CHAPTER I

INTRODUCTION

1.1 INTRODUCTION

The earth is the only object known in the entire universe capable of supporting life. This supporting property of our planet is due to its unique atmosphere. Atmosphere is the protective thick gaseous mantle, surrounding the earth which sustains life on earth and saves it from unfriendly environment of outer space. It was pure, virgin, undisturbed, uncontaminated and basically quiet hospitable for human kind.

Recently for the first time in entire cultural history, man has faced one of the most horrible ecological crises, the problem of pollution of environment. Pollution is an undesirable change in the physical, chemical or biological characteristics of air, land, and water that may or will harmfully affect human life or that of desirable species, our industrial process, living conditions, and cultural assets. In other words, pollution is the unfavourable alteration of our environment, largely as a result of human activities. Atmospheric pollution is one of the disastrous, undesired Calamity. It may be defined as the emission of substance that disturbs the physical and chemical properties of air. The main
pollutants are classified into primary and secondary pollutants. Primary pollutants such as sulphur dioxides, carbon dioxides, nitrogen oxides, hydrocarbons and particles are those stay in the atmosphere just as they were originally emitted by the source. Secondary pollutants that experience chemical changes as a result of a chemical reaction between two or more pollutants such as oxidants and some radicals like ozone. The adverse effects of atmospheric pollution causes diseases as tuberculosis, typhoid, lung cancer, cardiac vascular and respiratory diseases. It affects plant life such as premature leaf and inhibition of growth, reduction of photosynthesis.

Pollution accelerates corrosion on metals / alloy like copper, brass, aluminium and mild steel etc., deteriorates the quality and strength of buildings, textiles and rubber and imbalances the climatic condition through green house gases. Among the above listed, atmospheric corrosion on structural materials is one of the most important issues at both ecological and economical concerns. Worldwide studies have shown that the overall cost of corrosion amounts to atleast 2% to 4% of the Gross National Products (GNP) and that 20% to 25% of that cost could be saved by using appropriate corrosion control technology. Atmospheric corrosion is the major contributor to this cost.
1.2 CLASSIFICATION OF CORROSION PROCESS

The word 'Corrosion' is derived from Latin 'Corrosus' which means eaten away or consumed by degrees; an unpleasant word for an unpleasant process. Corrosion is defined as the destruction of materials caused by chemical or electrochemical action of the surrounding environment (Speller, 1951).

The corrosion process may be broadly classified as follows.

Corrosion Process

- Chemical Corrosion
  - Direct oxidation,
  - Corrosion by liquid metals, fused halides, non-aqueous solution, etc.
- Electrochemical Corrosion
  - Immersion
  - Underground
  - Atmospheric
  - Corrosion
Reaction of metals with dry air or oxygen is considered as chemical corrosion. High temperature oxidation of metals and tarnishing of metals like copper, silver etc., fall in this category. Of late this is also considered to be an electrochemical process with the diffusion of oxygen (inwards) and metal ions (outwards) through the oxide layer, the electromotive force at metal-oxide interface being the driving force.

Electrochemical corrosion occurs in the presence of electrolyte. The reaction is considered to take place at the metal-solution interface with the creation of local cathodic and anodic sites on the metal surface.

1.3 CORROSION MECHANISM

Atmospheric corrosion occurs as uniform corrosion through the operation of micro-galvanic cells on the surface which shifts in a disorderly way. It can be explained how it initiates on the metal surface and there by propagates into the surface.

1.3.1 Initiation

In a dry, clean atmosphere, the steel surface becomes covered by a 20% -50 % thick oxide film which practically
prevents further oxidation. This oxide film consists of an inner layer of Fe$_3$O$_4$ and an outer layer of polycrystalline Fe$_2$O$_3$. In atmospheres containing small amounts of water vapour, $\Gamma$-FeOOH may also form (Ali and Wood 1969, Cook et al 1998, RamaBalasubramanian et al 1999, Balasubramanian et al 2003).

