CHAPTER I

INTRODUCTION

1.1 Definition of corrosion

'Corrosion' is defined as the destruction of metals or alloys as a consequence of chemical or electrochemical reaction with the environment.

In nature metals are present in the form of chemical compounds, i.e., minerals. Some amount of energy is needed to extract metals from their minerals and the same amount of energy is evolved during the chemical or electrochemical reaction involving corrosion. Thus, in corrosion phenomenon, the metals revert to their natural state (1).

1.2 Costs of corrosion

1.2.1 Economic losses

The economic losses, due to corrosion, are divided into 1) direct losses and 2) indirect losses. Direct losses include the costs of replacing the corroded structures and machinery or their components. Indirect losses include shut down, loss of products, loss of efficiency, contamination of product and the costs due to over design (2).
Were it not so insidious and ubiquitous, corrosion could be classified as the greatest economic calamity known to the humankind. As it is, corrosion is the root cause of many industrial economic calamities (3).

1.2.2 Human life and safety

Corrosion takes an even more significant toll on human life and safety. Corrosion is scarcely reported as the cause of many fatal accidents, but a few examples can be cited readily. The spectacular airline accident in which part of the fuselage tore away during flight in Hawaii was in all probability due to the combined effects of cyclic mechanical stress and atmospheric corrosion in a semitropical environment (4).

The well-known bridge collapse at Pt. Pleasant, West Virginia, killed 46 people in 1967 and this has been attributed to stress corrosion cracking (5).

Selective corrosion of a welded liquid gasoline pipeline in Minnesota in 1986 (6) resulted in massive fire damage to the entire town and also in the loss of two lives.

Again in 1986, a steam pipe suffering from the combined effects of corrosion and erosion, burst at a nuclear power plant in Virginia, severely burning eight nearby workers, four of whom died later.
These are only a few examples of many such fatal accidents caused by corrosion.

1.3 Methods of corrosion prevention and control

The various methods employed for corrosion control are summarised in the form of a chart shown in Fig. 1.1.

1.4 Corrosion control by inhibitors

1.4.1 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.

1.4.2 Classification of corrosion inhibitors

Putilova et al., (7) 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.
CORROSION CONTROL METHODS

Modification of metal
  - Modification of composition of metal (Alloying)
    - S.S., Monel, Brass
  - Modification of metal surface
    - Coating
      - Surface alloying
        - Inorganic coatings
          - Organic coatings, Paints, Lacquers, Oil
          - Electro deposits (Zn, Cd, Ni, Cr, etc.)
        - Metallic coatings
          - Hot-dip coatings (Zn, Al)
          - Diffusion coatings (Cr, Al)

Modification of environment
  - Inhibitors
  - Dehumidification
    - Acetic
    - Vapour phase
    - Neutral and alkaline

Cathodic/anodic Protection
  - Use of non-metallic materials
    - Sacrificial anodes
    - Impressed current
    - Insoluble films on metals, using chelat of anodic

Fig. 1.1
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. (8), 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 polarization curves showing the pertinent processes at the metal/solution interface under impressed electromotive force (EMF) conditions (9).

Figure 1.2 illustrates the significant terms for a freely corroding metal. The line $E_aD$ represents the anodic reactions; line $E_cD$ represents the cathodic reactions. The point of intersection of anodic and cathodic reactions ‘$D$’ establishes the open circuit corrosion potential ($E_{corr}$) of the metal and indicates the magnitude of corrosion at $i_{corr}$ (corrosion current).
Fig. 1.2 Activation polarisation curves showing pertinent processes for metal/solution interface under impressed EMF conditions.
Fig. 13 Anodic and cathodic polarization curves

(a) significant terms for freely corroding metal

(b) relation of metallic corrosion protection and inhibition
Figure I.3b 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 maeti ons is more ofluotive. It is found that both anodic and cathodic type inhibitors reduce the corrosion current (anodic : A i ; cathodic : ^ h ) / <wJ thi.it the "mixed" inhibitor reducer. tho corrosion current moro effectively ( Ai ) .

