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Corrosion Examination in Peroxide Solutions under Acidic pH

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***Abstract:** In current investigation, results of electrochemical as well as weight loss test conducted on steels in acidic peroxide solutions have been discussed. Electrochemical polarization test E vs. time curve, potentiodynamic as well as cyclic polarization curve were performed on stainless steels SS304L, SS316L, SS2205 and 6% Mo in peroxide solutions having H_2O_2, 500 and 1000 parts per million (ppm). The pH of these solutions for electrochemical tests was kept 4 with chloride and without chloride. Chloride content varied from 0 to 1000 ppm. Weight loss test was also accomplished on above stainless steels in peroxide solutions with chloride content varied from 0 to 1000 ppm at same pH. Alongside an E-pH illustration of peroxide-water coordination were constructed. Electrochemical results of tested steels show soaring extent of localized corrosion while it is less relentless in crate of solutions exclusive of Cl^-. In general, It is accomplished that acidic peroxides among/lacking Cl^- are corrosive to steels to anecdotal amount furthermore their corrosives augments with boost in H_2O_2 as well as Cl^- substance. The optimal material for managing these media is recommended to be SS 2205. Results of Weight loss test showed that SS 304L is found to observe high degree of uniform corrosion hence cannot be suggested for handling these media. Duplex stainless steels therefore have to be used. Both electrochemical and weight loss tests on stainless steel showed increased resistance against corrosion in order of: SS304L< SS316L < SS2205~ 6% Mo.*

***Keywords:** Peroxide, steels, corrosion, E-pH*

I. INTRODUCTION

Paper manufacturing in bleach plants have conventionally engaged austenitic stainless steels since of their good mechanical as well as corrosion resistance properties. Nevertheless, , to hoard energy and to fulfill environmental regulations, practices introduced more than last ten years has ended bleaching medium additional corrosive. Predominantly, sluice water recycling consequences in elevated chloride concentration, lesser pH standards and elevated temperature. For above mentioned new condition the SS 316L and 317L material have become unacceptable so numerous mills have bowed to advanced alloyed steels [1]. By and large, bleach plants of paper mills uses chlorine along with chlorine dioxide whose acidic nature media is extremely corrosive. Accordingly, lots of bleach plant have been prepared by using titanium alloys because of their lofty corrosion confrontation properties. The paper mills which look forward to to utilize peroxide as a bleaching agent otherwise which may well exchange elemental chlorine free (ECF) in addition to total chlorine free (TCF) for titanium lodge for managing peroxide media.

The previous reported studies [2-5] showed titanium experiencing stern assault in alkaline peroxide solutions. In view of the fact that subsequently various studies [6-22] have been demeanor on corrosion recital of titanium and zirconium alloys in acidic peroxide solutions and these alloys also revealed an enhanced corrosion in acidic peroxide solutions. Subsequently opportunity, in hunt of appropriate resources for managing acidic peroxide solutions, is to asses steels adjacent to corrosion while they are amid frequently used materials owing to their extensive as well as speckled corrosion resistance together with strength plus construction properties. For this intention, an immersion in addition to electrochemical corrosion tests was act upon at pH 4.0. A Potential-pH illustration was also completed for H_2O_2-H_2O coordination through a vision to assist in perceptive corrosion reactions captivating in current case.

II. EXPERIMENTAL METHODS

The chemical compositions of samples used in corrosion study of long term immersion and as well as electrochemical tests are given in Table 1. The entire stainless steel coupons were annealed as per ASTM specification A240. Samples were bare in peroxide solutions with a pH 4.0 in addition to anecdotal Cl^-(0 to 1000 ppm) and peroxide concentration (0 to 1000 ppm). Meant for set up the, 30% H_2O_2 in refined water was applied. This solution was assorted into refined water in requisite quantity subsequently as have 500 furthermore 1000 ppm H_2O_2 in addition to their pH were attuned to 4.0 by means of CH_3COOH solution. The NaCl was additional in these solutions, so that have preferred echelon of Cl^- substance. The symphony of solutions was tartan for H_2O_2, Cl^- furthermore pH by means of regular procedure [23, 24] plus pH meter. The Table 2 demonstrates symphony of solutions. The immersion investigation was demeanor for assessment of corrosion tempo, in which ponder coupons were bared pro six months period at extent hotness. Apiece one coupon, built-in by way of jagged washers for commence crevice corrosion, arrangement as apiece ASTM G78 [25], was engrossed into test solutions (Table 2). Throughout in test, H_2O_2, Cl^- as well as pH of solutions was supervised furthermore uphold two times in a week. Subsequent to revelation, corroded coupons were unsoiled accordingly as in ASTM G1-10 [26] methods. Corroded coupons were afterward weighed up for guesstimate weight failure in sort to establish their corrosion tempo.

