Corrosion Problem in Pulp and Paper Industry

VISWANATHAN M.*, CHANDRASEKAR H.M.*

ABSTRACT

The paper deals with the factors influencing corrosion in pulp and paper industry. The corrosion effects experienced in various areas of the industry is explained, followed by ways of reducing corrosion. The authors share some experiences through this article.

Introduction :

In the pulp and paper industry, the exposure of the equipments in an extensive amount to water and water dispersions and also the solutions containing variety of materials is conducive to corrosion reactions.

Corrosion is the effect of exposure to environment conditions upon equipment. The corrosion may be conditioned by the effect of an aggressive environment or a mild environment. Also the material surface, on its part, may play a vital role in influencing corrosion either by being resistant or susceptible to corrosion. Hence the study of corrosion invariably requires an indepth knowledge about the factors responsible for corrosion and of means of modifying the environment towards greater protection of material surfaces. It is very much necessary to have a first hand information about various materials used for construction for guidance in the selection for equipments, required in a pulp and paper industry.

This paper deals with the aspects of corrosion on the following lines :—

1. The factors influencing corrosion.
2. The areas of corrosion in the industry.
3. Corrosion reduction.
4. Practical experiences.

1.0 Factors influencing corrosion—These can be studied under the following heads :

1. Affect of pH
2. Affect of dissolved gases.
3. Affect of dissolved solids.
4. Flow rate and temperature.

1.1 The most important factot in metallic corrosion is acidity. Under low pH conditions, in the absence of protective films, iron, steel, aluminimum, zinc and many other metals are susceptible for rapid corrosion. The effect of other corrosive agents such as chlorine, oxygen and salts is much more pronounced at a lower pH than at normal or alkaline conditions. The effect of dissolved oxygen in a low pH medium is drastic than the effect of low pH.

1.2 Other than dissolved oxygen, gases like CO_2, H_2S and SO_2 play a vital role in the corrosion phenomena.

The effect of CO_2 is due to the formation of carbonic acid whereas SO_2 forms sulphurous acid and sulphuric acid with moisture and oxygen. Corrosion as a result of CO_2 is pronounced in steam and condensate lines due to the release of CO_2 from boiler water as a result of decomposition of carbonates.

Hydrogen sulphide corrosion is experienced with the formation of metallic sulfides. Chemical and mechanical conditions will be the factors for determining the seriousness of corrosion either due to the formation of an adherent protective coating or exposure of fresh surface.

*Superintendents of Mysore Paper Mills Ltd., Bhadravati.

1.3 The presence of higher concentrations of ionifable salts greatly influences the rate of corrosion. Mineral salts like NaCl, Na_2SO_4, $CaCl_2$ and $MgCl_2$ add up to the corrosion rate extensively. The corrosion is due to the greater conductivity of the water resulting from these dissolved salts. The increased conductivity accelerates the galvanic action thus aiding in increased rate of corrosion.

The adherence of initial products of corrosion is a vital factor for preventing further corrosion. Salts make these films less adherent.

1.4 The rate of corrosion is influenced by flow rate and temperature. High flow rates help in the removal of products of corrosion, resulting in opening up of new surfaces for further corrosion. The effect of temperature is similar as the accelerating effect of chemical reactions. Hence proper selection of materials of construction involves a highly complex calculation of the resistance of the metal an idea of the environmental conditions, the cost in volved and the expected life. Invariably, the initial cost involved plays a vital role in the selection of the right type of material, for a longer life.

2.0 The areas prone for corrosion in the industry :

Corrosion is observed in varying degrees in the following areas of the paper industry.

1 Chemical recovery boiler
2. Evaporators
3. Chlorine handling and hypochlorite preparation plants
4. Pulp Mill
5. and Paper Machines 4

2.1 Chemical recovery boiler :

In the operation of a chemical recovery boiler, corrosion is experienced in,

i) Fire side exposures
ii) Tube side exposures
iii) Electostatic precipitator
iv) Areas around smelt spouts and air ports.

2.1.1 Fire side exposures : The main corrosion product is FeS, identified by a hard black scale. This product is tightly bonded to the tube surface. The formation of FeS is aided by the presence of elemental sulphur formed in the furnace operations.

$$Na_2S + 2CO_2 \rightarrow Na_2CO_3 + S + CO \quad .....(1)$$

$$2Na_2S + 3\,SO_2 \rightarrow 2Na_2SO_3 + 3S \quad .....(2)$$

$$H_2S + \tfrac{1}{2}\,O_2 \rightarrow H_2O + S \quad .....(3)$$

$$Fe + S \rightarrow FeS \quad ..... (4)$$

$$H_2S + O_2 \rightarrow \tfrac{1}{2}\,S + \tfrac{1}{2}\,SO_2 + H_2O \quad .....(5)$$

The rate of corrosion is low at 310°C. Increase of temperature results in increased rate of corrosion. Keeping the metal surface temperatures below this limit is critical for controlling this type of corrosion. The tube wall surface temperatures depend on local heat flux, the deposits within the tube, and the boiler water saturation temperature. It is observed that a layer of frozen smelt acts as a protective coating.

Literature states that $H_2S - O_2$ reaction is predominant in the case of wall drying units whereas Na_2S—CO_2 reaction plays a major role in the corrosion of suspension drying units. This invariably involves a reduced sulphur species and an oxidising medium.

