Investigations into Bleach Plant Corrosion Problems

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ABSTRACT

Corrosion, a natural menace, shows its destructive effects in Bleaching Section of a Paper mill to an extent greater than that in other sections. The targets are mainly steel equipment e g. washer vats, drum, pipe lines etc., concrete structures, which consequently loose their mechanical strength. The culprit being oxidising aqueous environment which are acidic/alkaline consisting of Cl-, ClO_2, hypochlorite etc. There are several alternatives to minimise the losses due to corrosion e.g appropriate material selection, protective coating, electro-chemical protection. Case studies presented show them economically viable too. However, to apply any of these alternatives effectively it is essential to have indigenous data on such aspects as corrosivity of different aqueous/gaseous media prevailing in Bleaching section, corrosion rate of various steel grades in these media tendency of experiencing localised corrosion, passivation, behaviour stability of protective coating in these media etc. etc. Unfortunately this data is almost completely missing in the case of Indian Paper Mills. With en aim of filling this gap, a research programme has been started at the institute. The present paper gives an account of the type of tests, both laboratory and mill tests, being carried as a part of this programme. Some of the results obtained are presented in the report. These pertain to corrosion rate determination, characterisation of rust and Electrochemical behaviour. The results have been analysed with respect to the chemical environment to which the coupons were exposed. Usability of these parameters has also been discussed. As the present report relates to only the initial stage of the research programme, anything conclusively cannot be drawn out presently. It needs further more tests, outlined briefly in the report, to be carried before concrete suggestions are put forth in terms of appropriate choice of steels, their corrosion rate, corrosivity of different media encountered in bleaching section, possibility of protection through application of electro-chemical systems, coating etc.

INTRODUCTION :

Chemical Industry, in general, are prone to vagaries of corrosion in terms of loss of economical value of material of plant equipment. The same is true about Pulp and Paper Industry also. In fact this is one of the first industries which used stainless steels quite widely[1]. It gives a qualitative idea about the degree of corrosivity in different sections. A survey conducted around 1970[2] estimated the worldwide cost per year of corrosion exceeding US $ 300 million in the manufacture of Pulp and Paper products. It was also concluded that corrosion may account for nearly 20% of the annual maintenance expenditure. Unfortunately no such authentic published data is available in the case of Indian Paper Mills as revealed by a recent survey conducted by NPC[3]. The survey estimated, conservatively the loss due to corrosion in Indian Mills at Rs 160 million, which might be much less than actual loss as per their apprehensions. Strangely the industry as a whole has so far tended to accept the huge loss due to corrosion with resignation treating it as an unavoidable phenomenon to be dealt with by unspecialized mill personnel as exigency demanded. This avoidable loss due to corrosion are going to increase dramatically due to basically two reasons—

(i) The inflationary cost of materials and labour.

(ii) Due to government rules for controlling environmental pollution, the mill will have to go for 'Close' systems which means recirculation of aqueous media giving rise to enhanced temperature, chemical concentration and lower pH's in some of the cases.

As such in coming years, the mills have to think in terms of taking protective measures against corrosion loss to keep the process 'economical'. This is further desired in view of the development of better corrosion resistant materials and protection methods.

Among the different sections, bleaching section presents most corrosive environment in a Paper mill. This is apparent from the study of a survey conducted

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in USA[4] that bleach plant is responsible for approximately 50% of the total cost due to corrosion. Here again no such data is available in case of Indian mills. In view of the above situation, a project has been under taken at the Institute for investigating corrosion problems pertaining to bleaching section.

There are four possible ways in which corrosion losses may be minimised. These are given below :

(i) Employing Suitable corrosion resistant alloys e.g. stainless steels, Incoloys, Hastelloy etc. or nometals.

(ii) Employ electrochemical protection systems[5].

(iii) Avoid contact between metallic surface and aggressive environment by putting corrosion resistant lining or by coating[6].

(iv) Change the environment to make it less corrosive.

Among the above, alternative (iv) is out of question. In view of the environmental pollution, all bleaching processes employing chlorine or its compound are to be replaced by a process making use of O_2, peroxide, ozone etc., and hence it is worth taking a look at the change in the corrosivity of environment due to above mentiond development. However, the present project does not aim at this aspect.

