"Applications of Cathodic Protection Systems for Power Plant Components"

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ABSTRACT

Corrosion of buried or submerged structures in Power plants especially in coastal plants is a known phenomenon. As a result of corrosion, many critical components become unavailable for operation and at times require shut down of unit or the power plant. Components such as Condenser Water Boxes, Heat Exchangers, external surfaces of buried fire fighting, naptha, make-up water, drinking water, cooling water, & effluent disposal pipelines, internal surfaces of cooling water & auxiliary cooling water ducts, seawater pumps, travelling water screens, bottom ash scrapper conveyor chains & body, etc are some of such components susceptible to severe corrosion and failure reducing their availability.

Recently many such cases were investigated at power plants both coastal and non-coastal and based on studies it was identified that these components could be well protected by application of suitable anti-corrosive coatings and properly designed cathodic protection systems. Accordingly identification of suitable anti-corrosive coatings and design & application of cathodic protection systems (both sacrificial & impressed current systems) were undertaken. After implementation of coatings and installation of cathodic protection systems availability of these systems were either improved or restored.

The paper intends to present a few cases such as those of seawater intake pump, internal surfaces of cooling & auxiliary cooling water ducts (seawater), external surfaces of make-up water pipelines, scrapper conveyor chain system, condenser water boxes, etc where either after failures or as a preventive measure suitable anti-corrosive coatings were identified & got applied and these were supplemented by application of in-house designed cathodic protection systems. These measures have improved the availability of the systems and failure rates have substantially reduced.

Key Words: *Cooling Water ducts, seawater intake pumps, fire-water pipelines, condenser water boxes, cathodic protection, anti-corrosive coatings.*

INTRODUCTION:

Power sector is an infrastructure industry and availability, reliability and efficient performance of these are critical for the growth of the industry/country. Corrosion of Power plant components is one of the leading source for the loss of availability, reliability and performance of the plant besides causing tremendous financial losses.

With the availability of fresh water declining and high demand for adding power generating capacity, more attention is being given to locating the power plants in the coastal belts of the

Country. Apart from availability of sea water as a cooling media, sea provides a convenient means of transporting coal especially from other countries for use as fuel in power plants. However; using sea water as cooling water results in many problems such as higher corrosion in the cooling water systems, scaling potential, and corrosion induced damages to RCC structures, corrosion in desalination systems, etc.

Chemical process plants such as refineries, petrochemical, desalination and power generation plant utilities on a coastal shoreline experience severe corrosion. The presence of dissolved salts, chlorides, mild acids (chemical sewers, process area drains, etc) microbiological contaminations result in chemical attack and degradation to most materials. The typical services are seawater cooling, firewater, ash handling, supply of fresh water to plant through desalination, control of SOx emission through FGD, etc. These services are usually critical to plant operation. Interruption in such services can result in forced outage of the plant. Direct repair cost may not be substantial, however; indirect costs associated with outages may be much more. If a system is problematic due to corrosion, often it will fail over and again until the system is revamped. These in-turn call for special care of the systems and application of better control measures such as more corrosion resistant alloys, close monitoring of cooling water systems, special protective measures, etc.

Equipment and Components in direct contact with cooling waters, service waters, ash slurry, fire water, soil, etc are susceptible to corrosion and the severity of corrosion increases manifold if the water is seawater and the plant is situated in coastal region. Components such as pumps, steel cooling water ducts & pipes, auxiliary cooling water pipes & valves, travelling water screens, trash racks, bottom ash scrapper conveyors, valves in contact with water/seawater and cooling water ducts, fire water pipes, etc in contact with soil (buried underground) are some of such components which are highly susceptible to corrosion, require specific corrosion protection measures.

The paper intends to present a few cases such as those of seawater intake pump, internal surfaces of cooling & auxiliary cooling water ducts (seawater), external surfaces of make-up water pipelines, scrapper conveyor chain system, condenser water boxes, etc where either after failures or as a preventive measure suitable anti-corrosive coatings were identified & got applied and these were supplemented by application of in-house designed cathodic protection systems. These measures have improved the availability of the systems and failure rates have substantially reduced.

THEORETICAL CONSIDERATIONS:

Corrosion of Buried or Submerged Metallic Structure:

When a metal corrodes in contact with an electrolyte neutral atoms pass into solution by forming positively charged ions and excess electrons are left in the metal. The process for iron may be represented as:

$$\mathbf{Fe \longrightarrow Fe^{2+} + 2e^{-}} \qquad \textbf{(1)}$$

Thus corrosion is accompanied by the flow of an electric current from metal to electrolyte due to the movement of positive ions into the electrolyte and of electrons into the metal. Any area to which current flows is referred to as an anodic area and the reaction is called an anodic reaction. The metallic ions may react with negative ions in the electrolyte to give insoluble corrosion products (for example, rust in the case of steel). Such reactions do not materially affect the corrosion process except where insoluble corrosion products stifle further corrosion attack.

