

# Corrosion in pulp & paper industry - prevention & control

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## ABSTRACT

This Article deals with the types of corrosion and the strategy to manage corrosion. Corrosion is prevented and controlled by (i) proper painting of equipment, pipe line and structures with suitable primers and top coats (ii) cathodic and Anodic protection (iii) Electrochemical protection (iv) Selecting and using non-corrosive materials - metallic, and FRP. All these methods have to be used depending upon the situation which have been reviewed. In addition to process equipment and structures, water side of boilers, condensate return lines and cooling water systems have also to be protected from corrosion. The normally adopted strategies for these are also briefly discussed.

It is necessary to know what is corrosion before attempts are made to combat it.

In simple terms corrosion can be explained from two stand points

- i) Thermodynamic
- ii) Electrochemical

Thermodynamically corrosion may be considered as a natural reversal process of metal and alloy production. Metals and alloys are made from their ores by input of energy and hence corrosion is the process through which these metals and alloys tend to return to their natural low energy state (1).

Electrochemically, corrosion can be considered as a process where a metal dipped into a electrolyte solution of its ions tends to dissolve. The metal gives out electrons and forms the anode. In this process, the metal atoms are converted to positively charged metal ions and are available to combine with any negative ions in the electrolyte. In water medium the metal ions combine with OH ions (Because water always has a definite part in the form of OH<sup>-</sup> and H<sup>+</sup> ions). Also if the water

has dissolved impurities such as chlorides, sulphates and carbonates, the positive metal ion tends to combine with these negative ions (2).

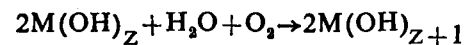
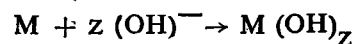
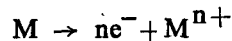
Now for corrosion process to continue, the electrons liberated should be captured.

In the absence of dissolved oxygen, the H<sup>+</sup> ions combine with electrons forming hydrogen molecule.

In the presence of oxygen, the cathodic reaction will be to absorb electrons and to generate further OH<sup>-</sup> ions.

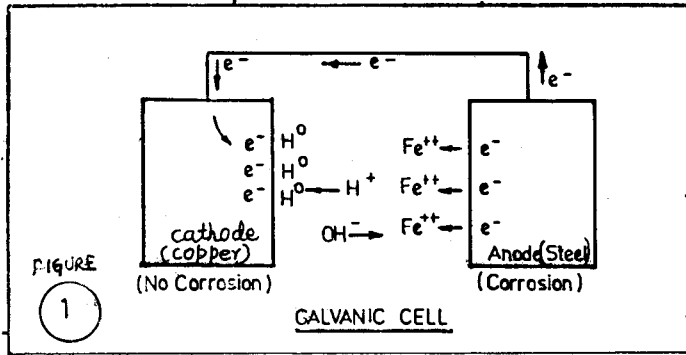
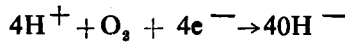
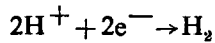
The reactions taking place at the anode and cathode can be symbolically expressed as below :

At the Anode (ie corroding metal surface)

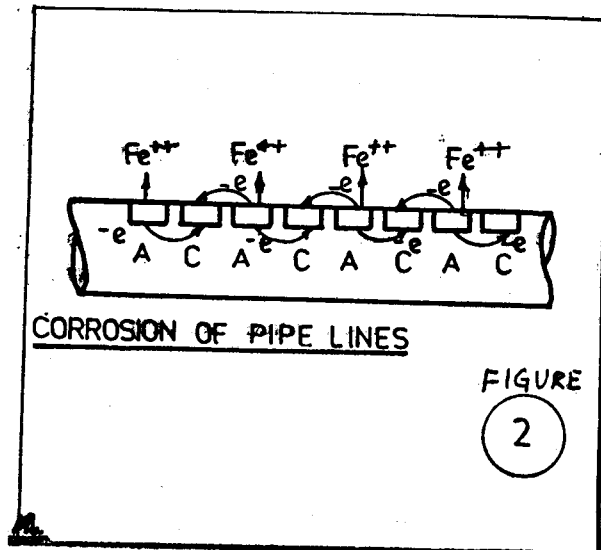


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At the cathode

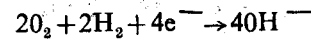


The rate of corrosion depends on Temperature, pressure, presence of oxidizing species, pH of the surrounding medium composition and the condition of the metal surface and exposure of the surface. Almost all commercial metals and alloys are to some extent nonhomogeneous. This discontinuity results in a series of tiny cells (Anode & Cathode) all over the metal surface. Thus the corrosion process sets in.



