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Research Article

Corrosion behavior of 304-stainless steel in aqueous sulphate Environment

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ABSTRACT

In different industries Stainless steel corrode in different environments. The various environments can affect the metal to different extents. The effect of pH and concentration of Aluminium sulphate in aqueous environment has been studied. The potentiodynamic polarization experiment was carried out at 0.003M, 0.03M and 0.15M concentration with the pH values of 5, 7, 9, 11, and 12.5. Weight loss experiment was also carried out at 0.003M, 0.03M and 0.15M concentrations. The results from potentiodynamic polarization technique indicate that when the pH value increases, corrosion potential shifts towards less negative values. Hence the metal becomes less susceptible to corrosion. Corrosion rate determined from the corrosion current density was compared with those obtained by weight loss method. From the above studies, it is observed that the corrosion of stainless steel is decreased with decrease in the concentration of Aluminium sulphate (0.003M to 0.15M) at constant pH or with increase in pH at constant concentration.

Keywords: Corrosion, 304-Stainless steel, Polarization, Aluminium sulphate

INTRODUCTION

Passivity of Chromium: Chromium behaves electrochemically similar to iron but certain important differences exist. The passivation potential of chromium is substantially lower than that of iron. The passivating current of chromium is further more a matter of a few mA per dm^2, whereas iron needs about 15-20 A/ dm^2. Chromium therefore passivated much easily than iron. Corrosion rate of chromium in the passive state is several magnitudes lower than that of iron.

Passivity of Stainless Steel: The fact that chromium and nickel are readily passivated accounts for these metals as alloying constituents in stainless steel. At chromium content of iron only iron 12-18 % the passivity

properties of chromium are approached. The value of passivation potential has almost shifted from that of iron to that of chromium. In the passive state, the corrosion current is about two orders of magnitude lower than for

pure iron. The result is an improvement of passivity and corrosion resistance. This means that stainless steel containing even these elements has substantially better corrosion resistance in non-oxidizing media and also more easily transferred to the passive state.

Properties of Passive Film: The passivated oxide film on e.g. stainless steel and Aluminium are extremely thin, usually in the range of 10-100Å. The first step in the passivation process is probably the formation of a film of chemisorbed oxygen on the metal surface. For iron-Chromium alloys it has been shown that chromium is enriched in the passive film although iron oxides generally predominate. For austenitic 18-8 nickel, the highest corrosion resistance is obtained at a film thickness of 30-50 Å. The oxide film is amorphous in nature. Thicker films are crystalline have a higher ionic conductivity and are remarkably less protective. These thick films may be considered as hydrated oxides as they contain up to 30% water, along with oxides of iron, chromium, nickel and silicon[1].

Applications include cooking utensils, textiles, food processing equipments, exterior architecture, and equipments for chemical industry, truck tailors, and kitchen sinks[2]. Among all metallic materials the austenitic stainless steel are the most popular because of their relatively low cost, ease of fabrication and reasonable corrosion resistance[3-4]. It is well known that stainless steel suffer from different forms of localized corrosion, mainly due to the halide ions, sulphate ions and particularly chloride ions[5-8].

The AISI 304 type stainless steel (SS) contains a high content and is commonly used engineering materials mainly because of its corrosion resistance. However it prevents a low surface hardness, a low – load bearing capacity and a poor wear resistance. For these reasons different approaches have been developed for improving the mechanical surface properties of such SS[9-12]. The effect of pH value and static corrosion on the mass loss is evaluated. The cavitation pattern and damage status of 304-stainless steel in corrosive liquid are observed[13]. The effect of alloy sulphur content and bulk solution composition of crevice corrosion initiation of type 304 Stainless steel in neutral chloride media solutions was studied, with particular emphasis on the solution composition that develops in the occluded region. Nitrate was a far stronger inhibitor for crevice corrosion than sulphate and operated via a mechanism and other than a supporting effect[14]. Sensitization of stainless steel has been posing serious problems to the industries. Characterizes sensitized surfaces of AISI 304 Stainless steel using impedance and Tafel extrapolation techniques[15]. The performance evolution by stainless association with corrosion in water and soil as well as remedies is described along with future problems are discussed[16].