The initiation of corrosion on clean metal surface in non-contaminated atmosphere is a very slow process even in atmospheres saturated with water vapour. In this case initiation may occur at surface inclusions such as MnS, which dissolve when the surface becomes wet (Okada and Shimada 1974, Stratman 1990, Leygraf 2002). A more important factor for the initiation of corrosion is the presence of solid particles on the surface. Settled airborne dust may promote corrosion by adsorbing SO$_2$ and water vapour from the atmosphere (Chandler and Stanners 1966, Takeshi et al 2003, Chen et al 2005). Of special importance are particles of hygroscopic salts, such as chlorides or sulphates, which form a corrosive electrolyte on the surface. In SO$_2$ polluted atmospheres at high relative humidities rusting is rapidly initiated on polished steel samples in the absence of any particles (Sydberger and Vannerberg 1972, Zaki Ahmad et al 2000).
1.3.2 Propagation

During the initiation period, anodic spots surrounded by cathodic areas are created. In the presence of an electrolyte film on the metal surface, conditions are created for propagation of the corrosion process. The process is stimulated by \( \text{SO}_2 \), which is adsorbed and oxidized in the rust layer to \( \text{SO}_4^{2-} \). In the corrosion cells, sulphate accumulates at the anode and thus creates so-called sulphate nests in the rust, which were first described by Schwarz (Schwarz 1965, Derek Peek 1999). In the initial stage, the surface is covered by a great number of small surface nests. With increasing exposure period the nests grow larger and their number per unit area decreases (Matsushima 1971). The size and distribution of the nests depend on, among other factors, the type of atmosphere and the degree of sheltering.

In atmospheres polluted with chlorides, the corrosion of carbon steel proceeds in isolated areas, which resemble the sulphate nests mentioned above (Henriksen 1969, Barton 1981, Mc Cafferty 2003). They may arise around chloride particles deposited on the surface, where the concentrated chloride solution locally destroys the passivating film of FeOOH. In the anodic areas so formed, the chlorides are
concentrated by migration, while the surrounding surface covered by rust acts as a cathode.

When the surface becomes wetted by rain, dew, or moisture adsorption, the sulphate nests in combination with the surrounding area form corrosion cells (Fig. 1.1).

The electrolyte is mostly very concentrated and has a low water activity. Anodes are located inside the sulphate nests, where the pH value and the redox potential become low. The conditions here correspond to a position in the Fe$^{2+}$ domain in the potential – pH diagram and local attack will take place on the steel surface. The surrounding area acts as a cathode. The corrosion reaction may be described in terms of an electrochemical cell of the type.

\[
\text{Fe}/\text{Fe}^{2+} (\text{aq}) \parallel \text{OH}^- / \text{O}_2 (\text{aq}) \rightarrow \text{Fe}_3\text{O}_4 \quad \text{1.1}
\]

Besides magnetite, hydroxide containing both divalent and trivalent ions, i.e., green rust, may serve as cathodes as they possess appreciable electronic conductivity.

The following equations may, in principle, describe the reactions taking place in the corrosion cells.
Fig. 1.1: Corrosion Cell at Sulphate Nest on Steel
At the cathode

The main cathodic reaction is considered to be reduction of oxygen dissolved in the electrolyte film:

\[
\frac{1}{2} O_2 + H_2O + 2 e^- \rightarrow 2 OH^- \quad ... \quad 1.2
\]

This process causes a local increase in pH at the cathodes and promotes precipitation of corrosion products at some distance from the anodes.

As soon as ferric corrosion products have been formed another cathodic process may take place:

\[
Fe^{3+} + e^- \rightarrow Fe^{2+} \quad ... \quad 1.3
\]

The cathodic step then consists of reduction of ferric rust to magnetite according to

\[
8 \text{FeOOH} + \text{Fe}^{2+} \text{(aq)} + 2 e^- \rightarrow 3 \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O} \quad ... \quad 1.4
\]

This process takes place during wet periods and has been verified through cathodic polarisation measurements on rusty steel specimens in sulphate solutions (Matsushima 1971, Hakkarainen and Ylasaari 1982).
At the anode

The basic anode reaction

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2 \text{e}^- \] ... 1.5

has different mechanisms in neutral and acid solutions. At low concentrations of sulphates, the mechanism of iron dissolution may be described as follows according to Heusler (Heusler 1958) and Bockris et al (Bockris et al 1961).

\[ \text{Fe} + \text{H}_2\text{O} \rightarrow \text{Fe (OH)}_{\text{ads}}^\text{ads} + \text{H}^+ \] ... 1.6

\[ \text{Fe (OH)}_{\text{ads}}^\text{ads} \rightarrow \text{Fe (OH)}_{\text{ads}}^\text{ads} + \text{e}^- \] ... 1.7

\[ \text{Fe (OH)}_{\text{ads}}^\text{ads} \rightarrow \text{Fe (OH)}^\text{+} + \text{e}^- \] ... 1.8

\[ \text{Fe (OH)}^- \rightarrow \text{Fe}^{2+} + \text{OH}^- \] ... 1.9

If insoluble corrosion products are formed at anodic sites, the corrosion rate may be reduced substantially due to passivation (Barton and Bartonova 1969). This may occur in rural atmospheres, where the content of sulphates and chlorides in the rust layer is very low.

