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Steel Structural and Functional Characteristics Focusing on Corrosion Mechanisms

Rajesh Kumar Singh (D. Sc) [1,]*, Vikas Kumar[2], Yashwant Ray Balwant[3]

Abstract

This research article examines steel structural and functional characteristics, focusing on corrosion mechanisms and inhibitor protection strategies. Steel corrosion affects numerous industries, causing significant economic losses and safety risks. Fundamental electrochemical processes behind various corrosion forms including uniform, pitting, crevice, galvanic, intergranular, and stress-induced corrosion are explained. The chapter highlights the steel industry's importance while investigating how corrosion impacts performance and longevity. Protection methods discussed include material selection, environmental modification, sacrificial anodic, impressed current and organic inhibitors. Special attention is given to corrosion inhibitor and their classification, action mechanisms, and design parameters. Inhibitor adsorption and precipitation behaviours are analyzed along with chemical compatibility requirements. The text covers raw materials, synthesis pathways, formulation strategies, and monitoring techniques for effective inhibitor implementation. Raw materials including fatty acids, amines, and their derivatives are detailed alongside formulation considerations such as solubility and stability. Testing methodologies for evaluating inhibitor performance under various conditions are presented, from static tests to dynamic flow simulations. This comprehensive information provides valuable insights for researchers and industry professionals seeking sustainable, cost-effective corrosion protection solutions for steel.

Keywords: Steel corrosion, electrochemical processes, corrosion mechanisms, corrosion inhibitors, corrosion protection, adsorption behaviour, steel durability

INTRODUCTION

Corrosion is a major problem in steel structures and systems across numerous industries. The damage caused by corrosion is observed not only in chemical and petrochemical industries but also in thermal power generation equipment, vehicles, sugar industry, pulp and paper industry, urban infrastructure, nuclear reactors, building construction, and railways [1].

Metallic corrosion represents the physicochemical interaction between a metal or alloy (in solid or liquid state) and its surrounding environment. This phenomenon can be characterized as the undesirable deterioration of metallic materials resulting from environmental exposure, which subsequently compromises their inherent properties and functional integrity. The corrosion process encompasses complex chemical, electrochemical, and bio-electrochemical mechanisms that occur at the interface between the metal substrate and its surrounding medium.

While predominantly associated with metals, similar degradation pathways can affect diverse material classes including vitreous materials, ionic crystalline solids, polymeric substrates, and multi-

*Author for Correspondence
Rajesh Kumar Singh (D. Sc)
E-mail: rks_jpujc@yahoo.co.in

[1]Principal, Subject Specialization Chemistry, JLNM College, Ghorasahan East Champran, India.
[2]Assistant Professor, Department of Chemistry, Government Engineering College, Siwan, India.
[3]Assistant Professor, Department of Chemistry, J.L.N.M College, Ghorasahan, East Champaran, India.

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component composite systems. These deterioration processes manifest across various environmental conditions, including but not limited to exposure to liquid metallic phases, gaseous atmospheres, non-aqueous electrolytic media, and anhydrous solution systems. The thermodynamic instability of refined metals in their processed states provides the fundamental driving force for these spontaneous degradation reactions, which represent a return toward more energetically favourable states [2].

The economic impact of corrosion is substantial, with annual costs estimated to be several percent of the global GDP. Beyond the financial implications, corrosion-related failures can lead to catastrophic consequences including environmental contamination, structural collapses, and loss of human life. This underscores the critical importance of understanding corrosion mechanisms and developing effective protection strategies.

FUNDAMENTALS OF STEEL CORROSION

Electrochemical Nature of Corrosion

When a metal comes in contact with an electrolyte solution, it develops an electrical cell, which has a tendency to dissolve metal as positive ion in solution. In solution, the concentration of both ions must remain electrically neutral when an equivalent number of some other positive ions must be removed as the metal corrodes.

