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Corrosion: Favoured, Yet Undesirable - Its Kinetics and Thermodynamics

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Abstract

This chapter describes the fundamentals of metal corrosion in relation to thermodynamics and kinetics. The chapter is so titled, because corrosion of metal is thermodynamically favourable. Moreover, it impacts negatively on economy and safety. Industries expend a substantial percentage of their budgets on corrosion control, and lose revenue due to corrosion damage. Effects of corrosion on industrial and public infrastructure cannot be overemphasized. Several accidents in the transportation and recreational industries have been linked to corrosion of metallic parts of respective gadgets. Some of these accidents are utterly catastrophic and fatal. Therefore, corrosion, albeit its thermodynamic favourability, is not desired by man. Metals corrode as a way of minimizing energy contents. Active metals are more stable in combined forms such as oxides, sulphides, and hydroxides, even though these forms are less useful to man. It appears the “price” to pay for extracting the pure forms of these metals from their ores is corrosion. This chapter presents fundamentals of thermodynamics and kinetics of metal corrosion, with emphasis on aqueous medium. It promises to serve as an introductory chapter for corrosion science students and as a concise material for tutors.

Keywords: corrosion, metallurgy, spontaneity, passivity, electrochemical

1. Introduction

Corrosion is a spontaneous disintegration of materials owing to their reactions with chemical constituents of the surroundings. Materials in this context may include metals, polymers and ceramics [1, 2]. However, corrosion is mostly used to refer to undesirable destruction of metals and alloys due to interactions with surrounding environment. The interactions or reactions as used here could be chemical or electrochemical in nature. More concisely, for the purpose of this chapter, corrosion would be described as chemical or electrochemical reaction between a metal and constituents of its environment. Emphasis will be placed on corrosion of metal in aqueous environments. Corrosion is a “favoured” process, requiring little or no energy input for its occurrence. Despite being naturally favoured, corrosion imposes a lot of economic strain, health and safety threat on human and society. It is a naturally favoured and an unavoidable process, yet, undesirable by man.

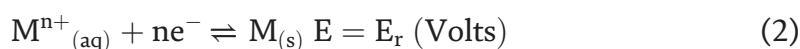
Corrosion is a way by which a metal assumes a low energy state, by combining with some other elements such as oxygen, hydrogen and sulphur. Metals are

naturally not favoured to exist in free states. They are found in combined forms, often as ores. Pure metals are extracted from their respective ores with a lot of energy input. No wonder corrosion is also touted as “retro-extractive metallurgy” [3], as depicted in Eq. (1).

Extractive Metallurgy



Corrosion of metals is essentially an electrochemical process. A metal could assume an immune, active or a passive state when exposed to the environment, depending on the nature of the metal and the environment [1]. An index of the possible state of a metal in an environment is its electrochemical/redox potential (E_r). The half-cell equation for the reduction of a metal (M) could be written as:



Metals with highly positive E_r are naturally immune to oxidation, examples include Au and Pt. Those with negative E_r are active in the environment. Some of them may assume an active-passive state, depending on the nature of the environment and the properties of their corrosive products.

Understanding the thermodynamics and kinetics of metal corrosion would make corrosion science students to appreciate why corrosion occurs and how its rate could be mitigated. It would also help corrosion science tutors to lay a good foundation of the course for their students.

2. The fate of a metal in an environment

The behaviour of a metal upon exposure to an environment depends on the nature of the metal and the conditions of the environment. A metal exposed to a corrosive environment could behave in one of the following ways [1]:

- i. Immune behaviour: the metal may be immune to an environment, such that it does not react in the environment. That is, the metal does not corrode. Such a metal is said to be thermodynamically stable in such an environment and would not undergo spontaneous corrosion. Metals with immune behaviour are very noble. They are un-reactive in virtually all environments. Examples include Au, Ag, Pt, and Pd.
- ii. Active behaviour: a metal is said to be of active behaviour in an environment when it reacts with the environment and thereby corrodes. If the environment is an aqueous solution, such a metal dissolves in solution and forms soluble non-protective corrosion products. Since the corrosion product is soluble and non-protective, the dissolution of such a metal is continuous. A metal with active behaviour suffers significant weight loss in an aggressive solution. Examples include Fe, Al, Zn, Mg, Cu etc. Activity of metals may vary with environmental conditions such as corrosive ions, immersion time, temperature, etc. In a recent study, Dong *et al.* [4] compared the corrosion rates of Zn, Fe and Mg in simulated physiological

solutions and found that Mg exhibited the highest corrosion rate. The study also illustrates how corrosion rate could vary with immersion time.

