

1.05 Basic Concepts of Corrosion

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1.05.1 Introduction

Modern technology has at its disposal a wide range of constructional materials – metals and alloys, plastics, rubber, ceramics, composites, wood, etc., and the selection of an appropriate material for a given application is the important responsibility of the design engineer. No general rule governs the choice of a particular material for a specific purpose, and a logical decision involves a consideration of the relevant properties, ease of fabrication, availability, relative costs, etc. of a variety of materials; often, the ultimate decision is determined by economics rather than by properties, and ideally, the material selected should be the cheapest possible that has adequate properties to fulfill the specific function.

Where metals are involved, mechanical, physical, and *chemical* properties must be considered, and in this connection, it should be observed that while mechanical and physical properties can be expressed in terms of constants, the chemical properties of a given metal are dependent entirely on the precise environmental conditions prevailing during service. The relative importance of mechanical, physical, and chemical properties depends, in any given case, on the application of the metal. For example, for railway lines, elasticity, tensile

strength, hardness, and abrasion resistance are of major importance, whereas electrical conductivity is of primary significance in electrical transmission. In the case of heat-exchanger tubes, good thermal conductivity is necessary, but this may be outweighed in certain environments by chemical properties in relation to the aggressiveness of the two fluids involved – thus, although the thermal conductivity of copper is superior to that of aluminum brass or the cupronickels, the alloys are preferred when high-velocity seawater is used as the coolant, as copper has very poor chemical properties under these conditions.

While a metal or alloy may be selected largely on the basis of its mechanical or physical properties, the fact remains that there are very few applications where the effect of the interaction of a metal with its environment can be completely ignored, although the importance of this interaction is of varying significance according to circumstances; for example, the slow uniform wastage of a steel structure of massive cross-section (such as railway lines or sleepers) is of far less importance than the rapid perforation of a buried steel pipe or the sudden failure of a vital stressed steel component in sodium hydroxide solution.

The effect of the metal–environment interaction on the environment itself is often more important than the actual deterioration of the metal. For instance, lead pipes cannot be used for conveying plumbo-solvent

[†]Deceased.

waters, since a lead level of >0.1 ppm is toxic; similarly, galvanized steel may not be used for certain foodstuffs owing to the toxicity of zinc salts. In many chemical processes, the selection of a particular metal may be determined by the need to avoid the contamination of the environment with traces of metallic impurities that would affect the color or taste of products or catalyze undesirable reactions; therefore, copper and copper alloys cannot be used in soap manufacture, since traces of copper ions result in the coloration and rancidification of the soap. In these circumstances, it is essential to use unreactive and relatively expensive metals, even though the environment would not result in the rapid deterioration of cheaper metals such as mild steel. A further possibility is that the contamination of the environment by metal ions due to the corrosion of one metal can result in an enhanced corrosion of another when the two are in contact with the same environment. Thus, the slow uniform corrosion of copper by a cuprosolvent domestic water may not be particularly deleterious to copper plumbing, but it can result in the rapid pitting and consequent perforation of galvanized steel and aluminum that subsequently comes into contact with the copper-containing water.

Finally, it is necessary to point out that for a number of applications, metals are selected in preference to other materials because of their visual appearance, and for this reason, it is essential that brightness and reflectivity are retained during exposure to the atmosphere; stainless steel is now widely used for architectural purposes, and for outdoor exposure, the surface must remain bright and rust-free without periodic cleaning. On the other hand, the slow-weathering steels, which react with the constituents of the atmosphere to form an adherent uniform coating of rust, are now being used for cladding buildings, in spite of the fact that a rusty surface is usually regarded as aesthetically unpleasant.

The interaction of a metal or alloy (or a nonmetallic material) with its environment is clearly of vital importance in the performance of materials of construction, and the fact that the present work is largely confined to a detailed consideration of such interactions could create the impression that this was the sole factor of importance in material selection. This, of course, is not the case, although it is probably true that this factor is most neglected by the design engineer.

