

DEFINITION OF METAL CORROSION.

Metal Corrosion can be defined as the destructive attack of a metal through interaction with its environment.

DRIVING FORCE FOR CORROSION.

Most metals used in the construction of facilities are subject to corrosion. This is due to the high energy content of the elements in metallic form. In nature, most metals are found in chemical combination with other elements. These metallic ores are refined by man and formed into metals and alloys. As the energy content of the metals and alloys is higher than that of their ores, chemical re-combination of the metals to form ore like compounds is a natural process.

FUNDAMENTAL MECHANISM OF ATTACK.

Corrosion of metals takes place through the action of [electrochemical cells](#). Although this single mechanism is responsible, the corrosion can take many forms. Through an understanding of the electrochemical cell and how it can act to cause the various [forms of corrosion](#), the natural tendency of metals to corrode can be overcome and equipment that is resistant to failure by corrosion can be designed.

The Electrochemical Cell.

As in all chemical reactions, **corrosion** reactions occur through an exchange of electrons. In electrochemical reactions, the electrons are produced by a chemical reaction, the [oxidation](#), in one area, the anode, travel through a metallic path and are consumed through a different chemical reaction in another area, the cathode. In some cases, such as the common dry cell battery, electrochemical reactions can be used to supply useful amounts of electrical current. In marine **corrosion**, however, the most common result is the transformation of complex and expensive equipment to useless junk.

Components.

In order for electrochemical reactions to occur, four components must be present and active. These components are the anode, cathode, electron path, and electrolyte.

Anode.

In an electrochemical cell, the anode is the site where electrons are produced through the chemical activity of the metal. The anode is the area where metal loss occurs. The metal loses electrons and migrates from the metal surface through the environment. The electrons remain in the metal but are free to move about in response to voltage gradients.

Cathode.

The cathode in an electrochemical cell is the site where electrons are consumed. For each electron that is produced at an anodic site, an electron must be consumed at a cathodic site. No metal loss occurs at sites that are totally cathodic.

Electron Path.

In order for electrons to flow from the anodic sites to cathodic sites, the electrons migrate through a metallic path. This migration occurs due to a voltage difference between the anodic and cathodic reactions. Electrons can move easily only through metals and some non-metals such as graphite. Electrons from electrochemical reactions cannot move through insulating materials such as most plastics nor can they directly enter water or air. In some cases, the electron path is the corroding metal itself, in other cases, the electron path is through an external electrical path.

Electrolyte.

Electrolytes are solutions that can conduct electrical currents through the movement of charged chemical constituents called ions. Positive and negative ions are present in equal amounts. Positive ions tend to migrate away from anodic areas and toward cathodic areas. Negative ions tend to migrate away from cathodic areas and towards anodic areas.

Anodic Reactions.

Metal loss at anodic sites in an electrochemical cell occurs when the metal atoms give up one or more electrons and move into the electrolyte as positively charged ions.

Typical Reactions.

The generic chemical formula for this metal loss at anodic sites is:



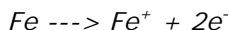
where:

M = uncharged metal atom at the metal surface

M^+ = positively charged metal ion in the electrolyte

e^- = electron that remains in the metal

This type of chemical reaction is called [oxidation](#) even though it does not directly involve oxygen but only results in an increase in positive charge on the atom undergoing oxidation. More than one electron can be lost in the reaction as in the case for iron where the most common anodic reaction is:



where:

Fe = metallic iron

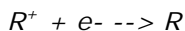
Fe^{2+} = ferrous ion that carries a double negative charge

Correlation Between Current Flow and Weight Loss.

For each specific anodic reaction a characteristic number of electrons are produced in the reaction of one metal ions. Thus, all other things being equal, the metal loss is proportional to the number of electrons that are produced. As the electrons produced migrate to cathodic areas through the electron path, the metal loss is proportional to the current flow. In cases where more positively charged ions are produced, more electrons flow for a given number of corroding metal atoms but the current flow remains proportional to the metal loss.

Cathodic Reactions.

The electrons that are produced at anodic sites are consumed at cathodic sites. The type of chemical reactions that consume electrons are called reduction and have the generic chemical formula:



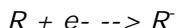
where:

R^+ = a positive ion in solution

e^- = an electron in the metal

R = the reduced chemical

In reduction, the chemical being reduced gains electrons and its charge is made more negative. In some cases, where the ion in solution has a multiple positive charge, the total positive charge on the ion may not be neutralized. In other cases, the chemical which is reduced may not be a positive ion but is a neutral chemical which then becomes a negatively charged ion in solution in a reaction such as:



Source: "Corrosion Control" September 1992

BASICS OF CORROSION – BIMETALLIC CORROSION

What is bimetallic corrosion?

Bimetallic corrosion is the accelerated corrosion of one metal placed in contact with a different more noble (less corroding) metal.

Why is it a problem?

Because, it is usually localized and if the area of the corroding metal is small compared to the metal it is in contact with can occur very rapidly.

Where does it occur typically?

Around fixings such as nuts and bolts, rivets or welds but generally in situations where different metals are in contact and can become wet.

Does it happen with all combinations of metals?

No. The metals have to be significantly different in terms of their nobility in the specific environment that they are exposed to. This can be looked up in a table.

Ranking in sea water (top of table is most noble)

Sea water is salty, contains about 2% NaCl.

Noble

Platinum

Gold

Titanium

Stainless Steel 316 (passive state)

Brasses

Tin

Lead

Stainless steel 316 (active state)

Carbon steel

Aluminium alloys

Zinc

Magnesium

Corrosive

How can bimetallic corrosion be prevented?

By isolating the metals electrically using insulators

By isolating the metals from the environment using a coating

By choosing metals that are close together in the table or coating one of them to achieve this.

Description of a Wet Corrosion Process

The main features of corrosion of a divalent metal M in an aqueous solution containing oxygen are presented schematically in Figure 1.

The corrosion process consists of an **anodic** and a **cathodic** reaction. In the anodic reaction (oxidation) the metal is dissolved and transferred to the solution as ions M^{2+} . The cathodic reaction in the example is reduction of oxygen. It is seen that the process makes an electrical circuit without any accumulation of charges. The electrons released by the anodic reaction are conducted through the metal to the cathodic area where they are consumed in the cathodic reaction. A necessary condition for such a corrosion process is that the environment is a conducting liquid (an electrolyte) that is in contact with the metal. The electrical circuit is closed by ion conduction through the electrolyte. In accordance with the conditions this dissolution process is called wet corrosion, and the mechanism is typically electrochemical.

In the example in Figure 1 the metal ions M^{2+} are conducted towards OH^- ions, and together they form a metal hydroxide that may be deposited on the metal surface.

If, for instance, the metal is zinc and the liquid is water containing O_2 but not CO_2 , the pattern in the figure is followed: Zn^{2+} ions join OH^- and form $Zn(OH)_2$. When CO_2 is dissolved in the liquid a zinc carbonate is deposited.

Corrosion of substances like iron and copper follow similar patterns with modifications: divalent iron oxide, $Fe(OH)_2$, is not stable, thus with access of oxygen and water it oxidizes to a trivalent hydrated iron oxide, $Fe_2O_3 \cdot nH_2O$, or an iron hydroxide, $Fe(OH)_3$, which also may be expressed as $FeOOH + H_2O$. $FeOOH$ is the ordinary red (or brown) rust. If the access of oxygen is strongly limited, Fe_3O_4 is formed instead of the trivalent corrosion products. Fe_3O_4 is black (without water) or green (with water). Divalent copper hydroxide, $Cu(OH)_2$, is not stable either and tends to be dehydrated to CuO .

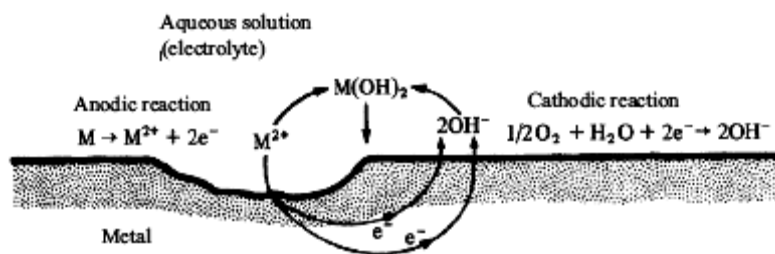


Figure 1. Wet corrosion of a divalent metal M in an electrolyte containing oxygen.

