

Chapter 1

Introduction

1.1 Introduction

Corrosion is “**The cancer of metal**”. All metals and alloys are susceptible to corrosion by one or more naturally available or man-made fluids. Normally metals exist in unstable form and try to get stable by reacting with the atmosphere [1-10]. Mild steel is the most versatile, least expensive and world widely used in many applications in industries like metallurgical process, chemical cleaning, fertiliser, desalination plants, bolts-nut, screw industry, storage tank, petroleum refineries, pharmaceutical industry, thermal power plant, construction material, and gas industry, sugar, paper, textile, boilers, automobiles, steam boilers, engineering purpose, mechanical purpose, chain, hinges, knives, magnets, military equipment, armour, vehicles (ships and cars) and pickling process etc., due to their stability, high strength, weld ability and good corrosion resistance [11-15].

Hydrochloric acid, sulphuric acid, phosphoric acid and organic acid like citric, oxalic, acetic acid are used to clean up the scales and rusts of the mild steel articles which are caused by corrosion of the exposed metal after the scales have been removed [16-40]. Sea water and base medium is another corrosive environment which causes drastic environmental degradation of various mild steel structures. Application of corrosion inhibitors is one of the best methods, among the various methods of mitigation of corrosion. They are generally heterocyclic organic compounds with presence of S, O or N atoms in the molecules (compounds) with a lone pair of electron, pi electron with multiple bonds. But most of the synthetic organic and inorganic inhibitor is toxic and harmful to human and other living system; this may cause temporary or permanent damage to the organ system [41-80]. Since the early 1990's in different areas of the world where platform in the sea are used to extract oil, environmental situations arise that challenge the use of corrosion inhibitor. Plant extracts have been explored as corrosion inhibitors due to their bio-degradability, non-toxicity, environmental friendly nature, easy availability, easy to handle, low cost and simple procedure [81-102]. In the present investigation, corrosion inhibition of mild steel in HCl has been studied in the presence of few green inhibitors (both in aqueous and alcoholic extract) mainly *Gloriosa superba* Linn, *Madhuca longifolia*, *Alangium lamarckii*, *Holoptelea integrifolia*, *Pithecellobium dulce* and *Schrebera swietenoides* and there are no reports in the literature on the use of these plants as corrosion inhibitors.

1.2 Basic Concept of Corrosion

Corrosion is “**Billion dollar thief**”. Corrosion has been classified as chemical and electrochemical, low and high temperature, wet and dry corrosion. Carbon and low alloy steel are widely used, mainly for economic reasons. Moreover, they may have different microstructures which influence their mechanical properties and corrosion resistance in certain environments [103].

1.3 Definitions

Ulick R. Evans the “**Father of Corrosion Science**” has said that corrosion is largely an electro chemical phenomenon, may be defined as deterioration of metals and alloys in the presence of an environment by chemical or electrochemical means.

In simple terminology, corrosion is an irreversible interfacial reaction of a material (metal, ceramic, and polymer) with environmental species [104-105].

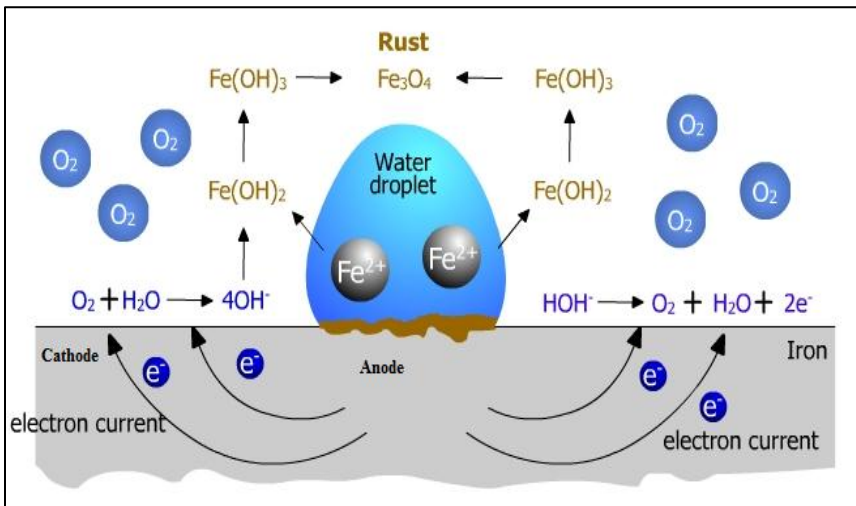


Fig. 1. Formation of Rust

For environments with water present, including moisture in the air, the electrons consume metal converting oxygen and water to hydroxide ions. All metal and alloys in those hydroxide ions in turn combine with iron ions to form [$Fe(OH)_2$]. Subsequent reactions form a mixture of **magnetite (Fe_3O_4)** and **hematite (Fe_2O_3)**. This **red-brown** mixture of iron oxides is called as **rust** [106-108].

