CHAPTER-I
INTRODUCTION
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Introduction

Corrosion is defined as the obliteration of materials caused by chemical or electrochemical action of the nearby surrounding environment. In our day to day livelihood very often we experience corrosion. The corrosion word is resulted from the latin corrosus which means eaten away or inspired by temperature. The common examples of corrosion are rusting, discoloration and tarnishing. Corrosion is normal procedure and is a consequence of the intrinsic affinity of metals to relapse to their most even compounds usually oxides. Majority of metals originates in nature in the form of a variety of chemical compounds called ores. In refining process; energy is added to the ore to produce metal. It is commonly seen on metals in the form of oxide films. However alike processes also occur in non-metals, such as plastic, concrete and ceramics except the corrosion is not electrochemical. Corrosion can be reduced but it is unprotectable because it is an unprompted occurrence (Pierre R. Roberge, 2006). The actual basic aspect of increase in the economy would be changed if corrosion is prevented. The cost of corrosion shows that the direct cost of corrosion was approximately about 4.2% of their Gross National Product. Direct cost of Corrosion includes substitute of corroded mechanism, using of corrosion resistant alloys, using coating or inhibitors, and electrochemical protection measures. While Indirect cost of corrosion may include failure of manufacture during down time, loss of product due to seepage, loss of effectiveness due to corrosion, contamination, Loss of human being life due to fire explosion etc. Millions of dollars is lost each year due to corrosion. To a great extent; this loss is due to the corrosion of iron and steel,
even if many other metals can corrode as well. The problem with Iron as well as many other metals is that due to oxidation there is formation of oxide which do not resolutely stick to the surface of the metal and results in causing "pitting". Due to pitting ultimately the structure gets weakened and the metal disintegrates. (Mark A.L et.al., 1994, Paul R.P & Hess T.R, 1991). Corrosion can be quick or sluggish. Polythionic acid is responsible for corrosion in sensitized stainless steel. Railroad tracks more often not give us an idea about slight rusting; which would not be sufficient to have an effect on the way of acting for many years. Almost 1600 years old; the famous iron Delhi Pillar in India was as good as new even if it has been opened to the elements responsible for corrosion (Srinivasan.S et.al., 2004).

Corrosion are of two types; chemical corrosion and electrochemical corrosion. In chemical corrosion direct oxidation occurs which may be due to liquid metals, fused halides, non-aqueous solutions etc. The electrochemical corrosion is further classified into immersion corrosion, underground corrosion and atmospheric corrosion. An electrochemical process may be due to oxygen diffusion and metal ions with the help of the oxide layer, and it occurs in the presence of electrolytes. The common types of Corrosion may include uniform, electrochemical, galvanic, concentration cell, erosion, embrittlement, stress corrosion, filiform, corrosion fatigue, intergranular, fretting, impingement, dezincification, and chemical reaction, Atmospheric, Galvanic, Stray current, General biological, Molten salt, Liquid metals, high temperature, crevice, pitting, localized microbiological, Intergranular, Dealloying, Cavitations and water drop impingement, stress cracking, hydrogen damage, liquid metal embrittlement, solid metal embrittlemet (Corrosion Control and treatment Manual, 1994, M.G.Fontana, 1987). The electrochemical
environment of corrosion leads to varied forms of attack. These are
determined by the series of mechanical, geometrical and
environmental factors. The recognition in the form of corrosion is of
very important to determine the cause of corrosion process; in
addition to prevention, control and protection of the material. The
classification of corrosion can be generalized, localized and selective
corrosion. By Generalized corrosion the whole surface of the metal is
affected and becomes very thin when it comes in contact with the
electrolyte. Depending upon the consistency of the corrosion attack, it
can be categorized into generalized uniform and generalized non
uniform corrosion. In localized corrosion the metallic surface is
affected in a very limited form and there is a formation of cavity
which depends upon the diameter externally against depth relation
named as pitting, craters and ulcers. The pitting corrosion is
sometimes seen in the form of piercing. Intergranular phenomenon
can be seen in the fissure. In selective corrosion dealloying occurs
and some part of the metal generates reduction due to chemical or
metallurgical reasons, which is proved to be attacking more easily.
Degradation is nothing but which indicates corrosion of materials
physical properties. Materials could be metals, polymers, ceramics or
a composite-mechanical mixture which has different properties.