For example, a sample of iron placed into a solution of copper sulfate will begin to corrode while copper ions are plated out of the solution simultaneously to form copper metal on the iron surface. The anodic and cathodic reactions can be written as follows:

$$Fe \rightarrow Fe^{2+} + 2e^- \text{ (Anodic reaction)} \quad (1)$$

$$Cu^{2+} \text{ (in solution)} + 2e^- \rightarrow Cu \text{ (Cathodic reaction)} \quad (2)$$

General electrochemical reactions, such as the anodic and cathodic reactions can be combined:

$$Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu \quad (3)$$

This reaction is self-stifling because the deposited copper acts as a barrier between the iron and solution, thus preventing further reaction.

When zinc is immersed in an acid solution, hydrogen is plated out of the solution to maintain electrical neutrality. The oxidation-reduction corrosion reactions can be written as follows:

$$Zn \rightarrow Zn^{2+} + 2e^- \text{ (Anodic reaction)} \quad (4)$$

$$2H^+ + 2e^- \rightarrow H_2 \text{ (cathodic reaction)} \quad (5)$$

The hydrogen gas can be removed as bubbles. The reaction is not self-limiting, and the formation of zinc chloride continues.

Formation of Corrosion Cells

Generally, three types of cells form when corrosive substances attack the metal surface [3].

Dissimilar Electrode Cell

It is also known as a bimetallic or galvanic cell. When a metal contains electrically conducting impurities on the surface of a base metal, a separate phase and one metal in contact with another metal are examples of the formation of a corrosion cell. Different electrode potentials develop between the two separate phases or metals; thus, corrosion reactions occur.

Concentration Cell

It is formed when two metallic electrodes are immersed into different concentration of electrolytic solution. Concentration cells can be classified into salt concentration and aeration cells.

Salt Concentration Cell

A concentration cell is formed when electrodes are dipped into different concentrations of electrolytic solutions; for example, Cu electrode is immersed into a concentrated $CuSO_4$ solution and another to a dilute $CuSO_4$ solution. An electrochemical cell is formed, and thus copper dissolves from the electrode in contact with the dilute solution, which behaves like an anode, and plates out on the other electrode, which behaves as a cathode. The dissolution and deposition reactions continue until the concentrations of solutions become the same.

Aeration Cell

The differential aeration cell is more important from a practical point of view. This includes two similar Fe electrodes dip in a dilute NaCl solution more aerated electrode behaves as a cathode and less deaerated electrode works as an anode. The difference in oxygen concentration produces a potential difference and causes current to flow. The practical example of this type of corrosion is crevice corrosion, in which crevices are formed at the interface of two coupled pipes or at threaded connections because the oxygen concentration is lower within the interface or at the threads than elsewhere [4].

Differential Temperature Cell

Electrodes of the same metal are immersed in an electrolytic solution of the same initial composition at a different temperature. The higher temperature area works as an anode and the lower temperature area behaves as a cathode; such corrosion cell is observed in radiators, evaporators, condensers, boilers, and other similar equipment [5].

Potential and pH

The corrosion of any metal depends on the potential as well as the pH value of the solution or environment. Chemical or electrochemical reactions in the aqueous medium depend on the oxidation potential and pH of the solution. Potential and pH values predict the spontaneous direction of reactions, estimate the composition of corrosion products, and predict environmental conditions that will prevent or reduce corrosive attack. Electrochemical reactions are produced by H^+ or OH^- ions:

$$M \rightarrow M^{n+} + ne^- \tag{6}$$

Chemical reactions undergo only H^+ ions or OH^- ions and do not involve electrons. This type of reaction is written as follows:

$$M^{2+} + 2H_2O \rightarrow M(OH)_2 + 2H^+ \tag{7}$$

Reactions involving both H^+ ions or OH^- ions and electrons:

$$H_2 \rightarrow 2H^+ + 2e^- \tag{8}$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \tag{9}$$

Water may be reduced with the evolution of hydrogen and may be oxidized with the evolution of oxygen. Potential and pH values are very useful in aqueous media and in electrode-deposition of metals and oxides. Metal corrosion gives a large number of substances in the dissolved and gaseous state [5].

