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# Tribocorrosion

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Additional information is available at the end of the chapter

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## Abstract

This chapter includes some of the definitions of corrosion as important problem in many industries. The main forms of corrosion have been discussed in this chapter which depended on the appearance of corroded surface with some details of their mechanisms and how can prevent them. This chapter reviews tribocorrosion and explains the simplest method for tribocorrosion test by certain set-up using electrochemical test with three electrodes. Tribocorrosion test is needs to special arrangement of cell to be predicted which also has been mentioned in this chapter.

**Keywords:** tribocorrosion, corrosion forms, electrochemical test, wear rate

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## 1. Introduction

Many materials such as metals and alloys, plastics, rubber, ceramics, composites, wood, etc. have a wide range of applications as a constructional material, and the selection of an appropriate material for a given application is the important. Generally, there are no general rules that govern the choice of a 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; frequently, the ultimate decision is determined by economics rather than by properties.

There are many properties that may be limited by the selection of the proper material, which includes mechanical, physical and chemical properties. Mechanical and physical properties can be expressed in terms of constants, while the chemical property is dependent on the presented environmental conditions during service.

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The term corrosion of non-metallic materials refers to their deterioration by chemical media, but a similar concept is not necessarily applicable to metals. Many authorities [1] consider that the term metallic corrosion includes all interactions of a metal or an alloy with its environment. Other definition of corrosion refers to the undesirable deterioration of a metal or an alloy. This definition is also applicable to non-metallic materials such as glass, concrete, etc. [2].

On the other hand, Fontana and Staehle defined the term [3] 'Corrosion' as the reaction of metals, glasses, ionic solids, polymeric solids and composites with its environments (such as liquid metals, gases, non-aqueous electrolytes and other non-aqueous solutions) [4]. Vermilyea defined corrosion as remove atoms or molecules from the material [5]. Finally, Evans defined the corrosion as a chemical thermodynamic and kinetic process, causing the introduction of electrochemical cells which deteriorate the lattice structure of a material [6].

## 2. Forms of corrosion

Corrosion forms can be classified according to the appearance of the corroded surface. This classification identifies the corrosion failure as a corrosion form by visual inspection, either by the naked eye or possibly by a magnifying glass or microscope. Since each form of corrosion has its characteristic causes, important steps to a complete diagnosis of failure can often be taken after a simple visual inspection [7].

On this basis, the following corrosion forms can be defined as follows:

1. Uniform (general) corrosion.
2. Galvanic (two-metal) corrosion.
3. Thermogalvanic corrosion.
4. Crevice corrosion (including deposit corrosion).
5. Pitting, pitting corrosion.
6. Intergranular corrosion (including exfoliation).
7. Selective attack, selective leaching (de-alloying).
8. Erosion corrosion.
9. Cavitation corrosion.
10. Fretting corrosion.
11. Stress corrosion cracking.
12. Corrosion fatigue.

A simple illustration of the various forms of corrosion is shown in **Figure 1**.

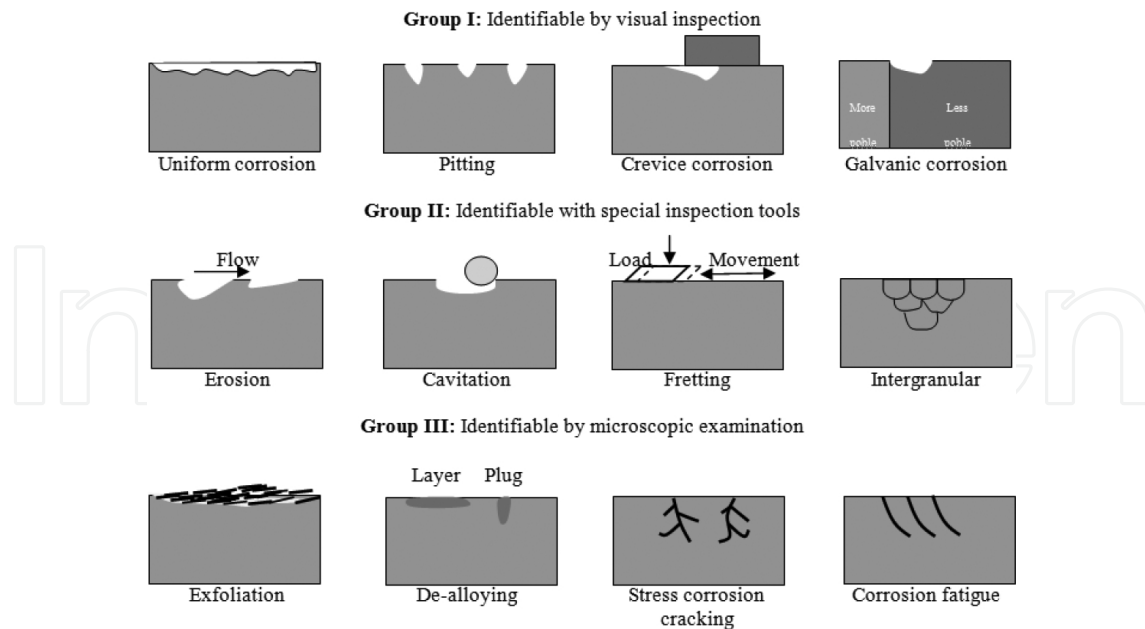


Figure 1. Main forms of corrosion grouped by their ease of recognition.

## 2.1. Uniform (general) corrosion

By definition, attacks of this type are quite evenly distributed over the surface, and consequently they lead to a relatively uniform thickness reduction. The necessary conditions for uniform corrosion have already been presented. Homogeneous materials without a significant passivation tendency in the actual environment are liable to this form of corrosion. The most common form of corrosion is uniform corrosion, but it is not a dangerous type of attack due to the following:

- By simple tests, we can predict the reduction in thickness and then we can add the corrosion allowance.
- Reducing the corrosion rate to acceptable level may be achieved by changing the environment or material or applying coatings and cathodic protection.

