CHAPTER -1

INTRODUCTION

1.1. Definition of Corrosion

Corrosion in a broad sense signifies the whole range of reactions between metals and their environments. Uhlig [1] describes corrosion as the reaction of a solid with environment. It is now generally accepted that corrosion is a reversion or a partial reversion from the metastable condition of the metal to stable condition of the mineral accompanied by the reduction in the free energy of the system. It is the commonest electrochemical phenomenon experienced in day-to-day living. Common examples are rusting of iron and steel, tarnishing of silver and copper, etc.,

1.2. Historical Background

Significant amounts of electricity were generated by the use of the phenomenon of corrosion by means of well known Voltaic pile. Nicholson and Carlisle [2], Davy[3] and subsequently Faraday [4] in 1834, established the close relationship between current and electrochemical reactions. In 1827, Bacquarel [5] proposed that corrosion took place when there was difference in metal ion concentration. Dela Rive [6] pointed out that if zinc was impure it dissolved faster in acid solutions. In 1847, Richard Adie [7] demonstrated that difference in
oxygen concentration in a flowing stream could give rise to a flow of current between two pieces of iron or zinc.

Trends in corrosion research changed rapidly over the years. In the fifties, polarisation studies and their applications had been the topic of interest [8-10]. In the seventies corrosion research was concentrated on the mechanistic studies on metal dissolution, localised corrosion and high temperature corrosion [11-17]. In recent years corrosion research has been diversified into several newer fields. The optical techniques have revolutionised the field. Surface analytical techniques play a major role since, surface analytical techniques give more insight into the understanding of the nature and influence of surface oxides on the corrosion of metals and alloys. These techniques are helpful to characterise thickness, structure and composition of films. Computers [18,19] and microprocessors [20] find application in analysing corrosion data.

The ultimate objective of all these investigations is to minimise corrosion failures.

1.3. Classification of corrosion

Corrosion of metals can be broadly classified as (i) dry or chemical corrosion and (ii) wet or electrochemical corrosion.

The reaction of metals with 'dry' air or oxygen is considered as dry or chemical corrosion. High temperature oxidation of metals and tarnishing of metals like Cu, Ag etc., fall in this category. Of late, this is also considered to be
an electrochemical process with diffusion of oxygen inwards and metal ions outwards, through the oxide layer and the electromotive force at the metal-oxide interface is considered as the driving force.

Wet or electrochemical corrosion occurs in presence of electrolytic solution. The reaction is considered to take at the metal-solution interface due to the presence of heterogeneity in the metal surface, which creates local cathodic and anodic sites in the metal.

1.4. Factors influencing corrosion

The nature and extent of corrosion depends on the metal and environment. The important factors influencing corrosion are:

| i) | Nature of the metal |
| ii) | Nature of the environment |
| iii) | Electrode potential |
| IV) | Nature of the corrosion products formed |
| V) | Hydrogen overpotential |
| Vi) | Concentration of various ions in solution |
| vii) | pH of the solution |
| viii) | Amount of dissolved oxygen |
| ix) | Conditions of flow of solution, and |
| x) | Temperature |
I.5. Corrosion – The basic electrochemical process [21]

Corrosion (or) cancer of metals arises from the thermodynamic instability. During the production of iron, ores such as haematite (Fe₂O₃) is reduced with carbon in the form of coke

\[ 2 \text{Fe}_2\text{O}_3 + 3\text{C} \rightarrow 4\text{Fe} + 3\text{CO}_2 \quad \text{--- 1.1} \]

\([\text{Ore}] \quad [\text{Coke}] \quad [\text{Iron}] \quad [\text{Gas}]\]

Energy is spent in this process and consequently steel, when exposed to moisture and air, tends to revert to its original form of lower energy state as indicated below

\[ 4\text{Fe} + 3\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O} \quad \text{--- 1.2} \]

\(\text{Iron} \quad \text{Rust}\)

In the presence of moisture and oxygen, the poor protective film present on the metal surface breaks and corrosion occurs. Micro galvanic cells with local anodes and cathodes are formed on the metal surface due to heterogeneities in the metal composition. Heterogeneities are due to defects, grain structures and variations in composition of solution such as differential aeration and differential concentrations (Fig.I.1). The above process is basically electrochemical in nature and can be written as follows:

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad \text{[anodic reaction]} \quad \text{--- 1.3} \]

\(\text{Iron} \quad \text{Ions} \quad \text{Electrons}\)
Fig. I.1 Diagrammatic representation of a steel surface showing anodes and cathodes
The cathodic reaction can be either hydrogen evolution or oxygen reduction.

\[
2\text{H}^+ + 2e \rightarrow \text{H}_2 \uparrow \quad \text{[acid solutions]} \quad \Delta G = -1.4
\]

\[
4\text{H}^+ + \text{O}_2 \rightarrow 2\text{H}_2\text{O} \quad \text{[aerated acid solutions]} \quad \Delta G = -1.5
\]

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4e \leftrightarrow 4\text{OH}^- \quad \text{[neutral solutions]} \quad \Delta G = -1.6
\]

1.6. Corrosion Thermodynamics [22]

In most of the cases, metallic state represents the state of high energy. Therefore, metals have a natural tendency to react with other substances and go back to lower energy state with subsequent release of energy. Except noble metals, which are found in native state in nature, all other metals show decrease in free energy by undergoing the reaction with the environment. Thermodynamic stability of any chemical compounds is determined by the sign and the change in the free energy (\(\Delta G\)).

The thermodynamic data have been accumulated for many metals [23], M. Pourbaix combined solubility data of oxides, hydroxides and other salts with equilibrium constants for reaction of these to produce potential - pH diagrams [24]. The potential - pH diagram presents, curves representing chemical and electrochemical equilibria which try to provide the boundary conditions under which immunity, corrosion or passivation may be expected. The potential pH diagram for Fe/H\(_2\)O system is shown in Fig.1.2.
Fig. 1.2 Potential – pH diagram for iron; iron concentration is $10^{-6}$ gram atoms per litre, temperature 25°C.
Each line represents a balanced reaction. A horizontal line represents equilibrium involving electrons but not H\(^+\) or OH\(^-\) ions, a vertical line represents one involving H\(^+\) or OH\(^-\) but not electrons; a sloping line indicates one involving H\(^+\) (or) OH\(^-\) (or) electrons. These diagrams provide conditions under which metallic ions are stable, the corrosion products are stable or metal is stable.

The horizontal line marked 'a' shows the potential of electrode equilibria.

\[ \text{Fe} \rightleftharpoons \text{Fe}^{2+} + 2 \text{e}^- \quad \text{---- 1.7} \]

The vertical line marked 'b' represents hydrolysis.

\[ \text{Fe}^{3+} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe(OH)}^{2+} + 2\text{H}^+ \quad \text{---- 1.8} \]

The sloping curve 'c' shows the possibility of equilibria of reductive dissolution of solid ferric oxide to ferrous ions in the liquid.

\[ 2\text{Fe}^{2+} + 3\text{H}_2\text{O} \rightleftharpoons \text{Fe}_2\text{O}_3 + 6\text{H}^+ + 2\text{e}^- \quad \text{---- 1.9} \]

Below the line 'a' corrosion does not occur and this region is known as the region of immunity.

The region in which Fe\(^{2+}\) ions are stable is the region of corrosion. When a solid corrosion film is formed, further entry of metal ions into solutions will be restricted and this area is the area of passivation. But their use is generally
limited by the fact that all diagrams published for metal – water – oxide systems are restricted to 25°C.

I.7. Corrosion kinetics

Corrosion is an electrochemical process consisting of simultaneous oxidation of metal, with accompanying reduction process of reducible species. Rates of corrosion reactions are determined by the kinetics of these reactions.

Activation controlled reactions:

The rate of an simple anodic reaction,

\[ M_{(s)} \rightarrow M^{+}_{(soln)} + e^{-} \]  \hspace{1cm} (1.10)

can be written in terms of current density as

\[ i_a = F \ K_a \]  \hspace{1cm} (1.11)

The rate of backward reaction can be written as

\[ i_c = - F \ K_c \ C^{+} \]  \hspace{1cm} (1.12)

where \( K_a \) and \( K_c \) are the potential dependent heterogeneous rate constants.

The potential dependence of the rate constant is given by

\[ K_a = K_a \left( \frac{\alpha_i F}{RT} \phi \right) \exp \]  \hspace{1cm} (1.13)
\[ K_c = K_c \left( \frac{-\alpha F}{RT} \phi \right) \exp \] —— 1.14

where \( \phi \) is the electrode potential, taken with reference to standard hydrogen electrode, \( \alpha_a \) and \( \alpha_c \) are the intrinsic kinetic parameters and have values of 0.5 for simple one electron transfer process.

