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INTRODUCTION

Most metals exist in nature as ores, oxides, sulfates, carbonates etc. when man refines them to pure metals, nature has its own way "CORROSION" for reverting them back to their parental state.

1.1 Corrosion - An inevitable but controllable phenomenon

Corrosion is a natural phenomenon in which the metal strives to go back to its original parental state. Similar to natural disasters like hurricane, tornado, landslide, earthquake etc. corrosion can also cause expensive damages to automobiles, structural buildings, bridges, energy production & distribution systems, drinking water systems and even human lives. Unlike weather-related disasters, corrosion can be controlled, but at some cost. The annual corrosion costs of a nation range from 1-5 % of the gross national product (**http://libback.uqu.edu.sa/hipres/Indu/indu10673.pdf).**

1.2 Significance of corrosion control

The need for more holistic and conciliatory solutions is vital for control of corrosion problems in and around the world. Though the corrosion control methods and strategies are innumerable, the costs involved are too high for most of them. A careful balance of innovative and inexpensive technologies for corrosion control is the need of the hour. A recent report published in a daily (***The Hindu*** dated April 20, 2014) calls for investment in the anti-corrosive measures. Dr. Samir Degan, Chairman of National Association of Corrosion Engineers, Mumbai, in his interview on the impact of corrosion and its prevention has emphasized that an investment in training and making people at every level aware of the correct procedures and protocols is necessary to ensure that our structures survive without any problems throughout their design life.

In an inaugural event to celebrate "100 years of stainless steel-towards building corrosion free India", ONGC Chief Managing Director Sudhir Vasudeva has mentioned that India loses more than USD 40 billion a year - about 4 percent of the size of the total economy - due to corrosion in infrastructure and industry segments. He also added that better corrosion control is needed through use of proper grade of stainless steel as capex on infra is exorbitant. Oil industry is the second largest after chemical industry that faces severe corrosion problems.

Considering the above mentioned facts, World Corrosion Organization (WCO) has designated 24th April as Corrosion Awareness Day. Corrosion problems spelled in various sectors are shown in the trapezoid list (Figure 1). As the spell of corrosion and losses due to corrosion is inevitable, awareness about the corrosion and timely measures can help in mitigating the corrosion to a larger extent. The corrosion preventive measures not only help the country economically by cutting down the costs, but also save hundreds of innocent human lives from the corrosion catastrophes. The newspaper clippings (Fig. 2) describe the major catastrophes due to corrosion around the world from 1984-2014.

