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Corrosive Environments and Types of Steel

1.1 Introduction

Corrosion is defined as the process by which metallic materials when interacting in a specific environment undergo a chemical or electrochemical reaction that degrades their properties. Any material, especially metal material, has its specific use in environment. Use in an unsuitable environment may lead to premature corrosion damage to the material and induce corrosion accidents, which will not only cause economic losses but even cause casualties and environmental pollution [1].

According to statistics, more than half of the steel is in service in the natural environment (atmosphere, soil, and water), another part is used in industrial acids, alkalis, salts, or high-temperature and high-pressure environment, and a very small part is used in extreme harsh environments, such as high-temperature, high-humidity, and high-salt spray extreme marine atmospheric environments, deep-sea environments below 300 m, and dry and hot desert environments. Therefore, the service environment of steel is extremely complex, the study also shows that the type of corrosion of steel in specific environments is also diversified, which leads to the complexity of steel varieties. Correct and comprehensive understanding of the corrosion environment and corrosion type of steel in the development of high-quality steel is the first major issue.

1.2 Natural Corrosive Environments

1.2.1 Atmospheric Corrosive Environments

Atmospheric corrosion environment accounts for more than half of the total corrosion environment. According to the humidity of the surface, it can be divided into three categories: (i) dry atmospheric corrosion: when there is a discontinuous liquid film layer on the surface, a very thin invisible oxide film is formed on the surface of the metal whose free energy of reaction is negative, for example, the thickness of the oxide film of iron is about 30 Å. (ii) Damp atmospheric corrosion: corrosion that occurs when there is a thin liquid film layer on the surface of the metal that is

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invisible to the naked eye, such as for example, rusting of iron when there is no rain or snow. (iii) Wet atmosphere corrosion: corrosion that occurs when the humidity of the air is close to 100%, or when moisture in the form of rain, snow, foam, etc., falls on the metal surface, and there is a film layer of condensed water visible to the naked eye on the surface of the metal. According to regional conditions and atmospheric characteristics, this can be divided into rural atmosphere, marine atmosphere, suburban atmosphere, industrial atmosphere, etc.

The main environmental factors that impact atmospheric corrosion are: (i) Humidity: the greater the humidity, the easier the metal surface condensation, the longer the electrolyte film exists, and the more the corrosion rate increases. There exists a critical humidity for metallic materials, and the corrosion rate of the material increases dramatically when the humidity is greater than the critical humidity level. For iron and steel, copper, nickel, zinc, and other metals, the critical humidity is about 50–70% between. (ii) Temperature: in other conditions are the same, areas with high average temperatures have higher atmospheric corrosion rates. (iii) Rainfall: rainwater may damage and wash away the rust layer on the material surface, accelerating corrosion. However, in some cases, rain can slow down corrosion to some extent by washing away dust, salt particles, or water-soluble corrosion products from the rust layer on the metal surface. (iv) Atmospheric composition: outside the basic composition of the atmosphere, atmospheric pollutants, such as sulfides, nitrides, CO, and CO_2, salt particles, and sand, can accelerate atmospheric corrosion to some extent. (v) The impact of abnormal climatic conditions: for example, acid rain can reduce the corrosion resistance of Fe, Zn, Cu, Pb, and other metal greatly. Due to the complexity of atmospheric factors, the corrosion behavior and rate of materials under specific atmospheric conditions can be determined through long-term field testing. The usual corrosive classification of the atmospheric environment is shown in Table 1.1.

1.2.2 Soil Corrosion Environments

Soil consists of a variety of granular minerals, moisture, gases, microorganisms, and other multiphase compositions, with biological activity, ionic conductivity,

Table 1.1 Classification of environmental corrosivity in terms of corrosion rates of different metals in the first year of exposure.

	Corrosion rate of metals				
Corrosion type	**Unit**	**Carbon steel**	**Zn**	**Cu**	**Al**
C1 (Very low)	g/m^2/a μm/a	<10 <1.3	<0.7 <0.1	<0.9 <0.2	<0.2
C2 (Low)	g/m^2/a μm/a	10–200 1.3–25	0.7–5 0.1–0.7	0.9–5 0.1–0.6	
C3 (Medium)	g/m^2/a μm/a	200–400 25–50	5–15 0.7–2.1	5–12 0.6–1.3	0.6–1.3
C4 (High)	g/m^2/a μm/a	400–650 50–80	15–30 2.1–4.2	12–25 1.3–2.8	
C5 (Very high)	g/m^2/a μm/a	650–1500 80–200	30–60 4.2–8.4	25–50 2.8–5.6	

and capillary colloidal properties. Soil is a special electrolyte, may induce uneven total corrosion of metals and severe localized corrosion [2]. Stray currents and microorganisms also cause soil corrosion.

Soil corrosion and other media electrochemical corrosion processes are due to the metal and the medium of the formation of electrochemical inhomogeneity of the corrosion of the primary battery. At the same time, as the soil medium has multiphase (phases such as soil, water, and air), inhomogeneity and relative stability, and other characteristics, soil environment caused by metal corrosion has its own unique corrosion mechanism and kinetic development process, such as soil macro-uniformity caused by corrosive macrocells; often soil corrosion plays a greater role.

The inhomogeneity of the soil medium is mainly due to the different permeability conditions of the soil. Under different permeability conditions, the rate of oxygen penetration varies greatly, strongly affecting the potential of the metal parts in contact with different areas of the soil, which is the basic factor contributing to the establishment of the oxygen concentration corrosion battery. Soil pH, salt content, and other properties of the change will also cause corrosion macrocells. Long-distance pipelines inevitably have to cross a variety of different conditions of the soil. The formation of long-distance corrosion macrocells is different from other media. Corrosion in the soil plays a role in the following types of macrocells: (i) Long-distance corrosion macrocells: The extended metallic infrastructure buried underground forms a long-distance corrosion macrocell through differential soil compositions and stratified geological structures. (ii) Corrosion macrocells resulting from soil localized heterogeneity: Areas of stone accumulation in the soil are less permeable than soil proper, making it easier for the metal in that area to become the anode of the corrosion macrocell during corrosion, while the metal in the soil-only area becomes the cathode. (iii) Corrosion macrocells caused by different burial depths and edge effects: Due to the different depths of burial and the presence of oxygen diffusion in the soil, an oxygen concentration corrosion cell effect can be formed in areas at different depths. As oxygen more easily reaches the edge of the electrode, the edge of the metal components on the same level becomes the cathode. Compared to the anode area (central part), corrosion of the material edge would be much lighter. (iv) Corrosion macrocells due to differences in metal states: corrosion macrocells formed as a result of dissimilar metal contact, temperature differences, stresses, and different surface states of metals in soil. This in turn induces localized corrosion of the material.

Environmental factors affecting soil corrosion mainly include: (i) Porosity (permeability): larger porosity is conducive to oxygen penetration and water transmission, and this is the initial occurrence of corrosion promotion factors. Good permeability accelerates the corrosion process of microcells. With poor permeability, the presence of anaerobic microorganisms in the soil leads to microbial corrosion. (ii) Soil temperature: the higher the temperature, the greater the corrosion rate. (iii) Soil water content: when the soil water content is very high (water saturation >80%), the diffusion of oxygen is hindered, and corrosion is reduced. With the reduction of water content, the depolarization of oxygen becomes easier, and the corrosion rate is increased. When the water content falls below 10%, the anodic polarization and the soil resistivity are increased, and the corrosion rate is reduced sharply. (iv) pH value: as soil acidity increases, soil corrosion increases. When the soil contains a large number of organic acids, its pH value is close to neutral, but its corrosiveness is still very strong. (v) Resistivity: generally, the smaller the soil resistivity, the more serious the soil corrosion. Soil resistivity can be used as a parameter for evaluating soil corrosivity. (vi) Soluble ions (salt): soil generally contains sulfates, nitrates, chlorides, and other inorganic salts. In the soil, the electrolyte cations are generally potassium, sodium, calcium, magnesium, and other ions; anions are carbonates, chlorides, and sulfate ions. A large salt content in the soil increases its electrical conductivity and the corrosiveness of the soil. (vii) Soil redox potential: soil redox potential and soil resistivity can also be used as a major indicator of soil corrosivity. Soil corrosivity is generally believed to be −200 mV (vs. SHE) below the anaerobic conditions if corrosion is intense and is susceptible to the role of sulfate-reducing bacteria. (viii) Microorganisms: microbiologically induced corrosion (MIC) is corrosion due to the presence and activity of microorganisms and/or the action of their metabolites. Bacteria, fungi, and other microorganisms play an important role in soil corrosion and the corrosion mechanism is complex. It has been found that there are large corrosion rates in soil due to the action of microorganisms. (ix) Stray current: stray current refers to the current flowing into other places from the leakage of the intended normal circuit, such as electrified railways, electrolysis and electroplating tanks, welding machines, electrochemical protection devices, and disturbances in the large geomagnetic fields. In many cases, stray currents flowing through underground metallic facilities result in severe corrosion damage.

The role of various soil environmental factors on corrosion is intricate and complex. The corrosion behavior and mechanism of metallic materials in specific soil environmental conditions need to be determined through long-term field tests. Usual soil environment corrosion contains uniform corrosion and pitting corrosion simultaneously, hence, grading must be evaluated simultaneously using both uniform and pitting corrosion factors, as shown in Table 1.2.

1.2.3 Natural Water-Corrosive Environment

Corrosion in the water environment generally includes freshwater corrosion, salt lake water corrosion, and seawater corrosion, of which freshwater generally refers to river water, lake water, groundwater, and other natural water with low salt content. Compared with seawater, freshwater has low salinity and variable water quality conditions, and freshwater corrosion is greatly affected by environmental factors of

Table 1.2 Carbon steel soil corrosion classification criteria.

Corrosion class	I (Excellent)	II (Good)	III (Moderate)	IV (OK)	V (Poor)
Corrosion rate/(g/dm^2/a)	<1	1–3	3–5	5–7	>7
Maximum corrosion depth/(mm/a)	<0.1	0.1–0.3	0.3–0.6	0.6–0.9	>0.9

water quality. Usually the salinity of lake water ≥50 g/l brine lake or those lakes with self-dissolving salt deposits are defined as salt lake.

Around 70.9% of the Earth's surface is the ocean. Corrosion of metallic materials in the ocean is quite serious. Marine corrosion losses account for about one-third of the total corrosion losses. In recent years, with the vigorous development of the marine economy, the problem of corrosion in various types of marine equipment has become increasingly prominent [3]. Seawater is a very complex composition of natural electrolytes. Surface seawater (1–10 m) is saturated with oxygen and carbon dioxide, with a pH value of 8.2 or so, and is a corrosive electrolyte solution at room temperature with a certain flow rate. It has high salt content, electrical conductivity, corrosivity, and biological activity. Seawater contains a large number of sodium chloride-based salts and is often approximated as a 3.5% NaCl solution. The temperature of seawater varies between 0 and 35 °C with geographic location, ocean depth, day and night conditions, seasons, and so on. Oxygen content in seawater is the main factor in seawater corrosion, and the surface layer of seawater is saturated with air under normal conditions at the sea surface. The pH in seawater is usually 8.1–8.3, but it varies greatly in local areas.

The marine environment is the world's most complex natural environmental corrosion system, which can be categorized into marine atmospheric zones, splash zones, tidal zones, fully immersed zones, and sea mud zones. According to the different depths of seawater, the fully immersed area can be divided into shallow water, continental shelf, and deep sea area. Marine atmospheric area refers to the sea surface splash zone above the atmospheric area and coastal atmospheric area, carbon steel and low-alloy steel used in this environment would be corroded seriously. Splash zone refers to the zone above the average high tide line where the waves splash and wet. Due to the full contact of seawater and air here, the oxygen content reaches the maximum degree, coupled with the impact of the waves, making the splash zone the most corrosive area. Tidal zone is the area between the average high tide level and the average low tide level, and its corrosion rate is slightly higher than the full immersion zone. However, for long-sized steel strip specimens, the corrosion rate in the tidal zone is lower than that in the total immersion zone. The mean low tide line below the part up to the bottom of the region is known as the total immersion zone. The marine mud area consists mainly of seafloor sediments. Unlike land soil, the sea mud zone has high salinity, low resistivity, and is more corrosive. Compared with the fully immersed zone, the oxygen concentration in the marine mud zone is low, and the corrosion rate of steel in the marine mud zone is usually lower than that in the fully immersed zone. The corrosion behavior of materials in the deep sea is as follows: with the increase in depth, the uniform corrosion is weakened, the local corrosion increases.

The main environmental factors of seawater corrosion are: (i) Salinity: The salinity in seawater is just close to the salt concentration required to maximize the corrosion rate of steel. When the salinity exceeds a certain value, the increase in salinity decreases the solubility of oxygen and the corrosion rate of the material decreases. (ii) pH: as the pH of seawater is generally neutral, the corrosion effect is not significant. In the deep sea, pH is slightly reduced, which is not conducive for the generation of protective carbonate layer on the metal surface. (iii) Carbonate saturation: in the pH conditions of seawater, carbonate saturation, easy to deposit on the metal surface, and the formation of a protective layer. The river water at the estuary dilutes the seawater, making the carbonate solution undersaturated. As a result, it is less likely to precipitate and form a protective layer on the metal surface, leading to an increase in corrosion. (iv) Oxygen content: if the seawater oxygen content increases, it can increase the metal corrosion rate. (v) Temperature: increase in the temperature can usually accelerate the reaction, but with the rise in temperature, the oxygen solubility decreases, and weaken the temperature effects. (vi) Flow rate: as the flow rate increases, the corrosion rate increases. However, for metals that can be passivated in seawater, an appropriate flow rate can promote the passivation and corrosion resistance of titanium, nickel alloys, and high-chromium stainless steel. When the seawater flow rate is very high, metal corrosion increases dramatically, which is the same as in freshwater, due to friction, impact, and other mechanical forces, abrasions, erosion, and cavitation. (vii) The influence of biological factors: the organisms and microorganisms in seawater can attach to the material surface, accelerating the corrosion of the material.

1.3 Industrial Corrosive Environments

Industrial environments involve high temperatures, high pressures, and corrosive media such as various acids, alkalis, salts, and chemical substances, which accelerate the corrosion failure process of materials. Typical industrial corrosive environment of petroleum, chemical, and nuclear power industry is also extremely complex.

1.3.1 Corrosive Environments in the Petroleum Industry

The petroleum industry consists of exploration, drilling, development, oil recovery, gathering, refining, and storage. All aspects of the petroleum industry are closely linked to steel, and most of the steel structures are in service in very harsh environments, leading to severe corrosion of equipment in the petroleum industry.