In sulphate-containing solutions, however, the anodic dissolution proceeds according to a mechanism proposed by Florianovitch and Kolotyrkin (Florianovitch and Kolotyrkin 1967).
Fe + H₂O → Fe (OH)₉⁻ + H⁺ + e⁻ ... 1.10

Fe (OH)₉⁻ + H₂O → Fe (OH)₂⁻ / ads + H⁺ + e⁻ ... 1.11

/ Fe (OH)₂⁻ / ads + SO₄²⁻ → FeSO₄ + 2 OH⁻ ... 1.12

FeSO₄ → Fe²⁺ + SO₄²⁻ ... 1.13

The pH regulating effect of FeSO₄ will result in maintaining a relatively low pH at the anodic sites and thus preventing precipitation of iron hydroxides directly on the metal surface. This creates favourable conditions for corrosion in the active state, the sulphate accelerating the anodic dissolution of iron. Tanner (Tanner 1964) identified the crystalline iron (II) sulphate at the steel/rust interface as tetrahydrate FeSO₄·4H₂O. Thus a reservoir of soluble sulphates exists within the sulphate nests, contributing to high stability.

In the rust layer the following reaction takes place

2 Fe²⁺ + 3 H₂O + ½ O₂ → 2 FeOOH + 4 H⁺ ... 1.14

This so-called oxidative hydrolysis plays an important role in most of the proposed mechanisms of atmospheric corrosion. According to Evans (Evans 1972), the magnetite
produced by cathodic reduction is reoxidized by oxygen in the presence of water.

$$\text{Fe}_3\text{O}_4 + \frac{1}{4} \text{O}_2 + \frac{3}{2} \text{H}_2\text{O} \rightarrow 3 \text{FeOOH} \quad ... \quad 1.15$$

The sulphate nest becomes enclosed within a semi-permeable membrane of hydroxide formed through oxidative hydrolysis of the iron ions. The electric current in the corrosion cell causes migration of $\text{SO}_4^{2-}$ ions into the nest. This will stabilise the existence of the nest.

Since the classical work of Vernon (Vernon 1935), the decisive importance of $\text{SO}_2$ in the process of atmospheric corrosion of steel has been recognised. Under atmospheric conditions $\text{SO}_2$ may be adsorbed at the steel surface, the adsorption rate on rusty and especially on polished specimens depends on the relative humidity. Investigations by Sydberger and Vannerberg (Sydberger and Vannerberg 1972) showed that the adsorption rate increases with relative humidity. At high humidities, a limiting value is reached which corresponds to the situation where every $\text{SO}_2$ molecule reaching the surface is adsorbed. Johansson and Vannerberg (Johansson & Vannerberg 1981) made an extensive analysis of the thermodynamic conditions for reactions of $\text{SO}_2$ in moisture layers on metal surfaces.
At low and medium SO₂ concentrations (< 1-10 ppm) and under atmospheric conditions there is a strong driving force for the reaction

\[ \text{SO}_2 \text{(aq)} + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2 \rightarrow \text{H}_2\text{SO}_4 \quad \ldots \quad 1.16 \]

as all sulphur (IV) species, in aqueous solutions are thermodynamically unstable. The rate of oxidation of SO₂ by oxygen in water is rather low. The reaction is, however catalyzed by, e.g., Fe²⁺ (aq) and Mn²⁺ (aq) as well as by oxides and hydroxides of iron which are present at the steel surface. The reaction is strongly pH-dependent, the reaction rate decreasing with pH (Johansson 1964, Mattsson and Holm 1968). Apart from oxygen, Fe³⁺ (aq) and solid ferric oxide hydroxide may also oxidise SO₂.

At high SO₂ concentrations, as already mentioned, Rozenfeld (Rozenfeld 1962) found in laboratory experiments that SO₂ in high concentrations has a marked depolarizing effect on cathodic reactions at polished metal surfaces. A high SO₂ content also creates a low pH on the surface film and consequently a low rate of sulphate production. Thus the surface film will contain appreciable amounts of tetravalent sulphur. Under these conditions, at SO₂ contents greater than approximately 10 ppm reduction of SO₂ to dithionite may take place according to the following reaction:
2 SO$_2$ (aq) + 2 e$^-$ → S$_2$O$_4^{2-}$ \hspace{1cm} ... 1.17