COST EFFECTIVENESS :

The desirability of taking up such a project depends upon whether the protective measures taken, on the basis of results of corrosion tests, lead to reduction in overall cost of production or not. Case studies given below suggest such measures to be economically viable

In manufacturing any plant, one can consider starting material as mild steel (ms) and then alloyed Steels (mainly SS) if the former is not economical to use. Following are given some aspects for ms and SS

	Mild Steel	Stainless Steel
Cost (per ton)	Rs. 5000/–	Rs. 40,000/–
Average Corrosion rate (in mpy)	50*	10**

* In some stages the rate is even higher than 100 mpy.

**There are no available values for Indian mills. The value given is for a typical canadian Paper Mill.

—Yield Strength of ms is 1/4th of that of SS (Cold-worked).

—Down time cost will be much higher in case of ms plant than in SS plant.

The above factors lead to conclusion that it is economical to use SS in place of ms where corrosion rates of ms $\geqslant$50 mpy. This is the situation considering uniform corrosion. However, due to presence of chlorine in various stages of bleaching section ms is prone to localised corrosion e.g. pitting, crevice corrosion. In such cases—SS-316, 316L, 317, 317L are used, which have much better resistance against localised corrosion, even in cases where ms corrodes at a rate lesser than 50 mpy.

It is hence useful to discuss economy by comparing cases of SS bleach plants. This discussion is to be centered around three situations—

I. UNPROTECTED :

Consider a plant having output of 100 TPD. Such a plant is expected to use 75 tonnes of steel in bleach plant. Steel selected to from such a plant has surface of$\sim$ 250 ft^2 /ton[6] Considering a time span of 10 years, the % of steel lost due to corrosion 40% (corrosion rate 10 mpy).

Cost of the Steel lost — Rs. 1.2 million

To make up for this loss, 30% of the steel has to be replaced.

Replacement cost 4·5x (cost of fabricated equipment)[7]

This comes out to be Rs. 3,60,000 per ton and hence total replacement cost is Rs. 8.10 million. Thus cost in 10 years due to corrosion losses comes out to be Rs. 9.3 million. For a mill is USA, this cost is $ 6,30,000[6] for plant of 800 TPD capacity. The difference in the price is basically due to much higher price of SS in India as compared to that in USA.

II. SYSTEM WITH PROTECTIVE COATING :

Normally the surface is done two-coat paint job. The actual figures for coating are not available in the

case of Indian Mills. However, from a rough estimate one can start with a rate of coating as 20/– per Sq. ft. (This does not include the cost for 'sand blasting' for surface preperation and another coat of primer material). To include these two as well. It will be safe to start with a figure of 60/– persq. ft. Total surface to be given initial cost is 19000 ft². Cost of initial coating will be Rs. 1.14 million. Cost of recoating in USA is about 4 time the cost of initial coating[6]. From that account the cost of recoating in India should be around Rs 240/- per sq. ft. According to normal standards 50% of the total surface should be recoated in 10 years of time in a bleach plant. From those standards, cost of recoating comes out to be Rs. 2.28m. Hence total cost due to corrosion loss in a system with protective coating comes out to be Rs. 3. 42 million. In a USA mill, this cost has been calculated as $ 3,30,000. This means as annul cost saving of $ 30,000 due to painted structure.

III SYSTEM WITH ELECTROCHEMICAL PROTECTION :

Another and more recentlly developed alternative[8] of protecting system is by electrochemical means. Since Electrochemical system still do not exist in Indian Mills, the example with be taken of a system in use in many north American Mills[4]. A 317L washer used here has a life expectancy of 5 years. Cost of washer drum is $ 250,000 Electrochemical protection system costs around $ 30,000. Running cost of such a protection system is negligible, considering return on investment at a rate of 12% it has been shown that 50% reduction in corrosion rate (thus enhancing life expectancy of washer drum from 5 to 10 years) gives an annual cost saving of $ 20,000. Similarly reduction of corrosion rate by a factor of 4 (life expectancy increased from 5 to 20 years) gives annual cost saving of 34,000. These calculation do not include any savings in maintenance and down time costs, in antichlor consumption Thus this method may prove to be much more economical than protective coating method.

