Performance of steels against corrosion in peracid bleach media

GAYAAN SINGH AND AJAY KUMAR SINGH

ABSTRACT: Peracids are being considered as bleaching media with low environmental impact. The performance of candidate alloys was evaluated by coupon tests and electrochemical polarization tests in pulp-free laboratory solutions of peracetic acid (a mixture of acetic acid and hydrogen peroxide), Caro's acid (a mixture of sulfuric acid and hydrogen peroxide), and mixtures of the two solutions. 0.1% or 0.2% chlorides were added to these test solutions. All the solutions could be handled in Alloy 2205. Type 304 stainless steel was adequate for some of the conditions tested.

Application: Long-term immersion and electrochemical corrosion tests help in identifying appropriate material of construction for handling peracid bleach media of lower pH.

The paper industry has adopted nonchlorine chemicals, such as hydrogen peroxide, peracids, oxygen, and ozone, with the aim of reducing pollution. The peracids (peracetic acid [P_a]), Caro's acid (P_x) and (P_{xa}) (mixture of P_a and P_x), have been used as activating agents for lignin and as brightening agents. Chemically, P_a is CH_3COOOH, with a molecular weight of 76.05 and active oxygen as 21%, whereas, P_x is peroxymonosulfuric acid (H_2SO_5), having a molecular weight of 114.08 and 14% active oxygen content. Peracids are considered equally effective for bleaching as peroxide and ozone. However, its selection is guided by associated safety hazards, ingredient costs, and effluent loads [1].

With the use of newer chemicals, their corrosive effects has also been studied. Thus Varjonen et al [2], while studying corrosion of titanium in peroxide, found that magnesium sulfate was not an effective inhibitor, in contradiction to Macdiarmid et al [3]. In a similar study, Wyllie et al [4] found sodium silicate and calcium nitrate to be an effective inhibitor for pH ~ 12, but not EDTA. Been [5] doubts the effectiveness of calcium as an inhibitor for titanium in peroxide media. Singh et al [6] studied the effect of chelants on the corrosivity of peroxide solutions. Pehkonen et al [7] studied corrosion of stainless steel in ozone and peracetic acid without chlorine (Cl^-). Sodium sulfate was found to inhibit the corrosive effect of Cl^- in ozonated solutions. This paper reports about the investigation on corrosion of stainless steels in peracids. The corroded samples were evaluated for localized and uniform corrosion for their possible use in a peracid bleach plant.

EXPERIMENTAL

Material

We selected plate samples for weight loss tests, and cylindrical samples for the electrochemical tests of austenitic stainless steel 304L, 316L, and 317L, and duplex stainless steel (2205). The composition of the stainless steels (**Table I**), from plate and cylindrical samples, do not differ much (difference among the respective chemicals not exceeding 0.06%) except for chromium (maximum difference of 0.99%), nickel (maximum difference of 0.65%), and molybdenum (maximum difference of 0.26%). All the samples were solution annealed, as per ASTM specification A240. Before exposure, the coupons were polished up to 600 grit, degreased using acetone solution, and weighed.

Alloy	C	Cr	Ni	Mo	Cu	Mn	P	S	Si	N
304L	0.02	18.10	11.52	—	—	1.92	—	—	0.59	—
316L	0.016	16.45	10.22	2.11	0.25	1.75	0.026	0.008	0.44	0.03
317L	0.019	18.19	13.23	3.11	0.42	1.78	0.031	0.001	0.55	0.047
2205	0.025	22.00	5.700	3.01	0.29	1.44	0.022	0.001	0.48	0.154

