

Introduction

1. INTRODUCTION

“Rust, corrosion, wind, rain. The nibbling teeth of mice and the acrid droppings of insects and the devouring jaws of years. The was of nature upon machines, of the planet's chaotic forces upon the works of humankind. The energy that man had pulled from the earth was being inexorably pulled back into it, sucked like water down a drain. Before long, if it hadn't happened already, not a single high-tension pole would be left standing on the earth”.

- Justin Cronin

Most people are familiar with corrosion in one form or another, particularly the rusting of an iron fence, the degradation of steel pilings, boats and boat fixtures. Pipelines are another major type of equipment subject to corrosion. This includes water pipes in the home, where corrosion attacks mostly from inside, as well as the underground water, gas, and oil pipelines that crisscross our land. Thus, it would appear safe to say that almost everyone is at least somewhat familiar with corrosion, which is defined in general terms as the degradation of a material, usually a metal, or its properties because of a reaction with its environment

Corrosion is defined as the deterioration of material by reaction to its environment (**NACE International**). Corrosion may be defined as a destructive phenomena, chemical or electrochemical, which can attack any metal or alloy through reaction by the surrounding environment and in extreme cases may cause structural failure. Corrosion occurs because of the natural tendency for most metals to return to their natural state; e.g., iron in the presence of moist air will revert to its natural state, iron oxide. Metals can be corroded by the direct reaction of the metal to a chemical; e.g., zinc will react with dilute sulfuric acid, and magnesium will react with alcohols.

The rapid industrialization of many countries indicates the competition for the metal resources. It is obvious that metals are extremely important in modern engineering, yet many can be badly affected by corrosion. With modern emphasis on health, safety and the environment, the case of managing corrosion has become an

imperative agenda. The importance of corrosion studies is three folds. The first is economic, including the reduction of material losses resulting from the wasting away or sudden failure of piping, tanks, metal components of machines, ships hulls, marine structures etc. The second is conservation, applied primarily to metal resources, the world's supply of which is limited, and the wastage of which includes corresponding loss of energy and water resources accompanying the production and fabrication of metal structures. The third is improved safety.

The petroleum, chemical, petrochemical, construction, manufacturing, pulp-paper and transportation (railroad, automotive and aerospace) industries are the largest contributors to corrosion expenditure. The cost of corrosion differs from country to country. For instance in USA, the transportation sector is the largest sector contributing to corrosion after public utilities, whereas in the oil producing countries, such as the Arabian Gulf countries, the petroleum industries. The latest surveys show that the worldwide direct cost of corrosion is around 3.1 to 3.5 percent of a nation's GDP (Gross Demand Product) value, **WCO (2012)**. The losses due to corrosion can be pictorially represented in **Figure 1.1**.