The corrosion of metal takes place because we use the
materials in such a way that it comes in direct contact with the
environment. eg: golden statue in Bangkok, Thailand is made up of a
metal which is stable in room temperature air (KSC.CTL,NASA). The
metals found in metallic state are copper, gold, platinum, and silver.
A metal named iron is made from minerals or ores into metals which
is found to be unstable in the environment.
All matter is made of atoms and it consists of protons, neutrons and electrons. The orbits consist of negatively charged electrons. e.g. figure 1.1 represents in a similar way as the planets range the sun in a solar system.

![Figure: 1.1. Planets in the range of solar system](image)

Atoms are neutral in charge and there are same number of protons and electrons. In all the atoms the numbers of neutrons are same and it indicates that it doesn’t have any impact on the element’s identity. The type of atom is determined by the number of protons whereas the number of protons and neutrons in the nucleus will determine the atomic mass. More than 100 elements have been discovered which is given in the periodic table of the elements. The element symbols are known and given from their Latin names.
There are very few elements which are common and corrosion is seen only on some metallic elements like aluminium, copper, iron and zinc which normally react with the nonmetallic elements like sulfur, oxygen, and chlorine.

When atoms or groups of atoms lose or gain electrons ions are formed. In order to form positively charged ions metals lose some of their electrons e.g. copper, aluminium, iron etc. while to form negatively charged ions nonmetals gain electrons e.g. sulfur, oxygen, chlorine etc. A group of nonmetals and metals which is formed as a separate chemical is called as compounds. e.g. H\textsubscript{2}O has two hydrogen atoms and one oxygen atom. Numerous molecules are shaped by electron sharing with nearby atoms. Similarly a water molecule has
nearby hydrogen and oxygen atom which shares electrons. A common compound which is present on the earth is water which is the basic necessity of life. It has a different constituent which has low concentration of $H^+$ and $OH^-$ ions. When water has excess $H^+$ ions it is called as acid, when the water has an excess amount of $OH^-$ ions it is known as base whereas the equal amount of hydrogen and hydroxide ions refers to be neutral. The strength of the acid and base is measured on the basis of pH scale. pH is a negative logarithm of Hydrogen Ion Concentration. In neutral environment the metals will not corrode although the metals will corrode at a faster rate when it comes in contact with acid or base e.g. zinc and aluminium. There are some other metals like steel which corrodes at a very high rate when it comes in contact with acid. The corrosion rate was found to be less in base and neutral environment. (KSC, NASA, CTL). Oxidation reaction in corrosion is the oxidation of neutral ion atoms to positively charged ions. Reduction reaction in corrosion is the reduction of atoms to form negatively charged ions. It is known that 90% of corrosion reactions takes place due to the reduction of oxygen. Hence the oxygen present in the environment and its tendency to absorb electrons is considered to be one of the important factors of corrosion or oxidation of metals.
Electrochemical Reactions:

When two metal strips are exposed in the same acid a similar kind of oxidation reaction occurs.

![Image of electrochemical reaction](image)

**Figure 1.3. Experiment on Electrochemical Reaction.1**

\[
\begin{align*}
Zn & \rightarrow Zn^{2+} + 2e^- \\
Cu & \rightarrow Cu^{2+} + 2e^- \\
\end{align*}
\]

Due to oxidation reaction the movement of electrons is inspired by reduction reaction.

The reduction reaction in copper is:-

\[
4H^+ + O_2 + 4e^- \rightarrow 2H_2O
\]

But the amount of dissolved oxygen in the acid the rate of corrosion in copper is incomplete.