Passivity and Its Characteristics

There are two recognized states for several metals and alloys: active and passive. While passive-state metals and alloys behave more noble, active-state metals and alloys exhibit higher activity in specific types of conditions. The rate of corrosion of a passive metal is extremely slow. The characteristic that gives many structural metals, such as aluminium, chromium, and stainless steel, their beneficial inherent resistance to corrosion is called passivity [6].

Anodic polarization produces current densities or exposure to passivating conditions, such as iron in CrO_4^{2-} or NO_2^- solutions, can render some metals and alloys passive. When the electrochemical behaviour of an active metal in the emf family, or an alloy made of these metals, resembles that of a significantly less active or noble metal, the metal is said to be passive.

A metal or alloy is considered passive if it significantly inhibits corrosion in a setting where the transition from the metallic state to the proper corrosion products is linked with a significant thermodynamic free energy loss. The passive corrosion occurs when lead is submerged in H_2SO_4, Mg in H_2O, or Fe inhibited pickling solution. When making these metals the anode of a cell, its polarization is not very noticeable. These metals include, among others, stainless steels, Cu alloys, nickel, molybdenum, titanium, zirconium, and chromium. Iron in dissolved chromates is one example of a metal that becomes passive in passivator solutions [7].

Characteristic of Passivation

When iron is dipped into H_2SO_4 and acts as an anode, its electrode potential is enhanced. The polarization current that results produces the necessary results, but not beyond, to keep the control potential in relation to a calomel electrode. This can be accomplished manually or, even better, with the help of a potentiostat, a device that automatically converts current to potential and is typically used in an appropriate electronic circuit.

According to Faraday's law, iron corrodes anodically as Fe^{2+} and is active at low current densities. An insulating layer made most likely of $FeSO_4$ builds over the electrode surface as the current rises. The current abruptly decreases at a critical current density of roughly 200 mA/cm^2, which is higher while stirring or when the environment's pH declines.

The corrosion product is Fe^{3+}, and low current density stays with further slow potential shift. The 1.2V potential is developed by O_2 electrode potential; however oxygen does not significantly evolve until the potential is several tenths of a volt higher than the equilibrium value (oxygen overvoltage). Short-time current-pulse experiments indicate that the genuine critical current density to achieve iron passivity slayer is roughly 10-20 mA/cm^2.

The passivity quickly decreases when the anodic current is cut off. The potential changes slowly after first changing its values that is passive on the hydrogen scale. Ultimately, it quickly decays to iron's active potential. It was discovered that the more acidic the solution in which passivity deteriorated, the more noble the noble potential that was reached right before rapid decay to the active value. This is a characteristic potential. Potentials (pH = 0) for nickel and chromium Cr-Fe alloys have less noble passive films than those for iron.

Passivation Groups of Metals

Metals can be passivated into three groups:

Group I (Ti, Cr, Sn)

These metals have a passivation domain partly below the stability domain of water for an extensive pH range. Therefore, the passivation will be very easy and will occur spontaneously even in the absence of an oxidizing agent. These metals can be activated with relative difficulty.

Group II (iron)

For pH values between 9 and 13 iron will passivate by weak oxidizing action. For other pH values, the oxidizing action will have to be strong.

Group III (Mn, Pb, Ag)

Passivation will be possible by means of a strong oxidizing action. However, these metals can be activated very easily.

TYPES OF CORROSION IN STEEL

When materials come in contact with corrosive environments, they exhibit various forms of corrosion. Some important forms of corrosion observed in hostile media include [8].

Uniform Corrosion

Uniform corrosion occurs on the whole surface area of materials, which is the most prevalent and easily recognized type of corrosion. An excellent illustration of atmospheric corrosion is found in steel tanks and structures. Increased material thickness, coating, and cathodic protection can all help control uniform assault [9].