1.05.2 Definitions of Corrosion

In the case of nonmetallic materials, the term *corrosion* invariably refers to their deterioration from chemical causes, but a similar concept is not necessarily

applicable to metals. Many authorities¹ consider that the term *metallic corrosion* embraces all interactions of a metal or alloy (solid or liquid) with its environment irrespective of whether this is deliberate and beneficial or adventitious and deleterious. Thus, this definition of corrosion, which, for convenience, is referred to as the *transformation* definition, includes, for example, the deliberate anodic dissolution of zinc in cathodic protection and electroplating as well as the spontaneous gradual wastage of zinc roofing sheet, resulting from atmospheric exposure.

On the other hand, *corrosion* has been defined² as 'the undesirable deterioration' of a metal or alloy, that is, an interaction of the metal with its environment that adversely affects those properties of the metal that are to be preserved. This definition – which is referred to as the *deterioration* definition – is also applicable to nonmetallic materials such as glass, concrete, etc. and embodies the concept that corrosion is always deleterious. However, the restriction of the definition to undesirable chemical reactions of a metal results in anomalies that become apparent from a consideration of the following examples.

Steel, when exposed to an industrial atmosphere, reacts to form the reaction product rust of approximate composition $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$, which, being loosely adherent, does not form a protective barrier that isolates the metal from the environment; the reaction thus proceeds at an approximately linear rate until the metal is completely consumed. Copper, on the other hand, forms an adherent green patina corresponding approximately to bronchantite, $\text{CuSO}_4 \cdot 3\text{Cu}(\text{OH})_2$, which is protective and isolates the metal from the atmosphere. Copper roofs installed 200 years ago are still performing satisfactorily, and it is apparent that the formation of bronchantite is not deleterious to the function of copper as a roofing material – indeed, in this particular application, it is considered to enhance the appearance of the roof, although a similar patina formed on copper water pipes would be aesthetically objectionable.

The rapid dissolution of a vessel constructed of titanium in hot 40% H_2SO_4 , with the formation of Ti^{4+} aquo cations, conforms to both definitions of corrosion, but if the potential of the metal is raised (anodic protection), a thin adherent protective film of anatase, TiO_2 , is formed, which isolates the metal from the acid so that the rate of corrosion is enormously decreased. The formation of this very thin oxide film on titanium, like that of the relatively thick bronchantite film on copper, clearly conforms to the *transformation* definition of corrosion, but not with the *deterioration* definition, since in these examples, the rate and extent of the reaction are not significantly

detrimental to the metal concerned. Again, magnesium, zinc, or aluminum is deliberately sacrificed when these metals are used for the cathodic protection of steel structures, but as these metals are clearly not required to be maintained as such, their consumption in this particular application cannot, according to the *deterioration*, be regarded as corrosion. Furthermore, corrosion reactions are used to advantage in technological processes such as pickling, etching, chemical, and electrochemical polishing and machining, etc.

The examples already discussed lead to the conclusion that any reaction of a metal with its environment must be regarded as a corrosion process irrespective of the extent of the reaction or of the rates of the initial and subsequent stages of the reaction. It is not illogical, therefore, to regard *passivity*, in which the reaction product forms a very thin protective film that controls rate of the reaction at an acceptable level, as a limiting case of a corrosion reaction. Thus, both the rapid dissolution of *active* titanium in 40% H₂SO₄ and the slow dissolution of *passive* titanium in that acid must be regarded as corrosion processes, even though the latter is not detrimental to the metal during the anticipated life of the vessel.