The reduction reaction in zinc is:-

\[
2H^+ + 2e^- \rightarrow H_2
\]
A bubble of acid indicates that there is alteration of hydrogen ions to hydrogen gas molecules.

If two metals are connected with wire and electrical energy is measured by connecting the wire, there is a difference in the potential of electrons. The rate of corrosion in copper decreases and in zinc increases. When the two metals are connected to the copper is prepared to cathode and zinc to anode. The rate of accelerated corrosion increases and the oxidation of copper stops which is protected from corrosion. This method refers as cathodic protection.

![Figure 1.4. Experiment on Electrochemical Reaction](image)

**Figure 1.4. Experiment on Electrochemical Reaction.2**

At the copper (cathode) the reaction is: \(2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\)

There is a reduction of hydrogen ion because of voltage shortage in copper point. The corrosion can be prevented by the electrical connection to the zinc anode.

At the zinc (anode) the effect relics similar, \(\text{Zn} \rightarrow \text{Zn}^{+2} + 2\text{e}^-\)

Due to the cleaner surface area of copper the rate of reaction increases and can grip for the reduction reaction at a higher rate. Hence the corrosion rate in copper is prevented; some place zinc corrosion cannot be prevented.
There are various forms of corrosion:

**Figure 1.5. Uniform Corrosion**

In Uniform Corrosion (UC) the surface is directly affected by the chemical this indicates consistent engraving of the metal.

**Figure 1.6. Galvanic Corrosion**

Galvanic corrosion (GC) occurs in the presence of an electrolyte and in an electron conductive path which is referred as electrochemical action of two different metals. This type of corrosion occurs when two different metals come in contact.
Concentration cell corrosion (CCC) is seen in different concentrations of the same solution when there is a contact of two or more areas of the surface of metal.

Pitting Corrosion (PC) is also known as localized corrosion which occurs on the metal surface. The depths are very often seen beneath the surface deposits which are caused due to accumulation of corrosion products.
Figure 1.9. Crevice Corrosion

Crevice corrosion (CC) may occur when there is a contact with metals and metals or metals and nonmetals. This kind of corrosion may be seen in protective films, washers, sand grains etc.

Figure 1.10 Filiform Corrosion

Filiform corrosion (FC) is a type of corrosion which occurs on plated or painted surfaces due to the interaction of moisture with coating. From the original corrosion pit a long branching filaments of rust products extend out which also results in the degradation of the coating protects.
When a metal or alloy gets affected on the particle borders then it is called as Intergranular corrosion (IC).

Stress corrosion cracking (SCC) is caused by the immediate effect of tensile stress and in an exact acidic environment. This kind of SCC is because of residual stress from the manufacturing process, applied loads etc.
Corrosion fatigue (CF) is seen due to the mutual effects of cyclic stress and corrosion. If the metal is in an acidic environment then none of the metal can be protected from reduction resistance to cyclic stressing.

The fretting corrosion (Frt.C) is seen due to the contact of highly loaded metal surfaces to vibratory motions.
Erosion corrosion (EC) is the result of a combination of destructive chemical environment and high fluid-surface velocities.

When an active component of the metal loses and retains the corrosion resistant constituent on the metal surface then it is called as
Dealloying corrosion (DC). Dealloying is an exceptional form of corrosion seen in gray cast iron, alloys of copper and other alloys.

![Figure 1.17. Hydrogen Damage](image)

A hydrogen damage (HD) problem is seen in some metals, titanium, and high-strength steels. It can be controlled by the usage of resistant alloys.

![Figure 1.18. Corrosion in Concrete](image)

Corrosion in concrete (CIC) is seen in structural material shatterproof with carbon steel rods, post-tensioning cables or
prestressing wires. The steel used is important for maintaining the strength but it focuses to corrosion.

Figure 1.19. Microbial Corrosion

Microbial corrosion (also called microbiologically -influenced corrosion or MIC) is corrosion that is caused by the existence and behavior of microbes. This corrosion can take many forms and it can be controlled by using biocides or by adopting some control methods like conventional corrosion.