- iii. Passive behaviour: a metal that exhibits passive behaviour might corrode at some instances but assume a non-responsive state over a period. Upon exposure to the corrosive environment, a metal with passive behaviour forms insoluble protective corrosion products, which cover the surface of the metal and shield it from further exposure to the corrosive environment. The protective film slows down further reaction with the environment. The films are usually more stable (less reactive) than the metals themselves. However, if the passive film is broken or dissolved, then the metal can revert to the active state, at which instance rapid dissolution of the metal could occur. In some cases, repassivation could follow the breakdown of passive film. Various factors could be responsible for passive film breakdown or instability. Among them are film thickness, nature of corrosive ions, pH, anodic potentials and so on. Feng *et al.* [5] observed that increased strain magnitude could also increase instability of passive film on carbon steel. A more detailed overview on the passivity of metals could be found in literature [6].

It is noteworthy that the behaviour of a metal depends on its “micro-environment”. The natural or real practical environments are characterized by variable factors. The conditions of the environment may change with time. There could be a change in the cell pH, fluid flow rate, and temperature. Some reactions in the environmental might also result in solid deposits. The actual environment to which a metal responds is the immediate local environment at or near its surface. It is this micro-environment that determines the behaviour of the metal. Though some metals exhibit nearly universal behaviour irrespective of the environmental conditions. Metals such as Au, Pt and Ag typically exhibit noble or immune behaviour regardless of the environment, while metals like Na, K and Mg are generally active in nearly all aqueous environments. Metals like titanium and tantalum assume passive state in a wide range of aqueous environments, though reactive in some other environments. Aluminium and zinc are very reactive metals and often exhibit active behaviour. However, they form stable protective passive films in some environments. The behaviour of such metals could be described as “active-passive” – active in some environments at some instances, and sometimes passive. The subsequent passivity is due to the change in the local environment at the surface of the metal, being occupied by the insoluble passive corrosion products.

Active-passive behaviour of iron in nitric acid was first observed in 1790 by Keir [7]. The thickness of passive films may vary with environmental conditions. Susceptibility of the film to breakdown also depends on the thickness [6]. Sato *et al.* [8] also reported that the composition and thickness of passive films on iron immersed in a borate solution could change with change in potentials. Luo *et al.* [9] observed that alloy 59 (a Ni-Cr-Mo alloy with the least Fe content and highest Cr-Mo content) develops thicker passive film in air than sulphuric acid solution, and the constituents of the film vary in the two environments.

3. Corrosion: thermodynamic driving force

As pointed out earlier, corrosion of a metal is a spontaneous process. A metal in its pure state has a considerably higher energy than its corresponding ore. Metal corrodes in an attempt to minimize its energy, while assuming a more stable state.

Minerals or Ores	Constituent metal oxide, hydroxide or Sulphide	ΔH_f (kJ/mol)
Hematite	Fe_2O_3	-825.50
Bauxite	Al_2O_3	-1675.69
Zincite	ZnO	-350.46
Sphalerite	ZnS	-206.00
Brucite	$\text{Mg}(\text{OH})_2$	-924.66
Chalcocite	Cu_2S	-79.50

Table 1.
Minerals or ores of some common metals, their chemical formulas and standard heats of formation.

Corrosion is therefore a means of energy minimization as a metal tends to return to its combined form in which it exists naturally. A basic illustration of this energy minimization is the exothermic nature of the formation of metal oxides, sulphides and hydroxides (**Table 1**). Formation of hematite (the world most important ore of iron) is accompanied by the release of a huge amount of energy (825.50 kJ/mol). Meanwhile, the relative energy of a free Fe atom is 0 kJ/mol. The same applies to other metals and their minerals.

3.1 Corrosion: electrochemical cell and electrode potential

Corrosion of metals is essentially an electrochemical process, involving both anodic oxidation and cathodic reduction reactions. A micro-electrochemical cell is established on the surface of a corroding metal. Perhaps for the sake of emphasis, electrochemical corrosion cell is a galvanic (or voltaic) cell. The progress of corrosion reaction is accompanied by flow of electric current (i), which has to do with movement of an electric charge across a potential difference. A corroding metal in an aqueous solution sets up a galvanic cell system comprising the metal (M) in contact with its metal ion (M^{n+}) such that an equilibrium is established. The site on the metal surface where dissolution of metal into its ion occurs is the anodic site. The cathodic site is set up not far from the anodic site. Each site constitutes a half-electrode reaction system, making up two half-cells, like that of a galvanic cell. The difference between the electrode potentials of the two half-cells can be expressed as:

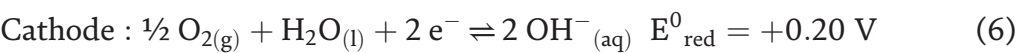
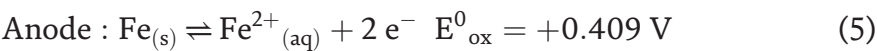
$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}} \tag{3}$$

In Eq. (3), both E_{cathode} and E_{anode} are reduction potentials. Since we are considering corrosion, the E_{cell} is equivalent to the corrosion potential, E_{corr} . For a spontaneous cell reaction as we have in corrosion, E_{anode} is always more negative than E_{cathode} , such that E_{cell} is always positive.