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The corroded as well as cleaned coupons were too outlook underneath microscope for ballpark figure pitting as well as crevice corrosion through evaluate maximum profundity of pitting assault on unlock surface as well as crevice assault beneath serrated washer of coupon, correspondingly [27]. For accelerated tests the electrochemical corrosion tests were conducted by a potentiostat.

III. RESULTS AND DISCUSSION

To comprehend a variety of response, accountable for corrosion of materials, a sequence is requisite on chemical group at hand in test solutions. In favor of this rationale an E-pH illustration [28] was created for H_2O_2-H_2O arrangement (Figure 1) uses subsequent reactions as well as their analogous equations (i to v) by way of quantity of H_2O_2 in use as 500 along with 1000 ppm, identical as individuals in test solutions.

$H_2O_2 = H^+ + HO_2^-$ (i)

$\mathrm{Log}\,[HO_2^-]/[H_2O_2] = -11.63 + pH$

$2H_2O = 2H^+ + 2e^- + H_2O_2$ (ii)

$EH_2O_2/H_2O = 1.776 - 0.0591pH + 0.0295\,\mathrm{Log}\,[H_2O_2]$

$2H_2O = HO_2^- + 3H^+ + 2e^-$ (iii)

$E\,HO_2^-/H_2O = 2.119 – 0.0886pH + 0.0295\,\mathrm{Log}\,[HO_2^-]$

$H_2O_2 = O_2 + 2H^+ + 2e^-$ (iv)

$EO_2/ H_2O_2 = 0.682 - 0.0591pH + 0.0295\,\mathrm{Log}\,[PO_2]/[H_2O_2]$

$HO_2^- = O_2 + H^+ + 2e^-$ (v)

$EO_2/H_2O_2 = 0.338 - 0.0295pH + 0.0295\,\mathrm{Log}\,[PO_2]/[HO_2^-]$

Figure 1 demonstrate assortment of potential inside which OCP standards of diverse stainless steels with respect to SCE lie from 187.1 to 271.3 mV (429.1 to 513.3 mV with respect to SHE), whilst bared in experimented test solution and assortment is mendacious close to line 2 which confirm H_2O_2/H_2O stability (reaction/equation ii), on the other hand O_2 reducing to H_2O_2 and H_2O_2 oxidizing to O_2 (equation iv and v), a resolution having peroxide at mentioned pH along with potential worth will have H_2O_2 and O_2 because chemicals into solution plus so will be answerable for subsequent reduction reactions :

$H_2O_2 + 2\,H^+ + 2\,e^- = 2\,H_2O$ (ii)

$O_2 + 4\,H^+ + 4\,e^- = 2\,H_2O$ (vi)

