



Behavior of Steels against Corrosion in Peroxide Solutions

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Abstract

Environment safety measurements have resulted in use of peroxide as bleaching chemical in place of chlorine and chlorine dioxide. Concentration and composition of chemicals affects corrosion aspects, the suitability of existing plant metallurgy and materials of construction of bleach plants. Accordingly long term immersion and electrochemical corrosion tests were conducted on stainless steel 304L, 316L, 2205 and mild steel (MS) in peroxide solutions of pH 10. The materials were tested for uniform corrosion, pitting and crevice corrosion and attack around the weld area. Corrosion attack estimated from long term immersion tests is found in agreement, by and large, with that analysed from electrochemical test. E-pH diagrams drawn for water-peroxide system have been used to understand the corrosivity of the peroxide media. Attempt has been made to suggest suitable material of construction for handling the test media on the basis of degree of corrosion attack along with cost and mechanical properties of the test materials.

Key Words : Corrosion, bleach plant, peroxide, stainless steel, material selection, pH.

1. Introduction

Chemical and Paper industries are adopting non-chlorine chemicals e.g. hydrogen peroxide, peracids, oxygen, ozone etc. with the aim of reducing pollution. With the use of newer chemicals, conditions in the concerned sections have changed thereby affecting the performance of machinery materials. This state has resulted into investigating the corrosion effects of these chemicals on the existing materials of plant machinery which in many cases has been observed to deteriorate. Accordingly, the corrosion investigations on newer materials of construction have become necessary so as to predict the metallurgy of the plants in the changed scenario of bleaching processes. Present work deals with the changes likely to be observed on adopting peroxide as the bleach chemical.

Literature cites several investigations related to corrosive effect due to peroxide. Among the earlier articles [1] suggested 300 series stainless steel to for most applications dealing with peroxide solutions. Bennett [2] studied the effect of peroxide addition to the chlorine dioxide bleaching stage on stainless steel 316L. Yau [3,5] discussed zirconium as a material of construction. Investigation was also done [6] on studying corrosion rates of titanium in the presence of hydrogen peroxide in alkaline peroxide bleach liquor with paper mill chemistry. Varjonen et al [7] while studying corrosion of Ti in peroxide found that $MgSO_4$ was not an effective inhibitor, in contradiction to Macdiarmid et al [4]. Similarly, sodium silicate and calcium nitrate were found to be effective inhibitor for pH ~ 12 but not EDTA [8]. In another [9] study the effect of

chelants on the corrosivity of peroxide solutions were investigated. In yet other study [10] investigations have been carried on transpassive corrosion of stainless steels in alkaline peroxide solutions. In the presence of phosphonate salts, often used as stabilizers of hydrogen peroxide, which are strong complexants of transition metal cations, transpassive corrosion of stainless steel is observed to occur and leads to coloration of the metal surface in hydrogen peroxide solutions.

A. D. Bauer and M. Lundberg [11] observed attack on 304L and other alloy steels in the strong oxidizing environment, such as provided in alkaline hydrogen peroxide section. Use of titanium showed increased corrosion with peroxide ion content. Been, [12] on the basis of his work cast doubts on the effectiveness of calcium as inhibitor for Ti in peroxide media. Another study [13] aims to evaluate the performance of titanium modified austenitic stainless steels in the simulated peroxide bleaching stage solutions through electrochemical measurements. Uniform corrosion of titanium was studied in alkaline hydrogen peroxide environments simulating pulp bleaching conditions [14]. Corrosion rates of unalloyed Grade 2 and alloyed Grade 5 were determined as a function of hydrogen peroxide anion (HOO^-) concentration. Influences of calcium and silicate inhibitors and iron and manganese were investigated. A consequence of conducting corrosion tests of various candidate materials in peroxide media is a recent report from Outokumpu, Finland [15]. This report indicates the replacement of traditional hydrogen peroxide reactor materials – the high-performance, high-alloyed austenitic stainless steel grade 904L or the more commonly used Duplex 2205 by

LDX2101®. LDX 2101®, which has a very low nickel content, is well adequate to handle the hydrogen peroxide reactor process, an environment with a low corrosion rate under alkaline conditions but high pressures up to 10 bars and temperatures around 110 degrees Celsius.