1.4 The energy cycle of Iron

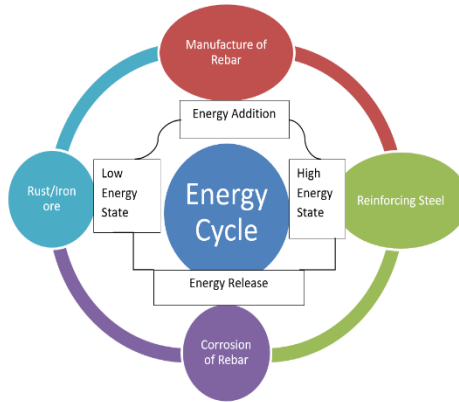


Fig. 2. The energy cycle of iron

1.5 Factor influencing corrosion

Environmental effects such as the role of various micro organisms present in **soil and water bodies, oxygen and other oxidizers, changes in flow rates (velocity), temperature, reactant concentrations and pH** would influence the rate of anodic and cathodic reactions. The definition for corrosion needs to be further widened and to be included in microbial influenced factors.

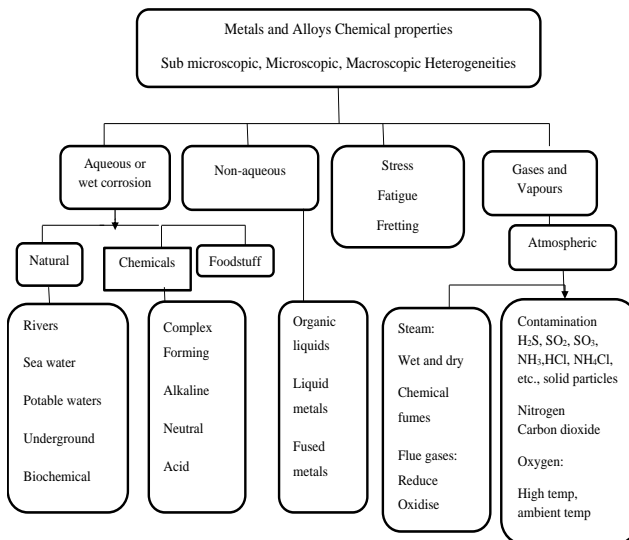


Fig. 3. Factors of various corrosion formations

1.6 Types of corrosion

The most important types of corrosion are

- General corrosion
- Localized corrosion
- Pitting corrosion
- Crevice corrosion
- Filiform corrosion
- Galvanic or bi-metal corrosion
- Environmental cracking
- Stress corrosion cracking
- Corrosion fatigue
- Flow-Assisted corrosion
- Cavitation corrosion
- Erosion
- Intergranular corrosion
- De-Alloying
- Exfoliation
- Fretting corrosion
- High temperature corrosion
- Corrosion via hydrogen embrittlement

