

Corrosivity of environment and material performance in bleach plant washers

B. Gaur, A. K. Singh, S. Kumar, N. J. Rao, and V. K. Tewari

Commercial grades of stainless steel and mild steel were tested in the chlorination and hypochlorite washers of a bleach plant to determine how suitable they are for the mill.

The bleaching section in a paper mill is among the worst affected by the ravages of corrosion, accounting for nearly 50% of total mill corrosion costs (1). The equipment is exposed to highly corrosive bleach liquors of low pH and moderately high temperatures. These liquors have high concentrations of residual oxidant, chloride, and hypochlorite ions.

The nature of corrosion attack in most of the cases is observed to be pitting, crevice corrosion, weld-associated corrosion, and stress corrosion cracking (2). Numerous articles have appeared (2-9) dealing with corrosion problems in bleach plants of North American and Scandinavian paper mills. The mills in India, however, use different types of papermaking fibrous raw materials and bleaching processes. Except for two recent reports (10, 11), practically no study has been performed on corrosion problems in the Indian paper industry (12).

It is in this context that we planned corrosion studies to be performed on locally available machinery material in bleach sections of local paper mills. The work was performed on locally available commercial grade mild steel and austenitic stainless steels. Test coupons from these steels were exposed to both gaseous and liquid media in the bleaching section of a nearby paper mill for a duration of three months. The corroded coupons thus obtained have been analyzed for their corrosion behavior with respect to the process conditions. Tests of this kind have not been reported previously by any mill in India.

Experimental procedures and results

Materials

Five different types of austenitic stainless steels (stainless

steel) and one commercial grade mild steel were taken for the corrosion tests. Chemical analysis of the stainless steel samples was done with the help of optical emission spectroscopy (13). Mild steel was chemically analyzed using standard procedures (14). Results of these analyses are given in Table I.

Test coupons 1 in. $\times$ 1.5 in. were cut from the steel samples. The surfaces of the coupons were wet ground on silicon carbide (SIC) paper starting from 120 grit down to 600 grit. They were polished using emery papers from Grade 1/0 to Grade 4/0 and finally on selvyt cloth sprinkled with fine polishing alumina. The polished samples were degreased with benzene, cleaned ultrasonically in detergent solution, and washed with a solution of acetone and water. These coupons were weighed before they were put through corrosion tests.

Mill exposure conditions

Test coupons were exposed in the bleaching section of a nearby paper mill: M/S Ballarpur Industries Ltd., Yamunanagar, North India. This mill uses a mixture of *eucalyptus*, pine, and bamboo as raw material for fiber. The bleaching process in this mill consists of the following stages: chlorination (C), a hypochlorite stage (H1), and a second hypochlorite stage (H2). This mill does not recycle filtrate.

The samples were put through tests on the washers of these three stages. The conditions of vat liquors from the washers are given in Table II. We determined the residual chlorine by the iodometric method and estimated chloride ion by Volhard's method (14). Sulfate was determined by standard procedure (14), but it was found to be below the detectable limit.

For exposure, the test coupons were mounted in racks. Each rack consisted of six samples (five stainless steel and one mild steel). To ensure that coupons would be exposed to both liquid and gaseous media, the racks were fixed inside vats at the inlets (vat) and near the shower pipes of washers (gaseous). The duration of tests was three months.

Gaur, Singh, Kumar, and Rao are affiliated with the Institute of Paper Technology (University of Roorkee), Saharanpur — 247001, India. Tewari works in the Dept. of Metallurgical Engineering, University of Roorkee, Roorkee — 247667, India.

I. Analyses of stainless steel and mild steel

	C	Si	Mn	Ni	Cr	Mo	Ti
Stainless steel							
304	0.04	0.59	1.92	11.52	18.10	...	...
304L	0.02	0.59	0.91	9.25	19.15	...	...
316	0.03	0.62	0.94	8.53	18.68	0.29	...
316L	0.02	0.48	1.66	13.86	18.42	1.95	...
321	0.05	0.69	1.30	9.38	18.63	...	0.41
Mild steel	0.18	0.04	0.66	...	...	...	...