For the corrosion reaction to proceed the overall electrical neutrality has to be maintained. Therefore, the movement of electrons into the metal and positive ions into the electrolyte at the cathode areas has to be counterbalanced by the consumption of electrons at other areas known as cathodic areas.

Various reactions can occur at the cathodic areas and these are known as cathodic reactions.

The following equations show the most common reactions that occur at cathodes:

$$\mathbf{O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-} \quad \mathbf{(2)}$$

Oxygen Water Electrons hydroxyl ions

$$\mathbf{2H^+ \quad 2e^- \longrightarrow H_2} \quad \mathbf{(3)}$$

Hydrogen ion Electrons Hydrogen Gas

$$\mathbf{2H_2O \quad 2e^- \longrightarrow H_2 + 2OH^-} \quad (4)$$

The first of these reactions occurs in the presence of dissolved oxygen and near neutral conditions.

The second is favoured by acidity (excess of hydrogen ions) while the third is dominant at pH values greater than neutral.

In aerated near neutral conditions, the iron ions produced at the anode react with the hydroxyl ions formed at the cathodic areas produce ferrous hydroxide:

$$\mathbf{Fe^{2+} + 2OH^- \longrightarrow Fe(OH)_2} \quad \mathbf{(5)}$$

The ferrous hydroxide is readily oxidized by dissolved oxygen to form hydrated ferric oxide Fe2O3H2O:

$$\mathbf{4Fe(OH_2 + O_2 \longrightarrow 2H_2O + 2Fe_2O_3.H_2O} \quad \mathbf{(6)}$$

Thus the overall reaction which proceeds through a series of intermediate steps may be written as:

$$\mathbf{4Fe + 3O_2 + 2H_2O \longrightarrow 2Fe_2O_3.H_2O} \quad \mathbf{(7)}$$

Hydrated Ferric Oxide (rust)

In practice the rate of corrosion is often determined by the rate at which the cathodic reaction can be sustained.

In near neutral anaerobic waterlogged environments sulphate reducing bacteria may give rise to a further type of cathodic reaction in the corrosion of iron and steel. These microbes reduce dissolved sulphates to sulphides possibly through the reaction:

$$SO_4^{2-} + 8H^+ + 8e^- \longrightarrow S^{2-} + 4H_2O \quad (8)$$

and the corrosion is characterized by the fact that it occurs:

a) In the absence of air; and
b) Sulphides are present in the corrosion products.

From the composition of the actual products formed it is probable that the corrosion mechanism involves cathodic depolarization which may be represented by the simplified equation (9):

$$4Fe + 4H_2O + SO_4^{2-} \longrightarrow 3Fe(OH)^2 + FeS + 2OH^- \quad (9)$$

Stimulation of the cathodic reaction depends on the bacteria possessing an enzyme (hydrogenase) to enable them to oxidize hydrogen found at the cathodic sites.

The sulphide ions produced by the reduction of sulphate can sometimes stimulate the anodic process of iron dissolution.

As shown in the following reactions, hydrogen gas can be produced at the cathode, and chlorine evolution and/or acidification of the electrolyte can occur at the anode.

Two possible reactions at the cathode are:

$$2H_2O + O_2 + 4e^- \rightarrow 4OH^- \quad (10)$$

$$H_2O + 4e^- \rightarrow H^0_{ADS} + 4H^- \quad (11)$$

At the anode, electrochemical activities can generate the following reactions:

$$2H_2O \rightarrow O_2 + 4e^- + 4H^+ \quad (12)$$

$$2Cl^- \rightarrow 2e^- + Cl_2 \quad (13)$$

In addition, the following chemical reaction can occur in the electrolyte:

$$H_2O + Cl_2 \rightarrow HCl + HClO \quad (14)$$

(Reactions (10) to (14) are important when Cathodic Protection is employed for rehabilitation of concrete subject to damages by chloride. The hydroxyl ions are produced at the cathode, the pH adjacent to the steel increases, which is beneficial for the rebar besides removal of chloride).

Corrosion control methods:

1. **Water Treatment -** Water treatment is a normal option for the corrosion prevention of the cooling water systems. However, generally all the cooling water treatment programs are multifunctional in nature to reduce corrosion/scaling/fouling/bio-fouling effects inside the condenser tubes and not for the corrosion of the mild steel surfaces as in the water boxes, cooling water ducts, etc.