EXPERIMENTAL

Material and Methods: The corrosion behavior of stainless steel was studied in an aqueous medium. The corrosion behavior was determined by using potentiodynamic polarization technique and the weight loss method. The experiments were carried out at different concentration ranging from 0.003M to 0.15M Aluminium sulphate dissolved in deionized water. All chemicals used were of analytical reagent grade.

ELECTROCHEMICAL POLARIZATION TECHNIQUE

The technique involves the following steps

Specimen preparation: The rods were cut into electrodes of required size. The electrode was polished first with emery paper to smoothen the surface. The electrode was then polished with a cloth mounted wheel. Polishing with the wheel helps to get fine smooth surface. The electrodes were then degreased with methanol. An area of one square centimeter on the surface of the specimen was selected and marked. A lacquer was applied on all the sides of the specimen exception the area of one square centimeter and some space for

electrical contact. The lacquered specimen was allowed to dry for half an hour and then used for the polarization studies

Preparation of the required solutions: The following table gives the weight of the salt taken for preparing the solution of corresponding molarity it is listed in **Table- 1.**

Table-1: Solution of corresponding molarity

Molarity (M)	Weight of the solute in 1000cc
0.003	0.00099
0.03	0.0102
0.15	0.501

Preparation of buffer solution: The EI digital pH meter model 111E was used to adjust the pH of test solution. A tablet of 9.2 pH was added to 100 Ml of deionized water. It was dissolved. This solution was used to calibrate the pH meter. Then the pH of the test solution was measured.

Preparation of 0.1% Nitric acid: 1.0 mL of Nitric acid solution was taken and made up to 100 mL in a standard flask.

Preparation of Sodium hydroxide: 2.5 gm of sodium hydroxide was taken and dissolved in 100 mL deionized water. Using the above solution of sodium hydroxide of nitric acid the pH of the test solution was adjusted to the required pH.

Polarization: In the potentiodynamic polarization studies a three electrodes cell assembly was used. A platinum foil was used as the auxiliary electrode. These can extent and uniform potential field on the working electrode. The standard calomel electrode was used as the reference. The prepared specimen which is the working electrode was immersed in the test solution taken in a dry test cell such that the exposed area of one square centimeter is completely immersed in the test solution. The time of immersion of each specimen was noted. The immersed specimen was left undisturbed for fifty five minutes. After the period of immersion was over the open circuit potential of the specimen was recorded. Then the potentiodynamic polarization of the specimen was carried out. A salt bridge was introduced between the test solution and the calomel electrode which was immersed in saturated potassium chloride taken in another beaker. The connections were then made to the specimen and to the counter electrode with the potentiostat. After the connections were established the polarization test were carried out. For each value of applied potential the resulting current was recorded. The logarithm of current was then plotted against the corresponding potential. The electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic tafel slope (b_a) and cathodic tafel slope (b_c) have been evaluated from the graph. These results were analyses to understand the electrochemical behaviour of stainless steel.

WEIGHT LOSS EXPERIMENT

Specimen preparation: The specimens were prepared in the similar manner to that employed for the polarization studies. The surfaces of the specimens were cleaned, polished and smoothened. The sharp edges were removed. Before polishing and cleaning the specimens were numbered and holes were drilled at one side of the specimen to hang them in the test solution using teflon tape. Before immersion the specimen in respective solutions, initial weight of the clean and dry specimen was taken.

Solution preparation: *The* same procedure as that employed for preparing test solution in electrochemical polarization method was employed. The concentration of the test solutions used were 0.003M, 0.03M and 0.15M Aluminium sulphate dissolved in deionized water. Each solution was taken in suitable clean, dry

container. The specimen in duplicate was immersed in corresponding test solutions. Each specimen was examined for color, luster, surface irregularities, and corrosion products. The duration of the test period was

382 hours. They were left undisturbed and were visually observed after every 24 hours. After the immersion period was completed each specimen was taken out from the solution and washed thoroughly with running water. They were chemically cleaned and dried with methanol. The dried specimen was weighed to get the final weight of the specimen gave the weight loss of the respective specimen.