The reactive dithionite is then either oxidised or further reduced by the metal to sulphide

S$_2$O$_4^{2-}$ + 8 H$^+$ + 10 e$^-$ → 2 S$^{2-}$ + 4 H$_2$O \hspace{1cm} ... 1.18

The situation may be illustrated by a potential - pH diagram, which shows that, at high SO$_2$ concentrations, FeS is the stable corrosion product in the pH range of 3-6 (Johansson and Vannerberg 1981). Sulphide containing corrosion products have, in fact, been reported in laboratory experiments at SO$_2$ > 10 ppm in several investigations (Langle 1968, Sydberger 1977, Johansson 1981). At the SO$_2$ concentrations found in polluted outdoor atmospheres, however, which are usually in the range 0.01 – 0.2 ppm, reduction of SO$_2$ does not take place. This applies especially to rusty surfaces, which strongly catalyze the oxidation of SO$_2$.

In conclusion, sulphates influence the corrosion of steel in the following ways:

They give rise to sulphate nests, which create the basis for the electrochemical process in atmospheric corrosion of steel.
They increase the conductivity in the thin surface electrolyte films, thus increasing the current in the electrochemical cells, i.e., the corrosion rate.

They accelerate the anodic dissolution of iron in the active state in the neutral to slightly acid pH range.

They influence the protective ability of the rust. If the rust formed becomes infested with sulphate nests, as may happen when steel is first exposed during the winter season, rust becomes less protective for some time. If, on the other hand, the first rust is formed during the summer season, it will generally be less contaminated by sulphate and as a consequence will be more protective.

### 1.3.3 Electrochemical Theory of Corrosion

Corrosion of metals in aqueous solution is an electrochemical process, as established in the first half of the 19th century. In other words, microgalvanic cells operate on the metal surface leading to the dissolution of metal (oxidation) at the anodic areas and reduction of oxygen or hydrogen ion at the cathodic areas. Thus for iron,

\[
\text{Fe} \rightarrow \text{Fe}^{++} + 2 \text{e}^- \quad \text{(Anodic site) (i_a)} \quad \ldots \quad 1.19
\]

\[
\text{H}^+ + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2 \quad \ldots \quad 1.20
\]
At the corrosion potential \( E_{corr} \), \( i = i_a = i_c = i_{corr} \). This suggests that the rate of corrosion can be measured by the measurement of anodic or cathodic current.

1.4 CLASSIFICATIONS OF THE ATMOSPHERIC ENVIRONMENT

The atmospheric environments may be classified as follows:

1. Marine
2. Industrial
3. Urban
4. Rural

The classification are mainly based on “geographical” locations and particulate air-borne contaminants associated with them.

A marine environment is characterized by proximity to the ocean and salt-laden air that can produce very severe corrosion damage on many structural materials, enhance galvanic corrosion, and accelerate deterioration of protective
coating systems. The principal culprit in marine environments is the chloride (Cl\textsuperscript{−}) ion derived from sodium chloride.

Industrial environments are associated with a host of industries emitting pollutants like oxides of sulphur, (SO\textsubscript{x} like SO\textsubscript{2} and SO\textsubscript{3}), smaller amounts of oxides of nitrogen (NO\textsubscript{x} such as NO\textsubscript{2}), ammonia and its salts (NH\textsubscript{3}, NH\textsubscript{4}) and hydrogen sulphide (H\textsubscript{2}S).

In urban environments, the principal contaminant is usually NO\textsubscript{x} species from automobile exhaust fumes, possibly SO\textsubscript{x} from long range transport and frequently, soot from home fuels. Rural environments are generally regarded as benign because they are characterized by either undetectable or trivial concentrations of the afore mentioned pollutants like (Cl\textsuperscript{−}, SO\textsubscript{x} and NO\textsubscript{x}).

1.5 CONDITIONS FOR ATMOSPHERIC CORROSION

Atmospheric corrosion may from the practical point of view, may be considered as a discontinuous process. It has been described (Barton and Bartonova 1969) by the equation

\[ K = \sum_{1}^{n} \tau_{n} V_{k}(n) \quad \ldots \quad 1.22 \]
where

\[ k = \text{accumulated corrosion product.} \]

\[ \tau_n = \text{Time of wetness, i.e. the period with an} \]
\[ \text{electrolyte layer on the surface.} \]

\[ V_k = \text{average corrosion rate during the individual} \]
\[ \text{periods of wetting.} \]

The total corrosion during a period is determined by the total time of wetness and the composition of electrolyte, together with other climatic parameters.