Pitting Corrosion

It is one of the most hazardous and damaging localized attacks that can lead to equipment and pipeline breakdowns as well as holes in metal or alloy. Because pits are small and frequently coated in corrosion products, they can be challenging to spot. The pits that form are often saucer-shaped when there is no mechanical stress present. When the surface diameter is roughly equal to or less than the depth, the term "pitting" is used. Pits vary greatly in quantity, size, and depth.

On a surface with distinct irregularities, a dotted look of the corrosion result is probably a sign of pits underneath. Pits rarely develop upward direction from the bottom of horizontal areas; instead, they typically grow toward gravity. The pits may occasionally begin on vertical surfaces. Pits can occasionally be uneven or undercut, giving the appearance of a honeycomb surface. Pitting is hard to assess [10].

The ratio of the average penetration of the ten deep pits to the depth of the deepest pit is known as the pitting factor. A calibrated microscope that focuses on the surface first, then the pit bottom, or a micrometer with a suitably formed top are two methods for measuring depth. Depending on the metal and the environment, pitting often requires an initial period that might vary significantly. Pits typically grow quickly after initiation.

Halide ions, such as chloride, bromides, and hypochlorite, are typically linked to pitting. Pitting tendencies are rather low for iodides and fluorides. Practically speaking, chloride and ions containing chlorine are the main cause of pitting failures. This is caused by the broader spread of chlorides in nature as well as their aggression. Chlorides, such as cupric, ferric, and mercuric halides, are quite aggressive when oxidizing metal ions. Halides of nonoxidizing metals ($NaCl$, $CaCl_2$) are less hostile. Pitting corrosion is also significantly influenced by critical concentration and critical potentials. Static circumstances are typically linked to pitting [11].

Self-stimulating autocatalytic activities take place in a corrosion pit when an aerated sodium chloride solution pits a metal. In terms of electrochemistry, a small anode encircled by a large cathodic surface is linked to the pit creation. Local heterogeneity or local passive film breakdown is the cause of small anodes. Chloride ions migrate to maintain electron neutrality since the pit is fast metal dissolution tends to create an excessively positive charge there. Consequently, there is a large concentration of M^+Cl^- in the pit, and hydrolysis occurs as follows:

$$M^+Cl^- + H_2O \rightarrow MOH + H^+Cl^- \tag{10}$$

A high concentration of hydrogen ions is the end outcome. Most metals and alloys dissolve when stimulated by hydrogen and chloride ions, and the process speeds up over time. There is no oxygen decrease in a pit because oxygen is essentially insoluble in corrosive solutions. The autocatalytic nature of pitting is the direct cause of the previously described gravity effect. Pits are more stable when they proceed in the direction of the earth gravitation force because a dense concentrated solution is required inside of them.

Crevice Corrosion

These attacks, caused by surface deposits, gasket surface holes, lap joints, and cracks beneath bolt and rivet heads, are usually associated with small amounts of stagnant solution. For a crevice corrosion area, it must be sufficiently large to allow liquid in while maintaining a stationary zone. Crevices usually occur at apertures as small as a few thousandths of an inch. When metal surfaces (gaskets) come into touch with nonmetallic surfaces, crevice corrosion may result. Fibrous gaskets or asbestos fabric provide ideal crevices. Metals or alloys that depend on oxide coatings to stop corrosion are more susceptible. Stainless steel is the most vulnerable [12].

Take into consideration a piece of riveted metal (M) submerged in aerated seawater (pH= 7). The oxidation ($M \rightarrow M^+ + e-$) and reduction ($O_2 + 2H_2O + 4e- \rightarrow 4OH^-$) reactions first take place evenly throughout the whole surface, including the crevice. Shortly after, the limited convection causes the oxygen in the fissure to be exhausted. The disintegration of metal M continues after the oxygen is exhausted. The movement of Cl^- ions into the crevice (hydroxide ions are less mobile) must balance the extra positive charge that is produced in the solution. An autocatalytic process, similar to that of pitting, then takes place.