2. **Anti-Corrosive Coatings -** Anti-corrosive coatings are used widely with varying degree of success. This depends on the nature of the circulating water, operating conditions and maintenance plans. Generally the major corrosion protection (~80%) is, provided by the anticorrosive coatings. Previously coal tar based coatings were used for the steel surfaces under submerged conditions, but due to the high temperature, turbulence, impingement, high flow rate etc, it may lead to the severe localized corrosion attack. Also Coal-tar based coatings are considered to be Carcinogenic in nature and to-day the trend is towards discontinuing coal-tar based products.

   There has been a substantial development in the field of anti-corrosive coatings. These coatings, despite high initial cost, are effective due to their ability to provide better corrosion protection for longer period and easy maintenance. These are therefore called "High Performance Coatings" and these can have life of over 15 years if applied properly. Solvent free 100% Solids Epoxy, Vinyl Ester Glass Flake Reinforced coatings, 100% Solids Polyurethane, Moisture Cured Polyurea, etc are considered suitable coatings for application on submerged structures.

   However, in-spite, of these preventive measures ~20% of the surfaces remains unprotected owing to imperfections and mechanical damages in the coatings. These areas primarily need only to be protected by the application of Cathodic protection system in a cost effective manner.

3. **Cathodic Protection -** One of the most proven and the assured method of controlling corrosion is Cathodic Protection as this is almost reversal of corrosion process. During the corrosion process, the electrons are transferred from one metal site to another also known as the electronic conduction. The current flowing through the circuit is proportional to the corrosion rate. Now the potential difference between the metal and its surrounding electrolyte varies with density and the direction of any crossing current interface. This variation is referred, to as "polarization". The potential difference is also dependent on the type of chemical reaction taking place at the metal/electrolyte interface. At the free corrosion potential (Ecorr) the anodic and the cathodic currents are equal in magnitude and opposite in direction. During this situation all the electrons evolved at the anodic reaction are consumed by the cathodic reaction. In case the potential of the metal surface (Anode) is decreased by the external source, the anodic reaction can be decreased and the cathodic reaction can be increased by making the metal more positive. As is evident from the Electro chemical series, metals like Magnesium, Aluminum, Zinc are more negative compared to Iron/Steel, and hence if metals are coupled with Iron/Steel, then they will become anode and would be corroding. On the other hand Iron/steel would become Cathode and in this process would be protected.

The basis for the protective potential is given by the Pourbiax Diagram (Pot.Vs. pH) of Iron in aqueous media. It can be seen that when the potential of Iron/steel shifts beyond -850mV.Vs. Cu/CuSO4, then Iron will be cathodically protected. This shift in potential will be achieved either by coupling with the metals like Zn, Al or Mg (where Iron will be saved at the expense of these metals), or it can be achieved by passing a current through some anode (Consumable/non-consumable type) from a DC source. The first method of protection is called "Sacrificial Cathodic Protection and the second type of protection is called "Impressed Current Cathodic Protection".

Types of Cathodic protection systems: As discussed before, there are two types of Cathodic Protection systems:

a) **Sacrificial Cathodic Protection System (SCCP)** - By coupling a given structure (say Fe) with a more active metal such as zinc or magnesium. This produces a galvanic cell in which the active metal works as an anode and provides a flux of electrons to the structure, which then becomes the cathode. The cathode is protected and the anode progressively gets destroyed, and is hence, called a sacrificial anode.

b) **Impressed Current Cathodic Protection System (ICCP)** - This method involves impressing a direct current between an inert anode and the structure to be protected. Since electrons flow to the structure, it is protected from becoming the source of electrons (anode). In impressed current systems, the anode is buried and a low voltage DC current is impressed between the anode and the cathode.

Principles of Cathodic Protection:

Cathodic protection is an electrochemical means of eliminating, or mitigating corrosion. Corrosion is no longer accepted as an inevitable part of nature, and cathodic protection is one of the most effective and widely used means to prevent this waste. The high degree of effectiveness of the cathodic protection process is due, in part, to the fact that it is almost a direct reversal of the basic corrosion reaction. Other aspects of the process enhance its ability to limit corrosion so that it may be as much as 99% effective in totally eliminating corrosion.
When a potential of a metal electrode is shifted negatively, the metal tends to attract the Fe^{++} ions and the anodic reaction is slowed down. When the potential is changed in a positive direction, the Fe++ ions are more easily released and the corrosion accelerates. Similarly, the cathodic reaction rate is increased when the metal becomes more negative and the reaction slows down when the potential becomes more positive.

The shift of the potential of an electrode is called **polarisation**. The effect of changing reaction rates with polarisation can be illustrated in an "Evans diagram" shown in Figure 1.