RESULTS AND DISCUSSION

Potentiodynamic polarization studies: A plot of potential (V) Vs current density (x10^{-6} A) gives the polarization curves at different concentrations and different pH values. **Fig.1** represents the Potentiodynamic polarization behavior of 304-stainless steel in 0.003M Aluminium sulphate dissolved in deionized water.

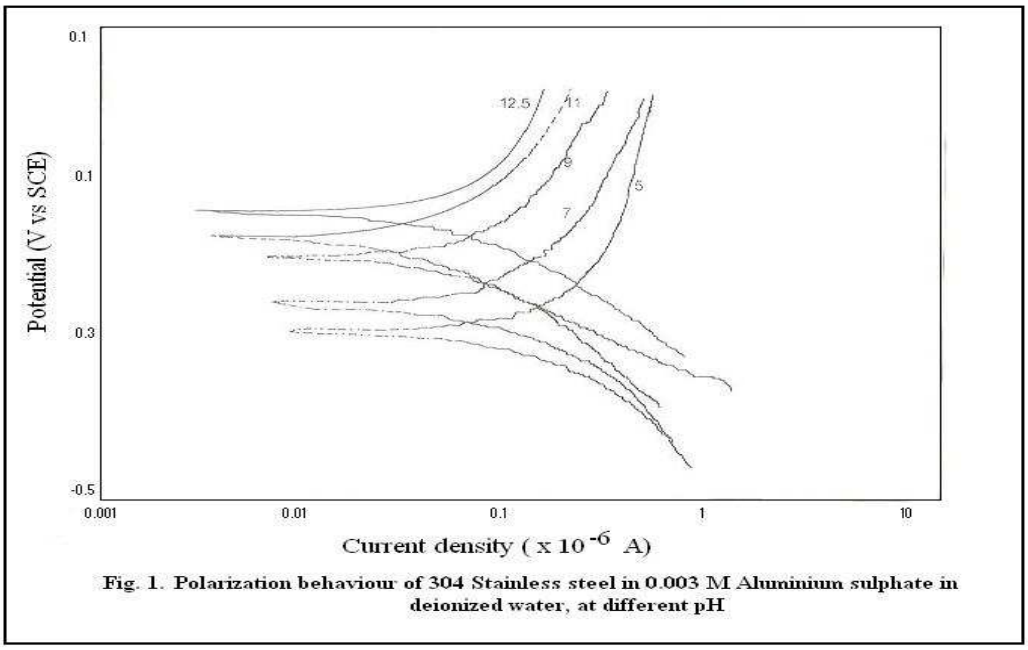

Fig. 1. Polarization behaviour of 304 Stainless steel in 0.003 M Aluminium sulphate in deionized water, at different pH

At 5 pH the cathodic curve is in the potential range of -0.460 V to -0.29 V. The anodic curve in the potential range of -0.29 V to 0.025 V. The cathode to anode transfer occurred at a potential of -0.290 V and at a current density of 0.009 x 10^{-6} A. In this system the current density ranges from 0.009 x 10^{-6} A to 0.8 x 10^{-6} A. At 7 pH the cathodic curve is in the potential range of -0.480 V to -0.250 V. The anodic curve is in the potential range of -0.250 V to 0.01 V. The cathode to anode transfer occurred a potential of -0.250 V and at a current density of 0.0075 x 10^{-6} A. In this system the current density ranges from 0.0075 x 10^{-6} A to 0.7 x 10^{-6} A. At 9 pH the cathodic curve is in the potential range of -0.360 V to -0.200 V. The anodic curve is in the potential range of -0.200 V to 0.02 V.

The cathode to anode transfer occurred at a potential -0.200 V and at a current density of 0.007 x 10^{-6} A. In this system the current density ranges from 0.007 x 10^{-6} A to 1.2 x 10^{-6} A. At 11 pH the cathodic curve is in the potential range of -0.380 V to -0.160 V. The anodic curve is in the potential range of -0.160 V to 0.03 V. The cathode to anode transfer occurred at a potential -0.160 V and at a current density of 0.0035 x 10^{-6} A. In this system the current density ranges from 0.0035 x 10^{-6} A to 0.6 x 10^{-6} A. At 12.5 pH the cathodic curve is in the potential range of -0.315 V to -0.14 V. The anodic curve is in the potential range of -0.14 V to 0.03 V. The cathode to anode transfer occurred at a potential -0.14 V and at a current density of 0.003 x 10^{-6} A. In this system the current density ranges from 0.003 x 10^{-6} A to 0.72 x 10^{-6} A.