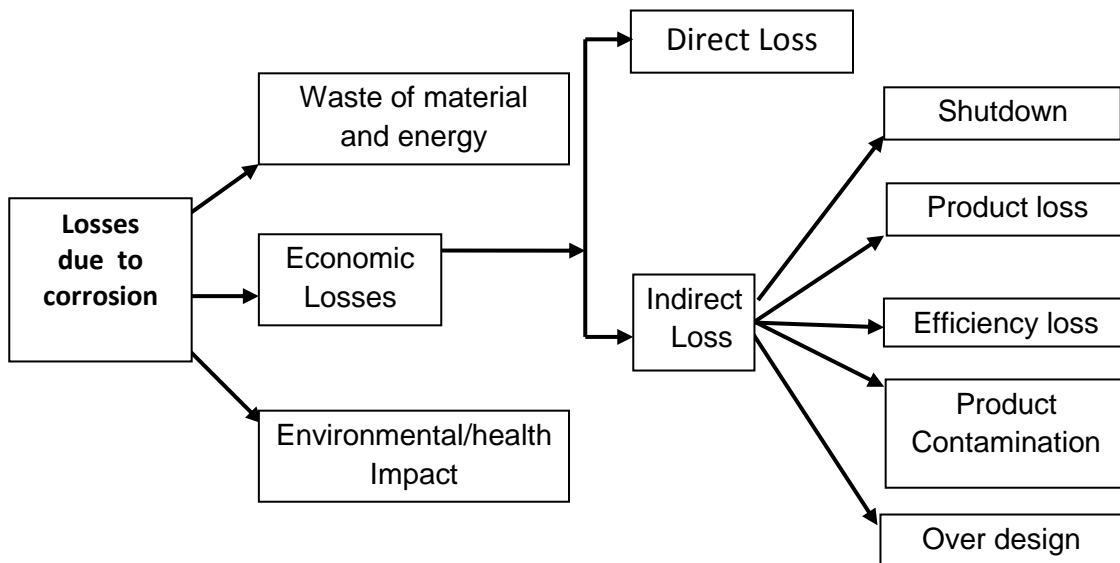


Figure 1.1. Losses due to corrosion

The indirect cost of corrosion was conservatively estimated to be equal to the direct cost. Lot of funds was utilized in many countries to study the cause and outcomes of corrosion every year. The main aim of research in corrosion protection is to reduce corrosivity of the desired material of choice. Beside the losses due to

corrosion, it severely affects the desired properties of the materials. Development of new technologies is held back by corrosion problems because materials are required to withstand high temperatures, pressures, and highly corrosive environment simultaneously. Nowadays corrosion research and quantum mechanics jointly play an important role in developing new alloy materials of desirable properties.

CORROSION CONTROL METHODS

Corrosion can be controlled by modifying either the material of choice or the environment. The materials can be modified by changing microstructure, composition, applying cathodic or anodic protection or coatings. The aggressive environment plays an important role in the extent of corrosion. The aggressiveness of the stagnant solution can be reduced by the removal of corrosive ions, changing operating variables and by the addition of inhibitors. The most economical way to control the corrosion can only be realized by applying a protective coating to the metal or by adding a corrosion inhibitor to the environment.

Corrosion Protective Coatings

Early attempts to mitigate corrosion of metals were empirical and centered largely on the use of organic and metallic coatings. There were obvious measures to protect metallic structures constructed by early artisans, often at the expense of much time and very hard labor (**Uhlig, 1971**). An organo-silicate hybrid coating was developed by **Khramov et al. (2005)** using sol-gel method. The organic corrosion inhibitors were preloaded in the coatings as a result of physical entrapment during film formation and cross-linking. It provided active corrosion protection when integrity of the coating is compromised. Organic compounds like mercaptobenzothiazole, mercaptobenzimidazole, mercaptobenzimidazole sulfonate, and thiosalicylic acid were tested for their inhibitive performance in the coatings, **Hayes and Kinlen (2011)**.

Khan et al. (2010) in their review article listed the various intrinsically conductive polymers with anticorrosive properties. It includes polyanilines, polypyrroles, polythiophenes and their derivatives. Many research articles showed the high corrosion inhibition performance of polyaniline based compounds in anticorrosive coatings. These compounds were used as such or in doped state or in the blended forms with paints or resins.

Corrosion Inhibitors

Inhibitors for acid corrosion of metals were known from middle ages. A corrosion inhibitor may be defined, in general terms, as a substance which when added in a small concentration to an environment effectively reduces the corrosion rate of a metal exposed to that environment (**NACE International**). Inhibitors are commonly used in four types of environments namely,

- 1) Cooling waters in the near neutral pH,
- 2) Primary and secondary crude oil productions and subsequent processes,
- 3) Volatile compounds are used in the aggressive gaseous environments such as boilers,
- 4) Pickling acid solutions for removal of rust and mill scale during the production and fabrication of metal parts or post-service cleaning of the parts.

A particular advantage of corrosion inhibitor is that it can be implemented or changed in situ without disrupting the actual process. The major industries using corrosion inhibitors are the oil and gas exploration and production industry, the petroleum refining industry, chemical industry, heavy industrial manufacturing industry, water treatment facilities and electroplating industries.

