

Corrosion studies of stainless steels in peroxide bleach media

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ABSTRACT: *Peroxide bleaching is an alternative to conventional bleaching because of its environmentally friendly advantages. This work is an investigation on the corrosion behavior of austenitic stainless steels and their suitability in peroxide solutions using simulated bleach media. In peroxide media of TCF bleaching, one may use stainless steel 304 or 316 without localized corrosion while stainless steel 316 is suitable for peroxide media of ECF bleaching. Chelant addition increases the upper limit of chloride content in liquors. The study suggests an economic way to use peroxide as bleaching media.*

KEYWORDS: *Chelating agents, chlorides, chlorine free bleaching, corrosion, corrosion tests, EDTA, hydrogen peroxide, magnesium sulfate, peroxide bleaching, simulation, sodium chloride, stabilizers, stainless steel.*

Growing concern about environmental degradation has forced some chemical industries to seek acceptable technology to replace conventional methods. The paper industry is an example, since bleach plants can create high pollution. Discharge from such plants contains hazardous by-products of chlorine including dioxin (1).

Consequently there is an active search for elemental chlorine free (ECF) or total chlorine free (TCF) bleaching sequences (1–3) that the paper industry can adopt without

major problems. One component of this search includes using nonchlorine chemicals such as peroxide, oxygen, ozone, etc., as alternatives for pulp bleaching. Peroxide is currently finding acceptability as an important part of new bleaching sequences for chemical pulps (4). Peroxide already finds use in bleaching mechanical pulps. An important consequence of changing to new chemicals can be a possible change in corrosion by the bleach media. Any modification therefore requires simultaneous investigations on

corrosivity of liquors for the proposed bleaching processes. One must also consider the suitability of presently used and alternative materials in handling new chemicals. Such work might suggest different metallurgy for future bleach plants.

The work presented in this paper relates the corrosion effects on stainless steel from peroxide bleach solutions. There have been previous articles on corrosion of materials in the presence of hydrogen peroxide (5–9). Bennett (6) studied the effect of peroxide addition to the chlorine dioxide bleaching stage on stainless steel (SS) 316L. Yau (7, 8) discussed zirconium as a material of construction. Bloom *et al.* (5) suggest stainless steel in the 300 series for most applications dealing with peroxide solutions. A recent report (9) investigates the study of corrosion rates of titanium in the presence of hydrogen peroxide in alkaline peroxide bleach liquor with simulated paper mill chemistry. This report also discusses corrosion reduction by potential corrosion inhibitors. It therefore is obvious that various efforts are in progress to seek alternative solutions to corrosion problems with peroxide media.

The main problem using stainless steels with peroxide is the tendency of increasing decomposition of hydrogen peroxide. Adding peroxide stabilizers—chelants—controls this phenomenon in pulp bleach plants. Austenitic stainless steels are the conventional materials for fabricating most bleach plant machinery.

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Bleach Plant Corrosion

This work therefore has investigated their corrosion behavior and tested their suitability in solutions of peroxide bleach media of varying chemical concentration. There were electrochemical corrosion tests on austenitic SS-316 and SS-304 with solutions normally encountered in the peroxide stage washer of chemical pulp bleaching. There was also an attempt to observe the effect of chelants on the corrosivity of the solutions. Although the presence of or contact with fibers would influence the corrosivity of such solutions, the study did not include this aspect.