The corrosion-prone environments in the oil extraction process are mainly in the drilling, oil extraction, and gathering and transportation projects. The corrosive medium in the drilling process mainly comes from the atmosphere, drilling fluid, and formation outputs, usually several components exist at the same time; oil extraction and gathering and transportation projects are mostly CO_2 and H_2S-corrosive environments; oil and gas gathering and transportation projects also have water-doped environments [4].

The main corrosive environment of the oil refining industry contains: (i) $HCI + H_2S + H_2O$ corrosive environment mainly exists in the normal decompression distillation unit, the temperature is lower than 150 °C parts; (ii) sulfide corrosive environment, including: room temperature sulfide stress cracking corrosion and dew-point corrosion and 240 °C higher than the corrosive environment formed by the heavy oil parts of sulfur, sulfide, and hydrogen sulfide; (iii) naphthenic acid corrosive environment exists between 220 and 400 °C; (iv) Hydrogen embrittlement (HE) environment mainly occurs at room temperature, hydrogen corrosion refers to the temperature above 200 °C, hydrogen partial pressure >0.5 MPa caused by corrosion.

Petrochemical equipment corrosion environment for: (i) high-temperature hydrochloric acid corrosion environment; (ii) high-temperature sulfuric acid corrosive environment; (iii) hydrogen fluoride, and hydrofluoric acid corrosive environment.

Petrochemical fiber equipment corrosion environment: (i) acetic acid, maleic acid, and other organic acids corrosion environment, (ii) sulfuric acid corrosion environment, (iii) hydrochloric acid corrosion environment. In addition, chemical fiber equipment also exists in the corrosive environment of adipic acid, terephthalic acid corrosive environment, and sodium hydroxide corrosive environment.

The common corrosive environments of large nitrogen fertilizer plants are: low-temperature $H_2S—CO_2—H_2O$ environment; high-temperature hydrogen corrosion environment; medium-temperature $CO_2—CO—H_2$ environment; $K_2CO_3—CO_2—H_2O$ environment; high temperature and high-pressure $H_2—N_2—NH_3$ environment; room temperature ammonia environment.

1.3.2 Corrosive Environments in the Chemical Industry

The chemical industry is the most complex man-made corrosive environment of the industrial field. The history of almost every new product and the emergence of new processes are accompanied by the emergence of new corrosive environment; almost all man-made corrosive environment exists in the chemical industry. According to its medium classification, it is mainly divided into acid corrosion environment, salt corrosion environment, and alkali corrosion environment.

Chemical industry acid and alkali corrosion environment include all organic acids, inorganic acid environment, and all alkali. Their corrosion of metal is serious, and corrosion law is also complex. Acid corrosion of metals, depending on whether it is oxidizing or nonoxidizing, is very different.

Chemical industry salt corrosive environment has a variety of categories of forms. According to the acidity and alkalinity, when the salt is dissolved in water, the salt can be divided into acidic, neutral, and alkaline salts and oxidizing and nonoxidizing salt distinction. Table 1.3 lists the classification of some inorganic salts.

1.3.3 Corrosive Environments in the Nuclear Power Industry

The main corrosive media and environments in the nuclear industry are: radiation and irradiation; high-temperature and high-pressure water, high-purity sodium and high-purity lithium; and strongly aggressive media. Vibration corrosion, scouring corrosion, and corrosion fatigue in nuclear reactor operation and oxidation of zirconium alloys in high temperature water vapor are important [5].

Rays and irradiation corrosion environment: the nuclear industry often see rays of α-particles, β-particles, X-rays, γ-rays, neutron flow, etc., in addition to proton flow, deuteron flow, and other charged heavy particle beams. These rays will more or less play a role in the corrosion of the material [6].

Table 1.3 Classification of acidity and alkalinity of some inorganic salts.

	Neutral salt	Acid salt	Alkali salt
Nonoxidizing	NaCl KCl Na_2SO_4 K_2SO_4 LiCl	NH_4Cl $(NH_4)_2SO_4$ MnO_2 $FeCl_2$ Ni_2SO_4	Na_2S Na_2CO_3 Na_2SiO_3 Na_3PO_4 $Na_2B_2O_7$
Oxidizing	$NaNO_3$ $NaNO_2$ K_2CrO_4 K_2CrO_7 $KMnO_4$	$FeCl_3$ $CuCl_2$ $HgCl_2$ NH_4NO_3	NaClO $Ca(ClO)_2$

High-temperature and high-pressure water, high-purity sodium, high-purity lithium, and high-purity helium corrosive environments: High-temperature and high-pressure water is mainly used in light-water reactors, and the environment of high-temperature and high-pressure water in the nuclear power industry is very strictly controlled. High-purity sodium is mainly used in liquid metal cooling reactors, and high-purity lithium is used in fusion reactors. There are also high-temperature gas-cooled reactors using high-purity helium. The presence of impurities in helium can cause corrosion problems.

Strongly aggressive media corrosive environment: uranium mining in the nuclear industry, the chemical treatment and processing of ores, the refining and enrichment of uranium compounds, the treatment of nuclear fuel elements after nuclear reactions in nuclear reactors, the separation and recycling of fission products, and the treatment process of radioactive waste liquids and wastes require the use of a large number of acids, alkalis, and salt compounds, which are all of different erosive properties. Corrosion problems at welds and wear and tear corrosion from mineral materials are serious. During the separation of uranium isotopes, uranium hexafluoride is chemically exceptionally active, and it reacts with water to form HF, which has an erosive effect.

1.4 Uniform Corrosion and Localized Corrosion

The forms of metal corrosion are generally divided into two major categories: uniform corrosion and localized corrosion. Localized corrosion can be further classified into pitting corrosion, crevice corrosion, galvanic corrosion, intergranular corrosion, selective corrosion, stress corrosion, corrosion fatigue, and erosion–corrosion, commonly referred to as the eight main forms of localized corrosion. Localized corrosion, in contrast to uniform corrosion, is characterized by the occurrence of corrosion limited to or concentrated on a specific part of the metal. When localized corrosion occurs, the anode and cathode areas are clearly separated and can be distinguished either by the naked eye or through microscopic observation. Additionally, secondary corrosion products may form at a third location where the anode and cathode regions meet. Statistics show that over 80% of corrosion incidents are caused by localized corrosion. Due to the difficulty in detecting its corrosion rate, localized corrosion poses a significant risk. Therefore, this chapter will focus on introducing several common types of localized corrosion, with corrosion under stress and erosion–corrosion discussed in the next chapter.

1.4.1 Uniform Corrosion

Uniform corrosion refers to corrosion occurring over the entire surface of a metal material, resulting in an overall thinning of the metal. Uniform corrosion is typically uniform, although it may sometimes appear as nonuniform corrosion. This phenomenon is widespread and can be caused by electrochemical corrosion, such as the self-dissolution process of some pure metals or homogeneous alloys in an electrolyte solution. The term “uniform corrosion” specifically refers to corrosion caused by electrochemical reactions.

The electrochemical characteristics of uniform corrosion, on a macroscopic level, show that the entire metal surface appears uniform, and the corrosive medium in contact with the metal surface is consistent, meaning that the electrochemical properties of the entire metal–electrolyte interface are homogeneous, with all surface regions following the same dissolution kinetics. From a microscopic perspective, there are energy fluctuations at different points on the metal surface over time; areas with higher energy act as anodes, while areas with lower energy act as cathodes. The anode and cathode areas of the corrosion cells are extremely small, and their positions shift over time, resulting in nearly the same degree of corrosion across the entire metal surface [7].

1.4.2 Pitting Corrosion

1.4.2.1 Definition and Characteristics of Pitting

Pitting corrosion, also known as small hole corrosion, is a form of corrosion that concentrates in a very small area on the metal surface and penetrates deeply into the metal, creating small, deep pits. The severity of pitting is indicated by the pitting factor, which is the ratio of the maximum pit depth to the average corrosion depth of the metal [8].

Pitting corrosion is one of the most destructive and insidious forms of corrosion. Its severity is second only to stress corrosion cracking (SCC). Although pitting causes minimal weight loss of the metal, the very small anode area leads to rapid corrosion, often resulting in perforation of equipment and pipe walls and causing sudden failures. Detecting pitting corrosion is challenging because pit sizes are small and often covered by corrosion products, making it difficult to quantitatively measure and compare the extent of pitting. Additionally, pitting is closely related to the occurrence of other forms of localized corrosion, such as crevice corrosion and stress corrosion [9].

1.4.2.2 Morphology and Conditions of Pitting

The morphology of pitting corrosion varies widely, depending on the material and the corrosive medium. The conditions for forming a specific pit shape are not yet clearly understood and may be related to the material's microstructure.

The occurrence of pitting corrosion generally requires the fulfillment of three conditions: material, medium, and electrochemical factors.

1) Pitting corrosion often occurs on metal materials that are prone to surface passivation (such as stainless steel, aluminum, and aluminum alloys) or on metals with cathodic coatings (such as carbon steel coated with Sn, Cu, or Ni). When the passivation film or cathodic coating is locally damaged, the damaged area and the undamaged area form a "passivation–activation corrosion cell" with a large cathode and small anode, leading to corrosion that progresses deeply into the substrate forming pits (Figure 1.1).
2) Pitting corrosion occurs in corrosive media containing specific ions. Stainless steel, for instance, is particularly sensitive to halide ions, with the sensitivity order being $Cl^- > Br^- > I^-$. These anions can cause uneven adsorption on the metal surface, which may lead to localized breakdown of the passivation film, thereby triggering pitting corrosion.
3) Pitting occurs above a certain critical potential, known as the pitting potential or breakdown potential, represented by E_b. If the polarization curve is reversed and returns to the potential corresponding to the passive current, this is called the repassivation potential or protection potential, denoted as E_p. The potential relationships for the initiation and development of pitting corrosion are as follows: when $E > E_b$, pitting initiates and develops rapidly; when $E_b < E < E_p$, no new pits form, but existing pits can continue to grow; when $E < E_b$, pitting does not occur. A higher E_b value indicates better pitting resistance of the material. The closer E_b is to E_p, the stronger the passivation film's repair ability. It is important to note that when using potentiodynamic scanning to measure E_b and E_p, the effect of scan rate must be considered.

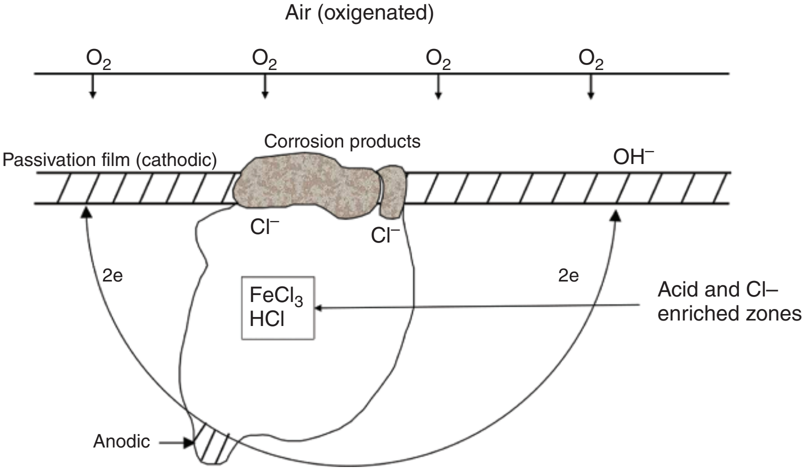

Figure 1.1 Pit corrosion diagram under Cl^- conditions.

1.4.2.3 Pitting Mechanism

Hoar and others proposed that the pitting corrosion process can be divided into two stages: pit nucleation (initiation) and pit growth (development).

Eroded Hole Nucleation (Occurrence) There are generally two viewpoints regarding the causes of pit nucleation: the passive film breakdown theory and the adsorption theory.

1) Passive Film Breakdown Theory: This theory suggests that as the electrode undergoes anodic polarization, the electric field intensity within the passive film increases. Corrosive anions (such as Cl^- ions), due to their small ionic radius, penetrate the passive film under the influence of this electric field, turning the local passive film into a highly conductive ion conductor. As a result, a high current density appears at this location, causing cations to move chaotically and become active. When the electric field intensity at the passive film–solution interface reaches a certain critical value, pitting occurs.
2) Adsorption Theory: The adsorption theory of passivation proposes that the passivation of metal is caused by an adsorption layer of oxygen or oxygen-containing particles on the metal surface. In contrast, the adsorption theory suggests that pit formation is due to the competitive adsorption between these anions and oxygen. This adsorption–replacement hypothesis is illustrated, where “M” represents the metal. In a degassed solution, the metal surface does not adsorb oxygen molecules but rather stable oxide ions formed by water. “ZX^-” represents chloride complex ions. Once chloride complex ions replace the stable oxide ions, the adsorption film at that site is destroyed, and pitting occurs. According to this theory, the pitting potential E_b is the potential at which corrosive anions can reversibly displace the adsorption layer on the metal surface. When $E > E_b$, chloride ions strongly compete for adsorption at certain points, leading to pitting at those locations.
3) Pitting-Sensitive Sites: Both theories suggest that pitting is the result of localized damage to the film caused by Cl^- ions at certain points on the metal surface. Which parts of the metal surface are most susceptible to pitting? The inhomogeneity of the microstructure and structure of the metal surface makes certain parts of the passive film weaker, making them prone to pit nucleation. Surface inhomogeneities primarily include grain boundaries, inclusions, dislocations, and heterogeneous structures.
4) Incubation Period of Pitting Corrosion: The period from when the metal comes into contact with the solution until pitting occurs is known as the incubation period of pitting corrosion. The incubation period shortens as the Cl^- concentration in the solution increases and the electrode potential rises. Engell and others discovered that, for low-carbon steel, the inverse of the incubation period for pitting corrosion has a linear relationship with the Cl^- concentration. That is: $\frac{1}{\tau} = k[Cl^-]$, where k is a constant. Pitting does not occur if the Cl^- concentration is below a certain critical threshold.

Eroded Hole Growth (Development) Once a pit forms, it develops rapidly due to significant changes in the electrochemical conditions within the pit, which greatly impact its growth. The primary theory regarding pit development is based on the formation of an "Occluded Cell," which subsequently leads to a self-catalytic "activation–passivation corrosion cell" theory.

1) Conditions for Occluded Cell Formation: The formation of an occluded cell generally requires the following conditions: Geometric conditions in the reaction system that hinder mass transfer in the liquid phase, such as the accumulation of corrosion products at the pit mouth, which can locally obstruct mass transfer. Similar situations can occur in crevices and cracks from stress corrosion. A local environment that differs from the overall environment; the presence of electrochemical and chemical reactions that create conditions locally distinct from those of the bulk environment.
2) Self-catalytic Development Process of Pitting: Once pitting occurs, a series of changes take place inside and outside the pit.