With a view to investigate corrosion performance of different stainless steels, which could be possible candidate materials, in peroxide bleach liquor having paper mill chemistry in a systematic manner, efforts were made to test mild steel and stainless steels (austenitic and duplex) in peroxide liquors of varying concentration as could be observed in bleach plant. For this purpose weight loss and electrochemical tests were performed. E-pH diagram was also constructed for $\text{H}_2\text{O}_2\text{-H}_2\text{O}$ system with a view to help in understanding the corrosion reactions taking place in the present case. Present report is based on this work.

2. Experimental

2.1 Materials

The test coupons were selected on the basis of their current use and possible use in future bleach plants. Accordingly, austenitic stainless steel 304L, 316L, duplex stainless steel 2205 and mild steel (MS) were opted for the test. Corrosion coupons from plate samples of mild steel, austenitic and duplex stainless steels were considered for the weight loss test. The stainless steel coupons were autogenously welded. Cylindrical samples from the rods of the above steels (except mild steel) were examined using electrochemical tests. The composition of the stainless steels, for plate and cylindrical samples, is shown in Table 1.

Table 1 : Composition of Test Materials										
Plate Samples										
Alloy	C	Cr	Ni	Mo	Cu	Mn	P	S	Si	N
MS	0.18	-	-	-	-	1.66	-	-	0.04	-
304L	0.036	18.11	8.01	0.26	0.46	1.84	0.024	0.001	0.44	0.058
316L	0.019	17.43	11.26	2.03	0.40	1.11	0.027	0.002	0.5	0.048
2205	0.022	22.13	5.55	3.16	0.21	1.47	0.02	0.001	0.35	0.188
Cylindrical Samples										
304L	0.02	18.10	11.52	-	-	1.92	-	-	0.59	-
316L	0.02	17.44	10.87	2.16	0.31	1.69	0.03	0.03	0.69	0.04
2205	0.02	22.25	5.48	3.08	-	1.45	0.026	0.002	0.52	0.15

All the stainless steel test samples were as received in the solution annealed condition as per ASTM spec A 240. Before exposure, they were polished up to 800 grit, then degreased using acetone solution and weighed in case of weight loss test.

2.2 Solutions

Samples were exposed in peroxide solutions having pH at 10 and varying Cl⁻ and peroxide concentration. For making these solutions, 50% H₂O₂ Analar grade in distilled water was used. This solution was mixed in distilled water in required amount so as to have 300 and 600 ppm H₂O₂ and their pH were adjusted to 10 using NaOH. NaCl was added in the solutions so as to have desired level of Cl⁻ content. The composition of the solutions was checked for H₂O₂, Cl⁻ and pH using standard techniques [16] and pH meter. Table 2 shows the composition of test solutions.

2.3 Tests

The immersion test was carried for corrosion rate estimation, in which weighed steel coupons were exposed for six months duration at room temperature. Each coupon, fitted with serrated washers for initiating crevice corrosion, was immersed in the solution (Table 2).

	Soln 1	Soln 2	Soln 3	Soln 4	Soln 5	Soln 6
Peroxide (ppm)	300	300	300	600	600	600
Chloride (ppm)	0	500	1000	0	500	1000

During the test, H₂O₂, Cl⁻ and pH of the solutions were monitored and maintained once in a week. During this period, the amount of H₂O₂ decreased from 5% - 15%, that of Cl⁻ from 2.5% - 5% and pH decreased from 3.3 – 5.1% of the respective target values. After the exposure, the corroded coupons were cleaned mechanically followed by treatment with cold solution of concentrated HCl with 50 g/L SnCl₂ and 20 g/L SbCl₃ [17]. The coupons were then weighed for estimating weight loss in order to determine corrosion rate using following equation:

$$\text{Corrosion Rate (mpy)} = (3.45 \times 10^6 \times w) / (\text{DAT})$$

W - weight loss in grams, D - density of metal in gm/cm³, A - area in cm² and

T - exposure time in hours

The corroded and cleaned coupons were also viewed under the microscope for estimating pitting, crevice corrosion and weld related attack by measuring the maximum depth of attack on the open surface, under the serrated washer and near the weld area of the coupon respectively.