For a typical case of iron (Fe) corroding in an aerated aqueous solution as:



The half-cell reactions equations can be expressed as:



In this case, $E_{\text{cell}} = (0.2 + 0.409) \text{ V} = 0.609 \text{ V}$. The more positive the E_{cell} , the more feasible the corrosion of the metal. Practically, the E_{cell} or E_{corr} is measured

using a potentiostat. In such measurements, a half-cell must be chosen as a reference, e.g. standard hydrogen electrode (SHE). Electrode potential for SHE is set at 0 V (E_{H^+/H_2}). The electrode is made up of 1 M hydrogen ion (H^+) and hydrogen gas (H_2) at 1 atm, supported with a platinum plate. When coupled with an half-cell of unknown E , the cell potential recorded by the potentiometer is the electrode potential of the system with unknown E .

Potentiostats with three-electrode system are often used to measure electrochemical corrosion parameters. The three-electrode system consists of the working electrode, WE (the metal or alloy whose corrosion is being studied), reference electrode, RE (against which the corrosion potential of the metal/alloy is measured), and auxiliary/counter electrode, CE, which supports or protects the reference electrode against passage of current. Commonly used reference electrodes include calomel electrode, which composed of Hg/Hg_2Cl_2 , sat'd. KCl, and silver-silver chloride electrode ($Ag/AgCl$, sat'd KCl). The latter is mostly used because of its relatively cheap cost and less toxicity compared to the mercury-based electrode.

Electrode potentials depend on concentrations of the species and temperature. Under the standard conditions of 25°C and 1 M concentration or 1 atm pressure of the species, it is referred to as the *standard electrode potential*. The standard electrode potentials (standard reduction potentials), E^0 for some species are listed in **Table 2**. The dependence of electrode potentials on concentrations of the species and temperature is expressed in the form of the Nernst equation, whose general form is:

$$E_r = E_r^0 - \frac{RT}{nF} \ln \left(\frac{[red]}{[oxi]} \right) \quad (7)$$

where n is the number of electrons transferred in the redox reaction, F is the Faraday constant, R is the gas constant and T is absolute temperature; $[red]$ and $[oxi]$ are the concentrations of the reduced and oxidized species, respectively.

3.2 Gibb's free energy and electrode potentials

Corrosion is characterized by lowering of Gibb's free energy or increasing electrochemical cell potential. For a corroding metal, a micro-electrochemical cell is created on the surface. The progress of metal corrosion is proportional to flow of current in the electrochemical cell. Thermodynamic parameters can be expressed for electrochemical systems. Since corrosion of metals is a constant pressure process, the Gibb's free energy (ΔG) is a good thermodynamic parameter for predicting its spontaneity. A spontaneous reaction is accompanied by energy minimization, which implies a negative ΔG , while a positive ΔG connotes non-spontaneous process. A non-spontaneous reaction requires energy input to proceed. For a system at equilibrium, $\Delta G = 0$. Corrosion being a spontaneous process has a negative ΔG . Thermodynamic favourability of metal corrosion could readily be predicted from the electrode potentials of the metal concerned. The change in Gibb's free energy (ΔG) per mole of an electrochemically reacting species is related to the electrode potentials as:

$$\Delta G = -nFE \quad (8)$$

where n is the valence of the species (number of electrons transferred), F is the Faraday's constant ($1 F = 96,485 C$) and E is the electrode potential (Volts). For a typical case of anodic dissolution of iron as it oxidizes from Fe to Fe^{2+} by losing two electrons ($Fe \rightleftharpoons Fe^{2+} + 2 e^-$); $n = 2$.