Reduction of oxygen is the dominating cathodic reaction in natural environments like seawater, fresh water, soil and the atmosphere. However, under certain conditions there are also other important cathodic reactions: the hydrogen reaction $2H^{+} + 2e^{-} \Rightarrow H_2$, reduction of carbonic acid (H_2CO_3) (in oil and gas production), reduction of metal ions etc.

Figure 1 illustrates an electrochemical cell, and the driving force for the electrochemical process (the corrosion) is the cell voltage, or in other words the potential difference between the anode and the cathode.

Crucial Mechanisms Determining Corrosion Rates

It is seen that the corrosion process in Figure 1 depends on the availability of oxygen. When corrosion products, such as hydroxides, are deposited on a metal surface, they may cause a reduction in the oxygen supply because the oxygen has to diffuse through the deposits, which may form a more or less continuous layer on the metal surface. Since the rate of metal dissolution is equal to the rate of oxygen reduction (Figure 1), a limited supply and limited reduction rate of oxygen will also reduce the corrosion rate. In this case it is said that the corrosion is under cathodic control. This is a very widespread mechanism for corrosion limitation by nature.

If the corrosion products are removed from the metal surface by mechanisms such as the corrosion medium flowing at high velocity and corresponding strong fluid dynamical forces, the corrosion rate may be greatly increased (see: erosion corrosion).

In certain cases, **if the corrosion products form a dense and continuous surface film** of oxide closely related to the crystallographic structure of the metal. Films of this type prevent the conduction of metal ions from the metal–oxide interface to the oxide–liquid interface to a great extent so that the corrosion rates may be very low (anodic control). This phenomenon is called passivation and is typical for materials like stainless steel and aluminium in many natural environments. Ordinary structural steels are also passivated in alkaline waters.

Passivation is promoted by ample access of oxygen on the material surface, which is obtained by high oxygen concentration in the liquid and by efficient transport of oxygen as a result of strong convection (high flow rates). Conversely, passivation may be hindered – or a passive film may be broken down – by the lack of oxygen. This often happens underneath deposits and in narrow crevices that obstruct the oxygen supply (see: crevice corrosion).

Aggressive species like chlorides are other major causes of the local breakdown of passive films that occurs in crevice corrosion, pitting and other forms of corrosion.

When more and less noble materials are placed in contact, the more noble material offers an extra area for the cathodic reaction. Therefore the total rate of the cathodic reaction is increased, and this is balanced with an increased anodic reaction, i.e. increased dissolution of the less noble material (see: galvanic corrosion).

If the more noble material (the cathodic material) has a large surface area and the less noble metal (the anodic metal) has a relatively small area, a large cathodic reaction must be balanced by a correspondingly large anodic reaction concentrated in a small area. The intensity of the anodic reaction, i.e. the corrosion rate (material loss per area unit and time unit) becomes high. Thus, the area ratio between the cathodic and the anodic materials is very important and should be kept as low as possible. It should be mentioned that in a galvanic corrosion process, the more noble material is more or less protected. This is an example of cathodic protection, by which the less noble material acts as a sacrificial anode.

Corrosion Prevention Measures

Corrosion prevention aims at removing or reducing the effect of one or more of the conditions leading to corrosion using the following measures.:

1. Selecting a material that does not corrode in the actual environment.
2. Changing the environment, e.g. removing the oxygen or adding anticorrosion chemicals (inhibitors).
3. Using a design that will avoid corrosion, e.g. preventing the collection of water so that the metal surface can be kept dry.
4. Changing the potential, most often by making the metal more negative and thus counteracting the natural tendency of the positive metal ions to be transferred from the metal to the environment.
5. Applying coatings on the metal surface, usually in order to make a barrier between the metal and the corrosive environment.

Expressions and Measures of Corrosion Rates

There are three main methods that are used to express the corrosion rate:

- a) Thickness reduction of the material per unit time.
- b) Weight loss per unit area and unit time.
- c) Corrosion current density.

Thickness reduction per unit time is the measure of most practical significance and interest. In the metric system this measure is usually expressed in mm/year. In some literature one can still find the unit mils per year (mpy) = 1/1000 inches per year, possibly also inches per year (ipy).

Weight loss per unit area and unit time was commonly used in earlier times, mainly because weight loss was usually the directly determined quantity in corrosion testing. Here the test specimens were weighed before and after the exposure to the corrosion medium. On this basis one could calculate the thickness reduction as weight loss per unit area/density.

From Figure 1 it can be understood that corrosion rate also can be expressed by corrosion current density. The dissolution rate (the corrosion rate) is the amount of metal ions removed from the metal per unit area and unit time.

This transport of ions can be expressed as the electric current I_a per area unit,
i.e. anodic current density i_a = corrosion current density i_{corr} .

If it is preferred to express the local corrosion current density in the anodic area in Figure 1, one has $i_{\text{corr}} = i_a = I_a/A_a$, where A_a is the *anodic area*. However, usually the average corrosion current density over the whole *surface area* A is given, i.e. $i_{\text{corr}} = i_a = I_a/A$.

The most suitable measure to employ for calculating the corrosion rate depends on which form of corrosion one is dealing with.

Corrosion current density is a particularly suitable measure of corrosion rate when treating corrosion theory and in connection with electrochemical corrosion testing.

Current density is also directly applicable for cathodic and anodic protection. In corrosion testing the unit A/cm² is most often used. When dealing with cathodic protection the units mA/m² and A/m² are used for the cathode (structure to be protected) and the anode, respectively.

The relationship between thickness reduction per time unit ds/dt (on each corroding side of the specimen/component) and the corrosion current density i_{corr} is determined from Faraday's equations:

$$\frac{ds}{dt} = \frac{i_{\text{corr}} M}{z F \rho} \text{ cm/s} \quad (2.1a)$$

or

$$\frac{\Delta s}{\Delta t} = 3268 \frac{i_{\text{corr}} M}{z \rho} \text{ mm/year}, \quad (2.1b)$$

where i_{corr} is given in A/cm²;

- z = number of electrons in the reaction equation for the anodic reaction (dissolution reaction) (per atom of the dissolving metal);
- M = the mol mass of the metal (g/mol atoms) (the numerical value of M is the atomic weight of the metal);
- F = Faraday's constant = 96,485 coulombs/mole electrons = 96,485 C/mol e⁻ \approx 96,500 As/mol e⁻ [2.2];
- ρ = the density of the metal (g/cm³).

Table below shows the conversion factors between the units of corrosion rates that are most frequently used in the literature. Note that, for most of the listed materials, a corrosion current density of 1 A/cm² corresponds to a thickness reduction of roughly 0.01 mm/year.

As an example of practical corrosion rates it can be mentioned that structural steels in seawater normally corrode by 0.1–0.15 mm/year which means 10–15 A/cm² on average. The corrosion rate can be a few times higher locally.

Table 2.1 Corrosion rate conversion factors.

Material/reaction	Corrosion current density	Weight loss per unit area and unit time	Average attack depth increment per unit time	
	$\mu\text{A}/\text{cm}^2$	mdd*	mm/year	mpy*
$\text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^-$	1	2.51	1.16×10^{-2}	0.46
$\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$	1	2.84	1.17×10^{-2}	0.46
$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$	1	2.93	1.5×10^{-2}	0.59
$\text{Ni} \rightarrow \text{Ni}^{2+} + 2\text{e}^-$	1	2.63	1.08×10^{-2}	0.43
$\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$	1	0.81	1.09×10^{-2}	0.43
$\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$	1	1.09	2.2×10^{-2}	0.89

* mdd = mg per dm^2 per day.
mpy = mils per year (1/1000 inches per year).