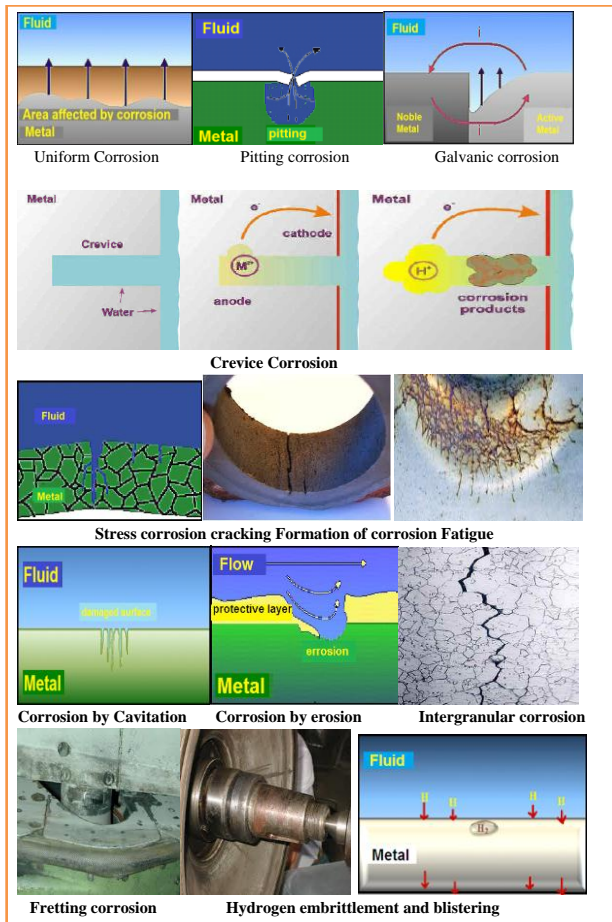


Fig. 4. Various forms of Corrosion

1.7 Principles of corrosion

Thermodynamic principle

Thermodynamic principles are applicable to corrosion processes involving **free energy, electrical double layer, Nernst equation for electrode potentials** and **Pourbaix diagrams**. It is used to determine whether corrosion is theoretically possible or not. Different metals have different tendencies to corrode in a given corrosive environment. Thermodynamic approaches have been also widely used to explain and understand the fundamental corrosion problems.

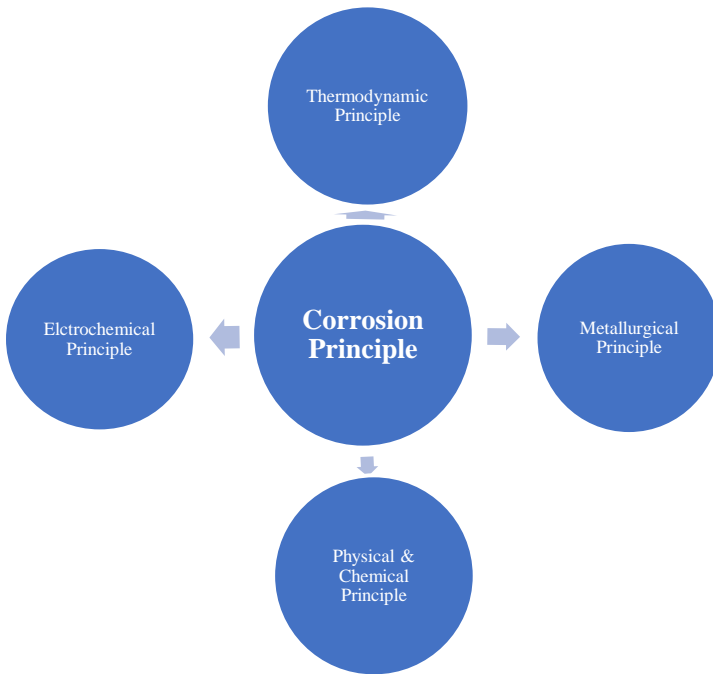


Fig. 5. Principles of Corrosion

1.8 Electrochemical Principle

Electrochemical corrosion is a spontaneous process that denotes the existence of anodic and cathodic zones, where an electrolyte is also required.

Anode reaction: $\text{Fe} \rightarrow \text{Fe}^{2+} + 2 e^{-}$

Cathode reaction: $2\text{H}^{+} + 2e^{-} \rightarrow \text{H}_2$; $\text{O}_2 + 2 \text{H}_2\text{O} + 4 e^{-} \rightarrow 4 (\text{OH}^{-})$

1.9 Metallurgical Principles

The corrosion behaviour of a metal is well understood by metallurgical principles. In many cases, the metallurgical structure of an alloy can be changed so as to improve its corrosion resistance.

1.10 Physical and Chemical Principles

The mechanism of corrosion reactions, the surface conditions of metals and other basic properties are understood by the physical and chemical principles. Physical corrosion is caused by impact, stress or exhaustion of the material. Chemical corrosion is caused by **oxygen, sulphur, fluorine, chlorine or other gases**, which act directly on the metal under environmental conditions that facilitate this phenomenon.

1.11 Theories of corrosion

There are two theories of corrosion, they are: 1. Homogeneous theory
2. Heterogeneous theory.

Homogeneous Theory

A corroding metal irrespective of the presence or absence of any micro heterogenetics can be regarded as a single electrode on which a reaction takes place. Therefore, it is necessary that the potential difference across the interface be more negative (anodic) than the equilibrium potential for the metal dissolution or more positive (cathode) than the equilibrium potential for the electro nation.