Galvanic Corrosion

Dissimilar metals must frequently be coupled in process flow systems, and when two dissimilar metals come into contact with a conductive or corrosive fluid, there is typically a potential difference between them. In contrast to how these metals behave when they are not in touch, the corrosion of the less corrosion-resistant material in the pair is often accelerated and that of the more corrosion-resistant material is decreased. The potential difference is what propels current and corrosion in this type of corrosion, which is also referred to as galvanic or two-metal corrosion.

The electrochemical series provides us with a decent idea of potential effects when actual experiments in a particular context are not available. The corrosion of two metals can be easily identified by the localized attack close to the junction, which decreases as one gets farther away from the junction, depending on the solution's conductivity. A pair with a tiny anode and a large cathode significantly accelerates the anode's rate of corrosion (by 100 or 1,000 times). While the anode area regulates the anode current density and, consequently, the severity of galvanic corrosion, the cathodic area controls the quantity of corrosion current.

Polarization is the primary factor limiting corrosion severity. Some couples, like Al-SS, polarize aggressively, resulting in only a slight corrosion current flowing, while other couples, like Al-Cu, polarize very little, maintaining the initial large corrosion current. Temperature causes some couples (like Fe-Zn) to reverse their polarity [13].

Intergranular Corrosion

The closely packed structure of the metal is its rare crystal lattice, and grain boundaries are high-energy areas but are usually only slightly more reactive than the lattice. However, under certain conditions, grain boundaries are very reactive and localized attack at and adjacent to grain boundaries with relatively little corrosion of the grains takes place, which is known as intergranular corrosion. The alloy disintegrates and/or loses its strength. Intergranular corrosion can be caused by impurities at the grain boundaries [14].

Stress Corrosion Cracking

Stress corrosion cracking (SCC) is the spontaneous cracking that may result from the conjoint action of tensile stress and corrosive media. Caustic embrittlement of steel boilers and seasonal cracking of brass cartridge cases are well-known examples of SCC. Even pure metals may be subjected to SCC, for example, pure Cu in cupric-ammonium complexes.

Alloys subject to cracking are normally considered the passive and noncorroding alloys. Environments in which cracking occurs are those in which corrosion can occur. If the initial localized corrosion is intergranular, the subsequent cracking is predominantly intergranular (e.g. Al-Cu alloys, Al-Mg alloys, Cu base alloys, mild steel, Mg alloys with impurities at grain boundaries, etc.). If the initial attack is in the body of grain, transgranular cracking develops, for example, Mg alloys, 18-8 stainless steel, and so on.

The microstructure and, in turn, the susceptibility to SCC are impacted by changes in composition, heat treatment, manufacture, and mechanical processing. Although SCC is commonly observed in a variety of aqueous media, it can also be found in nonaqueous inorganic liquids, fused salts, and some liquid metals. Cracking tendencies are often significantly impacted by the presence of oxidizers. As the temperature rises, SCC accelerates.

Current theories usually resolve themselves by two mechanisms: electrochemical mechanism oxide thin film barrier breaking or barrels shaped pitting corrosion modifications, and stress cracking involves in the reduction of surface energy by adsorptions components of the environments [15].

Hydrogen Damage

It is convenient to distinguish SCC from hydrogen cracking in which the cause of fracture is directly related to hydrogen. Some features of hydrogen cracking are similar to SCC but causes differ; cathodic polarization, for example, accelerates hydrogen cracking but inhibits SCC. Corrosion, application of sacrificial anodic protection, electrocoating, and other methods are bigger sources of H^+ in metals.