Experimental details

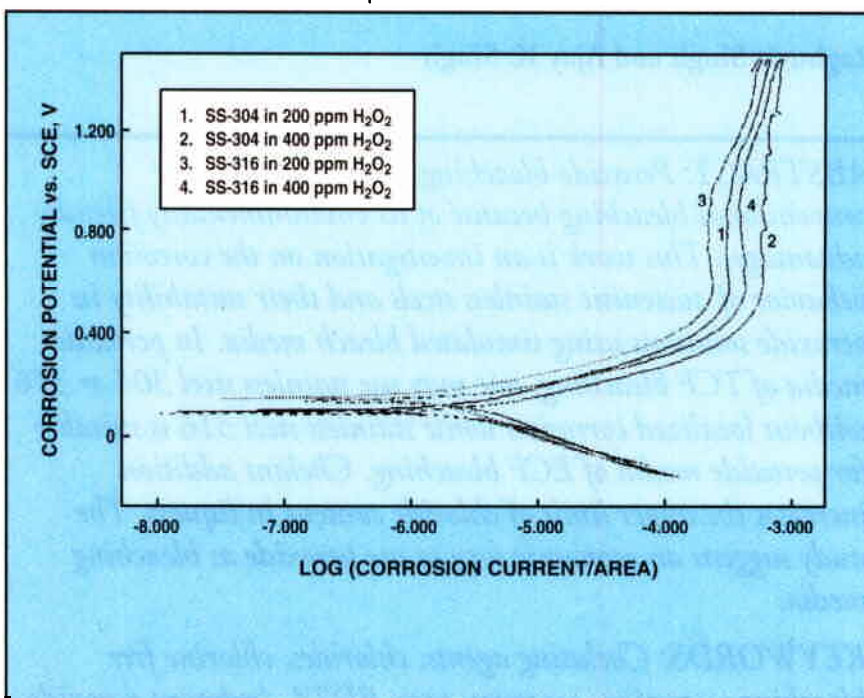
Well-characterized, austenitic SS-316 and SS-304 were the test subjects. **Table I** shows the chemical analysis obtained using standard procedures (10). The electrochemical polarization tests for studying corrosion behavior used samples of 2.5-cm length cut from rods of 1.5 cm diameter. Before testing, the samples underwent grinding with a silicone carbide paper through 600 grit followed by degreasing in acetone.

The experiments used three types of solutions containing 200, 400, and 600 ppm H_2O_2 . The first type of solution used an analytical reagent grade 30% H_2O_2 solution in distilled water. Titrating the solutions against sodium thiosulfate with starch as an indicator (11) checked the peroxide concentration. In some solutions, there was a requisite addition of NaCl to observe the effect of chloride ions. Volhard's method (11) checked the concentration of chloride. A second type of solution used peroxide with chloride containing the disodium salt of ethylenediaminetetraacetic acid (EDTA) and magnesium sulfate. These chemicals are chelants for stabilizing peroxide in a bleaching process. The percentage of chemicals charged in the peroxide stage (EDTA charged at 0.2–0.5% and $MgSO_4$ charged at 0.3–0.5%) determined the amount of addition for a 10% consistency level. The third type of solu-

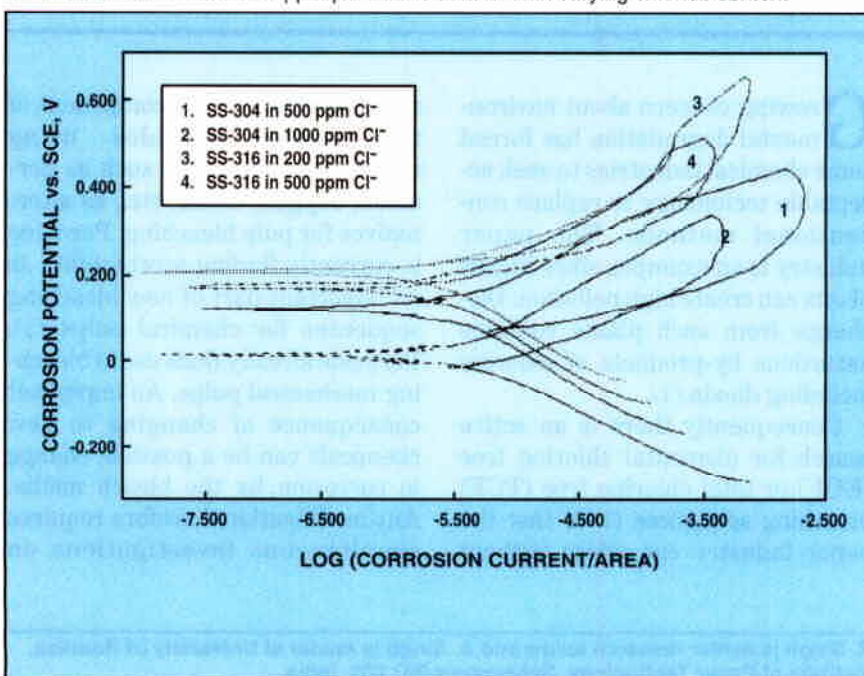
I. Chemical composition of stainless steels

