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INTRODUCTION

Corrosion and its Manifestations

By definition, "*corrosion is the physic-chemical interaction between a metal and its environment, which results in changes in the properties of the metal and which may often lead to impairment of the function of the metal, the environment, or the technical system of which these form a part*" (ISO 8044-1986).

Corrosion is the destructive attack on a metal by its environment through an unwanted, chemical or electrochemical reaction, starting at its surface. The term corrosion and rusting are often used interchangeably. The term 'rust' typically is applicable to ferrous materials, iron and steel. 'Corrosion' is used because it is inclusive of non- ferrous metals. Corrosion is an undesirable natural phenomenon which destroys the shine and splendor of the metallic objects and shortens their life. Corrosion has affected the quality of daily lives of people and also their technical progress ever since the ancient times. Corrosion is a natural process similar to all natural processes which tends the metal to revert back to its lowest possible energy states. Most of the metals and alloys have a natural tendency to react with water and oxygen present in the environment returning to its most stable state.

Corrosion takes place in different ways and classified depending upon the nature of the corrosive environment, mechanism of corrosion and appearance of the corroded metal. Based on these three factors, general forms of corrosion are classified as uniform or general corrosion, pitting corrosion, crevice corrosion, galvanic corrosion, erosion corrosion, inter-granular corrosion, stress corrosion and selective leaching.

1.1 Consequences of corrosion

Corrosion affects our society on a daily basis, causing degradation and damage to household appliances, automobiles, airplanes, highway bridges, energy production and distribution systems, and much more which are indirectly or directly associated with threat to lives of human. Some of the major consequences of corrosion are summarized below:

- Reduction in mechanical strength of the metal causing structural failure or breakdown
- Serious life threats or injuries to people due to structural failure or breakdown (e.g. bridges, cars, aircraft)
- Loss of time in repairing the industrial equipment damaged by corrosion
- Contamination of fluids in vessels and pipes which are corroded

- Perforation of vessels and pipes allowing escape of their contents and possible harm to the surroundings.
- Mechanical damage to valves, pumps, etc, or blockage of pipes by solid corrosion products
- Shutdown of nuclear plants, process plants, power plants and refineries may cause severe problems to industry and consumers.
- Loss of products, leaking containers, storage tanks, water and oil transportation lines and fuel tanks cause significant loss of product and may generate severe accidents and hazards

These consequences of corrosion results in huge economic loss and greatly affects the economic growth of all countries. The consequence of corrosion mainly affects the industries that are categorized under five major sectors viz, infrastructure, utilities, transportation, production and manufacturing and government. Based on these categories, the cost of corrosion for the industry sectors will be estimated. The cost of controlling this naturally occurring phenomenon and costs associated with the damage is substantial.

1.2 Cost of corrosion

The cost of corrosion in many countries ranges from approximately 1 to 5 percent of Gross National Product (GDP). In a widely-cited study (NACE Corrosion Costs Study) by the National Association of Corrosion Engineers (NACE), the direct cost of corrosion in the U.S. was estimated to equal $276 Billion in 1998, approximately 3.1 % of GDP.

1. A significant milestone in the effect of corrosion on the U.S. economy occurred in 2012 when the total cost of corrosion in the US exceeded $1 trillion annually for the first time. The annual cost of corrosion worldwide was estimated at $ 2.2 Trillion in 2010, which is about 3 % of the world's gross domestic product (GDP) of $ 73.33 Trillion.
2. NACE released the "International Measures of Prevention, Application and Economics of Corrosion Technology (IMPACT)" study, in which the global cost of corrosion was estimated to be US$2.5 trillion in 2016, roughly equivalent to 3.4 percent of the global Gross Domestic Product (GDP).
3. The two-year global study released at the CORROSION 2016 conference in Vancouver, B.C., examined the economics of corrosion and the role of corrosion management in establishing industry best practices. The study found that implementing corrosion prevention best practices could result in global savings of between 15-35 percent of the cost of damage, or between $375-875 billion (USD) (**NACE report, 2016**).

1.3 Best corrosion control practices:

Bob Chalker, CEO of NACE International has observed that, "Whether it is a pipeline, an airplane, a water treatment plant or highway bridge, corrosion prevention and control is essential to avoiding catastrophic events before it's too late". He also stated, it is necessary to minimize or control the corrosion of metals since the corrosion process is very harmful and the losses incurred are tremendous.

