

# Corrosion due to system closure in paper machine section and possible remedies

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## ABSTRACT

Increase in the population and industrialization has made fresh water a costly input which was till sixties a cheap commodity. Paper mills use large amounts of fresh water creating voluminous effluents. Stringent regulations to reduce pollution necessitates effluent treatment to bring down the amount of pollutants, also larger the effluent volume the more is the cost of treatment. Dilution is not a solution to the pollution problem as in most of the developed countries absolute amount of the pollutants per ton of the product and not the concentration is the criteria.

One of the methods to reduce the effluents volume is to recycle the process water. Complete or substantial closing of the system in paper machine section leads to considerable loading of process water i.e. higher temperature, higher acidic conditions (low pH) and higher concentration of ions. These conditions result in increased corrosion of various machinery part viz. pipe lines, stock and back water lines and the wire pits etc. Corrosion is more severe due to the presence of microbes and the growth of the microbes is rapid where water system has been closed completely. The microbiological corrosion has been observed in stainless steel in the form of pitting. Galvanic corrosion was prevalent in older mills where changes of equipment, pipes etc. with different metallurgies took place.

Partially closing the system rather than completely has been practiced without encountering severe problems of corrosion. Lowering the temperature of the system, removing corrosive species, addition of corrosion inhibitors, aeration of the process water, selective application of the biocides, use of proper material, protective surface coating, avoiding long detention of white water or stock are some of the measures which could substantially decrease the corrosion.

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In the last few years corrosion of equipments in paper Industry has become an almost universally encountered problem. The process changes which are actually responsible for the wide spread increase in corrosiveness include those made with the objective of saving energy and others made to curtail pollution. mechanical and chemical cleaning methods are necessary for maintaining the equipment but this could affect the form and rate of corrosion. Increased corrosion is being observed due to more acidic conditions and rising temperatures and chloride levels in process

waters. Corrosion in continuous digesters is not as serious as in batch digesters, because these are not subject to the frequent temperature cycling of batch digesters, and also because these are closed systems with little exposure of the metal to the air. Problems that do occur usually involve pitting and cracking of the welds. Most corrosion problems in the bleach plant are connected with piping, pumps and pulp

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washers in the chlorine stages because of the acidic conditions. Pitting, crevice corrosion, and some stress-corrosion cracking are the most common types of failure and are usually caused by the free chlorine concentrations in the bleach system. In recovery boiler, corrosion included leaks which can occur at tube welds which allow water or steam to mix with the hot smelt in the furnace region and may cause explosions. Corrosion problems in black liquor evaporators include erosion-corrosion in the vapour head, cracking and galvanic corrosion at mild steel-stainless steel welds and pitting on the liquor and vapour side of tubes. This article reviews the corrosion encountered in the paper machine area and current knowledge of the corrosivity of white water when the system is closed. The rate of corrosion and its control for different parts is also included.

We have been talking of the water reuse in paper mills for a longer time. But how will a closing of the system affect the equipments, is an important question. The use of stainless steel has apparently reduced the problem for mill running under standard conditions.

Closed cycle operations have imposed more stringent limitations on materials performance, particularly with regard to pitting and crevice corrosion.

There are in fact several reasons for the increased rate of corrosion. Firstly high temperature, causing faster chemical reactions. Secondly higher dissolved solids, causing increase in cell currents. And lastly high suspended solids, increasing system deposits and thus, anaerobic conditions under these deposits

#### WHITE WATER REUSE AND CORROSION

Past considerations of corrosion in white water environment were not specifically directed towards closed systems. Overbagh and Birchard reviewed some types of corrosion possible in paper mill (1). Muhonen showed that the effect of small changes in pH, temperature and certain additives used in paper making was insignificant on the polarization behaviour of type 304 and 316 stainless steel in white water (2).

The corrosion is one of the eight basic technical problems among the many difficulties encountered in water recycling (3,4) Table I.

TABLE I—WHITE WATER AND ITS EFFECT ON VARIOUS EQUIPMENT

S. No.	Equipment	Reason	Type of Corrosion
1.	Stock piping	Rough and uncleaned surface, presence of weld projections causing stock hand up.	Pitting or micro-biological attack, fatigue cracking of welds.
2.	Head boxes	Presence of embedded iron, iron oxides, weld spatter, slag, misuse of carbon brush for weld cleaning and pressure of pockets.	Crevice corrosion and pitting or microbiological corrosion particularly in head box apron and slice nips.
3.	Wet end structure	Accumulation of pulp deposit on metal surface.	Microbiological
4.	Vacuum pumps	Fresh water contamination by excessive White water carry over, use of white water as seal water, low flow rate of fresh water.	Erosion
5.	Suction rolls	Changes in design and machine environment (increased machine production & speed).	Corrosion thinning; pitting corrosion fatigue & stress corrosion cracking.
6.	Roll journals	Humid paper machine atmosphere splashing of white water, formation of damp pads exposure to cleaning chemicals.	Corrosion fatigue cracking.