1.5.1 Time of Wetness

The principle meaning of the term is the length of the time during which the metal surface is covered by a film of water that renders significant atmospheric corrosion possible. The time of wetness varies with the climatic conditions at the site. It depends on the relative humidity of the atmosphere, the duration and frequency of rain, fog and dew, the temperature of air and metal surface, as well as the wind speed and hours of sunshine.

1.5.2 Adsorption Layers

The amount of water adsorbed on the metal surface depends on the relative humidity of the atmosphere and on
the physical and chemical properties of corrosion products. The metal surface may be wetted if hygroscopic salts, deposited or formed by corrosion, absorb water from the atmosphere.

Such absorption occurs above a certain relative humidity (RH), called the critical relative humidity. Bukowiecki (Bukowiecki 1966) showed, by laboratory experiments, that its value depends on the nature of the metal and the surface contaminants. Usually corrosion sharply increases when the RH increases above the value at which the salt starts to absorb water and dissolves. This critical humidity corresponds to the vapor pressure above a saturated solution of the salt present. Capillary condensation may also contribute to the formation of adsorption layers of electrolyte on the surface (Skorcheletti and Teukeschimskig 1953, Sabah et al 2003).

The amount of water on the corroding surface is of great importance to the corrosion rate. Several laboratory investigations (BohrenKamp 1968, Barton and Schutz Gegen 1972, Schwarz 1972, Schikorr 1983) have shown that the corrosion rate above a critical humidity value increases sharply with increasing RH.
1.5.3 Rain

Rain causes even thicker layers of electrolytes on the surface than dew. The thickness of water layer retained on the surface has been estimated to be about 100 gm. /m². Precipitation in the form of rain affects corrosion by giving rise to phase layers of moisture on the materials surface and by adding corrosion stimulators in the form e.g. H⁺ and SO₄²⁻. On the other hand, rain also washes away pollutants deposited on the surface during the preceding dry period. Whereas the first two processes promote corrosion; the third, atleast in the case of steel – decreases corrosion. The significance of the two latter process is dependent on the ratio between dry and wet deposition of sulphur pollutants occurs, the washing effect of rain predominates. In less polluted sites, the corrosion action of rain is more important (Mikhailorski 1973).

1.5.4 Relative Humidity

The relation between actual water vapour present and the maximum possible content for the given conditions is called Relative Humidity and is designated by the symbol

\[
\text{RH} = \frac{\Gamma_d}{\Gamma_s^{1.23}}
\]
where

\[ \Gamma_d = \text{specific weight of water vapour present in the humid air in kgm/cm}^3. \]
\[ \Gamma_s = \text{specific weight of saturated vapour in kgm/cm}^3. \]

1.5.5 Temperature


On one hand, an increase in temperature stimulates the corrosion attack by enhancing the electrochemical and chemical reactions as well as diffusion processes. Thus, under constant humidity conditions a temperature increases promotes corrosion. On the other hand, an increase in temperature leads to more rapid evaporation of surface moisture created by dew or rain. Consequently, the time of wetness is shortened and the corrosion rate decreases (Berukshlis and Klark 1965, Moralesa et al, 2005).
solubility of oxygen and corrosive gases in the electrolyte layer also decreases with increasing temperature. Thus even if the temperature influences the corrosion rates strongly under certain conditions, it is not a decisive factor in the long time exposure period in the temperature climatic zone.

1.6 COMPOSITION OF SURFACE ELECTROLYTE

The electrolyte film on the surface contains various species deposited from the corroding metal. The composition of electrolyte is often of decisive importance. The main constituents and pollutants in the electrolyte film are discussed below.

1.6.1 Oxygen

Oxygen is a natural constituent of air and is readily absorbed from the air and the thin water film on the metal surface which may be considered saturated, thus promoting any oxidation reactions. Serious corrosive damage to iron alloys can be caused by 8-15% of oxygen at temperature of 3° - 500°C. It is confirmed by experiments. (Simon et al 1988).

1.6.2 Sulphur Dioxide

The main part of anthropogenic sulphur dioxide [SO₂] pollution is caused by combustion of fossil fuels. The SO₂ is
oxidised on moist particles or in droplets of water to sulphuric acid.

\[ \text{SO}_2 + \text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{SO}_4 \]..... 1.24

The main processes of deposition of sulphur compounds are:

Adsorption of gas \([\text{SO}_2]\) on materials surface – [dry deposition] and removal of gas and aerosols by precipitation – [wet deposition].

The dry deposition is adsorption of sulphur dioxide. The deposition is proportional to the concentration of sulphur dioxide in the atmosphere.