Since the types of corrosion are so numerous and the conditions under which corrosion occurs are so different, diverse methods are used to control corrosion. There are four common methods used to control corrosion which include material selection, cathodic protection, protective coatings and linings, and corrosion inhibitors.

- **Materials selection** refers to the selection and use of corrosion-resistant materials such as stainless steels, plastics, and special alloys to enhance the life span of a structure. Some of the most common materials used in constructing a variety of facilities, such as steel and steel-reinforced concrete, can be severely affected by corrosion.
- **Cathodic Protection** (CP) is a technology that uses direct electrical current to counteract the normal external corrosion of a structure that contains metal, such as an underground petroleum storage tank or natural gas pipeline. In new structures, CP can help prevent corrosion from the start itself whereas in existing structures, CP can help stop existing corrosion from getting worse.
- **Coatings and linings** are principal tools for protection against corrosion. Protective coatings are the most generally used method for preventing corrosion. The function of a protective coating is to provide a satisfactory barrier between the metal and its environment. These substances are often applied in conjunction with cathodic protection systems to provide the most cost-effective protection for a structure.
- **Corrosion inhibitors** are substances that, when added to a particular environment, decrease the rate of attack of that environment on a material such as metal. They can help extend the life of equipment, prevent system shutdowns and failures, avoid product contamination, prevent loss of heat transfer, and preserve the attractive appearance of structures.

1.4 Use of corrosion inhibitors

Among the various methods to prevent destruction or degradation of metal surface, the corrosion inhibitor is one of the best known and by far one of the most applied corrosion control strategy in oil-fields and many other industry sectors. This method is effective if the adsorption mechanism(s) of the adsorbed inhibitor compound at the metal surface is rightly defined. Generally, the inhibitors minimize the corrosion phenomenon by means of inhibiting action of

- chemically adsorbing (chemisorption) on the metal surface and forming a protective thin film with inhibitor effect or by combination between inhibitor ions and metallic surface;
- leading to a formation of a film by oxide protection of the base metal;
- reacting with a potential corrosive component present in aqueous media and the forming complex product.

1.4.1 Classification of inhibitors:

The corrosion inhibitors can be chemicals either synthetic or natural and could be classified as in Figure 1. (**Dariva and Galio, cdn.intechopen.com/pdfs/46243.pdf**)

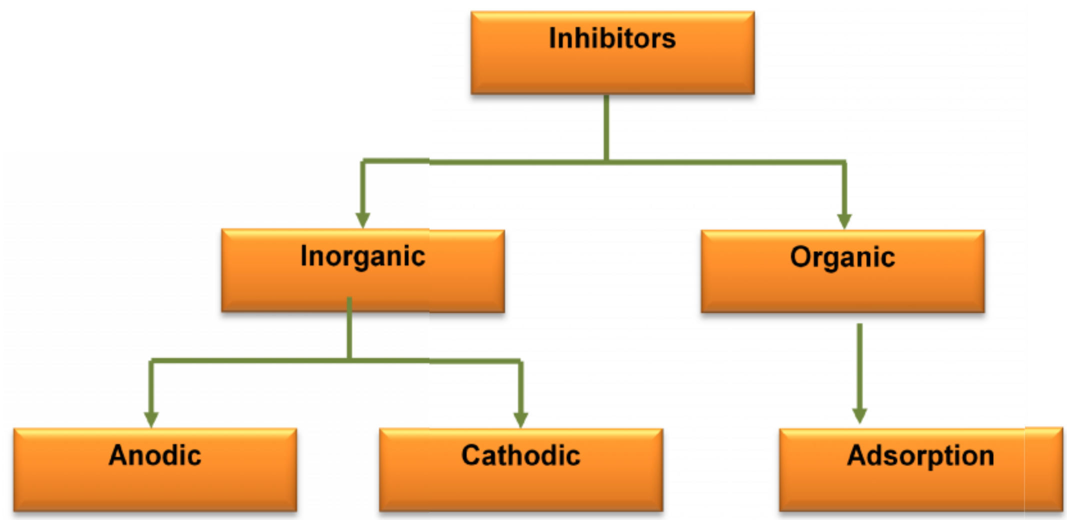

Figure 1 - Classification of Inhibitors

1) Inorganic inhibitors – Anodic inhibitors:

Anodic inhibitors (also called passivation inhibitors) act by reducing anodic reaction, that is, blocking the anode reaction and supporting the natural reaction of passivation metal surface, as well as, due to the forming a film adsorbed on the metal. In general, the inhibitors react with the corrosion product, initially formed, resulting in a cohesive and insoluble film on the metal surface. Examples for anodic inorganic inhibitors are nitrates, molybdates, sodium chromates, phosphates, hydroxides and silicates.

