Corrosion in Pulp and Paper Industry

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SUMMARY

Corrosion is a very serious problem faced by almost all industries in the world. Due to corrosion of pipelines, tanks, many other metal parts and even concrete structures, huge losses are incurred every year. In India the losses due to corrosion of materials is more than Rs. 150/- crores every year.

In this article, theory of corrosion, and corrosion as faced by the Pulp and Paper Industries, along with the preventive and remedial methods are discussed.

Corrosion problem is solved by taking proper actions, like selection of proper material of construction, coating the surfaces of tanks and pipelines etc. with epoxy paints in the initial stages of erection itself and thereafter at fixed intervals. Proper ventilation arrangements to let out the corrosive fumes and gases at a safer distance in the atmosphere.

INTRODUCTION

Corrosion and its problems is as old as the civilization itself. Corrosion of materials especially metals is inevitable because practically all environments are corrosive to a greater or smaller degree. It is a very common sight in day to day life, in homes, on roads, in the industrial plants to see the corroded materials. Corrosion of metals is therefore a greave problem facing mankind in similar way as air and water pollution as regarded by the civilized world.

Corrosion losses in the United States as estimated some years back is to the tune of 9 billion dollars. As per the survey of 1960–61, corrosion losses in India were estimated to be about Rs. 150 crores a year. This figure now, must have gone up with the increased industrialization in all spheres.

Wherever water is used, the corrosion of metals occur. This is especially true in pulp and paper industry as large quantity of water and other corrosive chemicals are used under conditions which promote corrosion. In pulping and recovery of chemicals various gases are produced like H_2S, mercaptans, sodium peroxide fumes, acid formations in bleaching, carbon dioxide and oxygen which are also highly corrosive.

A simple definition of corrosion is "that the deterioration of a substance, usually a metal because of a reaction with its environment."

THEORY OF CORROSION

Electrolytic theory of corrosion is the most commonly accepted. When a metal is in contact with water it provides both the anode and cathode electrodes, with water as the electrolyte. Pure water with dissociation, contains hydrogen ions (H^+) and hydroxyl (OH^-) ions along with water (H_2O) molecules. When a piece of metal say iron is immersed in water this balance is upset, as the metal, because of its solution pressure discharges positively charged ions into the solution. The positive electricity of the water is increased while that of the metal is decreased, leaving the metal negatively charged. Equilibrium is regained by the displacement from water of positively charged hydrogen ions, which migrate to the metal and this is neutralized by the negative charge of the metal. This results in the formation of thin film or "plating out "on the metal of molecules of hydrogen. This film protects the metal from further corrosion. But if oxygen is there in water, the reaction continues and the thin film protecting the metal is removed and corrosion is continued (1).

The corrosions are divided into (1) Galvonic corrosion (2) Electrolytic corrosion (3) Stress corrosion.

(1) Galvonic corrosion takes place when disimilar metals are in contact with each other. The action is similar to that which takes place in an electric battery.

(2) Electrolytic corrosion takes place when a stray current of electricity from an outside source finds its way to a metallic structure. The chief source of stray currents is the return currents of street railways and other electric systems.

(3) Stress corrosion is the accelerated corrosion of a metal under a continuing stress. Its effect are greater than those of either the corrosive environment or the stress alone. Stress corrosion attack is selective in nature and its end result is failure by cracking which is usually intragranular but may be transgranular. Stress

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corrosion cracks have been observed to propagate at rates as high as 0.5 cm/hr. (2).

CORROSION IN PULP AND PAPER INDUSTRY

Corrosion may show up as (1) internal and (2) external.

Internal corrosion is due to the storage of corrosive chemicals, in tanks, flow of liquids in pipe lines, rate of flow etc.

External corrosion takes place due to the corrosive environment which contains various fumes and gases like hydrogen sulphide, carbon dioxide, hydrochloric acid, mercaptans, sodium peroxide, sulphur dioxide etc.

Corrosion can be minimised by taking care of—

(1) Lay out of the unit which should be such that it gives maximum access for ventilation, so that chemical fumes and gases are carried away naturally.

(2) Proper coating of the steel and concrete structure with corrosion resistant paints and periodic inspection.

(3) Proper selection of suitable materials of construction and type of the equipment for handling particular media.

Corrosion in the Pulp and Paper Mill can be reviewed under the following heads:

(1) Corrosion of concrete structures, like columns, beams, towers especially in Pulp Mill and Recovery Section.

(2) Corrosion in Pulp Mill.

(3) Corrosion in Recovery Section

(4) Corrosion in Boiler House and

(5) Corrosion in Paper Machine.

(1) Due to the evolution of various gases and fumes in the atmosphere, the uneven surfaces of concrete structures which are embedded with steel structures for support, get corroded thereby weakening these concrete structures. In one of the major mill, it is observed that the concrete structures got saturated with these chemicals and flakes of concrete are falling out. One of the possible reaction can be visualised as under.

Hydrochloric acid and its fumes are evolved during chlorination. This reacts with the calcium oxide in concrete.

$$CaO \text{ (in concrete)} + H_2O = Ca(OH)_2 \quad \ldots\ldots(1)$$

$$Ca(OH)_2 + 2\,HCl = CaCl_2 + 2\,H_2O \quad \ldots(2)$$

$$CaCl_2 + CO_2 + H_2O = CaCO_3 + 2\,HCl \quad \ldots(3)$$

$$CaCO_3 + CO_2 + 2H_2O = Ca(HCO_3)_2 + H_2O \quad \ldots(4)$$

$$Ca(HCO_3)_2 = Ca + 2HCO_3 \quad \ldots\ldots(5)$$

These reactions can repeat endlessly, depending on the temperature and humidity reversals. Flakes of concrete are detached in each cycle, the pore size in concrete widens, reinforcement is corroded and concrete corrosion occurs with accelerated rates due to the infilteration of the structure by hydrochloric acid under osmotic pressure, until finally the structure collapses.