Basic Properties That Determine if Corrosion Is Possible and How Fast Material Can Corrode

The corrosion process in Table 2.1 is an example of a so-called spontaneous electrochemical cell reaction. The driving force of the reaction is a reversible cell voltage. The cell voltage can be expressed as the difference between the potentials of the two electrodes (anode and cathode). Reversible cell voltage and the corresponding reversible potentials of the electrodes are determined by *thermodynamic properties*.

These properties, mainly provide a possibility to determine the spontaneous *direction* which a given reaction tends to have. Applied to corrosion, the thermodynamics can tell us if corrosion is theoretically possible or not under given conditions.

The driving voltage of the cell reaction must cope with various types of resistance:

- resistance against charge transfer** between a metal and the adjacent electrolyte at the anode and cathode, respectively;
- resistance due to limited access of reactants** or limited removal of reaction products at the electrodes;
- ohmic resistance in the liquid** and possibly in the metal between the anode and the cathode. The driving voltage and the sum of the resistances will together determine how fast the reactions will proceed, i.e. how fast a given material will corrode. Resistances against the reactions and the resulting reaction rates are described and explained under *electrode kinetics*.

In other words by using kinetic relationships we can determine *how fast* a material will corrode under certain conditions. Thermodynamics and electrode kinetics make up the two main parts of corrosion theory. These are the key to understanding and explaining the majority of practical corrosion problems. It is normal to apply this corrosion theory in modern corrosion testing, and it provides a more rational basis for corrosion prevention and monitoring.

References

- 2.1 Pourbaix M. Lectures on Electrochemical Corrosion. New York–London: Plenum Press, 1973.
- 2.2 Zumdahl SS. Chemical Principles. Lexington, MA: D.C. Heath and Company, 1992.

EXERCISES

1. Which reaction is the dominating cathodic reaction by corrosion in natural environments, such as seawater, fresh water, soil and condensation in the atmosphere?
Write the reaction equation.
2. What types of corrosion products are usually deposited by corrosion in natural environments? What is rust? How can corrosion product deposits affect the corrosion rate?
3. Which property of the corrosion medium (the aqueous solution) is the most important prerequisite for electrochemical corrosion?
4. What can be said about the relationship between the anodic current I_a and the cathodic current I_c in a normal corrosion process?
5. A steel plate has corroded on both sides in seawater. After 10 years a thickness reduction of 3 mm is measured. Calculate the average corrosion current density.
1. Take into consideration that the dissolution reaction is mainly $\text{Fe} = \text{Fe}^{2+} + 2e^-$, and that the density and the atomic weight of iron are 7.8 g/cm³ and 56, respectively.
6. What are the roles of thermodynamics and electrode kinetics in corrosion theory?

Electrochemical corrosion nomenclature

The aim of this document is to provide scientific definitions in the field of corrosion. Because of their great practical importance, corrosion terms have already been defined for the purpose of technical standardization. The present document avoids disagreements with the earlier definitions, if possible and concentrates on a more complete or rigorous description of the physicochemical basis of corrosion terms. As a consequence, only the terms of fundamental importance will be discussed. Technical definitions refer to corrosion of metals, but corrosion also affects other materials. This fact is taken into account in the general definition of corrosion given below. The major part of corrosion reactions are of an electrochemical nature.

1. GENERAL TERMS

1.1. Corrosion

Corrosion is an irreversible interfacial reaction of a material (metal, ceramic, polymer) with its environment which results in consumption of the material or in dissolution into the material of a component of the environment.

Often, but not necessarily, corrosion results in effects detrimental to the usage of the material considered. Exclusively physical or mechanical processes such as melting or evaporation, abrasion or mechanical fracture are not included in the term *corrosion*.

1.2 Electrochemical corrosion

Electrochemical corrosion always involves *electrode reactions*. Typical examples are the corrosion of a metal by dissolution of metal ions or by formation of an oxide film.

1.3 Electrode reactions during electrochemical corrosion

There are at least two electrode reactions in electrochemical corrosion, one being *anodic*, the other one *cathodic*.

The electrode reactions proceed simultaneously on a uniform surface or on spatially separated areas. In the latter case an electric current flows between the anode and the cathode.

1.4. Corrosion potential (E_{cor})

The corrosion potential is the electrode potential spontaneously acquired by a corroding material in a particular environment.

1.5. Corrosion rate (V_{cor}), Corrosion current (I_{cor})

The corrosion rate is measured as the amount of substance transferred per unit time at a specified surface. Using Faraday's law, the corrosion rate can be formally expressed as an electric current which at the corrosion potential is called the corrosion current. E.g. for the anodic dissolution of one component of a material with V_{cor} in [mol/sec] and I_{cor} in [Amperes], one obtains

$$I_{cor} = n * F * V_{cor}$$

where

n is being the charge number of the electrode reaction
 F is the Faraday constant.

1.6. Polarization

Polarization is the difference of the electrode potential from the corrosion potential. It is measured like the overpotential.

1.7. Uniform corrosion

Corrosion is uniform if the time average of the corrosion current through a unit area of any macroscopic dimension is independent of the position on the surface.

1.8. Non-uniform corrosion

Corrosion is non-uniform if the time average of the corrosion current through a unit area depends on its position on the surface. Non-uniform corrosion can be due to inhomogeneity of structure or of composition of the corroding material, or to inhomogeneity of the environment. Special cases of non-uniform corrosion such as pitting or *intergranular corrosion* sometimes are called localized corrosion.

1.9. Selective corrosion

Selective corrosion is corrosion of a single phase having more than one component, when the ratio of the corrosion rates of the components differs from the ratio of bulk mole fractions. Selective corrosion changes the composition of the material in the *interfacial region*.

2. UNIFORM CORROSION OF METALS AND ALLOYS

2.1. Corrosion in the active state

Corrosion in the active state occurs by direct transfer (which may involve one or several steps) of metal ions from the metallic phase to the adjacent electrolyte. A metal when corroding in the active state is called an *active metal*.

The *corrosion current* of an active metal usually increases when the electrode potential is made more positive, other conditions remaining constant.

2.2. Corrosion in the passive state

The passive state is characterized by a continuous "passiv film" of solid corrosion products separating the metallic phase from the adjacent electrolyte.

Corrosion in the passive state involves growth of the passivating film layer and/or transfer of metal ions through the film into the electrolyte. A metal when corroding in the passive state is called a *passive metal*.

2.3. Passivation potential

The passivation potential is the most negative electrode potential at which the passive film is formed. The passivation potential is equal to or more positive than the equilibrium potential of formation of the phase constituting the film. Usually, the corrosion current goes through a maximum at the passivation potential.

2.4. Passivation

Passivation is the process of transition from the active to the passive state by formation of the passive film. Passivation is achieved by an *anodic current* which at the respective electrode potential must be larger than the maximum current referred to in 2.3, or by the presence of an oxidized substance in the neighboring solution which passivates by being reduced (passivator).

2.5. Activation

Activation is the process of transition from the passive to the active state by removal of the passive film.

A necessary condition for activation is an electrode potential negative to the equilibrium potential of formation of the passive film. Activation is achieved by *cathode currents*, by a reduced substance in the adjacent solution, or by contact with an electronic conductor having a suitably negative corrosion potential.

2.6. Component-currents of the passive film

At the interface between the passive film and the adjacent electrolyte the current consists of two or more component currents. For example, anodic component currents are the transfer of metal ions from the passive film into the electrolyte, and transfer of anions from the electrolyte into the film. The latter component current results in film thickening.

2.7. Steady-state corrosion of a passive metal

The steady state is characterized by the current and the film thickness both being independent of time. In the steady state, the component current involving anions is zero and the corrosion current is equal to the component current involving metal ions.

The *steady state anodic current* depends on the composition of the film at the interface with the electrolyte, apart from other parameters such as *electrolyte composition* and temperature. The composition of the film changes with the electrode potential, in general. Therefore, the steady state corrosion current in the *passive state* may increase or decrease with the electrode potential.

3. NON-UNIFORM CORROSION

3.1 Corrosion cell

A corrosion cell is a galvanic cell resulting from *inhomogeneity* in the material or in its environment (ref.3).