It follows that in deciding whether the corrosion reaction is detrimental to a metal in a given application, the precise form of attack on the metal (general, intergranular, etc.), the nature of the reaction products (protective or nonprotective), the velocity and extent of the reaction, and the location of the corrosion reaction must all be taken into account. In addition, due consideration must be given to the effect of the corrosion reaction on the environment itself. Thus, corrosion reactions are not always detrimental, and our ability to use highly reactive metals such as aluminum, titanium, etc. in aggressive environments is due to a limited initial corrosion reaction, which results in the formation of a rate-controlling corrosion product. Expressions such as 'preventing corrosion,' 'combating corrosion,' or even 'fighting corrosion' are misleading; with the majority of metals, corrosion cannot be avoided and 'corrosion control' rather than 'prevention' is the desired goal. The implication of 'control' in this context is that (1) neither the form nor the extent, nor the rate of the corrosion reaction must be detrimental to the metal used as a constructional material for a specific purpose and (2) for certain applications, the corrosion reaction must not result in the contamination of the environment. Corrosion control must involve a consideration of materials, availability, fabrication, protective methods, and economics in relation to the specific function of the metal and its anticipated life. At one extreme, corrosion control in certain environments may be effected by the use of thick sections of mild steel without any protective

system, at the other, the environmental conditions prevailing may necessitate the use of platinum.

The scope of the term 'corrosion' is continually being extended, and Fontana and Staehle have stated³ that '*corrosion*' includes the reaction of metals, glasses, ionic solids, polymeric solids, and composites with environments that embrace liquid metals, gases, non-aqueous electrolytes, and other nonaqueous solutions.

Vermilyea, who has defined corrosion as a process in which atoms or molecules are removed one at a time, considers that the evaporation of a metal into vacuum should come within the scope of the term, since atomically it is similar to other corrosion processes.⁴

Evans⁵ considers that corrosion may be regarded as a branch of chemical thermodynamics or kinetics, as the outcome of electron affinities of metals and non-metals, as short-circuited electrochemical cells, or as the demolition of the crystal structure of a metal.

These considerations lead to the conclusion that there is probably a need for two definitions of corrosion that depend upon the approach adopted:

1. Definition of corrosion in the context of Corrosion Science: the reaction of a solid with its environment.
2. Definition of corrosion in the context of Corrosion Engineering: the reaction of an engineering constructional metal (material) with its environment with a consequent deterioration in properties of the metal (material).

1.05.3 Methods of Approach to Corrosion Phenomena

The effective use of metals as materials of construction must be based on an understanding of their physical, mechanical, and chemical properties. The last, as pointed out earlier, cannot be divorced from the environmental conditions prevailing. Any fundamental approach to the phenomena of corrosion must therefore involve a consideration of the structural features of the metal, the nature of the environment, and the reactions that occur at the metal–environment interface. The more important factors involved may be summarized as follows:

1. *Metal* – composition, detailed atomic structure, microscopic and macroscopic heterogeneities, stress (tensile, compressive, cyclic), etc.
2. *Environment* – chemical nature, concentrations of reactive species and deleterious impurities, pressure, temperature, velocity, impingement, etc.
3. *Metal–environment interface* – kinetics of metal oxidation and dissolution, kinetics of the reduction

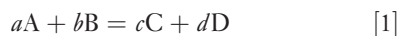
of species in solution, nature and location of corrosion products, film growth and film dissolution, etc.

From these considerations, it is evident that the detailed mechanism of metallic corrosion is highly complex and that an understanding of the various phenomena involves many branches of the pure and applied sciences, for example, metal physics, physical metallurgy, the various branches of chemistry, bacteriology, etc., although the emphasis may vary with the particular system under consideration. Thus, in stress-corrosion cracking, emphasis may be placed on the detailed metallurgical structure in relation to crack propagation resulting from the conjoint action of corrosion at localized areas and mechanical tearing, while in underground corrosion, the emphasis may be on the mechanism of bacterial action in relation to the kinetics of the overall corrosion reaction.

Although the mechanism of corrosion is highly complex, the actual control of the majority of corrosion reactions can be effected by the application of relatively simple concepts. Indeed, the Committee on Corrosion and Protection⁶ concluded that 'better dissemination of existing knowledge' was the most important single factor that would be instrumental in decreasing the enormous cost of corrosion in the United Kingdom.