Anodic inhibition runtuJ.ti; tn (jrcntor ijhiltu 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 tiding and the cathodic inhibitor ñhiltii thu wörrot.1lon potential towards cathodic side, whereas both shifts will be rualiuod in thu c.ūw o i <i niixwd Jnhi bi tui:. 
1.5 Theories of inhibition of corrosion

"Corrosion Inhibitors" has been the central theme of many reviews (7,10,11) and symposia (12,13).

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).

1.5.1 Adsorption-theory and effect of molecular structure

Machu (14,15) 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 (16) 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 (9) 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 (17 - 19).

The study of structure - corrosion inhibition relationship of organic compounds has received much attention from corrosion scientists. Hackerman and Hurd (20) plotted the degree of inhibition for ring-substituted N-methylamines vs the Hammett substituent constant. In 1965, Donahue and Nobe (21) 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 (17,22-27).

1.5.2 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 (28). Hackerman and Sudbery (29) pointed out that amines are adsorbed on the anodic and cathodic regions on the metal surface. Hoar and Holliday (30) 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.

1.5.3 Film formation theory

In order to explain the action of inhibitors in neutral and alkaline media, Evans (31) proposed the film formation theory. Evans attributed the inhibition to the formation of an insoluble film. According to Putilova et al. (7), in acid solution, inhibition is due to the formation of a layer of insoluble or slightly soluble corrosion product on the metal surface.

1.5.4 Electrochemical polarisation theory

Explaining the action of passivating inhibitors, Stern (32) 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 (7) 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.
1.6 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 (33) in the mid-thirties, who reported finding "compound filnis", such as formed by phosphate - chromate mixtures, to be roore effective than those of either alone.

The synergistic effect of halides and organic compounds as inhibitors has been frequently reported in the literature (34-37). 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 (38). At high concentrations, the two species on the iron surface transform from adsorption to the formation of a complex film (37-39).

Synergistic effect has been shown by various mixtures such as $\text{K}_2\text{CrO}_4$ and urotropine, $\text{NaV}_3\text{O}_8$ and potassium antimonyl tartrate (40) polyphosphate and orthophosphate (41), disodium sebacate and benzotriazole (42), potassium iodide and dicyclohexylamine (43), halides and benzyl amine (44).

Synergistic effects of mixtures of corrosion inhibitors have been reviewed and discussed at length (45, 46). The inhibiting effect of different organic phosphorus-containing compounds and the synergistic effect of various additives have been studied by
a new mathematical model (47).

Synergism was established in the inhibition of corrosion of steel in aqueous chloride media by a combination of inorganic oxidiser and monoethanolamine (48). Molybdate shows synergistic effect with various species such as nitrite (49, 50), phosphate (49, 51, 52), Zn$^{2+}$ (51-54), phosphonic acid (55), tolyltriazole (50), silicate (56), polymeric dispersants (55), monoethanolamine (57), and hydroxy carboxylates like sodium salicylate, sodium gluconate and sodium malate (58).

Sodium dodecyl succinate and sodium nitrite show synergistic effect in controlling the corrosion of steel in simulated cooling water circulates (59). A mixture of ethylxanthate and benzotriazole show synergistic effect in controlling the corrosion of copper in 0.1M NaCl at pH 7-11 (60).

A synergistic inhibitory effect of BiCl$_3$ and benzylthiocyanate (C$_5$H$_5$CH$_2$SCN) on corrosion of iron in IN H$_2$SO$_4$ 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 (61).

Synergistic effects of morganic cations like As$_3$$^{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 enhanced if another species was present in the solution that promoted the film formation (62).

A mixture of borogluconate and corrin-type inhibitors showed synergistic effect in preventing the corrosion of iron in neutral media (63).

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\(^{-}\) (64).

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 (65).

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, east iron, AlMg2 alloy and Al (66).

Phthalic anhydride, ATMP and zinc ion as a three component inhibitor has good adsorption and corrosion inhibition properties (67).
The corrosion inhibition efficiency of HEDP synergistically improved in the presence of ZnMoO$_4$ and Ca$^{2+}$ ions (68), Zn$^{2+}$ (53,60-71), Ca$^{2+}$, and Mg$^{2+}$ (69). A synergistic effect of Zn$^{2+}$ and HEDP in decreasing the corrosion rate of steel in seawater is observed. The protective cathodic film on the steel consists of Mg (predominant), P and Zn (70).