From this graph the electrochemical parameters have been determined for each system and one listed in **Table -2** observed that as the pH value increases the corrosion potential shifts towards less negative value

from -0.285 V to -0.125 V. Hence as corrosion potential becomes less negative the metal becomes less susceptible to corrosion. The shift in corrosion potential for increasing pH value is considerable. When the pH value increases the corrosion current density decreased from 0.30 x 10^{-6} A to 0.09 x 10^{-6} A. Since the corrosion current density is directly proportional to corrosion rate, the stainless steel becomes less susceptible to corrosion at this concentration also as pH value increases.

Table-2: Electrochemical parameters for each system determined for the graph

pH	Corrosion potential (V)	Corrosion current density (x 10^{-6})	Anodic Tafel slope (volt/decade)	Cathodic Tafel slope (volt/decade)
5	-0.285	0.1	0.1780	0.1460
7	-0.245	0.061	0.1810	0.1430
9	-0.180	0.057	0.1850	0.1560
11	-0.150	0.050	0.1860	0.1450
12.5	-0.100	0.045	0.1930	0.1450

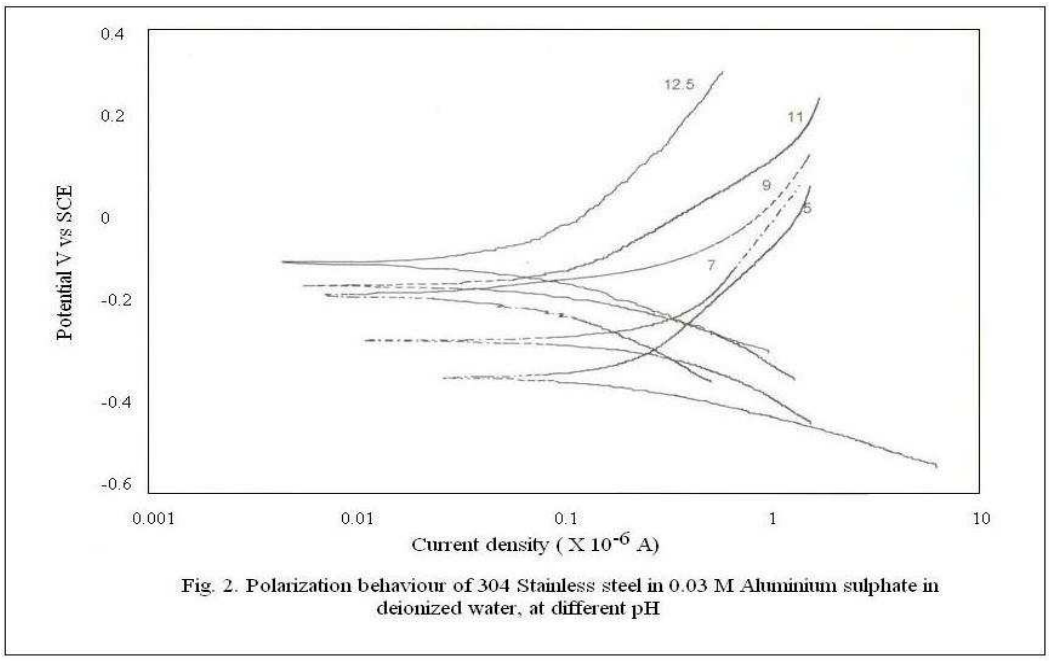

Fig. 2. Polarization behaviour of 304 Stainless steel in 0.03 M Aluminium sulphate in deionized water, at different pH

Fig.2: Represents the Potentiodynamic polarization behavior of 304-stainless steel in 0.03M Aluminium sulphate dissolved in deionized water.