The deposition rate differs on different materials. Sulphur dioxide is absorbed on rusty steel surfaces at high relative humidities. The deposition on copper and particularly on aluminium is much less (Sydberger and Vannerberg 1972, Sabah et al 2003, Syed Sabir 2006).

The interest in the effect of \(\text{SO}_2\) on atmospheric corrosion stems to a large extent from its role as one source for sulfate which is usually found in the corrosion products of metals exposed, indoors and outdoors, to the urban atmosphere. Despite the decrease in the \(\text{SO}_2\) levels in many countries,
sulphates are still a major corrosion product found on surfaces of copper, zinc and other metals exposed in the atmosphere, indicating that SO₂ still plays a very important role for the atmospheric corrosion. It may clearly be understood that the corrosion rate of copper, zinc and other metals in the atmosphere is related to the concentration of SO₂. The mechanism by which SO₂ accelerates the corrosion of copper, zinc and other metals is still not fully understood, although a great number of investigations have been devoted to this subject (Metal corrosion in the atmosphere, STP 435, Tanner 1964, Bukowiecki 1966, Walter 1991). The corrosion stimulating effect of SO₂ and its oxidised forms as it was suggested already in the early work by investigators that the oxidation of SO₂ to produce SO₄²⁻ influences the local pH on the surface (Tanner 1964, Evans Taylor 1972). This causes oxide dissolution and increase the corrosion rate. However, in controlled laboratory exposures, the reactions of SO₂ of copper in the absence of additional oxidants produce copper sulfites, the main reaction product (Vernon 1935, Sydberger 1972) and the oxidation of these copper sulfite layers to sulfate is quite slow in clean humid air.
1.6.3 NO\textsubscript{x}

Emission of NO\textsubscript{x} originates mainly from different combustion processes, road traffic and energy production being the main sources. In the combustion process, most of the nitrogen oxides are emitted as NO. In the atmosphere, NO is oxidised to NO\textsubscript{2}, according to

\[ 2\text{NO} + \text{O}_2 \rightarrow 2\text{NO} \ldots \ldots \ ... \ 1.25 \]

and at greater distance

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \ldots \ldots \ ... \ 1.26 \]

Nitrogen dioxide may be considered as the main nitrogen pollutant near emission sources. No\textsubscript{x} may be oxidised to HNO\textsubscript{3}.

\[ 2\text{NO} + \text{H}_2\text{O} + 3/2 \text{O}_2 \rightarrow 2\text{HNO}_3 \ldots \ldots \ ... \ 1.27 \]

Therefore in the vicinity of emission source, the contents of HNO\textsubscript{3} and nitrates are very low. At long distances from the emission source, wet deposition of nitrates seems to predominate. Near the source wet deposition is lower than dry deposition as NO, NO\textsubscript{2} have a low solubility in water and nitric acid. In two field corrosive tests (Grennfelt 1979, Smith 1980) the deposition of NO\textsubscript{x} was measured. The amount of
deposited NO\textsubscript{x} and NO\textsubscript{3} were found to be 10 to 100 times lower than the amount of sulphur dioxide.

1.6.4 Chlorides

Chlorides are deposited mainly in the marine atmosphere, as droplets or as crystals formed by evaporation of spray carried by the wind from the sea. Other sources of chloride emission are coal-burning and municipal incinerators. The importance of chloride as an atmospheric corrosion promoter in coastal line is emphasized by many investigators. (Brierly 1965, Mendoza and Corva 1999, Marco et al 2000, Morcillo et al 2000).

In marine environments, chloride deposition usually decreases strongly with increasing distance from the shore, as the droplets and crystals settle by gravitation. Deposition rates in marine areas are reported to be in the range of 5 to 1500 mg of NaCl/m\textsuperscript{2}/day as measured by the wet candle method (Johnson and Stanners 1981, Corros 1986, Mendoza and Corva 1999, Forseca et al 2004).

Airborne salt particles have been reported to play an important role for atmospheric corrosion. Concentrations of gaseous pollutants, such as SO\textsubscript{2}, NO\textsubscript{2} and O\textsubscript{3} are being reduced in many regions, and the relative importance of
Salinity particles is thus increasing. Sodium chloride (NaCl) and ammonium sulphate (NH₄)₂SO₄ particles are probably the most important airborne salt particles for atmospheric corrosion. Chloride deposition is a major contributor to the increased atmospheric corrosivity in marine environments. The main source for chlorine in the atmosphere is sea aerosol salt (Sereda 1960). Chlorides enter into the atmosphere in tiny droplets of salt solution originating from surf action and turbulent ocean states, and are transported inland predominantly by coastal wind patterns as solid particles or liquid droplets.