## 2.2. Galvanic corrosion

This form of corrosion occurs with contact between a more noble metal and a less noble one in the presence of an electrolyte, where the latter is oxidized and the other is reduced.

Galvanic corrosion can be prevented or made harmless in several ways:

- Select the proper material.
- Using weld consumable is more noble than the base metal.
- Avoiding the combination of a large area of cathode with a small area of anode.
- Using insulation materials to insulate the parts in galvanic couples.

5. Applying metallic coating on one of the materials similar to the other material.
6. Applying paints.
7. Using cathodic protection.
8. Adding corrosion inhibitors.
9. Preventing the access of humidity to be present between the contacted materials.
10. Avoiding electrolytic deposition of a more noble material on a less noble one.

### 2.3. Thermogalvanic corrosion

Thermogalvanic corrosion takes place when a material is subject to a temperature gradient in a corrosive environment. The hot surface is the anode and the cold one the cathode (see **Figure 2**) because of the anodic properties that are dependent on the temperature, as well as the variation in temperature affects the cathodic reaction in corrosion process.



**Figure 2.** Thermogalvanic corrosion.

This form of corrosion requires little information about the service conditions to distinguish between thermogalvanic and other forms [7]. Thermogalvanic corrosion can be prevented by several ways:

1. Selecting the proper design.
2. Avoiding uneven heating/cooling.
3. Checking the continuous insulation for heat-insulated pipes.
4. Applying cathodic protection or coatings.

### 2.4. Crevice corrosion

This form of corrosion concentrates in crevices that are sufficiently wide for liquid to penetrate into it and sufficiently narrow for the liquid to be stagnant. This attack can be seen beneath flange gaskets, paint-coating edges, nail and screw heads, tube plates in heat exchangers, in overlap joints and between tubes, etc. Most materials undergo crevice corrosion that is passive beforehand, or can easily be passivated such as stainless steels, aluminium, unalloyed or low alloy steels in corrosive media containing chlorides and can also occur in other salt solutions. This form of corrosion occurs in stagnant or slowly flowing seawater and even at higher velocities too [7].

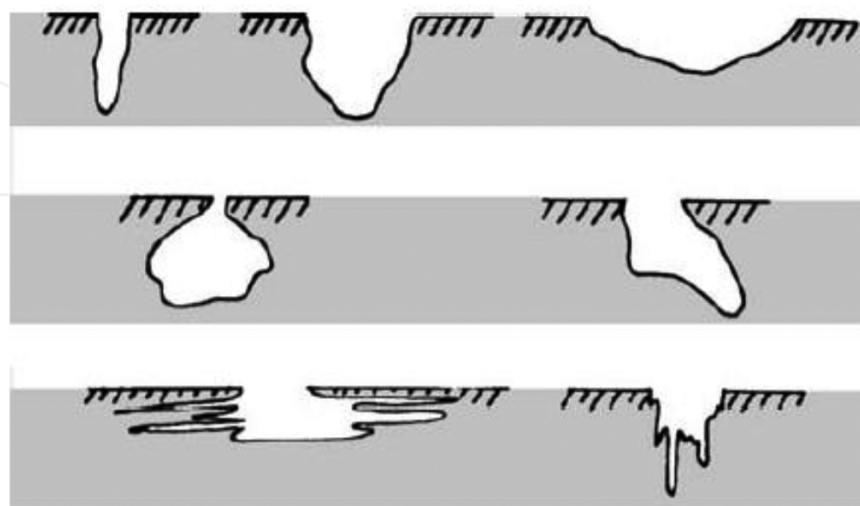
A special form of crevice corrosion that can develop on steel, aluminium and magnesium beneath a protecting film of lacquer, enamel, phosphate or metal is the so-called filiform corrosion, which leads to a characteristic stripe pattern. It has been observed most frequently in cans exposed to the atmosphere. Crevice corrosion is affected by several factors, of a metallurgical, environmental, electrochemical, surface physical, and last but not least a geometrical nature. One of the most important factors is the crevice gap.

Crevice corrosion can be prevented or reduced by several ways:

1. Selecting a proper material.
2. Avoiding crevices and deposition as far as possible.
3. Applying cathodic protection.
4. Measures for preventing deposition are as follows:
  - a. Inspection and cleaning during and between service periods.
  - b. Separation of solid material from flowing media in process plants.
  - c. Gravel filling around buried piping and structures.

## 2.5. Pitting corrosion

Pitting corrosion occurs on more or less passivated metals and alloys in environments containing halogen ions. The characterization of pitting shows narrow pits with a radius of the same order of magnitude as, or less than, the depth, and with different shapes of pits as illustrated in **Figure 3**. This form of corrosion is dangerous because penetration can occur without a clear warning in addition to difficult prediction of the pit growth.



**Figure 3.** Different shapes of corrosion pits.

Determining pitting corrosion in laboratory is difficult because it needs longer time for the pit to be grown, for example, many months before the pits are visible in addition to the critical size of the pit, that is, the maximum pit depth, which increases with increasing surface area.

Most materials liable to pitting are aluminium in environments containing chloride, stainless steels in strongly oxidizing chloride solutions, and copper and its alloys in fresh water at pH <7.4 and temperatures >60°C, and when the ratio of sulphate to carbonate is relatively high.

The mechanism of pitting consists of the following stages:

1. Local breakdown of passivity (pit nucleation).
2. Early pit growth.
3. Late or stable pit growth.
4. Repassivation (if possible).

There are many theories to interpret the mechanism of pitting: some authors suggested that pitting is initiated by the adsorption of halide ions that penetrate the passive film at weak points of the oxide film, for example, at irregularities in the oxide structure due to grain boundaries or inclusions in the metal. This absorption leads to strong increase of the ion conductivity in the oxide film [7].

Other authors suggested that the initial adsorption of aggressive anions at the oxide surface catalytically enhances the transfer of metal cations from the oxide to the electrolyte and then local thinning of the oxide film can occur. A third theory suggests that the attacks may be start at defects in the passive layer and then introduce.