Concentration of dissolved solids and gases, pH, temperature and velocity are the major causes of corrosivity of white water. These factors will vary widely with the type of clarification system used for recycled water and the grade of Paper being manufactured. The concentration of dissolved solids ranges from 1,600 to 5,000 ppm for fine papers while for board it is 6,000 to 70,000 ppm (5). The relative amount of each component of the dissolved solids in the water varies with the type of furnish, additives, and the hardness of feed water. The reported level of dissolved solids and ionic concentration for different categories of paper are given in table II & III (3, 4, 6,) respectively.

Because of the limited information, no specific comments could be made concerning the level of particular species build up for full closure among different paper categories. From the point of view of corrosion the anions like chlorides, sulphur compounds and

carbonates are very aggressive in nature while influential cations are the ferric and manganese ions as well as the calcium, magnesium and barium scale formers.

TABLE II—REPORTED LEVELS OF DISSOLVED SOLIDS IN WHITE WATER IN DIFFERENT MILLS MANUFACTURING DIFFERENT GRADES

Mill	Grade	Closure (%)	Dissolved solids (ppm)
1	Fine papers	70-100	5000
2	Paper board	70-100	7000
3	Newsprint	100	1600
4	Duplex	100	8000
5	Catalog	72	1900
6	Paper board	100	10-2000

TABLE : III PERCENTAGE OF EACH CONSTITUENT IN DISSOLVED SOLIDS IN WHITE WATER

CATEGORY	Fe	Cl	So <sub>4</sub>	Mg	Ca	Al	Si	P
FINE PAPER	0.17	5.12	39.3	0.48	0.84	2.67	7.56	0.25
	0.05	6.59	61.2	0.97	1.62	2.22	5.29	0.39
	0.27	5.56	54.9	0.54	1.28	1.01	1.43	0.06
PACKING DUPLEX	0.005	39.40	40.50	0.23	19.72	0.015	—	—
	0.010	41.60	37.80	0.74	19.80	0.018	—	—
	0.020	50.40	23.30	—	26.20	0.050	—	—
	0.180	20.00	33.40	3.40	42.10	0.770	—	—

Streebin and coworkers reported that the corrosion rate of mild steel, cast iron and brass more than doubled in going to a closed system in a paper reprocessing board mill (7). While the same increase was true for type (304) stainless steel, the corrosion rate however was insignificant.

The temperature in a fully closed system is reported to be in the range of 54.71°C. Corrosion kinetics are dependent on temperature and corrosion rate will increase as the temperature increases (5).

Very little data is available regarding the presence of dissolved gases in recycled water but it is expected that concentration of dissolved oxygen and carbon dioxide are very low in low pH, high temperature white water.

### KINETICS OF CORROSION PROCESS

The actual rate of corrosion in aqueous media can be assessed without considering the influence of physical/chemical parameters at a given level of pH. Uhlig has shown that the corrosion of unalloyed iron materials is increased by oxygen and carbon dioxide (8). While oxygen accelerates corrosion more than carbon dioxide, significant increases in corrosion rate are shown when both are present at increased temperatures. At 5cc of oxygen per liter of water, the corrosion rate of mild steel as a function of pH is greatest below pH 4 but remains significant until passivation at around pH 10. Fig. 1 shows the effect of chloride on corrosion of mild steel in distilled water adjusted to various pH values (9). Again corrosion is significant upto values of pH 9.5-10. Alum acid white water and carbonic acid are common causes of acidic conditions during paper making. Chloride attack can cause pitting corrosion under near neutral conditions (8) stainless steel alloys Type 304L and 316L are susceptible to pitting corrosion by chloride attack, regardless of the pH level.

In addition to the effects of pH and chloride, stainless steel alloys are vulnerable to localized corrosion caused by thiosulphate ions. In white water containing thiosouidhate, there is a synergistic effect with chloride that corrodes, even the higher alloyed types 316 and 317 stainless steel (10). Although thiosulphate is known to be active in biological processes, its roll in

conjunction with bacteria commonly found in paper-making system remains obscure (11). However, it is clear that the sulphate species contribute to one of the most devastating of all metal corrosion processes i, e. microbiological attack via. Sulphate reducing bacteria. The occurrence of sulphate reducers and the accompanying corrosion in alum-acid papermaking systems have been the subject of numerous reports (5, 11).