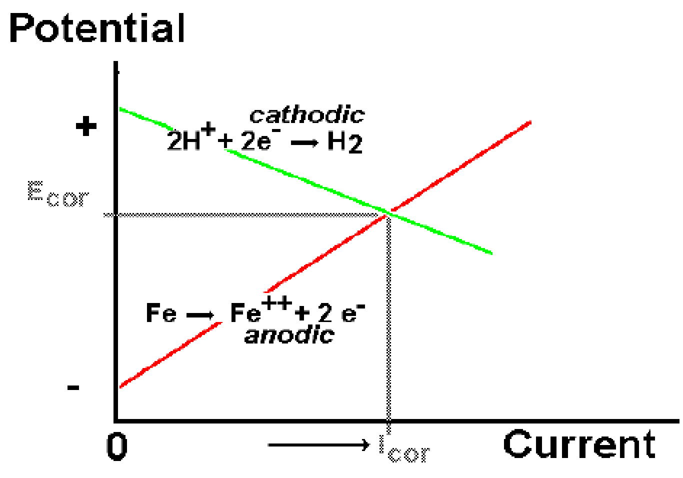


Fig. 1: Evans Diagram

The natural surface potentials of iron and steel in contact with soil or water are always negative when referred to either of the half-cells (Cu/CuSO4 or Ag/AgCl); nevertheless, different areas of the same metal surface may have different potentials. Potential-pH diagram (Pourbaix Diagram) of steel in water at 25 oC is indicated in Fig. 2 and Stability diagram of iron is indicated in Fig. 3 & 4.