NATURE OF STUDY

The above section gives ample justification for using any of the above protective methods in order to minimise Corrosion losses. It can be seen that to apply them, data on following aspects are needed with reference to Indian mills.

(i) Corrosivity of various stages and aqueous media encountered in bleach section.

(ii) Corrosion rate of different kinds of steels e.g. C—steel, SS—316, 316 L, 317 L, 430 etc. as are normally used in fabricating the plant equipment.

(iii) Resistance of such steels against localised corrosion e. g. pitting, crevice corrosion in above mentioned environment.

(iv) Tendency of above steels to passivate i.e. Electrochemical potentials of steels between which their corrossion rate becomes extremely low.

Properties at (iii) and (iv) above can be measured using electrochemical experiments eg. Tafal plot, potentiostatic polarisation etc. These are helpful in developing electrochemical protection systems.

(v) Cost of coating and recoating a steel equipment.

(vi) Stability of coating in the conditions present in bleach plant e.g. temperatures, mechanical stresses etc.

(vii) Ease and safety of application, surface preperation requirements, number of coats required, adhesion to new and old coatings or surfaces.

(viii) Corrosion reactions, rate etc. of steel surface beneath the coating.

As the information pertaining to above aspects with reference to Indian mills are hardly available in literature or otherwise it requires a large scale effort to be made in close co-operation between the mills and the Institute of Paper Technology. An inititative has been taken by the Institute in the form of a research project being carried since April 1986 with the financial assistance of Department of Science and Technology, Govt. of India. The project aims at gathering data related to aspects mentioned above at no(i) to (iv). These data should help in minimising corrosion losses through selection of appropriate material and development of indegenous electrochemical protection system in later years. Work on aspects related to protective coating has not been preferred at present due to apprehensions on long term integrity of steel-to-resin bond[5] Nevertheless the project is worth trying.

A brief idea is now being given about the tests that are currently undergoing/are to be performed, the results

obtained/are expected to obtain as a part of the project. In the end is presented a brief about the future plan of work.

EXPERIMENTS/TESTS

In a project of this nature, one has to perform tests in laboratory as well as on the actual mills sites Where as the former helps one in predicting the corrosivity of environment and behaviour of material in a controlled environment, the latter gives information on these aspects at actual site where the material is exposed to real life problems.

As such mill tests and laboratory tests have been/ are to be conducted to ascertain the corrosivity of the different stages of bleach section and different aqueous media encountered in it by the fabrication material. To begin with experiments were done with a co nmercial grade mild-steel (ms), whose chemical composition and microstructure was determined. Coupons of size 1.25 x 1 x 0.1" (for laboratory tests) and 2.5x1.5x0 1" (for mill tests) were cut from a single piece of above mentioned ms.

Corrosion reactions being surface reactions, it is necessary to have uniformally smooth (crack free) and identical (from microstructure point of view) surface in case of all coupons. Surface preparation of coupons is, therefore, a very crucial part of corrosion tests. For surface preparation following procedure was adopted. The coupons were heat treated at a temperature 725°C (austenizing temperature) and then annealed to ambient temperature. The coupons were then ground from coarse to fine emery paper (final finishing done with 600-grit paper) and finally buffed. These coupons were then ultrasonically cleaned and finally degreased in acetone—water to remove any oily patch. Before exposure the coupons were weighed and their surface area measured.

The prepared coupons were exposed, for laboratory tests, to bleach liquor of varying available Cl_2 concentration. The volume of bleach liquor (1 litre) and the time of exposure (1 day) was finalised. So that the nature of corroding medium does not change significantly.

In mill test, the coupons were exposed inside respective vats and at shower pipes of chlorination Buffered hypo and hypowasher stages of bleaching section of a paper mill.

Table 1—gives process parameters of a representative Indian Paper Mills.

After the exposure, rust from the coupons were taken away and coupons were cleaned completely using a standard procedure[9]. The clean coupons have been weighed for measuring weight loss and corrosion rate. Their surface has been microscopically analysed to know the nature of corrosion attack on them.