Cooling Water System – Scale Inhibitors

In addition to corrosion, scale formation is the major problem associated with cooling water systems. Moreover, the blowdown of the cooling water system could be recycled through the effluent treatment plants. The color and chemical oxygen demand (COD) of blowdown cooling water were reduced by the adsorption of inhibitors. Oxidative corrosion in cooling water system is substantially reduced by the addition of small amounts of sodium silicate and sodium glutonate, **Foroulis (1973)**. Schiff bases derived from diamines and *o*-hydroxy, *o*-methoxy aromatic aldehydes were investigated as corrosion inhibitor for mild steel in aqueous media by **Shokry et al. (1998)**. The naturally occurring compounds viz. *Azadirachta indica* (leaves), *Punica granatum* (shell), and *Momordica charantia* (fruits) were used as corrosion and scale inhibitors for the cooling water system, **Quraishi et al. (1999)**. Molybdate was capable of inhibiting the corrosion of mild steel in simulated cooling water, **Saremi et al. (2006)**. Sodium glutamate and monosaccharides derivatives were

used as corrosion and scale inhibitors for steel in simulated cooling water systems, **Tour et al. (2008 and 2009)**.

Volatile Corrosion Inhibitors

Corrosion inhibitors can be volatile or nonvolatile. Volatile Corrosion Inhibitors (VCI), also called Vapor Phase Inhibitors (VPI), are compounds transported in a closed environment to the site of corrosion by volatilization from a source. In boilers, volatile basic compounds, such as morpholine or hydrazine are transported with steam to prevent corrosion in condenser tubes by neutralizing acidic carbon dioxide or by shifting surface pH towards less acidic and corrosive values, **Vatsala et al. (1994)**. Superior performance and low cost of hydrazine fastly replaced morpholine in boiler systems. Increasing use of hydrazine pronounced toxic effects in humans, especially when it comes into contact with food stuffs. In closed vapor spaces like shipping containers, volatile solids such as salts of dicyclohexylamine, cyclohexylamine and hexamethylene-amine are used. **Koehan et al. (1999)** have formulated materials with ambient temperature vapour pressure using few organic compounds and their derivatives which were used as VCIs. Wood bark oils of *Cassia siamea-gonrai* (CS), *Cassia auriculata* (CA), *Crataeva religiosa* (CR) and *Strychnos nux-vomica* (SNV) were used as vapour phase corrosion inhibitors (VPI) for mild steel and copper in sodium chloride and sulphur dioxide environments, **Poongothai et al. (2005)**. Dicyclohexylamine and oleylamine were used as VCI for mild steel in CO₂ environment, **Jevremović et al. (2012)**.

Acid Corrosion Inhibitors

Nonvolatile compounds with electron donating centers can preferentially used as corrosion inhibitors for aqueous acid, basic or neutral aggressive medium. The acid corrosion inhibitors may be organic compounds, inorganic complexes, natural/plant materials or polymers.

Organic Inhibitors

Organic inhibitors are usually designated as 'film-forming', since they protect the metal by forming a hydrophobic film on the metal surface. The effectiveness of these inhibitors depends on the chemical composition, their molecular structure, and their affinities for the metal surface. The effect of different amino acids, aliphatic and aromatic carboxylic acids on the corrosion of aluminium in acid medium was reported

by **Saleh and Shams El Din (1972)**. The efficiency of the studied amino acids increased in the succession: alanine < glycine , iso-leucine < glutamic acid < methionine < cysteine. The adsorbability of the aliphatic carboxylic acids changed in the order, formic < acetic < propionic < butyric acid. Aromatic carboxylic acids were adsorbed through the carboxylic group and the aromatic rings.

Heterocyclic nitrogen compounds like pyridine, quinoline, acridine, n-hexadecyl-pyridine bromide, n-hexadecyl quinoline bromide, and n-hexadecyl acridine bromide were used as a corrosion inhibitor for SAE 1010 steel and OMMET pure iron in HCl medium, **Granese et al. (1992)**. The acridine and its derivative showed better inhibition performance while pyridine and its derivative showed the least inhibition efficiency.