1.05.3.1 Corrosion as a Chemical Reaction at a Metal-Environment Interface

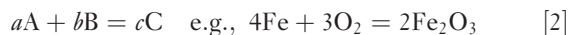
As the first approach to the principles which govern the behavior of metals in specific environments, it is preferable, for simplicity, to disregard the detailed structure of the metal and to consider corrosion as a heterogeneous chemical reaction that occurs at a metal-nonmetal interface and that involves the metal itself as one of the reactants (cf. catalysis). Corrosion can be expressed, therefore, by the simple chemical reaction:



where A is the metal and B the nonmetal reactant (or reactants), and C and D, the products of the reaction. The nonmetallic reactants are often referred to as *the environment*, although it should be observed that in a complex environment, the major constituents may play a very subsidiary role in the reaction. Hence, in the 'atmospheric' corrosion of steel, although nitrogen constitutes ~75% of the atmosphere, its effect, compared with that of moisture, oxygen, sulfur dioxide, solid particles, etc., can be disregarded (in the high temperature reaction of titanium with the atmosphere, on the other hand, nitrogen is a significant factor).

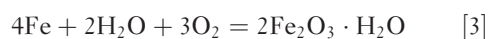
One of the reaction products (say, C) will be an oxidized form of the metal, and D will be a reduced

form of the nonmetal – C is usually referred to as the *corrosion product*, although the term could apply equally to D. In its simplest form, reaction [1] becomes



where the reaction product can be regarded either as an oxidized form of the metal or as the reduced form of the nonmetal. Reactions of this type, which do not involve water or aqueous solutions, are referred to as 'dry' corrosion reactions.

The corresponding reaction in aqueous solution is referred to as a 'wet' corrosion reaction, and the overall reaction (which actually occurs by a series of intermediate steps) can be expressed as



Thus, in all corrosion reactions, one (or more) of the reaction products will be an oxidized form of the metal, aquo cations (e.g., Fe^{2+} (aq.), Fe^{3+} (aq.)), aquo anions (e.g., HFeO_2^- (aq.), FeO_4^{2-} (aq.)), or solid compounds (e.g., $\text{Fe}(\text{OH})_2$, Fe_3O_4 , $\text{Fe}_3\text{O}_4 \cdot \text{H}_2\text{O}$, $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$), while the other reaction product (or products) will be the reduced form of the nonmetal. Corrosion may be regarded, therefore, as a *heterogeneous redox reaction at a metal-nonmetal interface in which the metal is oxidized and the nonmetal is reduced*. In the interaction of a metal with a specific nonmetal (or nonmetals) under specific environmental conditions, the chemical nature of the nonmetal, the chemical and physical properties of the reaction products, and the environmental conditions (temperature, pressure, velocity, viscosity, etc.) are clearly important in determining the form, extent, and rate of the reaction.

1.05.3.2 Environment

Some examples of the behavior of normally reactive and nonreactive metals in simple chemical solutions are considered here to illustrate the fact that corrosion is dependent on the nature of the environment; the thermodynamics of the systems and the kinetic factors involved are considered in subsequent chapters.

Gold is stable in most strong reducing acids, whereas iron corrodes rapidly, yet finely divided gold can be quickly dissolved in oxygenated cyanide solutions that may be contained in steel tanks. A mixture of caustic soda and sodium nitrate can be fused in an iron or nickel crucible, whereas this melt would have a disastrous effect on a platinum crucible.