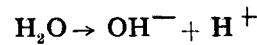
### Corrosion in presence of Oxygen :

In the presence of aerated water, the oxygen in the water provides the complementary electrode process.



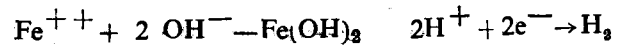
This electrode is capable of absorbing electrons and therefore of acting as a cathode.

For iron or steel metallic equipment :



**Anode reaction**

**Cathodic reaction**

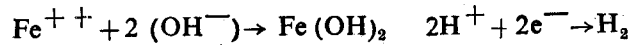


In the absence of dissolved oxygen in water, the following reactions take place.



**Anode reaction**

**Cathodic reaction**



Here, corrosion continues to spread if it is not limited by the absence of high pH or by saturation of the medium by  $Fe^{++}$  ions which cause a protective layer. Provided the layer is not carried away by movement of electrolyte (3).

### Types of Corrosion :

- i) Galvanic corrosion : This type occurs when two dissimilar metals are joined together in a conducting medium. The less resistant (ie active) metal becomes the anodic corrosion site while the resistant (ie nobler) metal becomes the cathode and is hence protected. It can be predicted by studying the Galvanic series given below which classifies metals into positive (noble) and negative (base) metals :

**TABLE-I Source : Water Treatment Hand Book, Degre-  
ment, 5th Edition**

Metal	Electrode reaction	Equilibrium potential, Volts (Theoretically determined)
Magnesium	$Mg \rightarrow Mg^{+2} + 2e^{-}$	- 2.34
Beryllium	$Be \rightarrow Be^{+2} + 2e^{-}$	- 1.70
Aluminium	$Al \rightarrow Al^{+3} + 3e^{-}$	- 1.67
Manganese	$Mn \rightarrow Mn^{+2} + 2e^{-}$	- 1.05
Zinc	$Zn \rightarrow Zn^{+2} + 2e^{-}$	- 0.762
Chrome	$Cr \rightarrow Cr^{+3} + 3e^{-}$	- 0.740
Iron	$Fe \rightarrow Fe^{+2} + 2e^{-}$	- 0.440
Nickel	$Ni \rightarrow Ni^{+2} + 2e^{-}$	- 0.250
Lead	$Pb \rightarrow Pb^{+2} + 2e^{-}$	- 0.126
Hydrogen	$H_2 \rightarrow 2H^{+} + 2e^{-}$	- 0.000 (By con- vention)
Copper	$Cu \rightarrow Cu^{+2} + 2e^{-}$	+ 0.345
Copper	$Cu \rightarrow Cu^{+} + e^{-}$	+ 0.522
Silver	$Ag \rightarrow Ag^{+} + e^{-}$	+ 0.800
Platinum	$Pt \rightarrow Pt^{+2} + 2e^{-}$	+ 1.2 (approx.)
Gold	$Au \rightarrow Au^{+3} + 3e^{-}$	+ 1.42
Gold	$Au \rightarrow Au^{+} + e^{-}$	+ 1.68

Hence It is necessary to take galvanic corrosion into consideration while designing materials with dissimilar metals.

Examples galvanic corrosion in pulp and paper industry are (1) Copper from a condenser or a feed water heater can plate out onto steam-generator tubes and set up localized corrosion cells. (ii) Denickelification of copper Nickel alloys and Dezinkification brass.

#### Pitting Corrosion :

Irregularities or destruction of protective layers on surfaces leads to this type of corrosion. The anodic sites will be on a small part of the surface and cathodic sites can be any where outside it. Crevice corrosion is similar to this.

#### Intergranular Corrosion :

This occurs at grain boundaries especially in heat-affected zones where the metal is not properly stabilized by annealing.