Ebenso et al. (1999) have studied the effect of functional groups and molecular structures on the mild steel acid corrosion by different amides and thiosemicarbazones. Urea, thiourea, acetamide, thioacetamide, semicarbazide, thiosemicarbazide, methoxybenzaldehyde thiosemicarbazone, 2-acetylpyridine-(4-phenyl)thiosemicarbazone, 2-acetylpyridine-(4-methyl) thiosemicarbazone, benzoin thiosemicarbazone and benzil thiosemicarbazone were considered to study the effect of functional groups on the inhibitive performance. Compounds with thiocarbonyl group have higher inhibition efficiency than the others and followed the trend thiosemicarbazide > thiourea > thioacetamide. The semicarbazone derivatives followed the order benzoin > benzil > methoxybenzaldehyde > 2-acetylpyridine-(4-methyl) > 2-acetylpyridine-(4-phenyl) thiosemicarbazones.

Natural Products as Inhibitors

However, most of the corrosion inhibitors used in aqueous heating and cooling systems are organic and are hazardous to health. Their toxic properties limit their application areas. The greatly expanded interest on naturally occurring substances, otherwise tagged as green corrosion inhibitors is attributed to the fact that they are cheap, non toxic, biodegradable and readily available in plenty. Some of the plant based products used as corrosion inhibitors in recent years for different metals and alloys include, *Citrus paradise* (**Olusegun et al. 2004**), *Xylopi ferruginea* (**Amira et al. 2011**), *Hibiscus sabdariffa* (**Oguzi et al. 2008**), *Andrographis paniculata* and *Pongamia pinnata* (**Singh et al. 2010 and 2011**), *Phyllanthus amarus* (**Okafor et al. 2008**), *Nicotiana tabacum* (**Idowu and Isaac, 2011**),

Parthenium hystophrous (Muhamath and Kulanthai, 2009) *Cyamopsis Tetragonaloba* (Subhashini et al. 2010) *Myristica frangans* (Karthikaiselvi and Subhashini, 2013) etc., The authors used seeds, leaves or stems, extracted the chemical compounds present in the material using acids or organic solvents and used as corrosion inhibitors.

Many researchers isolated a specific compound or a group of compounds from the plant materials and used as corrosion inhibitors. Dahmani et al. (2010) have isolated piperine from black pepper and compared its corrosion inhibition property with black pepper extract. Both the extract and piperine provided above 95% inhibition efficiency. Rajendran (2011) isolated flavonoids from the flowers of *Nerium oleander* and *Tecoma stans* and used as corrosion inhibitors for mild steel in sulphuric acid medium. The flavonoid compounds responsible for corrosion properties are Myricetin and Rutin respectively. Berberine an alkaloid isolated from *Captis* was studied for its anticorrosive properties for mild steel in acid media by Li et al. (2005). In most of the cases isolated compounds showed somewhat lesser inhibition compared to the whole extract, this is obviously due to the synergistic effect of all the organic compounds present in the extract.

The increasing awareness on health and environmental friendliness promotes the use of natural products. But the performance of natural inhibitor is not consistent. There may be variations in the extent of corrosion inhibition depending on the location where the plants are grown, Ferry et al. (2013).

Polymeric Inhibitors

Biodegradable polymeric materials are environment friendly, nontoxic, and relatively less expensive. Several researches have indicated that some polymers can be used as corrosion inhibitors because, through their functional groups, they form complexes with metal ions and on metal surfaces. These complexes occupy a large surface area, thereby blanketing the surface and protecting the metals from corrosive agents present in the solution.

This work is concerned with the use of biodegradable g-polymers for mild steel corrosion; the reported polymeric inhibitors are discussed elaborately in the literature review. The consistent performance of the polymers compared to the inconsistent nature of the plant products make polymeric inhibitors as the superior

and reliable ones. It has been shown that polymers especially the water soluble ones are efficient corrosion inhibitors in different aqueous media. Mechanism of corrosion inhibition are mainly attributed to adsorption which depends on the nature of metal and physicochemical properties of the polymers such as functional groups, steric factors, aromaticity at the donor atom and p orbital character of donating electrons, as well as the electronic structure of the polymers.