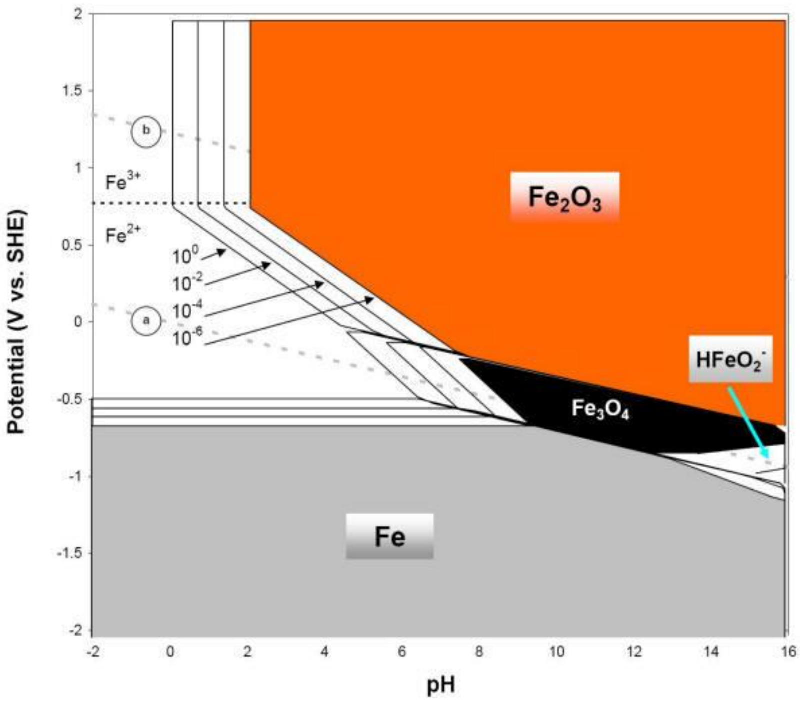


Fig. 2: Potential pH Diagram of steel in water at 25 oC

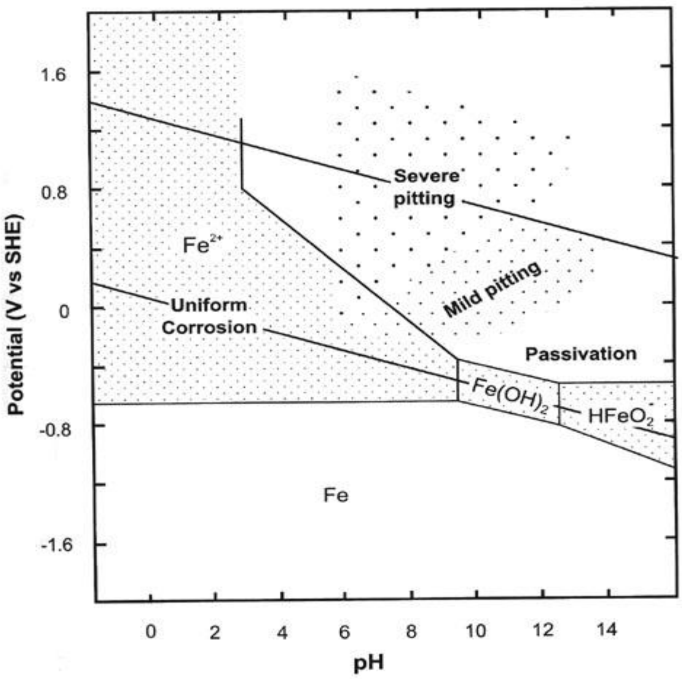
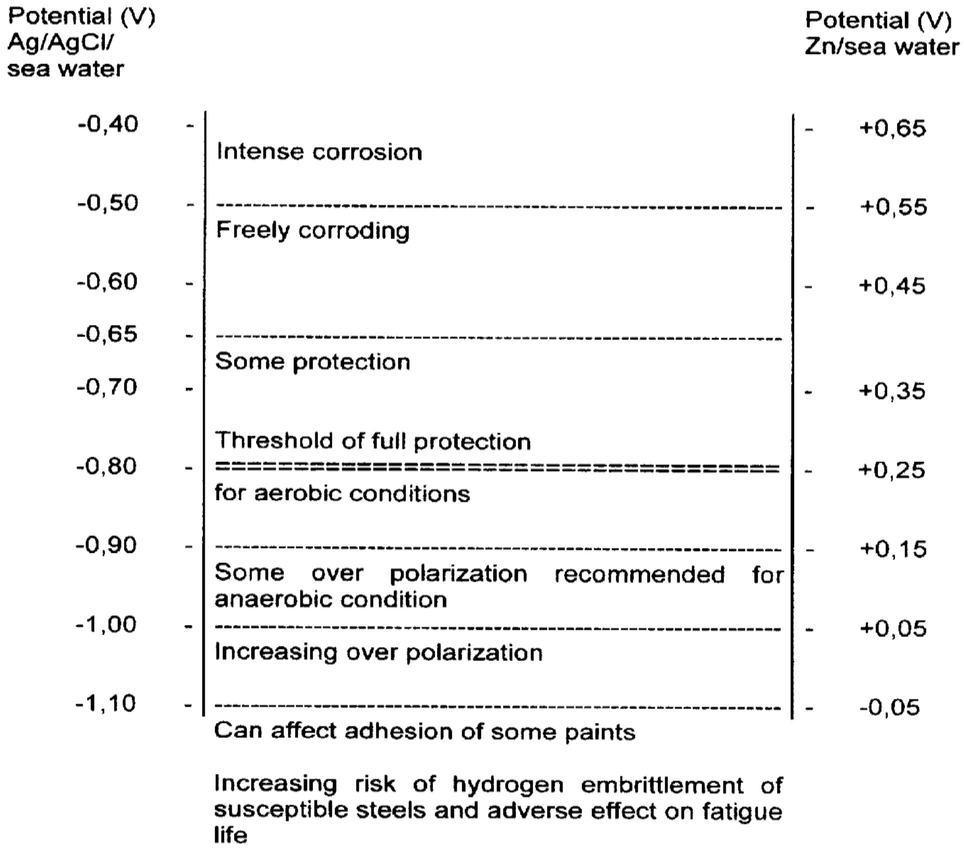


Fig. 3: Stability diagram of Steel



The corrosion, cathodic protection and over polarization regimes of steel expressed as a function of electrode potential

Fig. 4: Corrosion & Electrode Potential (Source: BS EN – General Principles of Cathodic Protection in Seawater)

Fig. 5 gives the galvanic series of metals.

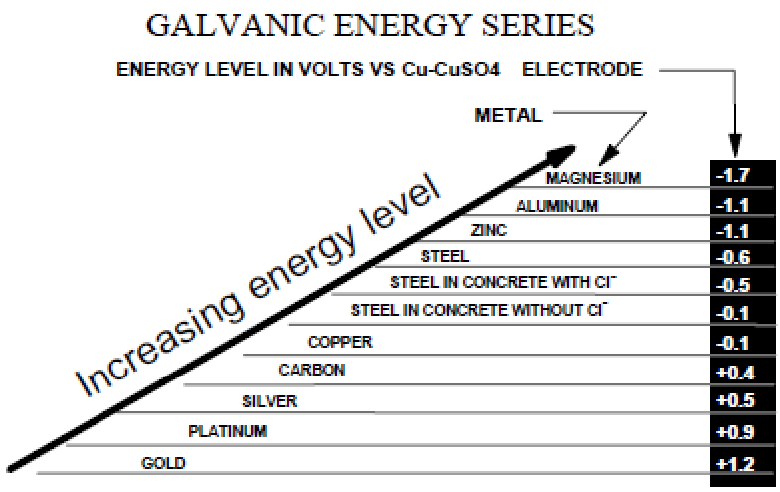


Fig. 5: Galvanic series of metals (Ref. Corrosion and Cathodic Protection Theory, James B. Bushman