First, the metal inside the pit begins to dissolve, as represented by the reaction: $M \rightarrow M^{n+} + ne$. In a Cl^- ion-containing aqueous solution, the cathodic reaction is an oxygen reduction reaction. This causes the oxygen concentration within the pit to decrease, while oxygen accumulates outside the pit, creating a "differential aeration cell."

The concentration of metal ions inside the pit continuously increases. To maintain the overall electro-neutrality of the reaction system, Cl^- ions from outside the pit migrate inward. The Cl^- concentration within the pit can rise to 3–10 times that of the bulk solution.

The metal salts formed inside the pit undergo hydrolysis: $M^{n+} + n(H_2O) \rightarrow M(OH)_n + nH^+$, leading to an increase in hydrogen ion concentration and a drop in pH within the pit, sometimes as low as 2–3. This severe acidification causes the metal inside the pit to be effectively in an HCl-like environment, resulting in an active dissolution state. Meanwhile, the solution outside the pit remains oxygen-rich and unchanged, with the surface still in a passive state. This creates an "activation (inside the pit)–passivation (outside the pit) corrosion cell," allowing pitting to progress in a self-catalytic manner.

When understanding the pit development process, one should not simply consider the interior of the pit as the anode and the exterior as the cathode. In essence, pitting is a multi-electrode system, with distinct differences in the cathodic reactions coupled inside and outside the pit.

Therefore, the formation of an occluded cell is essentially a process of transitioning the occluded region from oxygen reduction corrosion to hydrogen evolution corrosion. The essence of self-catalysis is the creation of a localized environment that accelerates the microcell process. The "activation (inside the pit)–passivation (outside the pit) corrosion cell" further accelerates hydrogen evolution corrosion within the pit.

1.4.3 Crevice Corrosion

1.4.3.1 Definition and Characteristics of Crevice Corrosion

Crevice corrosion is a form of localized corrosion that occurs in the presence of an electrolyte within narrow crevices formed between metal-to-metal or metal-to-nonmetal interfaces, where the movement of the medium is hindered.

In engineering structures, it is generally necessary to connect different structural components, making crevices unavoidable. Crevice corrosion reduces the effective geometric dimensions of components and decreases the degree of fit. The volume of corrosion products within the crevice increases, creating localized stress and making assembly difficult. Therefore, crevices should be minimized whenever possible to reduce this risk.

1.4.3.2 Gap Formation

Conditions that create crevices include:

1) Connections between different structural components, such as riveting and lap welding between metals, threaded connections, gaskets between various flanges, and contacts between metal and nonmetal materials.
2) Deposits, attachments, and coatings on metal surfaces, such as dust, sand particles, and deposited corrosion products.

Corresponding to these different crevice-forming conditions, there are several types of crevice corrosion, such as gasket corrosion, deposit corrosion, and filiform corrosion.

1.4.3.3 Characteristics of Crevice Corrosion

1) Crevice corrosion can occur on all metals and alloys, but it is particularly likely to occur on the surfaces of passivated, corrosion-resistant metal materials.
2) The medium can be any acidic or neutral corrosive solution, with chloride-containing solutions being the most likely to induce crevice corrosion.
3) Compared to pitting corrosion, crevice corrosion is more likely to occur on the same material. When $E_b < E < E_p$, existing pits can develop, but no new pits will form; however, crevice corrosion can both initiate and propagate within this potential range. The critical potential for crevice corrosion is lower than that for pitting corrosion.

1.4.3.4 Crevice Corrosion Mechanism

For a crevice to become a site of corrosion, it must be wide enough for the solution to flow into the crevice but narrow enough to maintain stagnant liquid within it (Figure 1.2). The crevice width most sensitive to crevice corrosion is typically around 0.025–0.15 mm.

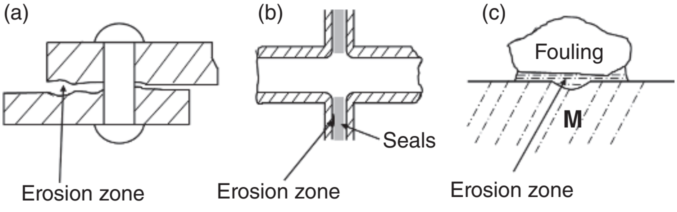

Figure 1.2 Schematic of crevice corrosion (a) intermetallic gap; (b) gap between metal and non-metal; (c) gaps between metal and limescale.

The occurrence of crevice corrosion can be divided into an initial stage and a later stage.

In the initial stage, the same anodic and cathodic reactions occur on the metal surfaces both inside and outside the crevice.

$$\text{Anodic Reaction}: \mathrm{M} \rightarrow \mathrm{M}^{n+} + n\mathrm{e};$$

$$\text{Cathodic Reaction}: \frac{1}{2}\mathrm{O}_2 + \mathrm{H}_2\mathrm{O} + 2\mathrm{e} \rightarrow 2\mathrm{OH}^-$$

After some time, once the oxygen inside the crevice is fully consumed, the oxygen reduction reaction ceases. Due to the lack of oxygen within the crevice and the abundance of oxygen outside, a “differential aeration cell” is formed. Metal dissolution inside the crevice produces an excess of M^+ ions, which induces the migration of Cl^- ions into the crevice. Subsequently, the hydrolysis of the metal salts formed inside the crevice leads to acidification, with the pH within some metal crevices dropping to as low as 2–3. The progression of crevice corrosion then follows a path similar to that of pitting corrosion.

1.4.4 Galvanic Corrosion

1.4.4.1 Definition and Characteristics of Galvanic Coupling Corrosion

Galvanic corrosion, also known as contact corrosion or dissimilar (bimetallic) metal corrosion, occurs in an electrolyte solution when two different metals or alloys come into contact (electrically connected). In this situation, the less noble metal with a more negative potential undergoes accelerated corrosion, while the more noble metal with a more positive potential is protected. This phenomenon is known as galvanic corrosion. In engineering, combinations of different metals are inevitable, as nearly all machinery, equipment, and metal structures are composed of components made from various metallic materials [10]. Therefore, galvanic corrosion is very common. Additionally, the principle of galvanic corrosion can be used to protect valuable components by employing sacrificial anodes made from less noble metals, providing cathodic protection through the sacrificial anode method.

1.4.4.2 Electric Coupling Sequence

As mentioned, galvanic corrosion is related to the potentials of metals in contact with each other in a solution. The difference in potential between contacting metals creates a corrosion cell, with the potential difference driving galvanic corrosion.

In electrochemical corrosion, the concept of the electromotive force series (EMF) or standard potential series is often referenced, where metals are arranged according to their standard electrode potentials. This thermodynamic equilibrium potential is measured under standard conditions with a metal placed in a solution containing its ions at an activity of 1. However, in practical corrosion systems, metals are rarely pure; they often contain impurities or are alloys, and their surfaces may have films. Likewise, the solution is typically not pure and does not contain only the metal ions at an activity of 1. Therefore, the EMF series is not applicable in real situations.

Instead, the galvanic series is used, which is an arrangement of the actual potentials (nonequilibrium potentials) of real metals or alloys in a specific medium. Different media produce different galvanic series.

It should be noted that, similar to the EMF series, a material's position in the galvanic series only indicates its corrosion tendency, not the actual rate of corrosion. In some cases, the potential of certain metals may even reverse in specific media. For example, when Al and Mg are in contact with neutral NaCl solution, initially Al has a more positive potential than Mg, making Mg the anode and causing it to dissolve. As Mg dissolves, however, the medium becomes alkaline, causing a potential reversal, and Al becomes the anode.

1.4.4.3 Galvanic Currents and Galvanic Corrosion Effects

To introduce the occurrence of galvanic corrosion from a physical perspective, let's consider two different metals, A and B, where metal A has a higher potential than metal B in a certain corrosive medium. When metals A and B are connected, the corrosion current changes. For simplicity and clarity, the anode and cathode areas of A and B are drawn separately, assuming that A and B have the same surface area.

When A and B are not yet connected: $i_{Aa} = |i_{Ac}|$, $i_{Ba} = |i_{Bc}|$;
When A and B are connected: $\mathrm{i}'_{Ac} - \mathrm{i}'_{Aa} = \mathrm{i}'_{Ba} - |\mathrm{i}'_{Bc}| = i_g$–galvanic current.

In the extreme case – when A is completely protected, $\mathrm{i}'_{Aa} = 0$, and $i_g = \mathrm{i}'_{Ac} = \mathrm{i}'_{Ba} - |\mathrm{i}'_{Bc}|$.

This means that in this case, within the galvanic cell formed by A and B, the cathodic current corresponding to the anodic dissolution (corrosion) of B is supplied jointly by the cathodic reactions on both A and B. Consequently, the corrosion of metal A itself stops, and the cathodic reaction on A is entirely directed to contribute to the corrosion of B.

Galvanic Corrosion Effect: This is the ratio of the corrosion current of the anodic metal B after coupling with metal A to the self-corrosion current of metal B when not coupled. This ratio is generally represented as i'_{Ba}/i_{Ba}.

$$\gamma = \frac{\mathrm{i}'_{Ba}}{i_{Ba}} = \frac{i_g + |\mathrm{i}'_{Bc}|}{i_{Ba}}$$

This formula indicates the extent to which the dissolution corrosion rate of the anodic metal B increases after coupling with metal A. The larger the ratio, the more severe the galvanic corrosion.

The same issue can also be understood using the galvanic corrosion polarization diagram. Since metals A and B are in the same corrosive medium, it can be assumed that the same cathodic reaction occurs on both metals.

As shown in the diagram, $\mathrm{i}'_{Ba} = |\mathrm{i}'_{Ac} + \mathrm{i}'_{Bc}| = i_g + |\mathrm{i}'_{Bc}|$, indicating that after the two metals are coupled, the anodic corrosion current of B is matched by the cathodic current composed of B's own cathodic self-corrosion current and the galvanic current (supplied by the cathodic reaction on A, with the anodic reaction on A ceasing in this scenario).

1.4.5 Intergranular Corrosion

1.4.5.1 Definition and Characteristics of Intergranular Corrosion

Intergranular corrosion is a form of localized corrosion that occurs along the grain boundaries or near the grain boundaries of metal materials in specific corrosive media, causing the grains to lose cohesion.

Intergranular corrosion is a highly destructive type of localized corrosion. Although it may not cause any visible changes macroscopically, it almost completely compromises the material's strength, often leading to sudden equipment failure. Additionally, intergranular corrosion frequently transitions into grain boundary SCC, serving as an origin for stress corrosion cracks. In extreme cases, the intergranular corrosion process can even be used to produce alloy powders.

1.4.5.2 Causes of Intergranular Corrosion

Like other types of corrosion, the occurrence of intergranular corrosion involves both internal (material-related) and external (environmental) factors.

First, in polycrystalline metals and alloys, there are differences in the structure and chemical composition between the grains and grain boundaries. The atomic arrangement at grain boundaries is more disordered, with concentrations of defects and stresses. Dislocations, vacancies, and other imperfections accumulate at the grain boundaries, making it easy for solutes (various impurities such as S, P, B, Si, and C) to adsorb and segregate there, or even precipitate phases (such as carbides or other phases). This creates a chemical composition difference between the grain boundaries and the grain interiors, forming the conditions necessary for a corrosion microcell.

When such metals and alloys are in specific corrosive environments, the grain boundaries and the grain interiors exhibit different electrochemical characteristics. Generally, the potential at the grain boundaries is lower, and their passivity is poorer. Therefore, in the corrosion cell formed by the grain boundaries and grains, the grain boundaries act as the anode, and the grains act as the cathode. Since the area of the grain boundary is very small, this creates a "small anode–large cathode" configuration, causing the dissolution current density at the grain boundaries to be much higher than that of the grain interiors.

1.4.5.3 Intergranular Corrosion Mechanism

The widely accepted theory regarding the mechanism of intergranular corrosion is the solute-depletion theory, specifically the Cr-depletion theory. Below, several common mechanisms of intergranular corrosion will be introduced.

1) Cr-Depletion Theory – Grain Boundary Carbide Precipitation: Ni—Cr austenitic stainless steels are typically used after solution treatment (held at 1050 °C for two hours). When solution-treated austenitic stainless steels with a carbon content above 0.03% are heated within the temperature range of 427–816 °C and then

slowly cooled (commonly referred to as sensitization), they experience severe intergranular corrosion when exposed to corrosive media.

The reason for this is that, after sensitization, continuous $Cr_{23}C_6$ carbides precipitate along the grain boundaries, causing a severe Cr-depletion zone at the grain boundaries. As carbides precipitate and grow along the grain boundaries, they consume C and Cr from the surrounding matrix, with diffusion from the grains toward the grain boundaries. Since C diffuses faster than Cr, almost all C in the solid solution is used to form carbides. During this period, only Cr near the grain boundaries is available to participate in the carbide formation reaction. As a result, a region with Cr content below the 12% needed for passivation forms near the grain boundaries. In mildly oxidizing environments, this Cr-depleted zone at the grain boundaries rapidly dissolves. This type of intergranular corrosion is most likely to occur in the active–passive transition region.

The situation with ferritic stainless steels is slightly different from that of austenitic stainless steels. Even ferritic stainless steels with very low C and N content can undergo intergranular corrosion when rapidly cooled (e.g. by quenching or air cooling) from temperatures above 900 °C. However, reheating to 700–800 °C can eliminate intergranular corrosion. This can also be explained by the precipitation of grain boundary carbides.

The carbide that causes intergranular corrosion in ferritic stainless steel is of the $(Cr, Fe)_7C_3$ type. This occurs because the solubility of C and N in ferrite is even lower than in austenite, and Cr diffuses in ferrite at a rate 2 orders of magnitude faster than in austenite. Thus, even with rapid cooling from high temperatures, carbides can precipitate along grain boundaries, forming Cr-depleted zones. Reheating to 700–800 °C promotes Cr diffusion, eliminating the Cr-depleted zones.

2) Anodic Phase Theory – Grain Boundary Phase Precipitation and Dissolution: With advances in smelting technology, it is now possible to produce large quantities of low-carbon and even ultralow-carbon stainless steel, greatly reducing intergranular corrosion caused by carbide precipitation. However, when ultralow-carbon stainless steels, especially high-Cr, Mo steels, are heated at 650–850 °C, they may still experience intergranular corrosion in strongly oxidizing media. This is due to the formation of phases composed of FeCr or MoFe intermetallic compounds at the grain boundaries. Under overpassivating conditions – that is, in a strongly oxidizing environment – these phases undergo severe selective dissolution.
3) Adsorption Theory – Impurity Atom Adsorption at Grain Boundaries: Occasionally, ultralow-carbon 18Cr—9Ni stainless steel undergoes intergranular corrosion in strongly oxidizing media (such as nitric acid with chromate) even after solution treatment at 1050 °C. This cannot be explained by carbide precipitation or phase precipitation at the grain boundaries. A possible reason is the adsorption of impurities like P and Si at the grain boundaries, altering the electrochemical properties of the grain boundaries.

