

A REVIEW ON CORROSION OF METALS AND PROTECTION

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Abstract

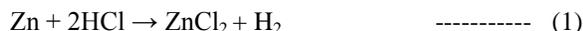
Corrosion is a complex series of reactions between different environmental conditions and metal surfaces. The importance of corrosion studies is threefold includes economic losses, improved safety and conservation. Corrosion control of metals is of technical, economical, environmental and aesthetical importance. The main cause of the structural deterioration of all metallic mains is external corrosion which is included by environmental and operation conditions. It is necessary to remember that the choice of a material depends on many factors, including its corrosion behavior. The engineering aspects of corrosion resistance cannot be over emphasized. Complete corrosion resistance is almost all media can be achieved by the use of either platinum or glass, but these materials are not practical. In this review, we study about the corrosion behavior of the iron and steel in different conditions and environment.

Keywords: corrosion, iron and steel, types of corrosion, environment and protection.

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1. DEFINITION OF CORROSION

We all know that what is the corrosion? Corrosion is the destructive attack of a metal and its properties by chemical (dry corrosion) or electrochemical (wet corrosion) reaction with its environment. Nonmetals are not included in the present definition[1][2]. Reaction can be divided into partial reactions of oxidation and reduction is termed as electrochemical[3]. For example, when zinc is placed in dilute hydrochloric acid, a vigorous reaction occurs; hydrogen gas is evolved and zinc dissolves, forming a solution of zinc chloride. The reaction is



This reaction can be written in the form



Equation (2) can be divided into two reactions, the oxidation of zinc and the reduction of hydrogen ions:

Oxidation (anodic reaction):



Reduction (cathodic reaction):



An oxidation is indicated by a production of electrons and reduction is indicated by consumption of electrons. The rate of electrochemical reaction is limited by physical or chemical factors. Hence, an electrochemical reaction is said to be polarized [4][5]. Metals that normally fall victim to corrosion will sometimes exhibit passivity to corrosion. Passivity is the characteristic of a metal exhibited when that metal does not become active in the corrosion reaction. Passivity is caused by the buildup of a stable, tenacious layer of metal oxide on the surface of the metal [6][10]. This oxide layer is formed by corrosion on a clean metal surface, where the corrosion products are insoluble in the particular environment to which the metal is exposed. Once the layer, or film, is formed, it acts as a barrier separating the metal surface from the environment.

For further corrosion to occur, the reactants must diffuse through the oxide film. Such diffusion is very slow or nonexistent, thus corrosion either decreases markedly or stops. Most metals used in the construction of facilities are subject to corrosion. This is due to the high energy content of the elements in metallic form. In nature, most metals are found in chemical combination with other elements. These metallic ores are refined by man and formed into metals and alloys. As the energy content of the metals and alloys is higher than that of their ores, chemical re-combination of the metals to form ore like compounds is a natural process. Metals corrode because we use them in environments where they are chemically unstable. Only copper and the precious metals

(gold, silver, platinum, etc.) are found in nature in their metallic state. All other metals, to include iron the metal most commonly used are processed from minerals or ores into metals which are inherently unstable in their environments. It is necessary to remember that the choice of material depends on many factors, including corrosion resistance, cost, fabricability, strength, etc. The cost and corrosion resistance of the material are the most important properties in most engineering applications requiring high chemical resistance. In this review we concerned with the metals steel and iron. Iron and steel are resistant to rapid corrosion in water despite the tendency of iron to oxidize [1].

2. TYPES OF CORROSION

Corrosion damage can occur in many ways, for example, in failure by cracking, loss of strength, etc. Forms of corrosion are uniform attack, galvanic corrosion, selective leaching, erosion corrosion, stress corrosion, crevice corrosion, pitting and intergranular corrosion [7][8].

