Electrochemical Studies of Structural Materials in Acidic Peroxide Media

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ABSTRACT

Corrosion in paper industries is responsible not only for weakening of metal structures but also for pollution of process liquors and contamination of products. The bleaching sections in pulp and paper industry are among the worst affected by the ravages of corrosion. In bleach plants the materials are exposed to highly corrosive bleaching liquors. Now day’s new norms of safety of environment are forcing paper industries to use peroxide as a bleaching agent instead of chlorine. So in the present study an effort has been done to propose an appropriate material for the construction of future bleach plants keeping in mind their mechanical factors and cost of the material. Accordingly electrochemical polarization tests, E vs. time curve, potentiodynamic polarization curve and cyclic polarization curve were performed on stainless steels samples of 316L, 317L, 2205 and 254SMO in peroxide containing solutions having H2O2, 500 and 1000 parts per million (ppm). The pH of these solutions was kept 4. The Chloride content varied from 0 to 1000 ppm. These tests was performed at room temperature. These tests showed increased resistance against corrosion in order of: 316L<317L<2205<254SMO. Thus 254SMO shows highest resistance for attack of corrosion but keeping in mind fabrication and cost aspects optimal material for treating these peroxide media is recommended to be SS 2205.

Key Words: Open circuit potential, Electrochemical polarization, Corrosion, Bleaching, Peroxide

Introduction

Bleach plant section of paper industries has conventionally worked with austenitic steel. This is because of the reason of decent resistance of these steels against corrosion. Also the mechanical properties of these steels are very good. Now in order to save energy and cost and also to fulfill with new environmental guidelines, bleach plants of these industries have become more corrosive. Mainly wash water area contains low pH, high concentration of chloride and also high temperatures which make it high corrosion prone area. In the view of these new circumstances 316L & 317L have become unacceptable material. Due to this reason many industries have crooked to new stainless steels with higher doping of alloys [1, 2]. Usually bleach plants of paper industries deals with liquid media containing chlorine dioxide. This liquid media is generally acidic in nature and is extremely corrosive. Keeping in mind this fact many mills have made their bleach plant machinery by using titanium since resistance of titanium against corrosion is extremely high. Some other studies [3, 4] showed serious corrosion on titanium in peroxide comprising solutions. Yet another study [5] it was found that constrained outcome of the calcium was not permanent. Numerous researches [6-11] performed on Zirconium & Titanium in the solutions comprising acidic peroxide showed boost in corrosion attack with increase in peroxide concentration, pH and temperature. Zirconium is also a suitable material for these peroxide media as it shows extraordinary resistance in comparison with SS and Titanium but it is a costly option.

On the other hand stainless steels have extensive and diverse resistance against corrosion together with these steels have good production properties and durability so these steels can also be the proper materials for handling peroxide media of bleach plants. A study regarding SS [12] also recommend that 300 series of stainless steel as an appropriate material for acidic media comprising peroxide. It was also found that at low values of pH
accumulation of peroxide was likely to start crevice type of corrosion. Another research [13] shows the suitability of 304L & 316L against pitting type corrosion attack. Use of peroxide in bleach plants can decrease the effect of chloride which breaks the protective layer formed over the steels. Results from and laboratory tests shows that SS 254SMO can also be used for fabrication of bleach plant machinery but under worst conditions it shows crevice corrosion attack and pitting attack. The alloy with high volume of Nickel and Chromium shows better resistance against crevice and pitting but they can suffer from transpassive corrosion [14]. Hence keeping in mind all the suggestions and recommendations obtained from above studies it is proposed to check the appropriateness of stainless steel in liquid media comprising chloride and peroxide for pitting and uniform corrosion attack. In view of this the current study explains various electrochemical tests conducted on the samples of austenitic and duplex stainless steel in liquid media containing varying amount of chloride and peroxide at pH 4.0.