1.5 Corrosion Under Stress

In actual use, metal materials are not only affected by corrosive media but subjected to various stresses, often resulting in more severe corrosion damage. These stresses can be externally applied, such as through tension, compression, bending, or torsion, which directly act on the metal, or they may be applied to the metal surface through relative motion at contact surfaces or the flow of high-speed fluids (possibly containing solid particles). Stresses can also originate internally within the metal, such as when hydrogen atoms penetrate the metal and create internal stresses.

Consequently, the resulting corrosion damage includes SCC, hydrogen-induced cracking, corrosion fatigue, erosion corrosion, and wear corrosion. Since the fracture of materials is caused by environmental factors, it is often collectively referred to as environmental cracking.

1.5.1 Stress Corrosion Cracking

1.5.1.1 Definition and Characteristics of Stress Corrosion Cracking

Stress corrosion cracking refers to the brittle fracture phenomenon that occurs in metal materials under a certain tensile stress in specific media due to the combined action of the corrosive medium and stress. Typically, in certain corrosive environments, a material may experience minimal corrosion when unstressed; however, when subjected to a certain level of tensile stress (which can be much lower than the material's yield strength), even highly ductile metals can suffer brittle fractures over time. This type of fracture generally occurs without any obvious warning and often leads to catastrophic consequences [11]. Common examples of SCC include "caustic embrittlement" in boiler steel, "nitrate embrittlement" in low-carbon steel, and "chloride SCC" in austenitic stainless steel.

1.5.1.2 Conditions and Characteristics of SCC Occurrence

It is generally believed that three conditions are necessary for SCC to occur:

1) Sensitive Material: The metal itself must be susceptible to SCC. Nearly all metals or alloys have some sensitivity to SCC in specific environments, with alloys and impurity-containing metals being more prone to SCC than pure metals.
2) Presence of a Medium that Triggers SCC: Each alloy is sensitive to SCC in specific environments, and not every medium can induce SCC. Typically, alloys are inert in SCC-triggering environments, often having a passive film on their surface, and even a small amount of the specific medium can lead to stress corrosion. The interaction between the material and environment is reflected in potential; SCC generally occurs within the potential range of the active–passive or passive–overpassive transition zone, where the passive film is incomplete.
3) Tensile Stress: A certain level of tensile stress is required for SCC to occur. This stress can be operational stress caused by external loads on the material, residual stresses such as thermal or deformation stresses formed during production, manufacturing, processing, and installation, or stress from the wedging effect of

corrosion products within cracks or from hydrogen generated by the cathodic reaction.

In addition, SCC also has the following characteristics:

1) SCC is a typical form of delayed failure, where, under the combined effects of stress and a corrosive medium, a material requires a certain period for crack nucleation, subcritical crack growth, and finally reaching a critical size, leading to unstable fracture. This delayed failure can be clearly divided into three stages: Incubation Period (t_{in}) – The crack initiation phase, which is the time required for crack nucleation and accounts for about 90% of the total time. Crack Propagation Period (t_{cp}) – The time from crack initiation to its growth to a critical size. Rapid Fracture Period – When the crack reaches a critical size, it undergoes instantaneous fracture due to purely mechanical effects. The total fracture time depends on the material, medium, and stress, ranging from a few minutes to several years. For a given material and medium, reducing the stress (and thereby the stress intensity factor) extends the fracture time. In most corrosion systems, there is a threshold or critical stress σ_{th} (or critical stress intensity factor K_I SCC), below which SCC does not occur.
2) SCC cracks are classified into three types: intergranular, transgranular, and mixed. The crack path depends on the material and medium; the crack path may change for the same material when the medium varies. Key characteristics of stress corrosion cracks include: the crack originates from the surface; the crack's length and width are disproportionate, differing by several orders of magnitude; the crack propagation direction is generally perpendicular to the main tensile stress; the crack typically appears branched or tree-like.
3) The crack propagation rate for SCC is generally between 10^{-6} and 10^{-3} mm/min, which is approximately 106 times faster than uniform corrosion but only about 10^{-10} of the speed of purely mechanical fracture.
4) SCC cracking is a form of low-stress brittle fracture. There is no obvious macroscopic plastic deformation before fracture, and in most cases, the fracture surface is brittle – cleavage, quasi-cleavage, or intergranular. Due to the effects of corrosion, the fracture surface appears dull in color, and microscopic examination often reveals corrosion pits and secondary cracks. Transgranular fractures typically exhibit patterns like river, fan, or feather markings, while intergranular fractures have a sugar-cube-like appearance.

1.5.1.3 SCC Mechanism

Various mechanisms have been proposed to explain the SCC phenomenon, but no universally accepted unified mechanism has been established. Since SCC is a corrosion-related process, its mechanism is necessarily linked to the anodic and cathodic reactions occurring during corrosion. Therefore, the mechanisms of SCC can be divided into two major types: anodic dissolution-type mechanisms and hydrogen-induced cracking-type mechanisms. The mechanism of hydrogen-induced cracking will be discussed in the next section, while the focus here will be on explaining the anodic dissolution-type mechanism.

The anodic dissolution mechanism suggests that in an environment where SCC occurs, the metal surface is typically covered by a passive film, preventing direct contact between the metal and the corrosive medium. When the passive film is locally damaged, crack nucleation occurs. Under the influence of stress, the crack tip becomes activated and dissolves along a preferential path, leading to crack propagation and ultimately fracture. Therefore, SCC progresses through three stages: film rupture, dissolution, and fracture:

1) Localized Film Rupture Leading to Crack Nucleation: The passive film on the alloy surface can be locally damaged due to electrochemical or mechanical forces, leading to crack nucleation.
   Electrochemical Effects: Local corrosion such as pitting or intergranular corrosion can initiate SCC cracks. When pitting occurs, SCC cracks may nucleate from the bottom of the pits under stress. In the absence of pitting, if the corrosion potential falls within the active–passive or passive–overpassive transition range, the instability of the passive film makes SCC cracks more likely to nucleate at weaker regions of the material surface, such as where intergranular corrosion occurs.
   Mechanical Effects: Due to the relatively poor ductility or strength of the passive film compared to the base metal, localized rupture of the film can occur when subjected to mechanical stress, leading to SCC crack initiation.
   Any defects on the metal surface, including submicroscopic cracks in the protective film, can serve as sites for SCC crack nucleation.
2) Crack Tip Directional Dissolution Leading to Crack Propagation: Once a crack is formed, its specific geometry creates a closed-off region. Similar to pitting and crevice corrosion, a “closed cell” forms inside the crack, leading to the creation of an “activation–passivation corrosion cell” between the crack tip and the crack walls. This establishes the electrochemical conditions necessary for rapid dissolution at the crack tip. This rapid dissolution process is also self-catalytic. Stress and material inhomogeneity (pre-existing active pathways) provide preferential corrosion routes, facilitating crack propagation. The pre-existing active pathways and strain-induced active pathways lead to both intergranular and transgranular SCC crack propagation.
3) Fracture: Once the SCC crack propagates to a critical size, the crack becomes unstable and undergoes a sudden mechanical fracture.

1.5.2 Hydrogen Cracking

1.5.2.1 Definition of Hydrogen Cracking

Hydrogen-induced cracking (HIC) is the phenomenon of brittle fracture caused by the ingress and diffusion of atomic hydrogen within the alloy’s crystal structure. It is sometimes referred to as HE or hydrogen damage. Strictly speaking, HE primarily involves the reduction of metal ductility, whereas hydrogen damage, in addition to the reduction in ductility and cracking, also includes the deterioration of other physical or chemical properties of the metal material, making its definition broader.

1.5.2.2 Behavior of Hydrogen in Metals

The process of hydrogen-induced cracking involves a series of steps, including the source of hydrogen, its transport, its eventual destination, and the resulting consequences. These steps describe how hydrogen atoms enter the metal, diffuse through it, accumulate at certain sites (such as grain boundaries or defects), and ultimately lead to brittle fracture or other forms of damage in the material.

Sources of Hydrogen The sources of hydrogen can be divided into two types: internal hydrogen and external hydrogen.

Internal hydrogen refers to hydrogen that already exists within the material before it is put into use. It is primarily absorbed during processes such as smelting, heat treatment, pickling, electroplating, and welding. External hydrogen, or environmental hydrogen, refers to hydrogen absorbed by the material during use when it comes into contact with hydrogen-containing media or undergoes cathodic hydrogen evolution reactions.

Hydrogen Solubility in Metals with Hydrogen Traps The accumulation of hydrogen in traps can lead to hydrogen-induced cracking. Oversaturated hydrogen atoms combine into molecular hydrogen within voids, generating very high pressures. For example, if the hydrogen concentration in steel is 4×10^{-6}, the corresponding hydrogen pressure at room temperature, based on the hydrogen solubility equation in steel, could exceed 104 MPa. This high pressure can cause significant damage to the material, potentially leading to cracking or other forms of failure.

Hydrogen Transport The average hydrogen content that causes hydrogen-induced cracking is generally very low. For example, in α-Fe, a hydrogen concentration of 4×10^{-6} corresponds to only 223 hydrogen atoms for every 10^6 iron atoms. Therefore, hydrogen-induced cracking requires local enrichment of hydrogen, which occurs through the transport of hydrogen within the metal. There are two mechanisms for hydrogen transport: diffusion and dislocation migration.

1) Diffusion: When there is a concentration gradient of hydrogen or a stress gradient within the metal, hydrogen will diffuse. In the presence of a concentration gradient, hydrogen will move from areas of higher concentration to areas of lower concentration. Under steady-state conditions, this process follows Fick's law. At room temperature, the presence of hydrogen traps significantly influences hydrogen diffusion behavior in the metal; however, at high temperatures, this effect is less significant.
2) Dislocation Migration: Dislocations act as special hydrogen traps. Dislocations not only capture hydrogen atoms around them, forming Cottrell atmospheres, but also facilitate hydrogen transport. Due to the fast diffusion of hydrogen in the metal, the hydrogen atmosphere can move along with the dislocation as it migrates. When a migrating dislocation encounters an irreversible trap with a stronger binding energy for hydrogen, the hydrogen is "dumped" into these traps.

Forms of Hydrogen Hydrogen in metals can exist in several forms:

1) H^-, H, H^+: Hydrogen can dissolve in metals in the forms of H^-, H, or H^+. One viewpoint is that in transition metals (such as Fe and Ni), the d-band electrons are not fully filled. When hydrogen enters the metal, it dissociates into protons and electrons, with the electrons occupying the d-band, while hydrogen exists in the metal as protons. Another viewpoint suggests that hydrogen has a very small atomic radius (0.53 Å), making it easy for hydrogen to exist in atomic form and occupy interstitial positions in the lattice. Additionally, in alkali metals (Li, Na, K), hydrogen can exist as H^-, such as in NaH.
2) Hydrogen Molecules: When the hydrogen content in the metal exceeds its solubility limit, hydrogen atoms tend to accumulate at defects in the metal, such as voids, cracks, or grain boundaries, and form hydrogen molecules.
3) Hydrides: Hydrogen has a relatively high solubility in IVB or VB group metals such as V, Ti, and Zr. However, once the solubility limit is exceeded, hydrides are formed, such as TiH_x (where $x = 1.58$–1.99). Nickel can also form hydrides under certain conditions.
4) Gas Clouds: Hydrogen can combine with dislocations to form gas clouds, which can be considered a distinct phase within the metal.

1.5.2.3 Classification of Hydrogen Cracking

Hydrogen-induced cracking (HIC) can be classified into two main types based on the relationship between HE sensitivity and strain rate:

First Type of Hydrogen Embrittlement:

In this type, the sensitivity to HE increases as the strain rate increases. That is, the material already contains some crack source before loading, and under stress, the formation and propagation of cracks are accelerated. This type includes three forms:

Hydrogen Corrosion: Hydrogen reacts with the second phase (such as inclusions or alloy additives) in the metal under high temperature and pressure, forming high-pressure gases (e.g. CH_4, SiH_4). This leads to material decarburization, internal cracking, and the formation of bubbles.

Hydrogen Bubbling: Oversaturated hydrogen atoms precipitate at defect sites (such as inclusions), forming hydrogen molecules. This leads to very high hydrogen pressure locally, causing surface bubbling or internal cracks.

Hydride-Type Hydrogen Embrittlement: Hydrogen has a strong affinity for IVB and VB group metals. When the hydrogen content is high, brittle hydride phases are easily formed, and under subsequent stress, these hydrides act as crack sources, causing brittle fracture.

These three situations result in permanent damage to the metal, reducing its plasticity or strength. Even if hydrogen is removed from the metal, the damage cannot be undone, and the plasticity or strength cannot be restored. Therefore, this is called irreversible HE.

Second Type of Hydrogen Embrittlement:

In this type, the sensitivity to HE decreases as the strain rate increases. That is, the material does not contain a crack source before loading, but under the interaction of stress and hydrogen during loading, crack sources gradually form, ultimately leading to brittle fracture. This type includes two forms:

Stress-Induced Hydride-Type Hydrogen Embrittlement: In metals capable of forming brittle hydrides, when hydrogen content is low or the hydrogen saturation in the solid solution is not high, hydrides cannot form spontaneously. Under stress, hydrogen accumulates at stress-concentrated areas. When the hydrogen concentration exceeds a critical value, hydrides precipitate. This stress-induced hydride phase transformation occurs only at lower strain rates and leads to brittle fracture. Once hydrides form, even if the stress is removed and hydrogen is dissipated, plasticity cannot be restored after a period of rest, hence, this is also irreversible HE.

Reversible Hydrogen Embrittlement: In this type, hydrogen-containing metals do not show brittleness during high-rate deformation. However, during slow deformation, hydrogen gradually accumulates at stress-concentrated areas. Under the interaction of stress and hydrogen, cracks nucleate and propagate, leading to brittle fracture. If the load is removed before crack formation and the material is rested, plasticity can be restored after high-rate deformation, meaning that the brittleness disappears once the stress is removed. This type is called reversible HE. When caused by internal hydrogen, it is called reversible internal HE, and when caused by external hydrogen, it is referred to as environmental HE. The most common and dangerous form of hydrogen-induced cracking is reversible HE.