Heterogeneous Theory

According to this theory corrosion is caused when the metal is exposed towards the moist atmosphere. Here corrosion is caused by local galvanic elements that arise on the surface of the corroding metal as a result of the chemical structure heterogeneity.

1.12 Losses due to Corrosion

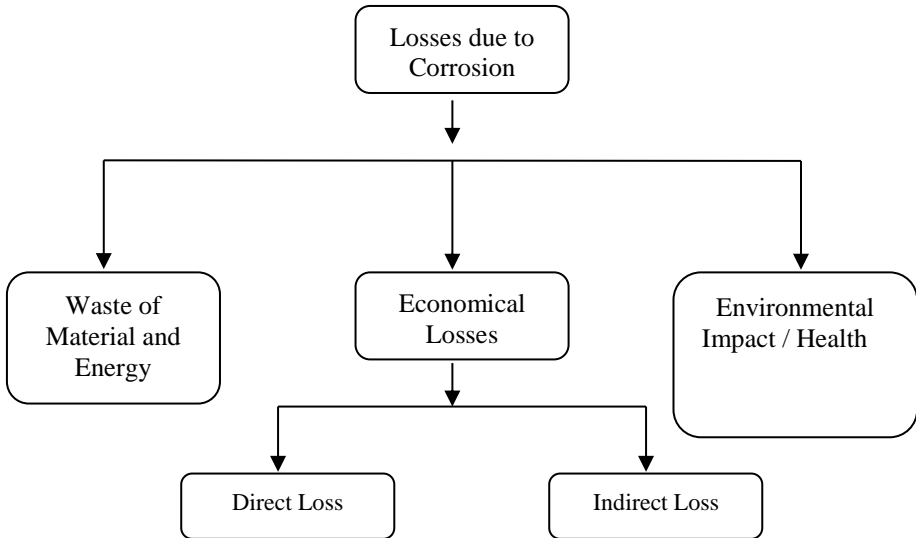


Fig. 6. Cost of Corrosion

1.13 Waste of Material and Energy

In India loss due to corrosion has been reported to account for more failure in terms of cost and tonnage than any other environment. Economical losses have been divided into: direct loss and indirect loss. The up-to-date study indicates that technological changes have provided a lot of new ways to prevent corrosion, and the better use of available corrosion management techniques. The cost was determined by analysing the following industrial sectors: Bridges, oil gas transmission pipelines, waterways, airports, railroads, motor vehicles, refining, agricultural and food processing, electronics & home appliances, pulp, paper, chemical, petrochemical, pharmaceutical, defence and nuclear waste disposal.

1.14 Economic Effects

In modern business environment, successful enterprises cannot tolerate major corrosion failure (bridges, aircraft, automobiles, gas pipelines, broken connections in pacemakers, and fracture of weight-bearing prosthetic devices, etc) especially those involving personal injuries (such as pins, screw, plates, hip joints, pacemakers, and other implants or even loss of life) fatalities, unscheduled shutdown and environmental contamination. Losses due to corrosion could be approximately Rs. 2.0 lakh crores per annum (in the year of 2015) in India [109].

1.15 Other effects

- Loss of time and corrosion products may contaminate dyes, chemicals, packaged goods, pharmaceuticals with direct penalties to consumers.
- Loss of metal strength leading to leaking containers storage tanks; water and oil transportation lines and fuel tanks cause (breakdown) significant loss of product and may generate severe accidents and hazards.
- International concern was aroused by the disclosure of the serious deterioration of the artistically and culturally significant gilded bronze statues in Venice, Italy.

1.16 Corrosion management and common methods of corrosion prevention

In most industrial situations it is virtually impossible to prevent corrosion but it can be minimised to a certain extent by corrosion resistance materials, rubber covered steel, resin bonded carbon.

- Increasing use of metals in all fields of technology. Use of rare and expensive metals whose protection require special precautions. Right metal in the right way in the right place is important (necessary).
- Use of new high strength alloys which are usually more susceptible to certain types of corrosive attack.
- Increase awareness, change policies, regulations, standards and management practices to increase corrosion savings through sound corrosion management.
- Improve education and training of staff in recognition of corrosion control.
- Advance life prediction, advance design practices for better corrosion management.
- Avoid metal-metal or metal-non-metallic contacting materials that facilitate corrosion.
- Bimetallic couple
- Designs that lead to erosion-corrosion and heterogeneity in the metal
- Use inorganic coatings e.g., (vitreous, enamel, glasses, ceramics) and organic coatings e.g., oil, enamels, white washing, paint, plastics.