X-ray diffraction

X-ray diffractograms of the surfaces of the stainless steel coupons after exposure in hypochlorite washer liquid phase were recorded on a Philips Norelco X-ray diffractometer using a Cu target and Ni filter.

Corrosion rates

Corrosion rates were calculated from weight loss experienced by test coupons as a result of mill exposure. For this purpose, loose rust was first scraped from the surface of corroded coupons. Then these were treated with a cold solution of concentrated HCl, 50 g/L SnCl₂, and 20 g/L SbCl₃ until they were completely clean (15). These cleaned coupons were weighed to determine weight loss. Proper corrections were done to take into account the amount of steel lost from cleaning. Table III gives the corrosion rates, in mils/year, for various steel samples exposed under different process conditions.

Results and discussion

Stainless steel coupons exposed in the liquid phase of H1 and H2 washers showed a smooth, shining violet-purple film that was also brown and green in some places. This film was insoluble in water, but it dissolved in acidic media. X-ray diffractograms of these coupons show strong peaks characteristics of Ni and Cr metal and weak peaks corresponding to their oxides, whose presence has also been indicated in an earlier study (16).

Pitting and crevice corrosion

After cleaning, the coupons were assessed for pitting and crevice corrosion. A crevice was formed on the coupons as a result of polyvinylchloride spacers in the rack. The localized attack has been assessed by estimating the fraction of exposed surface experiencing localized attack, f_{loc} . The severity of attack can be classified into one of three categories:

1. Excessive: $f_{loc} > 0.05$
2. Moderate: $0.015 < f_{loc} < 0.05$
3. Negligible: $f_{loc} < 0.015$.

Table IV presents this assessment for both pitting and crevice corrosion. Generally, the coupons experienced pitting in the gaseous phase and crevice corrosion in the

II. Conditions of the liquors from the three bleaching stages

Bleaching stage	Temp., °C	pH	Resultant oxidant, ppm	Chloride ion, ppm
Chlorination	29	2.80	0	621
Hypochlorite 1	33	7.53	2.38	941
Hypochlorite 2	32	8.10	19.50	449

The values are averaged over the duration of exposure.

liquid phase. However, the severity of the environment in the chlorination washer is such that both pitting and crevice corrosion occur in the liquid and gaseous phases. This observation indicates that process conditions in the chlorination washer are highly aggressive for the washer drum, which gets exposed to liquid and gaseous media periodically.

Table IV shows that gaseous environments in H1 and H2 washers are less aggressive than in the chlorination washer with regard to the pitting attack. On this basis, different materials can be put in the following order of increasing tendency of pitting:

SS-316L < SS-304 L ~ SS-316 < SS-304 < SS-321 < mild steel

This outcome is in accordance with the general understanding that an increasing amount of molybdenum in

III. Corrosion rates for steels under different conditions, mils/year

	<i>Mild steel</i>	<i>Stainless steel</i>				
		304	304L	316	316L	321
Chlorination						
Gaseous	9.39	6.97	5.25	5.00	2.57	4.56
Vat	39.85	0.10	0.07	0.09	0.03	0.07
Hypochlorite 1						
Gaseous	6.06	0.28	0.13	0.08	0.05	0.12
Vat	4.32	0.07	0.05	0.16	0.12	0.11
Hypochlorite 2						
Gaseous	8.23	0.06	0.03	0.04	0.03	0.05
Vat	16.31	0.86	0.09	0.73	0.65	0.74