1.5.2.4 Mechanism of Hydrogen Cracking

Hydrogen Corrosion Hydrogen corrosion was first discovered in pressure vessels used in the Haber process for the synthesis of ammonia in Germany. During hydrogen corrosion, hydrogen reacts with carbon (C) and iron carbide (Fe_3C) in steel to form methane (CH_4), causing severe decarburization on the surface and the formation of intergranular network cracks. The development of hydrogen corrosion can be roughly divided into three stages:

1) Incubation Period: During this stage, methane-filled microbubbles nucleate at the grain boundaries and nearby areas. The mechanical properties of the steel remain unchanged. The length of the incubation period determines the service life of the steel and reflects the steel's resistance to hydrogen corrosion.
2) Rapid Corrosion Period: Small bubbles grow and, once reaching a critical density, they connect along the grain boundaries to form cracks. The volume of the steel expands, and its mechanical properties degrade.
3) Saturation Period: As the cracks connect, the carbon (C) is gradually depleted. The mechanical properties and volume of the steel no longer change.

At high temperatures and pressures, hydrogen reacts with carbon to form methane gas bubbles.

Initially, hydrogen molecules diffuse to the steel surface, where they undergo physical adsorption (a → b). The adsorbed hydrogen molecules dissociate into hydrogen atoms or ions, which are then chemically adsorbed (b → c → d). These hydrogen atoms diffuse through the lattice and grain boundaries into the steel (e → f). The hydrogen in the steel reacts with carbon to form methane, which has poor diffusion ability in the steel and accumulates in micropores, such as at grain boundaries and inclusions. The continuous reaction causes the carbon concentration around the pores to decrease, while carbon from other areas diffuses to replenish it (g → h represents diffusion of carbon atoms in the carburized body; g′ → h′ represents diffusion of carbon atoms in the solid solution). This results in local high pressure.

At low methane pressure, the main mechanism for bubble growth is the diffusion of iron (Fe) atoms along the grain boundaries, causing the bubbles to enlarge. At higher methane pressures, the bubbles primarily grow due to creep in the surrounding matrix. Bubbles formed near defects such as inclusions close to the surface eventually cause surface bubbling, while bubbles formed inside the steel ultimately develop into cracks.

As described, hydrogen corrosion is a chemical reaction, so the reaction rate, hydrogen absorption, carbon diffusion, and crack propagation are all activation processes that overcome energy barriers. Therefore, increasing temperature and pressure can shorten the incubation period. Various steels have a threshold temperature for hydrogen corrosion initiation at a certain hydrogen pressure, typically above 200 °C. Below this temperature, the reaction rate is extremely slow, and the incubation period may exceed the normal service life. When the hydrogen partial pressure falls below a certain value, hydrogen corrosion will not occur, even at high temperatures; instead, only surface decarburization occurs, and the methane pressure is too low to cause bubbling or cracking.

When hydrogen contains oxygen or water vapor, it can reduce the rate at which hydrogen enters the steel, thus prolonging the incubation period. However, the presence of H_2S shortens the incubation period.

Steel's hydrogen corrosion is directly related to its carbon content. As carbon content increases, the incubation period shortens. When enough carbide-forming elements, such as Ti, Zr, Nb, Mo, W, and Cr, are added to the steel, carbides are less likely to decompose due to hydrogen, reducing the possibility of methane formation. MnS inclusions often act as crack initiation sites and should be minimized.

Heat treatment and cold working also influence hydrogen corrosion. Carbide spheroidization treatment reduces the surface area, decreases the interfacial energy, and helps prolong the incubation period. Fine-grain structures and steels deoxidized with aluminum, which provide more nucleation sites for bubbles, tend to shorten the incubation period. Cold working increases the inhomogeneity of the microstructure and stress, enhancing the diffusion capability of the grain boundaries and increasing nucleation sites for bubbles, thus accelerating hydrogen corrosion in steel.

Hydrogen Bubble In a wet H_2S environment, two types of cracking phenomena occur in steel:

Sulfide Stress Corrosion Cracking (SSCC): This typically occurs in high-strength steels and requires the presence of stress. The cracks are perpendicular to the direction of the principal stress and are a form of reversible HE.

Hydrogen-Induced Cracking (HIC): This occurs in low-strength steels and does not require stress. The cracks are parallel to the rolled plate surface, and bubbling forms near the surface, known as hydrogen bubbling. Cracks near the interior of the material may appear as straight lines or step-like patterns, referred to as step-wise cracking, which is the most dangerous form. Step-wise cracking is particularly hazardous because it leads to the gradual propagation of cracks through the material.

Studies have confirmed that nonmetallic inclusions are the main nucleation sites for cracks. In particular, type II MnS inclusions, due to their different coefficient of thermal expansion compared to the matrix, become flattened during the hot rolling process, creating voids between the inclusion and the matrix, which can be considered as two-dimensional defects. Hydrogen atoms accumulate at the edges of these voids, initiating cracks. Additionally, silicates, chain-like alumina, and larger carbides and nitrides can also serve as crack initiation sites. Low-strength steels mainly have a pearlite-ferrite microstructure, and cracks often propagate along abnormal structures caused by Mn and P segregation that result in low-temperature transformations (martensite or bainite), or along banded pearlite, leading to hydrogen bubbling.

Reversible Hydrogen Embrittlement Hydrogen in the material accumulates in regions with high three-dimensional tensile stress under the influence of the stress gradient. When the hydrogen concentration reaches a critical level in the accumulated areas, the material cracks due to the combined effect of the stress field. Typical examples of reversible HE include delayed fracture in high-strength steels, SCC in hydrogen sulfide environments, and internal HE in titanium alloys. The essence of both reversible internal HE and environmental HE is the same, with the difference lying in the source of hydrogen, which affects the process of HE and the rate of crack propagation.

HE has the following characteristics:

1) Delayed Fracture: Similar to stress corrosion, HE involves the combined effects of stress and hydrogen, leading to crack nucleation (incubation period), subcritical crack growth, and unstable fracture. It is a delayed failure process.
2) Sensitive to Hydrogen Content: As the hydrogen concentration in steel increases, the critical stress of the steel decreases, and its elongation reduces.
3) Sensitive to Notches: Under the same applied stress, the smaller the notch radius, the more likely HE will occur.
4) Most Sensitive at Room Temperature: HE generally occurs within a temperature range of −100 to 100 °C, with the most severe effects near room temperature (around −30 to 30 °C).
5) Occurs at Low Strain Rates: The lower the strain rate, the more sensitive the material is to HE. Impact tests and normal tensile tests cannot reveal whether a material is sensitive to hydrogen.
6) Discontinuous Crack Propagation: Monitoring through methods like electrical resistance, acoustic emission, and displacement sensors shows that the crack propagation in HE is discontinuous.

7) Cracks Are Generally Not on the Surface and Rarely Branch: The macrofracture surface is relatively flat, while the microfracture surface may involve more complex morphologies such as intergranular, quasi-cleavage, or ductile dimple patterns. These features are related to the stress intensity factor KIK_IKI at the crack tip and the concentration of hydrogen.

The mechanism of HE is still not fully understood, and there is no unified theory. However, all theories share a common idea: hydrogen atoms, induced by stress, diffuse and accumulate in high-stress areas, and only when the accumulated hydrogen concentration reaches a critical value C_{cr}, causing the material's fracture stress σ_f to decrease, will brittle fracture occur. However, how the accumulated hydrogen actually contributes to this process is still unclear. The four most popular theories are as follows:

1) Hydrogen Pressure Theory: This theory suggests that supersaturated hydrogen in the metal accumulates at defect sites, precipitates, and forms hydrogen molecules, creating significant internal pressure. This internal pressure reduces the external stress required for crack propagation. This theory can explain the existence of the incubation period, the discontinuous crack propagation, and the effect of strain rate. However, it struggles to explain phenomena such as cracking in high-strength steels at hydrogen partial pressures much lower than atmospheric pressure or the reversibility of HE. Nevertheless, when the hydrogen content is high, such as in irreversible HE-like hydrogen bubbling without external force, this theory is widely accepted.
2) Adsorbed Hydrogen Reduces Surface Energy Theory: Griffith proposed that the fracture stress of a material is influenced by the adsorption of hydrogen on its surface $\sigma_f = \sqrt{\frac{2E\gamma_s}{\pi a}}$. When hydrogen is adsorbed on the crack surface, the surface energy decreases, which in turn reduces the fracture stress and causes HE. This theory can explain the existence of the incubation period, the effect of strain rate, and brittle fracture at lower hydrogen partial pressures. However, this model is only applicable to brittle materials.
3) Weak Bond Theory: This theory suggests that when hydrogen enters a material, it reduces the interatomic bonding forces. The reason for this is that the 1s electron of hydrogen enters the d-band of transition metals, increasing the electron density in the d-band, which enlarges the overlap between the s and d bands. As a result, the interatomic repulsive forces increase, leading to a decrease in the bonding strength. This theory is simple and intuitive, making it easy for people to accept. However, experimental evidence is insufficient. For example, the material's elastic modulus is related to bond strength, but experiments have not found significant effects of hydrogen on the elastic modulus. Moreover, aluminum alloys, which do not have a 3d band, can also exhibit reversible HE, indicating that it is not possible for the hydrogen 1s electron to enter the metal's d-band.
4) Hydrogen-Promoted Local Plastic Deformation Theory: This theory suggests that hydrogen-induced cracking is essentially the same as general fracture processes,

both of which begin with local plastic deformation. When the deformation reaches a critical state, cracking occurs. The role of hydrogen is to promote local plastic deformation at the crack tip. Experiments show that the hydrogen atoms accumulated near the crack tip, due to stress-induced expansion, interact with the applied stress to facilitate large-scale dislocation proliferation and movement in the region, increasing the plastic zone at the crack tip and the amount of deformation within the plastic zone. However, due to the underdevelopment of metal fracture theory, the process of crack nucleation and propagation after local plastic deformation reaches a certain extent is not fully understood, and the role of hydrogen in this process still requires further investigation.

1.5.3 Corrosion Fatigue

1.5.3.1 Definition of Corrosion Fatigue

Corrosion fatigue (i.e. corrosion fatigue cracking) refers to brittle fracture that occurs in materials or components under the combined action of alternating stress and a corrosive environment.

General fatigue refers to the process where alternating stress causes the initiation, subcritical growth, and eventual unstable fracture of fatigue cracks. Alternating stress – fatigue stress – is the stress that varies in magnitude or both magnitude and direction over time. Stress that changes in a periodic manner according to a certain pattern is called cyclic stress or constant amplitude fatigue stress, while stress that changes randomly and without regularity is called random stress or variable amplitude fatigue stress.

The fatigue performance of engineering materials is determined through fatigue tests, which produce a fatigue curve (commonly referred to as the *S*–*N* curve), establishing the relationship between the stress amplitude σ_a and the corresponding number of cycles to failure N_f. As the fatigue stress decreases, the number of cycles required for fatigue failure increases. The maximum stress that can be experienced without causing failure after an infinite number of cycles is called the fatigue limit. It is related to the stress ratio R (also known as the stress asymmetry coefficient). The fatigue limit at this point is denoted as $\sigma - 1$. Typically, low and medium-strength steels exhibit a clear fatigue limit; however, high-strength steels, stainless steels, and aluminum alloys generally do not have a fatigue limit. Instead, the maximum stress that the material can withstand without fatigue failure for a fatigue life of N (in the range of 107–108 cycles) is referred to as the endurance limit or fatigue strength.

1.5.3.2 Characteristics of Corrosion Fatigue

Strictly speaking, only fatigue in a vacuum is considered true pure fatigue, as air is also a corrosive environment for fatigue. However, when we refer to corrosion fatigue, we typically mean the fatigue behavior in environments other than air. The involvement of corrosion significantly reduces both the time and number of cycles required for fatigue crack initiation and increases the crack propagation rate. The characteristics of corrosion fatigue are as follows:

1) Corrosion fatigue does not have a fatigue limit. The maximum stress that does not cause failure after a specified number of cycles is generally used as the corrosion fatigue strength to evaluate the material's corrosion fatigue performance.
2) Unlike SCC, pure metals can also experience corrosion fatigue, and it does not require a special combination of material and environment. As long as a corrosive medium is present, corrosion fatigue will occur under alternating stress. Metals in a corrosive environment can exist in either a passive or active state.
3) The corrosion fatigue strength of metals is related to their corrosion resistance. For materials with good corrosion resistance, the corrosion fatigue strength increases with tensile strength. However, for materials with poor corrosion resistance, the corrosion fatigue strength is not related to their tensile strength.
4) Corrosion fatigue cracks often originate from surface corrosion pits or defects, with multiple crack sources. Corrosion fatigue cracks are primarily transgranular, though sometimes they may appear as intergranular or mixed types. As corrosion progresses, the cracks tend to widen.
5) Corrosion fatigue fracture is brittle fracture, with no significant macroscopic plastic deformation. The fracture surface exhibits corrosion characteristics, such as corrosion pits, corrosion products, and secondary cracks, along with fatigue features, such as fatigue striations.

1.5.3.3 Corrosion Fatigue Mechanism

Since corrosion fatigue is the result of the combined effects of alternating stress and a corrosive medium, in mechanistic studies, the pure fatigue mechanism is often combined with electrochemical corrosion effects (which may also involve mechanisms of SCC or hydrogen-induced cracking). Various corrosion fatigue models have been established, and two representative models are introduced below.

1) Pit Stress Concentration Model: This model suggests that the corrosive environment causes the formation of pits on the metal surface. Stress concentration at the bottom of these pits generates slip. The dissolution of the slip steps prevents the surface from recovering during reverse loading, making it a crack source. Repeated loading leads to continuous crack propagation.
2) Slip Band Preferential Dissolution Model: In some alloys, during the corrosion fatigue crack initiation stage, no pits are formed, or even if pits are created, cracks do not initiate from these pits. Therefore, the slip band preferential dissolution model has been proposed. This model suggests that under alternating stress, a residual slip band is formed, and due to the high dislocation density at the extrusion and intrusion sites, or the deposition of impurities in the slip band, atoms in this region exhibit higher activity and are preferentially corroded, leading to the nucleation of corrosion fatigue cracks. The deformed region acts as the anode, and the undeformed region acts as the cathode, promoting crack propagation under alternating stress.

Corrosion fatigue cracks are easier to nucleate than stress corrosion cracks because of the different stress states. Under alternating stress, slip has a cumulative effect, and the surface film is more easily damaged. In static tensile stress, generating slip steps is relatively difficult, and stress corrosion cracks can only propagate if the dissolution rate of the slip steps exceeds the repassivation rate, thus requiring certain conditions from the medium.

The difference between corrosion fatigue and pure fatigue lies in the effect of the corrosive medium, which makes cracks easier to nucleate and propagate. In the case of lower alternating stress, pure fatigue crack nucleation is difficult and may not occur below a certain threshold, which leads to the existence of a fatigue limit. Increasing tensile strength also increases the fatigue limit. However, in the presence of a corrosive medium, crack nucleation is easy, and once nucleated, the cracks continuously propagate, meaning there is no corrosion fatigue limit. Since increasing strength has little impact on crack nucleation, the corrosion fatigue strength does not have a proportional relationship with tensile strength.