Now the rate of anodic and cathodic reactions may be written as

\[ i_a = F K_a \left( \frac{\alpha_a F}{RT} \phi \right) \exp \] —— 1.15

\[ i_c = F K_c \left( \frac{-\alpha_c F}{RT} \phi \right) \exp \] —— 1.16

The net current density

\[ i = i_a - i_c \] —— 1.17

at equilibrium net current is zero and \( \phi \) becomes \( \phi^* \)

The exchange current density \( i_0 \) is given by

\[ i_0 = F K_a \left[ K_c C_{M^*} / K_a \right] \alpha_a / \left[ \alpha_a + \alpha_c \right] \] —— 1.18
Therefore the net current density is given by

\[ i = i_o \exp \left( \frac{\alpha_a F}{RT} [\phi - \phi^*] \right) - \exp \left( \frac{-\alpha_c F}{RT} [\phi - \phi^*] \right) \quad \text{or} \quad 1.19 \]

\[ i = i_o \left( \exp \left( \frac{\alpha_a F}{RT} \eta \right) \right) - \exp \left( \frac{-\alpha_c F}{RT} \eta \right) \quad \text{----} \quad 1.20 \]

Where \( \eta = \phi - \phi^* \) \quad \text{----} \quad 1.21

This is the Butler – Volmer equation [25] for electrode kinetics of single step reaction.

For a multi electron process the above equation becomes [26]

\[ i = i_o \left( \exp \left( \frac{\alpha_a F}{RT} \eta \right) \right) - \exp \left( \frac{-\alpha_c F}{RT} \eta \right) \quad \text{----} \quad 1.22 \]

Where \( \alpha_a \) and \( \alpha_c \) are transfer coefficients of oxidation and reduction process, which are given as

\[ \alpha_a = \frac{V}{\nu} + \gamma \beta \quad \text{----} \quad 1.23 \]

\[ \alpha_c = \left[ n - \frac{V}{\nu} \right] - \gamma \beta \quad \text{----} \quad 1.24 \]
Where,

\[ \eta = \text{total number of electrons transferred in overall reaction} \]

\[ \beta = \text{symmetry factor} \]

\[ \gamma = \text{number of electrons involved in rate determining step} \]

\[ \nu = \text{stoichiometric number} \]

\[ V = \text{number of electrons transferred before r.d.s.} \]

At very high overpotentials \([\eta \gg \text{RT/F}]\),

\[ i_s = i_o \exp \left( \frac{\alpha_d F}{RT} \times \eta \right) \]  \[\text{[or]}\]

\[ \eta = a + b \log i_o \]

\[ \text{Where } a = \frac{-RT}{\alpha_d F} \ln i_o \]

\[ b = \frac{RT}{\alpha_d F} \]

The above equation is the Tafel equation [27] where 'a' is called Tafel constant, 'b' is the Tafel slope. A plot of \( \eta \) vs log current density gives the polarisation diagram in which the intercept and the slope correspond to \( i_o \) and \( b \) respectively.
1.8. Diffusion controlled reactions [22]

In a charge transfer process, the transport of an electroactive species from the bulk to metal/solution interface is a necessary step. If this transport is the controlling step, the reaction is said to be under diffusion control. The rate of a diffusion controlled process is given by Fick’s law

\[
i = nF \left( \frac{dc}{dx} \right)_{x=0}
\]

\[\text{--- 1.27}\]

The concentration gradient is a constant only for a short distance from the interface and the concentration changes in a linear fashion in the diffusion layer \([\delta]\)

Therefore, \[i = \frac{nFD}{\delta} [C_b - C_x = 0]\]

\[\text{--- 1.28}\]

where \(D\) is diffusion coefficient and \(\delta\) is thickness of the diffusion layer.

The concentration overpotential for a diffusion controlled reaction is given by

\[
\eta_c = \frac{RT}{nF} \ln \left[ \frac{i}{i_L} \right]
\]

\[\text{--- 1.29}\]

where, \(i_L\) = limiting current density.
Fig. 1.3 Polarisation conditions of corroding electrode; where — = real anodic or cathodic current, $i_a$ and $i_c$; ----- = outer (measurable) anodic or cathodic current, $I_a$ or $I_c$, $e_{corr} = \text{corrosion potential, } I_{corr} = \text{corrosion current}$
1.9. Mixed potential controlled reactions

Wagner and Traud [28] developed this concept. As the term implies, it is an irreversible, non-equilibrium potential formed by a mixing of the two electrode reactions coupled by a common current. The mixed potential is called as corrosion potential.

Fig. 1.3. shows the polarisation diagram of a corroding metal M with hydrogen evolution as the cathodic process. When the metal does not corrode the metal would assume the equilibrium potential, $e_{M,0}$. Similarly hydrogen reversible equilibrium $i_{H}$ and $e_{H,0}$ are the exchange current density and hydrogen equilibrium potential. During corrosion, the anodes tend to attain the potentials of cathodes and vice versa. The measurable electrode potential is a common intermediate potential called corrosion potential $e_{Cor}$. The local cell current in the absence of any external current is called corrosion current. The above figure is known as 'Evans diagram' after U.R. Evans.

1.10. Mechanism of electrochemical reaction [27]

Significant contributions of Bockris, Frumkin, Parsons, Vetter, Gerischer, Conway, Bagotsky, Delahay and Wroblowa have made it possible to develop the diagnostic criteria for the elucidation of the mechanisms of electrochemical reactions. Stages involved in the mechanism determination are:
The concept of reaction order has been developed by Vetter [29] and the same is determined from the plots of log anodic or cathodic current densities against log concentrations of any species taking part in the electrode reaction at constant electrode potential.

After determining the reaction orders of all components of the overall reaction, one writes down various seemingly possible consecutive reaction sequences in which the overall reaction might be brought about.

The determination of transfer coefficient, is helpful for determining the number of electrons transferred in the rds. It is obtained from the slope of the plots of n vs log current at a constant concentration of reactants. These coefficients are invariably multiples of 0.5.

For determining the number of times rds to occur for one act of overall reaction, the stoichiometric number (v) is got from the relationship.
CORROSION CONTROL METHODS

Fig. 1.4
Besides the above mechanistic parameters, determination of exchange current is essential for understanding the kinetics of the process. Various techniques have been developed for studying the kinetics of electrode process. The theory and application of these methods are reviewed by Yaeger [30] and Damaskin [31],

1.11. Methods of corrosion prevention and control

The various methods employed for corrosion control are summarised in the form of a chart shown in Fig. 1.4.

1.12. Corrosion control by inhibitors

1.12.1. Corrosion inhibitor definition

Corrosion inhibitor is defined as a chemical substance which when added to the corrosive environment at an optimum concentration, decreases the corrosion rate of metals or alloys significantly.
Fig. 1.5 Activation polarisation curves showing pertinent processes for metal/solution interface under impressed EMF conditions
1.12.2. Classification of corrosion inhibitors

Putilova et al., [32] classified corrosion inhibitors into three types:

Type 1: those which form a protective film on the metal surface.
Type 2: those which reduce the aggressiveness of the corrosive media.
Type 3: those which function by forming a protective film and at the same time reducing the aggressiveness of the corrosive agent.

Another classification is based on the environment. Inhibitors have also been classified into three types, viz., acid inhibitors, neutral and alkaline inhibitors, and vapour phase inhibitors.

Recent classification of inhibitors is due to Deans et al., [33] who have classified them into four types based on the mechanism of inhibitive action. They are: 1] barrier layer formers 2] neutralising inhibitors 3] scavengers, and 4] miscellaneous.

Another classification is as anodic inhibitors, cathodic inhibitors and mixed inhibitors. This classification requires the knowledge of polarisation data.

Figure 1.5. illustrates the schematic activation polarisation curves showing the pertinent processes at the metal/solution interface under impressed electromotive force (EMF) conditions [34].

Figure 1.6a illustrates the significant terms for a freely corroding metal. The line $E_A D$ represents the anodic reactions; line $E_C D$ represents the cathodic
Fig. 1.6 Anodic and cathodic polarisation curves

(a) significant terms for freely corroding metal
(b) relation of metallic corrosion protection and inhibition
reactions. The point of intersection of anodic and cathodic reactions 'D' establishes the open circuit corrosion potential \( E_{\text{Corr}} \) of the metal and indicates the magnitude of corrosion at \( i_{\text{Corr}} \) (corrosion current).

Figure 1.6b is a schematic diagram showing the relation of metallic corrosion (D), protection (F and G) and inhibition (P). Generally, the immersed metal may be corroding by reaction under anodic control \( (E_aF) \) by the use of anodic type inhibitors; under cathodic control \( (E_cG) \) by the use of cathodic type inhibitors; or by mixed control \( (E_a - E_cP) \) where the inhibitor controls both the anodic and cathodic reactions. It is readily apparent that an inhibitor which can control both the reactions is more effective. It is found that both anodic and cathodic type inhibitors reduce the corrosion current (anodic: \( \Delta i_1 \); cathodic: \( \Delta i_2 \)), and that the “mixed” inhibitor reduces the corrosion current more effectively (\( \Delta i_3 \)).