Engineering design is a complicated procedure that is included for the purpose of design, manufacturability, assessment, and repairs. The most important aspect which was overlooked was drained in the designing of manufactured products. One of the considerations often overlooked in designing manufactured products is drainage. For example in automobile corrosion panel corrosion could have been minimized by providing drainage so that the water and debris could be dropped off from the car instead of collecting and causing corrosion. Hence whenever designing is done each and every method of corrosion control should be adopted.

The world’s most useful first structural material is carbon which is inexpensive available in various varieties; machined, welded, shaped and most of the metal structures are made of carbon.
steel. A special form of carbon steel known as weathering steel is used to build the large statue known as Pablo Picasso near to Chicago city hall. ("Daley Center". Public Building Commission of Chicago, 2011) The weathering steel need not to be painted and it is misused in various situations where it could not drop off and a rust film is formed; which has given a varied status in the construction industry. In order to avoid corrosion various control methods could be adopted before using the more costly alternates to carbon steel. In the carbon steel a special type of corrosion is seen for e.g. hydrogen embrittlement.

Protective coatings, cathodic protection, and corrosion inhibitors are widely used to extend the existence of carbon steel structures and to allow their use in environments like in Kennedy Space Center where the environment is very corrosive.

![Figure 1.20. Kennedy Space Center shows Corrosive environment](image)

The second well known steel is stainless steel which is used in sports car. In comparison to the corrosion with carbon steel or aluminum; in stainless steel less corrosion is seen and is a good alternative to carbon steels too. The austenitic stainless steel with 18% chromium and 8% nickel are resistant to corrosion. In spite in
some environment the same steel may undergo pitting, crevice and stress corrosion cracking.

![Stainless Steel used in sports car](image1)

**Figure 1.21. Stainless Steel used in sports car**

The third well known steel is aluminium alloys which is widely used in applications of aerospace. It has very good atmospheric corrosion capabilities but the aluminium oxide films formed can rupture and permit to corrosion like intergranular corrosion which is the major problem in airplanes. This kind of corrosion may occur at bolt and at the cutouts where the smaller grain boundaries of the metal surface exposed. e.g. the highway guardrail located near Florida.

![Aluminium Alloys used in Aerospace](image2)

**Figure 1.22. Aluminium Alloys used in Aerospace**

The fourth well known steel is copper alloys. The common piping materials are brasses and bronzes used for valves and fittings but are focussed to stress corrosion cracking in the existence of...
ammonia compounds. It also undergoes delaying and galvanic corrosion. It is found that copper alloys are suffering from erosion corrosion. In order to avoid dezincification inhibited brasses can be used and is also available from 1930’s.

Figure 1.23. Copper Alloys

The last well known metal is titanium which is also one of the most common metal found in the environment. It is used in a very limited form because of which is expensive. In the United States it is more often used in aerospace industries whereas in Japan it is often used in chemical industries. The two types of titanium alloys are aerospace alloys and corrosion resistant alloys. The titanium is misused in a salt water application where the crevice corrosion is seen in aerospace alloys.

Figure 1.24. Titanium Alloys
The most common methods which are used for the corrosion control is protective coatings. It can be galvanized steel or a liquid paint. In protective coatings too filiform corrosion is seen underneath. In air conditions and aluminium airplane same type of corrosion problem could be seen. There are also some chemicals like corrosion inhibitors which are used to control and reduce the corrosion in various environments. For example chemicals added to automobile antifreezes. Most of the Kennedy Space Center's corrosion inhibitor research involves the efficiency of inhibitors added to protective coatings.

Cooling towers are generally giving out heat to the atmosphere mainly through one or more processes. It’s a very important factor of an integrated cooling system. Cooling tower consist of other structures like pumps, valves and recirculating water piping and it also provides a large amount of thermal energy and heat. The heat rejected is due to the water evaporated within the cooling tower. The evaporation of a pound of water requires about 1000 btu, makes the evaporative cooling tower which is considered as the most important effective means of the heat which is discarded. It is said that 75% to 80% of the heat is removed from cooling water due to evaporation.