1.6.5 Carbon - dioxide

Carbon-dioxide occurs in the atmosphere in a concentration of 0.03% to 0.05 % by volume varying slightly with the time of day and the season of the year. At equilibrium, the percentage mentioned corresponds to a concentration of the order of 10⁻⁵ moles / litre in the water film if its pH value is 6 or lower.

The most important role of CO₂, on atmosphere corrosion is to participate in the formation of secondary products, especially on non-ferrous metals. Serada (Serada 1960) discussed this point and concluded that the dissolution of CO₂ gave in electrolyte pH between 5 and 5.6. It was
reported that CO₂ has a strong effect on the NaCl-induced atmospheric corrosion of metals (Barton et al 1974, Kucera and Mattson 1974, Thomson 1981, Kucera 1981) and the corrosion was considerably lower at low CO₂ concentrations.

1.6.6 Ozone (O₃)

Ozone is gaseous compounds with colour produced in presence of ultraviolet light. They are chemically unstable gases that oxidize materials faster than oxygen. The main source of O₃ is by atmospheric reactions between hydrocarbons and nitrogen oxides under sunlight influence.

The stratospheric O₃ protects the earth from harmful ultraviolet radiation from the sun. However at ground level, elevated levels of O₃ are produced by photochemical reactions involving other air pollutants. Given sunlight and suitable meteorological conditions, nitrogen oxides and volatile organic compounds can react to form photochemical oxidants (also known as photochemical smog) of which O₃ is the principal component.

NO₂ and O₃ are believed to play important roles as oxidants of SO₂. As showed in several investigations, they can have synergistic effects with SO₂ and increase the corrosion rate several times (Barton 1974, Baker 1985). Another route
for SO$_2$ oxidation could be a metal catalyzed reaction, which is an important pathway in atmospheric microdroplets (Tomashov 1959).

1.7 CORROSION - PERIOD OF EXPOSURE

During an initial period, the corrosion rate is usually high because the rust formed is porous and has poor protective properties. After the initial period, the length of which is usually 1-5 years, depending on the corrosivity of the atmosphere, the protective properties improve and the corrosion rate decreases.

The penetration depth increases with time of exposure and non-linear relation with time are shown in a power law.

\[ p = kt^n \] \hspace{1cm} ... 1.28

where \( p \) is the penetration depth, \( k \) is a constant, \( t \) is the time of exposure, and \( n \) is a constant.

Such a time dependence has been reported by many authors (Pourbaix 1978). Removal of rust from the surface, due to dissolution, flaking, or erosion, however, will lead to higher values of \( n \). In exposure tests of steel, the \( n \) value has been found to vary between 0.4 and 0.8. In the long run a stationary state will be approached with constant thickness.
and porosity of the rust layer. Then the corrosion rate will become constant and the relationship between penetration and time becomes linear.

1.8 COMPOSITION OF CORROSION PRODUCTS

The composition of rust layer depends on the composition of the surface electrolyte and thus differs in different types of atmosphere. Fe (OH) may form in neutral to basic solutions. If atmospheres polluted by SO₂, however, the surface electrolyte is usually weakly acidic and Fe(OH)₂ does not precipitate. Some authors consider formation of the so-called green rust with the proposed formula 2 Fe (OH)₃·4 Fe (OH)₂·FeSO₄·XH₂O as an intermediate product in the oxidation of Fe (OH)₂ to FeOOH (Detournay 1975, Arroyave and Morcillo 1995). Several authors consider Γ-FeOOH to be the primary crystalline corrosion product (Hiller 1966, Engelhardt 1971, Karaivanon and Gawrilov 1973, Suzuki et al 1980, Masamistu et al 2003).

In weak acidic solutions, Γ-FeOOH is transformed into α-FeOOH, the process being dependent on the sulphate concentration and the temperature (Hiller 1966). α-FeOOH, seems to be the most stable modification of the ferric oxide–hydroxides. The solubility of α-FeOOH, is approximately 10⁵

The relative amounts of $\alpha$- and $\Gamma$-FeOOH depend on the type of atmosphere and on the length of exposure (Hiller 1966, Engelhardt 1971, Schwarz 1972, ). In freshly formed rust in SO$_2$ polluted atmospheres, $\Gamma$-FeOOH is usually slightly dominant. On prolonged exposure, the ratio of $\Gamma$ to $\alpha$ decreases.