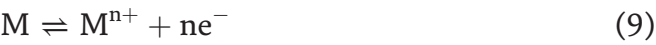
Reduction half-reactions	E ⁰ _{red} (V)
O ₃ + 2 H ⁺ + 2 e ⁻ ⇌ O ₂ + H ₂ O	2.07
H ₂ O ₂ + 2 H ⁺ + 2e ⁻ ⇌ 2 H ₂ O	1.776
Au ³⁺ + 3 e ⁻ ⇌ Au	1.68
PbO ₂ + 4 H ⁺ + 2e ⁻ ⇌ Pb ²⁺ + 2 H ₂ O	1.467
Cl ₂ + 2 e ⁻ ⇌ 2 Cl ⁻	1.3583
O ₂ + 4 H ⁺ + 4 e ⁻ ⇌ 2 H ₂ O	1.229
Pt ²⁺ + 2 e ⁻ ⇌ Pt	1.20
H ₂ O ₂ + 2e ⁻ ⇌ 2 OH ⁻	0.88
Hg ₂ ²⁺ + 2 e ⁻ ⇌ Hg	0.7961
Cu ⁺ + e ⁻ ⇌ Cu	0.522
O ₂ + 2 H ₂ O + 4 e ⁻ ⇌ 4 OH ⁻	0.401
Cu ²⁺ + 2e ⁻ ⇌ Cu	0.3402
2 H ⁺ + 2 e ⁻ ⇌ H ₂	0.000
Fe ³⁺ + 3 e ⁻ ⇌ Fe	-0.036
Pb ²⁺ + 2 e ⁻ ⇌ Pb	-0.1263
Sn ²⁺ + 2 e ⁻ ⇌ Sn	-0.1364
Ni ²⁺ + 2 e ⁻ ⇌ Ni	-0.23
Co ²⁺ + 2 e ⁻ ⇌ Co	-0.28
Fe ²⁺ + 2 e ⁻ ⇌ Fe	-0.409
Cr ³⁺ + 3 e ⁻ ⇌ Cr	-0.74
Zn ²⁺ + 2 e ⁻ ⇌ Zn	-0.7628
Mn ²⁺ + 2 e ⁻ ⇌ Mn	-1.04
Al ³⁺ + 3 e ⁻ ⇌ Al	-1.706
Mg ²⁺ + 2 e ⁻ ⇌ Mg	-2.375
Na ⁺ + e ⁻ ⇌ Na	-2.7109
K ⁺ + e ⁻ ⇌ K	-2.924

Table 2.
Standard half-cell reduction potentials for reactions.

3.3 Impracticability of equilibrium electrochemical corrosion potentials

Corrosion involves both anodic and cathodic reactions. Each of these reactions is reversible and has associated electrode potential (E), which tends to attain an equilibrium value. At equilibrium, ΔG = E = 0. However, attainment of this value is impracticable.

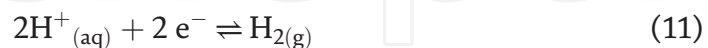
Practically, a bare (an oxide-free) metal surface releases metal ion into an aqueous solution (dissolution), leaving negatively charged electrons on the surface. This leads to an increase in the potential difference between the metal and the solution. The electrode potential becomes more negative. For the anodic dissolution of a metal, M, the half-cell reaction equation could be written as:



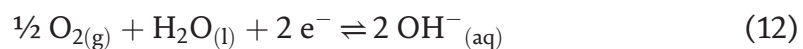
A more negative potential tends to retard dissolution but promotes deposition, according to Eq. (8) (i.e. ΔG is more positive for a more negative E). Since the process is reversible, continuous dissolution and/or deposition might lead to a stable (reversible) potential, E_r , which can be expressed in the form of Nernst Equation (for the reaction in Eq. (9)) as:

$$E_{r,M^{n+}/M} = E_{r,M^{n+}/M}^0 + \frac{RT}{nF} \ln a_{M^{n+}} \quad (10)$$

If a stable $E_{r,M^{n+}/M}$ is attained, dissolution would stop. However, in practice, $E_{r,M^{n+}/M}$ is never attained because electrons generated in Eq. (9) are always removed from the surface by the accompanied cathodic half-cell reaction, such as:



Or



in an acidic or basic medium respectively. The Nernst equation-type expressions for the reversible potential (E_r) for the cathodic reactions in Eqs. (11) and (12) respectively are:

$$E_{r,H^+/H_2} = E_{r,H^+/H_2}^0 - \frac{RT}{F} \ln \frac{P_{H_2}^{\frac{1}{2}}}{a_{H^+}} \quad (13)$$

$$E_{r,O_2/OH^-} = E_{r,O_2/OH^-}^0 - \frac{RT}{4F} \ln \frac{a_{OH^-}^4}{P_{O_2}} \quad (14)$$

where Eqs. (13) and (14) correspond to stoichiometrically adjusted forms of Eqs. (11) and (12) by multiplying the coefficients by $\frac{1}{2}$ and 2 respectively for reduction of 1 mole of H^+ and O_2 .

If E_r could be attained for reactions depicted by Eqs. (11) or (12), then E_r would be attained in Eq. (10). However, E_r in Eq. (13) or (14) is never stable due to continuous discharge of H_2 or consumption of O_2 . Hence, attainment of a stable $E_{r,M^{n+}/M}$ is practically impossible and corrosion of metal, M is continuous.