Anodic inhibition results in greater shifts in anodic Tafel slope and cathodic inhibition results in greater shifts in cathodic Tafel slope. In the case of mixed inhibition both anodic and cathodic slopes are shifted to an equal extent or there is not much change in the Tafel slopes.

The anodic inhibitor shifts the corrosion potential towards anodic side and the cathodic inhibitor shifts the corrosion potential towards cathodic side, whereas both shifts will be realised in the case of a mixed inhibitor.
1.13. Theories of inhibition of corrosion

‘Corrosion Inhibitors’ has been the central theme of many reviews [32,35,36] and symposia [37,38],

The action of inhibitor in acidic as well as in alkaline and neutral media has been mainly explained by adsorption and/or film formation. In the case of acid inhibitors, they can also act, in addition, by affecting the kinetics of hydrogen evolution (hydrogen overpotential theory).

1.13.1. Adsorption theory and effect of molecular structure

Machu [39,40] put forward the adsorption theory which predicts the formation of a porous layer of the inhibitive substance with high electrical resistivity, an essential characteristic of corrosion inhibition. Uhlig [41] considered that the inhibitors get adsorbed at the metal surface, thus blocking the active sites and affecting the potential of the metal by virtue of their net charge. Riggs [34] proposed that in the case of organic inhibitors, adsorption depends on the chemical nature of the inhibitor molecule, the environment, the nature of the metal surface and the electrochemical potential of the metal/solution interface. Adsorption was further classified as a) pi-bond orbital adsorption b) electrostatic adsorption and c) chemisorption.
Relationship between the characteristics of the electronic interaction at the metal/solution interface and the structure of the inhibitor molecules has been discussed in detail [42-44],

The study of structure - corrosion inhibition relationship of organic compounds has received much attention from corrosion scientists. Hackerman and Hurd [45] plotted the degree of inhibition for ring-substituted N-methylamines vs the Hammett substituent constant. In 1965, Donahue and Nobe [46] proposed a correlation between inhibition by organic compounds and their chemical structure and substituent constants. Subsequently, many investigations were carried out to correlate the effects of substituents in related molecules such as pyridines, aliphatic amines, benzoic acids, aliphatic sulphides and thiophenes, with inhibitive efficiencies and electron densities at functional groups as estimated from Hammett constants [42, 47-52],

1.13.2. Hydrogen overpotential theory

The action of acid inhibitors was explained by hydrogen overpotential theory. It was believed that inhibitors increased hydrogen overpotential, and thus, increased the cathodic polarisation [53]. Hackerman and Sudbery [54] pointed out that amines are adsorbed on the anodic and cathodic regions on the metal surface. Hoar and Holliday [55] pointed out that the shift in the initial potential of the metal in presence of organic inhibitors in the positive direction
indicates that they act on the anodic sites. This theory does not explain the inhibitive action of all types of systems.

1.13.3. Film formation theory

In order to explain the action of inhibitors in neutral and alkaline media, Evans [56] proposed the film formation theory. Evans attributed the inhibition to the formation of an insoluble film. According to Putilova et al., [32], in acid solution, inhibition is due to the formation of a layer of insoluble or slightly soluble corrosion product on the metal surface.

1.13.4. Electrochemical polarisation theory

Explaining the action of passivating inhibitors, Stern [57] suggested that inhibitors like chromate get reduced at the cathodic sites and consequently raise the electrode potential to more noble value bringing about passivation. Studies on passivating inhibitors [32] reveal that only a small amount of the total current could be associated with cathodic reduction of inhibitors. Thus, Stern’s theory also cannot explain the behaviour of all types of systems.

1.14. Synergistic effect and corrosion inhibition

Mixture of inhibitors frequently provides better inhibition than either of the individual components; i.e., the mixtures are synergistic. This was recognised by Speller [58] in the mid-thirties, who reported finding “compound films”, such as
formed by phosphate - chromate mixtures, to be more effective than those of either alone.

The synergistic effect of halides and organic compounds as inhibitors has been frequently reported in the literature [59-62]. It is suggested that the synergism could be interpreted as a co-adsorption of both halide anion and organic cation directly on the metal surface [63]. At high concentrations, the two species on the iron surface transform from adsorption to the formation of a complex film [62 - 64].

Synergistic effect has been shown by various mixtures such as $K_2CrO_4$ and urotropine, NaVOa and potassium antimonyl tartrate [65] polyphosphate and orthophosphate [66], disodium sebacate and benzotriazole [67], potassium iodide and dicyclohexylamine [68], halides and benzyl amine [69].

Synergistic effects of mixtures of corrosion inhibitors have been reviewed and discussed at length [70,71]. The inhibiting effect of different organic phosphorus - containing compounds and the synergistic effect of various additives have been studied by a new mathematical model [72].

Synergism was established in the inhibition of corrosion of steel in aqueous chloride media by a combination of inorganic oxidiser and monoethanolamine [73], Molybdate shows synergistic effect with various species such as nitrite [74,75], phosphate [74, 76, 77], Zn$^{2+}$ [76-79], phosphonic acid [80], tolyltriazole [75], silicate [81], polymeric dispersants [80], monoethanolamine
and hydroxy carboxylates like sodium salicylate, sodium gluconate and sodium malate [83],

Sodium dodecyl succinate and sodium nitrite show synergistic effect in controlling the corrosion of steel in simulated cooling water circulates [84], A mixture of ethylxanthate and benzotriazole show synergistic effect in controlling the corrosion of copper in 0.1 M NaCl at pH 7-11 [85],

A synergistic inhibitory effect of BiCh and benzylthiocyanate \([C_6H_5CH_2SCN]\) on corrosion of iron in 1N \(H_2SO_4\) was investigated using polarisation and impedance measurements, and it was shown that a composite protective film was formed on the iron surface by a combination of both the compounds [86],

Synergistic effects of inorganic cations like \(As^{3+}\), \(Sn^{2+}\), \(Cu^{2+}\), \(Ni^{2+}\), \(Hg^{2+}\) and organic cations of phenol, formaldehyde and hydroquinone on the inhibitive performance of propargyl alcohol on steel dissolution in boiling HCl solution has been reported. Propargyl alcohol controlled the corrosion rate by the formation of a surface layer at the interface. Its effect was enchanced if another species was present in the solution that promoted film formation [87].

A mixture of borogluconate and corrin-type inhibitors showed synergistic effect in preventing the corrosion of iron in neutral media [88].
The combination consisting of 25 ppm sodium borogluconate and 25 ppm nitrite ion showed synergistic effect in controlling the corrosion of mild steel in aqueous solution containing 100 ppm Cl⁻ [89].

It has been reported that the inhibitive power of gluconates and gluconic acids increases with the addition of borate ions because of their combined synergistic effect [90].

A mixture consisting of sodium salt of ATMP, phosphates, borate and silicate was found to be effective in inhibiting the corrosion of steel, Cr-Ni steel, cast iron, AlMg₂ alloy and Al [91].

Phthalic anhydride, ATMP and Zinc ion as a three component inhibitor has good adsorption and corrosion inhibition properties [92].

The corrosion inhibition efficiency of HEDP synergistically improved in the presence of ZnMoO₄ and Ca²⁺ ions [93], Zn²⁺ [78, 94-96], Ca²⁺, and Mg²⁺ [94]. A synergistic effect of Zn²⁺ and HEDP in decreasing the corrosion rate of steel in sea water is observed. The protective cathodic film on the steel consists of Mg [predominant], P and Zn [95].

Corrosion of iron-based alloys in a circulating water is decreased by a synergistic inhibitor mixture containing HEDP, hydroxyphosphonoacetic acid and sodium tolytriazole [97]. 2-Phosphonobutane-1, 2,4-tricarboxylic acid [PBTCA] shows synergistic effect with Zn²⁺ [98], Zn²⁺-HEDP combination [99] and MnCl₂·4H₂O [100]. When PBTCA is used along with Zn²⁺ in the corrosion
inhibition of mild steel in tap water, Zn(Ca) - PBTCA - Fe(III) sequestering film deposited on the surface of mild steel inhibited corrosion effectively [98],

1.15. Corrosion inhibitors in neutral aqueous environment

A wide variety of chemicals ranging from simple ions such as sulphate to complex molecules represented by tannins and polymeric substances can inhibit the corrosion of metals in neutral aqueous solutions. The properties of these inhibitors depend on the nature of the metal and the composition of the environment. These inhibitors may be used alone or in formulation containing other chemicals which may be present for synergism in the inhibition process. Health and safety requirements control the selection and use of inhibitors.