3.2 Contact corrosion, galvanic corrosion

Contact corrosion is the enhancement of the *corrosion rate* of the material with the more negative corrosion potential in a corrosion cell resulting from the contact between different electron-conducting phases.

3.3 Concentration-cell corrosion

Concentration-cell corrosion is the local variation of the *corrosion rate* due to the action of a corrosion cell resulting from inhomogeneous composition of the environment.

A common case of concentration-cell corrosion is that due to locally different concentrations of oxygen in the solution adjacent to the corroding material. Concentration-cells with locally different concentrations of oxygen are often called differential-aeration cells.

3.4 Pitting corrosion

Pitting corrosion is a special type of non-uniform corrosion of passive metals resulting in the formation of pits. Usually pitting corrosion occurs in the presence of certain anions at electrode potentials positive to a critical pitting potential.

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1. Corrosion of Metals and Alloys, Terms and Definitions, International Standard ISO 8044, TC 156
2. Electrode Reaction Orders, Transfer Coefficients and Rate Constants; Amplification of Definitions and Recommendations for Publication of Parameters; R. Parsons, Pure Appl. Chem. 52, 233 (1979)
3. Quantities, Units and Symbols in Physical Chemistry, Section 2.13 Electrochemistry, eds. I. M. Mills, T. Cvitas, K. Homann, N. Kallay and K. Kuchitsu, Blackwell Scientific Publications Ltd, Oxford

Natural environments

Air

Rural (farming, fertilisers, ammonia)
Coastal, marine (chloride)
Industrial, urban (sulphur dioxide, soot and acid rain)

Waters

Rivers, lakes, wells, water pipelines, dams; sea water (tidal, "splash zone"), estuaries, harbours (in most of these, chlorides are significant contaminants, as well as a variety of corrosive biological agents).

Soils

Clays, chalk, loam; drainage; acidity; access of air;
bacterial action (sulphate reducing bacteria).

Chemical environments

Urban and industrial atmospheres
Environmental pollutants creating aggressive mists
Interior of reaction and storage vessels in chemical plant.

Other environments

Embedded metals may react with non-metallic materials such as wood, plastics, and concrete. The porosity of some of these media allow contact with stagnant water.

Temperature

Increasing temperature usually causes increased rates of corrosion. A notable exception is when temperature increase reduces relative humidity or dries out the environment completely.

Incident radiation

Sunlight, ultraviolet light and thermal radiation, can activate short-lived reactive chemical species from contaminants in the environment, aggravating corrosion.

Stress

General or uniform corrosion causes progressive loss of cross-section and increased stress levels, while uneven and localised corrosion causes high stress concentrations.

Design should control extremes of stress and environment arising at any time in the life-cycle of the structure.

Think about the following ...

- Residual and thermal stresses arising from fabrication
- Transportation shocks and vibration
- Installation
- Performance and pressure testing, leading to overstressing, test fluids corrosion
- Operating and fault conditions
- Maintenance, including effects of modifications and repairs

Static stresses

The environment both inside and outside a structure can affect the strengths of the materials specified. For each alloy, *Stress Corrosion Cracking* (SCC) requires specific environmental corrosive conditions, with the alloy subjected to a critical tensile stress (residual or applied). SCC is very dangerous because of the progressive nature of the cracking, with ever rising risks of rupture, leakage, or loss of function.

Fluctuating stresses and corrosion fatigue

In a corrosive environment the stress level at which it could be assumed a material has infinite life is lowered or removed completely. Corrosion fatigue and fretting are both in this class. Much lower failure stresses and much shorter failure times can occur in a corrosive environment compared to a situation where the alternating stress is in a non-corrosive environment.

Hydrogen effects and stress

Atomic hydrogen released by cathodic reactions during corrosion can enter metals, causing several significant types of damage. Hydrogen has a strong tendency to travel along stress gradients and accumulate where there are high tensional stresses. By several mechanisms, this can cause cracking in steels. Hydrogen may also be introduced during welding or due to cathodic protection.

Electrochemistry:

Electrochemical Corrosion

Corrosion can be defined as the **deterioration of materials by chemical processes**. Of these, the most important by far is electrochemical corrosion of metals, in which the oxidation process $M \rightarrow M^+ + e^-$ is facilitated by the presence of a suitable electron acceptor, sometimes referred to in corrosion science as a *depolarizer*.

Introduction

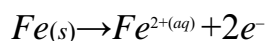
In a sense, corrosion can be viewed as the spontaneous return of metals to their ores; the huge quantities of energy that were consumed in mining, refining, and manufacturing metals into useful objects is dissipated by a variety of different routes.

The economic aspects of corrosion are far greater than most people realize; the estimated cost of corrosion in the U.S. alone was \$276 billion per year. Of this, about \$121 billion was spent to control corrosion, leaving the difference of \$155 billion as the net loss to the economy. Utilities, especially drinking water and sewer systems, suffer the largest economic impact, with motor vehicles and transportation being a close second.

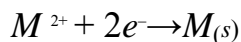
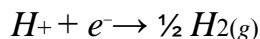
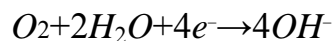
Corrosion cells and reactions

The special characteristic of most corrosion processes is that the oxidation and reduction steps occur at separate locations on the metal. This is possible because metals are conductive, so the electrons can flow through the metal from the anodic to the cathodic regions. The presence of water is necessary in order to transport ions to and from the metal, but a thin film of adsorbed moisture can be sufficient.

A corrosion system can be regarded as a short-circuited electrochemical cell in which the anodic process is something like



and the cathodic steps can be any of



where M is a metal.

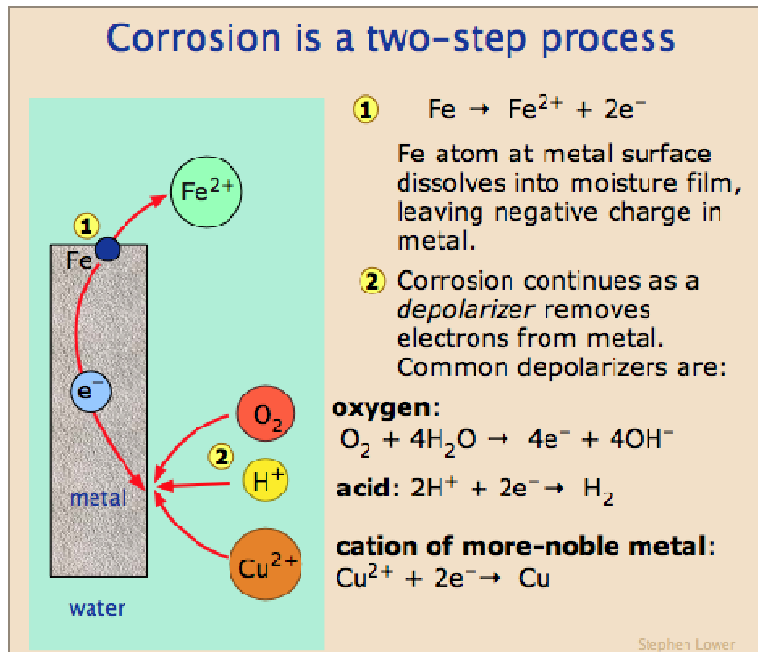


Figure 1.: Electrochemical corrosion of iron. Corrosion often begins at a location (1) where the metal is under stress (at a bend or weld) or is isolated from the air (where two pieces of metal are joined or under a loosely-adhering paint film.) The metal ions dissolve in the moisture film and the electrons migrate to another location (2) where they are taken up by a depolarizer. Oxygen is the most common depolarizer; the resulting hydroxide ions react with the Fe^{2+} to form the mixture of hydrated iron oxides known as rust.

Which parts of the metal serve as anodes and cathodes can depend on many factors, as can be seen from the irregular corrosion patterns that are commonly observed. Atoms in regions that have undergone stress, as might be produced by forming or machining, often tend to have higher free energies, and thus tend to become anodic.