3.4 Corrosion tendency based on electrochemical potentials and pH

Thermodynamics of electrochemical corrosion could be described as a function of electrode potential and hydrogen ions concentration (pH). This is often charted as potential-pH diagram, popularly called the Pourbaix diagram, named after the original inventor. Pourbaix, a Belgium electrochemist and corrosion scientist invented the potential-pH diagram in 1963 for the description of thermodynamics of electrochemical corrosion. Pourbaix diagrams provide theoretical description of stability of a phase of metal/electrolyte system at a particular pH and potential. It is a kind of phase equilibrium diagram, though with different axes parameters compared to thermodynamics phase equilibrium diagram. Potential-pH diagram is often plotted at 25°C, 1 atm, and 10^{-6} M concentration of the ionic species. A typical Pourbaix plot comprises the redox potential on the vertical axis and the pH on the horizontal axis. Potential-pH diagram for iron in aqueous environment is shown in **Figure 1**. The diagram clearly shows the stable and passive regions for iron, based

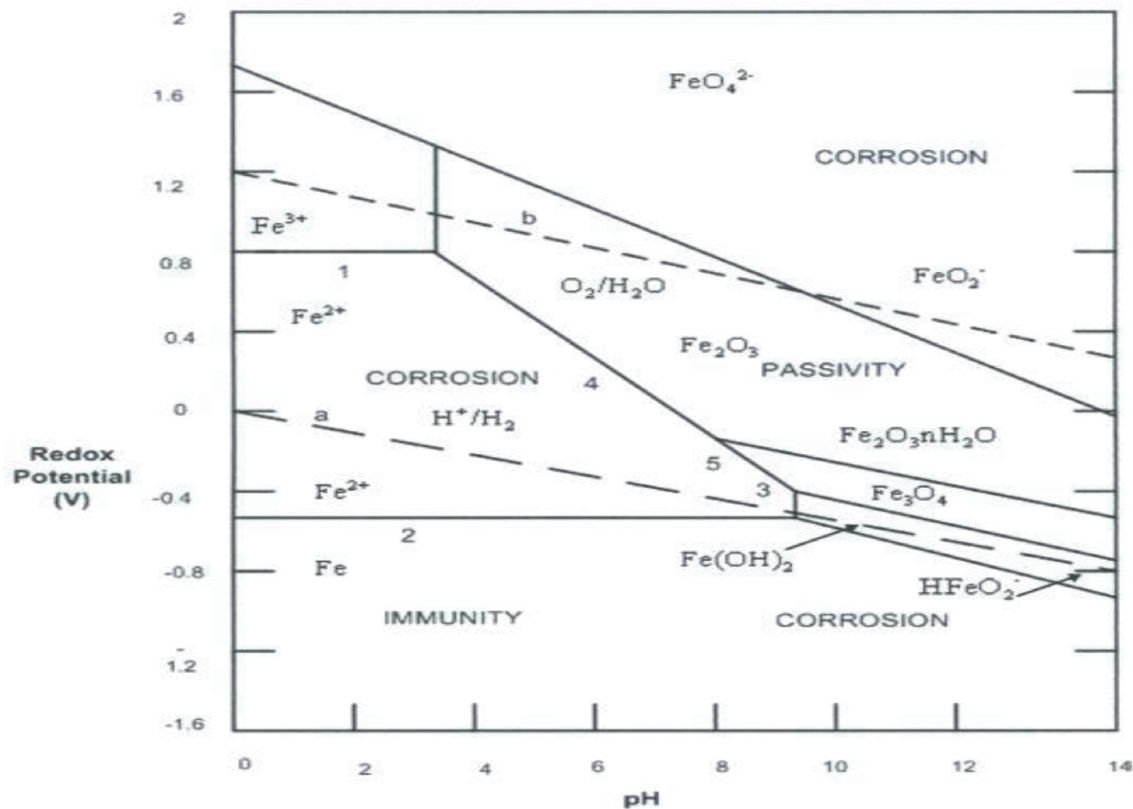


Figure 1.
Potential-pH diagram for iron in aqueous medium [10].

on the combination of potential and pH. At the very top of the diagram is corrosive region, where the potential is highly positive (above 1.8 V). At this region, iron would corrode at any combination of potential and pH. The region marked immunity at the lower portion of the diagram indicates the area where iron does not corrode. This region spans over a wide range of pH, and a limited range of highly negative potentials. Within this region, iron is immune to corrosion at various combinations of potentials and pH. In-between the two extreme top and bottom regions are regions where corrosion and/or passivity could occur, depending on the operating potentials and pH. The region marked “corrosion” between lines 1 and 2 covers a large area compared to the one at lower right-hand side. This implies that corrosion of iron at intermediate potentials between -500 mV and 1000 mV would progress more favourably in acidic pH than neutral and alkaline pH. At moderately positive potentials and neutral or alkaline pH, iron forms passive oxide film on the surface, which blocks further corrosion.