At 5 pH the cathodic curve is in the potential range of -0.530 V to -0.350 V. The anodic curve in the potential range of -0.350 V to -0.06 V. The cathode to anode transfer occurred at a potential of -0.350 V and at a current density of 0.025 x 10^{-6} A. In this system the current density ranges from 0.025 x 10^{-6} A to 6.1 x 10^{-6} A. At 7 pH the cathodic curve is in the potential range of -0.450 V to -0.270 V. The anodic curve is in the potential range of -0.270 V to 0.05 V. The cathode to anode transfer occurred a potential of -0.270 V and at a current density of 0.011 x 10^{-6} A. In this system the current density ranges from 0.011 x 10^{-6} A to 1.3 x 10^{-6} A. At 9 pH the cathodic curve is in the potential range of -0.360 V to -0.170 V. The anodic curve is in the potential range of -0.170 V to 0.12 V. The cathode to anode transfer occurred at a potential -0.170 V and at a current density of 0.007 x 10^{-6} A. In this system the current density ranges from 0.007 x 10^{-6} A to 1.4 x 10^{-6} A.

At 11 pH the cathodic curve is in the potential range of -0.280 V to -0.160 V. The anodic curve is in the potential range of -0.160 V to 0.25 V. The cathode to anode transfer occurred at a potential -0.160 V and at a current density of 0.0057 x 10^{-6} A. In this system the current density ranges from 0.0057 x 10^{-6} A to 1.7 x 10^{-6} A. At 12.5 pH the cathodic curve is in the potential range of -0.350 V to -0.14 V. The anodic curve is in the potential range of -0.100 V to 0.300 V. The cathode to anode transfer occurred at a potential -0.100 V and at a current density of 0.0042 x 10^{-6} A. In this system the current density ranges from 0.0042 x 10^{-6} A to 1 x 10^{-6} A.From this graph the electrochemical parameters have been determined for each system and one listed in **Table- 3.**

Table- 3: Electrochemical parameters for each system determined for the graph

pH	Corrosion potential (V)	Corrosion current density (x 10^{-6})	Anodic Tafel slope (volt/decade)	Cathodic Tafel slope (volt/decade)
5	-0.320	0.180	0.1610	0.1100
7	-0.265	0.170	0.1720	0.1350
9	-0.190	0.072	0.1880	0.1810
11	-0.155	0.069	0.1900	0.1400
12.5	-0.105	0.046	0.2000	0.1660

We observed that as the pH value increases the corrosion potential shifts towards less negative value from -0.350 V to -0.090 V. Hence as corrosion potential becomes less negative the metal becomes less susceptible to corrosion. The shift in corrosion potential for increasing pH value is considerable. When the pH value increases the corrosion current density decreased from 0.180 x 10^{-6} A to 0.046 x 10^{-6} A. Since the corrosion current density is directly proportional to corrosion rate, the stainless steel becomes less susceptible to corrosion at this concentration also as pH value increases.