Corrosion of iron-based alloys in a circulating water is decreased by a synergistic inhibitor mixture containing HEDP, hydroxyphosphonoacetic acid and sodium tolyltriazole (72). 2-Phosphonobutane-1,2,4-tricarboxylic acid (PBTCA) shows synergistic effect with Zn$^{2+}$ (73), Zn$^{2+}$-HEDP combination (74) and MnCl$_2$.4H$_2$O (75). When PBTCA is used along with Zn$^{2+}$ 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 (73).

I.7 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.

1.7.1 Chromates

Chromate is a very effective passivating inhibitor. Chromate passivation usually involves formation and maintenance of a protective ferric oxide film (76). Chromates are usually referred to as anodic inhibitors. However, cathodic inhibition has also been reported (77, 78). Passivation with chromate is sensitive to various common anions such as chloride and sulphate (79, 80). The use of chromates at high concentration has declined in recent years because of health and safety considerations.

1.7.2 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 (81) and mild steel in neutral aqueous solutions (82). Molybdates when used alone, are anodic inhibitors. Molybdate is found to be an efficient inhibitor in aerated distilled water but inefficient in deaerated water (83).
1.7.3 Pertechnetate

The protection of carbon steel in 13 ppm $\text{K}^7\text{TeO}_4^-$ 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 $\text{Te}^{IV}$ (84).

1.7.4 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 (85, 86). Bacterial decomposition of nitrite is a factor which discourages the use of nitrites in open recirculating systems (87). 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 (88).

1.7.5 Phosphates

Phosphates are frequently used in the polyphosphate form. They control the corrosion of ferrous metals. Polyphosphates act as cathodic inhibitors (89-91). The effectiveness of polyphosphates as inhibitors is increased by the movement of solution, but decreased by rise in temperature.
1.7.6 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 (92).

1.7.7 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 (93).

1.7.8 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 (94, 95). The organic surfactant, 1-decylimidazole, inhibits the corrosion
of iron in neutral solution of 3 percent sodium chloride (96). The inhibition of \( \alpha^+ \) and \( \gamma \) 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 (97).

1.7.9 Carboxylates

Several carboxylates such as sodium salicylate (98), sodium cinnamate (99), anthranilate (100), and adipate (101) have been used as inhibitors. Inhibitive anions like benzoate, phthalates and other carboxylates (102-104) 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 \( 0^- \). Carboxylates are anodic inhibitors. Therefore they are sensitive to the presence of higher concentrations of aggressive ions.

1.7.10 Tannins

Tannins are of vegetable origin and are good corrosion inhibitors (105-107). They are inoffensive towards the environment. Sodium tannate has been used in the inhibition of corrosion of mild steel in neutral solutions (108).
1.8 Review of literature on phosphonates as inhibitors

The need to develop inhibitor formulations free from chromates, nitrites and inorganic phosphorous compounds has stimulated research work on "Phosphonates as corrosion inhibitors".

Phosphonates are sodium, potassium or ammonium salts of phosphonic acids. Phosphonates provide the following key aggregation of properties:

a) They form complexes with metal ions at stoichiometric concentrations.

b) Corrosion inhibition: In the presence of other chemicals (synergists) they provide corrosion inhibition.

c) Scale inhibition: They inhibit precipitation of typical scalants at substoichiometric inhibitor concentrations.

d) Hydrolytic stability: They resist decomposition in aqueous solutions even at elevated temperatures and extremes in pH.

e) Chlorine stability: They resist degradation by ppm levels of available chlorine.

Because of these properties, studies on phosphonates as inhibitors in cooling water systems have gained considerable importance.
Phosphonates by themselves are not effective corrosion inhibitors. However, several Chemicals synergise the corrosion inhibition by phosphonates. Phosphonates show synergistic effect with 2-aminothiophenol \((109)\), zinc \((1:10-114)\), dichromate \((110,115-117)\) and carboxylic acids \((111)\).

Among the phosphonates, amino(trimethylene phosphonic acid) (ATMP) and 1-hydroxy-ethane-1,1-diphosphonic acid (HEDP) are widely studied.