Pourbaix diagram could be used as a route to first principle corrosion simulation [11], a model for optimizing corrosiveness of a medium and designing materials with desired corrosion resistance. In a recent study, Nave and Kornev [12] constructed and applied 3D Pourbaix profile to establish the conditions for thermodynamic stability of tungsten-based compounds and describe the anodic dissolution of tungsten in aqueous solutions of potassium hydroxide. Beyond pure metals, Pourbaix profiles for multielement system such as Ni-Ti alloys having different ratios of the element have been proposed [13]. In an effort to overcome the challenges associated with developing Pourbaix profiles for complex compounds, a recent study by Patel *et al.* [14] introduced a more robust algorithm for modelling Pourbaix diagram for multicomponent materials.

4. Corrosion kinetics

Having discussed the propensity of metals to corrode, it is important to also highlight the rate at which metals corrode and mechanisms of corrosion reactions.

4.1 Corrosion rate

In a general term, corrosion rate (C_R) refers to the amount of metal loss to corrosion per unit time. The rate at which a metal corrodes can be monitored by various methods. This also determines the kind of C_R expression and units. Both the methods and expression (together with units) are in turn dependent on the technical system and type of corrosion being investigated. These methods may be classified as chemical, electrochemical, spectroscopic, and surface analysis based methods. Basically, corrosion rate (C_R) may be monitored by measuring any parameter that changes as corrosion reactions occur. For example:

- monitoring the change in weight of the metal upon corrosion (weight loss measurements);
- pressure of gas evolved (e.g. monitoring the H_2 gas evolution level);
- change in temperature upon corrosion reactions (thermometric measurement);
- spectroscopic analysis of amount of metal that goes into solution upon corrosion (e.g. AAS analysis of Fe in solution);
- amount of current that flows in the system (electrochemical measurements).

Each of these methods have associated merits and demerits. Corrosion rate may be expressed as weight-loss of a metal per unit time per unit area according to the equation:

$$C_R = \frac{\Delta w}{At} \quad (15)$$

where Δw is the weight difference of the metallic block or plate at a set time interval (exposure time), t , and A is the exposed area of the metal. Being an analytical measurement, the ideal practice is to conduct repetitive measurements of Δw and utilize the average value in Eq. (15). This measurement is mainly applicable to general or uniform corrosion. However, it is the most used measurement of corrosion rate. For corrosion systems in which the metal/environment composition vary significantly with time and non-uniformity over the sites on corroding surface, measurement of C_R using Eq. (15) may be deficient. The results of such measurements must at least be supported with additional information such as the type of corrosion, dependence of corrosion rate on time and other relevant factors that prevail during the experiment. Eq. (15) is the simplest form of such expression, for which the units of Δw (g or nearest mg), A (nearest cm^2), and t (nearest h) would give the units of C_R as $gcm^{-2}h^{-1}$ or $mgcm^{-2}h^{-1}$. These units may not be applicable in reporting C_R in some other technical reports, for example, if C_R is to be expressed in the form of penetration rate (depth per unit time).

In an electrochemical experiment, corrosion rate could be measured as corrosion current density, in the form of corrosion current (mA) per unit area (cm^2) of

	mA cm^{-2}	mm year^{-1}	mpy	$\text{g m}^{-2} \text{day}^{-1}$
mA cm^{-2}	1	3.28 M/nd	129 M/nd	8.95 M/n
mm year^{-1}	0.306 nd/M	1	39.4	2.74 d
mpy	0.00777 nd/M	0.0254	1	0.0694 d
$\text{g m}^{-2} \text{day}^{-1}$	0.112 n/M	0.365 /d	14.4 /d	1

Table 3.
Conversion factors for various units of C_R [15].

corroding metal, i.e. mAcm^{-2} . Conversion factors from one C_R unit to another are listed in **Table 3**.
where:

- mpy = milli-inch per year
- n = number of electrons freed by the corrosion reaction
- M = atomic mass
- d = density

e.g.: $1 \text{ mA cm}^{-2} = (3.28 \text{ M/nd}) \text{ mm y}^{-1} = (129 \text{ M/nd}) \text{ mpy} = (8.95 \text{ M/n}) \text{ g m}^{-2} \text{ day}^{-1}$

4.2 Factors affecting corrosion rate

Besides basic requirements for electrochemical corrosion to occur, which include the presence of anodic and cathodic sites, electrolyte and connectivity between the sites (to promote ionic conduction), there are secondary factors that affect corrosion rate. These factors are briefly discussed as follow.