	C	Mn	Si	Cr	Ni	Mo
SS-304	0.074	1.49	0.41	19.80	8.45	-
SS-316	0.071	1.90	0.48	17.49	12.70	2.18

1. Polarization curves in chloride free peroxide solutions



2. Polarization curves in 200 ppm peroxide solutions with varying chloride content



II. Electrochemical parameters of SS-316 in peroxide solutions with and without chloride

H_2O_2 , ppm	Cl^- , ppm	E_{corr} , mV	E_p , mV	E_c , mV	I_{corr} , $\mu A/cm^2$
200	0	168	-	1650–1700	1.82
	200	183	211	325–375	1.40
	500	151	147	230–280	1.64
	1000	127	235	100–150	1.61
	2000	90	-	Pitting occurs	-
400	0	155	-	1650–1700	3.25
	500	153	207	300–350	3.60
600	0	145	-	1650–1700	3.70
	500	152	191	275–325	3.06

III. Electrochemical parameters of SS-304 in peroxide solutions with and without chloride

H_2O_2 , ppm	Cl^- , ppm	E_{corr} , mV	E_p , mV	E_c , mV	I_{corr} , $\mu A/cm^2$
200	0	118	-	1575–1625	3.26
	200	110	103	Pitting occurs	3.47
	500	92	50	Pitting occurs	2.57
	1000	-2	-31	Pitting occurs	3.04
	2000	-	-	Pitting occurs	-
400	0	116	-	1650–1700	3.56
	500	111	61	Pitting occurs	3.62
600	0	93	-	1650–1700	3.93
	500	87	76	Pitting occurs	5.98

tion contained only NaCl (chloride < 3000 ppm). The pH of all the solutions was 11. This value did not change significantly during the measurements. The test temperature was 50°C.

Most failures of stainless steels in bleach plants are due to localized corrosion—pitting and crevice corrosion (12). We therefore attempted to determine the susceptibility of SS-316 and SS-304 to these types of corrosion attack in the peroxide bleach environment. We performed cyclic polarization and potentiostatic tests on stainless steel samples using a commercially available, computer controlled corrosion measurement system. Each case involved recording of the polarization curve after sample immersion in the solution for approximately one hour. That was

the observation point for attaining stable open circuit potential. Calculation of corrosion current, I_{corr} , used a commercially available program for corrosion analysis. Saturated calomel electrode (SCE) was the reference electrode in these experiments. All the potential values in the text use SCE as a reference unless otherwise noted.

Results

Due to the oxidizing nature of peroxide, the corrosion potentials, E_{corr} , for steels in peroxide solution are approximately 770–780 mV more anodic compared to those in NaCl solution. **Figures 1 and 2** show polarization curves of SS-316 and SS-304 in peroxide solutions with and without chloride respectively. In cases

where it was difficult to determine pitting attack from these curves, potentiostatic curves measured the potential range within which the value of critical pitting potential, E_c , might fall. **Tables II and III** give this potential range and other parameters— E_{corr} , I_{corr} , and protection potential, E_p , derived from polarization curves—for SS-316 and SS-304, respectively.

Polarization curves of the stainless steels in chloride-free peroxide solutions depict the oxidation kinetics of the peroxide reaction on passive electrodes. Addition of chloride in these solutions destabilizes the passive layer. This shows the vulnerability of the steels to localized attack. Two parameters—margin of safety (MOS) against pitting ($E_c - E_{corr}$) and crevice corrosion ($E_p - E_{corr}$)—quantify this. We observed that MOS for SS-316 decreases with increasing chloride (Table II) in peroxide solution. SS-304 showed pitting and crevice corrosion at all levels of chloride (Table III and Fig. 2).