2.1 Uniform attack

Uniform corrosion is the attack of a metal at essentially the same at all exposed areas of its surface (Fig.1). At no point is the penetration of the metal by corrosion twice as great as the average rate. Rusting steel in the atmosphere and the corrosion of copper alloys in seawater are common examples where uniform corrosion is usually encountered. Steel submerged in seawater also suffer uniform corrosion but can also suffer from non-uniform attack under some circumstances [7].

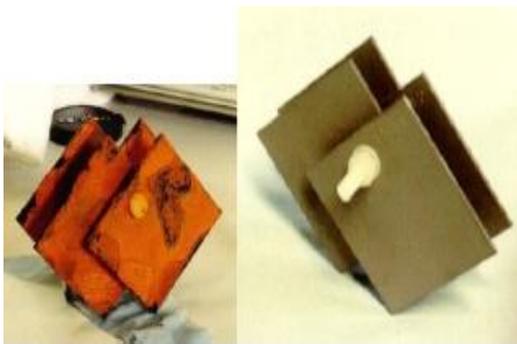


Fig-1: Uniform attack of metal

2.2 Galvanic Corrosion

Galvanic corrosion tends to occur when dissimilar conducting materials are connected electrically and exposed to an electrolyte (Fig.2). The following fundamental requirements therefore have to be met for galvanic corrosion:

1. Dissimilar metals (or other conductors, such as graphite).
2. Electrical contact between the dissimilar conducting materials (can be direct contact or a secondary connection such as a common grounding path).
3. Electrolyte (the corrosive medium) in contact with the dissimilar conducting materials.

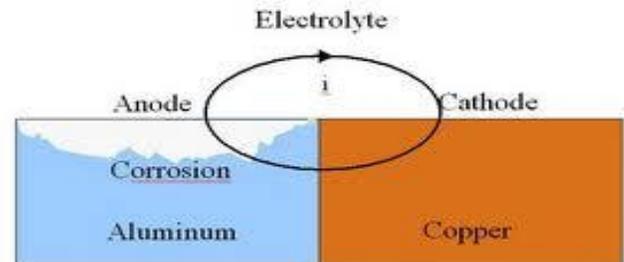


Fig-2: Galvanic corrosion

2.3 Crevice Corrosion

Crevice corrosion is a localized form of corrosive attack. Crevice corrosion occurs at narrow openings or spaces between two metal surfaces or between metals and nonmetal surfaces (Fig.3). A concentration cell forms with the crevice being depleted of oxygen. This differential aeration between the crevice (microenvironment) and the external surface (bulk environment) gives the crevice an anodic character. This can contribute to a highly corrosive condition in the crevice. Some examples of crevices are Flanges, Deposits, Washers, Rolled tube ends, Threaded joints, etc.



Fig-3: Crevice corrosion of metal

2.4 Pitting

Pitting corrosion is a localized form of corrosion by which cavities or "holes" are produced in the material. Pitting is considered to be more dangerous than uniform corrosion damage because it is more difficult to detect, predict and design against. Pitting corrosion (Fig.4) can produce pits with their mouth open (uncovered) or covered with a semi-permeable membrane of corrosion products. Pits can be either hemispherical or cup-shaped[9].



Fig-4: Pitting corrosion of metal

2.5 Intergranular corrosion

Intergranular corrosion is very relevant for the brewery industry. It consists of a localized attack, where a narrow path is corroded out preferentially along grain boundaries of a metal. This type of corrosion may have extreme effects on mechanical properties, resulting in a loss of strength and ductility(Fig.5).



Fig-5: Intergranular corrosion of metal

2.6 Selective leaching

It is also known as 'parting' or 'dealloying' is the selective removal of one element from an alloy leaving an altered residual structure. The most common example is the selective removal of zinc in brass alloy (dezincification) (Fig.6).