CASE STUDIES:

1. **Failure Assessment and Corrosion Protection of Sea-intake Pump:**

   A seawater vertical intake pump failed during service. The pump was taken out of service. Preliminary analysis indicated that the cast iron casing pipe had been damaged, a large piece of the pipe was found to be missing (Fig. 6 & 7), there were body cracks initiated from flanges and many bolts were found missing and SS shaft was pitted (Fig. 8 & 9). Detailed failure analysis was carried out which indicated that the main cause of failure was graphitization of cast iron casing pipe and corrosion fatigue initiating from crevice corrosion of bolts fixed on the flanges. Severe microbiologically induced corrosion was also observed. Subsequently it was observed that proper corrosion protection measures of the seawater pumps were missing (anodes of sacrificial cathodic protection system were either missing or had completely dissolved, electrical connections to the impressed current cathodic protection system were broken, no protective coating was observed, etc).

   Based on the failure analysis carried out, multi-dimensional corrosion protection measures were framed and implemented. To name a few: design & implementation of sacrificial cathodic protection for externals of pump body & internal surfaces of casing pipe, impressed current cathodic protection system for pump internals, application of suitable coating for pump body, control of microbiologically induced corrosion, etc (Fig. 10 to 15). All those were developed in-house and implemented. Same approach was adopted for rest of the pumps. Now the pumps are working satisfactorily without any problem.

Fig. 6 & 7: Failed Casing Pipe of Sea-Intake Pump

Fig. 8: Cracks on the Flange & Body

Fig. 9: Pitted SS Shaft

Fig. 10: Corroded Internals

Fig. 11: Broken ICCP Cables

Fig. 12: Missing Sacrificial Anode **Fig. 13: VEGF Coated Internal Surface**

Fig. 14: New MMO Anode (Internal) **Fig. 15: New Al-Zn-In Anodes installed**

2. Corrosion Protection of Condenser Water Box:

Condenser water boxes are the source of input and output of cooling water in the condensers. There could be number of water boxes depending on condenser design and heat load. The cooling water could be fresh water. The circulating water is cooled through induced draft cooling towers in this process the cooling water gets saturated with the oxygen. This high level of oxygen coupled with the elevated temperature of operation (around 50°C) aggravates the rate of corrosion of mild steel.

The large size of these boxes requires welded plate fabrication. The weld areas and crevices formed by flanges, promote local cell action, which is accelerated by the high oxygen content of the circulating water. However, the largest affected areas are the galvanic sites at the tube/tube plate joints. The other areas are the water box surfaces, which despite the preventive anticorrosive coatings are susceptible to localized corrosion effect. The holidays and the air pockets of the coatings on the water boxes come in contact with the circulating water and the severe localized corrosion damage occurs.

Furthermore the inlet side of the condenser tube is subjected to severe erosion-corrosion due to high influx of the water entering the tubes. Because of the high silt content, velocity of the water, vibration and rapid temperature changes, coatings alone are not able to give full protection to the water boxes. Cathodic protection in conjunction with suitable anti-corrosive coatings can provide good corrosion protection to the condenser water boxes.

Compared to most structures requiring cathodic protection, condenser water boxes have extremely high current requirement. The high oxygen content and water velocities contribute to rapid depolarization at the cathodic surfaces. The potential difference between the tube plate and water box indicates that major current goes to tube sheet. Typical current required to maintain protective potentials in water boxes under load varies from 650 mA/sq.m to 1600 mA/sq.m for bare steel. The requirement is reduced on coated steel.

Design of cathodic protection systems for many condenser water boxes have been undertaken at different power plants. Many condensers were provided with zinc based sacrificial cathodic protection but after the anodes had dissolved/damaged/coated with corrosion products, fresh design of cathodic protection system based on magnesium anodes were designed for fresh water systems. Aluminium-Zinc-Indium based systems have been designed for seawater based systems. However; as seawater based condensers are fitted with titanium tubes with titanium/titanium clad steel tube sheets they should be preferably protected through impressed current cathodic protection system as titanium is susceptible to hydriding at potentials > (-) 1.5 V vs Ag/AgCl. Fig. 16 & 17 show the typical Magnesium based anodes used for condenser water boxes, while Fig. 18 shows the typical impressed current cathodic protection system for condenser water boxes.

