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Introductory Chapter: Protection of Materials

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1. Introduction

The science and technology of materials have as objective provided access to specific knowledge in this field and besides generated matters of interest for the development of original researches leading to new materials and, as a consequence, to proper protection methods to achieve high economic impact.

Since iron and steels constitute a group of widely used materials in civil and industrial construction, this chapter describes firstly the fundamental concepts of metal corrosion and the most frequent failures originating on service. Besides, in this chapter, it was considered of interest to include aspects inherent to the physicochemistry of fire and its mechanism of spreading because of the significant human and material losses produced year after year by action of the fire.

It is appropriate to mention that the different chapters of this book describe innovative methods of surface treatment to control the kinetics of metallic corrosion and the action of fire on several materials.

2. Metallic corrosion and failures

Accidents arising from the *metallic corrosion* can produce injury or death of people by explosion, fire, and so on. The economic losses are classified into direct and indirect; the first includes the replacement of corroded materials, labor, periodic maintenance (coatings, cathodic protection, inhibitors in closed circuits, etc.) while the last involve aspects such as the discontinuity in the productive system, the loss and the contamination of raw materials and finished goods, and so on. The indirect losses are usually between 8 and 10 times the direct ones.

In industrialized countries, the total economic losses reach values between 3.5 and 4.5% of gross national product, despite applying all available technologies. It should also be mentioned

that the frequency of failure in metals by the various forms of corrosion reaches an average level of 60% (the remaining 40% is due to mechanical failures).

Metallic corrosion is usually defined as the destructive attack of a metal by chemical or electrochemical reaction with the environment [1]. Chemical corrosion involves the alteration of a metal in a non-ionic medium, such as gases or non-condensed vapors, high temperature, and so on. On the other hand, the electrochemical corrosion occurs with a simultaneous transport of electricity through the metal and the electrolyte (saline, atmosphere, seawater, etc.).

The most common metallic corrosion takes place electrochemically; it requires, as it is already put, electrical conductivity. Metals are electronic conductors of first specie while solutions and pure liquids are electrolytes of second specie.

Metallic or electronic conductors transport electricity through the electrons. The metals consist of a relatively rigid network of positive ions and of mobile electrons. When an electrical potential is applied, the electrons move in one direction while the positive ions remain static; the quoted electricity transport is produced without appreciable movement of matter. Since the electrons have a negative charge, the direction in which they move is the opposite at which is conventionally considered as positive current.

Meanwhile, the electrolytes carry the electric current through ions, that is, with a significant movement of matter. Ions are atoms or groups of atoms that have lost or gained electrons, reaching in this way positive charges (loss of electrons) or negative (gain of electrons), **Figure 1**. The positive ions (cations) move in the direction of current and the negative ions (anions) in the opposite one.

The determinant factors of metallic corrosion are the heterogeneity of metal (phases in alloy, remainder mechanical stresses, etc.) and/or of electrolyte (gradients of concentration, differential aeration, etc.). Meanwhile, the chemical nature of electrolyte (ion conductivity or equivalent) significantly influences the kinetics of the corrosive process and the geometry of the corrosion cell (higher conductivities usually favor the location of electrodes more distant from each other than solutions of high resistivity).