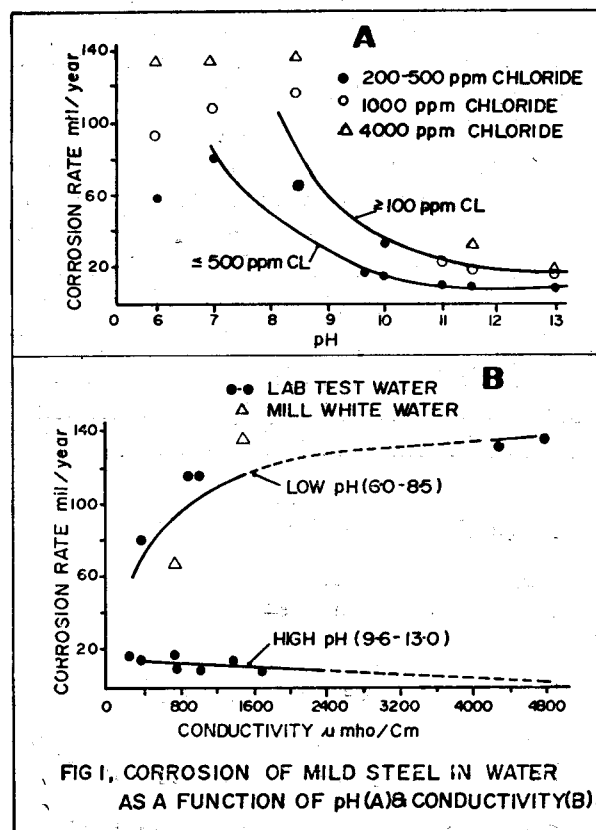


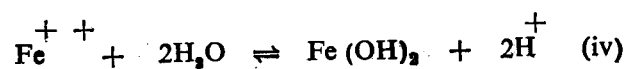
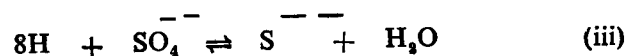
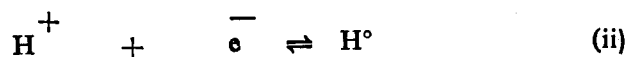
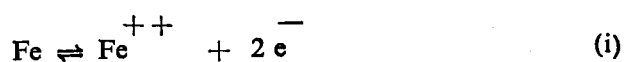
FIG. 1. CORROSION OF MILD STEEL IN WATER AS A FUNCTION OF pH (A) / CONDUCTIVITY (B).

Organic constituents together with dissolved solids efficient nutrients for various species of microorganisms. Oxygen dissolved in the process water first accelerate the growth of aerobic bacteria which then quickly absorb dissolved oxygen, Hence it results in a low concentration of dissolved oxygen in closed systems, Now such low oxygen content favours growth of anaerobic bacteria. Thus depending upon the prevailing physical characteristics and chemical composition, system specific population develops within a short time as it is difficult to maintain the conditions like pH at about 6, temperature at about 30°C and dissolved oxygen content at between 0 and 2 mg/liter (12).

## TYPES OF CORROSION & THEIR MECHANISM

The major forms of corrosion noticed are micro-biological, impingement (erosion), galvanic, cavitation and crevice or deposit attack. Usually several forms of corrosion will occur simultaneously (13).

Microbial corrosion can be difficult to detect and monitor. It is a type of corrosion which is initiated and accelerated by the action of microbes and usually it is associated with the absence of oxygen. In paper machine water and stock system conditions are favourable for the growth of microbes because of the presence of nutrients in the form of dissolved organic materials, dissolved inorganic salts, and a favourable temperature, the aerobic bacteria thiobacilli form sulphuric acid from sulphur, sulphite or thiosulphate and if localized by deposits, this can cause pitting corrosion. The details of the microbiological corrosion of iron and steel have been reviewed by Updegraff (14) and the electrochemical reaction of anaerobic corrosion in the presence of sulphate reducing bacteria described. The following reactions have been proposed :



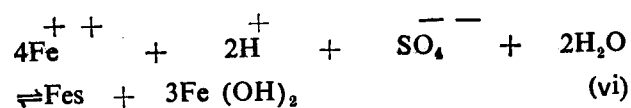
The resulting decrease of the amount of hydrogen absorbed on the steel stimulates further discharge of hydrogen which accelerates the dissolution of steel. The dissolved iron ion will get hydrolyzed,

The  $\text{S}^{--}$  ions produced react with iron or other metal ions to form a sulphide deposit e.g. ,



Such sulphides are a characteristic product of corrosion in the presence of sulphate reducing bacteria.