2) Cathodic inhibitors:

During the corrosion process, the cathodic corrosion inhibitors prevent the occurrence of the cathodic reaction of the metal. These inhibitors with metal ions have the ability to produce a cathodic reaction that precipitate selectively on cathodic sites, deposit over the metal a compact and adherent film, restricting the diffusion of reducible species in these areas. Thus, increase the impedance of the surface and the diffusion restriction of the reducible species, causing high cathodic inhibition. The cathodic inhibitors form a barrier of insoluble precipitates over the metal, covering it. Thus, restricting the metal contact with the environment, even if it is completely immersed, preventing the occurrence of the corrosion reaction. Due to this, the cathodic inhibitor is independent of concentration, thus, they are considerably more secure than anodic inhibitor. Examples of inorganic cathodic inhibitors are the ions of magnesium, zinc, and nickel that react with the hydroxyl (OH^-) of the water forming the insoluble hydroxides such as ($Mg(OH)_2$, $Zn(OH)_2$, $Ni(OH)_2$.

3) Organic inhibitors

Organic compounds used as inhibitors, occasionally, act as cathodic, anodic or together as cathodic and anodic inhibitors.They nevertheless, as a general rule, act through a process of surface adsorption, designated as a film- forming. Naturally the occurrence of molecules exhibiting a strong affinity for metal surfaces compounds showing good inhibition efficiency and low environmental risk. These inhibitors build up a protective hydrophobic film adsorbed molecules on the metal surface, which provides a barrier to the dissolution of the metal in the electrolyte. They must be soluble or dispersible in the medium surrounding the metal. The efficiency of an organic inhibitor depends on the:

- chemical structure, like the size of the organic molecule;
- aromaticity and/or conjugated bonding, as the carbon chain length; type and number of bonding atoms or groups in the molecule (either π or σ);
- nature and the charges of the metal surface of adsorption mode like bonding strength to metal substrate;
- ability for a layer to become compact or cross-linked,
- capability to form a complex with the atom as a solid within the metal lattice;
- type of the electrolyte solution like adequate solubility in the environment

Examples are amines, urea, Mercaptobenzothiazole (MBT), heterocyclic nitrogen compounds, sulfur-containing compounds and acetylenic compounds and also ascorbic acid, succinic acid, tryptamine.

Many industrial systems and commercial regions where inhibitors are applicable are cooling systems, refinery units, pipelines, chemicals, oil and gas production units, boilers and water processing, paints, pigments, lubricants, etc. Some of the commercial inhibitors used in these industries are listed below:

- Silicates, Chromates, nitrate, polyphosphates in Recirculation cooling water
- Benzoate, borax, phosphate, nitrite in Automotive coolants
- Ammonia, amines in steam condensates
- Chromates, nitrite in Sea water and brines
- Primary, amido-, quaternary amines, imidazoline in oil refineries

Now a days, due to changes occurring in the market of corrosion inhibitors, some industrial corrosion inhibitors are being unused. Normally in the field, these compounds are added in small concentrations to coolants, hydraulic fluids, or any other fluid (liquid or gas) surrounding the metal substrate, like alkyl aminophosphates and zinc dithiophosphates in fuel oil. Phosphates, and other inorganic sub-stances (e.g. chromates, dichromate and arsenates) are known to have detrimental environmental effect and human health impact and as such their usage is against modern safety regulation for the industrial chemicals with severe criticism. Currently, there is an increasing quest for limiting field applications involving toxic compounds. Hence the search for greener alternatives by reformulating the existing products or by identifying new chemistries for developing safer products (**Killaars & Finley, 2001**). Due to high toxicity of chromate, phosphate and arsenic compounds, related to various environmental and health problems, strict international laws were imposed. Reducing the use of these and therefore increasing the need for the development of other inhibitor to meet the inadequacy in this area. However, the new inhibitor should present similar anti corrosive properties as that of the existing better inhibitors.

1.5 Polymers for corrosion inhibitors

Polymers were found to be better choice for being used as corrosion inhibitors since they possess multiple functional groups thereby forming metal complexes with the metal ions and protect the metal surface from corrosion environment. The large molecular size of the polymers can cover a large surface area as a blanket on the active sites of the metallic surface. Attention towards polymers is principally due to its easy availability and cost effectiveness in addition to their inherent stability. Many researchers reviewed the exploitation of polymers as metal corrosion inhibitors (**Umoren (2009), Umoren and Solomon, 2014, Ali Fathima Sabirneeza *et al.*, 2015**).