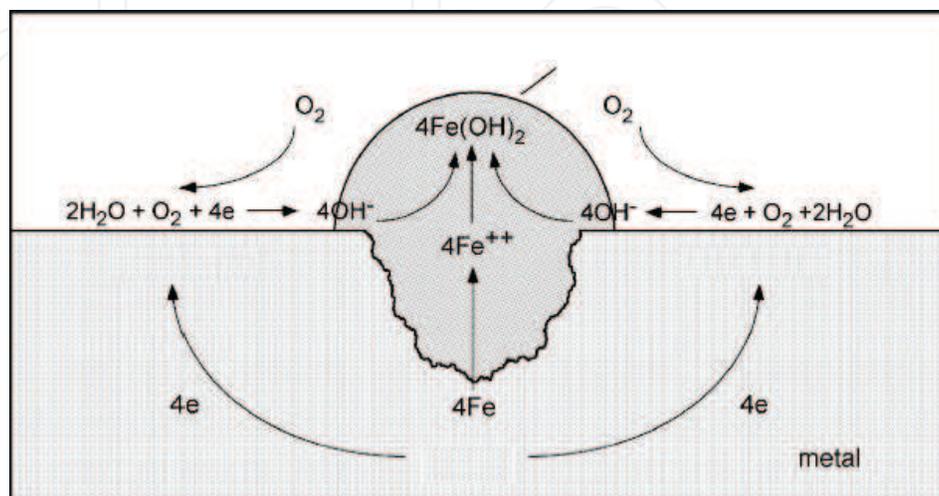


Figure 1. Corrosion mechanism.

A measure of the electrochemical kinetics (rate of reaction on electrode) is given by the equation $i = z F V$, where i is the current density (current per unit area of electrode), z the number of equivalents per mole, F the Faraday constant (96,500 Coulomb/equivalent), and V the rate of reaction in moles per unit area and time.

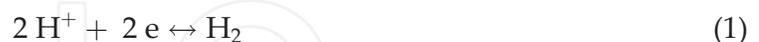
The abovementioned heterogeneity leads at the metal-solution interface to a gradient of electric potential between two adjacent areas. From a thermodynamic point of view, the quoted potential gradient is correlated with a difference of free energy ΔG . This is a thermodynamic function that is used as a criterion of spontaneity; it depends only on the initial and the final states, that is, that it is independent of the path: it decreases its value in a spontaneous transformation, either of physical or of chemical nature at constant temperature and pressure. Accordingly, it is possible to conclude that metal surfaces with high free energy are thermodynamically unstable and therefore tend to spontaneously evolve into a state of lower energy and greater stability.

The free energy is related to the electromotive force of a corrosion cell through the equation $\Delta G = -z F E$, where E is the reversible potential in volt, z the number of equivalent by mol, and F the Faraday constant.

Consequently, ΔG is the electrical work carried out by corrosion cell; it is observed that a reaction occurs spontaneously, at a constant temperature and pressure, when the value of E is positive.

Electrochemical corrosion is actually a network of shorted galvanic cells arranged on the metallic surface. Metal dissolves in the anode areas in equivalent relation to the reaction that takes place in the cathodic areas. In general, the anodic reaction is faster in almost all media, that is, that cathodic reaction is usually the decisive stage of the overall speed of corrosion process.

The *cathodic reaction*, in deaerated solutions, involves the reduction of protons (fast in acid and slow in neutral and alkaline media); instead, the quoted reaction, in aerated solutions, is accelerated by the reduction of dissolved oxygen:



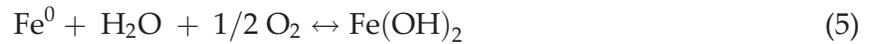
In both cases, there is an alkalization of the cathodic area, either by the decrease of the concentration of protons or directly by the generation of hydroxyl groups.

Meanwhile, the *anodic reaction* involves loss of electrons, from atoms of higher free energy, arranged on the metallic surface:



As a result of the ferrous and/or ferric ions reacting with ions hydroxyl of the medium for generating hydroxides, acidification of the anodic area occurs.

The sum of the anodic and cathodic hemi-reactions, in aerated media, is as follows:



The reaction in a corrosion cell involves the formation of hydrated ferrous oxide (ferrous hydroxide), which forms a first barrier for the diffusion of oxygen (polarization). This hydroxide is white in its pure state and has a pH of 9.5 in saturated solution. In a second sequential reaction, the hydrated ferrous-ferric oxide, which is the intermediate layer, is formed. This product, black in color, has magnetic properties. Subsequently, the reaction leads to the generation of hydrated ferric oxide, which makes up the third (external) layer of the oxidized system. This compound is orange/dark red in color and has a nearly neutral pH in saturated solution; exists as $\alpha\text{Fe}_2\text{O}_3$ (non-magnetic, with higher free negative energy of formation, i.e., more stable) and as $\gamma\text{Fe}_2\text{O}_3$ (magnetic).