The electrochemical tests namely E vs. t, potentiodynamic (Fig.1)

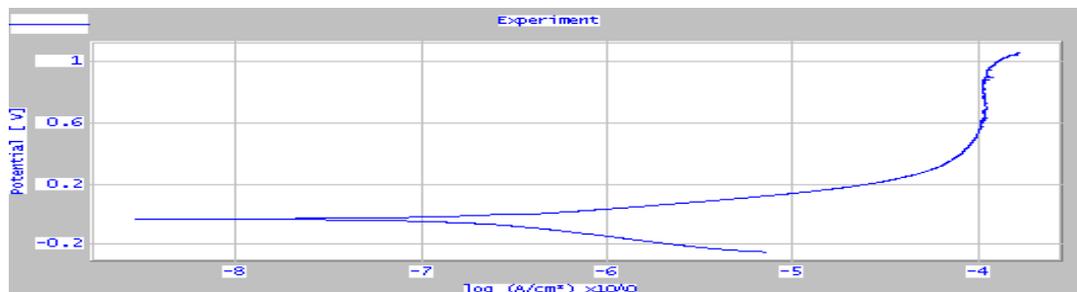


Fig. 1 : Potentiodynamic Polarization Curve of 2205 in Peroxide solution 6

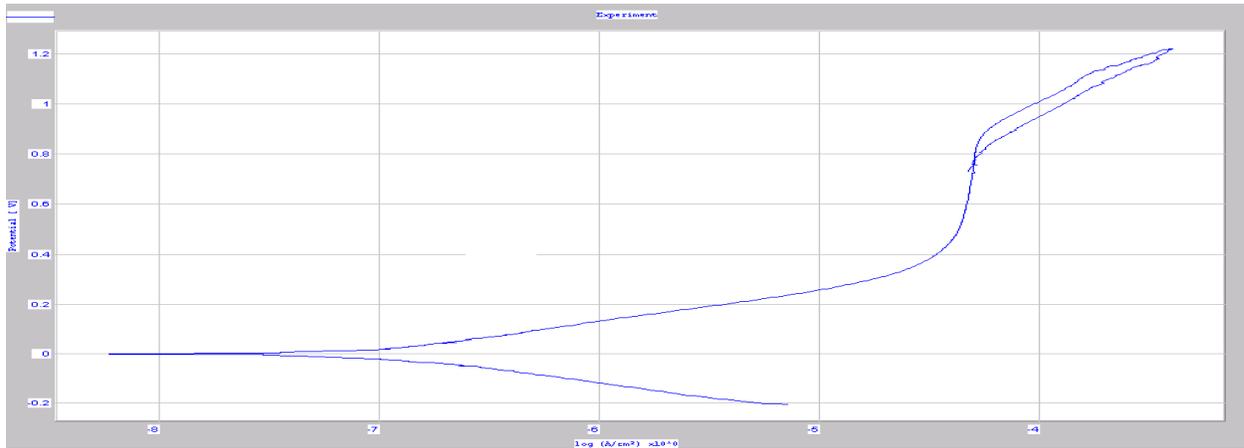


Fig. 2 : Cyclic Polarization Curve of 2205 in Peroxide solution 6

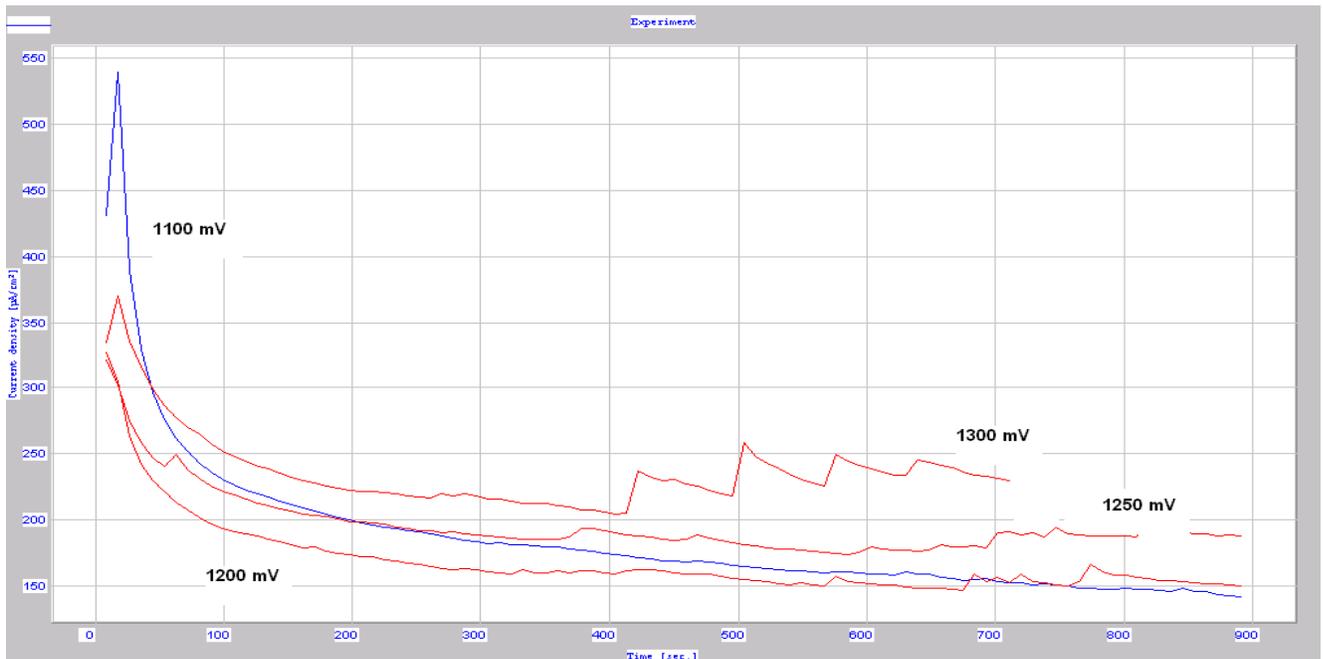


Figure 3 : Potentiostatic Curves for Stainless Steel 316L in Solution 4

Were carried out in the solutions as mentioned in table 2. The corrosion measurement system included a potentiostat and a polarization cell having five necks meant for a working electrode, two counter electrodes, saturated calomel electrode (SCE) as reference electrode and for gas purging. Open circuit potential (OCP), corrosion (E_{corr}), pitting (E_p) and repassivation (E_c) potential were evaluated from these tests.

3. Results and Discussion

It is important to understand various reactions which are responsible for the corrosion of materials in the peroxide solutions. This in turn requires the information on the chemical species present in the solutions. For this purpose an E-pH diagram (so-called Pourbaix diagram) was constructed for $\text{H}_2\text{O}_2\text{-H}_2\text{O}$ system (Fig.4).

	Soln 1	Soln 2	Soln 3	Soln 4	Soln 5	Soln 6
(MS)	6.26	6.8	6.98	6.39	7.82	9.43
SS-304L	1.18	1.18	1.21	1.23	1.27	1.49
SS-316L	0.11	0.19	0.19	0.20	0.22	0.25
2205	0.001	0.005	0.01	0.011	0.012	0.013

NMA – No measurable Attack

*measured as maximum depth of attack, over open area, under the crevices and at welded joint respectively