Although the structure of ATMP is quite different, it shares many of the properties of the polyphosphates.

1. It forms complexes with calcium and other polyvalent metal cations.
2. It is a good peptizing agent and dispersant.
3. It stabilises iron and manganese-bearing water \((118)\).
4. It stabilises supersaturation with respect to calcium carbonate and calcium sulphate \((119,120)\).
5. It forms protective films on metal surfaces \((110,115,121)\).

Kubicki et al., have investigated \((111)\) the inhibitive property of ATMP in preventing the corrosion of iron in neutral aqueous solution; The influence of ATMP, in combination with carboxylic acids and zinc salts upon the change of the double layer capacitance on iron and the inhibitive properties of the
mixture were examined. The greatest decrease of capacity and the
greatest protective effectiveness were obtained for tri-component
compositions containing ATMP, phthalic acid or oxalic acid, and
Zn$^{2+}$ ions.

The results of the potentiodynamic cathodic polarisation
tests of Carter and Denohue (122) show that increase in pH (6.5
to 8.0) and calcium (as CaCO$_3$) increase corrosion inhibition.
They also observed that with ATMP, the metal surface did not have
any visible film. With chromate based treatments, interference
colours, indicating adherent protective films, are present.
Film formed with ATMP alone is thin and rapidly breaks down
under severe conditions such as high flow rate, low pH or heat
transfer. To overcome these inherent disadvantages, phosphonates
were formulated along with zinc or organic inhibitors.

The influence of the inhibitor system consisting of ATMP,
oxalic acid or phthalic anhydride, and zinc sulphate on the rate
of corrosion of steel in simulated industrial water of variable
Chemical composition and in water being chlorinated has been
studied by gravimetric method. This formulation is considered as
a perspective inhibitor for the corrosion protection of
industrial cooling and heating water installation (123).

It has been observed that the addition of sodium sulphite to
Zn$^{2+}$-ATMP formulation increases the degree of protection of iron
in a certain range of inhibitor concentration. This is attained by the effective slowing down of the reduction of oxygen on the steel (124).

The influence of divalent ions and ATMP on corrosion inhibition of low carbon steel in neutral water (NaCl 30 + Na₂SO₄ 70 mg/l) has been evaluated by polarisation resistance and weight-loss method. It has been reported that the protective properties depend on the solubility products of hydroxides of the metal-complexing agents and on the stability of the complexes of the metals with the ligand. An equation was obtained relating the minimal protective concentration of the inhibitor with the indicated parameters. A comparative analysis was also made of the protective properties of complexonates based on ATMP with that based on HEDP. The source of the differences in their properties has been indicated (125).

HEDP has been used as corrosion and scale inhibitor for mild steel (126). Addition of triazole to 'phosphonate-zinc combination is shown to improve the corrosion protection of mild steel. The corrosion inhibition efficiency of HEDP can be improved by combination with dichromate (115-117) or zinc salts (71,127) or Ca²⁺ (127).

The corrosion of steel and iron has been studied in neutral solutions containing NaCl, Na₂SO₄ and HEDP and its complexes with
transition metals. The corrosion rate and the electrode potential were measured as a function of the electrolyte composition and temperature. The possibility of passivation due to hydroxide formation and the participation of \( \text{OH}^- \) in the corrosion protection have also been discussed (128).

Corrosion inhibiting properties of HEDP and its sodium salt in neutral aqueous solution containing \( \text{HCO}_3^- \), \( \text{Ca}^{2+} \), \( \text{Cl}^- \) and \( \text{SO}_4^{2-} \) have been investigated (129). The influence of HEDP and combinations of HEDP and molybdate species on the corrosion of iron was studied in both buffered and unbuffered electrolytes (130).

The mixture consisting of sodium salt of HEDP, sodium gluconate and zinc sulphate effectively inhibited the corrosion of steel in water (131). It has been observed that decomposition of phosphonate inhibitors by chlorine in industrial cooling waters is decreased or prevented by treatment with water soluble sulfamic acid at 0.25 ppm/ppm chlorine. These phosphonates include HEDP and tris(aminomethane phosphonic acid) (132).