1.15.1. Chromates

Chromate is a very effective passivating inhibitor. Chromate passivation usually involves formation and maintenance of a protective ferric oxide film [101]. Chromates are usually referred to as anodic inhibitors. However, cathodic inhibition has also been reported [102,103]. Passivation with chromate is sensitive to various common anions such as chloride and sulphate [104,105]. The use of chromates at high concentration has declined in recent years because of health and safety considerations.
1.15.2. Molybdates

Molybdate based treatments for open recirculating cooling systems have become popular since the early 1980s as an alternative to the toxic and ecologically unacceptable chromate based inhibitors. Molybdate has been used as inhibitor to prevent the corrosion of iron [106] and mild steel in neutral aqueous solutions [107]. Molybdates when used alone, are anodic inhibitors. Molybdate is found to be an efficient inhibitor in aerated distilled water but inefficient in deaerated water [108],

1.15.3. Pertechnetate

The protection of carbon steel in 13 ppm K\textsuperscript{4+}Tc\textsuperscript{0} has been reported. A protective oxide film is formed on the metal surface. Technetium is reduced from the heptavalent to the tetravalent state. Structures in water can be protected against corrosion and fouling by coating the metal with \textsuperscript{99}Tc [109],

1.15.4. Nitrite

Nitrite ion is a well known oxidising type of cooling water inhibitor because of its unique role in forming and repairing the oxide film [110, 111], Bacterial decomposition of nitrite is a factor which discourages the use of nitrites in open recirculating systems [112]. The effectiveness of nitrite is impaired by the presence of aggressive ions such as chloride, sulphate and nitrate; when these
are present above the critical concentration, localised attack will be developed [113].

1.15.5. Phosphates

Phosphates are frequently used in the polyphosphate form. They control the corrosion of ferrous metals. Polyphosphates act as cathodic inhibitors [114-116]. The effectiveness of polyphosphates as inhibitors is increased by the movement of solution, but decreased by rise in temperature.

1.15.6. Silicates

Silicates have the advantages of low cost and non-toxicity. Sodium silicate has been used as a corrosion control agent for open-circulating cooling water system [117].

1.15.7. Cations

Cations in adequate concentrations act as cathodic inhibitors. The cations form insoluble salts with the constituents of the solution in alkaline medium at local cathodes. These insoluble deposits screen the cathode from dissolved oxygen, thereby polarising the cathodic process, and thus, inhibiting the corrosion. Aluminium cations, for example, are effective inhibitors for mild steel in water. The corrosion inhibition is due to the precipitation of hydrous aluminium
oxide. The inhibition efficiency may be improved by the presence of thiourea [118].

5.15.8. Organic inhibitors

Several organic compounds have been used as inhibitors of corrosion of mild steel in aqueous neutral environment. Gluconates and gluconic acids are known to be effective non-toxic inhibitors for iron and mild steel in cooling water [119, 120]. The organic surfactant, 1-decylimidazole, inhibits the corrosion of iron in neutral solution of 3 percent sodium chloride [121]. The inhibition of a- and y- pyrophthalones on the corrosion of iron and mild steel in near neutral aqueous sulphate solutions has been studied. The inhibition is explained by adsorption of the organic molecules on the metal surface as well as by their incorporation into the oxide film [122],

1.15.9. Carboxylates

Several carboxylates such as sodium salicylate [123], sodium cinnamate [124], anthranilate [125], and adipate [126] have been used as inhibitors. Inhibitive anions like benzoate, phthalates and other carboxylates [127 - 129] stabilise the oxide film on the iron surface. Presumably, their inhibitive action results from the bonding of the anion to the metal surface by excess electrons on the O'. Carboxylates are anodic inhibitors. Therefore they are sensitive to the presence of higher concentrations of aggressive ions.
1.15.10. Tannins

Tannins are of vegetable origin and are good corrosion inhibitors [130 - 132]. They are inoffensive towards the environment. Sodium tannate has been used in the inhibition of corrosion of mild steel in neutral solutions [133].

1.16. Review of literature on phosphonates as inhibitors

Phosphonates are sodium, potassium or ammonium salts of phosphonic acids. However, proprietary, branded acids are also referred to in general terms as "phosphonates". In this thesis, this word is used in general terms. Phosphonic acids are compounds having carbon atoms directly bonded with phosphorus atoms. The active phosphonic acid group is $0=\text{P} (\text{OH})_2$. General arrangement of acid molecule is as follows:

$$C (X, Y, Z) - \text{P} \text{O}_3\text{H}_2$$

Where X, Y and Z are various groups or atoms.

Phosphonates are introduced alone or in combination with other metal ions. Research in this area has been stimulated by the need to develop inhibitor formulations that are free from chromates, nitrates, nitrites, inorganic phosphorus compounds etc. Addition of phosphonic acids even to chromates [134], nitrites [135] reduces the corrosion rate. Phosphonates contain phosphorus-carbon bonds (P-C) in contrast to phosphorus-oxygen bonds (P-O) in inorganic
Phosphates. The P-C bonds are much more resistant to conversion into orthophosphate than the P-O bonds in inorganic phosphates.

Phosphonates when blended with certain metal ions, organic compounds and polymers further reduce the optimal inhibitor concentration needed for inhibition due to synergistic effect of the components. Synergism is one of the important effects in inhibition process and serves the basis for all modern corrosion inhibitor formulations [136]. Very few reviews are available in the literature regarding the use of phosphonic acids as corrosion inhibitors and each one discusses one particular aspect. Pandya.V.H. [137] discussed the use of phosphonic acids especially HEDP and ATMP. The other review discusses the acidic, complexing, adsorptive and anticorrosive properties of aminophosphonic acids [138], Kuznetzov.Yu.I [139] discussed several scientific aspects of metal corrosion by inhibitor, based on phosphonic acids. The author showed special attention to the influence of chemical structure of phosphonic acid inhibitors and of the nature of complex formed on metal. In this review, the corrosive environment in which the phosphonic acids are tested for corrosion inhibition, the metal and alloy to be protected by phosphonic acids, inhibitor composition containing multicomponent systems and other corrosion related applications of phosphonic acids are discussed.
5.16.1. Properties of phosphonic acids

Phosphonates provide the following key aggregation of properties:

a) Sequestration to complex metal ions at stoichiometric concentrations.

b) Deflocculation - The ability to disperse solid particles.

c) Corrosion inhibition - In the presence of other chemicals they provide synergistic corrosion inhibition.

d) Scale inhibition - The inhibition of precipitation of typical sealants at substoichiometric inhibitor concentrations.

e) Hydrolytic stability - The resistance to decomposition in aqueous solutions even at elevated temperatures and extreme pH values.

f) Crystal growth modification - The property of distorting normal crystal growth patterns.

g) Chlorine stability - The resistance to degradation by ppm levels of available chlorine.

1.16.2. Types of phosphonic acids

Alkyl and aryl phosphonic acids

1-Phenylethane-1,2,2-triphosphonic acid [140], Methylphosphonic acid [141], Phenyl phosphonic acids etc.

Hydroxy substituted alkyl and aryl phosphonic acids

HEDP [142], Hydroxy mono, di, tri-phosphonic acids [143], Hydroxy substituted mono and bisphosphonic acids [144], etc.
Hydroxy, carboxy substituted alkyl or aryl phosphonic acids

R-C (OH) (PO$_3$H$_2$) $X$COOH, ($R$ = alkyl, alkenyl, cycloalkyl, aryl, $X$ = alkylene, alkenylene and arylene) [145] e.g. 3-Hydroxy-3-phosphonobutanoic acid, etc.

Aminoalkyl or aryl phosphonic acids

1-Aminoethylidine phosphonic acid ammonium salt [146, 147],

N-Substituted 1-aminophosphonic acids

ATMP [148], 1-Aminophosphonic acid [149], Acetylamino ethanediphosphonic acid [150], HOOCCH (NEt$_2$) P(O) (OH)$_2$ HClH$_2$O [151], N-phosphonomethyl glycine [152], etc.

Cyclic phosphonic acids

4-Phosphonomethyl-2-hydroxy-2-oxo-1,2,4-oxazaphosphinane-1-oxide [153], 4-Phosphonomethyl-2-hydroxy-1,2,4-oxazaphosphorinane [100], etc.

Phosphonic acids with multifunctional groups

Thiazenealkane phosphonic acid [154,155], Benzimidazodyl-2-alkane phosphonic acid [156], 2-Phosphonomethylenethio-1,3-benzotriazole [157], etc.
Polyphosphonic acids

Poly (hydroxyphosphonic acid) [142, 158], Phosphonated hydrolytic polymaleic anhydride [159], Phosphono (carboxylic acid) [160], Polyvinyl phosphonomethyl aminocarboxylates [161], Polyamides containing phosphonic acid and N-Methylene phosphonic acid groups [162], etc.