Factors Influencing Corrosion Process

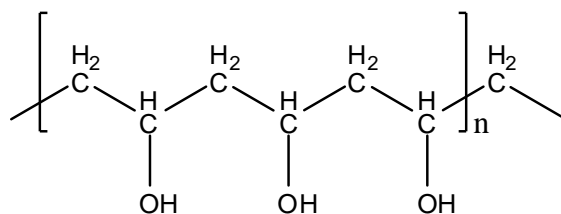
The major influencing factors for the type, rate, and cause of metal corrosion are nature of metal, relative areas of anode and cathode, climatic conditions, temperature and pH. Some metals have high tendency to corrode compared to others. Variations in size and shape of metal can indirectly affect the corrosion resistance property of the metal. Corrosion will be severe if the anodic area is small and the cathodic area is large. The environmental conditions under which metal is exposed greatly affect corrosion characteristics. The materials constantly exposed to sea water and salt air are highly susceptible for corrosion. The impact of the temperature on the corrosion rate of the material is usually very high, because the speed of electrochemical attack is increased in a hot, moist climate. The corrosion rate is maximum for MS when the environment is more acidic ($\text{pH} < 5$) and minimum when the environment is more alkaline ($\text{pH} > 11$).

SELECTION OF POLYMER MATRIX AND MONOMERS

Polyvinyl alcohol, polyvinylpyrrolidone, polyethylene glycol, pectin, dextran, cellulose etc., are water soluble ecofriendly polymer matrices. These polymers are readily available and economically feasible. PVA is a well known water soluble ecofriendly polymer with large number of hydroxyl groups, very good flexibility and wide commercial availability. It is composed mainly of 1,3-diol and a few percent 1,2-diols depending on the condition of polymerization. It exhibits excellent film forming, emulsifying, hygroscopic and adhesive properties. It can be used as a emulsion polymerization aid, as a protective colloid to make dispersions. The biodegradable and bioadaptable nature of polyvinyl alcohol find its role in feminine hygiene, adult incontinence products and embolization agent in medical procedures. The corrosion inhibition properties of polyvinyl alcohol has been reported by several investigators

for different varieties of metals **Khairou and El-Sayed, (2003); Rajendran et al. (2005); Umoren et al. (2006a) and Umoren et al. (2007a)**. Though several authors studied the inhibition performance of PVA it was not a highly efficient inhibitor having less than 80% inhibition efficiency. To achieve maximum inhibitor performance, **Ebenso et al. (2006); Umoren et al. (2006b and 2007b)** have studied the synergistic effect of halide ions on PVA. The synergism effect of the halide ions increased the inhibition performance of PVA to a greater extent.

Polyvinyl alcohol is a water soluble synthetic polymer exhibiting crystallinity. Polyvinyl alcohol (MP: 230 °C, MW: 1,40,000 g/mol; 86% hydrolysed) was selected on the above basis as a supporting matrix for the study. Based on the solubility of PVA the concentration was chosen to be less than or equal to 10 weight percent.



Polyvinyl alcohol (PVA)

Amino acids are selected as monomers for grafting to enhance the corrosion inhibition properties of PVA on the basis of the literature survey. Amino acids were selected, due to the rich source for heteroatom with electron donating centers and bio acceptability. The corrosion inhibition properties of various amino acids were reported in literature by **Ashassi-Sorkhabi et al. (2004 and 2005a); Badawy et al. (2006) and Barouni et al. (2008)**. Most of the amino acids provided good inhibition against corrosion of iron/steel, alloys of Cu etc. Though they are efficient corrosion inhibitors, their biological importance and high cost restricts their use as industrial corrosion inhibitors. Alpha L- amino acids selected for the study and are tabulated in **Table. 1.1**.