- *Concentrations of dissolved oxygen (i.e. oxygen and oxidizers)*: corrosion rate and mechanism could be affected by the amount of dissolved oxygen. This is because, both anodic dissolution of metal and cathodic reactions are oxygen dependent. Generally, the higher the concentration of dissolved oxygen the higher the corrosion rate. Since anodic dissolution is an oxidation reaction, increased oxygen content in the microenvironment would increase the rate of metal oxidation. More so, when oxygen reduction predominates the cathodic reaction, dissolved oxygen increases the rate of cathodic reaction, which in turn speeds up the anodic reaction for charge balancing purpose. In other words, the rate of metal dissolution is directly proportional to the rate of oxygen reduction. A limited oxygen reduction or dissolved oxygen would lead to a decrease in metal dissolution and overall corrosion rate. Hydroxide and oxide deposits and protective film reduce the rate of oxygen diffusion onto the metal surface. They also tend to prevent conduction of metal ions from metal-oxide interface to oxide-liquid interface. Hence, they reduce corrosion rate, usually by passivation.
- *Concentration of dissolved salts*: dissolved salt increases conductivity of an electrolyte system. Since a requirement for corrosion to progress in ion mobility, increase in conductivity of the electrolyte due to dissolved salt increase corrosion rate. Generally, corrosion rates tend to increase when water conductivity increases. For this reason, corrosion rate is higher in saline water than freshwater. The

corrosion rate in seawater is a function of numerous mutually dependent factors. However, according to Kirk and Pikul (1990) [16], if salinity exceeds 3%, water corrosivity decreases. This is due to decrease in oxygen solubility in water with > 3% salinity, as posited by Weiss (1970) [17].

- *Temperature and pressure:* Generally, temperature increases the rate of metal corrosion, so does pressure. Just like every other electrochemical reactions, increase in temperature increases fluid flow and ionic mobility. Temperature can also affect scale formation and gas fugacity, which indirectly affect corrosion rate. Most corrosion models are accurate only within prescribed temperature ranges. For corrosive involving gases such as CO₂ and H₂S increase in operating pressure could increase the partial pressure of the corrosive gases. It should be noted that the reduction potential of the metal is dependent on fugacity of the gases present, according to the Nernst Equation. The dependence of corrosion rate (C_R) on temperature could be expressed in the form of Arrhenius equation as:

$$C_R = A \exp(-E_a/RT) \quad (16)$$

where A is the pre-exponential factor, E_a is the activation energy, R is the gas constant and T is temperature.

- *Associated fluid dynamics:* increase in fluid flow rate increases the rate of metal loss. Fluid flow rate the reason for the particular type of corrosion, the “Flow-Accelerated Corrosion”. Accelerated fluid drives corrosive ions to the reactive sites faster than a stagnant or unstirred solution. Fluid flow also has mechanical effects on passive films or deposits by driving them out of site, exposing the metal surface to direct attack of corrosive ions. Flow-accelerated corrosion is usually found at high flow rates around pipe/tube blockages, tube inlet ends, or in pump impellers.
- *Concentration of corrosive electrolyte:* generally the higher the concentration of corrosive electrolyte the higher the rate of metal corrosion. Though, change in concentration of corrosive electrolyte often lead to change in pH of the medium, which can affect corrosion rate and mechanism in different ways.
- *pH of the medium:* this affects the kind of reactions that take place at the cathode. For instance, in acidic pH, hydrogen ion reduction/hydrogen gas evolution predominates at the cathode. Oxygen reduction could also occur if the medium is aerated. Oxygen reduction is the primary cathodic reaction in neutral/basic solutions.

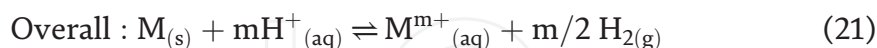
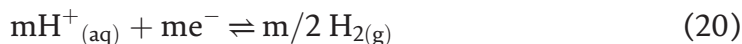
4.3 Corrosion mechanism

Corrosion, like many other chemical reactions usually involve more than one definable step. Interests often lie in the slowest step. Electrochemical corrosion involves release of ions and movement of electrons. Corrosion requires presence and movement of ions and electrons. A typical mechanism of corrosion of Fe in acidic medium is:

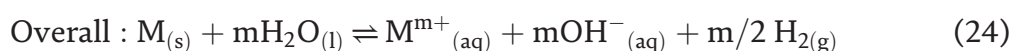
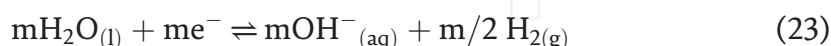


The process is often more complex such that, metal ions may go into solution as complexes or even; precipitate as hydroxides, oxides, sulphides etc.