On the other hand, the failures of metals take place by different causes due to the great amount of variables involved; as previously mentioned, the frequency of failure in the metals by corrosion reaches average levels of 60% in the different productive sectors. The types of corrosion failure and their frequency are given in **Table 1**.

Uniform corrosion. It is characterized in that the cathodic and anodic areas are modified alternately in space and time; as examples, it is possible to cite the case of a metal in direct contact with a solution of reduced electrical conductivity (the corrosion products, due to the reduced distance between the electrodes, are deposited simultaneously on the anodic and cathodic areas controlling the kinetics of process) and also the case in which the metal is exposed to

Type of failure	Failure frequency, %
Uniform corrosion	31.2
Corrosion-fatigue and corrosion under tension	23.4
Corrosion by pitting	15.7
Inter-granular corrosion	10.2
Corrosion-erosion, corrosion-wear and corrosion-cavitation	8.4
High-temperature corrosion	2.3
Corrosion by welding	2.1
Thermo-galvanic corrosion	2.0
Galvanic corrosion and corrosion in concentration cells	1.4
Corrosion by electrolysis	1.1
Corrosion by selective attack	1.0
Microbial corrosion	0.7
Corrosion by hydrogenation	0.5

Table 1. Types of failure and frequency.

high temperature in a relatively dry atmosphere. Preventive measures generally include selecting suitable materials for each aggressive medium, changing or inhibiting the electrolyte (closed systems), specifying resistant coatings, and designing anodic protection (passivation).

Corrosion fatigue. It is characterized by the action of alternating tensions in the presence of a corrosive medium. The causes are basically the same that can be attributed to static fatigue but adding cyclic loads. The deteriorating effect of combined fatigue and corrosion is much greater than the sum of individual damages. The most suitable measures to avoid this type of corrosion are to eliminate the cyclic tensions, increase the size or thickness in critical sections, reduce the concentration of stresses or redistribute them, provide sufficient flexibility to diminish over-fatigue by thermal expansion, control the vibration or shocks, eliminate the sudden changes in loads, temperature, or pressure, specify the right surface finishing, and select the appropriate protective system.

Corrosion under tension. It consists of premature breakage caused by the combined action of corrosive medium and residual or applied stress on the piece of metal, that is, that it takes place by combining high efforts and the presence of an electrolyte. Efforts by static charges in the metal surface and corrosive action that diminishes the section of the piece may exceed the elastic limit and even the breaking load. The forms of controlling this failure are to reduce mechanical tensions, ensure a sufficient flexibility, increase the size of the critical sections, select materials in the joints with a similar expansion coefficient, design adequate protection, and use a medium of suitable nature and composition.

Corrosion by pitting. It is a localized phenomenon that produces an appreciable penetration in the metal, generating either cavities or a discontinuity of the protective coating that lead to the formation of a concentration cell. To avoid this pathology, it is convenient to control the properties and the main characteristics of protective film (dry and wet adhesion, thickness, permeability, etc.), select a good geometry to prevent attacks, and specify properly the electrolytic medium.

Inter-granular corrosion. It is the preferred attack on grain boundaries of a metal or an alloy; it is characterized by a selective deterioration and an inter-crystalline cracking along inter-granular streaks (e.g., in stainless steels in chrome-deprived areas). Frequently, the specifications contemplate to select materials with a suitable thermal treatment for each particular case and realize weldings that do not generate temperatures superior to those used in the pretreatment of material.

Corrosion-erosion. The failure generated by the relative movement of the electrolytic medium (generally accelerated by abrasion due to the presence of solid particles in suspension) releases the corrosion products adhered to metal (depolarization) and also causes surface wear. For satisfactory corrosion-erosion control, it is appropriate to decrease the fluid velocity to achieve laminar movement, suppress the localized turbulence and the discontinuous flows, eliminate the abrupt changes in the direction of flow (aligning sections of ducts), avoid the obstructions, increase the material thickness in critical areas, design anodic parts so they can be changed quickly, specify the surface roughness, select the suitable coatings, and carry out cathodic protection.