1.17 Scope of the present investigation

Studies in a number of countries have attempted to determine the national cost of corrosion. For this reason, considerable efforts are generally employed in corrosion control at the operational phase. Actually, something can and should be done to prolong the life of metallic structure and components exposed to the corrosive environments. ***Therefore, there is a need for a plant extract that provides an excellent inhibition, low cost, and is environmentally safer.*** There is growing demand for corrosion inhibitors that are less toxic and biodegradable compared to current formulations. In this present study, the plant extracts in 1N HCl medium as a corrosion inhibitor in mild steel as a research study to investigate the inhibiting effect of aqueous

and alcohol extract using *weight loss method and EIS, Tafel, SEM and FTIR* technique. Green inhibitors displaying substantially improved environmental properties will be the inhibitors most widely used in the future.

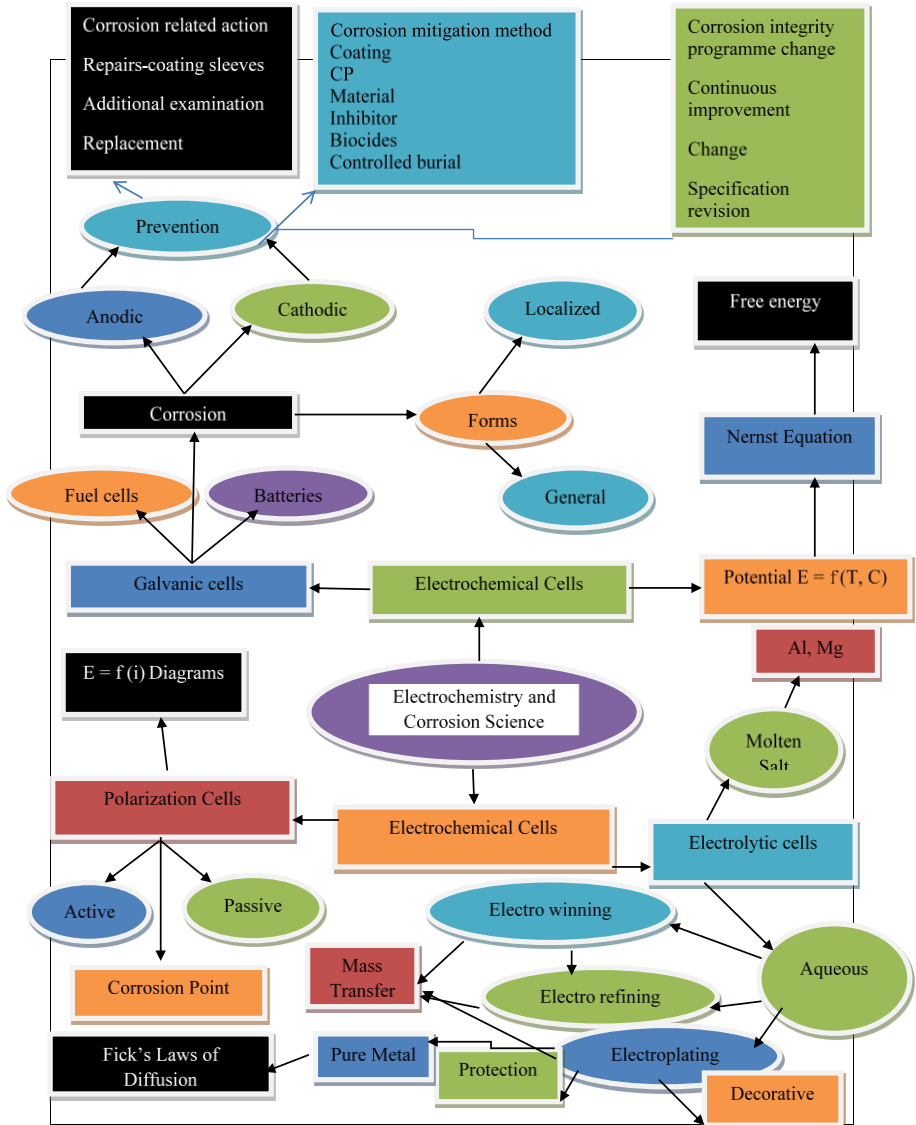


Fig. 7. Representation of Corrosion Control Plan

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