1.16.3. Corrosion inhibition using phosphonates in different corrosive environments

Chloride environment

Wide range of chloride concentrations are used for testing corrosion inhibition of phosphonic acids. The concentration of chloride used depends on the purpose of the study [163-172]. Gunasekaran G et al., [163, 164] used 60 ppm chloride for the testing of 2-Carboxyethylphosphonic acid (2CEPA). 3% NaCl was used for checking the corrosion inhibition efficiency of some of the phosphonic acids [165-169], Kuznetzov. Yu. I and Sardasheva. T. I [169] used 0.01 M NaCl for testing iminoparboxy phosphonic acids and HEDP. Sekine. I and Hirakawa. Y [171] used 0.3% NaCl for HEDP. Sodium chloride is taken as the chloride source in most of the experiments. Sometimes calcium chloride and potassium chloride also have been used [171, 172],
Sulphate environment

Sulphates are used in the range of 100 ppm to 35,000 ppm (0.5 M) for testing phosphonate inhibitors [173-180]. 200 ppm of sulphate is used by Kuznetzov.Yu.I et al., [178] for testing the corrosion inhibition efficiency of NTMP and Kubicki.J et al., [175] used 105 ppm sulphate solution for ATMP. The source of sulphate is sodium sulphate and sometimes potassium sulphate [174].

Environment containing hardness causing ions

Water hardness is mainly due to calcium and magnesium salts. The performance of phosphonates as corrosion inhibitors is also tested in presence of carbonates of calcium, magnesium, potassium and sodium. The corrosion inhibition efficiency of HEDP is tested by Terekhin.S.N et al., [181] using 300 ppm of total hardness but Kuznetzov.Yu.I. et al., [182] used equal or less than 10 mg equiv/L calcium harness for HEDP. Boffardi. B.P [183] used 318 ppm hardness water with respect to calcium carbonate to study the corrosion inhibition efficiency of ATMP. VanLoyen.D et al., [184] used different carbonate hardness to check the corrosion inhibition efficiency of HEDP. Sodium bicarbonate and potassium carbonate have also been used to identify the corrosion inhibition efficiency of phosphonic acids [175, 177],
Effect of pH

pH is a crucial factor for the determination of corrosion inhibition efficiency of phosphonic acids. Most of the phosphonic acids are pH selective. The nature of pH selectivity of phosphonic acids depends on the metal, the composition of inhibitor etc. Nitrogen containing phosphonic acids are effective at decreased pH (acidic) levels. Thomas.M [185] used a composition containing ATMP at pH 1-4. Kruchenko.V.P and Sabirova.A.A [170] used NTMP at pH5. Zhou.M.P et al., [228] used ATMP in 0.1 M sulphuric add. Notoya.T et al., [186] used Bis (benzotriazoly) methyl phosphonic acid in acid medium. Horvath.T and Kalman.E [187] used diethylenetriaminepentaphosphonic acid in acid solutions. Some of the phosphonic acids not having nitrogen group were also tested in low pH. eg., 1,6-hexane diphosphonic acid [173], HEDP [168], HEDP, Zinc ions combination even works at alkaline pH [168],

Effect of temperature

Temperature dependence on the use of phosphonic acids for the system like cooling water, boiler etc., has been studied [170, 188-191], He.Baocai [188] and Wang.G [189] prepared inhibitor compositions containing ATMP or ATMP with HEDP for boilers. Kuznetzov.Yu.I et al., [191] used HEDP at elevated temperature for studying the corrosion inhibition efficiency and Kruchenko.V.P and Sabirova.A.A [170] used NTMP at 90°C.
### Table I.1: Phosphonic acids studied for corrosion inhibition of different metals and alloys

<table>
<thead>
<tr>
<th>Metals and Alloys</th>
<th>Phosphonic acids</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>HEDP</td>
<td>[171, 172, 174, 180, 182, 184, 192-210]</td>
</tr>
<tr>
<td></td>
<td>ATMP</td>
<td>[166, 175, 177, 187, 211]</td>
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<td></td>
<td>NTMP</td>
<td>[170, 178, 212, 216]</td>
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<td></td>
<td>HPA</td>
<td>[144, 219-221]</td>
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<tr>
<td></td>
<td>1,6-hexanediolphosphonic acid</td>
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<td>1,4-phenylenebisphosphonic acid</td>
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<td>N-phosphonomethyl glycine</td>
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<td>Disodium monoalkyl phosphonate</td>
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<td></td>
<td>Orthohydroxy benzene phosphonic acid</td>
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| Material   | HEDP          | ATMP          | NTMP          | Reference  
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<td>thio-1,3-benzotriazole</td>
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<td>Brass</td>
<td>HEDP</td>
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<tr>
<td>Mg₂Al</td>
<td>NTMP</td>
<td>[212]</td>
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</tbody>
</table>
For different metals and alloys

Iron

Phosphonic acids have been used to protect frequently iron and its carbon alloys (Refer Table 1.1) in neutral medium. HEDP is the phosphonic acid which is widely used to protect iron and its carbon alloys [171, 172, 174, 180, 182, 184, 192-210]. Kuznetzov. Yu. I et al., did enormous study on the corrosion inhibition of mild steel using HEDP and its combination with zinc ions. The other phosphonic acids which are frequently used for the corrosion inhibition of iron and its carbon alloys are ATMP [168,175,177,187,211], Nitrilotri(methylene) phosphonic acid (NTMP) [170,178,212,216], 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) [217, 218] and Hydroxyphosphonoacetic acid (HPA) [144, 219-221]. Other phosphonic acids such as 1,6-hexanediphosphonic acid (HBP) [173], phenylenediphosphonic acid [176], ethylenediaminetetramethylene phosphonic acid [222, 223], diethylenetriaminepentamethylene phosphonic acid [224], methylphosphonic difluoride [224], N-phosphonomethyl glycine [152], disodium dodecylphosphonate [191], disodium monoalkylphosphonate [168], orthohydroxybenzenephosphonic acid [168], 2-carboxyethylphosphonic acid [163, 164] and orthohydroxybenzenephosphonic acid [226] are also used for the corrosion inhibition of iron and its carbon alloys.
Stainless steel

Very few references are available in the literature regarding the corrosion inhibition of stainless steel using phosphonic acids. Bartonicek.R et al., [212] used NTMP for the protection of Chromium-Nickel steel and Sekine.I et al., [227] used HEDP to protect SS-304 stainless steels. Zhou.M.P et al., [228] used various phosphonic acids such as ATMP, methyaminodimethyleneephosphonic acid [228], n-butylaminodimethyleneephosphonic acid, and HEDP for the corrosion inhibition of Cr-13 stainless steels in acid medium. Zabielski.C.V. and Levy.M [225] used methylphosphonic diflouride for the corrosion inhibition of 316L stainless steel and 304 stainless steel.

Aluminum

Next to iron and its carbon alloys, Aluminum and its alloys are protected by phosphonic acids. Nitrogen containing phosphonic acids especially NTMP is used for the corrosion inhibition of Aluminum and its alloys [169, 212, 216, 229-233], Kuznetzov.Yu.I et al., [231] used HEDP for the protection of Aluminum and its alloys. The other phosphonic acids which are used for the corrosion protection of Aluminum and its alloys are Aminomethyleneephosphonic acid (AMP), iminocarboxyphosphonic acids, ATMP and Gem-diphosphonates.
Copper

Nitrogen containing phosphonic acids are mostly preferred for the corrosion inhibition of copper. The exception is HEDP [234], NTMP has been used by Bartonicek.R et al., [212] and Falewicz.P et al., [216] for the corrosion inhibition of copper. Sherwood. V and Alfano.N.J [235] used 2-Acrylamido-2-methyl propylphosphonic acid and 2-methylacrylamido-2-methylpropyl phosphonic acid for the corrosion inhibition of copper. Yamada.Y et al., [236] used ATMP-benzotriazole mixture and Notoya.T et al., [186] used bis [(1-benzotriazolyl) methyl] phosphonic acid for the corrosion inhibition of copper. Zhu.C.F and Zhou.W (104) used a phosphonic acid with a thio group such as 2-phosphonomethylenethio-1,3-benzotriazole (PMPB) for the corrosion inhibition of copper.

Brass

The use of phosphonic acid to corrosion inhibition of brass is lower in comparison with the use of phosphonic acids to corrosion inhibition of copper. Very few examples are available in the literature for the corrosion inhibition of brass using phosphonic acids [135, 179, 212, 216, 234], VanLoyen.D [234] used HEDP for the corrosion inhibition of brass. Bartonicek.R et al., [212] and Falewicz.P et al., [216] used NTMP for the corrosion inhibition of brass.
Other metals and alloys

Phosphonic acids such as NTMP and HEDP were used for the corrosion inhibition of copper, zinc and aluminium alloys CuZn20A12 [234], copper, aluminum and magnesium alloy (AlCu4Mg1) [216] and copper, nickel, iron and manganese alloy (CuNi10Fe1Mn) [234]. In case of corrosion inhibition of Magnesium [225] and its alloy (Mg2A1) [212] methylphosphonic diflouride and NTMP were used.