IV. Coupon assessments for both pitting and crevice corrosion

		Stainless steel				
Mild steel		304	304L	316	316L	321
<u>Pitting</u>						
Liquid phase						
Chlorination	Exc.	...	...	Neg.	...	Neg.
Hypochlorite 1	...	...	...	...	...	...
Hypochlorite 2	...	...	...	...	...	...
Gaseous phase						
Chlorination	Exc.	Exc.	Exc.	Exc.	Mod.	Exc.
Hypochlorite 1	Exc.	Mod.	Neg.	Neg.	Neg.	Mod.
Hypochlorite 2	Exc.	Neg.	Neg.	Neg.	Neg.	Mod.
<u>Crevice corrosion</u>						
Liquid phase						
Chlorination	Mod.	Mod.	Mod.	Mod.	Mod.	Mod.
Hypochlorite 1	Mod.	Mod.	Mod.	Exc.	Exc.	Exc.
Hypochlorite 2	Exc.	Mod.	Neg.	Mod.	Exc.	Exc.
Gaseous phase						
Chlorination	Neg.	Exc.	Exc.	Exc.	Exc.	Mod.
Hypochlorite 1	...	...	...	...	...	...
Hypochlorite 2	...	...	...	...	...	...

Ellipsis indicates no localized attack on coupon.

stainless steel improves its resistance against pitting (5).

Crevice corrosion is generally more severe in the H1 and H2 washer vats than in chlorination vat conditions (Table IV). SS-321 experiences maximum crevice corrosion, while SS-304 and 304L experience minimum crevice corrosion in the H1 and H2 vats. In the C vat, however, the degree of crevice corrosion is similar for all samples. No particular trend with regard to variation in the degree of crevice attack is observable in relation to varying amounts of Mo and Cr in stainless steel. This could be the result of there being little variation in the amount of Mo (Table I) (17) and to the lesser influence of Cr on crevice attack (3).

In our study, for the chlorination washer, one can observe excessive pitting in mild steel in the liquid phase; in the gaseous phase, we see excessive pitting in all stainless steels except 316L. Nearly all materials experience

excessive crevice corrosion in the gas phase and moderate corrosion in the liquid phase. In general, however, the process conditions are less severe in this washer than in its counterpart in American and Scandinavian mills (4, 5, 7, 9), where even 316L and 317L have been found to experience severe pitting results in complete perforations after an exposure of nearly three months. In these mills, stainless steels of high molybdenum content (e.g., 904L, 254SMO) and nickel-based alloys have been suggested as suitable materials (5, 9). The lower rate of corrosivity in Indian mills appears to rest with the practice of not recycling filtrate, which is also reflected in the negligible residual Cl_2 , lesser Cl^- , lower temperature, and higher pH in the chlorination stage in comparison to those in North American mills (5). Corrosion in the bleach plant increased enormously in these mills as soon as they started recycling filtrate (9).

In the hypochlorite washers, the process conditions are less corrosive, basically because of higher pH. Crevice corrosion is less aggressive in the liquid phase, perhaps because there is a higher concentration of residual oxidant in H vats than in C vats (Table II) (8). SS-304 and SS-316 can be used economically in these environments if crevices are avoided. However, the possibility of failure of SS-304 as a result of chloride stress corrosion should be accounted for (9). The conditions in Indian mills are not very different from those in North American and Scandinavian mills.

Weight loss

Corrosion rates calculated on the basis of weight lost by the steel coupons are shown in Table III. Several observations can be made. First, the gaseous phase of the chlorination washer is more corrosive than that of the H1 and H2 washers, because of the moist chlorine present in the gaseous phase around the chlorination washer (5, 9). Second, liquid media in the H2 washer appears more corrosive than in the H1 washer. Possible reasons for this could be (a) the addition of sulfamic acid in the H1 stage, which may be showing inhibitive action, and (b) a higher amount of residual oxidant in the H2 stage. (Experiments for studying the effect of sulfamic acid on the corrosiveness of bleach liquor are being carried out presently.) Third, in the H2 washer, the coupon material experienced a lower corrosion rate in the gaseous phase, probably because there was not a significant amount of moist chlorine in the gaseous phase in this washer.

For stainless steel, the gaseous phase of the chlorination washer is the most aggressive among all of the six different environments studied. This finding has been suggested in earlier studies (5, 9). The H1 gas phase is more corrosive than the H2 gas phase, perhaps because of the presence of moist chlorine around the H1 washer as a result of its closer proximity to the chlorination washer.