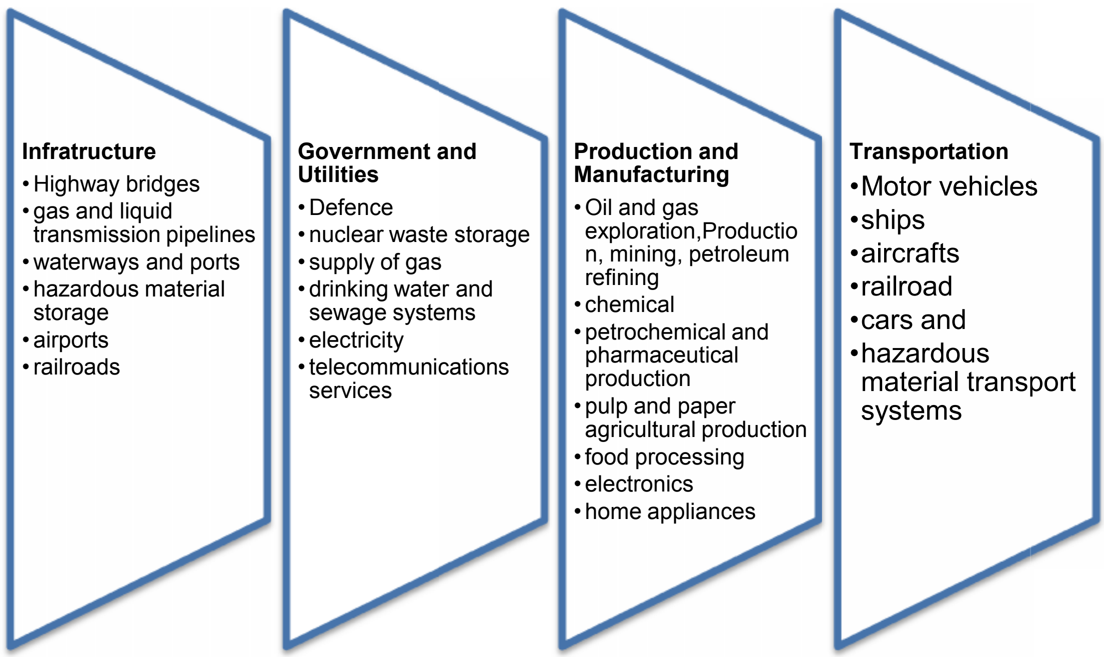

Figure - 1 Trapezoid list showing corrosion in various industries

Figure - 2 Newspaper clippings of World's most disastrous corrosion catastrophes

1.3 Corrosion of iron and its alloys

Iron and its alloys such as mild steel, carbon steel are used worldwide in industries and household articles because of their relatively low cost and availability. Mild steel is a type of steel alloy that contains a carbon (0.2% to 2.1%) as one of the major constituent and is used in construction, car manufacturing industries, and manufacturing of bullets, knives, armours, bolt & nut, hinges, chains, pipes and so on. Stainless steel is preferred over mild steel for its near zero corrosion property. The different amount of carbon present in the steel decides the strength and ductility of the steel. The carbon atoms affixed in the interstitial sites of the iron lattice make it stronger. So, when the carbon content is high, the steel is stronger and stiffer but has low ductility and highly prone to corrosive attack. Inspite of their good mechanical properties, susceptibility to corrosion attack cannot be ruled out. Mild steel is exposed to different environments like acid, Underground (soil), Atmosphere, Salt water, and Fresh water. The metallic material made using steel is usually cleaned with hydrochloric acid and sulphuric acid to remove the rust and scales and the process is called as pickling which further enhances corrosion. The pipelines made of mild steel come into contact with underground soil and gets corroded. Bridges, highways and electric poles made of mild steel are some of the examples where atmospheric corrosion takes place. Chloride rich sea water is another environment which when comes into contact with steel causes severe corrosion and produces scales on the metals. Mild steel suffers from corrosion in the recirculating systems such as cooling towers.

1.4 Corrosion control methods in practice

The most prevalent corrosion control methods include conditioning the metal and conditioning the corrosive environment **(http://www.npl.co.uk/upload/pdf/ basics of corrosion control.pdf).**

i. **Conditioning the metal**

Conditioning the metal can be achieved by coating the metal or alloying the metal. ***Coating of the metal,*** through which a protective layer is applied on the surface of the metal as a barrier between metal and corrosive environment.

The coating can be

- Metallic coating by other metal e.g. Zinc or tin coating on steel.
- Metallic oxide coating formed by the metal itself, e.g. Aluminium oxide on aluminium.
- Organic coatings in the form of paints, resins, pigments, oils, enamels and greases.

Alloying the metal, through which a more corrosion resistant metal can be obtained. *E.g*. Stainless steel, which is produced by alloying with chromium and nickel.

ii. Conditioning the environment

Removal of Oxygen: Oxygen is one of the component responsible for corrosion in water systems having the pH range of 6.5-8.5. Hence the removal of oxygen from such systems by the use of strong reducing agents like sulphite can help in corrosion control.

Use of corrosion inhibitors: A corrosion inhibitor is a chemical additive, which when added in small quantity to a corrosive environment reduces the rate of corrosion remarkably. Inhibitors generally function by getting adsorbed on the metal surface. Several organic, inorganic, polymeric and natural inhibitors are studied and recommended as corrosion inhibitors for metals subjected to harsh environments including aqueous, nonaqueous, molten salts, and dry atmospheres.

iii. Electrochemical control

Since corrosion is a electrochemical process, corrosion reactions can be studied by measuring the potential changes with respect to time or applied voltage. Similarly, the corrosion can also be controlled by passing anodic/cathodic currents into the metal. For e.g. If a DC current is passed into the metal the anodic reaction gets stifled due to the external supply of electrons, while the cathodic reaction is enhanced. This is called cathodic protection as the cathodic reaction forms a protective oxide film. If a current is passed such that the electrons are removed from the system, anodic reaction gets accelerated initially, but later formation of protective oxide film controls the corrosion reaction.

The scope of the present study involves the use of corrosion inhibitors for corrosion mitigation during pickling. Hence a detailed insight into the inhibitors and their properties are discussed in the following sections. The inhibitors are generally developed and used by trial and error experimental method. The selectivity of the inhibitors is an important tool before its application, because the activity of inhibitor varies with respect to the environmental conditions. The following parameters have to be taken into account for proper selection of inhibitors **(Patel and Mehta, 2012).**

- solubility
- compatibility with the corroding system;
- durability of the inhibitor with respect to various environmental conditions including temperature, pH and time;
- pollution to the environment through the effluents containing the inhibitor and cost

1.5 Classification of corrosion inhibitors

Corrosion inhibitors are generally classified as in Figure 3 and described in the following sections.