1.5.4 Wear-Related Corrosion

The synergistic effects of stress and environmental media on materials not only are observed when metals are subjected to static or dynamic loads such as tension, compression, bending, or torsion, but also occur when metals experience wear. Wear refers to the damage to a metal surface and its underlying material caused by frictional mechanical forces during contact and relative movement with solid, liquid, or gas. Wear can be viewed as a special fracture process occurring on the metal surface and the adjacent substrate, which includes plastic strain accumulation, crack nucleation, crack propagation, and eventual detachment from the substrate.

In engineering, many wear-related issues involve the chemical and electrochemical effects of corrosive environments. The failure of materials or components is the result of the interaction between wear and corrosion. Below, we will focus on discussing erosion–corrosion related to fluid movement, cavitation corrosion, as well as corrosion wear, fretting corrosion, and other types of wear occurring on friction surfaces [12].

1.5.4.1 Erosion by Washing Away and Corrosion

Definition and Characteristics of Washout Corrosion Erosion–Corrosion (also called Erosion–Corrosion Wear) is the metal damage caused by the relative high-speed movement between the metal surface and a corrosive fluid. Typically, in a stagnant or low-velocity flowing corrosive medium, corrosion is not severe. However, when the corrosive fluid moves at high velocity, it disrupts the protective surface film or corrosion product layer on the metal surface. The thinning or removal of this surface film accelerates the corrosion process of the metal. Therefore, erosion–corrosion is the result of the combined action of fluid impingement and corrosion.

Erosion–corrosion commonly occurs in various metals and alloys exposed to moving fluids in industrial fields such as offshore and marine engineering, oil and gas production and transportation, petrochemicals, energy, and papermaking. It is especially severe in areas where the flow direction, velocity, and turbulence are changed, such as elbows, tees, pumps, valves, impellers, mixers, and the inlet and outlet heat exchangers. The metal surface affected by erosion–corrosion typically shows grooves, cavities, tear-drop shapes, and horseshoe shapes. The surface is shiny and free of corrosion products, with a distinct dependence on the flow direction. It usually forms along the local flow direction of the fluid or the irregularities on the surface that create turbulence.

Scouring Corrosion Mechanism Erosion–corrosion is characterized by the combined effects of the fluid's impact on electrochemical corrosion behavior, the mechanical forces generated by the fluid, and the interaction between these two factors. The acceleration of corrosion due to erosion mainly manifests in the enhancement of mass transfer processes, promoting the arrival of depolarizers such as O_2 to the metal surface and the removal of corrosion products from the surface.

The mechanical effects of erosion are primarily manifested as shear stresses and pressure changes caused by high fluid velocities, as well as the impact of solid particles or bubbles in multiphase flows. These mechanical forces can cause the thinning, rupture, or plastic deformation of the surface film, dislocation accumulation, and local energy increase, creating "strain difference cells," which accelerate corrosion. Additionally, erosion can cause partial delamination of the protective film, exposing fresh substrate. This exposes the metal to accelerated corrosion due to the galvanic corrosion effect between the pore and the film.

Conversely, corrosion also promotes the erosion process. Corrosion can roughen the surface, creating localized micro-turbulence. It can also dissolve the metal's work-hardened surface layer, exposing a softer substrate. Moreover, corrosion can expose and cause the detachment of wear-resistant hardened phases.

1.5.4.2 Cavitation

Definition and Characteristics of Cavitation Corrosion Cavitation corrosion (also known as cavitation and pitting corrosion) is a special form of erosion–corrosion caused by the collapse of bubbles in the liquid near the metal surface. This results in surface roughening and the formation of numerous volcanic-like pits of varying diameters, ultimately leading to the loss of serviceability. Cavitation corrosion only occurs under high-velocity turbulent flow conditions, especially when the liquid flows over surfaces with complex shapes where significant pressure changes occur, such as in water turbine blades, propellers, pump impellers, valves, and the tube ends of heat exchangers.

Formation and Bursting of the Vacuole According to Bernoulli's principle in fluid dynamics:

$$p + \frac{pv^2}{2} = C$$

In the equation, p is the pressure, v is the flow velocity, ρ is the fluid density, and C is a constant. In a localized region, when the flow velocity becomes so high that the static pressure drops below the liquid's vapor pressure, numerous small bubbles rapidly form within the liquid. These bubbles are primarily filled with water vapor. As the pressure decreases, the bubbles grow larger, and the flow transitions from a single-phase to a two-phase flow. The bubbles, carried along with the fluid, continue to be compressed as the external pressure increases and eventually collapses (implode).

Because the collapse time is extremely short, about 10^{-3} seconds, the space left behind by the collapsing bubbles is quickly filled by the surrounding liquid, generating powerful shock pressures that can reach up to 103 MPa. The repeated collapse of numerous bubbles in a specific region on the metal surface can induce strain fatigue and crack initiation, leading to cavitation corrosion damage.

Mechanism of Cavitation Corrosion The mechanical damage caused by cavitation was initially thought to be due to the shock waves generated by the collapse of bubbles. However, later studies revealed that the high-speed microjets produced during the collapse also play a significant role. This indicates that fluid dynamics (mechanical) factors are the primary contributors to cavitation corrosion. However, in a corrosive environment, electrochemical factors cannot be overlooked, and there is a synergistic interaction between the two.

The collapse of the bubbles destroys the surface protective film, promoting corrosion. On the other hand, the formation of pits further facilitates bubble nucleation. The existing pits can also concentrate stress, accelerating the detachment of material from the surface and substrate. Generally, when the stress is not too high, corrosion and mechanical factors have an equal influence. Corrosion factors – such as the composition of the medium, the alloy's corrosion resistance and passivity, electrochemical protection, or the use of inhibitors – greatly affect cavitation corrosion. However, when the stress is high, such as under intense water impact, the mechanical factors become more significant.

1.5.4.3 Corrosion and Wear

Definition of Corrosive Wear Corrosion wear is the combined effect of mechanical wear on the contact surfaces of friction pairs and the chemical or electrochemical corrosion occurring with the surrounding environmental medium, leading to the loss of surface material. It commonly occurs in contact components of mining machinery, construction machinery, agricultural machinery, metallurgical machinery, and parts that directly friction with materials such as sand, stones, coal, and ash, including equipment such as coal mills, ore crushers, ball mills, chutes, vibrating screens, screw feeders, scraper conveyors, and cyclone dust collectors [13].

Mechanism of Corrosive Wear The mechanisms of mechanical wear include adhesive wear and abrasive wear.

1) Adhesive Wear: This occurs when two solid surfaces move relative to each other under a certain pressure, causing the protruding or raised areas on the surfaces to undergo plastic deformation. Under high local pressure, the areas weld together.

As the surfaces continue to slide, material from one surface is peeled off and adheres to the other surface, resulting in wear. During this process, small particles or debris are often generated, further intensifying surface wear.

2) Abrasive Wear: This occurs when a rough and hard surface slides against a softer surface under pressure, or when free, hard solid particles slide between two friction surfaces, causing wear. Unlike adhesive wear, no micro-welding occurs in abrasive wear.

In the absence of these mechanical wear mechanisms, materials experience minimal corrosion due to the protection provided by the surface protective film in a corrosive environment. When mechanical wear is present, the protective film is locally damaged, allowing corrosion to proceed, and the frictional heat accelerates the corrosion rate. On the other hand, the detached protective film typically exists as solid debris between the two surfaces, causing abrasive wear. Therefore, in many cases, the total loss from corrosion wear is often greater than the sum of losses from pure corrosion and pure wear. In a few cases, when the corrosiveness of the medium is weak and has certain lubricating properties, corrosion wear losses may be less than dry wear losses under the same friction parameters, producing what is known as a “negative interaction.” Additionally, when the surface film consists of soft and tough substances such as chlorides, sulfides, phosphates, and fatty acid salts, wear may cause local film detachment but does not result in severe corrosion wear.

Corrosion wear rarely occurs in harsh corrosive conditions; it is more common in atmospheric or natural water environments. In dry atmospheric conditions, it is mainly chemical oxidation, while in humid atmospheres and natural waters, it is electrochemical corrosion, with corrosion being less pronounced.

1.6 Corrosion in the Natural Environment

Corrosion of metallic materials in natural environments is the most common type of corrosion. The natural environment refers to the soil, seawater (including freshwater), and atmosphere corresponding to the land, sea, and air in the natural world, as well as microorganisms that are closely related to and widely present in all three. In these three typical natural environments, the characteristics of corrosion vary depending on the changes in the environment or medium. However, in principle, corrosion of metals in natural environments falls under the category of electrochemical corrosion. Therefore, the basic process of corrosion should follow electrochemical principles.

1.6.1 Atmospheric Corrosion

1.6.1.1 Definition and Characteristics of Atmospheric Corrosion

Corrosion of metallic materials exposed to air, caused by the chemical and electrochemical interactions of water and oxygen in the air, is called atmospheric corrosion. Atmospheric corrosion is the most common type of corrosion, and a quick glance around us reveals many examples of rusted steel components. Over 60% of the world's steel production is used in atmospheric environments, and metal losses due to atmospheric corrosion account for more than 50% of total corrosion losses. For certain functional materials (such as microelectronic circuits), decorative materials, and cultural heritage items, even minor atmospheric corrosion is sometimes unacceptable. The reality is that with the overuse of mineral resources and increasing air pollution, atmospheric corrosion of materials is becoming more severe.

Atmospheric corrosion is not a specific form of corrosion but rather a general term for a category of corrosion. In most cases, atmospheric corrosion primarily involves uniform corrosion, but other forms such as pitting, crevice corrosion, galvanic corrosion, fretting corrosion, stress corrosion, and corrosion fatigue can also occur.

1.6.1.2 Classification of Atmospheric Corrosion

In the atmosphere, the corrosion rate, characteristics, and controlling factors of metallic materials change with atmospheric conditions. The main components that cause atmospheric corrosion are water and oxygen, with water – especially the water that moistens the metal surface – being the key factor determining the corrosion rate and progression. It shows the relationship between the atmospheric corrosion rate and the thickness of the water film on the metal surface [14]. Generally, atmospheric corrosion is classified into three types based on the moisture level of the metal surface and the presence of the electrolyte film:

1) Dry Atmospheric Corrosion: Corrosion that occurs when the metal surface does not have a liquid film layer due to very dry air conditions is called dry atmospheric corrosion. The characteristic is that the thickness of the adsorbed water film on the metal surface does not exceed 10 nm (100 Å), and no continuous electrolyte film is formed (zone I). The corrosion rate is very low, and chemical oxidation plays a larger role. For example, metals like Cu and Ag lose their luster in air polluted with sulfur compounds, forming a visible thin film.
2) Damp Atmospheric Corrosion: When the relative humidity of the atmosphere is high enough and a thin liquid film exists on the metal surface, invisible to the naked eye, the corrosion is called damp atmospheric corrosion. At this point, the water film thickness can range from tens to hundreds of molecular layers, around 10 nm to 1 μm, forming a continuous electrolyte film (zone II). Electrochemical corrosion begins, and the corrosion rate increases dramatically. For example, iron rusts when it is not exposed to rain or snow.
3) Wet Atmospheric Corrosion: Corrosion that occurs when the air humidity is close to 100% and water in the form of rain, snow, or mist directly contacts the metal surface is called wet atmospheric corrosion. The characteristic is that the water film is visible to the naked eye, with a thickness ranging from 1 μm to 1 mm. As the water film thickens, oxygen diffusion becomes more difficult, and the corrosion rate decreases (zone III). When the water film thickness exceeds 1 mm, it is essentially like the metal being completely immersed in an electrolyte solution, and the corrosion rate remains almost constant (zone IV).

It should be noted that in the actual atmospheric corrosion process, due to environmental changes (such as the transition from sunny to rainy or snowy conditions, or day to night), these three types of corrosion occur alternately.

1.6.1.3 Atmospheric Corrosion Mechanism

As mentioned above, atmospheric corrosion is the corrosion process that occurs when a metal is under a thin surface electrolyte film. Therefore, atmospheric corrosion is primarily an electrochemical corrosion process that follows the general principles of electrochemical corrosion. At the same time, because the electrolyte film is relatively thin and often undergoes cycles of wetting and drying, the electrode processes involved in atmospheric corrosion have their own distinctive characteristics [15].

Mechanism of Atmospheric Corrosion in the Initial Stage When a continuous electrolyte film forms on the metal surface, the electrochemical corrosion process begins.

Cathodic Process: Typically, this involves the depolarization reaction of oxygen, which is as follows: $O_2 + 2H_2O + 4e \rightarrow 4OH^-$.

Under the thin liquid film condition, oxygen diffusion is easier compared to the fully immersed state. Therefore, even metals with more negative potentials (such as magnesium and magnesium alloys), when transitioning from corrosion in a fully immersed state to atmospheric corrosion, shift from a cathodic process dominated by hydrogen depolarization to one dominated by oxygen depolarization.

Anodic Process: In the thin liquid film, the anodic process of atmospheric corrosion is significantly hindered. The main reasons for anodic polarization are the difficulties in anodic passivation and the hydration process of metal ions.

As a general rule, as the electrolyte film on the metal surface becomes thinner, the cathodic process of atmospheric corrosion becomes easier, while the anodic process becomes increasingly difficult. For damp atmospheric corrosion, the corrosion process is mainly controlled by the anodic process. For wet atmospheric corrosion, the corrosion process is controlled by the cathodic process, but it is much weaker compared to corrosion in a fully immersed electrolyte solution. It is clear that as the thickness of the water film changes, the characteristics of electrode process control change significantly. Understanding this is important for implementing appropriate corrosion control measures. For example, in anodically controlled corrosion processes with low humidity, alloying to improve anodic passivation is effective, while it has little effect on cathodically controlled processes. In such cases, measures to reduce humidity and decrease harmful components in the air should be taken to mitigate corrosion.

Mechanism of Corrosion after Rust Layer Formation For a long period, it was believed that the cathodic process of atmospheric corrosion of steel materials only involved the reduction of oxygen. However, subsequent research has shown that under certain conditions, the corrosion products that have already formed can influence the electrochemical processes of subsequent atmospheric corrosion. Evans proposed that under wet conditions, the rust layer can act as a strong oxidizing agent.

The anodic reaction occurs at the metal/Fe_3O_4 interface:

$$Fe \rightarrow Fe^{2+} + 2e$$

The cathodic reaction occurs at the Fe_3O_4/FeOOH interface:

$$8FeOOH + Fe^{2+} + 2e \rightarrow 3Fe_3O_4 + 4H_2O$$

That is, the reduction reaction occurs within the rust layer, where the rust layer participates in the cathodic reaction process.