Inhibitor composition and its effect on corrosion rates

Phosphonic acids alone

HEDP

Wang.H et al., [237] used 12 ppm of HEDP and chlorine as algicide and bactericide in circulating cooling water in a plant manufacturing butadiene. The corrosion rates of test periods of 33, 49 and 52 days were 0.039 mm/yr, 0.049 mm/yr and 0.056 mm/yr respectively.

Impedance spectra of carbon steel in presence of HEDP were studied in neutral solutions by Kalman.E et al., [197]. Results of these studies show that at low concentration, HEDP inhibits carbon steel corrosion by a precipitative mechanism by forming insoluble iron complexes and repairing the porous oxide layer formed on the metal surface. Increasing the HEDP concentration beyond
the optimal value, decreases its corrosion inhibition efficiency due to the
dissolution of the oxide layer. Zocher.G [238] also studied the corrosion
inhibition of HEDP and its sodium salt.

NTMP

Venables.J.D [229] studied the corrosion rate of Aluminum and steel
surfaces in presence of NTMP. He found that NTMP is inhibiting both Aluminum
and steel. Zamucchi.P.J et al., [230] treated Aluminum with NTMP and
examined the surface with Infra-Red spectroscopy and X-Ray photoelectron
spectroscopy. These measurements show that NTMP reacts with the Aluminum
surface to form a coating which is an effective inhibitor.

1,1 -Di( 1 -phosphonopropionic acid)

1,1-Di(1-phosphonopropionic acid) and its sodium salts showed excellent
corrosion inhibition and scale prevention in stabilization of water [239],

N-Methyl aminophosphonic acid

Pyrwanow.B et al., [222] studied the sorptive properties and
thermodynamic properties of adsorption of ethylenediaminetetra
phosphonic acid and n-octaminedimethylenephosphonic acid on solid iron
electrode in a neutral medium using electrical double layer differential
capacitance. The inhibiting properties of components were determined using
The corrosion inhibiting properties of phosphonic acids were interpreted in terms of localized chemisorption on the metal surface.

**Alkyl phosphonic acids**

Using the current potential curves of pure iron in 0.5 M sodium sulphate as a standard, the corrosion inhibition effect of 1,4-phenylenebisphosphonic acid on corrosion of iron was investigated by Erbil.M [176] with a rotating disc system under oxygen and hydrogen atmosphere, current-potential curves in 0.5 M sodium sulphate with and without the inhibitor and the kinetic results showed that within 4 < pH < 5, 1,4-phenylenebisphosphonic acid is a weak surface active inhibitor under hydrogen atmosphere.

Isopropenylphosphonic acid copolymers were used by Becker.L.W [240] for the corrosion inhibition of steel and it acts as an effective inhibitor and antiscalar. The influence of disodium monoalkyl phosphonates R(P0$_3$H$_2$)$_2$ (R = C$_4$H$_9$, CsHn, C$_6$H$_{13}$, C$_7$H$_{15}$, C$_8$H$_{17}$, C$_{10}$H$_{21}$) on the corrosion rate of steel type XC38 was examined by voltametric and impedance technique [168]. The formation of a relatively compact adherent film of disodium monoalkylphosphonates caused a decrease in the corrosion rate.

**Phosphonic acid-metal ions mixtures**

Except very few phosphonic acids, most of the phosphonic acids as such are not good corrosion inhibitors. Their corrosion inhibition properties were
Table 1.2: Studies on synergistic effect of phosphonates along with different metal ions

<table>
<thead>
<tr>
<th>Phosphonic acid</th>
<th>Metal cation</th>
<th>References</th>
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<tr>
<td>HEDP</td>
<td>Zn$^{2+}$</td>
<td>172,181,182,234,241-243</td>
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<td>ATMP</td>
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<td>241,244</td>
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<td>Iminophosphonic acid</td>
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<td>N-phosphonomethyl derivatives</td>
<td>Zn$^{2+}$</td>
<td>245</td>
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<tr>
<td>HEDP</td>
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<tr>
<td>N-phosphono derivatives</td>
<td>Metavanadate, ion</td>
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</table>
increased by addition of metallic ions [Table.1.2], These metallic ions form insoluble complexes with phosphonic acids and repair the porous oxide layer and prevent further corrosion. Predominantly Zinc ions are used for elevating the corrosion inhibiting properties of phosphonic acids. The Zinc-phosphonate complexes give very good corrosion inhibition compared to other metallic cation phosphonate complexes. The other metallic cations tested for using in phosphonate inhibitor mixture are Ca\(^{2+}\), Mg\(^{2+}\), Co\(^{2+}\), Ni\(^{2+}\), Cd\(^{2+}\), Mn\(^{2+}\), Sn\(^{2+}\), Cu\(^{2+}\), Ba\(^{2+}\), Sr\(^{2+}\), Al\(^{3+}\), Cr\(^{3+}\) etc.

Phosphonic acids along with Zinc ions

Corrosion inhibition efficiency of HEDP and Zinc ions mixture was elaborately studied by many authors [241]. The effect of HEDP on the corrosion rate of copper, brass and other copper alloys in cooling water were studied gravimetrically by using a recirculating loop by VanLoyen.D [234]. HEDP decreases the corrosion rate of copper and its alloys in presence of Zinc ions.

Terekhim.S.N. et al., [181] studied the effect of HEDP and Zinc ions on the corrosion rate of steel ST-3 with varying hardness and temperature. Radioactive tracers and potentiometry were used to determine the effect of Zinc ions concentration on the adsorption of HEDP on a low alloy steel and its corrosion inhibition efficiency by Konya.J et al., [172]. When the HEDP concentration is in the range of 0.0003-0.0005 M, adsorption on steel in 0.5 M sodium perchlorate solution attained a maximum at Zinc ions/ HEDP ratio of 2.
Kuznetzov.Yu.I et al., [182, 242, 243] studied the protection of low carbon steel from corrosion by HEDP and its combination with Zinc sulphate in the presence of calcium and magnesium salts as well as stability of solutions at pH 5.7-8.3. The introduction of HEDP and Zinc ions improves the protection of steel from corrosion. The use of Zinc ions-HEDP complexes is more effective in water with calcium hardness less than or equal to 10 mg equiv/L in hard water for stabilizing the solutions: their pH must additionally be controlled. The corrosion rates of steel in presence of the supporting electrolyte, sodium chloride 30 mg/L and sodium sulphate 70 mg/L were also determined using weight loss method.

Hydroxyphosphonoacetic acid (HPA) with Zinc ion is a suitable ferrous alloy corrosion inhibitor for cooling towers that is nontoxic to aquatic life and decomposes to simple compounds. The testing sequence included aerated solution bottle tests (corrosion rate 0.3 mm/yr) recirculating water rig tests alone and with additives, pilot cooling water rig tests and a field trial. HPA was compatible in formulations containing polymers for scale control, nonferrous metal inhibitors, biocides for sludge control and Zinc ions for soft water conditions.

In aqueous cooling and heating systems, scale formation and corrosion are prevented by addition of an organophosphonic acid such as ATMP with Zinc ions. Dricker.B.N. et al., [244] used the mixture of Zn₃ [N(CH₂P0₃)₃] (10-40 wt%) and Zns [N(CH2P0₃)]2 (60-90 wt%). Kuznetzov.Yu.I and Bardasheva.T.I [169] used electrochemical and weight loss methods to study the pitting action of
complexes in aqueous solution of chlorides for Aluminum. The effect of inhibitors increases during the use of iminophosphonates in a composition with cation-complexing agents in particular with Zinc ions. Depending on the hydrodynamic conditions, the temperature and the solution pH, as well as composition of Zinc-phosphonates they are capable of slowing down the occurrence of both electrochemical reactions. The studies were made in borate buffer solution, primarily at pH 7.36 containing 0.1 M NaCl as well as aqueous solution of KCl and calcium chloride at different concentrations.

Kalman.E et al., [245] prepared N-phosphonoaminocarboxylic acids from aminoacids. They studied the corrosion inhibition efficiency of these phosphonic acids with and without Zinc ions using impedance spectroscopy, weight-loss and potentiostatic polarisation methods in order to show the significance of CH$_2$PO$_3$H$_2$ substitution.