The over all reaction may be written as follows.



Similar equations apply to the production of  $\text{Fe}_2\text{O}_4$  and  $\text{Fe}_2\text{O}_3$  and to the corrosive attack on other metals and alloys e.g. on stainless steels.

Slime deposits cause aeration cells. Beneath thin slime deposits, which are oxygen rich, the metal surfaces lose electrons, setting up a corrosion cell.

The increasing velocity and level of suspended solids concentration in white water in closed loops cause impingement corrosion. Precipitates which may also form, have a high abrasiveness. The grits usually present in the sludge from clarifiers is one of the causes of acceleration of erosion.

Galvanic or dissimilar metal corrosion is prevalent in those mills that are old or have, over the years, been patched up with many different metallurgies.

The recycled water acts as a stronger electrolyte as its concentration and temperature are quite high. Lower pH will also aid this corrosion and concentrations of high solids yield ions of metals.

Cavitation is caused by formation and collapse of vacuum bubbles of the metal surface. The high impacts wear away protective film, exposing metal to corrosive effects. This is seen at points of high vacuum and also on the impellers of the pumps.

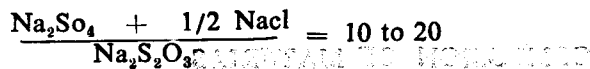
Crevice corrosion is a form of pitting which can quickly cause metal perforation, even with 316 stainless steel when the protective chromium oxide film is damaged. The presence of fibers in fouling processes (e.g. . scaling ) pervade all areas of paper making. Crevice corrosion beneath fiber deposits on stainless steel has been reported to be influenced by the wicking action of the fiber to transport bulk water to the shielded metal surface. The corrosion at the wet metal interface is influenced by a number of factors like the composition of back water, surface metal and stagnation time etc.

In the presence of aggressive anions such as chlorides, the safe potential is narrowed. If a certain critical potential is exceeded, chloride ions can even attack the stainless steel surface. This attack will develop the pits because passive film break down occurs only in isolated locations, such as weak spots in the film due to defect in the underlying metal. Pitting attack is favoured by the following conditions.

- Higher chloride concentration.
- Higher temperature.
- Highly oxidizing conditions.
- Low pH.
- Stagnant or low velocity conditions.
- Lower molybdenum content in the stainless steel.

A new chloride pit tends to repassivate unless the favourable conditions for initiation are maintained until the pit has become established. And thus metal becomes anodic in the pit with respect to the surrounding metal outside, which becomes cathodic because of ready access to dissolved oxygen for the reduction of half of the net corrosion reaction. The generation of free hydrogen ions, produced as a result of anodic dissolution and later hydrolysis of metal ions, will promote the diffusion of additional anions into the pit to maintain charge neutrality. The chloride ions which are more mobile than sulphate ions migrate into the pit. The solution inside a growing pit may have a solution of hydrochloric acid and pit growth may continue almost independently of external conditions.

Thiosulphate is an aggressive pitting agent, particularly for stainless steels that do not have molybdenum. Thiosulphate pitting occurs below a certain critical potential - the thiosulphate reduction potential. The reduction of thiosulphate in the presence of hydrogen ions produces an adsorption of sulphur monolayer on the metal surface. This adsorbed sulphur reactivates the anodic dissolution of the metal and hinders repassivation. The worst case for thiosulphate pitting occurs with in the molar concentration ratio :



The pits once formed are very stable and are not subject to spontaneous repassivation. Scratches encourages the initiation of pits. Few, large pits tend to form rather than many, small pits, as in chloride pitting.

#### CORROSION CONTROL METHODS :

Improved corrosion control can be obtained through strict pH, temperature, deposition and corrosivity monitoring at a number of positions in the system.

By preventing reaction (1) from taking place, the problem of metal dissolution will be solved. By this the second reaction will be automatically controlled. This control could be based entirely on the selection of a particular metal or alloy in consideration of its engineering and corrosion resistance properties, in preference to all other metals or alloys, or the rejection of metals in favour of a non metallic material (15) on the hand corrosion may also be controlled by choosing less corrosion resistant material and bringing down the aggressiveness of white water by (16, 17)

#### (i) Measuring and controlling

- the concentration of (a) Al<sup>+++</sup>, (b) chloride ions and (c) thiosulphate (5) and 10 ppm for equipment made of type 304 and 316 stainless steel (18).
- pH ( > 4.4 )
- Sulphate reducing bacteria, slime.