Discussion

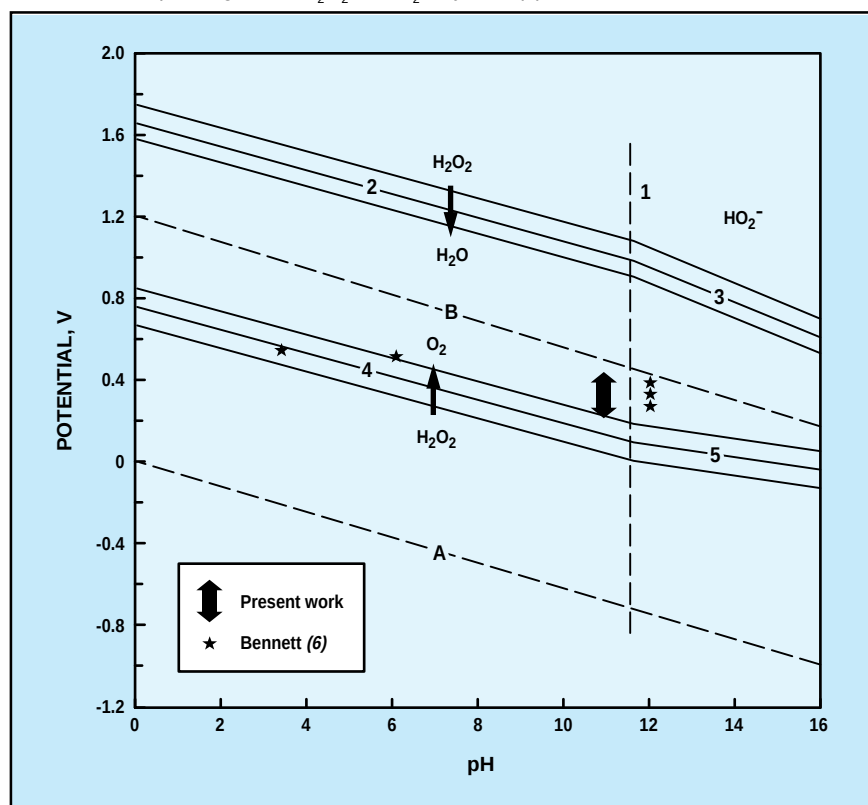
Polarization measurements on SS-316 and SS-304 in chloride-free solutions show practically the same passivation range with breakdown potential at approximately 1675 mV (Fig. 1). The results do not show any tendency for crevice corrosion. The potential vs. pH diagrams of chromium and molybdenum (13) help in understanding the similar passivation behavior of the two stainless steels. The experimental point representing E_c , the pH values corresponding to E_{corr} of carbon-steel (–183.1 mV) that is mainly iron, and the pH of the solutions (11) lie in the passivation domain of the potential vs. pH diagram of chromium. Passivation behavior of both of the stainless steels is therefore similar, and it is mainly due to chromium. In chloride containing solutions, however, the passive film on both stainless steels appears to break at much lower potential (Fig. 2). This shows the sus-

Bleach Plant Corrosion

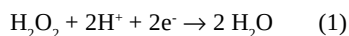
ceptibility to localized attack characterized by E_c and E_p (Tables 2 and 3). The MOS against pitting and crevice corrosion of SS-316 decreases with increasing chloride content, but SS-304 experiences pitting and crevice corrosion. The experimental E and pH point corresponding to the conditions of occluded cell corrosion (OCC) in stainless steels falls in the corrosion region of the potential vs. pH diagram of chromium in chloride solutions (13) and in the passivation region for the molybdenum diagram (14). Since resistance of SS-304 against localized corrosion is due to chromium, it pits and experiences crevice corrosion. Due to presence of molybdenum, however, SS-316 still shows a non-zero, though decreased, magnitude of MOS. SS-316 is therefore superior to SS-304 against localized corrosion in solutions containing chloride ions. This property is due to the presence of molybdenum in SS-316 (Table I) as earlier literature indicates (15).