Due to higher potential of H_2O_2 reduction (reaction ii) and reduction reaction (i) and (iv) which are existing equation at acidic pH provides extra hydrogen ion which increase the reduction rate and it govern in persuade corrosion of steels in peroxides. H_2O_2 diminutions will upshot in augment the pH of solutions since corrosion keep on, the same as was pragmatic while examine pH all through immersion investigation. Also the gap between line 2 and 4 is decreasing which is an indication of higher potential and materials will likely experienced pitting at lower potential. The corrosion tariff for diverse steels in different solutions is specified into Table 3. Individual scrutinize peroxides devoid of Cl^- to subsist slightest corrosive. Accumulation of Cl^- along with augmented H_2O_2 deliberation demonstrates elevated corrosion tariff for particular materials. Degree of pitting in addition to crevice corrosion on different steels in test solutions (Table 4) are as well originate, usually, to augment with elevated H_2O_2 and Cl^- stuffing. Consequently peroxide solution through no chloride as well as 500 ppm peroxide is slightest corrosive; whilst amid 1000 ppm Cl^- along with 1000 ppm peroxide demonstrate uppermost extent of corrosivity. Augmented corrosivity of solutions by way of H_2O_2 may be assigned to H_2O_2/ H_2O reaction (reaction ii, Figure 1). The position of corrosion rates, by Table 3, is SS304L > SS316L > SS2205 ~ 6% Mo SS. In preponderance of cases, 6% Mo material illustrate vaguely better concert. An interesting observation from Table 4 is that SS 304L is found to carry out roughly equivalent as SS 316L [29]. Table 5 demonstrates results derivative from electrochemical polarization tests. Accordingly OCP standards are mendacious in assortment 187.1 to 271.3 mV with reverence to SCE. Cyclic polarization curvature for SS 316L along with SS304L explain E_C plummet exceedingly quickly with preamble of Cl^-. In support of duplex steel 2205, E_C, E_P in toting up to MOS are pragmatic to be pretty elevated, representing a lot enhanced resistance of material yet into container of peroxides having 1000 ppm and 1000 ppm Cl^- (Figure 2). The 6% Mo SS is anticipated to carry out flat better than SS2205 seeing as previous steel has advanced quantity of Mo plus N even though a modest lesser quantity of Cr as contrast to SS2205. These explanations can accredit to pitting resistance equivalent number (PRE No. equal 30% N+ % Cr + 3.3% Mo) [30]. The PRE number used for 6% Mo material is 46, whilst of 2205 is 37.6, demonstrating previous steels to carry out enhanced against restricted corrosion it has been pragmatic earlier [31] as well. Occurrence of Cr rally round in development $Cr(OH)_3/Cr_2O_3$ while Mo forms MoO_2, which are protecting sort [32,33]. An assessment of on the whole material performance adjacent to corrosion points toward 2205 SS as best material.

Table1: Composition of tested materials

Cylindrical and plate coupons										
Alloys	C	Cr	Ni	Mo	Cu	Mn	P	S	Si	N
SS304L	0.03	18.1	8.0	0.3	0.5	1.8	0.02	0.001	0.4	0.06
SS316L	0.02	17.4	11.3	2.0	0.4	1.1	0.03	0.002	0.5	0.05
SS2205	0.02	22.1	5.55	3.2	0.2	1.5	0.02	0.001	0.3	0.19
6%Mo	0.01	19.9	17.9	6.1	0.7	0.4	0.02	0.001	0.3	0.20

Table 2: Compound symphony of tested solutions (pH = 4.0)

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

Table 3: Corrosion rate of steels into peroxides (mpy*)

	Sol 1	Sol 2	Sol 3	Sol 4	Sol 5	So 6
SS 304L	01.211	01.431	01.272	01.491	_	_
SS 316L	00.290	00.322	00.371	00.390	00.391	00.422
SS 2205	00.012	00.017	00.032	00.050	00.073	00.078
6% Mo	_	_	_	_	00.007	00.008

* mpy – mils per year

Table 4: Crevice, pitting and welded hit* (deepness into µm)

Samples		Sol 1	Sol 2	Sol 3	Sol 4	Sol 5	Sol 6
SS-304L	Pitting	54	88	105	102	_	_
	Crevice Corrosion	NMA	43	45	48	_	_
SS-316L	Pitting	63	72	113	110	1304	140
	Crevice Corrosion	42	70	80	78	88	112
SS2205	Pitting	NMA	NMA	49	63	70	75
	Crevice Corrosion	NMA	NMA	NMA	NMA	47	56
6% Mo	Pitting	_	_	_	_	65	72
	Crevice Corrosion	_	_	_	_	NMA	NMA

NMA (no measurable attack); *considered as utmost deepness of hit, over unbolt region and underneath crevices.

Table 5: Electrochemical stricture

Samples		Sol 1	Sol 2	Sol 3	Sol 4	Sol 5	Sol 6
SS 304L	E_{corr}	201.05	234.31	233.91	219.70	-	-
SS 316L	OCP	224.10	241.70	237.81	248.00	234.31	226.21
	Ecorr	212.90	281.12	208.51	273.91	-	266.81
	$(Ec)_{pot}$	650.00	1150.0	700.02	700.10	-	600.00
SS 2205	OCP	194.51	256.71	247.41	228.21	265.10	271.31
	Ecorr	198.41	-	233.31	264.82	193.21	214.32
	$(Ec)_{pot}$	650	650	1000	1400	1300	1300

	MOS	-	-	965.70	886.81	838.12	784.10
6% Mo SS	OCP	-	-	-	-	252.41	187.12
	Ecorr	-	-	-	-	245.10	227.31
	(Ec)pot	-	-	-	-	1100.01	1350.00
	MOS	-	-	-	-	487.71	404.91

All constraint are in ‘mill volt’, calculated with respect to SCE; * cyclic measurement, MOS (margin of safety), (Ec)pot , (Ec)cyclic obtained from potentiodynamic and cyclic polarization measurements, respectively.