#### Stress Corrosion :

This results from residual stresses from metal working operations or externally applied stresses. It also depends on the concentration of corrodant at a specific location. Most of the metals and alloys can be affected by this. For example copper based alloys are affected by this type of corrosion in presence of ammonia and austenitic stainless steel by chloride induced corrosion. Caustic induced corrosion of this type is called caustic embrittlement. Hydrogen liberated at the cathode can lead to cracks and decarburization.

#### Other Types of Corrosion :

Corrosion by (dry) gaseous environment, usually at elevated temperatures where the corrosion reaction is a chemical combination between the metal and oxidizing component. Corrosion is also possible by solvents such as liquid metals and fused salts in which the corroding metal may be directly soluble.

#### Management of Corrosion :

T. R. B. Watson (2) has mentioned the following methods to control/Prevent Corrosion.

- (i) Isolate the metal from its environment so it has nothing to combine with.
- (ii) Treat the environment to make it less corrosive.
- (iii) Use resistant alloys and nonmetals.
- (iv) Employ electrochemical means of corrosion control.

The first includes coating the structures, equipment etc. with an essentially free from minute pin holes protective film.

The second is usually impracticable in the pulp and paper industry as the environment is imposed. However this may be possible as break throughs in technology may lead to better environments. Nevertheless as we stand today, we have to live with the environment.

The third depends on the availability and cost of suitable metal or alloy or nonmetallic material.

Now we can discuss each strategy in some detail :

#### Painting Structures and Equipment :

David C. Bennett (4) has considered three alternatives to compare cost for bleach plant service :

- a) No coating applied—in this case a part of the structures and equipment need replacement.
- b) Use of minimum acceptable two-coat paint job on the new steel.
- c) Use of 'high quality' three-coat system on the new steel.

A comparison of the costs and asset value at the end of 10 years has indicated (c) as the best strategy. Even here, it is essential to preventively maintain the paintings applied.

#### Coating Selection :

The most important requirement is to enclose the steel of structures and equipment with air tight and moisture resistant protective film.

Hence for bleach plant service, Mr. Bennett considers the following properties.

1. Chemical resistance, especially to aggressive bleaching chemicals
2. Very low moisture and gas permeability
3. Suitable temperature resistance
4. Easy repairability

The properties are all collectively obtainable to some extent in the following generic coatings.

1. Chlorinated rubber
2. Vinyl
3. Amine cured epoxy
4. Amide cured epoxy
5. Coal tar epoxy
6. Polyurethane.

#### Chlorinated Rubber :

They have good resistance to acids, alkalis and permeation. These are produced by chlorinating natural rubber latex. It has been observed that for coating metals, more the number of coats, better the performance with minimum thickness of 152 to 150  $\mu\text{m}$  for good performance leading to higher costs.

#### Vinyl :

These are basically copolymers of vinyl acetate and vinyl chloride. After drying, have good resistance to acids, alkalis, aliphatic solvents and oils. Have low water & gas permeability as also abrasion resistance. Some of the disadvantages are strong odour of the solvent, need for well prepared metal surface and can be applied usually by spraying. Some of these can be overcome by having precoat of proper primers before vinyl is applied.

#### Polyurethane Coatings :

They develop chemical and abrasion resistant films but less resistant to alkalis.

Basically isocyanate groups react with hydroxyl groups (either from atmosphere for single component ones or from a hydroxyl containing chemical such as polyesters, acrylics, polyethers or castor oil.

#### Epoxies :

The generally used variety is condensation product of Bisphenol-A and epichlorohydrin.

Also cross linking can be done using polyamines and polyamides.

Comparatively, amine cured epoxies have better solvent resistance and good hardness as against amide cured ones. But amide cured ones have better adhesion, better resistance and better wettability.

Combination of coaltar, epoxy and curing compound gives a coaltar epoxy. This imparts better water resistance as also to acids, alkalis, salt water, oil and fats. However, the major disadvantage is the recoating problem.