When the rust layer dries, meaning when the external relative humidity decreases, the local battery between the rust layer and the underlying base metal becomes open circuited. Under the action of oxygen in the atmosphere, the Fe^{2+} within the rust layer is reoxidized to Fe^{3+}. This reaction is:

$$4Fe_3O_4 + O_2 + 6H_2O \rightarrow 12FeOOH$$

Therefore, under conditions of alternating wet and dry periods, the corrosion of steel with a rust layer is accelerated.

In general, the corrosion rate of steel exposed to the atmosphere for an extended period gradually slows down. There are two main reasons for this: first, the thickening of the rust layer increases the electrical resistance and makes the penetration of oxygen more difficult, which weakens the cathodic depolarization effect of the rust layer. Second, the inner layers of the rust layer, which have good adhesion, reduce the active anode area and increase the anode polarization.

The Structure and Protective Properties of Rust Layers Due to changes in atmospheric corrosion conditions and material composition, the composition and structure of the rust layer also change. Typically, the rust layer consists of two layers: the outer layer is loose and prone to peeling, while the inner layer has better adhesion, is denser in structure, and provides a certain level of protection. It shows a schematic of the cross section of the atmospheric corrosion rust layer on iron. In industrial atmospheres, steel rust layers often contain salt crystals, such as $FeSO_4 \cdot 7H_2O$, $FeSO_4 \cdot 4H_2O$, and $Fe_2(SO_4)_3$. The presence of these crystalline salts reduces the protective effect of the rust layer.

The rust layer on carbon steel primarily consists of α-FeOOH, β-FeOOH, and Fe_3O_4, with the composition varying depending on the environment. It is generally believed that α-FeOOH is initially formed on the steel surface, which then transforms into β-FeOOH and Fe_3O_4. This transformation is influenced by factors such as atmospheric humidity and pollution. Among the components of the rust layer, α-FeOOH plays an important role in corrosion resistance. Under typical atmospheric conditions, with prolonged exposure, the content of α-FeOOH increases. In industrial areas with SO_2 or coastal regions containing Cl^-, α-FeOOH is less prevalent, while β-FeOOH or Fe_3O_4 is more abundant. In areas with less pollution, such as forests, α-FeOOH is more common. Further research indicates that α-FeOOH is more likely to form at lower pH levels, while β-FeOOH and Fe_3O_4 are more likely to form at higher pH levels. The relationship between the composition of the rust layer and its corrosion resistance is still not fully understood.

Characteristics of the Rust Layer Structure of Weathering Steel Weathering steel, also known as atmospheric corrosion-resistant steel, is a low-alloy steel that contains certain alloying elements such as Cu, P, Cr, Ni, and Mo, which provide excellent resistance to atmospheric corrosion. The reason weathering steel has superior corrosion resistance is primarily due to the formation of a dense, continuous, and amorphous product layer containing elements like Cu, Cr, and P between the porous outer corrosion product layer and the steel substrate after exposure to the atmosphere for a period of time. This process is typically referred to as the stabilization of the rust layer. The dense, continuous amorphous inner oxidation layer and the α-FeOOH layer not only effectively isolate the corrosion medium from the steel substrate but also, due to their extremely high impedance, significantly slow down the electron migration between the corrosion anode and cathode, thereby reducing the rate of electrochemical reactions and leading to a significant decrease in the corrosion rate of weathering steel.

1.6.2 Soil Corrosion

1.6.2.1 Definition and Characteristics of Soil Erosion

The corrosion of metals and their components buried in soil is called soil corrosion, which is one of the most important corrosion issues in real-world production and daily life. With the development of modern industry, an increasing number of oil pipelines, water pipes, and gas pipelines have been laid underground, forming the "underground arteries." In addition, there are many cables, communication facilities, and various underground buildings. Their corrosion problems are significant, causing substantial losses and often leading to a series of issues.

1.6.2.2 Electrode Processes in Soil Corrosion

Characteristics of the Anodic Process The anodic process of iron in moist soil is similar to its corrosion in a solution, with no significant hindrance to the anodic process. In dry and well-aerated soil, the anodic process closely resembles the anodic behavior in atmospheric corrosion, meaning that the anodic process is greatly polarized due to difficulties in passivation and ion hydration. Generally, metals corrode much more severely in moist soil than in dry soil. During long-term corrosion, due to the shielding effect of insoluble corrosion products generated by secondary reactions, an increase in anodic polarization can be observed.

Based on the anodic polarization behavior of metals in moist, poorly permeable soils containing chloride ions, four categories can be identified:

1) Metals with no significant anodic polarization during anodic dissolution, such as Mg, Zn, Al, Mn, and Sn.
2) Metals with low anodic dissolution polarization, which is determined by the overpotential of the metal ionization reaction, such as Fe, carbon steel, Cu, and Pb.
3) Metals with high initial polarization due to anodic passivation, where anodic passivation is broken at higher anodic potentials due to the presence of Cl^- ions in the soil, such as Cr, Zr, and chromium or chromium-nickel stainless steels.
4) Metals that do not undergo anodic dissolution under soil conditions, such as Ti and Ta, which are fully passivated and stable.

Characteristics of the Cathodic Process The cathodic process of common metals like steel in soil corrosion mainly involves the depolarization of oxygen. In strongly acidic soils, the hydrogen depolarization process may also play a role. In some cases, microorganisms may participate in the cathodic reduction process.

The oxygen depolarization process in soil also consists of two basic steps: the transport of oxygen to the cathode and the cathodic reaction of oxygen ionization. The oxygen ionization reaction in soil is similar to that in ordinary electrolytes, but the transport process of oxygen is more complex than in electrolytic solutions. In the multiphase structure of soil, oxygen is transported through both the gas and liquid phases and is carried out in two ways:

1) Directional flow of the gas or liquid phase in the soil. The degree of directional flow depends on the periodic fluctuations in the soil surface temperature, atmospheric pressure, changes in soil moisture, rainfall, wind, and fluctuations in groundwater levels. These changes cause the intake and flow of air and saturated air moisture, making the oxygen transport rate much faster than the purely diffusion process. For loose, coarse-grained soils, oxygen is transported quickly via this method; in compact, moist soils, this method has little effect. This leads to differences in the rate of oxygen transport in different types of soil.
2) Diffusion in the gas and liquid phases of the soil. The diffusion of oxygen is the primary way oxygen is supplied in the soil. The diffusion rate of oxygen depends on the thickness, structure, and moisture content of the soil layer. Thick soil layers will hinder oxygen diffusion, and as the moisture content and clay component content increase, the oxygen diffusion rate can decrease by 3–4 orders of magnitude. During the diffusion of oxygen to the metal surface, the oxygen must ultimately pass through the thin electrolyte layer and corrosion product layer formed in the soil's capillary pores beneath the metal surface.

Control Characteristics of Soil Corrosion Based on the above analysis of the anode and cathode processes of soil corrosion, the control characteristics of the corrosion cell under different soil conditions can be predicted.

For most soils, when corrosion is determined by the corrosion microcell's action, the corrosion process is strongly controlled by the cathode process, similar to the situation where the metal is fully immersed in stagnant electrolyte. In loose and dry soils, the corrosion process shifts to be primarily controlled by the anode process, which is closer to the control characteristics of atmospheric corrosion. For soil corrosion influenced by long-distance macrocells, such as the oxygen concentration differential corrosion cells formed when underground pipelines pass through soils with different permeability, the soil's resistance becomes the main corrosion control factor. In this case, the control characteristics are cathode-resistance mixed control, or even resistance-controlled dominance.

1.6.2.3 Corrosion Batteries in the Soil

Soil corrosion, like electrochemical corrosion in other media, is primarily caused by the corrosion galvanic cell effect formed due to the electrochemical heterogeneity between the metal and the medium, which is the fundamental cause of corrosion.

Additionally, soil media have characteristics such as multiphase and inhomogeneity, so in soil corrosion, besides the potential formation of corrosion microcells related to the metal's microstructure, the corrosion macrocells caused by the macroscopic inhomogeneity of the soil medium often play a larger role [16].

The inhomogeneity of the soil medium is mainly caused by the different permeability of the soil. Under different permeability conditions, the rate of oxygen penetration varies greatly, which significantly affects the potential of different metal parts in contact with different regions of the soil, leading to the formation of oxygen concentration differential corrosion cells. Changes in soil properties such as pH and salt content also contribute to the formation of corrosion macrocells. Moreover, long-distance underground pipelines often have to pass through soils with various conditions, forming long-distance corrosion macrocells that are different from those in other media.

Types of corrosion macrocells that occur in soil include:

1) Long-Distance Corrosion Macrocells: Long-distance metal components buried underground can form long-distance macrocells as they pass through soils with different compositions and structures. A cell is formed where one soil (I) meets another (II): steel|soil (I)|soil (II)|steel. In one case, the difference in oxygen permeability between soils can cause an oxygen concentration differential cell. Steel buried in dense, moist soil (clay) acts as the anode and corrodes. Another case is when one of the soils contains sulfides, organic acids, or industrial wastewater, where the change in soil properties can also form a corrosion macrocell.

   Long-distance corrosion macrocells can generate considerable corrosion currents (also called long-line currents). Reports show that their current intensity can reach 5 A, and the flow range can exceed 1.5 km. The higher the conductivity of the soil, the larger the value of the long-line current.
2) Corrosion Macrocells Caused by Local Inhomogeneity in the Soil: In the soil, inclusions such as rocks have lower permeability than the soil itself, causing the metal in that area to become the anode of the corrosion macrocell, while the metal in contact with the soil body acts as the cathode. Therefore, when underground metal components are buried, the density of the backfill soil must be uniform, and it is important to avoid inclusions.
3) Corrosion Macrocells Caused by Different Burial Depths and Edge Effects: Even when metal components are buried in uniform soil, different burial depths can cause oxygen concentration differential corrosion cells. Therefore, deeper parts of underground metal components exhibit more severe local corrosion. Even on large-diameter horizontal pipelines, corrosion is often more severe on the lower part of the pipe than on the upper part.

   Similarly, due to the edge effect, where oxygen is more readily available at the edges of electrodes, the edges of metal components in the same horizontal plane become cathodes, leading to less corrosion compared to the central parts, which become anodes. This type of corrosion is often observed in large underground storage tanks.
4) Corrosion Macrocells Caused by Differences in the Metal's State: Corrosion macrocells can also form due to the contact between different metals,

temperature differences, stresses, and variations in the surface condition of metals in the soil. This leads to local corrosion. It shows an example where a new and old pipeline connected underground forms a corrosion cell.

1.6.3 Freshwater and Saltwater Corrosion

1.6.3.1 Freshwater Corrosion

Characteristics of Freshwater Corrosion Freshwater generally refers to natural waters with low salt content, such as river water, lake water, and groundwater. Table 1.4 shows the average values of dissolved substances in river water worldwide. The corrosivity of freshwater is weaker than that of seawater, but its corrosion principles, research methods, and protective measures share many similarities with those of seawater corrosion. Here, only the general principles of freshwater corrosion will be briefly introduced.

Freshwater Corrosion Mechanism The corrosion of metals in freshwater is primarily an electrochemical corrosion process controlled by oxygen depolarization, usually governed by the cathodic process. Taking iron as an example, the reaction process is as follows:

The anodic reaction: $Fe \rightarrow Fe^{2+} + 2e$

The cathodic reaction: $\frac{1}{2}O_2 + H_2O + 2e \rightarrow 2OH^-$(Oxygen absorption reaction)

In the solution: $Fe^{2+} + 2OH^- \rightarrow Fe(OH)_2$

Further oxidation: $4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3$

The iron hydroxide partially dehydrates to form rust:

$$2Fe(OH)_3 - 2H_2O \rightarrow Fe_2O_3 \cdot H_2O$$

or: $Fe(OH)_3 - H_2O \rightarrow FeOOH$

Factors Affecting Freshwater Corrosion The corrosion of metals in freshwater is greatly influenced by environmental factors.

1) pH Influence: The corrosion rate of steel is related to the pH of freshwater.
   Within the pH range of 4–9, the corrosion rate is independent of pH. This is because a hydroxide film forms on the surface of steel, and oxygen must pass through the film to perform depolarization. When pH is lower than 4, the film dissolves, and hydrogen evolution occurs, causing corrosion to intensify. However, when the water contains Cl^- and HCO_3^-, corrosion is very fast even at pH around 8. When the alkalinity is very high, the passive film is disrupted again, and iron forms soluble NaFeO, which increases the corrosion rate.

Table 1.4 Average dissolved solids in world rivers/%.

CO_3^{2-}	SO_4^{2-}	Cl^-	NO_3^-	Ca^{2+}	Mg^{2+}	Na^+	K^+	$(Fe, Al)_2O_3$	SiO_2	Total
35.15	12.14	5.68	0.90	20.39	3.14	5.76	2.12	2.75	11.57	100.00

2) Effect of Dissolved Oxygen: The corrosion of freshwater is controlled by the cathodic process. Therefore, except for water with strong acidity, the corrosion rate is proportional to the dissolved oxygen concentration and the consumption of oxygen. When the dissolved oxygen exceeds a certain level, the metal becomes passive, and the corrosion rate decreases sharply. In waters with high acidity or high salt content, metals are difficult to passivate.
3) Effect of Dissolved Components: As the salt content increases, the water's electrical conductivity rises, which in turn increases the local current. At the same time, corrosion products are more easily removed from the metal surface, leading to an increase in corrosion rate. However, when the salt content exceeds a certain concentration, the solubility of oxygen decreases, which reduces the corrosion rate.
   In freshwater, the general cations (such as K^+, Na^+, etc.) have little effect. However, if the water contains dissolved heavy metal ions with oxidizing properties, such as Cu^{2+}, Fe^{3+}, Cr^{3+}, and Hg^{2+}, they will promote the cathodic reaction. On the other hand, ions like Ca^{2+}, Zn^{2+}, and Fe^{2+} have some corrosion protection effects. Natural freshwater with a high content of Ca and Mg salts is classified as hard water, while water with low content of these salts is considered soft water. In general, soft water is more corrosive than hard water because the calcium carbonate ($CaCO_3$) in hard water forms a protective film on the steel surface, preventing the diffusion of dissolved oxygen.
   Anions are generally harmful. For example, halide ions like Cl^- are one of the causes of pitting and stress corrosion. SO_4^{2-} or NO_3^- have less impact than Cl^-. Other harmful anions include ClO^- and S^{2-}. On the other hand, anions like PO_4^{3-}, NO_2^-, and SiO_3^{2-} have corrosion-inhibiting effects, and the presence of HCO_3^- and Ca^{2+} together also helps to reduce corrosion.
4) Effect of Water Temperature: When corrosion speed is controlled by the diffusion of oxygen in the water, for every 10 °C increase in water temperature, the corrosion rate of steel increases by approximately 30%. In the pH range of 4–10, as temperature rises, the chemical reaction rate accelerates, while the dissolved oxygen in the solution decreases. It shows the effect of temperature on iron corrosion in 3% saltwater. As the temperature rises, the corrosion of iron increases, with the maximum corrosion occurring at 80 °C. Beyond this temperature, corrosion slows down due to the reduction in dissolved oxygen. In a closed system, as the temperature rises, the dissolved oxygen cannot escape, and the corrosion rate continues to increase.
5) Effect of Flow Rate: The influence of flow rate is complex and interrelated with other factors. It shows the relationship between metal corrosion rate and water flow rate. At low flow rates, the corrosion rate increases with flow rate due to the increased oxygen reaching the metal surface, enhancing the micro-cathodic reaction. When the flow rate reaches a certain level, the speed of oxygen reaching the surface creates strong oxidative conditions, causing the steel to enter a passivation state, and the corrosion rate sharply decreases. If the flow rate increases further, mechanical erosion can damage the protective layer on the metal surface, leading to an increase in corrosion rate again.