I. Composition of test materials.

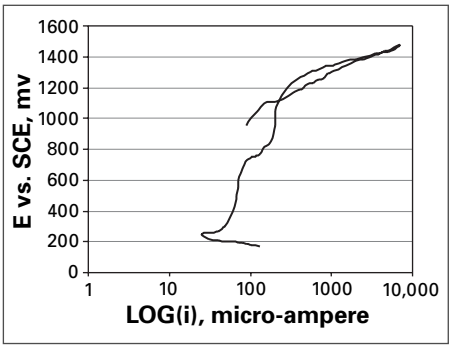
Solution	Chemical charge (as % A.O.)*	pH	Cl^- (ppm)
P_x 1	0.47±0.05	5±0.10	1000±0.20
P_x 2	0.47±0.05	5±0.10	2000±0.20
P_{xa} 1	0.94±0.05	5±0.10	1000±0.20
P_{xa} 2	0.94±0.05	5±0.10	22000±0.20
P_a 0	0.47±0.05	5±0.10	0
P_a 1	0.47±0.05	5±0.10	1000±0.20
P_a 2	0.47±0.05	5±0.10	2000±0.20

* A.O. – active oxygen

II. Chemical composition of the solutions.

Solutions

Samples were exposed to peracid solutions (P_a, P_x, and P_{xa}), prepared as described by Amini and Webster [1]. Accordingly, we prepared P_a by adding glacial acetic acid to hydrogen peroxide (1 molar ratio) containing 1 mL of concentrated sulfuric acid as a catalyst. The mixture was then warmed to 45°C, held at this temperature for 2 hours, and stored overnight in a refrigerator to allow the mixture to come to equilibrium. P_x was prepared by adding sulfuric acid to hydrogen peroxide (1 molar ratio) while maintaining the reaction temperature at 30°C–35°C. P_{xa} solutions were prepared by adding the required amount of glacial acetic acid to the cold Caro's acid. We added sodium chloride in the solutions to get the desired level of Cl^-. We kept these solutions at a pH of 5 by adding sodium hydroxide. **Table II** gives the test conditions and composition of the solution.



1. Cyclic polarization curve for 317L in P_a1 solution.

Tests

In the weight loss test, the steel coupons were exposed for 6 months at 50°C and at room temperature. Each coupon was immersed in the solution (Table II) with serrated washers to initiate crevice corrosion. During the test, the percent active oxygen (AO) and pH of the solutions were monitored and maintained each day. While pH did not change much (±0.1), decrease in percent AO was compensated, to keep it within limit, as per Table II, by adding requisite amounts of peracetic acid or Caro's acid. After the exposure, the corroded coupons were cleaned mechanically and further cleaned by treating them with a cold solution of concentrated hydrogen chloride with 50 g/L stannous chloride and 20 g/L antimonous chloride [8]. The coupons were then weighed to determine corrosion rate and viewed under the microscope to estimate the extent of localized attack. The electrochemical tests were conducted using a potentiostat and polarization cell having five necks meant for a working electrode, two counter electrodes, a reference electrode (saturated calomel electrode), and for gas purging. Corrosion (E_{corr}), pitting (E_p), and repassivation potential (E_c) were evaluated from these tests.

RESULTS

Corrosion rate, extent of pitting (evaluated by measuring the maximum depth of pits formed on freely exposed surface), and crevice corrosion (estimated by measuring the maximum depth of attack (in millimeters) on occluded surface formed by serrated washers) are given in **Table III**. These tests did not show any pitting attack.

Solutions	Materials	Corrosion rate, mpy		Degree of crevice corrosion, mm	
		Room Temp.	50°C	Room Temp. Max	50°C Max
P_x1	304L	—	—	—	0.08
P_x2	304L	0.45	0.71	0.21	0.29
	316L	0.12	1.71	0.06	NVA
P_{xa}1	304L	0.37	0.70	NVA	0.05
P_{xa}2	304L	0.03	0.03	0.09	0.15
P_{xa}2	316L	0.23	0.31	0.09	0.11
P_{xa}2	317L	—	0.18	—	0.08
P_a0	304L	—	0.12	—	0.03
P_a1	304L	0.52	—	0.15	—
P_a1	316L	1.64	1.77	0.12	0.21
P_a1	317L	0.02	0.02	NVA	NVA
P_a2	316L	4.24	—	0.54	—
P_a2	317L	0.09	0.023	NVA	NVA
P_a2	2205	0.44	—	0.09	0.06

