic region electrons are consumed. Result is anodic region maximum in corrosion rate and cathodic region slower in corrosion rate.

For example, In process of tinning, tin is coated over iron. Tin is act as cathodic and iron act as an anodic. Large in coated surface this is act as a cathodic. Result is higher the corrosion rate due to the anodic area is smaller compared to the cathodic area.

1.7.1.4 Nature of the corrosion product

Nature of the corrosion product is more depends on the corrosion rate. Corrosion product is formed protective film on metal surface. Product may be stable or unstable or volatile in nature. Stable product decreases the corrosion rate by forming a protective film. Protective layer continue to form on the metal surface, which act as a barrier between the new metal surface and corrosion environment. Corrosion products is unstable the corrosion continuous without any reduction. New metal surface is continuously exposed on corrosion environment. The metal surface is corroding takes place continuously. Corrosion product does not have any protective value, and then also the corrosion product formed either the soluble medium/ formed away from the cathodic and anodic sites.

1.7.1.5 Hydrogen overvoltage

Less hydrogen overvoltage increase corrosion in metal surface. Hydrogen gas is very easy to release and the rate of cathodic reaction becomes faster. This makes anodic reaction also become faster thereby overall

corrosion reaction. Higher hydrogen overvoltage slower corrosion in metal surface, cathodic reaction is also slower. Higher overvoltage lower will be the corrosion rate.

Any electrolyte has its own decomposition potential but an extra potential is required to continuous electrolysis this is called overvoltage. Some metal can give electron H^+ ions easily and hence overvoltage will decrease because H_2 will easily form. Some metal cannot easily give electron to H^+ ions to form H_2 . This cause increase in over potential.

1.7.2 Secondary factors

1.7.2.1 P^H of the medium

The p^H medium is lower than the rate of corrosion. Rate of corrosion will be higher. Some metals undergo corrosion very fast in high alkaline solution.

1.7.2.2 Temperature

Temperature increases with increasing the rate of chemical reaction. As the temperature increases the rate of corrosion is also increases. At high temperature, the conductance of the corrosion medium is increases which is also increasing rate of corrosion. In the case of corrosion resistance of passive metal, increase in temperature decrease the passive range and increasing the corrosion rate.

1.7.2.3 Nature and concentration of the electrolyte

Usually mineral acids more corrosive if concentration increases then corrosion increases. Since H^+ ions will be more and cathodic reaction increases.

1.7.2.4 Polarization

During the corrosion process both polarization of anodic and cathodic region are decreasing the corrosion rate. Anodic polarization, anodic metal goes on oxidation is decreases and the rate of metal dissolution as metal ion is also decreases. Anode reaction is become slower and overall rate of corrosion will be decreases.

Cathode polarization delays cathodic reaction due to chemical polarization of the cathode which hinders the combination of cathode reactant and the electron. Some case of cathodic polarization, cathodic reaction forming product on metal surface or removal of cathodic reaction product on metal surface it also makes cathodic reaction slower. (Wasim et al., 2018)

1.8 Prevention of corrosion

1.8.1 Materials selection

Prevention is to select the correct metal and alloy for a particular corrosive operation. This is the most effective way to prevent or reduce corrosion damage.

1.8.1.1 Metal purification

A pure metal corrosion resistance is superior to one that contains impurities/ small quantities of other metals. Usually pure metals are very expensive, soft and weak. For example aluminium which is inexpensive and it is in pure metal state. Commercially pure metals are used to handling H_2O_2 where, the presence of other elements can cause decomposition due to the catalytic effect. In another case, alloy containing segregation of impurity iron that gives localized attack of aluminium equipment. Which reduce the maximum iron content, which was acceptable to both producer and consumer, eliminates the localized attack on aluminium and obtained better equipment performance without added in the cost of material.

1.8.1.2 Non metallic

This category includes integral/ solid non-metallic construction as well as considerable thickness sheet linings or covering. There are five types of classification rubbers (natural/ synthetic), plastics, ceramics, carbon and graphite, and wood.

Rubber and plastics are generally compared to the metal and alloys they are much weaker, softer, and more resistant than chloride ion and hydrochloric acid, less resistance than oxidizing acids like nitric and strong sulphuric acid, less resistance than solvents and have almost low temperature. Ceramics have excellent corrosion and high temperature resistance, with brittleness and lower tensile strength being the main disadvantages. Carbon is good corrosion resistance but it is easily broken or damaged. It is electric and heat conductivity. In aggressive environments, wood is attacked.

1.8.2 Cathodic protection and anodic protection

- ❖ **Cathodic protection:** - “This method is protecting a metal or alloy from corrosion by converting it completely into cathodic and no part of it is allowed to act as anode”. Metals normally undergo electrochemical corrosion in contact with each other through the formation of anodic region and cathodic region. Corrosion of metals occurs in the anodic region whereas the metal is not affected in the cathodic region. Corrosion avoided by removing anodic sites and entire metal converting into cathodic area. This can be done in two ways as follows:
 - **Sacrificial anodic protection:** - Here, the metal is protected and connected with a more active metal, it acts as an anode. Thus this anode metal act as sacrificial anode and protects the main structure. Once this metal is completely corroded, it will be replaced by the fresh one. Normally zinc, magnesium are used for this process. Its major advantages to include low maintenance and instalment cost. These suffer from the disadvantages of interchanging sacrificial anode frequency.
 - **Impresses current cathodic protection:** - In this method direct current is applied, which strength is greater than the corrosion current. The metal to be protected is connected to the cathode source and it becomes cathodic in nature. The source anode is connected to an inert anode to complete the circuit. One of the main disadvantages of this method is that the metal surface is susceptible to corrosion, because if there is a slight variation in the direct current.
- ❖ **Anodic protection:** - “The prevention of corrosion by the impressed anodic current is called as anodic protection”. This based on formation of protective film on a metal surface by applied externally anodic current. When metal is made as anode and applied a current and increasing the dissolution level of the metal. However, in passive metals have active passive transitions like nickel, iron, chromium, titanium and their alloys, the metal application appropriate to makes them passive and decrease the metal dissolution rate.

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