Phosphonic acids along with metal ions other than Zinc

The metal ions other than Zinc ions such as Ca$^{2+}$, Mg$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Cd$^{2+}$, Mn$^{2+}$, Sn$^{2+}$, Cu$^{2+}$, Fe$^{2+}$, Ba$^{2+}$, Sr$^{2+}$, Al$^{3+}$, Cr$^{3+}$ and metavanadate ions are also used with phosphonic acid to increase the corrosion inhibition efficiency of phosphonic acids. Usually Zinc ions are hazardous to environment, Zinc ions were converted to Zinc sulphide by sulphate reducing bacteria. This Zinc sulphide is cathodic to mild steel resulting in localized corrosion. Some of the authors tried to eliminate Zinc from phosphonic acid inhibitor mixture by substituting environmental friendly metal ions. The widely used other metal
cation is calcium ions. Much of the study on calcium ions adsorption has been
done by Kalman. E et al., [172,195,196,198,245,246]. They used various
corrosive media and studied the adsorption of HEDP and calcium ions on the
surface of steel. Potentiometry and Radioactive tracers [172] were used to
determine the effect of calcium ions concentration on the adsorption of HEDP on
a low-alloy steel and on its corrosion inhibition efficiencies in presence of 0.5 M
of sodium perchlorate. The adsorption of HEDP increases with increase of
Ca/HEDP mole ratio.

X-Ray induced photoelectron spectroscopy, Auger spectroscopy and
radioisotopes were used by Kalman.E and Karmanne.D [195] for the
identification of the effect of calcium ions on the adsorption of HEDP at steel
surface. Calcium ions also used with ethylenediaminetetramethylene
phosphonic acid and its corrosion rates were determined [223], Kuznetzov.Yu.I
et al.,I [139, 214, 215, 243] discussed the effect of various metal ions such as
Mg$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Cd$^{2+}$, Mn$^{2+}$, Sn$^{2+}$, Cu$^{2+}$, Ba$^{2+}$, Sr$^{2+}$ and Al$^{3+}$ on phosphonate
complexing agents. Terekhim. S.N et al., [181] and Rodin V.M et al., [174] used
Fe$^2$, Co$^{2+}$, Mg$^{2+}$, Al$^{3+}$ and Cr$^{3+}$ on HEDP and studied the effect of this inhibitor
mixture on corrosion inhibition efficiencies. These studies reveal that the
corrosion inhibition efficiencies of phosphonic acid - Zinc ions mixture is much
better than phosphonic acid - other cations mixtures.
Table 1.3: Studies on synergistic effect of phosphonates along with different metal ions and organic/inorganic compounds

<table>
<thead>
<tr>
<th>Phosphonic acid</th>
<th>Metal cation</th>
<th>Organic/or Inorganic compounds</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEDP</td>
<td>Zn(^{2+})</td>
<td>Di-Na EDTA, NaN(_2)NO(_2), Nitrobenzoic acid.</td>
<td>[193]</td>
</tr>
<tr>
<td>HEDP+ATMP</td>
<td>Zn(^{2+})</td>
<td>Polysodium potassium silicate, Humate.</td>
<td>[189]</td>
</tr>
<tr>
<td>HEDP</td>
<td>Zn(^{2+})</td>
<td>Sodium gluconate</td>
<td>[184][194]</td>
</tr>
<tr>
<td>PBTC</td>
<td>Zn(^{2+})</td>
<td>Acrylic acid polymer, Orthophosphate, Tolyltriazole.</td>
<td>[247]</td>
</tr>
<tr>
<td>NTMP</td>
<td>Zn(^{2+})</td>
<td>Phthalic acid anhydride</td>
<td>[213][216]</td>
</tr>
<tr>
<td>ATMP</td>
<td>Zn(^{2+})</td>
<td>Phthalic acid anhydride</td>
<td>[175]</td>
</tr>
<tr>
<td>NTMP</td>
<td>Zn(^{2+})</td>
<td>Oxalic acid</td>
<td>[216]</td>
</tr>
<tr>
<td>Diethylenetriamine pentamethylene phosphonic acid</td>
<td>Zn(^{2+})</td>
<td>Ethanolamine phosphate</td>
<td>[248]</td>
</tr>
</tbody>
</table>
Multicomponent inhibitor mixture with metal ions

Addition of organic and inorganic compounds to inhibitor mixture, not only increases the corrosion inhibition efficiency of the inhibitor mixture but also reduces the requirement of phosphonic acids and metal ions [Table. 1.3], Thus addition of organic and inorganic compounds to inhibitor mixture reduces the cost of the inhibitor system markedly and reduces the pollution of water.

Phosphonic acid along with metal ions and organic compounds

The effect of corrosion inhibitor, sodium salt of HEDP with and without addition of Zinc ions and sodium gluconate on the corrosion inhibition of unalloyed steel in cooling water with different carbonate hardness was studied by VanLoyen.D et al., [184, 194] using recirculating loop. The optimal inhibition is attained by using sodium salt of HEDP, Zinc ions and sodium gluconate.

The NTMP, phthalic acid anhydride and Zinc sulphate as a three component inhibitor has good adsorption and corrosion inhibition properties [213], The corrosion inhibition rate of steel, even for multifunctional systems is over 90% for this solution. Kubicki.J et al... [175] did statistical optimization of the following corrosion inhibitor composition : ATMP, phthalic acid anhydride and Zinc sulphate for the protection of steel in water containing calcium chloride (330 ppm), sodium sulphate (105 ppm) and sodium carbonate (170 ppm). The optimal inhibitor composition was 45 ppm of ATMP, 8 ppm of phthalic acid anhydride and 8 ppm of Zinc ions. The corrosion inhibition efficiency is 98%.
Falewicz.P and Kuczkowska.S [216] studied the inhibitor mixture which contains NTMP, oxalic acid or phthalic acid anhydride and Zinc sulphate. Using gravimetric techniques, the influence of this mixture on the rate of corrosion of steel ST38 in stimulated industrial water of variable chemical composition and in water being chlorinated were studied. The influence of this mixture on the rate of corrosion of copper, brass, Zinc and aluminum alloy were studied and a considerable decrease of the corrosion rate by the inhibitor mixture has been established. NTMP in combination with phthalic acid anhydride and Zinc ions has therefore been considered as a perspective inhibitor for the corrosion protection of industrial cooling and heating water installations.

Phosphonic acid, metal ions with organic and inorganic compounds

The corrosion and electrochemical behaviour were studied for ST3 and Armco iron in neutral media (temperature in the range of 40° to 90°C) in the presence of HEDP, Zinc ions, the disodium salt of EDTA, sodium nitrite and benzoic acid by Kuznetzov.Yu.I and Isaev.V.A. [193]. The inhibition of steel corrosion by the complexon is a consequence of the simultaneous formation of insoluble complexons on its surface and alkylation of the near electrode layer depending on the nature of oxidising agent and the solution temperature.

Wang.G et al., [189] used a corrosion inhibitor in recirculating water system which comprises the sodium salt of HEDP (5-15 wt%), sodium salt of ATMP (5-15 wt%), polysodium potassium silicate (20-40 wt%), water soluble
sodium humate (5-15 wt%) and Zinc carbonate (1-5 wt%). The composition is suitable for use in boilers for scale control.

The composition for preventing corrosion and scale in aqueous recirculation system comprises, an aqueous solution with pH 2-13.5 containing 2-phosphonobutane-1,2,4-tricarboxylic acid (PBTC) or its water soluble salts, a water soluble Zinc complex with 1: (3.2) wt ratio with Zinc ions polymer species and a water soluble orthophosphate at weight ratio with Zinc ions of 1.5:1 [247]. The polymer is a terpolymer comprising acrylic acid, methacrylic acid and N-alkylated acrylamide monomer having molecular weight of 2500-25000. Additionally the composition may contain components such as tolyltriazole, polyphosphates, phosphonic acids and acrylic polymers. Thus one effective composition for cooling water systems containing mild steel in hard water was Zinc ions (1 ppm), orthophosphate (4 ppm), PBTC (2 ppm), tolyltriazole (2 ppm) and acrylic acidmethacrylic acid-N-t-butylacrylamide copolymer (7.5 ppm) (water basis).

In a system with stimulated recycle conditions, a decarbonated well water with relatively high calcium hardness was concentrated to 1/3 of its volume in 2 days and held for 12 days under constant condition. The inhibitor added contains diethylenetriaminepentamethylene phosphonic acid, ethanolaminephosphate, anionic polymeric dispersants, azole components, Zinc salts, chromates, phosphates etc. After 14 days, the corrosion inhibition was 86.1% [248].
Metal free inhibitor composition

Very few examples in the literature are available for metal free composition for corrosion inhibition. Mostly and widely used phosphonic acid for metal free composition is HPA [220, 249-251]. Mitchel.W.A. [249] prepared a metal free composition by using HPA and the copolymer formed from 2-acrylamido-2-methylpropane sulphonic acid and acrylic acid and methacrylic acid. The respective corrosion rates of steel coupons in recirculating line and in the tank in the test solution containing the inhibitor composition is 11.7 mils/yr is 30.8 and 34.3 mils/yr for the coupons in the test solution containing no inhibitor. Hwa.C.M and Mitchell.W.A. [220] prepared a inhibitive formulation using HEDP, HPA and an azole compound. The corrosion inhibitor in water preferentially was 5-200 ppm of HEDP and HPA and 0.4-50 ppm of azole compound. The water is suitable for heat exchangers and cooling water systems. SAE1010 steel coupons were immersed for 3 days in hard water at 130°F and pH 8-8.5 and flow rate 2 ft/s. Corrosion rate was 5.6 mils/yr when the inhibitor, 5 ppm each of HEDP and HPA and 1.94 ppm of sodium toyltriazole and 8.1 mils/yr at 10 ppm HPA and 1.94 ppm of sodium toyltriazole and 87.5 mils/yr without the inhibitor.