The next stage proceeds essentially by the anodic dissolution inside the pit (at the bottom) and the cathodic reaction outside the pit. Metal chlorides form at the bottom and then hydrolyze to produce an acidic solution, which also may allow an additional cathodic reaction represented by the reduction of hydrogen ions. Metal cations from the dissolution reaction migrate and diffuse toward the mouth of the pit where they react with OH<sup>-</sup> ions to form metal hydroxide deposits that may cover the pit.

There are many factors affecting pitting as follows:

- a. pH and chloride concentration: the pitting potential and pitting resistance normally increase with increasing pH and decreasing chloride concentration. The negative effect of increased Cl<sup>-</sup> concentration on the pitting potential  $E_p$  is of great significance. For an 18-8 CrNi steel,  $E_p$  can be expressed by

$$E_p = 0.168 - 0.0881 \log a_{Cl^-} \quad (1)$$

where  $a_{Cl^-}$  is the activity of chloride ions.

While for aluminium

$$E_p = -0.504 - 0.124 \log a_{Cr} \quad (2)$$

- b. Flow velocity: this factor has a complex effect on corrosion rate. At high velocity, washing away the corrosive environment in the pit can occur, but it leads to increase the transport of oxygen to the active area, so the pit may be passivated before it gets the chance to grow. Then, the cover of pits washes away to a higher extent, and pit initiation in the neighbourhood of an active pit occurs more easily. The result of this process is smaller but more numerous pits, which makes pitting corrosion less serious.
- c. The gravity force: heavy pitting occurs on horizontal top surfaces, while hard pitting occurs on underside surfaces. Vertical surfaces are intermediate as to the extent of pitting due to the higher density of corrosive environment in the pits.
- d.  $\text{Cu}^{2+}$  and  $\text{Fe}^{3+}$  ions have more noble potentials that cause initiation of pit and acceleration of pit growth.
- e. Metallurgical properties: some impurities, inclusions and secondary phase participate in the localization of pits on materials because they act as efficient cathodes.
- f. The insulating ability of the oxide: the oxide layer plays a good role in slowing the growth of pits if it has efficient insulation.
- g. Surface roughness: the smooth surfaces get few, large pits while rough surfaces get numerous smaller pits.
- h. Temperature: pitting potential decreases with increasing temperature.
- i. Galvanic contact: the tendency of pitting increases with contact to more noble material.

There are many methods to prevent pitting corrosion:

1. Selecting a proper material such as aluminium alloys with magnesium (e.g. AlMg 4.5 Mn), stainless steels with sufficient content of Cr, Ni and Mo, some Ni alloys and titanium.
2. Applying cathodic protection using sacrificial anodes of Zn or Al alloys.
3. Changing the environment.

## 2.6. Intergranular corrosion

Intergranular corrosion occurs on or at grain boundaries and it is a dangerous form of corrosion due to decreasing of the cohesive forces between the grains and it cannot withstand tensile stresses, followed by reducing the toughness of the material, and fracture can occur without warning. Finally, the grains may fall out to form pits or grooves on the surface.

This form of corrosion is presented in the presence of galvanic elements in or at the grain boundaries, which may be the impurities that segregate at the grain boundaries, larger amount of a dissolved alloying element at the grain boundaries or smaller amount of a dissolved alloying element at the grain boundaries.

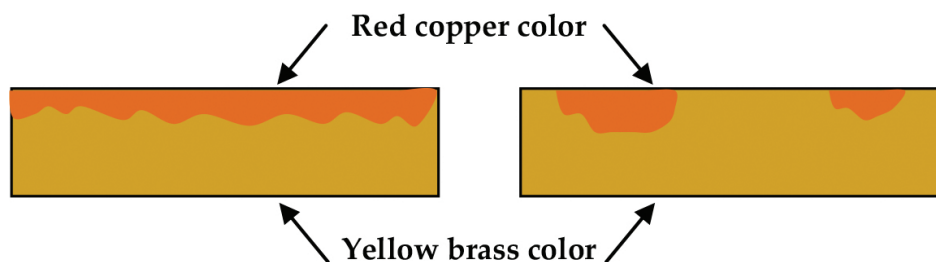


In most cases, the zone of less noble material in/at the grain boundaries acts as an anode and the other parts of the surface form the cathode. But in some cases, precipitates at the grain boundaries may be more noble than the bulk material and then they act as efficient local cathodes [7].

## 2.7. Selective corrosion (selective leaching)

This form of corrosion occurs in alloys that contain clearly less noble metal than the other. In this attack, the less noble element is removed from the material leaving a porous material with very low strength and ductility. The selectively corroded areas are sometimes covered with corrosion products or other deposits and it is difficult to be discovered. Serious material failure may therefore occur without warning. The most common example of selective corrosion is dezincification of brass (**Figure 4**), which occurs by removing the zinc from the alloy and retaining the copper. The Zn-depleted regions have a characteristically red copper colour in contrast to the original yellow brass. Dezincification occurs in two forms:

- a. Uniform dezincification which occurs in the presence of high Zn content and acidic solutions.
- b. Localized dezincification which occurs in the presence of lower Zn content and in neutral, alkaline and slightly acidic solutions.



**Figure 4.** (a) Uniform dezincification and (b) Localized dezincification of brass.

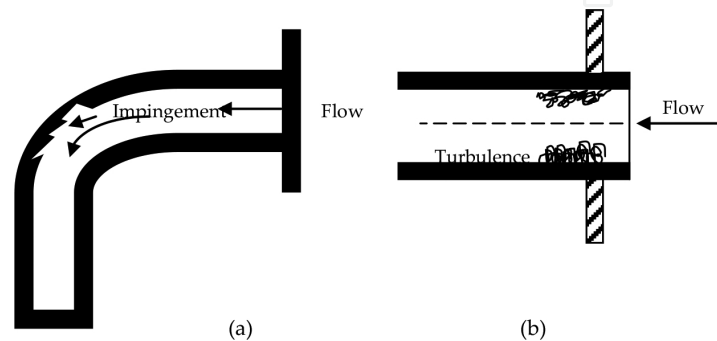
The dezincification increases with increasing Zn content and temperature and is promoted by a stagnant solution, porous surface layers and oxygen in the corrosive medium.