The rust samples obtained from the coupons are being analysed by Mossbauer spectroscopy. This will help in identifiying the nature of corrosion products formed and hence in understanding the behaviour of material in the aggressive environment and protective nature of rust.

Cylindrical shaped specimens have been prepared of ms (1.5 cm diameter, 1 cm height) for performing electrochemical tests in bleach liquor. The experimental set-up include a microprocessor controlled potentio/ galvauostat, polarisation cell and an x-Y recorder. Here tests are being performed to know corrosion potential, Tafel behaviour and potentiodynamic polarisation behaviour of ms.

TABLE — 1.
Details of Process Parameters

Stage	Temperature (°C)	pH	Available cl_2 (gpl)	NaOH
Chlorination (C)	Ambient	2–2.5	3.2	—
Buffer (E/H)	60–65°	7.5–8.5	Depending upon the running capacity of plant	
Hypochlorite (H)	45–50	7.5–8.0	20 0	—

The exposure was done for 15 & 45 days.

RESULTS

Some of the results obtained in above mentioned experiments/tests have been accepted for presentation in an International Conference on Corrosion Scheduled in November 1987[10]. However a part of that finding and results obtained later will be shared here.

Laboratory Tests :

These indicate that corrosion rate of ms increases with available Cl_2 concentration upto 6 gpl (1163 mdd) and then starts decreasing with further increase in concentration. Similar indication is also given by ECORR measurement of ms in bleach liquors.

Rust obtained from laboratory corroded coupons indicates β=FeOOH and Fe_3O_4 as corrosion products.

The nature of corrosion attack appear to be non-uniform type.

Miil Tests :

Weight loss tests (Table 2) indicate chlorination washer having highly aggressive environment. Buffered hypowasher has lesser aggressive while hypowasher is observed to have least aggressive environment.

Presently this can be said to be due to lowest pH ranges in chlorination and highest pH ranges in hypo washer.

FUTURE PLAN :

The future plan of the work includes following :

1. Corrosion tests to be performed on stainless e g. SS 316, 316L, 317, 317L, 430 etc. in different stages of bleaching section. This will help in selection of appropriate fabrication material.
2. Tests on ms and SS exposed to Cl_2 water, Buffered hypo liquor, filterates of washers of different stages. This will help in appropriate selection of material for pipe lines and will also tell about the suitability of filterate for recycling purpose
3. Perform tests on ms and SS by putting them in pipe-lines on mills. This will expose to real environments consisting of moving aqueous media, pulp slurry at higher temperatures.
4. Electrochemical behaviour of ms and SS in different aqueous media (with and without pulp) at ambient and high temperatures. It will give information on tendency of experiencing localised corrosion, potentials between which the material remains in passivated state in the given aqueous medium. This information is expected to help in the development of an indigenous electro-chemical protection system.

TABLE — 2

Corrosion rate of mild Steel (in mpy)

Time of Exposure (Days)	Chlorination Stage		Buffer stage		Hypochlorination Stage	
	Vat	Shower pipe	Vat	Shower pipe	Vat	Shower pipe
15	1211	157	49	75	–	34
45	–	72	27	49	–	24

The rust removed from mill corroded coupons is observed to have β–/r– FeOOH and Fe_3–v O_4 as corrosion products. Since Fe_3O_4 is considered to act as a protective layer, the determination of its relative amount is expected to predict the corrosion rate.

Coupons exposed to chlorination and Buffered hypo washer are observed to show the tendency of pitting.

CONCLUSION :

The first corrosion tests performed in Indian mill environments and in aqueous medium of bleach section clearly indicate that these are highly corrosive in nature and mild steel in these show tendency of experiencing pitting making it unsuitable for use. It has, therefore, been planned to perform such tests in case of stainless steels by exposing them to the different mill environment and to different aqueous media. This will help in

selection of appropriate material of fabrication and help in identifying filterates suitable for reuse. Electrochemical tests have also been planned on ms and SS to see the feasibility of development of protection system suitable for Indian mills. For working on this proposal, it is necessary to have close collaboration and helping attitude between mills and the Institute. With this attitude it should be possible to usher into a new era, in a span of about 5–10 years, where Indian paper mills will be rolling out their products more economically by minimising corrosion losses.

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