D. C. Bennett has Ranked the above paints taking their resistance into consideration which is given below :

TABLE—II

Coating	Water resist- tance	Abrasion resist- tance	Acid resis- tance	Alkali resis- tance	Bleach chemical resis- tance
Chlorinated rubber	9	6	8	8	8
Vinyl	10	6	10	9	10
Amine-cured Epoxy	8	9	9	9	9
Polyamide-cured Epoxy	8	9	7	9	7
Coal tar-epoxy (polyamide)	10	9	9	10	9
Polyurethane	9	10	9	7	8

10 : Excellent, 8 : Good 6 : Fair

To select the required type of paint for specific applications, it is necessary to consider the properties required as also earlier experience regarding their use,

As a rule, suitable primer should be applied to the properly prepared metal surface. The primers are mainly of three types (i) Barrier Primers (ii) Inhibitive primers (iii) Zinc-rich primers.

**Barrier primers** are impermeable films such as chlorinated rubber or aluminium-flake loaded catalyzed epoxies.

**Inhibitive primers** are commonly composed of oil base, alkyd or phenol-alkyd vehicles that contain small additions of soluble inhibitor such as chromates or nolyledates,

**Zinc rich primers** are highly loaded with metallic zinc.

**Red oxide primers** : These primers are more popular in India.

**Other points on paints and painting** : Rick A. Huntley (15) has opined that it may be more economical to repair the damaged areas (i. e. areas of random corrosion or mechanical damage that require repainting)

and apply a topcoat over the entire surface. To ensure satisfactory performance, he suggests that the steps to be taken as (i) Survey (ii) Adhesion characteristics (iii) System compatibility (iv) Application procedure.

Thomas P. Delany (16) suggest the use of following coating systems for steel in moist atmosphere in waste water plants.

—Epoxy primer and Epoxyenamel, 3 coats, 150 $\mu$ m thick

—Epoxy primer and high build epoxy, 2 coats, 150  $\mu$ m thick

—Vinyl primer and top coats, 3 coats, 150–175 $\mu$ m thick

—Chlorinated rubber primer and top coats, 3 coats, 150-175 $\mu$ m thick

He adds that for exterior exposures, a Vinyl system may be preferred to epoxy because of better chalk resistance and gloss retention upon exposure to sunlight. More recently the trend has been toward use of an epoxy-urethane 3-coat system applied with dry film thickness of 175 to 225  $\mu$ m because of their outstanding protection and appearance.

For normal work a second coat (after primer application) of suitable material described above is to be applied. For severe corrosion areas a third coat of suitable paint is needed. Primer coat : 75 to 100  $\mu$ m thick, Second coat : 125-150  $\mu$ m thick and third coat when needed : 50  $\mu$ m thick.

#### Cathodic & Anodic Protection :

Paper Industry is one of the industries plagued by corrosion but which has been late in considering cathodic and Anodic protection. Though this has caught up in the west, it is yet to take root in India.

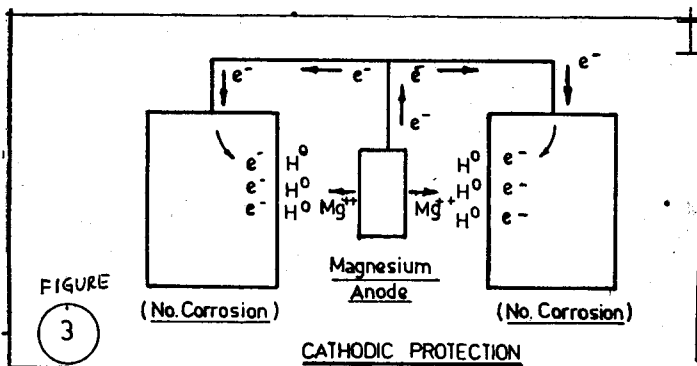
As has been described in the beginning, metals contain energy (Referred to as Gibbs energy) which varies for different metals or alloys. This gives the driving force for corrosion.

The article by T. R. B. Watson (1) gives a good account of cathodic protection in Pulp and Paper industry.

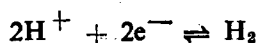
If a metal piece is immersed in water or an electrolyte containing the ions of the metal, a few of the metal

atoms on the surface ionize and escape into the surrounding solution leaving free electrons on the surface of the metal. The metal develops negative charge and the metal ions positive charge. Under defined conditions this reaction will come to equilibrium.