## 2.8. Erosion and abrasion corrosion

Erosion corrosion occurs in metallic material immersed in corrosive fluid with a relative movement between the material and medium by wearing of the corrosion products, deposits or salt precipitates, which lead to the metallic surface being metallically clean and more active. Erosion corrosion accompanies with pure mechanical erosion, by tearing out the solid particles in the fluid and causing plastic deformation and leaving grooves or pits with a pattern determined by the flow direction and the local flow conditions. The corrosive fluid in erosion may be two-phase or multiphase flow, that is, liquid-gas and liquid-solid particle flow. This form of corrosion takes place in pumps, turbine parts, propellers, valves, heat exchanger tubes, bends, nozzles and equipment exposed to liquid sputter or jets [8].

The mechanism of erosion and abrasion corrosion can be divided into three types:

- a. Impingement corrosion which occurs in two-phase or multiphase flow as shown in **Figure 5a**.
- b. Turbulence corrosion which occurs in the regions of strong turbulence such as the inlet end of heat exchanger tubes as shown in **Figure 5b**.
- c. Removal of corrosion products leads to increase in corrosion by wearing the particles moving along the corroding surface, or by wearing between components in moving contacts with each other.



**Figure 5.** Type of erosion: (a) Impingement and (b) turbulence corrosion (nest).

In some cases, deposits may also be removed by high shear stresses. The shear stresses may vary considerably as a consequence of flow fluctuations or repeated impacts. The pure erosion rate can be expressed by the following formula:

$$W \text{ (mm/y)} = K_{\text{mat}} \times K_{\text{env}} \times c \times v^n \times f(\beta) \quad (3)$$

where  $K_{\text{mat}}$  is a material factor depending on a complex manner on (among other properties) hardness and ductility of the substrate,  $K_{\text{env}}$  is an environmental factor that includes the effects of size, shape (sharpness), density and hardness of the particles,  $c$  is the concentration of particles,  $n$  is the so-called velocity exponent,  $v$  is the particle velocity and  $\beta$  the impact angle. This equation is very useful in connection with erosion testing in the laboratory [7].

## 2.9. Cavitation corrosion

This corrosion form is similar to erosion corrosion and its appearance is deep pits grown perpendicularly to the surface. These pits localize close to each other or grow together over smaller or larger areas to produce a rough and spongy surface.

Cavitation corrosion occurs at high-flow velocities and fluid dynamic conditions causing large pressure variations, as often is the case for water turbines, pump rotors, propellers and the external surface of wet cylinder linings in diesel engines. The mechanism starts by rapidly collapsing vapour bubbles formed in low-pressure zones when they suddenly enter a high-

pressure zone. This collapse causes a concentrated and intense impact against the metal, which induces the high local stress and then local plastic deformation of the material can occur. Repeating these steps leads to microscopic fatigue and crack formation, and subsequent removal of particles from the material itself.

### **2.10. Fretting corrosion (fretting oxidation)**

Fretting corrosion occurs in fitting components in the presence of slightly relative motion (slip) between them. This motion may be ranged from less than a nanometre to several micrometres. This form of corrosion takes place in joints, press fits, and other components which subjected to load.

The fretting corrosion involves mechanical contribution including elements of adhesive wear and microscopic fatigue crack development, and then delamination in metal lattice can occur. The formed debris adheres to the fretting surfaces and tappers between these, and may partly escape [7].

The mechanism of fretting corrosion proposes that the relative motion between the parts may promote oxidation of the surface. This formed oxide film is partly worn off, and the fresh metal surface is highly active and oxidizes again. The repeating of this circular process leads to fretting damage. Another explanation is that, firstly, metal particles are released from the metal surface by adhesive wear, and then the particles oxidize forming debris, which moves out from the interfacial area between the components. Repeating of this process leads to deterioration at a high rate.

Fretting corrosion may be reduced or prevented by the following:

1. Use of lubricants, gaskets or sealing materials, which hinder the access of oxygen and then decrease adhesive wear.
2. Using proper and hard materials in components.
3. Applying coating on soft material.

### **2.11. Stress corrosion cracking**

Stress corrosion cracking occurs by crack formation caused by static tensile stresses and corrosion. This stresses may be formed by external or internal stresses. The initial crack is discoloured and brittle, dull or darkened by oxide layers, and the crack may be discovered as a pit being narrow, and filled or covered by corrosion products. The factors affecting stress corrosion cracking are as follows:

1. Environmental and electrochemical factors.
2. Metallurgical factors.
3. Mechanical stress and strain.

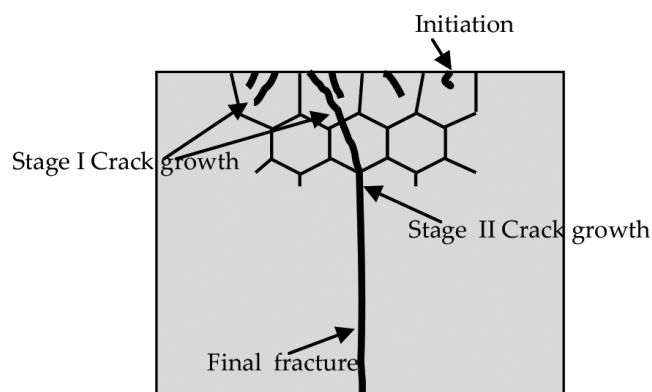
Stress corrosion cracking can be prevented by affecting one or more of the above factors as follows:

- a. Selecting the right material.
- b. Achieve annealing to remove residual stresses in materials to below the threshold values.
- c. Changing the environment to be less corrosive.
- d. Applying cathodic protection by sacrificial anodes.
- e. Adding corrosion inhibitors.