Fig. 16 & 17: Typical Magnesium Based anodes for Condenser Water Boxes

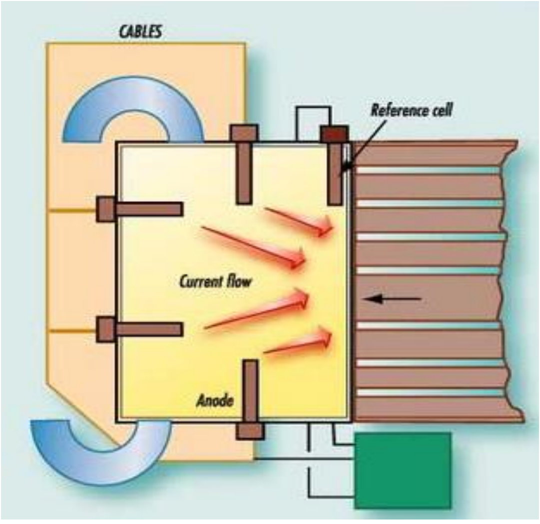


Fig. 18: Typical Impressed Current Cathodic Protection of Condenser Water Box

3. **Corrosion Protection of Buried Critical Make-up Water Pipeline:**
   Two numbers of water pipelines each about ten kilometres in length and 1.2 m diameter are supplying make up water to a power plant. These pipes are laid underground. These are one of the critical pipelines as stoppage of water supply will immediately affect the running of the power plant it may have to be shut down completely. In order to prevent failure of the pipelines from soil side corrosion, an impressed current type cathodic protection system had been provided. As per Design, a pipe to soil potential of -1.46 V with reference to Cu-CuSO4 electrode is being maintained continuously for the protection from DC Rectifier and a deep bed anode system. During field analysis, it was found that only 5 KM of pipe line is completely protected whereas rest of the pipelines were having less protection against corrosion. The PSP was deteriorating continuously at the pump end while at plant end, 5 Km of pipeline was well protected. PSP at plant end ranged from (-) 1.4 V to (-) 850 mV while at the pump end the PSP was found to in the range of (-) 280 to (-) 350 mV. The data showed that the present cathodic protection system was inadequate and could lead to failure of pipelines at pump end.

   The problem was studied and a fresh design of an additional cathodic protection system was developed in-house and is under execution. The initial design was again based on deepwell anode system using MMO string anodes. However; as the soil in the area was backfilled soil, the anode bed design was changed to Horizontal Bed. The system is under commissioning. The study highlighted that regular monitoring of such protective systems is essential to prevent any catastrophic failure. (Fig. 19 – 22)

Fig. 19: PSP measurements **Fig. 20: DC Rectifier for Potential Control**

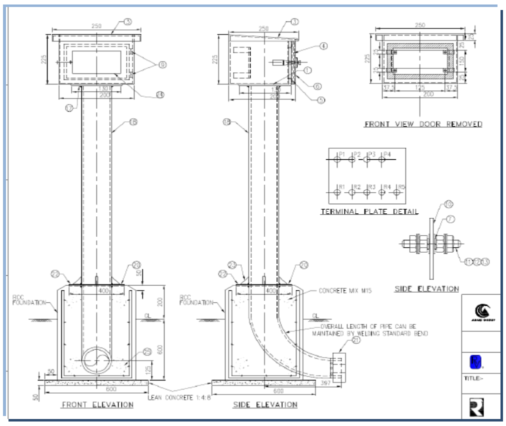


Fig: 21: Deepwell anode bed

Fig. 22: Installation of Horizontal anode Bed

4. **Corrosion Protection of Seawater based Cooling Water Ducts, Auxiliary Cooling Water Ducts & Associated Valves:**

Cooling Water ducts supplying seawater as cooling water to condensers of power stations are made of carbon steel. The diameter of these ducts varies from 3.2 m to 2.2 m for ducts with butterfly valves of 900 mm/2.2 m diameter. The length of these ducts runs upto 2 km and there are number of such connected to different units. The ducts are buried underground with soil with resistivity ranging from 2 to 100 ohm m and chloride level upto 2000 ppm.

The ducts were internally coated with three layer epoxy (Chinese product) and some zinc based anodes were placed. From the soil side Magnesium based anodes were installed along with coal tar tape coating. It was observed that pieces of zinc anodes were breaking and were damaging coating inside the ducts and condenser water boxes. The epoxy coating has been replaced with vinyl ester glass-flake reinforced coating (1.5 mm thickness) and fresh design of cathodic protection system based on Aluminium-Zinc-Indium anodes was prepared and implemented in phased manner in all the units. Systems are performing well. For the soil side Pipe-to-soil potential measurements are being carried out to assess the condition of pipes from soil side.