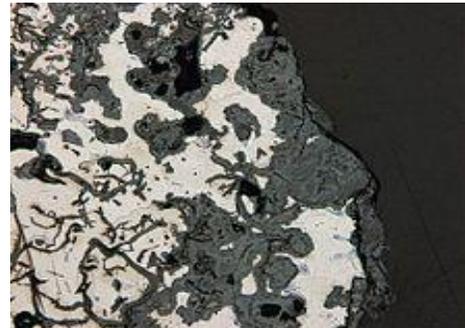


Fig-6: Selective leaching of zinc

2.7 Erosion corrosion

Erosion corrosion is the acceleration or increase in the rate of deterioration or attack on a metal because of relative movement between a corrosive fluid and the metal surface (Fig.7).



Fig-7: Erosion corrosion of metal

2.8 Stress corrosion

Stress corrosion cracking (SCC) refers to the cracking caused by the simultaneous presence of tensile stress and a corrosive environment. The impact of SCC on a material usually falls between dry cracking and the fatigue threshold of that material(Fig.8).

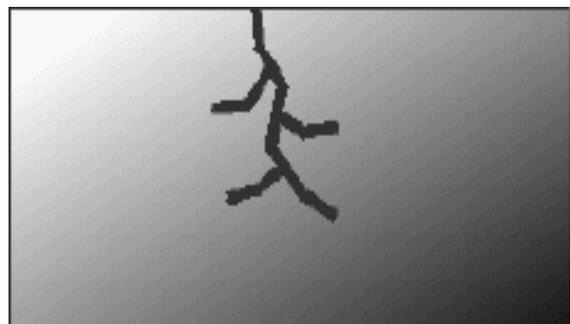


Fig-8: Stress corrosion of metal

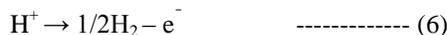
3. IRON AND STEEL

Steel is an alloy that consists mostly of iron and has a carbon content between 0.2% and 2.1% by weight, depending on the grade. Carbon is the most common alloying material for iron, but various other alloying elements are used, such as manganese, chromium, vanadium, and tungsten. Varying the amount of alloying elements and the form of their presence in the steel (solute elements, precipitated phase) controls qualities such as the hardness, ductility, and tensile strength of the resulting steel. Steel with increased carbon content can be made harder and stronger than iron, but such steel is also less ductile than iron.

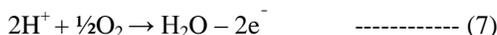
The electrochemical theory of corrosion was described as the short circuited galvanic cells on the metal surface. Metal ions go into solution at anodic areas in an amount chemically equivalent to the reaction at cathodic areas. At anodic areas the following reaction takes place:



This reaction is rapid in most media. When iron corrodes, the rate is usually controlled by the cathodic reaction, which is much slower (cathodic control). In deaerated solutions, the cathodic reaction is



This reaction proceeds rapidly in acids, but only slows in alkaline or neutral aqueous media. The cathodic reaction can be accelerated by dissolved oxygen in accord with the following reaction, a process called depolarization.



Dissolved oxygen reacts with hydrogen atoms adsorbed at random on the iron surface, independent of the presence or absence of impurities in the metal. The oxidation reaction proceeds as rapid as oxygen reaches the metal surface. From (5) and (7) and the reaction



Ferrous oxide $[\text{Fe}(\text{OH})_2]$ will then reacts with oxygen to give iron oxides: Fe_2O_3 (red) and Fe_3O_4 (black).

Iron and steel corrosion rates can vary with different environments and factors like aqueous environment, metallurgical factors and atmosphere.

3.1 Aqueous environment

3.1.1 Influence of oxygen

In air saturated water, the initial concentration rate at the room temperature reaches high and this rate diminishes over a period of days as rust film is formed and acts as a barrier to oxygen diffusion. The corrosion rate of iron is proportional to oxygen concentration. In the absence of oxygen, the corrosion rate at room temperature is negligible both for iron and steel[15].

3.1.2 Influence of velocity

The velocity is affected by the factors like presence of oxygen, depends on characteristics of metal and environment to which is exposed. If the agitation increases, corrosion rate is also increases when oxygen presents in small amounts. In the distilled water, the critical concentration of oxygen above which corrosion decreases. This value increases with dissolved salts and with temperature, and decreases with increase in velocity and pH.