## 2.12. Corrosion fatigue

Corrosion fatigue is crack formation due to varying stresses combined with corrosion. The crack development can be divided into four stages:

1. Initiation.
2. Crack growth stage I, with crack growth direction about  $45^\circ$  relative to the tensile stress direction.
3. Crack growth stage II.
4. Fast fracture as shown in **Figure 6**.



**Figure 6.** The stages of development of a fatigue fracture.

The mechanism of corrosion fatigue follows the following steps:

- i. Stress concentrations in certain site lead to form corrosion pit and groove.
- ii. Mutual acceleration of corrosion and mechanical deterioration.
- iii. Absorption and adsorption of species from the environment, including absorption of hydrogen and resulting embrittlement.

## 3. Tribocorrosion

Tribocorrosion is a material degradation resulting from simultaneous action of wear and corrosion. Under these conditions, the material selection is a challenge since the material has

to effectively withstand wear, corrosion and their combined effect. The importance of tribology and tribocorrosion is to know the equipment failure due to wear and corrosion. Potential financial savings in the industry by reduction in maintenance, downtime, breakdowns and replacement of equipment are considerable [8–10].

Application of good practices and known tribological principles can save industry and society from this cost. Research within tribology contributes thereby to an increase in efficiency and availability of production processes, longer lifetime of equipment and safer operation [9–11].

Wear and friction together with lubrication form the scientific discipline called 'tribology'. A major area of tribology is to design surfaces sliding and rolling against each other in such a way that friction and wear are minimized. By reducing friction and wear, many benefits, both economical and environmental, can be achieved in several technological fields of application. When developing technical equipment, the choice of material for a certain detail is often a compromise. Usually, it is not possible to optimize all material properties (mechanical, tribological, electrical and chemical) at the same time. The best material choice with respect to one property might not be possible to use due to poor performance with respect to another property [9, 10].

Sometimes the application of any material needs to knowledge about the surface of the component. For instance, low wear and low friction are mainly controlled by the surface properties. An elegant way to achieve this can be to use a material with poor tribological performance but otherwise optimal properties, for example, high toughness, low weight or low price, as base material and coat it with a thin layer of a wear resistant material with low friction coefficient.

Wear is very complex phenomenon and usually involved progressive loss of material. Wear processes can be categorized into five main forms:

**Abrasion Wear:** The definition of abrasion wear is produced by a hard/sharp particle or protuberance imposed on and moving on a softer surface.

**Adhesion Wear:** It is defined as localized bonding between contacting solids leading to material transfer or loss from either contacting surface.

**Corrosion Wear:** Corrosive wear occurs when the sliding of surfaces is in corrosive environment. This wear action generally takes place in two stages. First, there is corrosive attack on the surface. Then, the sliding action wears off the corroded surface film.

**Surface fatigue:** Contacts between asperities with very high local stress that are repeated a large number of times during sliding or rolling, with or without lubrication. High plastic deformation causes crack initiation, crack growth and fracture.

**Erosion Wear:** As illustrated in previous section, the erosion is referred to the continuous loss of a solid surface due to mechanical interaction between the surface and a fluid, which may be a multiphase fluid or impinging solid or liquid particles.

Accurate prediction of the rate of erosion requires detailed investigation of the solid particle motion before and after impact. The difficulty arises mainly from the fact that most flows

occurring in industrial processes are turbulent, which makes the particle path and impact characteristics difficult to predict [12].

#### 4. Measurement of corrosion under normal conditions

The exposure of material to corrosive medium leads to reduction in weight or thickness of material. This reduction in weight or thickness refers to corrosion rate measurement. The common expression of this loss is mils per year (mpy), inches per year (ipy) and milligrams per square decimeter per day (mdd). Conversion of ipy to mdd or vice versa requires knowledge of the metal density.

To determine the corrosion rate, a specimen with known surface area is exposed to the corrosive environment for a period of time and then the loss in weight has been determined by the weighting of corroded specimen. The corrosion rate (C.R.) of the metal can be calculated using the formula:

$$C.R. = \frac{\Delta W}{\text{area} \cdot \text{time}} (\text{mdd, gmd} \dots) \quad (4)$$

$$C.R.(\text{mpy}) = \frac{22.237 \Delta W}{\text{density} \cdot \text{area} \cdot \text{time}} \quad (5)$$

where  $\Delta W$  is in grams, density in  $\text{g} \cdot \text{cm}^{-3}$ , area in  $\text{inch}^2$  and time in days, and then weight loss to penetration loss can be converted by the following relation:

$$C.R.(\text{mpy}) = \frac{1.44}{\text{density}} C.R.(\text{mdd}) \quad (6)$$

According to Faraday's law:

$$Q = \frac{nFW}{M} \quad (7)$$

where  $Q$  is the charge passed (Coulombs),  $n$  is the number of electrons involved in the electrochemical reaction,  $F$  is Faraday constant,  $W$  is the weight of electroactive species (g) and  $M$  is the molecular weight (g).

$$W = \frac{QM}{nF} \quad (8)$$

$$W = \frac{QE.W.}{F} = \frac{it(E.W.)}{F} \quad (9)$$

Or

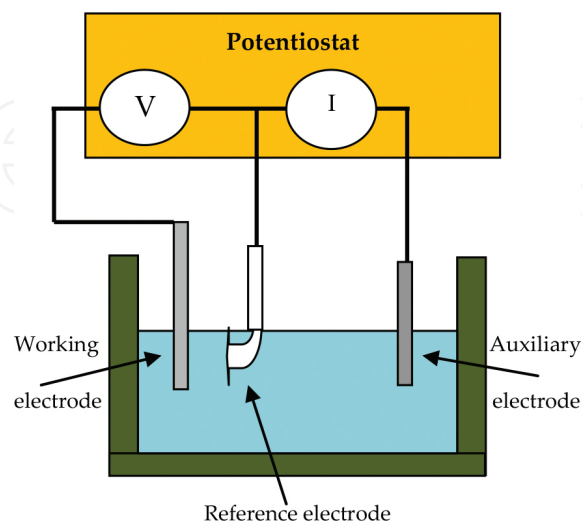
$$\frac{W}{t} = \text{Corrosion Rate (C.R.)} \left( \frac{\text{g}}{\text{s}} \right) \quad (10)$$

$$\text{C.R.} \left( \frac{\text{cm}}{\text{s}} \right) = \frac{i(E.W.)}{dFA} \quad (11)$$

$$\text{C.R. (mpy)} = \frac{i(E.W.) \times 31.6 \times 6 \times 10^6 \times 10^3}{dFA \times 2.5 \times 10^6} \quad (12)$$