The remaining heat is removed by shifting to the considerable air flow transitory through the cooling tower. For example, a 1000 ton rated cooling tower is designed to have a heat rejection of 12 million btu/hr, 12,000 btu/hr/ton. At 80% heat rejection by evaporation, this unit will evaporate 26.55 gpd/ton, or 26,550 gpd. (Timothy Keister, CWT, 2008). In the cooling tower evaporation of water leads to increase in the concentration of dissolved salts which in turn increase the scale formation, biological fouling and corrosion. Apart from the increase in concentration of salts 1000 ton unit operates at a design air
flow rate of 271,000 cfm through the unit. It is known that cooling is very efficient “air scrubber,” where huge amount of air is passed and results to the adding of airborne dust and waste to the water of the cooling tower. In cooling tower the cooling effect is only due to evaporation of the recirculation of cooling water. For this purpose there is a need of continuous supply of water or the make up water for the loss of water during evaporation. Due to evaporation the water is lost and there is a formation of concentrated dissolved solids in cooling tower because dissolved solids is already present in make up water of municipal water. If the dissolved solids are not cleared then it will lead to the formation of sludge and finally leading to scaling in the cooling tower. (Jose Otavio Silva et.al., 1987). In order to avoid such problems more make up water is required. The recirculating water is also lost from “windage” or “drift” owed to put back of entrained water droplets in the mass flow of exist air. It will vary according to the green environment, tower safeguarding, management of chemical range, and the hard work of each producer to reduce “drift” by providing “drift removal”. The problems raised in the cooling tower may differ like where the cooling tower is installed and also depends on the make up water used in the cooling tower. The amount and excellence may differ and the discharge from the blow down may also differ according to the area and time. Typically, windage will be between 0.01% and 0.05% of the cooling water recirculation rate. In various countries one of the most important issues is formation of scale because of deprived makeup water quality which is responsible for cyclical, whereas additional areas are harshly imperfect to the maximum obtainable. In this case there is a need of chemical treatment of the cooling water which is required in many areas to allow cycling process, to decrease the use of water, of a
cooling tower without the scale formation. Scaling results to blockage in pipelines, equipments etc. There is an increase in the usage of energy in chillers used in cooling comfort of the cooling tower. e.g, The ordinary cooling water calcium carbonate has a thermal conductivity about 6.4 btu/hr(ft$^2$)F/in, whereas the thermal conductivity of copper is 2674 btu/hr(ft$^2$)F/in. A minute quantity of scale is important for the energy cost penalty. A calcium carbonate scale of just 1.5 mil thickness is predictable to reduce the thermal effectiveness by 12.5 %, which on a 1000 ton chiller would add to yearly energy costs by concerning $72,000/yr in existing energy costs and usual HVAC service loads.(Timothy Keister, 2008). Water is known to be as “universal solvent” which is responsible for dissolving almost all materials and is also responsible for corroding all materials at various rates. It is found that the lowest cost construction material is steel used in the cooling systems and is almost responsible for leading to corrosion due to cooling water. The cooling system life span can be increased by the usage of corrosion inhibitors. (William W. Wheeler et.al., 1979).The increase in the content of dissolved solids is a good medium for the growth of microorganisms which will definitely lead to various severe problems. There is a possibility of increase in the risk of disease known as Legionnaires disease, whereas the biofilms leads to the blockage of water pipelines, helping to speed up the rate of corrosion and the effectiveness of heat exchange efficiency is reduced. Hence even if a system is scale free, the presence of biofilm may lead to the use of more amount of energy. Therefore to avoid such problems, “biocides” a toxic chemical should be added to the cooling towers inorder to have a control on the growth of microorganisms in the cooling water. (Timothy Keister, 2008, John. C. Smedley, 1986