Electrochemical corrosion mechanism of an active metal in an aqueous environment can be expressed generally as [18]:

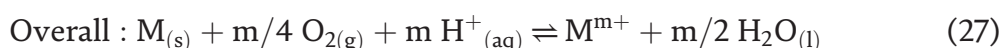
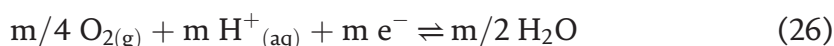


In a deaerated acidic medium. Or.



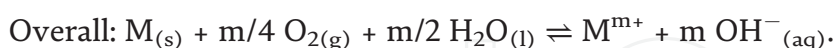
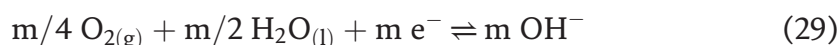
In a deaerated neutral/basic medium.

In an aerated environment, oxygen plays a prominent role in the reaction and the mechanisms look like [18]:



In an aerated acidic environment.

Or



In an aerated neutral or basic environment.

5. Corrosion control methods

As contained in the previous sections, whether a material would corrode or not depends on a number of factors. The extent and rate of corrosion also varies, depending on the nature of the metal or alloy, corrosive medium, pH, temperature and so on. While it may be difficult to “work against nature”, to completely stop metal corrosion, several methods of abating corrosion damage have been identified. Most of these methods reduce corrosion rate, rather than “inverting” the thermodynamics. Although, thermodynamic susceptibility might be influenced in some instances. Choosing a suitable corrosion control method requires proper understanding of corrosion type and mechanism. No particular method had been adjudged universally effective to mitigate all forms of corrosion. Common corrosion control methods are highlighted below.

- *Material selection:* this method entails careful selection of metal or alloy that is immune to corrosion in an environment. While this sounds as a good idea, such

materials do not often possess the desired mechanical properties for prospective technological design. Besides, using such materials for engineering purposes could be very expensive. In other words, striking a balance between material cost, mechanical properties and corrosion resistance is not a straightforward task.

- *Engineering design*: careful structural design might reduce or eliminate certain forms of corrosion. A design that eliminate accumulation of water on metal surface might reduce the rate of top-of-line corrosion (TLC), which is greatly associated with water accumulation [19]. Crevice corrosion could be minimized if engineering design minimizes stagnation of fluids and adopts welded rather than bolted joint. Design that eliminates or reduces turbulence flow could reduce the rate of erosion corrosion [20]. The major limitation to using engineering design to control corrosion is that the choice of a design might not meet other important criteria of the structure, aside reducing corrosion propensity of the material. A wrong design might be costly and yet not suitable for optimum application of the structure [21, 22].
- *Cathodic and anodic protection*: electrochemical potentials of a metal could be modified to suppress cathodic or anodic corrosion by shifting the potential cathodically or anodically, respectively. This could be achieved via impressed current system [23]. Cathodic shift increases the immunity of the metal by reducing electron uptake for the cathodic reaction [24]. A more positive or anodic shift of the potential increases the passivity behaviour of the metal [22, 25]. The use of sacrificial materials known as sacrificial anode/cathode is also a known practice. A more active metal (sacrificial anode) could be used to protect a metal of interest. Parthiban *et al.* [26] reported the use of magnesium alloy anode for the cathodic protection of steel embedded in concrete. It was observed that the mechanism of cathodic protection with the sacrificial anode could be correlated to the removal of corrosive ions such as chloride from the vicinity of steel.
- *Protective coatings*: organic or inorganic coatings are often used to protect the surface of active metals. Such coatings could serve as barrier protection and/or chemical inhibition. Besides corrosion mitigation, special coating materials could provide aesthetic functions, improving the surface appearance of the metal [27]. An extensive review on protective coating on magnesium alloy is available in literature [28].
- *Corrosion inhibitors*: chemical substances could be added to corrosive solution in trace quantities to reduce corrosion rate of metal. These additives, which often reduce the rate of metal corrosion by adsorbing as thin film on metallic surface are called corrosion inhibitors. Several corrosion inhibitors have been designed. Notable among them are benzotriazole (a popular inhibitor of copper corrosion) [29], quinoxalines [30–32], benzimidazoles [33], pyrimidines [34, 35], pyridazines [36], hydantoins [37], ionic liquids [38] and so on. Most organic corrosion inhibitors contain heteroatoms and pi-electron systems that aid adsorption of their molecules onto active sites on the metal surface. There are also inorganic inhibitors such as salts of zinc, copper, nickel, and arsenic. Earlier efficient inorganic corrosion inhibitors are chromate based, but their use have been discouraged due to their high toxicity.

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