**Experimental Solutions**

In experimental solutions the concentration of peroxide and chloride was taken 500ppm and 1000 ppm separately. The pH of these solutions was taken 4.0. These solutions were prepared by adding required amount of peroxide in distilled water. For wanted amount of chloride ion NaCl was added to these solutions [15]. The concentrations of peroxide and chloride were checked by iodometric titration and Scan test method [16]. The pH of these solutions were checked by using a pH meter and adjusted by adding CH$_3$COOH in the solutions. Table 1 shows the chemical composition of experimental solutions.

| Soln 1 | Soln 2 | Soln 3 | Soln 4 |
|--------|--------|--------|--------|
| Chloride (ppm) | 500 | 500 | 1000 | 1000 |
| Peroxide (ppm) | 500 | 1000 | 500 | 1000 |

**Materials**

These electrochemical tests were performed on the rectangular samples duplex SS 2205 and austenitic SS316L,317L and 254SMO. Among these samples duplex SS is a recent addition due to its better corrosion resistance against stress cracking in addition to better strength to weight ratio(Fig. 1). The electrochemical corrosion tests were performed on these samples to investigate their corrosion mechanism and behavior in the experimental test solutions. The composition of these test samples is given in table 2.

| Alloy | C  | Cr  | Mn  | Ni  | Mo  | Cu  | P   | N   | S   | Si   |
|-------|----|-----|-----|-----|-----|-----|-----|-----|-----|------|
| 316L  | 0.020 | 17.44 | 1.12 | 11.25 | 2.04 | 0.41 | 0.028 | 0.047 | 0.002 | 0.51 |
| 317L  | 0.034 | 18.67 | 2.11 | 12.78 | 3.06 | --  | 0.038 | 0.112 | 0.040 | 0.62 |
| 2205  | 0.023 | 22.12 | 1.46 | 5.56 | 3.17 | 0.22 | 0.019 | 0.187 | 0.002 | 0.36 |
| 254SMO | 0.012 | 19.92 | 0.42 | 17.92 | 6.08 | 0.68 | 0.023 | 0.202 | 0.002 | 0.30 |

**Sample preparation**

The surface of these samples was prepared according to the norms of American Society for Testing and Materials [17]. Every sample was cut in pieces of 1sq. cm and then embedded in a non-reacting plastic and a conducting wire was spot welded with it (Fig. 1). This system acted as working electrode. The saturated calomel electrode was used as reference electrode while graphite electrodes were used as auxiliary electrodes. The surface finishing was done by abrading the specimens on emery or silicon carbide paper with grit varying from starting from 120 to 1200. These papers were fitted on a motor driven polishing wheel. The coupons were held
by hand and water stream was made to fall continuously during the grinding and polishing process. This was done to avoid any heat generated metallurgical damages. Moderate to heavy pressure was applied evenly on the test coupons. It was ensured that the surface was completely scratch free. Finally the test coupons were degreased in 50% acetone solution in distilled water and then dried.

![Test Samples](image1)

Figure 1. Test Samples

Tests

The electrochemical tests namely E vs. t, potentiodynamic and cyclic polarization were conducted on the test samples in these test solutions. For this purpose a corrosion measurement system was used. This system consists of a potentiostat with a polarization cell (Fig. 2). This cell has five inlets for fitting of different electrodes. By these tests values of OCP (open circuit potential), Ecorr (corrosion potential) and (Ec) pot (passivation potential) of different test samples were measured.

![Electrochemical Corrosion Measurement System](image2)

Figure 2. Electrochemical Corrosion Measurement System
Results and discussion

The values of different type of potentials obtained from these electrochemical tests are given in Table 3. From this table it is clear that range of OCP varies from 186.87 to 271.31 mili Volts. The potential above OCP is vulnerable to corrosion. In general the value of $E_{C_{orr}}$ is less than the value of OCP so for proper measurement of OCP the test must be run for long period of time. Due to this reason value of potential increases because a corrosion film is formed over the metal. The cyclic corrosion polarization curves for 316L and 317L shows that value of $E_c$ decreases towards solution 4 which is a result of increasing concentration of Cl$^-$. Generally high value of $(E_c)_{pot}$ shows better resistance of metals against pitting and crevice attack. For 316L and 317L the value of $(E_c)_{pot}$ is very low which shows their weak performance against localized corrosion and crevice corrosion in these solutions. On the other hand duplex SS 2205 shows higher values of $(E_c)_{pot}$ in comparison with 316L and 317L and also its passivation range or MOS is quite high even in solution 4 in which peroxide and chloride have highest concentration. This shows better performance of 2205 for corrosion attack in such severe conditions. It is also clear from table 3 that with increase in peroxide and chloride concentration its resistance shows minor drop only. This performance of 2205 may be due to higher chromium amount. The austenitic SS 254SMO is supposed to show little better performance than 2205 because of its higher PRE No. (Pitting Resistance Equivalent Number) which can be calculated by the following relation [17].