Copper is relatively resistant to dilute sulfuric acid, but corrodes if oxygen or oxidizing agents are present in the acid, whereas austenitic stainless steels are stable in this acid only if oxygen or other

oxidizing agents are present. Iron corrodes rapidly in oxygenated water, but extremely slowly if all oxygen is removed; if, however, oxygen is brought rapidly and simultaneously to all parts of the metal surface, the rate will become very low, owing to the formation of a protective oxide film. Lead dissolves rapidly in nitric acid, more slowly in hydrochloric acid, and very slowly in sulfuric acid. These examples show that the corrosion behavior of a metal cannot be divorced from the specific environmental conditions prevailing, which determine the rate, extent (after a given period of time), and form of the corrosion process.

1.05.3.3 Metal

Heterogeneities associated with a metal have been classified in **Table 1** as atomic (see **Figure 1**), microscopic (visible under an optical microscope), and macroscopic, and their effects are considered in various sections of the present work. It is relevant to observe, however, that the detailed mechanism of all aspects of corrosion, for example, the passage of a metallic cation from the lattice to the solution, specific effects of ions and species in solution in accelerating or inhibiting corrosion or causing stress-corrosion cracking, etc. must involve a consideration of the detailed atomic structure of the metal or alloy.

The corrosion behavior of different constituents of an alloy is well known, since the etching techniques used in metallography are essentially corrosion processes that take advantage of the different corrosion rates of phases as a means of identification, for example, the grain boundaries are usually etched more rapidly than the rest of the grain owing to the greater reactivity of the disarrayed metal.

Macroscopic heterogeneities, for example, crevices, discontinuities in surface films, bimetallic contacts, etc.

have a pronounced effect on the location and the kinetics of the corrosion reaction and are considered in various sections throughout this work. Practical environments are shown schematically in **Figure 2**, which also serves to emphasize the relationship between the detailed structure of the metal, the environment, and external factors such as stress, fatigue, velocity, impingement, etc.

1.05.4 Types of Corrosion

Corrosion can affect the metal in a variety of ways, which depend on its nature and the precise environmental conditions prevailing, and a broad classification of the various forms of corrosion, in which five major types have been identified, is presented in **Table 2**. Thus, an 18Cr–8Ni stainless steel corrodes uniformly during polishing, active dissolution, or passivation, but locally during intergranular attack, crevice corrosion, or pitting; in certain circumstances, selective attack along an ‘active path’ in conjunction with a tensile stress may lead to a transgranular fracture. Types of corrosion are dealt with in more detail in Appendix A.

Ideally, the metal selected, or the protective system applied to the metal, should be such that no corrosion occurs at all, but this is seldom technologically or economically feasible. It is necessary, therefore, to tolerate a rate and a form of corrosion that will not be significantly detrimental to the properties of the metal during its anticipated life. Thus, provided the corrosion rate is known, the slow uniform corrosion of a metal can often be allowed for in the design of the structure; for example, in the case of a metal that shows an active–passive transition, the rate of corrosion in the passive region is usually acceptable, whereas the rate in the active region is not. It follows that certain forms of

Table 1 Heterogeneities in metal

1. <i>Atomic</i> (as classified by Ehrlich and Turnbull, ⁷ see Figure 1). <ol style="list-style-type: none"> a. Sites within a given surface layer (‘normal’ sites); these vary according to the particular crystal plane (Figure 3). b. Sites at edges of partially complete layers. c. Point defects in the surface layer: vacancies (molecules missing in surface layer), kink sites (molecules missing at edge of layer), molecules adsorbed on top of complete layer. d. Disordered molecules at point of emergence of dislocations (screw or edge) in metal surface.
2. <i>Microscopic</i> <ol style="list-style-type: none"> a. Grain boundaries – usually, but not invariably, more reactive than grain interior. b. Phases – metallic (single metals, solid solutions, intermetallic compounds), nonmetallic, metal compounds, impurities, etc. – heterogeneities due to thermal or mechanical causes.
3. <i>Macroscopic</i> <ol style="list-style-type: none"> a. Grain boundaries. b. Discontinuities on metal surface – cut edges, scratches, discontinuities in oxide films (or other chemical films) or in applied metallic or nonmetallic coatings. c. Bimetallic couples of dissimilar metals. d. Geometrical factors – general design, crevices, contact with nonmetallic materials, etc.