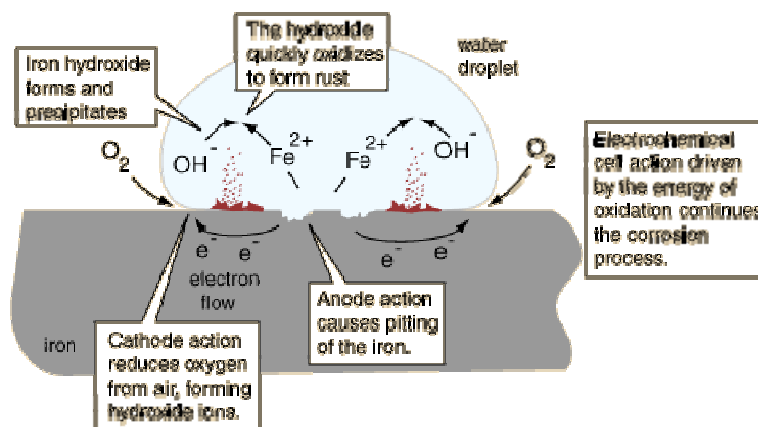


Figure 2: Schematic diagram of corrosion cells on iron.

If one part of a metallic object is protected from the atmosphere so that there is insufficient O_2 to build or maintain the oxide film, this "protected" region will often be the site at which

corrosion is most active. The fact that such sites are usually hidden from view accounts for much of the difficulty in detecting and controlling corrosion.

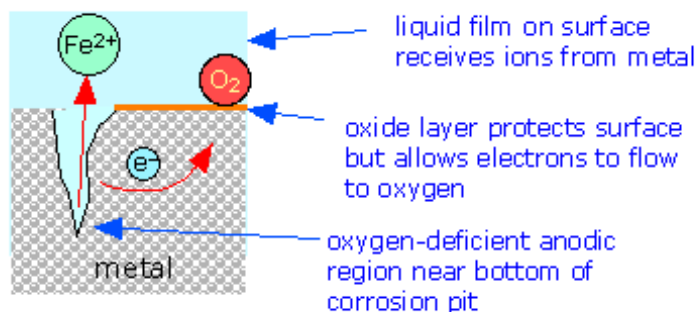


Figure 3: Pitting corrosion Most metals are covered with a thin oxide film which inhibits anodic dissolution. When corrosion does occur, it sometimes hollows out a narrow hole or pit in the metal. The bottoms of these pits tend to be deprived of oxygen, thus promoting further growth of the pit into the metal.

In contrast to anodic sites, which tend to be localized to specific regions of the surface, the cathodic part of the process can occur almost anywhere. Because metallic oxides are usually semiconductors, most oxide coatings do not inhibit the flow of electrons to the surface, so almost any region that is exposed to O_2 or to some other electron acceptor can act as a cathode. The tendency of oxygen-deprived locations to become anodic is the cause of many commonly-observed patterns of corrosion

Rusted-out cars and bathroom stains

Anyone who has owned an older car has seen corrosion occur at joints between body parts and under paint films. You will also have noticed that once corrosion starts, it tends to feed on itself. One reason for this is that one of the products of the O_2 reduction reaction is hydroxide ion. The high pH produced in these cathodic regions tends to destroy the protective oxide film, and may even soften or weaken paint films, so that these sites can become anodic. The greater supply of electrons promotes more intense cathodic action, which spawns even more anodic sites, and so on.



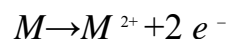
Figure 4.: Rusted out car.

A very common cause of corrosion is having two dissimilar metals in contact, as might occur near a fastener or at a weld joint. Moisture collects at the junction point, acting as an electrolyte and forming a cell in which the two metals serve as electrodes. Moisture and conductive salts on the outside surfaces provide an external conductive path, effectively short-circuiting the cell and producing very rapid corrosion; this is why cars rust out so quickly in places where salt is placed on roads to melt ice.

Dissimilar-metal corrosion can occur even if the two metals are not initially in direct contact. For example, in homes where copper tubing is used for plumbing, there is always a small amount of dissolved Cu^{2+} in the water. When this water encounters steel piping or a chrome-plated bathroom sink drain, the more-noble copper will plate out on the other metal, producing a new metals-in-contact corrosion cell. In the case of chrome bathroom sink fittings, this leads to the formation of Cr^{3+} salts which precipitate as greenish stains.

Control of corrosion

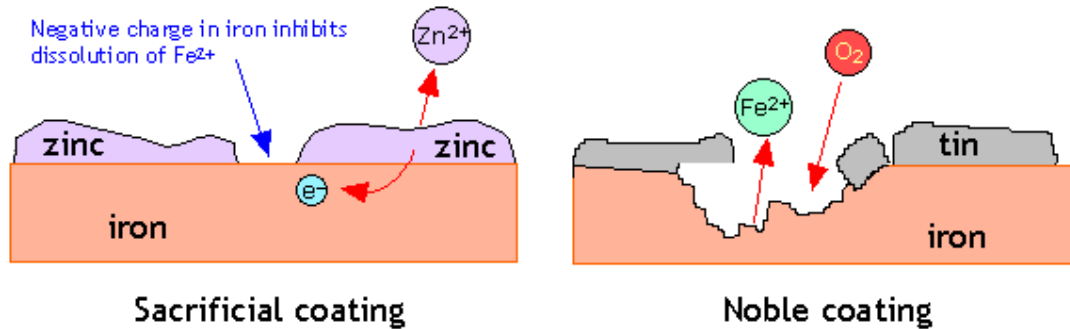
Since both the cathodic and anodic steps must take place for corrosion to occur, prevention of either one will stop corrosion. The most obvious strategy is to stop both processes by coating the object with a paint or other protective coating. Even if this is done, there are likely to be places where the coating is broken or does not penetrate, particularly if there are holes or screw threads. A more sophisticated approach is to apply a slight negative charge to the metal, thus making it more difficult for the reaction



to take place.

Sacrificial coatings

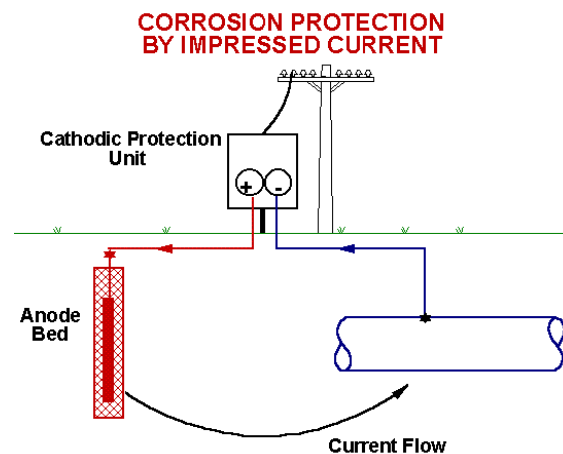
One way of supplying this negative charge is to apply a coating of a more active metal. Thus a very common way of protecting steel from corrosion is to coat it with a thin layer of zinc; this process is known as galvanizing. The zinc coating, being less noble than iron, tends to corrode selectively. Dissolution of this sacrificial coating leaves behind electrons which concentrate in the iron, making it cathodic and thus inhibiting its dissolution.



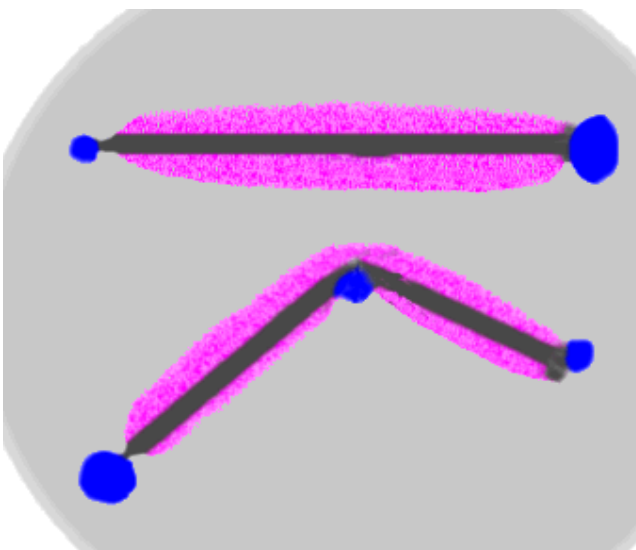

The effect of plating iron with a less active metal provides an interesting contrast. The common tin-plated can (on the right) is a good example. As long as the tin coating remains intact, all is well, but exposure of even a tiny part of the underlying iron to the moist atmosphere initiates corrosion. The electrons released from the iron flow into the tin, making the iron more anodic so now the tin is actively promoting corrosion of the iron! You have probably observed how tin cans disintegrate very rapidly when left outdoors.