The corrosion due to the formation of pyrosulphate $N_2S_2O_7$ in the upper regions of furnace namely boiler bank, super heater and economiser is pronounced at high SO_3 concentrations. These high concentrations of SO_3 result from excessive gasification in the furnace, insufficient sodium volatilization and excessive oxygen concentrations in the flue gas.

$$Na_2SO_4 + SO_3 \rightarrow Na_2S_2O_7$$

$$Na_2S_2O_7 + H_2O \rightarrow 2\,NaHSO_4$$

The freezing point of $Na_2S_2O_7$ is 400°C which gets reduced to 280°C in the presence of Potassim salts.

The attack by reduced sulphur species occurs if unburnt entrained black solids is mixed in the deposits. The presence of chloride bring down the melting point of protective layer of slag. Also smelt by itself is corrosive in the absence of a protective barrier.

Moreover, the tendency to form acids by the component of flue gas when it is cooled below

the dew point aggravates the corrosion problem. The oxides of sulphur and Hydrochloric acid cause corrosion in precipitator, ID fan, ducting and parts of economiser.

2.1.2 Tube side corrosion : This can be prevented by a strict control of the dimineralised water properties. The cracking of steam tubes on the water side is caused by various factors such as Hydrogen embrittlement, caustic embrittlement, oxygen, and stress corrosion cracking, all related to impurities in feed water or inadequate pH control. Monitoring of these impurities either directly by measuring Hydrogen, Oxygen, chloride or Sodium levels or indirectly through conductivity or pH measurements is important to know about the correlation with process variables and corrosion.

2.1.3 The corrosion of electro static precipitator is attributed to the less temperature of flue gas entering the chamber and the incomplete even distribution of flue gas in the chamber. The presence of oxides of sulphur at a lower temperature aggravate the rate of corrosion. It is being recommended that the temperature of the flue gas stream entering the electrostatic precipitation must be atleast 15°C. Normally a temperature of 30°C above the dew point is a safe operating temperature. Dew point temperature is a complex function of moisture content and sulphur trioxide. The temperature is raised by an increase in moisture and increase in sulphur trioxide concentration. Also increasing the black liquor concentration and better control over air distribution reduce Hydrogen sulphide emissions. Thereby the problem of corrosion can be controlled.

2.1.4 The ability of the molten smelt to react very rapidly with iron and steel poses a serious problem. Continued cantact results in complete destruction. A protective layer of frozen smelt by cooling the metal acts as a barrier to corrosion. Every effort should be made to have a continuous supply of sprout cooling water to avoid corrosion, atleast as long as smelt flow is there in the spouts.

2.2 Evaporators : The corrosion of the tubes in the multiple effect evaporators is due to the compounds of sulphur, entrained with the vapour. The corrosion product formed is again FeS. Black liquor oxidation either in the weak black liquor or strong black liquor minimises the corrosion due to the oxidation of Na_2S to $Na_2S_2O_3$ at 70°C.

$$2\,Na_2S + 2\,O_2 + H_2O \rightarrow Na_2S_2O_3 + 2\,NaOH$$

(exothermic reaction)

Also the malodorous non condensible gases with evaporator condensates gets substantially reduced. Proper venting of the non condensible gases brings down the corrosion substantially.

2.3 Chlorine handling and hypochlorite plants : The recommendations are to use iron as the material of construction when handling dry chlorine and for moist chlorine, rubber lined steel, Hastelloy C, tantalum and sarn lined steel.

For hypochlorite, rubber lined steel, or saran or saran lined steel is advocated.

2.4 Cold soda mechanical operations are conducted under alkaline conditions but the equipments are subjected to erosion by the nature of the process of the fibrous material. The presence of low pH conditions in paper machines requires the use of stainless steel piping as materials of construction.

3.0 Corrosion reduction : Complete knowledge about the requirement of material of construction for the corrosive media is a necessity. A balance has to be struck between the initial cost and the life of the equipment. Periodic monitoring of the areas prone for corrosion is necessary for taking any preventive action. A good record keeping about the changes happening in a system will go a long way in knowing about the behaviour of the system, acting as a guide for further actions to bring down the corrosion.

In chemical recovery boiler, corrosion protection is provided by close spaced pin studs, flame or plasma metallizing, weld overlaying or composite tubing. When the protection is intact, corrosion is less. The protective measures need the use of advanced metallurgies or extensive studding of tubes in the critical regions. Due to this, actions on the fire side, a tendency to limit steam pressures and tempera-

tures obtainable from such units is possible. Strict maintenance of quality of boiler feed water is a must for prevention of tube side corrosion.

4.0 Experiences in Mysore Paper Mills :

The corrosion phenomena is observed in the following areas.

1. Electrostatic precipitator
2. Super heater area.

A reason for the extent of corrosion in the electrostatic preciptator was traced to the vapours coming out of the ash mixing tank and getting through the rotary feeder into the chamber. Providing sufficient height for the vent minimised the vapours entering the system. The presence of a by pass duct to electrostatic precipitator helps in initial start ups and shut downs.

Corrosion of super heater tubes in the secondary stage is observed in contrast to the primary super heater coil which is not affected. A study is being conducted to findout the reason for this tube punctures, happening near the bends joining the main outlet.

In conclusion, a thorough knowledge about the environment and the medium handled is vital for corrosion prevention A strict monitoring of the parameters is important. The authors express their gratitude to Sri PS Adyanthaya, General Manager for the encouragement and guidance in bringing out this paper.

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