Table. 1.1. Selected Amino Acids and its properties

Aminoacid	Structure	Nature of side Chain	Molecular Weight	Melting point
L-Leucine (Essential)	$ \begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{CH}_2 \\ \\ \text{CH}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array} $	Hydrophobic	131.17 g/mol	295 °C
L-Histidine (Essential)	$ \begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{CH}_2 \\ \\ \text{N} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{NH} \end{array} $	Polar Charged	105.09 g/mol	284.5 °C
L-Serine (Nonessential)	$ \begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{CH}_2 \\ \\ \text{OH} \end{array} $	Polar Uncharged	131.17 g/mol	228 °C
L-Cysteine (Nonessential)	$ \begin{array}{c} \text{O} \\ \parallel \\ \text{H}_2\text{N}-\text{CH}-\text{C}-\text{OH} \\ \\ \text{CH}_2 \\ \\ \text{SH} \end{array} $	Special case	121.16 g/mol	240 °C

SELECTION OF MATERIAL

Iron and its alloys find utility in a wide spread spectrum of many industrial units because of its high abundance, low-cost and excellent mechanical properties. Despite the developments in corrosion resistant alloys over the past few decades, mild steel and carbon steel still constitutes an estimated 99% of the material used in the oil industry. Mild steel (MS) is an important material of choice for fabricating various reaction vessels, pipes, tanks, etc., Susceptibility of MS to rusting in humid air and its very high dissolution rate in acid medium are the major obstacles for its use on larger scale. Thus, much attention is given for its protection from the hostile

environments. For this reason, the corrosion behavior of these materials has attracted the attention of several electrochemists.

MS experiences series drawback owing to corrosion especially under aggressive environments during acid pickling, acid cleaning, oil well oxidizing, etc., which results in awful degradation. The rate of degradation is not only affected by the nature of acid but also their concentration and operating temperature.

SELECTION OF TEST MEDIUM

Acids are widely used for pickling, descaling and cleaning of industrial equipments. Among the various commercial acids, the most frequently used acid is hydrochloric acid. In steel and ferrous alloy industry, hydrochloric acid is used as pickling agent, and its greater application is removal of undesirable scales and rust present on steel materials. The use of hydrochloric acid in pickling of metals, acidization of oil wells and in cleaning of scales is more economical, efficient and trouble free compared to other mineral acids. But it requires corrosion inhibitor to reduce metal wastage for effective performance. Therefore the current work was carried out in 1M analar grade hydrochloric acid.

Considering the above factors in the present study L-amino acids like leucine, histidine, serine and cysteine were selected for grafting on to poly vinyl alcohol matrix to improve its inhibition efficiency for mild steel corrosion in 1M hydrochloric acid.

OBJECTIVES OF THE STUDY

- ❖ To synthesize graft polymers such as Poly(vinyl alcohol-leucine), Poly(vinyl alcohol-histidine), Poly(vinyl alcohol-serine) and Poly(vinyl alcohol-cysteine).
- ❖ To optimize the weight ratio of PVA and L-amino acids (leucine/histidine/serine/cysteine) for grafting based on inhibition efficiency using Taguchi experimental design.
- ❖ To Characterize the grafted polymers using UV-Visible, Fourier Transform Infra red spectra, (FTIR) Scanning electron microscope-Energy dispersive X-ray spectroscopy (SEM-EDX) and X-ray diffraction techniques
- ❖ To predict a possible mechanism for grafting.
- ❖ To study the thermal stability of the graft polymers using Thermogravimetry (TG), Differential thermal analysis (DTA) and Differential scanning calorimetry (DSC).
- ❖ To examine the corrosion inhibitive nature of the graft polymers on mild steel in acid medium using electrochemical impedance spectroscopy, linear polarization, potentiodynamic polarization and gravimetric methods.
- ❖ To confirm the adsorption of inhibitor through surface analytical techniques such as SEM-EDX, Atomic force microscopy (AFM) and Laser profilometry.
- ❖ To propose a probable mechanism for the corrosion inhibition process based on quantum chemical properties of graft polymers (using Hyperchem.7) and potential zero charge of mild steel.