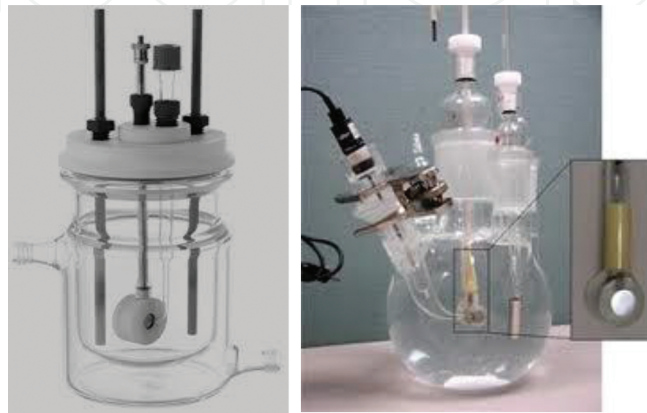
$$\text{C.R. (mpy)} = \frac{0.13 \times i_{\text{corr}} (E.W.)}{d} \quad (13)$$

where mpy is milli-inches per year,  $i_{\text{corr}}$  is the corrosion current density ( $\mu\text{A}\cdot\text{cm}^{-2}$ ), E.W. is the equivalent weight of the corroding species (g) and  $d$  is the density of the corroding species ( $\text{g}\cdot\text{cm}^{-3}$ ).



**Figure 7.** Arrangement of electrodes in corrosion test.

The most exact method to determine corrosion rate is achieved using Potentiostat. This device controls the voltage difference between a working electrode and a reference electrode. Three electrodes used in this method include an auxiliary electrode (such as Pt and Graphite) to inject the current into the cell, and then the current flow will be recorded by Potentiostat, another electrode is a reference electrode (such as Calomel and Ag/AgCl) to measure the potential of a specimen, which represents the third electrode as working electrode. These three electrodes are arranged as in **Figure 7**, which are connected to Potentiostat. This arrangement is obtained using electrochemical cell as in **Figure 8**.



**Figure 8.** Standard electrochemical cells.

#### 4.1. Measurement of corrosion potential ( $E_{\text{corr}}$ )

The potential of the specimen (working electrode) is measured with respect to a reference electrode, which is kept in a separate container and connected electrically with the working electrode placed in a container in contact with the electrolyte via a salt bridge (Luggin). The potential of the working electrode is measured by a voltmeter, which is connected between the working and the reference electrode through the negative terminal of the voltmeter connected to the working electrode and the positive to the reference electrode. The corrosion potential is also referred to as the open-circuit potential (OCP) as the metal surface corrodes freely and it is called mixed corrosion potential. After applying voltages with  $\pm 200$  mV around OCP, we can get polarization behaviour of working electrode in environment, which is immersed in it. The obtained polarization is the behaviour of the material in active region only, and by drawing the tangents to the anodic and cathodic curves, both the corrosion current density ( $i_{\text{corr}}$ ) and corrosion potential ( $E_{\text{corr}}$ ) can be determined (which is extrapolated to the point of intersection) using the four-point method [13].

#### 4.2. Measurement of corrosion current density ( $i_{\text{corr}}$ )

When applying the voltages on working electrode through Potentiostat, the current of working electrode can be recorded by auxiliary electrode through ammeter, which is connected between the working and auxiliary (counter) electrode.



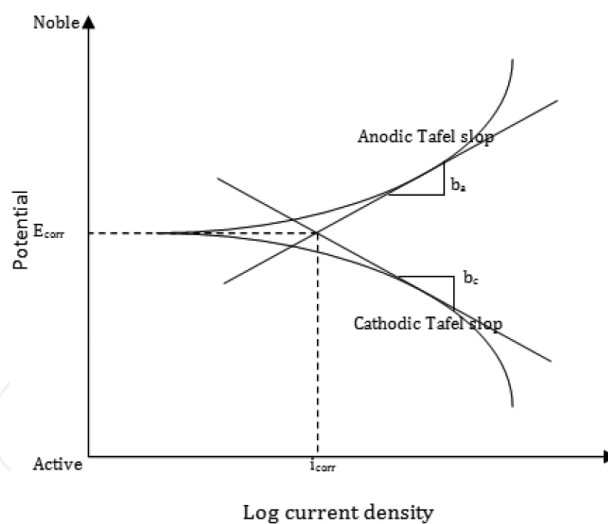
The anodic polarization is tended in the noble direction starting from the OCP and the overpotential is positive, since the polarized potential is more positive than the equilibrium potential. The cathodic polarization has a small overpotential and is tended in the active direction; however, at a sufficiently large overpotential, only one reaction, either anodic or cathodic, takes place depending on which direction the potential is impressed [13].

When a metal is corroded in its environment, the anodic process (represented by oxidation reaction) intersects the cathodic process (represented by reduction reaction) at the corrosion potential ( $E_{\text{corr}}$ ). The current corresponding to  $i_{\text{corr}}$  is the corrosion current density ( $i_{\text{corr}}$ ), which can be determined from the intersection with X-axis.