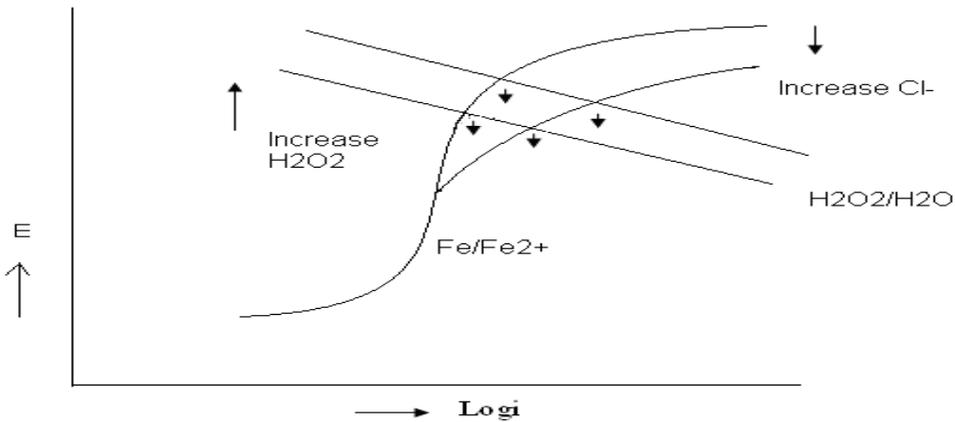


Figure 5 : Redox Curve for Fe-H₂O₂ system

		Soln 1	Soln 2	Soln 3	Soln 4	Soln 5	Soln 6
MS	Pitting	-	-	-	-	-	59
	Crevice Corrosion	72	88	90	73	79	102
	Weld Area Attack	-	-	-	-	-	-
SS-304L	Pitting	40	36	45	50	71	85
	Crevice Corrosion	NMA	35	40	41	52	53
	Weld Area Attack	NMA	NMA	NMA	63	78	115
SS-316L	Pitting	58	81	84	60	75	109
	Crevice Corrosion	47	67	71	41	85	105
	Weld Area Attack	NMA	40	43	35	62	78
2205	Pitting	39	36	48	55	57	64
	Crevice Corrosion	NMA	NMA	40	NMA	44	46
	Weld Area Attack	NMA	NMA	41	NMA	41	44

* mpy – mils per year

Table 4 shows extent of pitting, crevice corrosion and weld area attack on different steels in the test solutions. As per this table, all the three types of localized attack are found by and large to increase as one considers solutions with higher H₂O₂ and Cl⁻ contents. Thus peroxide solution with no chloride and 300 ppm peroxide is least corrosive while that with 1000 ppm chloride and 600 ppm peroxide shows highest degree of corrosivity. Localized corrosion too, therefore, is found to increase as H₂O₂ and Cl⁻ increase. The increased corrosivity of the solutions with H₂O₂ may be assigned to H₂O₂/H₂O reaction (eqn.2). Nernst equation for this reaction is given by:

$$E_{\text{H}_2\text{O}_2} = 1.776 - 0.059 \text{ pH} + 0.0295 \log [\text{H}_2\text{O}_2] \quad (4)$$

Increase in concentration of H₂O₂ will shift E_{H₂O₂} to higher values thereby increasing OCP and corrosion rate of metal (Fig.5). Whereas enhanced corrosivity due to increased level of Cl⁻ may be attributed to decreased passivation range of stainless steels, which in turn will increase corrosion rate and may enhance possibility of localized corrosion as well (Fig.5). Thus corrosivity of the peroxide solutions is likely to increase with increased residual peroxide levels and higher chloride levels which might be a consequence of filtrate recycling, a practice adopted to control discharge of pollutants to nearby stream. According to Table 3, corrosion rates are observed to vary as per following trend