PRE No. = 1% Cr + 3.3% Mo + 16% N

PRE No. of 254SMO SS and 2205 are 46 and 38 respectively. For 317L and 316L its values are 30 and 25 respectively. So value of this number for different steels shows better resistance of 2205 and 254SMO against pitting. The pitting is a result of contravention of protecting layer. This process is enhanced by the introduction of chloride. It is earlier observed that Cr, Mo and N enhance the formation of this passive layer. Existences of the nitrogen ion overturn the immersion of Cl$^-$ on this protective film or slow down their admission towards this film. This process improves constancy of this passive film [12]. This noble behavior of 254SMO shows this glimpse in the present study also. From table 3 it is clear that its $E_{corr}$ is nearly equal to 2205 but it shows much improved behavior in solution 4 which contains worst conditions of liquid media of this study. In this solution it has highest value of $(E_c)_{pot}$ which indicates its best resistance against pitting and crevice attack in this solution. An assessment of complete performance of materials against corrosion generally shows 2205 much better than other steels except in solution 4 where performance of 254SMO was found much better. Now if we keep in mind other aspects as cost, strength fabrication etc. then SS 2205 is found more suitable then other steels for dealing with these acidic peroxide media.

| Table 3 | Electrochemical Corrosion Parameters |
|---------|-------------------------------------|
|         | Soln 1 | Soln 2 | Soln 3 | Soln 4 |
| SS-316L |         |        |        |        |
| OCP     | 237.81  | 248.02 | 234.31 | 226.24 |
| Ecorr   | 208.52  | 273.93 | 250.03 | 266.84 |
| $(E_c)_{pot}$ | 700.14 | 700.01 | 588.12 | 600.04 |
| SS-317L |         |        |        |        |
| OCP     | 238.8   | 248.12 | 234.31 | 236.2  |
| Ecorr   | 210.51  | 273.98 | 251.59 | 266.8  |
| $(E_c)_{pot}$ | 694.21 | 700.08 | 600.11 | 604.12 |
|     | OCP   | Ecorr  | (Ec)pot | MOS   |
|-----|-------|--------|---------|-------|
| 2205 OCP | 247.41 | 233.33 | 1000.12 | 965.74 |
|      | 228.20 | 264.84 | 1400.11 | 886.82 |
|      | 265.11 | 193.23 | 1300.14 | 838.12 |
|      | 271.31 | 214.34 | 1300.24 | 784.13 |
| 254SMO OCP | -     | -     | -       | 487.73 |
|      | -     | -     | 1100.04 | 404.92 |

All values are in millivolts. MOS stands for margin of safety

**Conclusion**

In this work different types of electrochemical polarization corrosion tests were conducted on different type of steel samples in test solutions comprising chloride and peroxide. These tests were conducted at room temperature and at 4.0 i.e. acidic pH values. On the basis of these tests it is suggested that (1.) At low values of pH the value of MOS also decreases so at these values of pH accumulation of peroxide is not suggested for stainless steel 316L and 317L. (2.) With increase in chloride concentration MOS generally decreases which can accelerated pitting corrosion. (3.) SS 254SMO shows highest value of (Ec) pot but on the other hand ss2205 shows maximum margin of safety. Hence keeping in mind availability, cost and fabrication parts duplex SS 2205 is recommended to be best material for treating these liquid media.

**Recommendations**

In paper industries actual conditions are somewhat different than laboratory conditions for example value of temperature is higher than laboratory conditions. So in simulation with paper industries these tests should also be performed at high temperatures.

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