#### (ii) Lowering the temperature of the system (≤44°C)

(iii) Removing corrosive species — preventive control of the fiber material, fillers and additives.

#### (iv) Adding corrosion inhibitors.

(v) Washing of the system and giving good biological treatment ,

(vi) Keeping system clean and avoiding long detention of white water or stock.

(vii) Aeration of the process water.

(viii) Well balanced selective application of biocides.

The effective corrosion control may be brought about by the implementation of following steps.

- Selection of material.
- Modification of metal.
- Change in design.
- Change in corrosive environments.
- Protective surface coating and
- Change of electrode potential of metal/corrosive medium.

The most common method of corrosion control is, the proper selection of material for a particular corrosive environment based on the characteristics of the medium as well as of the materials.

The material of construction of paper machine equipment include—

- (a) Unalloyed iron (cast iron & steel)
- (b) Alloys of copper (brass and bronze) and
- (c) Stainless steels (type 304 and 316)

Experiments have revealed that type 316 stainless steel has much improved resistance to microbiological corrosion over types 304 and others. Use of type 316 as therefore will eliminate most of the microbiological corrosion. This infact is due to higher cotent of molybdenum content, which has been found to be resistant in most mill studies (Table IV). A good surface finish on the material selected will be an added advantage in controlling the corrosion. To avoid microbiological corrosion the surface of the material should be free of any oxide film from welding. Welding joints should be shielded with argon on the front and back sides of the weld (17).

For reducing galvanic corrosion, the dissimilarity of metals in electrolyte (white water) should be avoided. Therefore possible use of same metal be maintained in the construction of equipment. Galvanic corrosion can be overcome by cathodic protection which may be provided by a rectifier or a replaceable sacrificial galvanic anode. The couch roll corrosion can be overcome by a combined deposit control/corrosion inhibitor programme, monitored corrosion coupons and copper analysis of water.

In addition the following steps should also be regarded as essential in relation to the efficiency of above methods of controlling the corrosion—

- Testing and monitoring of corrosion
- Supervision and inspection.

#### CONCLUSION :

In largely or completely closed water systems, corrosion problems have been a frequent handicap. The main cause of corrosion is the increase in incidence and severity of pH, temperature, level of concentration, specific environmental species, sulphate reducing bacteria, slime etc. due to system close up. The higher temperature and presence of nutrients in the system favoured the growth of microbes which caused

TABLE : IV—CHEMICAL COMPOSITION OF MATFRIAS

ALLOY	C	Mn	Si	P	S	Cl	Ni	Mo	Cu	Co
304	0.059	1.38	0.52	0.025	0.014	18.15	8.89	0.15	0.12	0.15
304 L	0.019	1.76	0.47	0.024	0.018	18.33	9.52	0.40	0.31	0.25
316 L	0.022	1.75	0.52	0.029	0.016	17.16	10.40	2.07	0.33	—
317 L	0.019	1.83	0.54	0.033	0.026	18.37	13.64	3.18	—	—

microbiological corrosion. The closing of the system did not even spare stainless steel from corrosion. Microbial attack on iron or stainless steel appeared in the form of pitting. And in most of the cases it was visible in the form of physically unstable crusts made up either of black ferrous sulphide or white ferrous hydroxide. Hence the control of microbial activity and corrosion is essential to the cost effective closure of machines

The concentration of corrosion aggressive ions ( $Al^{+++}$ ,  $Cl^-$ ,  $S_2O_3^{--}$  and  $SO_4^{--}$ ) should be controlled. The concentration of thiosulphate ions should be kept 5 to 10ppm for equipments made of type 304 and 316 stainless steels so as to minimize pitting attack. The efforts should be made to increase the pH ( $> 4.4$ ) and to reduce to temperature ( $< 44^\circ C$ ). If the concentration of dissolved oxygen is maintained between 1.5 to 2 mg/liter, the conditions of the process water may be improved and hence the corrosion may be controlled considerably.

Steps should be taken for the possible control of the fiber, fillers and other wet end additives. Integration of biological and physical treatment stages, aeration of the process water and selective use of biocides will definitely help in controlling the corrosion of equipment.

The use of higher quality of steel Type 316, 321 will also help in overcoming the problem of corrosion.

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