### 4.3. Determination of corrosion rate by electrochemical measurements

#### 4.3.1. Tafel extrapolation method

When the polarization curves for the anodic and cathodic reactions are obtained by applying potentials about  $\pm 200$  mV around OCP, the corrosion potential and THE corresponding current will be recorded. Plotting the logarithms of current ( $\log I$ ) versus potential and extrapolating the currents in the two Tafel regions gives the corrosion potential and the corrosion current density  $i_{\text{corr}}$  and this is the principle of Tafel technique as illustrated in **Figure 9**. By knowing  $i_{\text{corr}}$ , the rate of corrosion can be calculated in desired units by using Faraday's law [13].



**Figure 9.** A hypothetical Tafel plot.

#### 4.3.2. Polarization resistance (linear polarization) method

In this technique, the potential-current density plot gives approximately linear in a region of within  $\pm 10$  mV of the corrosion potential with slope represented by  $(\Delta E)/(\Delta I)$ . When both anodic and cathodic reactions proceed in the vicinity of corrosion potential ( $E_{\text{corr}}$ ), they are exponentially dependent upon the applied potential. Over a small potential range (20 mV),

the exponents are linearized and an approximate linear potential-current relationship is obtained [13].

Polarization resistance ( $R_p$ ) of a corroding metal is defined using Ohm's law as the slope of a potential (E) versus current density (log i) plot at the corrosion potential ( $E_{corr}$ ). Here,  $R_p = (\Delta E)/(\Delta I)$  at  $\Delta E = 0$ . By measuring this slope, the rate of corrosion can be measured. The correlation between  $i_{corr}$  and slope  $(dI)/(dE)$  is given by (Figure 10):

$$\frac{\Delta E}{\Delta I} = \frac{b_a b_c}{2.3 i_{corr} (b_a + b_c)} \quad (14)$$

where  $b_a$  and  $b_c$  are Tafel slopes.

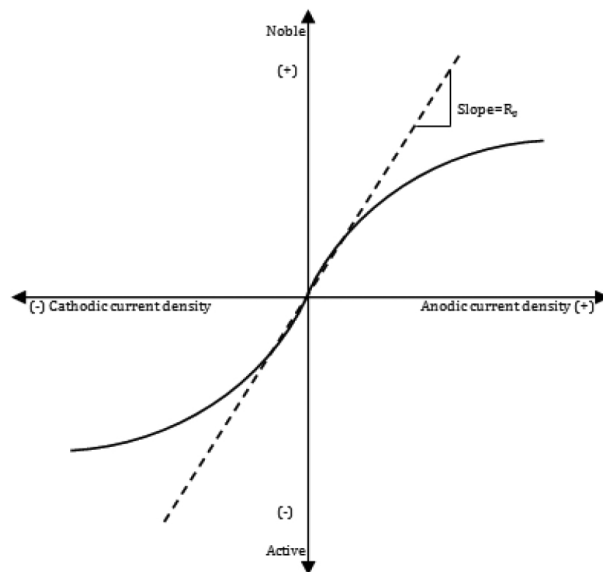
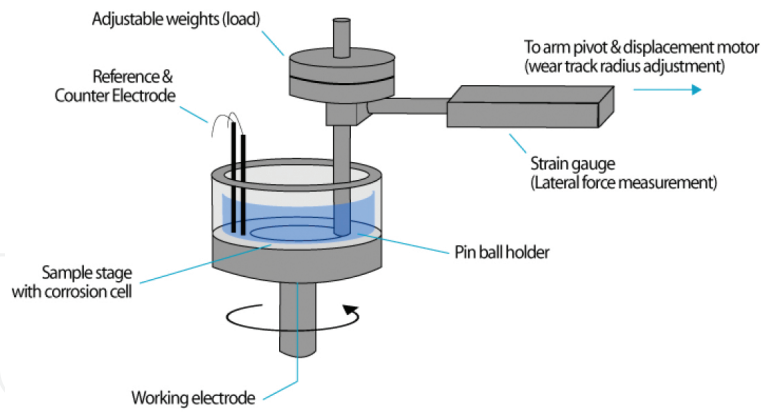


Figure 10. Hypothetical linear polarization plot.

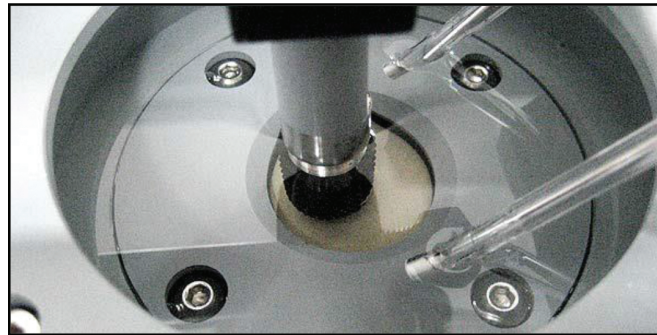
## 5. Tribocorrosion test principle

Tribocorrosion test can be achieved depending on the basic principles of electrochemical test using Potentiostat. This technique requires three electrodes: counter, reference and working electrode. The working electrode (experimental specimen) is mounted as O-ring with a known surface area, which is exposed to the electrolyte (see Figures 11 and 12).

Tribocorrosion test is achieved by applying a known force on a pin, or a ball, in contact with the surface of specimen to create the wear, and then OCP, linear polarization and cyclic polarization can be recorded in situ. The wear rate of the material calculates from the volume lost.



**Figure 11.** Schematic of the tribocorrosion test.



**Figure 12.** Tribocorrosion module of the pin-on-disk tribometer.

### 5.1. Tribocorrosion test at open-circuit potential

Using three-electrode cell as illustrated in **Figure 11**, a platinum wire, a Ag/AgCl, NaCl (sat) and mounted specimen with Tribometer are used. After applying the force on material surface, OCP can be recorded beyond maintaining the specimen in the electrolyte for 1 h to obtain a stable OCP, followed by the tribocorrosion test for 10 min (1000 cycles). After the wear process, the sample was kept in the solution for another 10 min to allow surface repassivation. Dry wear tests must be performed at the same condition for comparison.