Auxiliary Cooling Water (ACW) pipes made of Chinese steel were neither coated internally nor were cathodic protection system installed. The pipes started corroding severely resulting in leakages. There was no approach to internal surfaces. It was decided that during overhaul of each unit, damaged ACW pipes would be replaced and all pipe sections shall be provided with suitable manhole. Entire ACW pipelines were coated with vinyl ester glass-flake reinforced coating (1.5 mm thickness) and supplemented with newly designed cathodic protection system. Both sacrificial cathodic protection system based on Aluminium-Zinc-Indium anodes and Impressed current cathodic protection system based on MMO probe anodes were designed. However; due to practical considerations sacrificial protection system has been implemented. (Fig. 23 – 26).

Fig. 23: Old Zinc Anode in CW Duct

Fig. 24: New Aluminium based Anode

Fig. 25: Corroded ACW Pipe System

Fig. 26: VEGF Coated Valve of ACW

5. Corrosion Protection of Bottom Ash Scrapper Chain Conveyor, Trash Racks & Travelling Screens in Seawater:

Bottom Ash Scrapper Chain Conveyor system of a plant was getting corroded due to use of seawater in the system. Sacrificial cathodic protection system based on

Aluminium-Zinc-Indium anodes was developed and implemented. This resulted in good corrosion protection of chain system (Fig. 27 & 28).


Fig. 27: Chain Conveyor without Anode Fig. 28: Chain conveyor with anodes.

Trash racks and travelling water screens in contact with seawater are subject to severe corrosion. Sacrificial cathodic protection systems have been designed and is being implemented (Fig. 29 & 30).

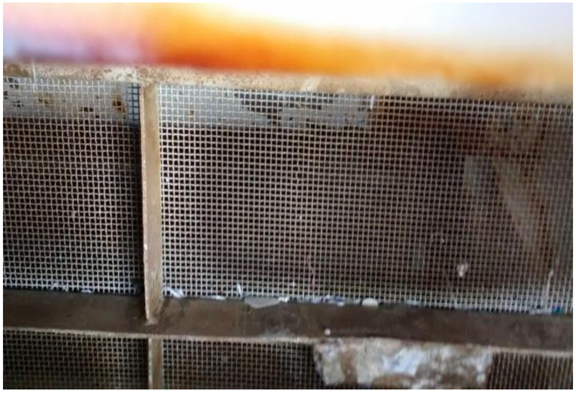



Fig. 29: Travelling Water screen Fig. 30: Trash Rack damaged anode

6. Corrosion Protection of RCC Structures (Cooling Towers) in Coastal Plants:

RCC structures such as cooling towers operating on seawater are subject to severe corrosion induced damages. Chloride ions penetrate the concrete surfaces and break the passive film on steel reinforcement resulting in corrosion induced damages. Generally patch repairs are used but the chloride that has penetrated the concrete remains there. Moisture and dissolved oxygen are already present in cooling waters. Once the passive film on the reinforcement is broken, dissolved oxygen and moisture aggravate the corrosion of steel. Electrochemical methods for repair & rehabilitation of concrete structures such as cathodic protection and electrochemical chloride extraction are the means of removing the chloride embedded in concrete as per reactions 12 -14 above.

Many cooling towers (both induced draft and natural draft) were found to be affected by chloride induced damages. Three different designs – 1) impressed current cathodic protection system based on MMO mesh/ribbon anodes, 2) spray coating of Aluminium-Zinc-Indium alloy and installation of Aluminium-Zinc-Indium alloy based anodes on concrete surfaces were developed, but due to high cost involvement actual implementation could not be carried out. Some trail installation of Aluminium-Zinc-Indium anodes on RCC surfaces of induced draft cooling tower using seawater has been carried out and is giving good results. (Fig. 31 – 34).

Fig. 31: Corrosion induced damage NDCT **Fig. 32: Corrosion Induced Damage IDCT**

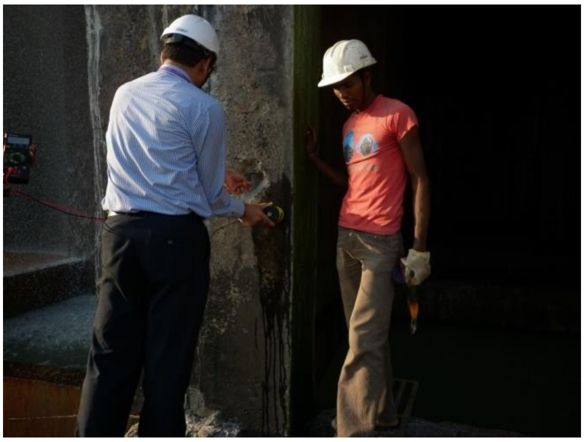


Fig. 33 & 34: Trial Cathodic protection of RCC structure of IDCT Columns & beams

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