Cathodic protection

A more sophisticated strategy is to maintain a continual negative electrical charge on a metal, so that its dissolution as positive ions is inhibited. Since the entire surface is forced into the cathodic condition, this method is known as *cathodic protection*. The source of electrons can be an external direct current power supply (commonly used to protect oil pipelines and other buried structures), or it can be the corrosion of another, more active metal such as a piece of zinc or aluminum buried in the ground nearby, as is shown in the illustration of the buried propane storage tank below.



Corrosion gallery

 <p>The diagram shows two nails immersed in a moist agar gel. The top nail is straight, and the bottom one is bent. The areas of the nails that were stressed (the ends of the straight nail and the bend of the bent nail) are highlighted in blue, indicating anodic regions where iron is released. The surrounding agar is highlighted in pink, indicating cathodic regions where the environment becomes alkaline.</p>	<p style="text-align: center;">Corrosion of a nail</p> <p>The nails are immersed in agar which forms a moist solid gel. The agar also contains phenolphthalein and hexacyanoiron(III) $\text{Fe}(\text{CN})_6^-$ which forms a deep blue color ("prussian blue") in the presence of Fe^{2+}. The blue colors are clearly associated with those parts of the nail that have been stressed, thus facilitating the anodic release of Fe^{2+} from the metal. The pink color shows the cathodic regions that have been made alkaline by the reaction</p> $\text{O}_2 + 2 \text{H}_2\text{O} + 4e^- \rightarrow 4 \text{OH}^-$ <p>This clearly shows the separation between the anodic and cathodic processes in corrosion.</p>
<p>Water distribution main</p> <p>If you live in the older part of a city where the mains are 50-100 years old, the water you drink may well have passed through a pipe in this condition!</p> <p>Severe corrosion like this is more common in areas where the water is acidic. Such water comes from mountain snowmelt and runoff, and usually acquires its acidity from dissolved atmospheric carbon dioxide.</p> <p>Waters from rivers, lakes, and especially groundwaters from wells have usually been in sufficiently long contact with carbonate-containing sediments to have been neutralized. Water-works administrators like to make the water slightly alkaline and slightly supersaturated in calcium carbonate in order to maintain a thin coating of solid carbonate on the interior of the pipe which acts to protect it from corrosion.</p>	 <p>A photograph showing a cross-section of a pipe that has undergone severe internal corrosion. The interior surface is heavily pitted and eroded, with a large, irregular opening in the center. The remaining material is a thick, rust-colored crust.</p>

Corrosion of reinforcing bars in concrete

All large concrete structures contain steel reinforcing bars ("rebars") that help ensure structural integrity under varying load conditions and especially during earthquakes. Intrusion of water, even in the form of fog or mists, can lead to serious corrosion damage, as seen in this picture of this column which supports a highway overpass.



Corrosion at metallic joints

The picture shows two steel structural members joined by cast iron flanges which have been bolted together. For some reason, one of the pieces has become more anodic than the other, leading to extensive corrosion of the upper part.

Bacterial-assisted corrosion

This gas pipe was buried in a red soil that contained iron pyrites (FeS.) The bacterium *thiobacillus ferrooxidans* derives its energy by oxidizing Fe^{2+} to the more soluble Fe^{3+} , transferring the electrons to O_2 . It also oxidizes the sulfur, producing sulfuric acid. The resulting chemical cocktail has eaten a hole into the pipe.



These galvanized bolts were used to join wooden beams together. Subsequent movement of the beams due to varying load conditions abraded the zinc coating. A lack of oxygen near the centers of the bolts also likely contributed to the corrosion by preventing the formation of a protective oxide film.



Pitting corrosion



Summary

Make sure you thoroughly understand the following essential ideas which have been presented above. It is especially important that you know the precise meanings of all the highlighted terms in the context of this topic.

- **Electrochemical corrosion of metals** occurs when electrons from atoms at the surface of the metal are transferred to a suitable electron acceptor or *depolarizer*. Water must be present to serve as a medium for the transport of ions.
- The **most common depolarizers** are oxygen, acids, and the cations of less active metals.
- Because the electrons flow through the metallic object itself, the anodic and cathodic regions (the two halves of the electrochemical cell) can be at widely separated locations.
- **Anodic regions** tend to develop at locations where the metal is stressed or is protected from oxygen.
- **Contact with a different kind of metal**, either direct or indirect, can lead to corrosion of the more active one.
- **Corrosion of steel can be inhibited** by *galvanizing*, that is, by coating it with zinc, a more active metal whose dissolution leaves a negative charge on the metal which inhibits the further dissolution of Fe^{2+} .
- *Cathodic protection* using an external voltage source is widely used to protect underground structures such as tanks, pipelines and piers. The source can be a sacrificial anode of zinc or aluminum, or a line-operated or photovoltaic power supply.

Additional readings:

- [Chem1 Virtual Textbook](#)

Electrode Potential and Galvanic Corrosion

An introduction to the electrochemical series and corrosion of metals

The **potential difference** between an anode and a cathode can be measured by a voltage measuring device. The absolute potential of the anode and cathode cannot be measured directly. Defining a standard electrode, all other potential measurements can be made against this standard electrode. If the standard electrode potential is set to zero, the potential difference measured can be considered as the absolute potential.

Standard Hydrogen Electrode

- The half-cell in which the hydrogen reaction takes place is called the **Standard Hydrogen Electrode - SHE**

Standard Electrode Potential

- The potential difference measured **between** metal M, and the Standard Hydrogen Electrode - SHE

The electrochemical series consists of a list of metals which have been arranged in order of their standard electrode potentials.

Element	Electrode Potential (Volts)
Lithium	-3.04
Rubidium	-2.92
Potassium	-2.92
Calcium	-2.87
Barium	-2.80
Sodium	-2.71
Magnesium	-2.37
Aluminum	-1.67
Zinc	-0.76
Chromium	-0.74
Iron	-0.44
Nickel	-0.24
Tin	-0.14
Lead	-0.13
Hydrogen	+0.00
Copper	+0.34
Iodine	+0.54
Silver	+0.80
Gold	+0.80
Mercury	+0.80
Iodide	+0.54
Bromine	+1.07
Chlorine	+1.36
Fluorine	+2.87

IMPORTANT! Metals which are higher in the electrochemical series displace metals which are lower in the sequence, which means when connecting two metals, the metal with lowest potential will corrode.

Corrosion Problems Connecting Copper and Iron/Steel

A very common connection in piping systems is copper and iron/steel. In a connection like this iron/steel will corrode **many times faster** than iron/steel alone.