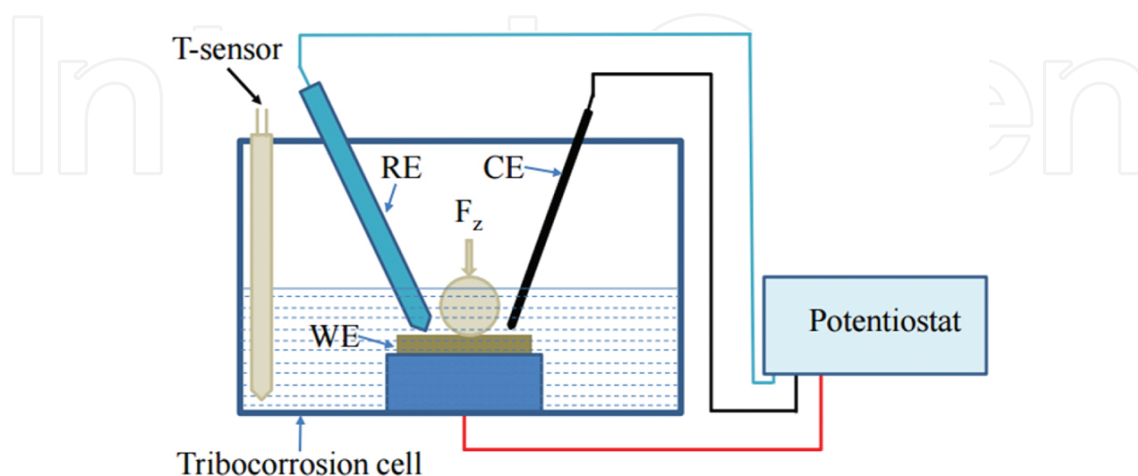
### 5.2. Tribocorrosion test at controlled potentials

Cathodic and anodic polarization conditions are carried out after OCP test by changing the applied potentials  $\pm 200$  mV around OCP to show the acceleration of corrosion process by wear. The evolution of the current was monitored before, during and after the wear process. The wear rate,  $K$ , was evaluated using the formula:

$$K = \frac{V}{F \times S} = \frac{A}{F \times n} \quad (15)$$

where  $V$  is the worn volume,  $F$  is the normal load,  $s$  is the sliding distance,  $A$  is the cross-section area of the wear track and  $n$  is the number of revolution.

The set-up of simultaneous measurements of wear and electrochemical parameters (open-circuit potential) is shown in **Figure 13**.



**Figure 13.** Schematic tribocorrosion test, WE: working electrode, RE: reference electrode and CE: auxiliary (counter) electrode.

### 5.3. Tribocorrosion tests at anodic/cathodic potential

In order to further emphasize and demonstrate the contribution of corrosion in tribocorrosion, the tribocorrosion tests are performed at anodic/cathodic potentials. The synergistic effect of severe corrosion and wear leads to the formation of a substantially larger wear track. By contrast, the tribocorrosion test that performs at a cathodic potential exhibits a lower wear rate showing the importance of corrosion suppression for tribocorrosion protection.

The tribocorrosion studies take a wide range of researches due to wide applications in a variety of industries, such as mining, food, oil, automotive, offshore marine, nuclear and biomedical. Tribocorrosion is a surface degradation process resulting from simultaneous tribological and electrochemical actions in a corrosive environment (*Wood, Landolt, Stack and Mischler*). Mathew et al. highlighted the study tribocorrosion behaviour of  $Ti_6Al_4V$  coated with a bioabsorbable polymer for biomedical applications to predict OCP of  $Ti_6Al_4V$  immersed in artificial saliva solution at  $37^\circ C$  in contact with  $Al_2O_3$  in addition to evaluate the coefficient of friction [14]. Mathew et al. in another study highlighted tribocorrosion in the hip joint [15]. These studies confirm the importance of tribocorrosion tests.

These studies cannot be predicted from the knowledge of wear and corrosion of the material because tribocorrosion can accelerate the mass loss in synergistic effects of wear and corrosion. The degradation of materials can cause tribocorrosion and affect the friction, wear and lubrication behaviour of the materials [16]. According to ASTM G 119, wear and corrosion form a synergistic couple:

$$T=W_o+C_o+S \quad (16)$$

where T is the rate of total material loss due to tribocorrosion,  $W_o$  is the rate of mechanical wear in the absence of corrosive agent,  $C_o$  is the rate of corrosion in the absence of mechanical agent and S is the change in the rate of material loss due to wear-corrosion synergy.

To obtain synergy (S), the following tests are performed: *Test 1*: electrochemical polarization to find corrosion potential ( $E_{\text{corr}}$ ) and corrosion current ( $i_{\text{corr}}$ ) to calculate  $C_o$ . *Test 2*: wear test in corrosive environment, no external potential or electrical current to obtain T. *Test 3*: repeat Test 2 to obtain electrochemical corrosion rate in the presence of wear ( $C_w$ ) and *Test 4*: repeat Test 2 with a potential of 1 V cathodic to  $E_{\text{corr}}$  to obtain  $W_o$ .

$$S = \Delta C_w + \Delta W_c \quad (17)$$

$$\Delta C_w = C_w - C_o \quad (18)$$

$$\Delta W_c = T - (W_o + C_w) \quad (19)$$

$$\text{Total synergism factor} = \frac{T}{(T - S)}$$

$$\text{Corrosion augmentation factor} = \frac{C_w}{C_o}$$

$$\text{Wear augmentation factor} = \frac{W_o + \Delta W_c}{W_o}$$

## 6. Conclusion

- Corrosion is an important problem in many industries, so it is necessary to know how one can discover this problem before the failure can occur.
- There are some difficulties to discover many types of corrosion because the appearance of metallic surface may be covered by corrosion products; therefore, it is necessary to know some details about service conditions.
- Tribocorrosion is a dangerous form of corrosion because it leads to reduction in material surface and then the failure can occur without clear warning.
- The prediction of tribocorrosion rate needs some requirements to be accurate and then using some methods to reduce it or continuously monitor it.

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