Ciba.G [250] prepared corrosion inhibitor composition with HPA together with acrylic acid-lower alkylhydroxy acrylate polymers or sulphonated styrene -maleic acid anhydride copolymers or sulphonated styrene copolymers or combined, which was effective against metal corrosion and scale deposition. Dabosi.F et al., [252] used oleylaminopropyleneamine with ATMP as corrosion
Inhibitor for carbon steel in 3% solution. Maleic acid anhydride polymer and ATMP combination is used by Boffardi.B.P [183] as corrosion inhibitor for steel 1010 poly (acrylic acid), benzotriazole, high molecular weight sulphonated polystyrene and hexamethylene diaminetetramethylene phosphonic acid mixture was used as corrosion inhibitor by Lipinski.R.J [253],

Inhibitor in the form of microemulsion

The corrosion inhibition of microemulsion composed of disodium 1-dodecanamido-1-methylethylphosphonate (DAMEPNa₂) heptane-pentanol-tapwater was studied by Zhu.H et al., [254] using weight loss method, polarisation curves and electron microscope. The results showed that DAMEPNa₂ in the microemulsion have an excellent inhibition effect. The efficiency of corrosion inhibition was above 90% but it was only 16.2% in the ion-micro emulsion system.

Other applications of phosphonates for corrosion inhibiton

For concrete structures

Corrosion of steel reinforcement members in concrete is inhibited by adding phosphonic acid to the slurry. Alternatively an existing concrete structure is repaired by pouring a concrete slurry containing the corrosion inhibitor on the top and allowing it to migrate through the structure and contact the reinforcing members. Neagle.W et al., [255] studied the polarisation resistance of EN33
mild steel electrodes in a simulated chloride solution containing 100 ppm HPA. The resistance was 4300 kilo ohms cm$^2$ after immersion for 12 - 25 days in inhibitor solution compared to only 12.1 kilo ohms cm$^2$ for the specimens exposed to the solution not containing the corrosion inhibitor. Morita.H et al., [256] added HEDP-Zn salt to reinforced mortar which effectively prevented rust formation of steel bars.

In surface coatings

Matienzo.L.J et al., [257] used phosphonic acid and silanes to improve the durability of adhesion between aluminum and polymeric coatings. Of the silanes and phosphonates tested, NTMP is the effective corrosion inhibitor for the prevention of environmental degradation and improvements of adhesion between etched aluminum alloy substrates and epoxy coatings as determined by the wedge test. Dofman.A.M et al., [258] studied the corrosiveness of modified polyethylene in metal polymer structures. Corrosion of steel coated with low density polyethylene containing 3-22% of fireproofing agent, poly(vinylmethylphosphonate) completely eliminated the possibility of atmospheric moisture getting on steel fire proofed polymer interface.

Along with rubber compounds

Lobacheva.G.K et al., [259] used flouro rubber acrylonitrile grafted EPDM rubber blends for improved corrosion and ozone resistance. It is prepared by addition of 1-30 parts of unsaturated chlorinated polyethylene (25-30% Cl) and 1-
30 parts bis (1-acryloyloxy-3-chloro-2-propanol) methyl phosphonate to mixtures of F2C=CF(CF3)-F2C=CF2 copolymer 10-75%, EPDM rubber containing 15-29% grafted acrylonitrile 25-90%, ZnO 5-10%, MgO 1-10%, 1,1-di(tert-butylperoxy)-1,4-diisopropylbenzene 4-10% and carbon black 30-80%. Niess.R et al., [260] also prepared rubber compounds for metal surfaces using (2-chlorovinyl) phosphonate.

Combined cathodic and inhibitive protection of steel

Kuznetsov.Yu.I et al., [261, 262] used combined protection of steel in sea water by phosphonate inhibitor and cathodic polarisation. The cathodic polarisation sharply decreases the corrosion rate of steel in sea water with the use of 10 ppm Na2H2P04 and HEDP. Synergistic effect of Zn-HEDP is observed. The protective cathodic film on the steel consists of Mg(predominant), P and Zn. The combined protection method is useful for ballast compartments of ships.

Anticorrosive water thinned inks for ball point pens

The anticorrosive water thinned inks for ballpoint pens is prepared by Suzuki.S [263] by using a mixture of C.I acid Red 8.75%, ethylene glycol 15.0%, glycerin 10%, polyoxynyl phenyl ether 0.3%, ATMP 0.1%, phenol 0.1% and water 69.5%. The ball point pen filled with above ink wrote smoothly initially and after one month storage at 50°C and produced no rust when kept in partial
Contact with a steel bar at 40°C for 10 days while a control without ATMP wrote scratchily after the storage and produced rust on steel.

Other miscellaneous applications

Bonnke. M and Bothe.L [264] used [(hydroxyphenyl) alkyl] phosphonates corrosion inhibitor for polyolefin molding compositions. Paladini.M [265] used hydroxydiphosphonic acid derivatives of caprylic, lauric, palmitic, stearic, undecenoic, oleic or hexane carboxylic adds for the preservation of organic products. Thus a steel rod of 8.4 cm$^2$ was immersed in a test tube filled with 6g of fatty acids and containing laurylhydroxy diphosphonic acids as inhibitor. After 3G hours, the iron content in fatty acids was 21.1 ppm or 12.05 ppm when the inhibitor concentration was 800 ppm or 1600 ppm compared with 104.4 ppm when no inhibitor was added. Boron.K and Dabrowieki.K [266] used 50 ppm ATMP, 150 ppm sodium phosphate mixture for controlling corrosion of steel in steel spray cooler. French.E and Braga.T.G [267] used PBTC for corrosion inhibition in coal slurries. Wilson.J.C [268] used disodium methylphosphonate (0.002-0.006 wt%) and sodium mercaptobenzotriazole (0.2-0.3 wt%) for the effective corrosion inhibition for high Pb solders in aqueous alcohol containing antifreeze systems for internal combustion engine radiators. Hirozawa, S.T et [269] prepared corrosion inhibitors for antifreeze coolants using 1-hydroxy-1,1 -diphosphonic acid. Cook.B [270] used hydroxy, carboxy phosphonic acids as fouling agents in aqueous systems. Hydroxycyanomethyl phosphonic acid [271] is used as corrosion inhibitor for preventing tartar and stabilizing tooth enamel.
Review of literature indicates that the mechanistic aspects of corrosion inhibition are largely based upon the results of the weight-loss studies and electrochemical methods. Surface examination techniques like x-ray diffraction, UV-visible reflectance spectroscopy, UV-visible luminescence studies and FTIR spectroscopy have rarely been used so far in examining the nature of the film. The review of literature also shows that no studies have so far been carried out on the influence of sodium gluconate, sodium potassium tartrate and sodium citrate on the corrosion inhibition efficiency of the 2-chloroethylphosphonic acid-Zn$^{2+}$ system in chloride environment.

Summary

In general phosphonic acids are very good complexing agents. Many of the phosphonic acids including polymeric phosphonic acids are easily prepared in the laboratory conditions. The corrosion inhibition efficiencies of phosphonic acids are tested using various conditions such as chloride, sulphate, hardness (calcium and magnesium hardness), pH, temperature etc. Usually phosphonic acids are as such not good corrosion inhibitors except in very few cases. But the corrosion inhibition is increased by addition of metal cations especially Zinc ions.

The amount of Zinc ions and phosphonic acid required for corrosion inhibition is reduced by addition of organic compounds. Some authors tried to eliminate the metal ions by addition of polymers, azole compounds with phosphonic acids. Phosphonic acids are frequently used for the protection of
iron and its alloys. The other metals and alloys benefited are Aluminum, copper, brass, stainless steel, Zinc, Magnesium and copper alloys.

The phosphonic acids are not only used as corrosion inhibitors in cooling water systems, but they are also used as inhibitors in concrete, coatings, rubber blends, acid cleaners, antifreeze coolants, ship ballast compartments, preservation of organic products, coal slurries etc. The above applications show that phosphonic acids have excellent role in corrosion inhibition as compared to that of any other group of compounds.

The general aspects of corrosion and controlling methods especially using inhibitors have been discussed in this chapter. The need, objectives and scope of the present study are presented in the next chapter.