3.1.3 Influence of temperature

Temperature increases the rate of almost all chemical reactions. In an open vessel, allowing dissolved oxygen to escape, the rate increases with temperature to about 80°C and then falls to a very low value at the boiling point. The falling of the corrosion is indicated that decrease of oxygen solubility in water as the temperature raised. In a closed system, oxygen cannot escape and the corrosion rate continues to increase with temperature until all oxygen is consumed. The rate of corrosion of iron and steel increases with temperature especially in media in which evolution of hydrogen accompanies corrosion[11].

3.1.4 Influence of pH

The corrosion rate for iron as a function of pH. In the range of pH 4 to pH 10, the corrosion rate of iron is relatively independent of the pH of the solution. In this pH range, the corrosion rate is governed largely by the rate at which oxygen reacts with adsorbed atomic hydrogen, thereby depolarizing the surface and allowing the reduction reaction to continue. For pH values below 4.0, ferrous oxide (FeO) is soluble. Thus, the oxide dissolves as it is formed rather than depositing on the metal surface to form a film.

In the absence of the protective oxide film, the metal surface is in direct contact with the acid solution, and the corrosion reaction proceeds at a greater rate than it does at higher pH values. It is also observed that hydrogen is produced in acid solutions below a pH of 4, indicating that the corrosion rate no longer depends entirely on depolarization by oxygen, but on a

combination of the two factors (hydrogen evolution and depolarization). For pH values above about pH 10, the corrosion rate is observed to fall as pH is increased. This is believed to be due to an increase in the rate of the reaction of oxygen with $\text{Fe}(\text{OH})_2$ (hydrated FeO) in the oxide layer to form the more protective Fe_2O_3 (note that this effect is not observed in deaerated water at high temperatures).

3.1.5 Influence of galvanic coupling

The actual penetration of iron increases when iron is coupled to a more noble metal. For the diffusion of depolarizer is controlling, the general relation between penetration p (proportional to corrosion rate) of a metal having area A_a coupled to a more noble of area A_c , where p_o is the normal penetration of the metal uncoupled, is given by

$$P = p_o(1 + A_c/A_a)$$

If the ratio of areas A_c/A_a is large, the increased corrosion caused by coupling can be considerable.

3.1.6 Influence of dissolved salts

The corrosion rate first increases with salt concentration, then decreases, the value falling below that for distilled water when saturation is reached. Various salts like sodium chloride, Alkali-metal salts, Alkaline-earth salts, Acid salts etc. can affect the corrosion rate of iron and steel in various manners[12].

3.2 Metallurgical factors

3.2.1 Types of iron and steel

Pure iron corrodes in acids at much lower rate than an iron or steel high in residual elements such as carbon, nitrogen, sulfur, etc. The high nitrogen content of steel makes it more sensitive than open heart steels to stress corrosion cracking in hot caustic solutions. Cast iron in natural waters or in soils corrodes initially, but provides much longer service life than steel [13].

3.2.2 Influence of composition

Carbon content of a steel has no effect on the corrosion rate in fresh waters, a slight increase in rate has been observed in seawater as the carbon content is raised from 0.1 to 0.8%. In acids, the corrosion rate depends on the composition as well as the structure of the steel and increases with both carbon and nitrogen content. Both alloyed sulfur and phosphorus markedly increase rate of attack in acids. Arsenic is present in some steels in small amounts. In quantities up to 0.1% it

increases the corrosion rate in acids; in large amounts (0.2%) it decreases the rate.

In addition to influencing microstructure characteristics such as ferrite: pearlite ratio and carbide content, composition also affects the fracture behavior of annealed ferritic Ductile Iron. The influence of carbon content on notched impact properties is primarily on the upper shelf energy, which decreases with increasing carbon content, as shown in Fig.9. The influence of carbon in this region, in which fracture occurs by the formation of voids on graphite nodules, and the growth and coalescence of these voids, is to increase the number and size of nodules. Increasing carbon content thus reduces the plastic deformation required to grow and coalesce voids, resulting in reduced plastic fracture energy. This relationship between carbon content and limiting plastic fracture strain is consistent with the observation that elongation and other indicators of ductility in ferritic Ductile Iron increase with decreasing carbon content. (Fluidity, microstructural and shrinkage considerations normally require carbon levels above 3.2 per cent[14].)