Mild steel experiences more corrosion loss in liquid media than in the gaseous phase in the chlorination washer. Since the iron oxide-oxyhydroxide film (rust) dissolves in acidic media, resulting in exposure of fresh metal surface, the corrosion rates for mild steel are high in the liquid phase in this stage (18). However, for the stainless steels, the presence of 8-10% Ni renders them more resistant to attack in acidic chloride media (19), resulting in lower corrosion rates of stainless steel in the liquid phase than in the gaseous phase (Table III).

As expected, the corrosion rate of mild steel in the H2 vat is less than in the C vat. For stainless steel, however, the liquid phase in the H2 vat is more corrosive than that of the C vat. At this time, we are unable to give a satisfactory explanation for this observation. Among the possible reasons are the difference in the nature of residual oxidants (e.g., Cl_2 in the C washer, OCl^- ion in the H2 washer), their varying amounts, and different kinetic electrochemical parameters (such as exchange current density and Tafel slopes) for mild steel and stainless steel. Study on these aspects forms part of our future plans.

Except for the H1 and H2 liquid phase, 316L shows maximum corrosion resistance in all environments. In the H1 and H2 liquid phases, 304L experienced the least corrosion. Before drawing any conclusion, we should recheck this observation, however. SS-304L and SS-316L

have better corrosion resistance than 304 and 316, respectively. This difference could be due to the fact that cementite is a phase of low-hydrogen overvoltage, which leads to low-carbon steel experiencing less corrosion than high-carbon steel (18).

Overall, none of the studied materials is suitable to use in the chlorination gas phase. SS-316L can be used in the chlorination liquor with the condition that crevices are avoided. It also can be used in the H1 and H2 gaseous phases. SS-304L may be considered for use in H1 and H2 liquors. In this context, it may be worth considering the materials currently in use in bleach plants of Indian mills. In many of them, 316 and 317L are used in pipes for transporting stock, in washer wires and drums, and for washed pulp in the chlorination stage, whereas hypochlorite washers are using 304 and cast iron as well (12). Some of these materials may not be suitable for the purpose; in some places, it may be more economical to use a material that is less resistant to corrosion.

The need for conducting corrosion tests is involved in selecting materials for aggressive environment. In this study, we have not considered such alternatives as (a) mild steel or cast iron lined with rubber or FRP (fiberglass-reinforced polyester) and (b) acid resistant, tile-lined concrete. These materials are also in use in some of the local mills (12).

Conclusions

In general, the chlorination washer is more corrosive than the hypochlorite washers. The studied materials have all experienced severe-to-moderate pitting in the chlorination washer. Crevice corrosion is more aggressive in the H washers. On the basis of weight loss studies, the liquid media of the H2 washer appears more corrosive than that of the H1 washer. This difference may be due to the presence of more residual oxidant in H2 and the addition of sulfamic acid in H1. Further tests are in progress. The gaseous phase of the H1 washer is more aggressive than that of the H2 washer, possibly because there is more moist chlorine around the H1 washer, due to its closeness to the chlorination washer.

A surprising observation is more weight loss of stainless steel in the H2 washer than in the chlorination washer liquid phase. This needs further study.

After considering both localized attack and corrosion rate, we can conclude that 316L has the best corrosion resistance among the materials studied in all sections except in the H1 and H2 liquid media, where 304L performs better.

There is a need to perform corrosion tests in different Indian mills for selecting viable materials for making process equipment economically. This is important because process conditions usually vary from mill to mill.

North American and Scandinavian mills have had to replace 316L and 317L because of severe perforations in the aggressive atmosphere in mills where liquor recycling is practiced. These mills found steels high in molybdenum to be more resistant. In the Indian mill, where no recycling is practiced, SS-316L experienced less corrosion attack. These Indian mills will have to review the materials of construction if liquor recycling is adopted as a mill closure strategy for pollution control. □

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The authors thankfully acknowledge the Ministry of Science and Technology (Dept. of Science and Technology), Govt. of India, New Delhi, for funding the project. We also thank the management of M/S BILT Yamunanagar for providing facilities for performing mill tests.

Received for review June 1, 1989.

Accepted July 17, 1989.