Corrosion wear. It is defined as the deterioration located at the interface between two surfaces in contact, accelerated by a relative movement of sufficient amplitude to produce slippage. Generally, it occurs under heavy loads and instantaneous movements produced by high-frequency vibrations; the wear of surface-protective film (inorganic primers, organic coatings, etc.) can initiate a corrosion process. The main prevention methods to avoid corrosion wear are to eliminate the transmission of vibrations, introduce barriers between metals that slip, increase the load to slow the movement, provide protective layers to porous materials or use suitable lubricants, isolate those moving parts of the static ones, and finally increase the abrasion resistance.

Corrosion cavitation. It is associated with vapor bubbles arranged inside the liquid that collapse on the surface of the solid. Repeated collapses on a metal surface can deteriorate the protective film and severely deform the surface, fracturing it or generating fatigue. Low-pressure areas are created by divergent flows, vibrations, and so on. To control these damages, it is very important to select conditions that diminish absolute pressure, reduce hydrodynamic pressure differences, control the vibration, design the system to avoid formation or accumulation of bubbles, prevent the entry of dispersed air, select resistant materials or coatings, specify the finishing polishing, use cathodic protection, and so on.

Corrosion by high temperature. It is associated to the effect of atmospheric conditions and the presence of gases, metals, and/or molten salts at high temperature; the kinetics depends on the nature of the metals, the composition of the medium, and the time of exposure. The reduced dimensional stability of the corrosion products (hydration/dehydration by thermal changes) produces tangential cutting stress to the surface leading to the partial detachment of the different oxide layers, generating heterogeneities that favor corrosive processes. The most recommended therapies are to select materials stable to the thermal action, adjust the nature and/or composition of the medium, and regulate, if possible, the contact time.

Corrosion by welding. A weld can have low corrosion resistance due to the chemical nature of the electrode (e.g., it should be used with those having a low hydrogen content), to the residual stress and to the metallurgical structure of the weld zone. Corrosion in welding joints can be avoided by careful selection of materials, of the technique used, and of the type of finishing.

Thermo-galvanic corrosion. It is the result of the operation of a galvanic cell generated from a temperature gradient; the heating and the heat dissipation in heterogeneous form are the responsible factors for the formation of this cell. The most efficient actions are to avoid point heating and/or unequal cooling, use a continuous and adherent coating, and introduce thermostated components from the outside to the system.

Galvanic corrosion. It involves the corrosion associated with the current resulting from the contact of different electrodes (metals of dissimilar chemical nature) arranged in a conducting electrolyte that closes the circuit of the cell. The most important preventive measures are to eliminate interaction of diverse metals or to produce a complete dielectric insulation, avoid contact of a small anode and a large cathode, extend the distance between dissimilar metals in conductive media, design the anodic parts that can be easily replaced or apply thicker

protective films, use suitable protective systems and regulate the degree of aeration, temperature, composition, or movement of the medium that is suitable for the metal coupling.

Corrosion by concentration cells. It is made up of a galvanic cell in which the electromotive force is due to the concentration difference of one or more reagents. The main causes are given either by differential aeration (different partial pressure of oxygen) generated in cracks, adherent deposits, and deep depressions that influence the diffusional process of oxygen and the existence of gradients of concentrations in the electrolyte generated by different causes. The most effective measures are to reduce surface irregularities especially in areas of heat transfer or where chemical reagents or oxygen are introduced, design drainage and a uniform environment, select forms that allow easy cleaning and application of protective layers, remove solids in suspension by filtration, use continuous welds, suppress porosity and cracking, and eliminate fibrous and/or absorbent packings.

Corrosion by electrolysis. It is generated by a current flow, that is, electric currents generally of an alternating nature, which cannot be controlled; they are often originated by sources external to the structure (e.g., bad ground connections, etc.), which enter through a conducting medium. It is convenient to connect properly the equipment to ground, isolate the apparatus from structures, use non-conducting fluids, eliminate errant or vagabond current sources, and incorporate sacrificial (cathodic protection) plates in the anodic areas near insulation joints.

Corrosion by selective attack. It is based on a process of extracting a soluble component from an alloy; generally, the percolation of the alloy occurs by the action of a solvent on an element of the metal (e.g., zinc, aluminum, etc.), which separates and consequently generates a corrosive action. The most appropriate measures involve selecting materials suitable for performing efficiently in the electrolytic medium in which the part or structure is inserted, reducing the aggressiveness of the medium if feasible (e.g., in closed systems), and using suitable protection methods.