However, if two metals from the Galvanic series (Table-I) are coupled externally, the one with higher negative potential becomes the anode and the other the cathode. Also, the cathodic metal becomes more negative than the solution potential. (Please refer Figure No. 1)



This prevent the escape on metal ions from the cathode, The electrons escaping from the surface of cathode in turn convert H<sup>+</sup> ion into hydrogen molecule



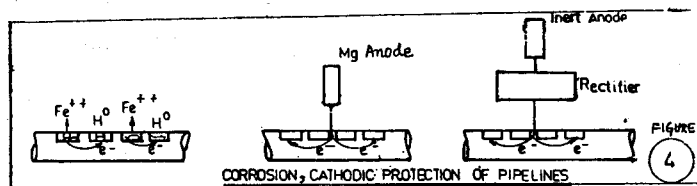
The hydrogen thus liberated form a film on the surface of the cathode leading to what is called "Polarization". This film prevents further escape of electrons.

Now we can observe that the cathode is made highly negative such that corrosion is practically avoided or to put it in other words, it is "Cathodically Protected."

Because of imperfections in metals, tiny cells of anode and cathode are formed leading to corrosion of the metal at anode sites. (Please see Figure No. 2)

The above corrosion can be stopped by introducing a magnesium (or Al or Zinc) anode in between. Now the anode of the original circuit is protected as Mg sacrificially corrods and pumps electrons into the corroding metal, converting it into a cathods and polarizing it. (Please see Figure No. 3)

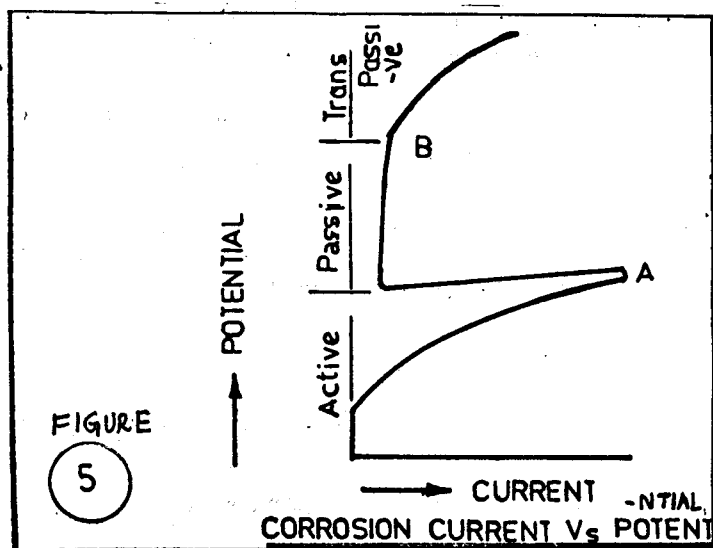
On the same principle, the burried metallic structures such as pipe lines, and internal structures of tank-ages etc. can be cathodically protected. (please see Figure No. 4)



Cathodic protection can be designed based on the sacrificial electrode principle or by suitable external DC supply.

#### Anodic Protection :

A metal anode corrodes. More anodic potential it is made more the corrosion. At a particular potential, however, the metal passivates and corrosion reduces to a very low value. The potential at which the passivation starts is called 'Flade potential.' If the metal is maintained at the passivation potential, corrosion is minimized. The small amount of corrosion taking place ensures that the passive layer is repaired regularly.



In Chemical Industries, steel tanks used for storing H<sub>2</sub>SO<sub>4</sub> are protected this way. This is likely to become a important method for digester corrosion control.

**Electrochemical protection :**

The paper published by L.H. Laliberte and A. Garner indicates that this method can be successfully applied to control corrosion of 317 L SS. (5).

**Process Equipment made of FRP :**

These material are becoming popular mainly because of their excellent resistance to corrosion and also their ability, when the appropriate additives have been incorporated to resist heat and/or fire (6).

FRP is a composit material consisting of a thermo-setting polymer, often a type of polyester, reinforced with glass fibres.

There are six types of FRP resins : isophthalic, orthophthalic, chlorendic, bisphenol A fumerate, furan and vinylester.