To understand the redox reactions responsible for corrosion of steel in peroxide solutions, it is important to know the nature of any chemical species present in the solutions. **Figure 3** provides the potential vs. pH diagram of hydrogen peroxide in water for this purpose (13). In this diagram, line 1 represents a pH value of 11.63. It shows the transition from H_2O_2 to HO_2^- . Lines 2 and 3 show reduction of H_2O_2 and HO_2^- , respectively, to H_2O . Lines 4 and 5 show oxidation of H_2O_2 and HO_2^- to O_2 depending upon the pH of the solution. The experimental points corresponding to E_{corr} of SS-316 and SS-304 and the pH of the experimental solutions lie within the thick arrow in Fig. 3. This line is in the stability region of O_2 . This means that most of the H_2O_2 and HO_2^- in the solutions have oxidized to O_2 . Earlier work suggested this transformation (16). Note that Fig. 3 shows the experimental points from earlier work (6). This also suggests similar transformation. Evo-

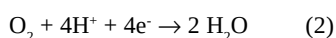
3. Potential vs. pH diagram of H_2O_2 and H_2O system (3)



lution of O_2 occurred as bubbles appearing over the sample in contact with the peroxide solution in our experiments. The test solution in our studies was therefore a mixture of O_2 and H_2O_2 . Earlier purging of the test solution with N_2 to draw out dissolved oxygen did not change the corrosion behavior of stainless steel. These observations agree with an earlier study (17). In a mixture of H_2O_2 and O_2 , however, the following equations show that H_2O_2 dominates the effects on the corrosion potential of stainless steel (16) due to its higher oxidation potential:



$$E = 1127 \text{ mV at pH 11}$$



$$E = 580 \text{ mV at pH 11}$$

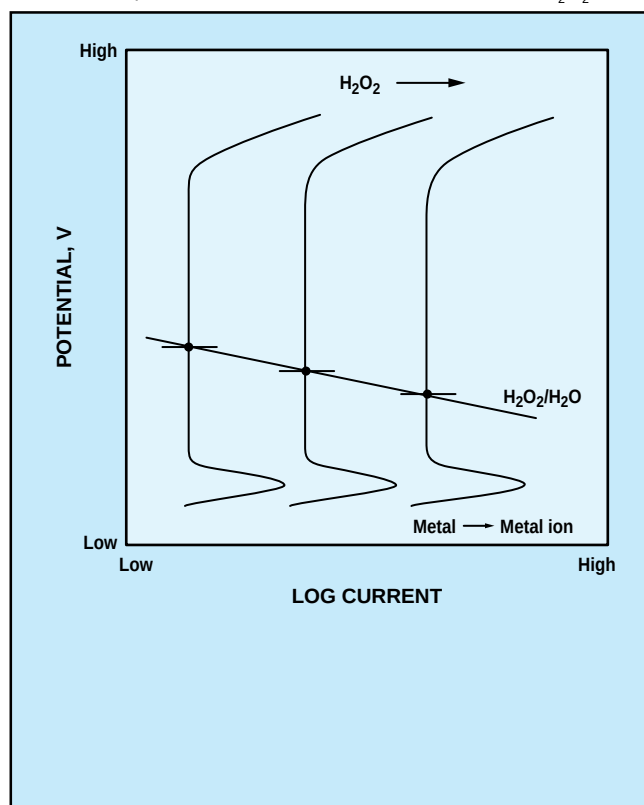
A level of H_2O_2 in the ppb range is sufficient to observe the saturation value of the corrosion potential of

stainless steel (16). We can consequently infer that the specimens in our work are corroding from H_2O_2 reduction as in Eq. 1. The E_{corr} of SS-316 and SS-304 observed earlier (16) match those of our results when considering the effect of temperature. For a similar reason, the corrosion behavior of stainless steel is unlikely to change significantly despite the change in the level of H_2O_2 observed during the polarization tests.