MS > 304L > 316L > 2205

The trend is as per the chemical composition of the test materials. According to Table 4, mild steel is observed to experience only crevice corrosion while pitting is experienced in one case only. An interesting observation is that 304L is found to perform better than 316L in terms of pitting and crevice corrosion. Normally, it is expected that 316L will show better resistance than 304L. Such a behavior has been observed earlier also [19,20,21] and though some explanation has been suggested, the authors feel that a detailed study is required in this regard. It is, therefore, necessary to measure potentiodynamic polarization curves to know E_p and margin of safety (MOS) in case of 304L to further corroborate this observation. Localized corrosion attack on 2205 is observed to be least (Table 4). Attack on weld area is found maximum on 304L which is followed by 316L and 2205. Thus by and large, different materials may be graded in terms of their resistance against uniform and localized corrosion in the following manner:

2205 > 316L > 304L > MS

Table 5 shows the electrochemical results derived from electrochemical polarization tests. Thus OCP values are lying in the range -23.95 to 76.5 mV (218.05 to 318.5 mV w.r. to NHE). Generally E_{corr} < OCP because for OCP measurement, one has to run experiment for longer duration so potential rises with built up of oxide layer. For 316L, E_p (1076 → 373.7 → 274.7 mV) and margin of safety (MOS) (1105 – 390.2 – 302.3 mV) fall very rapidly with introduction of Cl⁻. Because of this behavior, cyclic polarization curves were not recorded in Cl⁻ containing solutions since E_c would have turned out to be lower than E_{corr}. It indicates the vulnerability of 316L to attack by pitting and crevice corrosion in alkaline peroxide solutions having Cl⁻. This observation has another implication on effect of filtrates recycling on enhanced corrosivity and therefore possible premature failure of machinery equipment if constructed of 316L.

For 2205, E_c, E_p and passivation range (MOS) comes out to be pretty high indicating much better resistance of this steel even in case of peroxides with Cl⁻ (upto 1000 ppm level). For increased peroxide level, there is a slight reduction in the resistance against localized corrosion. Better resistance of 2205 as compared to 316L may be associated with higher amount of Cr, Mo and N in the former steel. PRE Number [20,22-24] (in chloride containing oxidizing media), which depends upon Cr, Mo and N content, for 2205 is 34.814 indicating that this is expected to perform better against localized corrosion than other steels.

Table 5 : Electrochemical Corrosion Parameters							
		Soln 1	Soln 2	Soln 3	Soln 4	Soln 5	Soln 6
SS-304L	OCP	-23.95	-11.97	16.44	43.37	55.6	-
SS-316L	OCP	43.67	28.2	-17.74	48.42	48.3	46.2
	E _{corr}	-29.7	-18.32	-27.59	3.16		11.4
	(E _c) _{pot}	1076	373.7	274.7	1151		288.8
	(E _c) _{cyclic}	?	?		?		
	(E _c) _{potstatic}				1275		
	E _p						
	Passiv.range	1105.7	390.02	302.3	1147.8		277.4
2205	OCP	45.38	15.48	26.77	28.22	65.1	62.8
	E _{corr}		-35.2	47.8/16*			36.2/0*
	(E _c) _{pot}		966.6	955			1027
	(E _c) _{cyclic}			946.5			877.9
	(E _c) _{potstatic}			1125			> 1100
	E _p			938.2			766
	Passiv.range		1001.8	907/930.5			990.8/877.9

All parameters are in 'milli volt', measured w.r.t. SCE, * cyclic measurement

A comparison of overall material performance against corrosion attack indicates best material to be 2205. Better cost/strength ratio of 2205 makes it all the more suitable for handling peroxide media with/without Cl⁻ content.

Conclusion

Electrochemical polarization and Weight loss test were performed at room temperature alongside construction of E-pH diagram of peroxide-water system in the present program. It is concluded that (i) alkaline peroxide solutions with/without Cl⁻ are corrosive to tested stainless steel to varying extent and their corrosivity increases with increase in H₂O₂ and Cl⁻ content. (ii) the optimum material for handling these media is suggested to be 2205 (iii) in the event of mills going for filtrate recycling, test should be made to check the corrosion resistance of the tested steels which is likely to deteriorate in view of the enhanced levels of Cl⁻ and oxidant.

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