Corrosion resistance of different types are given in table-III,

TABLE—III Comparitive corrosion resistance of various types of FRP's  
( Data from Ref. 6 )

	Acids	Alkalis	Pero- xides	Hypochlo- rites	Solvents	Flameretar dance	Structural Strength	Thermal Insulation
Isophthalic	B	B	C	C	B	C	A	A
Orthophthalic	C	C	C	C	C	C	B	A
Chlorendic	A	C	A	A	B	A	A	A
Bisphenol A fumerate	A	A	B	B	B	C	A	A
Furan	A	A	C	C	A	B	A	A
Vinylester	B	A	B	B	B	C	A	A
Carbon steel	C	B	C	C	A	A	A	C
Stainless steel	B	B	C	C	A	A	A	C

A : High resistance, B : Moderate resistance, C : Low resistance

TABLE IV  
Heat-resistance characteristics of FRP Laminates and resin castings.

	Continuous operating temp. of FRP laminates system containing 65% glass	Heat deflection temp. of clear cast resin containing no glass reinforcement
Isophthalic	135°C	97°C
Vinyl Ester	121°C	100°C
Bisphenol A fumerate	145°C	132°C
Chlorendic	182°C	150°C

While selecting FRP material, it is necessary to evaluate cost, resistance to chemicals to be in contact, pH, temperature, abrasion, etc. In addition to the corrosion control and prevention of process equipment, pipe lines and structures, (including those of fresh water and effluent systems), it is also necessary to prevent and control of corrosion of boilers, cooling water systems and condensate systems. These will be briefly mentioned.

#### **Boiler :**

The necessity of boiler water side corrosion and scaling control has been well recognized by most of the mills.

The parameters which need control are hardness PH, oxygen content, dissolved iron and copper, dissolved solids and silica. In past much attention has been directed at over heating of boiler metals, because of scale-build up. Newer mills operating at higher pressure with D. M. make up take into account the potential of caustic corrosion of boiler metal. Also iron has evolved as the major source of problem facing pulp and paper industry utility personnel today (7). Many mills are still using zolite/limesoda process for softening water to produced boiler feed water. However, the trend is towards use of D. M. water which has many advantages.

The boiler feed water is then deaerated and conditioned with pH controlling chemicals, oxygen savengers, polymeric dispersants and phosphates(8).

For D. M. water make up systems, the trend is towards use of volatile alkalizers and oxygen scavengers to minimize dissolved solids and also to reduce blow downs(9).

#### **Condensate Systems :**

Condensate polishing has become a popular and effective method for control and reducing the migratory corrosion products entering the boiler, However, to prevent condensate return line corrosion, neutralizing amines (such as morpholine) and film forming amines (such as cyclhexylamines) have to be used. The popularity of these chemicals in pulp and paper mills in India is not as much as it should be; looking into the benefits.

The principal chemical causes of condensate system corrosion are (10) :

- i) Carbonic acid attack
- ii) Attack by dissolved oxygen
- iii) Process contamination of condensate
- iv) Steam carryover

When properly supplied, in most steam generating systems, neutralizing and film forming amines can provide adequate control of both general and localized corrosion. Using catalyzed hydrazine with amines further enhance their action (11).

#### **Cooling Water System :**

The earliest chemicals used for scale and corrosion prevention were the polyphosphates. A serious drawback of this treatment approach is the potential reversion of the polyphosphates to orthophosphates leading the fouling and pitting type corrosion. The next chemical used was chromate. This being an anodic inhibitor may actually increase corrosion if insufficiently added and is also toxic. In some mills, the cooling water treatment is confined to treating the water with only sulphuric acid to control langlier index and to dose hypochlorite in shock doses to control slime growth.

The latest addition to this source are organophosphonates which function as good antiscalants and inhibitors (12, 13).

Acid cleaning of Paper Machine Poshporbroze wire Moulds and other metallic equipment such as boiler tubes, heat exchangers etc.

It is essential to prevent excessive acid corrosion during these operations which can be done effectively by use of inhibitors available in the market (14).

From the foregoing it is apparent that corrosion management needs a scientific approach in terms of material selection, paint selection, preventive painting, cathodic and Anodic protection.

#### **Acknowledgements :**

We are thankful to the Management of the Sirpur Paper Mills Limited, for permitting us to publish this paper.



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