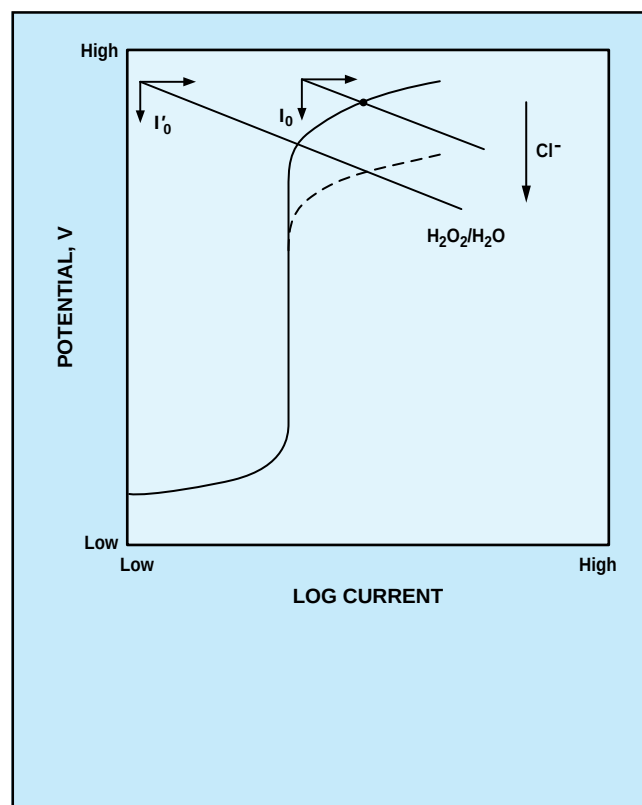
Peroxide solutions without chloride

Without chloride ions, both stainless steels do not show localized corrosion. The fact that E_{corr} is less than the breakdown potential is also evidence of this. Figure 1 showing cyclic polarization without hysteresis behavior is further evidence. Addition of H_2O_2 shows an increase in passivation range. This suggests improvement in resistance of stainless steel against localized attack. The

4. Corrosion potential of stainless steel with addition of H_2O_2



5. Corrosion potential of stainless steel with addition of chloride



corrosion rates for both stainless steels (Table 2) increase in peroxide solutions. Since these steels are in the passivation region in these solutions, the increase in corrosion rate is an indication of the increase in passivation current. Upon destabilization of the protective layer, a new film forms quickly. This results in an increase in passivation current. In this manner, resistance against localized corrosion also improves (higher passivation range). This reasoning also explains the change of E_{corr} to more active values with addition of H_2O_2 up to 600 ppm as **Fig. 4** shows. The authors feel that increase in passivation current due to H_2O_2 may result in increased concentration of iron. Iron will catalyze decomposition of H_2O_2 (18). As noted above, such a reaction does occur thermodynamically.

Effect of chloride

Presence of chloride ions in H_2O_2 solutions drastically reduces E_c and

therefore MOS against localized corrosion (Tables II and III and Fig. 2). Susceptibility of stainless steels to localized corrosion in chloride containing solutions is a common phenomenon. Corrosion potential for both types of steels decreases with increasing chloride content (Tables II and III). This behavior shown in **Fig. 5** could be due to the decrease of E_c and shifting of the cathodic polarization curve of H_2O_2 and H_2O toward lower current values with an increase in chloride. The later change occurred in cathodic polarization experiments on a platinum electrode in solutions containing H_2O_2 and chloride.

SS-304 experienced pitting and crevice corrosion, but SS-316 did not undergo corrosion attack until chloride increased above 1000 ppm (Fig. 2). To check this further, potentiostatic tests measured E_c to corroborate the above results (Tables II and III). With increased chloride, the stainless steel obviously

becomes more susceptible to localized attack. The corrosion rate of SS-316 in the passive state or under localized corrosion is less than SS-304 provided H_2O_2 concentration is approximately 200 ppm. Above this level of H_2O_2 , both steels corrode at identical rates.