NVA – No visible attack

III. Corrosion parameters in peracid solutions (long-term immersion test).

Solutions	Materials	Ecorr, mv		Ec, mv	Ep (Potentio-static), mv	Ep (Cyclic), mv
		E vs. t	Cyclic			
P_x1	304L	335	120	900	1375	1250
P_x2	304L	335	190	1470	1125	—
P_x2	316L	360	100	1480	1425	—
P_{xa}1	304L	100	200	1000	1225	1200
P_{xa}1	316L	125	210	1100	1275	1270
P_{xa}2	304L	100	200	1220	825	1330
P_{xa}2	316L	125	300	1290	925	1420
P_{xa}2	317L	135	210	1400	1125	1430
P_a0	304L	293	160	950	1275	1300
P_a0	316L	330	225	1100	1325	1320
P_a1	316L	330	—	—	325	
P_a1	317L	440	250	1150	775	1250
P_a2	316L	330	—	—	—	—
P_a2	317L	440	300	1020	625	1180
P_a2	2205	—	200	1170	1225	1370

IV. Electrochemical results.

Solutions	P_x1	P_x2	P_{xa}1	P_{xa}2	P_a1	P_a2	P_a0
Room Temp.	304L	2205	304L	304L	2205	2205	304L
50ºC	304L	2205	304L	2205	2205	2205	304L

V. Materials of construction for peracid bleach plant.

The potentiostatic test was conducted to evaluate E_p, which decides the vortex potential required for recording the cyclic polarization curves (**Fig.1**). The closed loop in Fig. 1 indicates that localized corrosion has begun. The downward curve therefore shows a weighted average of the alloys behavior in the base solution and the localized corrosion environment. E_{corr}, E_p, and E_c obtained from these tests are given in **Table IV**. A comparison of E_p and E_c, in some cases, show $E_c > E_p$. This is because E_c has been obtained from cyclic and E_p from potentiostatic measurement.

DISCUSSION

Corrosivity of solutions

The corrosion rates of stainless steel show maximum uniform corrosion in P_a solutions. Analysis of crevice attack shows it to be higher for P_a solutions than others. A comparison of (Ec-Ecorr) and (Ep-Ecorr) for 304L shows P_{xa} to be

more corrosive than P_x. Similarly, comparison of these parameters for 317L shows P_a2 to be more corrosive than $P_{xa}2$. In general, these solutions can be put in the following order of increasing corrosivity: $P_x < P_{xa} < P_a$. Variations in corrosivity of these solutions can be assigned to the mildly inhibitive properties of sulfate ions, as reported in a wide variety of other media. Increased Cl^- decreases the passivation range, as expected. A comparison of peracids with those of peroxide and chlorine dioxide solutions [6, 9], on the basis of weight loss and electrochemical tests, shows peracids to be less corrosive, compared to peroxide and chlorine dioxide, up to 1000 ppm Cl^-. Chlorine dioxide solutions are found to be most corrosive.

Material performance

In P_x2 and P_a1 at room temperature and in $P_{xa}1$ and $P_{xa}2$ at 50°C, 316L shows lesser crevice attack than 304L. In the case of $P_{xa}2$ and P_a1, 316L shows higher corrosion rate and crevice attack than 317L at 50°C, while 2205 shows intermediate resistance between 316L and 317L in P_a2 solution. In general, the comparison shows 304L to be least resistant to corrosion attack, followed by 316L, 317L, and 2205.