1.6.3.2 Sea Water Corrosion

Characteristics of Seawater Corrosion The ocean covers about seven-tenths of the Earth's surface. Seawater contains various salts and is the largest and most corrosive natural electrolyte in the environment. Most common metals and alloys suffer corrosion in seawater. For example, various types of ships, offshore oil platforms, mineral extraction and underwater transportation and storage equipment, coastal facilities, and equipment using seawater for cooling all experience severe corrosion from seawater. The ocean is not only the cradle of life but also rich in natural resources. Researching, understanding, and solving the problem of metal corrosion in seawater is of great significance for the development of marine transportation, marine exploration, and strengthening national defense.

Properties of Seawater The salts dissolved in seawater are primarily sodium chloride, and seawater is commonly approximated as a 3% or 3.5% NaCl solution. The salinity of seawater is typically expressed in terms of salinity or chloride concentration. Salinity refers to the total grams of dissolved solid salts in 1000 g of seawater, while chloride concentration indicates the grams of chloride ions in 1000 g of seawater. These are often expressed in percentage or per thousand units. Salinity is usually derived from chloride concentration (Cl‰) using the empirical formula: S‰ = 1.80655Cl‰. The salinity of normal seawater typically ranges from 32‰ to 37.5‰, with 35‰ (corresponding to a chloride concentration of 19‰) being the average for oceanic seawater. Table 1.5 lists the main salts in seawater. The total salinity of seawater varies by region; for example, near river mouths, seawater is diluted, and salinity is reduced. In semi-enclosed seas like the Mediterranean and the Red Sea, evaporation is rapid, and salinity can reach up to 40‰. The average salinity of coastal waters in China is approximately 32.1‰.

Seawater has a high electrical conductivity, with an average value of about 4×10^{-2} S/cm, much higher than that of river water (2×10^{-4} S/cm) or rainwater (1×10^{-5} S/cm).

The temperature of seawater varies from 0 to 35 °C depending on geographical location, ocean depth, time of day, and season.

Table 1.5 The content of major salts in seawater.

Ingredients	Salt content (g/100 g seawater)	Percentage of total salt content
NaCl	2.7123	77.8
$MgCl_2$	0.3807	10.9
$MgSO_4$	0.1658	4.7
$CaSO_4$	0.1260	3.6
K_2SO_4	0.0863	2.5
$CaCl_2$	0.0123	0.3
$MgBr_2$	0.0076	0.2

Dissolved oxygen is the primary factor affecting seawater corrosion. Under normal conditions, the surface layer of seawater is saturated with air, and oxygen concentration generally ranges from $(5\text{–}10) \times 10^{-6}$. Dissolved oxygen decreases slightly as temperature and salinity increase.

The pH of seawater typically ranges from 8.1 to 8.3, with variations depending on depth. If plant life is abundant, the reduction in CO_2 leads to an increase in dissolved oxygen concentration, and the pH can rise to around 9.7. In conditions where anaerobic bacteria proliferate at the seabed, oxygen levels are low, and the presence of hydrogen sulfide (H_2S) can cause the pH to drop below 7.

Electrochemical Process of Seawater Corrosion Seawater is a typical electrolyte, and the basic laws of electrochemical corrosion apply to seawater corrosion. However, seawater has its own unique characteristics, which result in specific electrochemical processes for corrosion.

1) Anodic Polarization in Seawater:
   For most metals (such as iron, steel, zinc, copper, etc.), anodic polarization in seawater is very limited. This is because halide ions, like chloride ions, in seawater can interfere with and disrupt the passivation of metals. The mechanisms of this destruction include:
   a) Oxide Film Destruction: Chloride ions penetrate the oxide film and degrade the gel-like protective film.
   b) Adsorption: Chloride ions adsorb more easily than some passivating agents.
   c) Electric Field Effect: Chloride ions form a strong electric field on the metal surface, which induces the release of metal ions.
   d) Complex Formation: Chloride ions can form complexes with metals, accelerating the anodic dissolution of metals. The hydrolysis of these chloride complexes further lowers the pH.
      These effects reduce anodic polarization resistance, making it difficult to prevent corrosion of iron-based alloys by increasing anodic resistance, which is different from atmospheric corrosion. However, recent studies of the rust layers on seawater-resistant steels have shown that adding certain elements to steel can form a dense, continuous, and adherent rust layer, improving the corrosion resistance of low-alloy steels in seawater.
      Since chloride ions destroy passivation, even stainless steel suffers from severe localized corrosion in seawater. Only a few metals, such as Ti, Zr, Nb, and Ta, can remain in a passive state in seawater, showing significant anodic resistance.
2) The cathodic process of seawater corrosion is primarily oxygen depolarization, which is the controlling step of the corrosion process. At the pH levels of seawater, the equilibrium potential for the hydrogen evolution reaction is approximately −0.48 V. Metals such as Pb, Zn, Cu, Ag, and Au do not undergo hydrogen evolution corrosion in seawater. Iron (Fe) at $pH = 8.8$ and chromium (Cr) at $pH = 10.9$ may undergo hydrogen evolution, but the rate is very slow.
   The oxygen depolarization reaction in seawater is as follows, with an equilibrium potential of +0.75 V: $O_2 + 2H_2O + 4e \rightarrow 4OH^-$. Oxygen reduction occurs more

easily on metals such as Cu, Ag, and Ni, followed by Fe and Cr. On metals like Sn, Al, and Zn, the overpotential is larger, making the reaction more difficult. Therefore, Cu, Ag, and Ni are more stable only in low dissolved oxygen conditions.

Additionally, in oxygen-depleted seawater with high concentrations of H_2S, the cathodic depolarization effect of H_2S may also occur. Cu and Ni are more susceptible to H_2S corrosion. High-valent metal ions such as Fe^{3+} and Cu^{2+} can also participate in the cathodic reaction. Copper (Cu) reduced from Cu^{2+} ions can form an effective cathode on the surface of metals such as Al. Therefore, if seawater contains Cu^{2+} ions at concentrations higher than 0.1 g/g, aluminum alloys should not be used.

3) The resistive hindrance effect of seawater corrosion is minimal, and contact between dissimilar metals can cause significant galvanic corrosion. The good conductivity of seawater makes the galvanic effect of dissimilar metal contacts more intense and widespread. For example, a bronze propeller on a seaworthy ship can cause corrosion on the steel hull of the ship, extending up to several tens of meters away.
4) In seawater, localized damage to the passive film makes pitting and crevice corrosion very likely. In high-velocity seawater, erosion corrosion and cavitation are also prone to occur.

Factors Affecting Seawater Corrosion Seawater is a complex solution in equilibrium with various salts. It also contains organisms, suspended sediments, dissolved gases, decaying organic matter, and pollutants. As a result, the corrosion behavior of metals in seawater is influenced by the combined effect of these factors. The potential factors affecting corrosion in seawater are listed in Table 1.6.

Taking iron as an example, the following tendencies are observed: (i) oxygen is the main factor accelerating corrosion; (ii) an increase in pH favors the formation of protective scale (silicate type); (iii) increasing flow rate promotes corrosion, especially when there are impurities present; (iv) temperature rise accelerates erosion;

Table 1.6 Factors affecting corrosion in seawater environments.

Chemical factors	Physical factors	Biological factors
(1) Dissolved gas O_2 CO_2 (2) Chemical equilibrium Salinity pH Solubility of carbonates	(3) Flow rate Air bubble Suspended sediment (4) Temperature (5) Stress	(6) Biological pollution Shellfish Non-shell type Swimming and semi-swimming classes (7) Plant life Production of oxygen Consumption of carbon dioxide (8) Animal Life Oxygen consumption The production of carbon dioxide

(v) pressure increase and pH decrease, as in deep-sea conditions, make it difficult for protective carbonate scale to form; (vi) biological fouling can reduce erosion or cause localized corrosion cells.

Classification of Marine Environments and Characteristics of Corrosion According to the contact between metals and seawater, the marine environment can be divided into five zones: the marine atmospheric zone, splash zone, tidal zone, fully submerged zone, and seabed zone. Based on the depth of seawater, the fully submerged zone can be further divided into shallow water, continental shelf, and deep-sea.

The marine atmospheric zone refers to the air zone above the marine splash zone and the coastal atmospheric zone. The corrosion rate of carbon steel and low-alloy steel in the marine atmospheric zone is approximately 0.05 mm/a, which is lower than in other zones.

The splash zone refers to the section above the average high tide line where seawater splashes and wets. In this area, seawater comes in full contact with the air, resulting in the highest oxygen content. Combined with the impact of sea waves, the splash zone becomes the most corrosive area. In the splash zone, the corrosion rate of carbon steel is approximately 0.5 mm/a, with a maximum of up to 1.2 mm/a.

The tidal zone refers to the area between the average high tide level and the average low tide level. Marine corrosion test results show that for isolated specimens, the corrosion rate is slightly higher than that in the fully submerged zone. However, for long steel strip samples, the corrosion rate in the tidal zone is actually lower than that in the fully submerged zone. This is because, for isolated specimens, corrosion mainly occurs due to microcell corrosion, with corrosion rates controlled by oxygen diffusion, and thus corrosion is faster in the tidal zone than in the fully submerged zone. For long specimens, in addition to microcell corrosion, oxygen concentration cells also affect the corrosion. In the tidal zone, parts of the sample that are sufficiently oxygenated act as cathodes, offering some protection, while parts close to the low tide line in the fully submerged zone, where oxygen supply is relatively insufficient, become anodes, accelerating corrosion.

The fully submerged zone refers to the area below the average low tide level, extending down to the seabed. In this zone, the corrosion rate of carbon steel is approximately 0.12 mm/a.

The marine mud zone refers to the part of the seabed below the fully submerged zone, mainly composed of seabed sediments. Unlike terrestrial soil, the marine mud zone has high salinity and low resistivity and is more corrosive. Compared to the fully submerged zone, the oxygen concentration in the marine mud zone is lower, and thus the corrosion rate of steel in the marine mud zone is usually lower than in the fully submerged zone.

1.7 Chapter Summary

Steel components are mostly in service in the natural and industrial environments, and the types of corrosion that occur are usually total corrosion, galvanic coupling corrosion, pitting, crevice corrosion, stress corrosion, and corrosion fatigue, as well as microbial corrosion and other types of corrosion. No matter which type of corrosion, the corrosion of steel components is in line with the characteristics of the electrode process and mechanism of electrochemical corrosion, generally this process is divided into three:

i) Initial Stage of Corrosion: when a thin layer of continuous electrolyte is formed on the metal surface, the electrochemical corrosion begins. The cathodic process mainly relies on the depolarizing effect of oxygen; even if the potential of the metal is extremely negative, the full immersion changes from electrolyte corrosion to atmospheric corrosion. The cathodic process mainly changes from hydrogen depolarization to oxygen depolarization. In the strong acidic solution, the full immersion mainly relies on hydrogen depolarization for corrosion. In the urban pollution of the atmosphere formed by the acidic water film, the corrosion of these metals mainly relies on the depolarizing effect of oxygen. This is because oxygen diffusion is easier in thin liquid film conditions than in full immersion. Under thin liquid film conditions, the anodic process is more hindered. Anodic passivation and difficulties in the hydration process of metal ions are the main causes of anodic polarization.

ii) In the second stage, the corrosion mechanism and process after the formation of the rust layer on the metal surface are as follows: when the air-corroded rust layer is under wet conditions, it can act as a strong oxidizer. Within the rust layer, an anodic reaction occurs at the metal–Fe_3O_4 interface: $Fe \rightarrow Fe^{2+} + 2e$; a cathodic reaction occurs at the Fe_3O_4–FeOOH interface: $6FeOOH + 2e \rightarrow 2Fe_3O_4 + 2H_2O + 2OH^-$, that is, $Fe^{3+} \rightarrow Fe^{2+}$ reduction reaction occurs within the rust layer, and it is visible that the rust layer is involved in the cathodic process. When the rust layer is dry, that is, when the relative humidity of the external gas decreases, the local battery of the rust layer and the base metal at the bottom opens, and the rust layer is reoxidized to form an oxide of Fe^{3+} under the action of atmospheric oxygen. It can be seen in the dry and wet conditions, when the rust layer of steel can accelerate the corrosion process. Generally, when the steel is exposed to the atmosphere for a long time, its corrosion rate gradually slows down. One of the reasons is that the thickening of the rust layer will lead to an increase in its resistance and difficulty in the penetration of oxygen, which weakens the cathodic depolarization of the rust layer; well-adhered inner rust layer can promote anodic polarization, so that the atmospheric corrosion rate is slowed down.

iii) In the third stage, a stable structure of the rust layer is formed. The main crystal structure of the rust layer changes with the environment. It is generally believed that the rust layer on the steel surface is first formed by γ-FeOOH and then transformed to α-FeOOH and Fe_3O_4. The degree of transformation is affected by the humidity of the surrounding atmosphere, pollution, and other factors. In industrial areas, as the atmosphere contains SO_2, the rust in the Fe_3O_4 content is very little. In coastal areas affected by Cl^-, there is less γ-FeOOH and more Fe_3O_4. In forested areas with little pollution, there is more α-FeOOH. The low pH of rust layer liquid film easily generates γ-FeOOH; the high pH easily generates α-FeOOH and Fe_3O_4.

Marble-resistant steel is more resistant to atmospheric corrosion than ordinary carbon steel, as the protection of its rust layer is better than that of ordinary carbon steel. Usually, after two to four years, a stable protective rust layer is formed, and the corrosion rate is reduced to a very low level; hence, it can also be used directly without painting.

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