TCF bleaching processes at sites having fresh water with almost no chloride will have negligible chloride content. SS-304 and SS-316 therefore probably would not undergo localized corrosion attack. If H_2O_2 levels are higher than 200 ppm, one might consider using SS-304, since this steel is lower cost. For H_2O_2 levels over 200 ppm, SS-316 might be a better alternative. Note that with 10% consistency, 1–3% H_2O_2 charge, and 20% residual peroxide in the washer for peroxide bleaching of chemical pulp (18), the H_2O_2 content in the liquid media would be 200–600 ppm. If chloride is over 500 ppm in the solutions, one may use SS-316, since it would not undergo localized

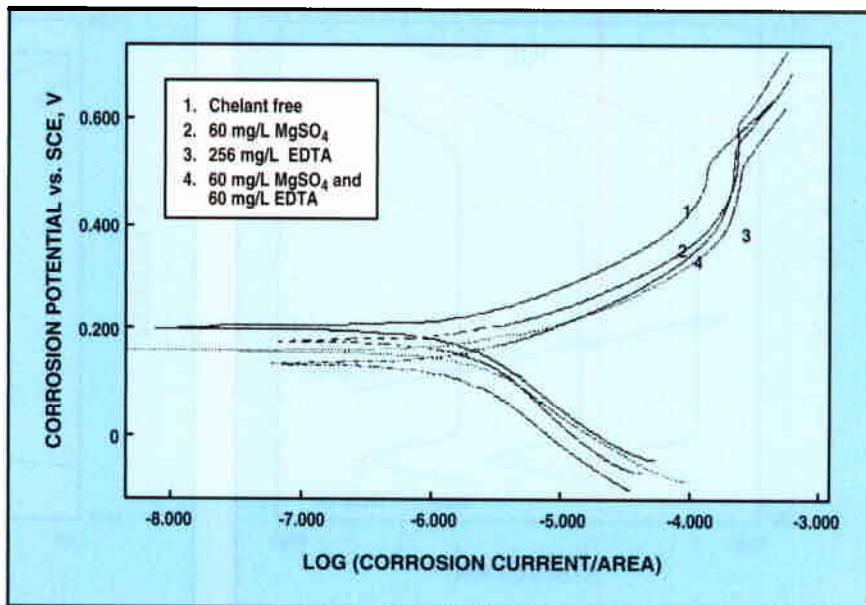
Bleach Plant Corrosion

attack. It is worth mentioning that in bleaching sequences with chlorine, chlorine dioxide, or both, SS-316 is not suitable. Mills prefer to use 4% or even 6% molybdenum containing austenitic stainless steels (19). The introduction of TCF or even ECF bleaching sequences with peroxide may therefore use less expensive materials for handling liquors compared to the bleaching processes today. Although SS-316 has significant MOS in peroxide solutions, the magnitude is less even at moderate levels of chloride compared to those in other liquid media such as white water (20).

Effect of chelants

The peroxide solutions having 200 ppm chloride and 200 ppm H_2O_2 had added chelants. This allowed checking the effect of adding $MgSO_4$ and EDTA. It also allowed determination of the effect of their simultaneous addition on corrosion behavior of stainless steels as Fig. 6 and Table IV show. On addition of $MgSO_4$ to the solution, E_{corr} of SS-316 decreases and E_c increases. The latter could come from a higher sulfate to chloride ratio, since addition of $MgSO_4$ is greater. The net result is that the MOS against pitting increases 1.5 times with addition of 60 mg/L of $MgSO_4$. Addition of $MgSO_4$ in the 100–500 mg/L range inhibits corrosion in a NaOH solution with H_2O_2 (9). With addition of EDTA to a peroxide solution, both SS-316 and SS-304 show resistance to pitting (MOS values in Table IV). The former also shows resistance against crevice corrosion in these solutions. With chelants in peroxide solution added mainly for stabilizing H_2O_2 , both stainless steels can handle higher chloride content without the risk of pitting. The effect of adding both $MgSO_4$ and EDTA simultaneously is additive in improving the resistance of stainless steels against localized corrosion. The MOS of SS-316 and SS-304 therefore improves more in the simultaneous

6. Polarization curves of SS-316 in 200 ppm peroxide solution with 200 ppm chloride and chelants



presence of both the chelants (Table IV). In our tests, we observed that with addition of $MgSO_4$ and EDTA SS-316 may handle below 1500 ppm and SS-304 below 200 ppm chloride without experiencing pitting.