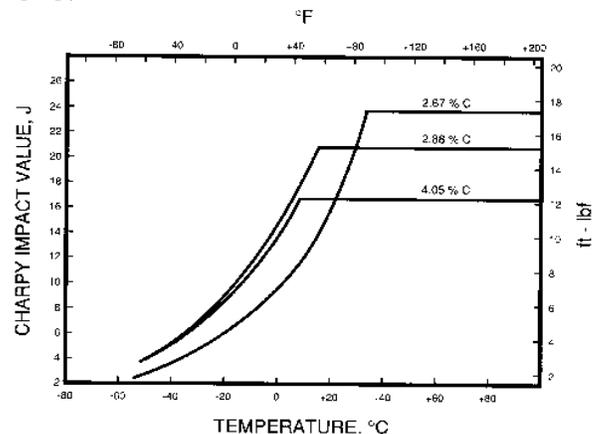


Fig-9: Influence of carbon content

3.2.3 Influence of heat treatment

Heat treating of steel is the process of heating and cooling of carbon steel to change the steel's physical and mechanical properties without changing the original shape and size. Heat Treating is often associated with increasing the strength of the steel, but it can also be used to alter certain manufacturability objectives such as improve machinability, formability, restore ductility etc. Thus heat treating is a very useful process to help other manufacturing processes and also improve product performance by increasing strength or provides other desirable characteristics.

High carbon steels are particularly suitable for heat treatment, since carbon steel respond well to heat treatment and the

commercial use of steels exceeds that of any other material. Carbon steel quenched from high temperatures has a structure called martensite. In dilute acids, the corrosion rate of the martensite is relatively low. Interstitial carbon reacts in large part with acids to form a complex hydrocarbon mixture and some residual amorphous carbon, which is observed as a black smut on the steel surface. On slowly cooling a carbon steel from the austenite region above 723°C, cementite, assumes a lamellar shape, forming a structure called pearlite. Corrosion rate increases as the size of iron carbide particles decreases. Pearlite structures corrode faster than spheroidized ones, and steels containing fine pearlite corrode more rapidly than those with coarse pearlite.

3.3 Atmospheric corrosion

In the absence of moisture, iron exposed to the atmosphere corrodes at a negligible rate. Corrosion does not depend only on moisture content of air but also on the dust content and gaseous impurities which favor condensation of moisture on the metal surface. The average of corrosion rates of metals is generally lower when exposed to natural water or to soils. Stainless steels (i.e. steels containing at least 12% chromium) show greatly improved resistance to atmospheric corrosion. The austenitic alloys containing 8% nickel and 18% chromium are still more resistant, and alloys containing in addition 2-3% molybdenum are almost completely unaffected by weathering in industrial atmospheres.

Factors affecting the corrosivity of soils are

- Porosity (aeration)
- Electrical conductivity or resistivity
- Dissolved salts (depolarization or inhibitors)
- Moisture
- Acidity or alkalinity

Corrosion rates tend to increase with depth of burial near the soil surface, but not invariably. Bureau of Standards tests on steel specimens exposed 6-12 years and buried 30-120 cm below the surface showed greater depth for soils but the reverse trend for two soils.

A soil containing organic acids derived from humus is relatively corrosive to steel, zinc, lead, and copper. The measured total acidity of such soil appears to be a better index of its corrosivity than pH alone.