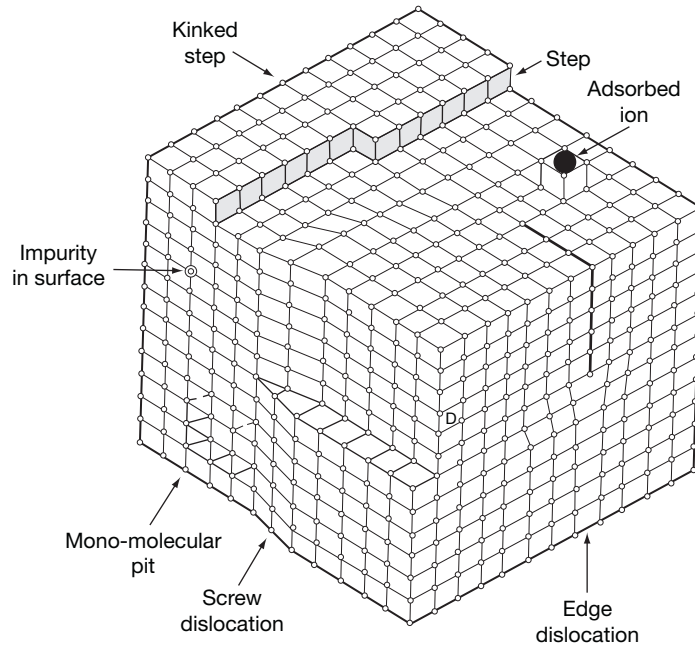


Figure 1 Surface imperfections in a crystal. Reproduced from Ehrlich, G.; Turnbull, D. *Physical Metallurgy of Stress Corrosion Fracture*; Interscience: New York and London, 1959; p 47, with permission from Interscience.

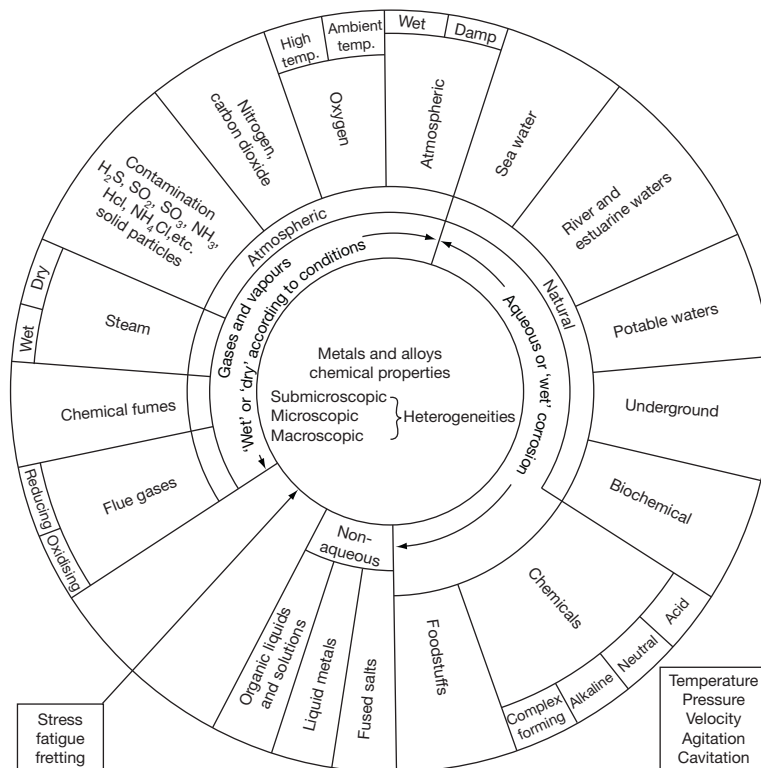


Figure 2 Environments in corrosion.

corrosion can be tolerated and that corrosion control is possible, provided that the rate and the form of the corrosion reaction are predictable and can be allowed for in the design of the structure.