A comparison of E_p, E_c, and the passivation range of 304L and 316L in P_x2, $P_{xa}1$, $P_{xa}2$, and P_a0 solutions show 316L to be more resistant than 304L against pitting and crevice corrosion. The better resistance of 316L can be assigned to ~ 2% molybdenum content, whereas 304L does not have any molybdenum (Table I). We compared the behavior of SS-316L and 317L in P_a solutions. We observed the E_p of 316L, from the potentiostatic test, to have very low value in both P_a1 and P_a2 solutions and quite close to the E_{corr} values in the respective cases. Stainless steel 317L, however, shows much higher E_p, E_c, and passivation range. The better resistance of 317L, in comparison to 316L, against localized corrosion is in accordance with higher PRE no., critical pitting temperature (CPT), and critical crevice temperature (CCT) of the former. This in turn can be attributed to higher amount of chromium, molybdenum, and nitrogen in it than 316L (Table I). Duplex stainless steel 2205 shows higher values of E_p, E_c, and passivation range in P_a2 solution (Table IV), thereby exhibiting better corrosion resistance in comparison to 317L in this solution. This behavior can be attributed to still higher values of PRE no., CPT, and CCT values for 2205 [10].

Material selection

The E_p, E_c, and passivation range of 304L and 316L are quite high in the case of P_x, P_{xa}, and P_a0 solutions, so they are expected to show good resistance against pitting and crevice corrosion. Stainless steel 316L, however, shows very low values of E_p (potentiostatic), which are quite close to the respective E_{corr} values in P_a1 and P_a2 solutions. It is likely to experience localized attack in these solutions. Stainless steel 317L shows acceptable performance in P_a1 and P_a2 solutions. Duplex stainless steel shows even better resistance in these solutions. The test coupons do not show pitting in long-term immersion test. The material selection, therefore, has been attempted considering the degree of crevice corrosion and its comparison with the in-plant data of Tuthill [11], suggesting guidelines for acceptability of material. On considering cost per unit strength and fabrication aspects, 2205 appears less costly than 316L and even 317L [10]. In cases where 316L, 317L, and 2205 show acceptable performance, 2205 may be considered an appropriate material of construction (**Table V**). Thus 304L is suitable for handling P_a (without Cl^-), P_x, and P_{xa} (up to 1000 ppm Cl^-), whereas 2205 may be considered for handling other peracids.

CONCLUSION

Peracids are among the potential nonchlorine bleach chemicals in papermaking. This study reports the corrosion effects on machinery materials and their suitability in liquors likely to be encountered in peracid bleaching. The following can be concluded on the basis of this work:

- Peracetic acids are most corrosive while Caro's acids are least. The mixture of peracetic acid and Caro's acid showed an intermediate level of corrosivity.
- Tested materials can be put in the following order of increasing corrosion resistance: 304L < 316L < 317L < 2205.
- SS-304L can be used for handling liquors under lesser corrosive conditions (P_a solution without Cl^- and P_x and P_{xa} solution with Cl^- up to 1000 ppm and up to 50°C), while for more corrosive conditions, 2205 is likely to be the more cost-effective option.
- Peracetic and Caro's bleaching solutions at pH 5 could be handled in the acid stages of existing bleach plants with equipment built for previous CEDED type bleaching sequences or today's chlorine dioxide/peroxide sequences. **TJ**

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INSIGHTS FROM THE AUTHORS

Optimum use of the available materials in the present scenario of changing bleach chemicals is probably one factor in economizing the paper making process. We chose this research keeping those economic factors in view. This work is actually part of one author's doctoral work, which relates to finding the optimum material of construction for handling chemicals for different bleaching processes.

Variation of composition during the test was the most difficult aspect of the work presented here. We tackled the challenge by frequently monitoring the parameters and correcting as and when required.

The work's most interesting finding was that the bleach plants used to handle chlorine dioxide bleach media can be used to handle peracids without modification of metallurgy. Mills planning to change over to peracid bleaching as a part of a pollution control strategy may do so using the same bleach plant machinery as meant for chlorine dioxide bleaching.

To supplement results of the present test, we now plan to perform in-plant testing in a peracid bleach stage.

G. Singh and A.K. Singh are with the Department of Paper Technology, Indian Institute of Technology, Roorkee, Saharanpur Campus, P.B. 83, Saharanpur-247001, India.

G. Singh