4. PROTECTION OF STEEL AND IRON FROM CORROSION

The most common method to prevent the corrosion is the selection of proper material for a particular service. Stainless steel is not stainless, it is not the most corrosion resistant material, and it is not a specific alloy. Stainless steel is a

generic name for a series of more than 30 different alloys containing from 11.5 to 30% chromium and 0 to 22% nickel, together with other alloy conditions. Stainless steel has widespread application in resisting corrosion, but it should be remembered that they do not resist all corrosives. Stainless alloys are more susceptible to localized corrosion such as intergranular corrosion, stress corrosion cracking and pitting attack than ordinary structural steels. The quality of the stainless steels is checked by the magnet. The nonmagnetic stainless steels represent good alloys and stainless steels that are magnetic are inferior [16].

4.1 Metal quality

The corrosion resistance of a pure metal is usually better than that of one containing impurities or small amounts of other elements. However, pure metals are usually expensive and are relatively soft and weak. For example Aluminum is not expensive in a fairly pure state. The commercially pure metal is used for handling hydrogen peroxide, where the presence of other elements may cause decomposition because of catalytic effects. In other case, localized attack of aluminum equipment occurred because of segregation of impurity iron in the alloy.

4.2 Environmental changes

- **Lowering temperature** usually causes a pronounced decrease in corrosion rate. Under some conditions, temperature changes have little effect on corrosion rate. In other cases, increasing temperature decreasing the corrosion rate.
- **Decreasing velocity** is used as a practical method of corrosion control. Metal and alloys that passivate, such as stainless steels, generally have better resistance to flowing mediums than stagnant solutions. Erosion corrosion effects can occur because of very high velocity rates.
- **Removing oxygen** is the very old corrosion control technique. Boiler feed water was deaerated by passing it through a large mass of scrap steel. In the modern practice this is accomplished by vacuum treatment, inert gas sparging, or through the use of oxygen scavengers.
- **Changing concentration** is usually effect in corrosion rate. In many processes, the presence of corrosive is accidental. For example, corrosion by the water coolant in nuclear reactors is reduced by eliminating chloride ions. In other cases, corrosion can be reduced by increasing acid concentration.

4.3 Inhibitors

An inhibitor is a substance that, when added in small concentrations to an environment, decrease the corrosion rate.

An inhibitor can be considered as a retarding catalyst. There are numerous inhibitor types and compositions[17].

- **Adsorption type inhibitor:** These are the organic compounds which adsorb on the metal surface and suppress metal dissolution and reduction reactions. In most cases, it appears that adsorption inhibitors affect both the anodic and cathodic processes.

- **Hydrogen evolution poisons:** These substances are very effective in acid solutions but are ineffective in environments where other reduction processes such as oxygen reduction are the controlling cathodic reactions.

- **Scavengers:** These substances act by removing corrosive reagent from solution. EX: sodium sulfite and hydrazine, which remove dissolved oxygen from aqueous solution. These inhibitors will work effectively in solutions where oxygen reduction is the controlling corrosion cathodic reaction but not be effective in strong acid solutions.

- **Oxidizer:** chromate, nitrate, and ferric salts also act as inhibitors in many systems. They are generally used to inhibit the corrosion of metal and alloys that demonstrate active passive transitions, such as iron and stainless steel.

- **Vapor-phase inhibitors:** these are very similar to the organic adsorption type inhibitors and possess a very high vapor pressure. These materials are used to inhibit atmospheric corrosion of metal without being placed in direct contact with the metal surface.

5. CONCLUSION

1. The atmospheric corrosion of metals caused by acid deposition is mainly a local problem restricted to areas close to pollution sources.

2. The main corrosive effect is caused by dry deposition of air pollutants.

3. The influence of acid precipitation may differ for different materials and depends on the pollution level.

4. The effects of S-pollutants, especially SO₂, are of greatest importance.

5. According to existing knowledge, NO_x has a limited influence on the corrosion of steel and zinc in outdoor atmospheres. There are indications that NO_x in combination with SO₂ can promote corrosion of, for example, copper and calcareous stone materials.

6. Corrosion in soil is a complicated process and dose-response relations between the corrosion rate and pH or acidity are lacking. Indications that soil acidification may increase the risk of corrosion of important technical materials and constructions exist.

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