Related Topics

- [Miscellaneous](#) Miscellaneous engineering related topics like Beaufort Wind Scale, CE-marking, drawing standards and more
- [Electrical](#) Amps and electrical wiring, AWG - wire gauge, electrical formulas, motors and units
- [Corrosion](#) Corrosion in piping systems - caused by thermodynamic and electrochemical processes - corrosion problems and methods of protection and prevention

Related Documents

- [Metals and Corrosion Resistance](#) Common metals and their corrosion resistance to aggressive fluids as acids, bases and more
- [Piping Materials & Galvanic Corrosion](#) Connecting pipes of common piping materials may cause galvanic corrosion and serious damage
- [Types of Corrosion](#) Uniform, pitting, galvanic, crevice, concentration cell and graphitic corrosion
- [Oxygen and Steel Pipe Corrosion](#) Oxygen concentration, temperature and corrosion of steel pipes
- [Potassium - Thermophysical Properties](#) Thermophysical properties of potassium
- [Metals - Galvanic Series in Seawater](#) Galvanic series in seawater

Metals - Galvanic Series in Seawater

Galvanic series in seawater

Galvanic series in seawater at 25°C are indicated below

Noble metals (from top) to more active metals (bottom)

- Platinum
- Gold
- Graphite
- Titanium
- Silver
- Chlorimet 3 (62 Ni + 18 Cr + 18 Mo)
- HASTELLOY® alloy C (62Ni + 17 Cr + 15 Mo)
- INCONEL® alloy 625
- INCONEL® alloy 825
- Stainless steel, type 316 (passive)
- Stainless steel, type 304 (passive)
- Stainless steel, type 410 (passive)
- Monel alloy 400
- INCONEL® alloy 600 (passive)
- Nickel 200 (passive)
- Copper alloy C71500 (Cu 30% Ni)
- Copper alloy C23000 (red brass 85% Cu)
- Copper alloy C27000 (yellow brass 65% Cu)
- HASTELLOY® alloy B
- INCONEL® alloy 600 (active)
- Nickel 200 (active)
- Copper alloy C46400
- Copper alloy C46500
- Copper alloy C46600
- Copper alloy C46700 (naval brass)
- Tin
- Lead
- Lead-Tin solders
- Hastelloy A
- Stainless steel, type 316 (active)
- Stainless steel, type 304 (active)
- 50 - 50 lead tin solder
- Stainless steel, type 410 (active)
- Cast iron
- Wrought iron
- Low carbon steel
- Aluminum alloy 2117
- Aluminum alloy 2017
- Aluminum alloy 2024
- Cadmium
- Aluminum alloy 5052

- Aluminum alloy 3004
- Aluminum alloy 3003
- Aluminum alloy 1100
- Aluminum alloy 6053
- Galvanized steel
- Zinc
- Magnesium alloys
- Magnesium

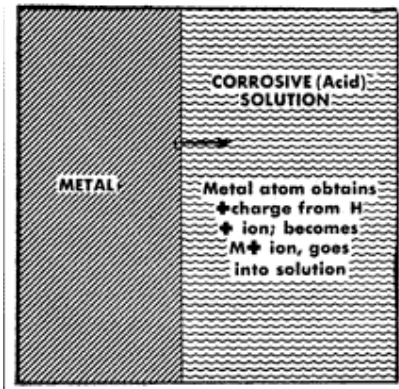
Related Topics

- [Material Properties](#) Material properties - density, heat capacity, viscosity and more - for gases, fluids and solids

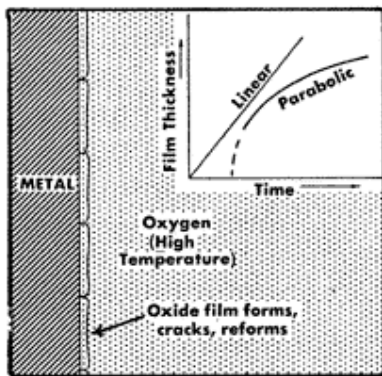
Related Documents

- [Electrode Potential and Galvanic Corrosion](#) An introduction to the electrochemical series and corrosion of metals
- [Piping Materials & Galvanic Corrosion](#) Connecting pipes of common piping materials may cause galvanic corrosion and serious damage

Other Types of Corrosion

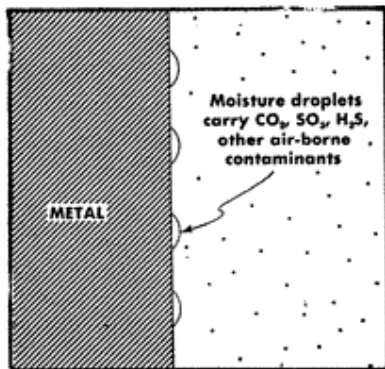


Direct Chemical Attack is also fundamentally electrochemical in nature. However, no current flow is detectable, nor are there any definite anodic or cathodic areas. The theoretical rate of a chemical attack can be affected by the formation of a protective film on the metal surface, through secondary reactions involving the products of corrosion, and the mechanical removal of protective films, such as by erosion, flexing of the metal surface, or by temperature changes.



Dry Oxidation and Tarnish result when the clean surfaces of metals are exposed to air or other gasses to form oxides or other compounds on the surface of the metals. Many of these films are invisible at room temperature, but at higher temperatures these films may reach considerable thickness. The rate of film growth is usually greater at higher temperatures.

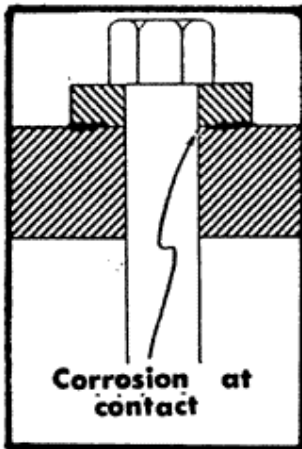
At higher temperatures, and more particularly under changes of temperature, the film may crack or spall to expose fresh metal to attack. Bending or stressing the metal can induce or increase the spalling. The presence of sulfur-bearing gasses may greatly increase the rate of attack. And the presence of moisture will accelerate attack, and complicate it by permitting electrolytic corrosion.



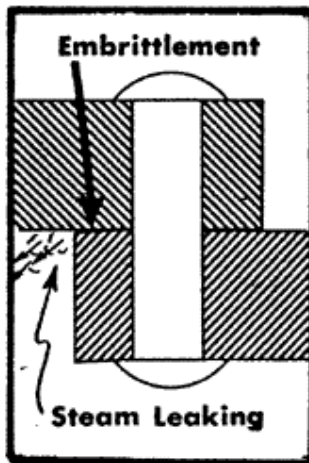
Atmospheric Corrosion combines electrochemical attack, direct chemical attack and oxidation. The many structures created by man which are subject to atmospheric corrosion, and the many specialized methods which have been developed to combat it, justify it for consideration as a basic type of corrosion.

Temperature changes, alternate wetting and drying, and the washing action of the elements of weather modify the rates of film removal.

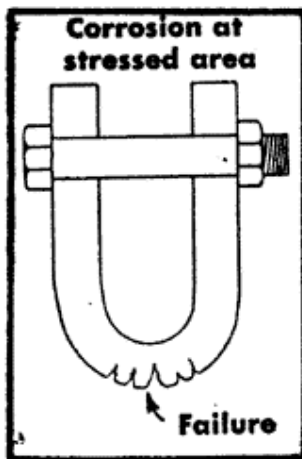
Rural atmospheres differ from industrial, and industrial atmospheres differ from one another to such an extent that special tests and consideration must be given for the optimum selection of protective coatings and application methods.



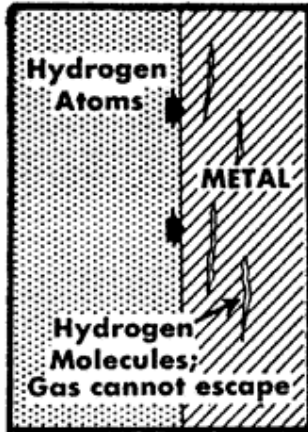
Crevice Corrosion is the attack on the surface of a metal partly shielded from contact with the corroding fluid, usually by a non-metallic materials. Typically, this is a concentration cell effect, the shielded area being anodic.



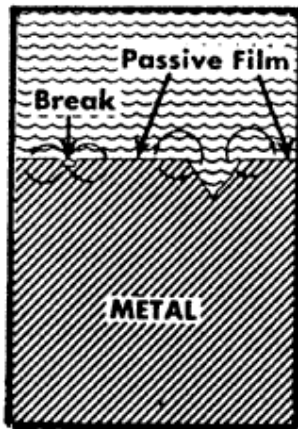
Caustic Embrittlement is usually the result of steam escaping through a crevice, such as between boiler plates or pipe flanges. The escaping water, usually in a fissure of steam, becomes highly concentrate, and the increased alkalinity of the concentrated water causes failure by stress corrosion.