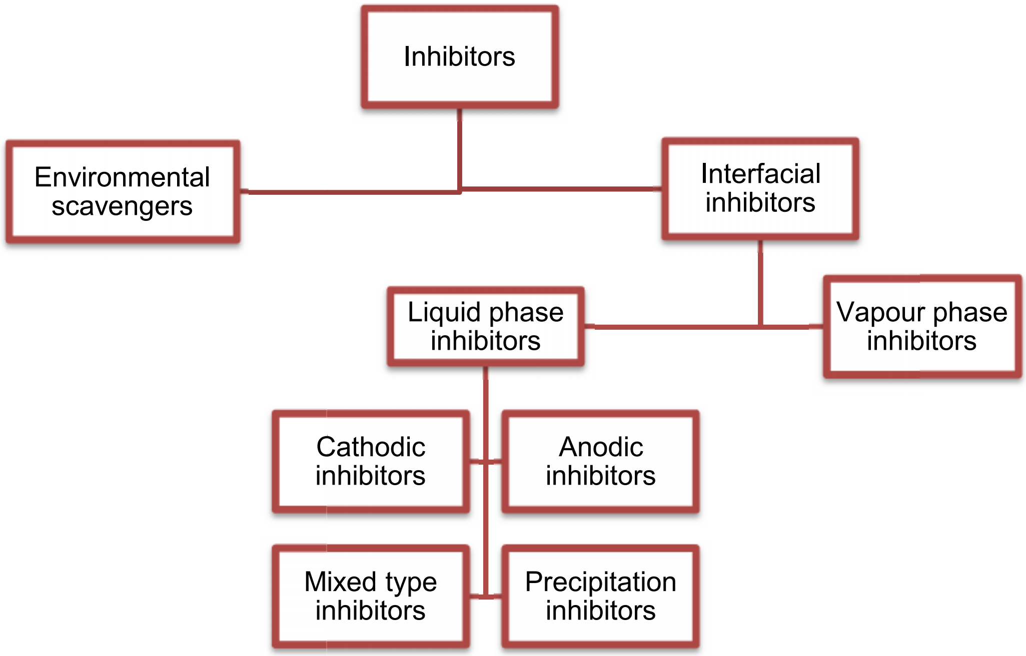

Figure - 3 Classification of inhibitors

1.5.1 Environmental scavengers

Environmental scavengers are substances that are used to condition the environment, i.e. to remove the corrosion causing species from the environment. In near neutral or alkaline solutions, oxygen reduction is a cathodic reaction that aggravates the corrosion. Hence, the removal of oxygen by environmental scavengers like hydrazine helps in combating the corrosion. The mechanistic aspect of the scavenging reaction can be given as follows:

$$O_2 + H_2O + 4e^- \rightleftharpoons 4OH^-$$
$$5O_2 + 2\,(NH_2\text{-}NH_2) \rightleftharpoons 2H_2O + 4\,H^+ + 4\,NO_2^-$$

1.5.2 Interfacial inhibitors

This type of inhibitors control corrosion by directly coming into contact with the metal/environment interface. The inhibitors form a protective film on the metal surface and prevent contact with the corrosive medium. These are further classified as vapour phase and liquid phase inhibitors.

i) Vapour phase inhibitors

Vapour phase inhibitors (VPI) are volatilized inhibitors that get adsorbed on material surfaces to form thin protective unimolecular films. They may also get absorbed on the electrolyte films that are already formed on the surface. They are mostly used in environment where free flow of air is not present like packaging containers, fuel tanks and gear boxes, distillation columns and boilers. For e.g. in boiler systems, the VPIs such as morpholine or hydrazine is volatilized by the steam which function either by neutralizing the CO_2 or shifting the surface pH to less acidic values. The VPIs are preferred inhibitors due to their durability, and uniform corrosion mitigating ability without enhancing other forms of corrosion **(Skinner, 1993).**

ii) Anodic Inhibitors

Anodic inhibitors generally function by interfering the anodic reactions by formation of protective oxide film. As a result the anodic sites are reduced in the metallic surface causing a large anodic shift from the corrosion potential. Since these inhibitors function by passivation of metal surface, they are also called as passivation inhibitors. Examples for the passivating inhibitors/film forming inhibitors include inorganic salts added to neutral or alkaline media. E.g. Chromates, nitrates, tungstates, molybdates etc.,

iii) Cathodic Inhibitors

Cathodic inhibitors generally function by interfering in the cathodic reactions. These inhibitors reduce the cathodic sites by formation of a barrier film thereby polarising the cathodic regions causing a cathodic shift from the corrosion potential. Most of the organic compounds containing electron rich hetero atoms like N,O, S and P are examples for cathodic inhibitors. These hetero atoms act as reaction centre and help the compound to get absorbed on the metal surface either in ionic or molecular form. Some cathodic inhibitors function by precipitating an insoluble species on the cathodic sites thereby preventing the cathodic reaction. Since these type of inhibitors function by adsorption mechanism, the inhibitors are also called adsorption-type inhibitors.