1.6 Eco-friendliness- A fundamental requirement for corrosion inhibitors

Nowadays, environmental criteria have been a prerequisite for every product and process. Considering the environmental safety, impact of the human's health factor and ecological balance, the usage of toxic substances and the process which emit them are prohibited. The inorganic, organic, polymeric inhibitors and some of their hazardous organic counterparts, despite of their better performance towards metallic corrosion even at lower concentration could not fulfill the requirement of the environmental protection standards. Obviously, the need of the hour is to switch over to the eco-friendly inhibitors. As per environment regulations, the development of new corrosion inhibitors should replace the toxic compounds by so-called "Green chemicals" which are of the type non-toxic, environment-friendly and biodegradable. Moreover the choice of the inhibitor is restricted for a particular application by several factors viz, environment safe profile of the inhibitor, environment friendly scheme of synthesizing process and mode of inhibition action to achieve effective corrosion inhibition (Figure 2). Therefore, enormous scientific efforts have been made by researchers in recent times to develop new eco-friendly corrosion inhibitors to meet the environmental regulations. The term ''green inhibitor'' or ''eco-friendly inhibitor'' refers to the compounds which possess biocompatible nature with the environment.

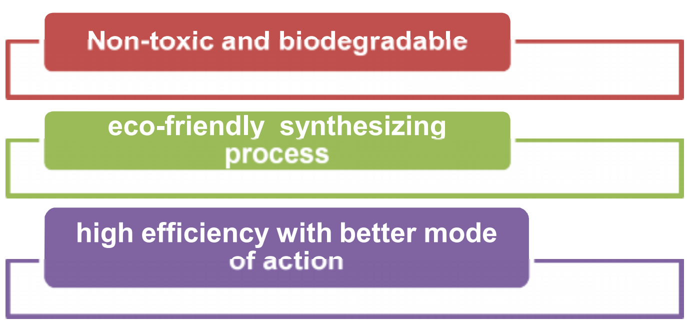

Figure 2 - Requirement of the eco-friendly inhibitor

1.6.1 Eco-friendly Inhibitors – Naturally occurring polymers for the corrosion protection

Recently, naturally occurring polymers, synthetic biopolymers and their derivatives have attracted the interest of the researchers since they meet the environmental requirements for better corrosion inhibition application. Naturally occurring polymers are biodegradable and do not contain heavy metals or other toxic substances.

Natural polymers are being used in many of application fields ranging from medicine, waste water treatment and so on. They are also found effective in corrosion inhibition since they represent a very good environment profile of biodegradability, biocompatibility, comprising of eco-friendly compounds which are chemically stable (Figure 3). As these compounds are extracted from the natural sources, they are regarded as low cost, renewable and readily available alternatives with essential and active ingredients responsible for the corrosion inhibition **(Rahim *et al*., 2008).**

Advantages of natural polymers- Eco-friendly inhibitors			
Non toxic and Cost effectivenes	Presence of multi functional groups which can don ate their lone pairs of electrons to metal surface forming protective layer	These lone pair of electron can participate in the bond formation whose strength depends on the electron donating group	The protective layer formed will be chemically stable

Figure 3 - Advantages of using Natural polymers as corrosion inhibitor

Objectives and Scope of the research work

- To synthesize environment friendly Chitosan Schiff bases with multiple functional groups and hetero atoms.
- To confirm the formation of imine groups in the polymer matrix using Elemental analysis, UV, FT-IR Spectroscopy and to determine the thermal stability of the Chitosan derivatives using thermo gravimetric analysis (TGA/DTA).
- To evaluate the corrosion inhibition performance of Chitosan Schiff bases on mild steel in 1M HCl at various times, concentration and temperature by weight loss and electrochemical methods.
- To monitor the adsorption behaviour of the Chitosan Schiff bases on the mild steel surface by cyclic voltammetric studies and to calculate the thermodynamic adsorption parameters using adsorption isotherms.
- To confirm the protective layer formation on the metal surface using surface analytical techniques.

- To determine the relationship between inhibition ability of Chitosan Schiff bases and their quantum chemical parameters using theoretical calculations.
- To propose a mechanism for adsorption of Chitosan Schiff bases with supporting evidences
- To explore the applicability of polymers as scale inhibitors in synthetic water samples.