Microbial corrosion. Bacteria and fungi, individually or together, and the subproducts of the biological activity attack the metal and/or the coating. The mentioned products (e.g., organic and inorganic acids and alkalis) display a significant aggressiveness to materials. Consequently, considering the causes described, it is convenient to avoid contamination, use specific biocides, control chemically the environment, select properly the protective coatings, and clean the surfaces as often as necessary.

Corrosion by hydrogenation. It is manifested by the reduction of the mechanical resistance produced by the inclusion of hydrogen gas in the crystal structure of the metal. The most common causes are linked to an inadequate de-oxidation and, fundamentally, to an oversizing of the cathodic protection. The most suitable therapies are to perform a suitable surface preparation, select properly coating systems, induce compressive stresses, heat the metallic substrate to 90–150°C, and systematically control the electrical potential of the metal substrate modified by the cathodic protection.

It is worth mentioning that coating systems are the most convenient methods for controlling the kinetics of metallic corrosion from a technical-economical viewpoint [2–6].

3. Fire action on materials

Fire is an energetic manifestation that constantly accompanies human activity; therefore, the emerging risk must be assumed.

Fire develops strongly exothermic chemical reactions, starting when oxidizer and combustible are in a sufficient energetic state (activation energy). The combustible includes substances that are not in their maximum oxidation state; in general, any material containing carbon and/or hydrogen can be oxidized and therefore be combustible. The most important oxidizer is air, which is composed in its fifth part by oxygen; during combustion, the other components remain unchanged (except at very high temperatures) and accompany the products of combustion in the fumes. Part of the energy released in the reaction is dissipated, generating an increase in the temperature of the medium and the remainder is transferred to the reaction products providing the activation energy for the process to continue; if this is not enough, the combustion stops.

The knowledge of the physicochemical theory of combustion has allowed the development of products and systems of defense against fires. Nevertheless, the losses occasioned continue to be one of the greatest tragedies of modern civilization. Taking into account the current technology of fire-retardant treatments (impregnation, coatings, etc.), it is important to mention the generic concept of "passive protection against fire," in which the efficiency is independent of human activity.

The research and development studies are thus significant to reduce the combustibility of materials and the speed of propagation of the flame front as well as to keep during the conflagration the mechanical properties of structures based on either combustible and non-combustible materials. The design of the constructions also plays a very important role.

The true magnitude of the fire problem is remarkable when considering the human and material losses occurring year after year. Thus, for example, 25% of the deaths caused by fire are due to people remain trapped inside buildings; the majority of victims are younger than 10 or older than 70 years. Considering accident deaths, those caused by the fire action are only surpassed by the car crashes.

With regard to economic losses, they reach in many countries a value nearly to 0.25% gross national product. Fire generates significant problems in civil constructions, ships, offshore structures and industrial plants; in many cases, the use of both untreated materials and conventional coatings contribute to the fire spreading.

Often, there are also significant indirect losses of difficult evaluation such as the decrease of income by the total or partial interruption of the activity of a company, the decrease in customers, the increase of replacement costs of installations and equipment, and so on. It is estimated that out of every five companies that have had a major fire, four of them disappear within three years of the incident.

In relation to cultural heritage and historical buildings, material losses are remarkable. For example, the Argentinian Theater of La Plata (Buenos Aires, Argentina) was completely

destroyed by a fire and the Theater della Scala (Venice, Italy) was seriously affected by another conflagration, in the decades of the 70 and 90 of the previous century, respectively.

As a consequence of the spectacular fires in historic and massive concurrence buildings, many countries adopted regulations for the control of materials flammability. The latter led to developments of intrinsically fire-resistant materials, retardant treatments, and a large number of test methods to evaluate the reaction to fire of the materials. It is also important to mention that for many years now, insurance companies have found that the way to deal with fire is through the prevention and the use of fire-proofing materials.

Stability of construction materials. The fire action on construction materials is significant; thus, for example, calcareous collapses rapidly by dilation and by contraction during drying.