Cooling tower water consists; the main branch of the use of industrial water. In each plant a large amount of water is consumed but in cooling tower water is very often reused to save the cost and water. As the cooling tower water is reused problems related to corrosion, scale and slime is caused due to the presence of soluble salts in the system, evaporation and emissions from the cooling water therefore a proper management strategy should be adopted to have a safer and corrosion free cooling tower. (William R. Hollingshad, 1972). Make up water is the water which is reused again and again in the cooling tower. A day to day or monthly analysis of cooling tower water samples should be carried out in order to check the water quality parameters. Makeup water is added to the system to recompense for loss of water due to evaporation, emission or blow down. Concentration of ratio is the ratio of the quality of circulating water to that of make-up water. (Water Quality Standards by Yasumonto Magara,). If a good cooling water treatment program is adopted then it may help to reduce the rates of corrosion. Some of the accepted average levels miles/year is Mild Steel 1 to 2, Copper Alloys 0.1 to 0.2, Aluminum 1 to 2, Zinc 2 to 4. (Timothy Keister, 2008, Bureau of Indian Standard Cooling tower, 1999).

Corrosion is one of the problems which are faced by every other industry in and around the world. Hence, In present investigation an attempt has been made to evaluate the impact of such problems and its associated environmental corrosion accelerators remedial action.
Study Area

The first study area preferred for the research was basynthan plant cooling tower of chemical industry and cooling tower of fertilizer industry (ammonia plant and utility plant). The site selected for study purpose is located in Turbhe (MIDC) and Taloja (MIDC), Thane, Maharashtra. The latitude and longitude of the area is $19.0538^0 \text{ N } & 72.99777^0 \text{ E}$. The maximum and minimum relative humidity of the area is 86% & 67%. Both the cooling towers are of the closed circulating system and is commonly found in most of the industries. The MIDC water is used as a make-up water in both the cooling towers. The most important factor of the tower is to expose the maximum level of water to the maximum flow for a longer period. The Cycle of Concentration for both the towers ranged from 2 to 2.5 per week & 4 to 5 per week and the make-up water quality is $50 \text{ m}^3/\text{day} & 1500 -1600 \text{ m}^3/\text{day}$. The second study area selected was appliances like geyser and water bath. The location of both the appliances was one from residential and the other from institutional laboratory. The water used in geyser was MIDC water whereas the water used in water bath was borewell water. This indicates that the environmental conditions of both the locations of appliances were totally different. The latitude, longitude and relative humidity of the appliances selected area was found to be same as highlighted above. The investigation period selected for the research was from April 2010 to March 2012. The next aspect of study was to know the corrosion inhibition of mild steel by using herbal and chemical inhibitors named Tagetus erecta(Marigold), Hibiscus rosal-sinensis(Shoe flower)& Alizarin Red, Zirconyl Nitrate at various temperature levels by weight and loss method, polarization
measurements, Electrochemical Impedance spectroscopy and Scanning Electron Microscopy instrumental techniques.

Figure 1.25. Location of the Study Area Turbhe and Taloja area, Mumbai.

Aims and Objectives of the study:-

- To assess the outline of cooling towers of two different industries.
- To survey the outline of two domestic appliances.
- To fix the sampling station for the collection of water samples from two different industries cooling towers and domestic appliances.
- To analyze the collected water samples for various environmental water parameters.
• To assess the impact of water quality on both the areas named cooling tower and domestic appliances.
• To assess the status of water quality parameters collected from cooling towers (chemical and fertilizer industry) and grey water samples collected from both the appliances (geyser and water bath) in the absence and presence of herbal inhibitors (Te & Hr).
• To revise the inhibition efficiency of chemical and herbal inhibitors by using mild steel coupons.
• To evaluate the efficiency of inhibitor by using weight and loss method on mild steel coupons.
• To learn the corrosion potential of mild steel coupons with the help of instrumental techniques like polarization measurement, Electrochemical Impedance spectroscopy (EIS) and Scanning Electron Microscopy (SEM).
• To suggest control measures to prevent corrosion by adopting corrosion control methods.
• To know Cost Benefit Analysis for corrosion inhibitors.