The corrosion of iron in 0.1M \( \text{Na}_2\text{SO}_4 \) exposed to air at pH 6 was inhibited by 1,6-hexane diphosphonic acid (133). Corrosive organic products are stored in non-aqueous phase in steel containers after addition of 100 to 1500 ppm of corrosion inhibitors optionally serving as a colour stabiliser. Thus, laurylhydroxy diphosphonic acid reduced the corrosion rate of
Phosphonate-terminated carboxylate-based telomers have been used as scale/corrosion inhibitors and/or fouling agents in aqueous systems (135). Corrosion inhibition of carbon steel by 2-phosphonobutane-1,2,4-tricarboxylic acid is based on formation of an inhibiting film (136). It has been reported that corrosion of carbon steel can be inhibited by addition of an organic phosphono carboxylic acid (e.g., 2-phosphonobutane-1,2,4-tricarboxylic acid) and/or phosphino carboxylic acid and manganese ion (137). Corrosion inhibiting compositions containing carboxylated phosphoric acid (hydroxy phosphono acetic acid or 2-phosphonobutane-1,2,4-tricarboxylic acid) and a sequestrant selected from tartaric acid, citric acid, gluconic acid, and sulphur-containing lignosulphonates have been studied (138).

The composition containing the steel corrosion inhibitor hydroxyphosphono acetic acid and the copper corrosion inhibitor, tolyltriazole, has been used as scale inhibitor (139). A corrosion inhibitor for iron-based alloys in an aqueous system (tap water) comprises hydroxyphosphono acetic acid or its water soluble ammonium or alkali metal salt and a co-polymer formed from 2-acrylamido-2-methylpropane sulphonic acid' and acrylic acid or methacrylic acid (140). Carboxyhydroxymethyl phosphonic acid is a suitable ferrous alloy corrosion inhibitor, for cooling
towers. This inhibitor is nontoxic to aquatic life and decomposes to simple compounds (141). Hydroxy- and/or carboxy-substituted phosphonic acid and diphosphonic acids usable as corrosion and scale inhibitors have been reported (142).

Aminophosphonic acid/phosphate mixtures for controlling corrosion of steel and inhibiting calcium phosphate precipitation in cooling water has been reported (143). Water in open cooling system is treated with diethylenetriamine-penta(methylene) phosphonic acid as its sodium salt, along with ethanolamino phosphate esters to prevent corrosion and scaling. Optionally, the effect is increased by adding anionic polymeric dispersants, azole compounds, zinc salts, chromates, phosphates, etc. (144). Scale and corrosion of metal surfaces in contact with industrial process waters is inhibited by treated waters with an amido alkyl phosphonate containing acrylic acid polymer (145). The inhibiting properties of phosphonic acid derivatives of polyamides in the inhibition of corrosion of carbon steel in water has been studied (146). The formulation consisting of a water soluble organic phosphonate and an N-substituted acrylamide tpolymer' has been used for inhibiting scale formation and/or cäispersing ions in reverse osmosis systems (147).

Phosphonoalkyl benzene has been used as inhibitor of corrosion and scale on metals (148).
Bis(2-chloroethyl) phosphonate and bis(2-chloroethyl) vinyl phosphonate have been used in corrosion inhibiting rubber compounds for steel surface (149). A phosphono-N-phosphonomethylated derivative of caproamide has been used as inhibitor for metal corrosion (150). Phosphonated hydrolysed poly(maleic anhydride) is an excellent anti-corrosion agent and seal inhibitor in a cooling water system containing < 40,000 ppm Cl\(^-\) (151).

The effect of zinc phosphonates on the cathodic protection of steel in sea water has been discussed (152). Corrosion protection of aluminium alloys in aqueous solutions of chloride, by zinc phosphonates has been reported (153).

The corrosion behaviour of L-62 brass was studied in water containing 230 ppm Cl\(^-\) and 620 ppm S\(_4\)O\(_4\)^{2-}, and in the presence of phosphonic acids (154). The effects of corrosion prevention of benzotriazole phosphonic acid derivatives on elution of copper in acidic or sodium chloride solution have been discussed (155).