Material of construction

Efforts to select an appropriate material for handling peroxide media have compared the performance of titanium, zirconium, and SS-316L (5, 7, 8). This comparison indicated that titanium is least resistant to H_2O_2 solutions for general corrosion and pitting. Titanium also decomposes H_2O_2 . Zirconium shows equivalent and sometimes better resistance than SS-316 but has a susceptibility to localized corrosion in the presence of chloride ions. Zirconium does not decompose H_2O_2 , however. Fabricated vessels of titanium and zirconium cost 3–4 times more than SS-316 without considering corrosion allowance.

Our tests show resistance of SS-316 to pitting to a certain level of chloride. There is H_2O_2 decomposition, however. Chelant addition will avoid this. Chelants enhance resistance of SS-316 and SS-304 stainless steels against localized corrosion and

extend the allowable upper limit of chloride in peroxide solutions. Earlier reports propose no such limit for zirconium. Since SS-316 and SS-304 are cheaper and more available than titanium and zirconium, the former steel may be economical to use for chloride below 1500 ppm or below 200 ppm in peroxide media with chelants.

These important, preliminary observations have used electrochemical tests on the effect of chelants in enhancing the upper allowable chloride limit in peroxide solutions without the risk of localized corrosion of the studied steels. It is necessary to explore these limits considering zirconium through short- and long-term experiments on localized corrosion, however. Such tests would assess the suitability of using stainless steels compared to zirconium in handling peroxide solutions for a given chloride level.

Conclusion

This work investigated the corrosion behavior of austenitic SS-316 and SS-304 in peroxide bleach media. It considered the effect of chloride and the addition of chelants to stabilize

IV. Effect of chelants on performance of stainless steels in 200 ppm peroxide solution

Solution	$E_{corr}/OCP,^a$ mV	$E_c,$ mV	MOS, mV
SS-316			
Cl ⁻ = 200 ppm	183	325–375	142–192
Cl ⁻ = 200 ppm, MgSO ₄	161.6	400–450	238.4–288.4
Cl ⁻ = 200 ppm, EDTA	143.8	400–450	256.2–306.2
Cl ⁻ = 200 ppm, MgSO ₄ + EDTA	120.7	425–475	304.3–354.3
Cl ⁻ = 1000 ppm, MgSO ₄ + EDTA	71	130–180	59–109
Cl ⁻ = 1500 ppm, MgSO ₄ + EDTA	58	60–110	2–52
SS-304			
Cl ⁻ = 200 ppm	110	Pitting	N. A.
Cl ⁻ = 200 ppm, MgSO ₄	116.1	Pitting	N. A.
Cl ⁻ = 200 ppm, EDTA	120.4	165–215	44.6–94.6
Cl ⁻ = 200 ppm, MgSO ₄ + EDTA	99.1	155–205	55.9–105.9

^aOCP = Open circuit potential

H₂O₂. For peroxide media of the TCF bleaching process where chloride ions are negligible, use of both stainless steels is possible without the risk of localized corrosion. In the presence of chloride such as with the peroxide media of ECF bleaching, SS-316 would not undergo localized corrosion at chloride levels below 500 ppm. The addition of chelants enhances the resistance of both steels. In the peroxide bleach liquor with simulated paper mill chemistry, SS-316 can handle higher chloride contents of over 1500 ppm and SS-304 can tolerate up to 200 ppm without experiencing pitting. The study therefore suggests an economic benefit for changing to an en-

vironmentally friendly bleaching process such as peroxide. It will be possible to use the less costly and more available SS-316 and SS-304 to handle the liquor compared to the chlorine and chlorine dioxide stages of conventional bleaching processes. In those cases, replacement of steel due to excessive corrosion requires more expensive stainless steel products having higher molybdenum content. Titanium and zirconium are also competitive materials to the 300 series stainless steels. SS-316 and SS-304 may prove economical compared to zirconium in handling peroxide media containing chelants depending on the chloride level. 

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