In marine atmospheres where the surface electrolyte contains chlorides, $\beta$-FeOOH is found. $\beta$-FeOOH has been shown to contain up to 5% by weight of chloride ions in marine locations (Misawa 1971, Suzuki et al 1980, Masamistu et al 2003). $\delta$-FeOOH has not been reported in rust formed under atmospheric conditions on carbon steel.

Magnetite, Fe$_3$O$_4$, may form by oxidation of Fe(OH)$_2$ or intermediate ferrous – ferric species such as green rust (Miswa 1973). It may also be formed by reduction of FeOOH in the presence of a limited oxygen supply (Bentley et al 1968, Schwarz 1972, Antonio et al 1999, Sabah et al 2003) according to

$$8 \text{FeOOH} + \text{Fe} \rightarrow 3 \text{Fe}_3\text{O}_4 + 4 \text{H}_2\text{O} \quad ... \quad 1.29$$
Magnetite is usually detected in the inner part of the rust adhering to the steel surface on specimens which have been subject to prolonged exposure, where depletion of oxygen may occur (Misawa 1971, Schwarz 1972). An exception is rust formed in a marine atmosphere, where Fe₃O₄ has been found to be the main constituent.

The rust layer formed on unalloyed steel generally consists of two regions (Suzuki et al 1980).

1. An inner region, next to the steel / rust interface, often consisting primarily of dense amorphous FeOOH with some crystalline Fe₃O₄.

2. An outer region consisting of loose crystalline α-FeOOH and γ-FeOOH.

The composition of the two layers may, of course, differ with the length of exposure and the exposure conditions, i.e., the type of atmosphere.

The general sequence of atmosphere corrosion of copper is well known. Initially oxygen and water react with a fresh copper surface forming a sequential structure consisting of Cu₂O/CuO/Cu(OH)₂ or CuO·xH₂O) the main component being
Cu$_2$O, Cuprite (Graedel 1987). Cuprite is an electrically conducting compound and is known to play a decisive role in the protectiveness of corrosion layers on copper. (Yamashita et al 1994, Crolet et al 1998). Further oxidised as follows

$$\text{Cu}_2\text{O} + 2\text{H}^+ \rightarrow 2 \text{Cu}^{2+} + \text{H}_2\text{O} + 2\text{e}^-.$$

This is later followed by reaction with pollutants present as gases (e.g. SO$_2$, O$_3$, Cl$_2$, HCl. and H$_2$S) as ionic constituents of aerosol particles or as ions in precipitation. Eventually a patina of several different compounds forms on top of the initially formed cuprite layer. Important copper compounds found as patina constituents are Cu$_2$Cl(OH)$_3$. atacamite, Cu$_2$SO$_4$(OH)$_6$.H$_2$O(Posnjnkate) and Cu$_2$SO$_4$(OH)$_6$ (brochantite), in rural and urban areas. In urban areas Cu$_2$SO$_4$(OH)$_6$ (antlerite) and Cu$_2$CO$_3$(OH)$_2$ (malachite) are also found (Graedel 1987). It has been reported that when chloride concentration is high brochantite can react with chloride ions to form basic chlorides (Veleva et al 1996, Almeida et al 1997).

$$\text{Cu}_2\text{SO}_4(\text{OH})_6 + 2\text{Cl}^- \leftrightarrow \text{Cu}_4\text{Cl}_2(\text{OH})_6 + \text{SO}_4^{2-}.$$
1.9 OBJECTIVES OF THE PRESENT STUDY

The main objectives of the present research are as follows.

- to utilize the atmospheric corrosion study as a passive monitor in understanding the complex natures of polluted atmosphere.

- to determine the rate of corrosion of selected engineering metals such as mild steel, copper and aluminium for different periods at various environments.

- To determine the corrosiveness of different environment according to classification of atmospheric categories.

- to determine the durability factor for non-ferrous metals at different environments.

- to study the effect of climatic factors and pollutants on the metals / alloy.

- to determine the seasonal variation of rate of corrosion on metals / alloy in different environments.
• to examine the correlation of the corrosion rate with the atmospheric parameters like rainfall, relative humidity, temperature $SO_2$, $NO_2$ and chloride content using statistical regression analysis.

• to analyse the corroded product of metals / alloy by Fourier Transform Infra Red (FTIR) spectral analysis.

• to study the morphology and surface characteristics of corroded mild steel by using Electron Scanning Microscope (SEM).

• also to evaluate the effectiveness of some of the commercially available paints for atmospheric corrosion protection.