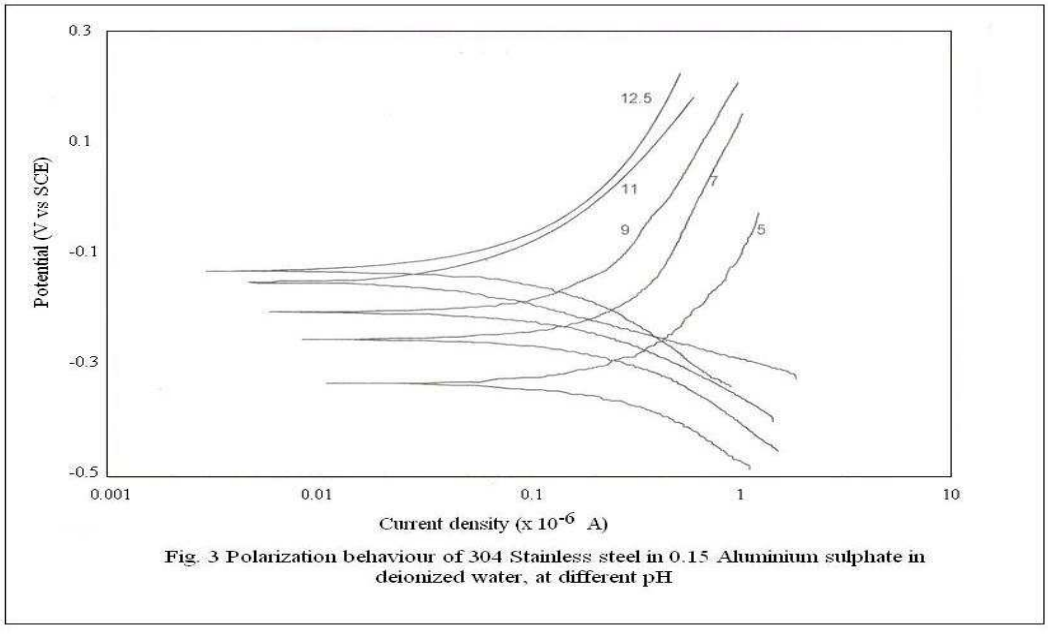

Fig. 3 Polarization behaviour of 304 Stainless steel in 0.15 Aluminium sulphate in deionized water, at different pH

Fig. 3: Represents the Potentiodynamic polarization behavior of 304-stainless steel in 0.15M Aluminium sulphate dissolved in deionized water.

At 5 pH the cathodic curve is in the potential range of -0.490 V to -0.330 V. The anodic curve in the potential range of -0.330 V to -0.004 V. The cathode to anode transfer occurred at a potential of -0.330 V and at a current density of 0.01 x 10^{-6} A. In this system the current density ranges from 0.01 x 10^{-6} A to 1.1 x 10^{-6} A. At 7 pH the cathodic curve is in the potential range of -0.460 V to -0.260 V. The anodic curve is in the potential range of -0.260 V to 0.140 V. The cathode to anode transfer occurred a potential of -0.260 V and at a current density of 0.008 x 10^{-6} A. In this system the current density ranges from 0.008 x 10^{-6} A to 1.2 x 10^{-6} A. At 9 pH the cathodic curve is in the potential range of -0.400 V to -0.210 V. The anodic curve is in the potential range of -0.210 V to 0.190 V. The cathode to anode transfer occurred at a potential -0.210 V and at a current density of 0.0058 x 10^{-6} A. In this system the current density ranges from 0.0058 x 10^{-6} A to 1.2 x 10^{-6} A. At 11 pH the cathodic curve is in the potential range of -0.330 V to -0.150 V. The anodic curve is in the potential range of -0.150 V to 0.16 V. The cathode to anode transfer occurred at a potential -0.150 V and at a current density of 0.0042 x 10^{-6} A. In this system the current density ranges from 0.0042 x 10^{-6} A to 1.9 x 10^{-6} A. At 12.5 pH the cathodic curve is in the potential range of -0.340 V to -0.130 V. The anodic curve is in the potential range of -0.130 V to 0.210 V. The cathode to anode transfer occurred at a potential -0.130 V and at a current density of 0.0029 x 10^{-6} A. In this system the current density ranges from 0.0029 x 10^{-6} A to 0.9 x 10^{-6} A.From this graph the electrochemical parameters have been determined for each system and one listed in **Table- 4**

Table- 4: Electrochemical parameters for each system determined for the graph

pH	Corrosion potential (V)	Corrosion current density (x 10^{-6})	Anodic Tafel slope (volt/decade)	Cathodic Tafel slope (volt/decade)
5	-0.320	0.180	0.1610	0.1100
7	-0.265	0.170	0.1720	0.1350
9	-0.190	0.072	0.1880	0.1810
11	-0.155	0.069	0.1900	0.1400
12.5	-0.105	0.046	0.2000	0.1660

We observed that as the pH value increases the corrosion potential shifts towards less negative value from -0.320 V to -0.095 V. Hence as corrosion potential becomes less negative the metal becomes less susceptible to corrosion. The shift in corrosion potential for increasing pH value is considerable. When the pH value increases the corrosion current density decreased from 0.200 x 10^{-6} A to 0.065 x 10^{-6} A. Since the corrosion current density is directly proportional to corrosion rate, the stainless steel becomes less susceptible to corrosion at this concentration also as pH value increases.