Concerning the concrete, it exhibits satisfactory response to high temperatures if perfectly anchored. For its part, reinforced concrete presents adequate behavior up to 300–330°C if its aggregates are small in size; the iron framework begins to lose resistance when reaching a critical temperature of 500–550°C.

As regards gypsum, it is gradually dehydrated above 120°C and up to 180°C, losing cohesion at 700–800°C.

The load-bearing iron and steel structures (made by forging or rolling) are plastically deformed by the action of heat, essentially when the pressure leads to lose their static equilibrium; at approximately 500°C, these materials halve their structural strength.

Wood and wood products were widely used in the construction of historic buildings; in spite of behaving like combustible materials and to be vulnerable in cases of fire, in general they display a considerable fire resistance (small decrease of area attributable to the low thermal conductivity of the superficially formed carbonaceous layer). Untreated wood begins to burn at 300°C but that treated with suitable fire retardants does not release so much smoke (the gases are non-toxic and non-combustible). The losses in cases of conflagration are always lower than in the constructions with iron and other metals and, once the origin of the fire has been eliminated, the wood is characterized by exhibiting a behavior corresponding to a self-extinguishing material.

All the abovementioned values have a singular meaning, since the average temperature of the fire ranges usually between 700 and 800°C.

Fire spreading. The speed of propagation of the flames plays a preponderant role in the advance of the fire front; as mentioned, the toxicity of gases and fumes is a significant variable. The room propagation involves the three forms of heat transfer (convection, radiation, and conduction): in the interior of a building, by conduction through the walls when the thermal insulation is reduced or by convection when there are open stairs while between adjacent buildings by radiation through the openings, doors, and windows.

It is worth mentioning that in the buildings under construction, expansion, or demolition, the probability of fire is particularly high during (i) the heating, welding, and cutting processes; (ii) the transport of flammable liquids and materials; and (iii) the use of electrical equipment with precarious installations.

Total thermal load and fire load. It is significant to determine the degree of risk and adequate security measures, particularly for civil buildings designed to permanently or transiently accommodate a large number of people (schools, libraries, hospitals, hotels, restaurants, auditoriums, theaters, cinemas, shops, etc.) and industrial units built to store and/or manufacture products, equipment, and appliances (petrochemicals, automotive terminals, medical laboratories, sawmills, etc.).

The total combustion risk of a building is calculated by considering the caloric content of the building (fire load including the building itself) and the enthalpy level of the content (fire load involving human lives and properties). The Pourt method was developed from the value of fire load and is widely used to determine the total risk of buildings; the fire charge density, calculated by dividing the fire load by the building surface, is also a widely considered variable.

Performance of coatings in fire. Coatings in particular and coating systems in general play well-defined actions against fire action [7–19]; they may

- Promote the spreading. Generally, conventional coatings have a low ignition point, so by thermal action they release combustible gases, which ignite and release caloric energy; the last one in turn becomes the energy of activation that promotes the spreading of conflagration front.
- Display inertia. Some commercial products of reduced efficiency do not alter the fire performance of the bare substrate or only achieve a limited retarding action.
- Delay evolution or extinguish fire. The retarding effect interrupts, in one or more stages, the combustion; the process ends in an acceptable lapse, often before the ignition takes place, **Figure 2**.

Testing methods. The analysis of the current regulations in the world indicates the existence of a great number of tests of different characteristics to determine the reaction, the resistance, and the stability against fire of the constructive elements. The results depend on the type and shape of the specimen, the intensity and time of action of the external energy source, and so on.



Figure 2. Left, panel without treatment and right, film of intumescent coating, both after the fire action.

The main variables considered include the size and position of specimen, the type and magnitude of energy source, the way and rate of heating, the duration of test, and valued indices; the fire performance varies according to the method applied.

In many occasions, the abovementioned is a technological barrier for the export/import of either fire retardants or treated materials. A political decision must be taken to impose common test methods at least at the regional or continental level, resulting in adequate reproducibility, that is, that in the case of operators working in different laboratories or in the same laboratory at different times, achieve comparable individual results (low dispersion of the mean value) by using the same method on an identical material.

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