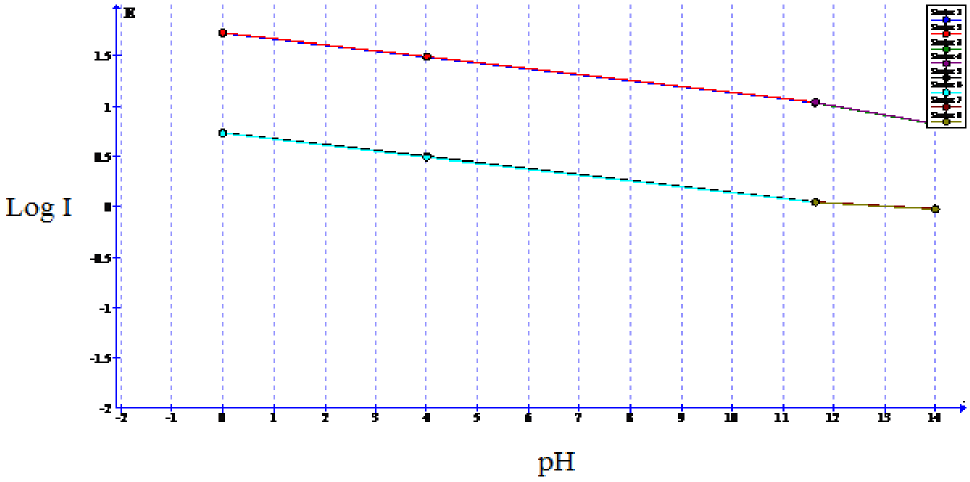

Figure 1: An E-pH illustration for H_2O_2/H_2O structure at room temperature

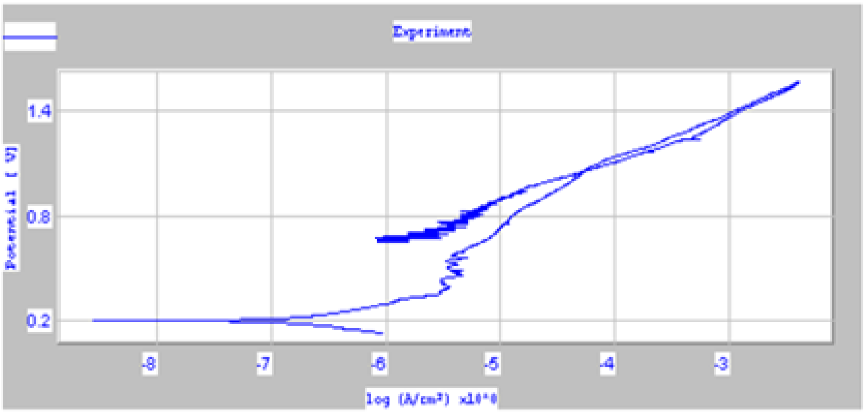

Figure 2: Cyclic polarization curve of SS 2205 in Solution 5

IV. CONCLUSIONS

In current exertion, electrochemical tests as well as immersion test were executed scheduled different stainless steels into Cl^- included peroxides. To comprehend a variety of reactions accountable meant for corrosion of tested steels into peroxides, an E-pH diagram of peroxide-H_2O arrangement is as well tired. It is accomplished so as to acidic peroxides among/exclusive of Cl^- are corrosive for tested steels to anecdotal amount in addition to their corrosivity increase with augment in H_2O_2 and Cl^- substance. The duplex SS2205 illustrated utmost resistance adjacent to corrosion assault as a result most favorable material for managing these media is recommended to be SS 2205. Supplementary in occurrence the mills obtainable in support of filtrate recycling, in-plant tests ought to be completed toward make sure corrosion conflict of steels which is expected to depreciate into observation of superior echelon of Cl^- moreover oxidant.

At the lower pH MOS reduced so it may be concluded that addition of H_2O_2 at low pH is not advisable for SS304L and SS316L equipments. Chloride concentration and temperature are also the factors which reduced or even eliminate the MOS and leading to localized corrosion.

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