In recent years various phosphonates and polymeric compounds have been claimed to show corrosion-inhibiting properties. In this regard phosphonic acid like hydroxyphosphono acetic acid (156) has been used. The use of polymers include polyacrylic acid, polymethacrylic acid (157), sulphonate containing polymers (158, 159), the most important ones being based on 2-acrylamido-
2-methylpropanesulphonic acid (160). N-Phosphonomethylated derivatives of polyamides have been used as inhibitors for metal corrosion (161). An alkaline cooling water treatment programme with ATMP and sodium polyacrylate has been reported (162). The performances of HEDP and acrylic acid based terpolymer have been studied (163).

The calcium phosphonate stabilising capacity of the co-polymer, acrylic acid-hydroxyl ethylacrylate sulphate ester, is a useful property in all organic cooling water formulations (164).

A brief review on the mechanistic aspects of corrosion inhibition is also worth mentioning here. The influence of salts of various phosphonic acids on the chemical passivation of pure iron and mild steel in neutral aqueous solution by dissolved oxygen has been investigated. It is shown that the chemical passivation is not attainable in the presence of phosphonates. In fact, the passive state of iron or mild steel surface achieved in air-saturated sodium benzoate solution is destroyed by the phosphonates (165).

The role of the ligand nature in inhibition of metal corrosion by phosphonates has been reviewed. It is shown that the corrosion inhibition is due to the formation of metal complexes with different solubilities (166).
The use of phosphonic acids (e.g., Cublen K60, Skiantan W Kf Trisphon) as corrosion inhibitors for carbon steel pipes of a cooling water system has been examined and the inhibition mechanism is on the formation of oxid-free calcium phosphonate protective layer (167).

Corrosion inhibition of carbon steel (in 3% NaCl solution) by disodium monoalkyl phosphonates has been reported. The formation of a relatively compact, adherent film of disodium monoalkyl phosphonates is responsible for the decrease in the corrosion rate (168).

Increase in corrosion rate with increasing inhibitor (phosphonate) concentration beyond the optimum value is explained by the formation of corrosion product-inhibitor complexes (169).

Aluminium corrosion inhibitors based on gem-diphosphonates have been prepared and examined in water/glycol solution. The inhibitor protected aluminium by forming a waxy, hydrophobic film (170).

It has been reported that some phosphonic acids may exert inhibition effect in HCl solution. These effects depend on the structure of phosphonic acids, i.e., the numbers and position of nitrogen atoms and phosphono groups (171).
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The corrosion of iron and low carbon steel in neutral aqueous media in the presence of complexons and compositions gised on them has been studied. On the basis of studies using jnc phosphonate inhibitors of corrosion, it was found that an extremely effective protection of steel over a wide pH range, jow rate and temperature is possible owing to the formation of a elatively thin but insoluble films on the metal surface (172).

The corrosion rate of steel has been investigated in 0.5M $\text{SO}_4^{2-}$ as a function of pH. The influence of adding 0.1 M HEDP nd 0.1M solution of $\text{Fe}^{2+}$, $\text{Co}^{2+}$, $\text{Mg}^{2+}$, $\text{Zn}^{2+}$, $\text{Al}^{3+}$ and $\text{Cr}^{3+}$ was examined. As a result of the formation of insoluble surface ompounds in slightly acidic or near neutral sulphate solutions, he rate of corrosion significantly decreased (173).

The Ca ion concentrations have little- effect on the orrosion inhibition of HEDP. However, the mechanism of orrosion inhibition is different frora high to low Ca$^{2+}$ oncentrations. When Ca$^{2+}$ concentration is low, HEDP is adsorbed n the surface of steel and performs as a mixed inhibitor. At higher concentrations of Ca$^{2+}$, HEDP forms a complex film with $\text{Ca}^{2+}$ deposited on the steel surface, and acts as a cathodic inhibitor to prevent corrosion (174).
Increased cathodic polarisation is shown as the principal inhibitive function of the ATMP – zinc mixture (110). It has been shown by infrared and X-ray photoelectron spectroscopies, that ATMP reacts with aluminium surface to form a coating which is an effective inhibitor (175).

Our 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 simple monophosphonates like ethyl phosphonate, 2-chloroethyl phosphonate and phenyl phosphonate.