Metals do not allow the molecular form of hydrogen (H_2) to diffuse. The only species that can diffuse through steel and other metals is atomic hydrogen (H). Localized deformation and, in certain situations, total vessel wall disintegration are the outcomes. Using clean steel, impermeable coatings, or inhibitors can all help avoid blistering. The eliminating toxins that cause hydrogen degradation, such as phosphorous ions, cyanides, arsenic compounds and sulfides and replacing alloys (nickel steel and Ni alloys have extremely low hydrogen diffusion rates) [16].

Hydrogen Embrittlement

This is also brought on by hydrogen seeping into a metal, which causes it to lose its tensile strength and ductility. Brittle hydride compounds are created when dissolved hydrogen combines with titanium and other potent hydride-forming metals.

The mechanism is based on slip interference by dissolved hydrogen by (1) decreasing the rate of corrosion, (2) changing the plating conditions, (3) baking, (4) switching out alloys, (5) using suitable welding technique sand embrittlement can be avoided. Utilizing clean steels has essentially no impact [17].

OTHER FORMS OF CORROSION

Fatigue Corrosion

Fatigue is the tendency of a metal to fracture when subjected to repetitive cyclic straining that is significantly lower than its ultimate tensile strength. Corrosion fatigue is a detrimental impact caused by the simultaneous action of corrosion and cyclic stressors. If the environment is such that the metal is subject to corrosive attack in addition to cyclic straining, the deterioration will be even more pronounced [18].

Fretting Corrosion

Fretting is the term used to describe the fast corrosion that happens at the interface between contacting, heavily loaded metal surfaces when they are subjected to modest relative vibrations. Deep pits in areas where there have been minor relative movements and surface discolorations are typically characteristics of fretting [19].

Cavitation Corrosion

Cavitation is mainly the wearing away of metal by the creation and collapse of voids in a fluid as a result of repetitive impact impacts. When separation and cavity creation in the flow system cause the constant pressure to drop under the liquid's steam pressure, voids are created [20].

Erosion Corrosion

Degradation The relative movement of a corrosive fluid and the metal surface causes corrosion, which is the acceleration or increase in the rate of attack on a metal. Metal is expanded mechanically from the interface of metal in the form of solid products or as dissolved ions.

CORROSION PROTECTION STRATEGIES

Significant financial losses result from corrosion. Despite being unavoidable, rust can be greatly minimized in cost. A corrosion engineer's job is to use scientific knowledge to prevent corrosion in a cost-effective and practical way [21]. On the other hand, the corrosion scientist conducts research and development to enhance current procedures, such as cathodic protection, inhibitor use, and the creation of novel corrosion-resistant alloys that include appropriate heat treatment.

Several schemes are used for the prevention of corrosion:

i. Selection of Metal or Alloy
ii. Use of Non-metallic Materials
iii. Alteration of Environment
iv. Cathodic and Anodic Protection
v. Use of Proper Design
vi. Use of Inhibitors
vii. Use of Coatings

Selection of Proper Metal or Alloy

The pure metals have high corrosion obstruction with respect of one possesses impurities other elements. But purified metals are costly, and their strength and hardness values are low. There are two examples of nonferrous metals used in the pure form: aluminium available not too valuable in a pure state (>99.5%). It is used for handling hydrogen peroxide. The presence of other elements may cause decomposition of hydrogen peroxide. Arc-melted zirconium is more corrosion-resistant than induction-melted zirconium which has more impurities in it.

In most engineering works, where strength and hardness are always required, alloys have to be used instead of pure metals. However, alloys can be designed in a manner that they possess not only strength and toughness but also resistance to corrosion. Alloying has proved to be a very effective method of improving the resistance of metals to attack by corrosive environments at either ordinary or elevated temperatures.

In alloy selection, there are available quite a few "natural" metal-corrosive combinations. These combinations of metal and corrosive usually represent the maximum amount of corrosion resistance for the least amount of money. Tantalum is a metal which is used anticorrosion-resistant material. It has corrosion resistance power against acids at any concentrations and temperatures. It is used implants in the human body [22] because less corroding effect.

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