Pitting is regarded as one of the most insidious forms of corrosion, since it often leads to perforation and to a consequent corrosion failure. In other cases, pitting may result in a loss of appearance, which is of major importance when the metal concerned is used for decorative architectural purposes. However, aluminum saucepans that have been in service for some

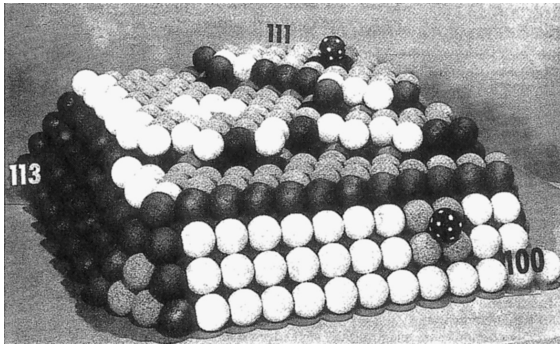


Figure 3 Hard-sphere model of face-centered cubic (fcc) lattice showing various types of sites. Numbers denote Miller indices of atom places and the different shadings correspond to differences in the number of nearest neighbors. Reproduced from Ehrlich, G.; Turnbull, D. *Physical Metallurgy of Stress Corrosion Fracture*; Interscience: New York and London, 1959; p 47, with permission from Interscience.

time are invariably pitted, although the pits seldom penetrate the metal, that is, the saucepan remains functional and the pitted appearance is of no significance in that particular application.

These considerations lead to the conclusion that the relationship between corrosion and the deterioration of properties of a metal is highly complex and involves a consideration of a variety of factors such as the rate and the form of corrosion and the specific function of the metal concerned; certain forms of corrosion such as uniform attack can be tolerated, whereas others such as pitting and stress corrosion cracking that ultimately lead to complete loss of function cannot be.

The implications of the terms *predictable* and *unpredictable* used in the context of corrosion require further consideration, since they are clearly dependent on the knowledge and expertise of the engineer, designer, or corrosion designer who takes the decision on the metal or alloy to be used, or the procedure to be adopted, to control corrosion in a specific environmental situation. On this basis, a corrosion failure (i.e., failure of the function of the metal due to corrosion within a period that is significantly less than the anticipated life of the structure) may be the result of one or more of the following possibilities:

1. *Predictable.* (1) The knowledge and technology are available, but have not been utilized by the designer; this category includes a wide variety of

Table 2 Types of corrosion

Type	Characteristic	Examples
1. Uniform (or almost uniform)	All areas of the metal corrode at the same (or similar) rate	Oxidation and tarnishing; active dissolution in acids; anodic oxidation and passivity; chemical and electrochemical polishing; atmospheric and immersed corrosion in certain cases
2. Localized	Certain areas of the metal surface corrode at higher rates than others due to 'heterogeneities' in the metal, the environment or in the geometry of the structure as a whole. Attack can range from being slightly localized to pitting	Crevice corrosion; filiform corrosion; deposit attack; bimetallic corrosion; intergranular corrosion; weld decay
3. Pitting	Highly localized attack at specific areas resulting in small pits that penetrate into the metal and may lead to perforation	Pitting of passive metals such as the stainless steels, aluminum alloys, etc., in the presence of specific ions, for example, Cl ⁻ ions
4. Selective dissolution	One component of an alloy (usually the most active) is selectively removed from an alloy	Dezincification; dealuminification; graphitization
5. Conjoint action of corrosion and a mechanical factor	Localized attack or fracture due to the synergistic action of a mechanical factor and corrosion	Erosion – corrosion, fretting corrosion, impingement attack, cavitation damage; stress corrosion cracking, hydrogen cracking, corrosion fatigue