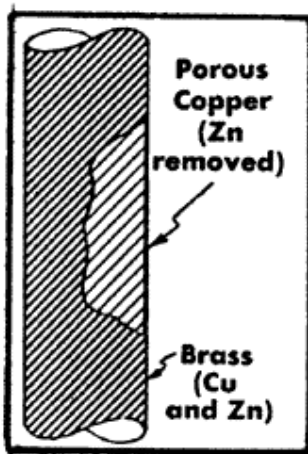
Stress Corrosion Cracking results when even a very small pit forms in a metal under stress. The concentrated stress may either deepen and extend the pit, or crack any protective film which might tend to form. Under continued exposure to the corrosive medium and stress, the crack extends by alternate corrosion and stress failure.



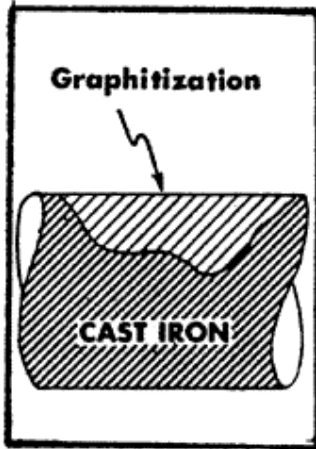
Hydrogen Embrittlement and hydrogen attack results when atomic hydrogen, contained in chemical and refinery processes or produced electrolytically by the process, penetrates onto the grain boundaries of steel producing microcracks, blistering and loss of ductility. The atomic hydrogen combines into molecules, cannot escape, resulting in blistering and laminations.



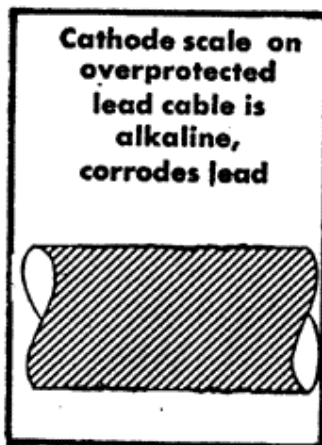
Pitting is caused by electrolytic corrosion and is the result of galvanic attack at the anodes of the metal surface. This can be seen where local failures in the film on stainless steel may be anodic to the remainder of the surface. This is more commonly seen on aluminum, and most commonly on steel in heterogeneous soil.



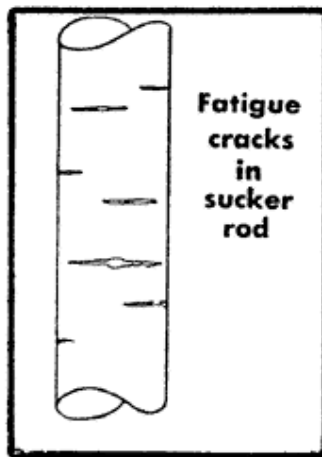
In **Dezincification**, one constituent of an alloy, such as the zinc in brass or bronze, may be selectively removed, leaving a porous replica of the original part. Often the whole alloy is initially dissolved, with one element redeposited in spongy form.



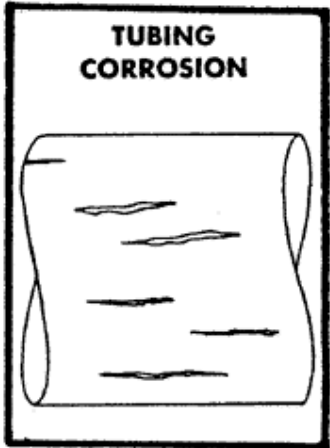
Graphitization is most often seen as the electrolytic corrosion of cast iron, and often takes a form very similar to the dezincification of brass. Iron is removed selectively, leaving a replica composed of carbon or graphite.



Cathodic Corrosion. Although the cathode of an electrolytic cell is not in itself corroded as a direct result of the electrolytic process, the cathode may be attacked by the reaction products formed by the process. A typical example is the corrosion of lead in the very alkaline environment produced at the cathode of cathodically protected lead cable.



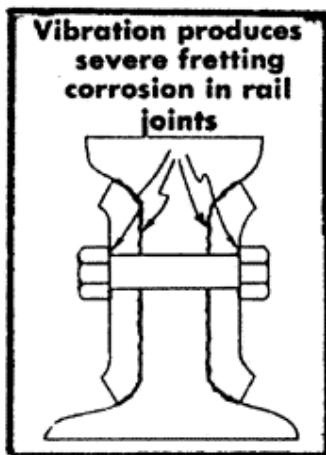
Corrosion Fatigue occurs when a metal is subjected to alternating stress and relief in a corrosive environment. Metal failure occurs much more rapidly under the alternating stress than under either stress or relief alone. Continuous removal of protective films, and the repeated exposures of clean metal by small stress failures cause corrosion fatigue.



Erosion Corrosion, as the name implies, occurs when the corrosion products which would normally afford a protective film are scoured off by moving fluids, particularly if the fluids contain abrasive materials. The erosion will expose clean metal, and develop a physical pattern so obviously a result of erosion that the corrosive factor may not be recognized.



Cavitation or Impingement Attack is a process which is very similar to erosion. In cavitation, collapsing gas bubbles in regions of turbulence and local pressure fluctuations may activate serious corrosion. Condenser tubes and pump impellers are subject to this type of attack.

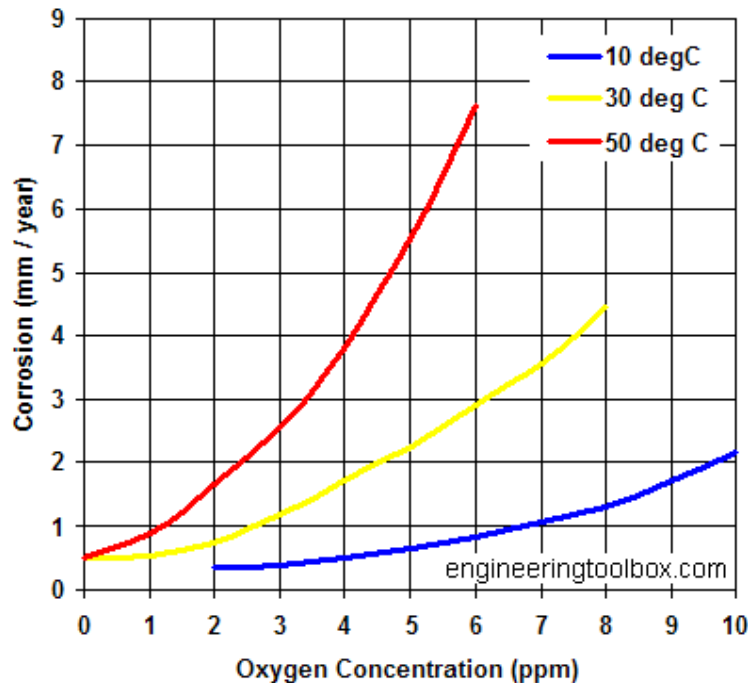


Fretting Corrosion. Metal surfaces in close physical contact, in a corrosive environment, and subjected to vibration, can accelerate corrosion attack by the continuous removal of protective films. Machine parts with small relative motion and high unit loads are subject to fretting corrosion.

Oxygen and steel pipe corrosion

Oxygen concentration, temperature and corrosion of steel pipes

Effects of oxygen concentration and temperature on the corrosion of low-carbon steel pipes are indicated in the diagram below.



- $1 \text{ mm} = 0.03937 \text{ in}$
- $T(^{\circ}\text{F}) = [T(^{\circ}\text{C})](9/5) + 32$

Related Topics

- [Corrosion](#) Corrosion in piping systems - caused by thermodynamic and electrochemical processes - corrosion problems and methods of protection and prevention

Related Documents

- [Electrode Potential and Galvanic Corrosion](#) An introduction to the electrochemical series and corrosion of metals
- [Metals and Corrosion Resistance](#) Common metals and their corrosion resistance to aggressive fluids as acids, bases and more
- [Corrosion Protection of Pipes](#) Corrosion protection tutorial of piping systems
- [Types of Corrosion](#) Uniform, pitting, galvanic, crevice, concentration cell and graphitic corrosion
- [ppm - parts per million](#) ppm - parts per million - is commonly used as unit of concentration