WEIGHT LOSS EXPERIMENT

The corrosion rate is determined by weight loss method was compared with the values calculated from the corrosion current density and are presented in **Table- 5.**

At all concentrations both the techniques yield the rate values in the same order of magnitude. As sulphate concentration was increased from 0.003 M to 0.15 M the corrosion rate increased from ~2 x 10^{-4} mpy to 8 x 10^{-4} mpy. This clearly indicates that the metal becomes more susceptible to corrosion which increases in the concentration of Aluminium sulphate in deionized water. This is also observed from the corrosion rate values

calculated from corrosion current density. The corrosion rate obtained from the corrosion current density is relatively less compared to that obtained from weight loss method. This may probably be occurring due to excess metal removal while cleaning the corroded sample. All the values are however acceptable and in the ranges.

Table- 5: Corrosion rate by weight loss method and compared with the values calculated from the corrosion current density.

pH	Corrosion potential (V)	Corrosion current density (x 10^{-6})	Anodic Tafel slope (volt/decade)	Cathodic Tafel slope (volt/decade)
5	-0.320	0.180	0.1610	0.1100
7	-0.265	0.170	0.1720	0.1350
9	-0.190	0.072	0.1880	0.1810
11	-0.155	0.069	0.1900	0.1400
12.5	-0.105	0.046	0.2000	0.1660

CONCLUSION

(i) From Potentiodynamic polarization technique:

- At all concentration of Aluminium sulphate, when the pH value increases the corrosion potential shifts towards less negative values.
- Similarly when the pH values increases the corrosion current density decreases.
- At any pH as the concentration increases the corrosion potential shifts towards more negative values.
- Similarly when the concentration increases the corrosion current density increases

(ii) From weight loss method:

It is observed that, when the concentration increases the corrosion rate will be increased.

REFERENCES

1. Gosta Wranglen, An Introduction to corrosion and protection of metals, publishers Great Britian by Buttler and Tanner LTd., Frome and London, Jan – **1972.**
2. T.Michler , Y. Lee ,R.P. Gangloft , J.Naumann J. Influence of macro segregation on hydrogen environment embrittlement of sus 316 L stainless steel.
3. M.K. Lei,X.M.Zhu, *Biomaterials*, 2001**, 22** , 641
4. M.E. Chabica, D.L.Williamson, R.Wei, P.J. Wilbur, *Surf. Coat.Technol*. 1992, **51,** 24.
5. U. Kamachi Mudali, T.Sundararajan, K.G.M. Nair, R.K. Dayal, *Mat. Sci, Forum*,1999, **531,** 318
6. J. Baszkiewicz, M. Kaminski, A. Podgrsky, J. Jagielki, G. Gawlik, *J. Corros. Sci*.,1992, **33** , 815
7. T. Hong, M. Nagumo, *Corros. Sci. ,1997***, 39** , 285
8. P.Q. Zhang, J.X. Wu, Q. Zhang, X.Y. Lu, K. Wang, *J. Corros. Sci*.1993, **34**, 1343.
9. G. Dearneley, Radiat. Eff., 1982, **63,** 1.
10. R. Wei, P.J. Wilbur, O. Ozturk, D.L. Williamson, *Nucl. In-str. and Meth*. B, 1991, **59/60**, 731.

11. G. Dearneley, *Nucl. Instr. and Meth.* B, 1990, **50,** 358.
12. L.J.Bredell, J.B.Malherbe, *Thin Solid Films*, 1993, **228,** 267.
13. Tsujino, Tomoji, Mizuta, Takamitsu, Inoue, Kenjiro, Mumamato Daigaku Kyoikugakuba, Kiyo, Shizen Kagaku, 1997**, 46,** 177.
14. C.S. Brosia, R.G.Kelly, Centre for electrochemical science. *Corrosion, Houston*, 1998, **54** (2), 145.
15. Mukherjee. S. Muralidharan, G.T.Parthiban, D.Jeyaperumal, S.P.Manoharan, *Journal of british corrosion control* 1996, **43 (6)**, 410.
16. Nemoto Rikio, Fushoku, Boshoku BBumon Inkai shiryo, Sato, Yoshikazu Busuoku. Bumonpon Zairyo Gakkai, 1998, **202,** 35.

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