This can be prevented by providing a suitable barrier for the entry of moisture into the concrete structure. The preventive measures are best carried out at the time of construction and commissioning of the struture. It is important to water proof the foundations and roofs so that underground or rain water does not enter into the structure. For this purpose, chemically resistant bituminous mastics may be used. Usage of hoods for Brown stock washers and Bleach washers such that corrosive gases are let out of the building, will be of great help.

(2) Due to highly corrosive nature of white liquors, pittings may occur in digesters, washers, screens and pipelines. In one of the mill, a digester commissioned few years back has already shown number of pittings inside surface of the digester. This probably is due to the faulty selection of material of construction. Carbon steels are more susceptible to corrosion if the carbon content of the steel is more.

(3) Corrosion of black liquor equipment in a soda mill is not a serious problem but in a sulphate mill it may become of considerable importance. The presence of sodium sulphide in the black liquor and the formation of organic sulfides and sulfonic acid derivatives, together with other organic acids, in the destructive distillation taking place in the evaporator, accelerates the corrosion of steel equipment. Stainless steel of the 18% chromium, 8% nickel composition has proved to be fully resistant to the action of sulphate black liquor and the corrosive condensate formed in its evaporation. Evaporator tubes of this metal that have been in operation under conditions of high temperatures, concentrations and erosion for a period of 18 years show no discernible wear or corrosion (3).

The major source of maintenance and repair expense in the causticizing system is the corrosive character of the liquor. Sulphide content is the main cause of corrosion. It is proved that higher sulphidity leads to increased corrosion. Corrosion is not a serious factor in those parts of the system where the liquor is week, the green liquor clarifier, dreg washers, and white liquor mud washers will frequently operate 5 to 10 years without need of repairs.

Corrosion is most severe with strong white liquor and it is aggravated by high local velocities, by the presence of lime sludge and by aeration. The presence of chlorides in the liquor circuit may also increase it to a point where under worst conditions liquor will eat through a 13 mm steel plate in two weeks. Very rapid corrosion occurs in the lime slaker and classifier, the causticizers and white liquor clarifiers and inter-connecting pipings. As stainless steel is expensive, use of extra heavy steel plate should serve the purpose, for large tanks. White liquor clarifier tanks of 13 mm plate should last 15 to 20 years.

(4) Corrosion in the boiler and power plant is primarily caused by the dissolving gases, mainly carbon dioxide, either naturally present or due to breakdown, of carbonates and bicarbonates. Corrosion can be controlled by installing deaerating heaters for the removal of dissolved gases and by correcting the alkalinity of the feed water. The boilers are protected also by the use of oxygen absorbing chemicals such as sodium sulphite and film forming treatments with materials such as tannins or lignin derivatives. Corrosion in equipments where steam is condensed such as dryer rolls, heat exchangers and in return condensate lines may be controlled by reducing the carbonates in the feed water to a minimum by lime treatment or by the use of ion exchange softeners.

(5) In paper machine section, the corrosion may be accelerated by low pH due to the use of acid or alum. Slime and other bacterial conditions, dissimilar metals, stray electrical currents, or improper use of mercurials may cause corrosion or embrittement of copper alloys.

A common method for alleviating corrosion in the paper mill system is to increase the pH of the process water wherever possible. The use of acid and alum should be kept to a minimum. If necessary alkaline materials like caustic soda and/or sodium aluminate may be used. The formation of slime which often causes corrosion can be eliminated or greately reduced by proper slime control. Bacteria which develop in dead spots and stagnant areas protected from the mill stream of water or by lack of air, cause slime to develop unless general mill cleanliness is observed. Corrosion due to metallic salts used for slime control and other slime preventives such as mercurials should be controlled by guarding against excessive dosages and by application at proper points in the system.

MEASURING CORROSION

The rate and to some extent, the type of corrosion experienced throughout the mill are measured by the installation of coupons or pieces of various types of metals suspended in the system, or by sections of pipe near where corrosion is being experienced. In most cases, the use of speciman testing requires individual study for each system, as there is no standard procedure, which entirely satisfactory. The details are available in any standard books on corrosion.

PREVENTION OF CORROSION

A few general recommendations are enumerated below, which will help in the effective control of corrosion.

(1) Timely detection of corrosion
(2) Assessment of its nature and extent
(3) Remedial measures to check its growth
(4) Scientific investigation to decipher the causes
(5) Permanent cure by positive actions
(6) Flow detectors which work on electronic principle can be used to detect cracks, loss of thickness of the plates due to corrosion in digesters pipelines etc.

Some of the remedial actions are—

(1) All new pipelines metal parts, checkered plates and other equipments should be properly painted before these are actually installed.

(2) Points of serious corrosion in various departments be marked for attention round the year, to save valuable metal and material.

(3) Anticorrosive chemicals can be used for cleaning the tubes, vessels etc. at regular intervals.

(4) A corrosion cell consisting of engineers, may be formed to study corrosion in various plants and make effective recommendations for the prevention of corrosion.

REFERENCES

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