iv) Mixed-type inhibitors

Inhibitors that are capable of retarding both cathodic and anodic reactions are called mixed-type inhibitors. i.e. it impedes the anodic metal dissolution and cathodic hydrogen evolution. A mixed type inhibitor is harmless, if the anodic reaction suppressing ability is higher than the cathodic reaction suppressing ability, and vice versa.

v) Precipitation inhibitors

The precipitation inhibitors are film forming inhibitors, for e.g. silicates and phosphates. They are similar to mixed type inhibitor by blocking both anodic and cathodic sites, but they precipitate on the metal surface to form a protective barrier. They act in two different ways by simply slowing down the corrosion or completely ceasing the corrosion attack.

1.6 Water soluble polymers as Corrosion Inhibitors

Water soluble polymers represent a diverse class of polymers ranging from biopolymers that are inevitable for the life processes to synthetic polymers having profound commercial applications. The water soluble polymers have gained an economical and environmental importance because water is an easily available and environmental friendly solvent. Moreover water solubility is an appreciable quality when compared to the traditional solvent solubility. The advantage of utilizing water soluble macromolecules as corrosion inhibitors for metals in different media has been discussed. The water soluble polymer can be utilized as corrosion inhibitors in acid, neutral and basic mediums. Several researches **(Ali fathima Sabirneeza *et al.,* 2014; Umoren and Solomon, 2014)** have reviewed the use of polymers as corrosion inhibitors. PVA was reported as good corrosion inhibitors in different media for various metals. The inhibition efficiency of PVA can be improved by introducing more functional groups in its structure. Grafting is an attractive method to impart a variety of functional groups to a polymer. In this context, efforts are made to modify PVA by grafting with AA/AAm/VSA/PVBS through chemical process and the following water soluble grafted terpolymers have been synthesized:

i) PVA-AAm-VSA (Polyvinyl alcohol-g-poly(acrylamide-vinyl sulfonate)
ii) PVA-AA-VSA (Polyvinyl alcohol-g-poly(acrylic acid-vinyl sulfonate)
iii) PVA-AAm-PVBS (Polyvinyl alcohol-g-poly(acrylamide-p-vinyl benzene sulfonate)
iv) PVA-AA-PVBS (Polyvinyl alcohol-g-poly(acrylic acid-p-vinyl benzene sulfonate)
v) PVA-VSA-PVBS (Polyvinyl alcohol-g-poly(vinyl sulfonate-p-vinyl benzene sulfonate).

Grafting of polymers can be carried out in three different ways: Graft-from, graft-onto, graft-through methods **(Bhattacharya and Misrab, 2004)**. In the graft-from method, the reaction initiating site is created on the backbone polymer from which the polymerization of the other monomer takes place. The initiating site on the backbone can be a free radical, anion, cation or Zieglar-Natta type catalysts. The main advantages of this type include extensive cross-linking and formation of products of high mechanical strength. The disadvantages include production of homopolymers, uncontrollable chain length and grafting units. When the polymer chains are attached through chain-end moieties on a polymer backbone, the process is called grafting-onto method. Though this type of reaction does not initiate monomer polymerization, controlling grafting units and removal of ungrafted monomers is cumbersome. This research work is focussed on the synthesis of water soluble grafted terpolymers by graft-from method through free radical polymerisation and to analyse their inhibition efficiency on mild steel in acid medium.

1.7 Objectives and Scope of the research work

- To synthesize some water soluble grafted terpolymers: PVA-AAm-VSA, PVA-AA-VSA, PVA-AAm-PVBS, PVA-AA-PVBS and PVA-VSA-PVBS.
- To characterize the polymers using UV, FT-IR spectra, NMR Spectra, thermogravimetric analysis (TGA/DTA) and differential scanning calorimetry (DSC).
- To evaluate the terpolymers as corrosion inhibitors for mild steel in 1 M HCl by weight loss and electrochemical methods at different environmental conditions.
- To determine the adsorption of terpolymers on mild steel surface by surface analysis techniques.
- To arrive at a possible mechanism for the inhibition process.
- To investigate the applicability of the synthesized terpolymers as oil field inhibitors on N80 steel in HCl, NaCl and simulated oil well water.