

Study of Influence of Zinc Plated Mild Steel Deterioration in Seawater Environment

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The corrosion resistance of electrolytic zinc-coating on mild steel in seawater was investigated. Mild steel samples were zinc electroplated at voltage varied (0.6, 0.8, 1.0, 1.5 V) and for plating time also varied (20, 30, 40, 50, 60 minutes). Focused ion-beam scanning electron microscopy was used to observe the surface morphology of the plated surface. The visual observation of plated samples revealed that samples plated at 0.6 V for 20 and 60 minutes; 0.8 V for 30 minutes and 1.0 V for 40 minutes showed the best physical properties such as colour, brightness, fineness, streak and strong adhesion. The plated samples were then subjected to seawater environment for 30 days. The electro-potentials mV (SCE) was measured daily. Weight loss was determined at intervals of five days for the duration of the exposure period. Experimental result showed little corrosion attack on the zinc-plated samples on the fifteenth and twenty-fifth day's exposure. The severity of attack decreases with increasing weight of zinc coated on substrate. Significant increases in the corrosion resistance were achieved for the plated samples compared with that of the substrate. The pH of the seawater became more alkaline at the end of the thirty days test.

Keywords: Zinc plating; Mild steel; Corrosion resistance; Seawater

1. INTRODUCTION

Unprotected mild steel has no place in marine applications because of its propensity to corrode, but it is a good material if suitably protected. [1-3] Since, acid solution are widely used in the industries, the most important field of application of mild steel being acid pickling, marine, industrial acid cleaning, acid decaling, oil well oxidizing and manufacturing. Because of general aggressiveness of acid solutions, the practice and mechanics of deposition were engaged to reduce the corrosion attack on

metallic materials.[1-5] Coatings are the most commonly used method to protect steel from the aggressiveness of the marine environment where it is widely used. The basic concept is not electrochemical in nature but simply to isolate the steel component or construction from the environment. Since zinc is anodic to steel, it protects the base metal even if the deposit is porous. [10] This is usually achieved by adding a layer of zinc-“galvanizing” which has two benefits; firstly, zinc has good resistance to chemical corrosion and, secondly, it will corrode preferentially to the steel in the presence of an electrolyte.[6-9]An acid zinc bath is used where it is desirable to have a high plating rate with maximum current efficiency. Zinc is applied with greater ease and at lower cost than other metallic coatings such as tin, chromium, nickel, or aluminum [8-11]. The objective of this research work is to investigate the corrosion behavior of mild steel and its zinc plated counterpart in seawater.

2. MATERIALS AND METHOD

Mild steel substrate is the material used in this investigation and was obtained from Continental Limited (CSL), Apapa, Lagos, Nigeria. The chemical composition shown in Table 1 was obtained using energy dispersion spectrometer.

Table 1. Chemical composition of mild steel used in the experiment

Elements	Composition (wt%)
Carbon	0.150
Silicon	0.180
Manganese	0.450
Sulphur	0.031
Phosphorus	0.010
Nickel	0.008
Aluminum	0.005
Iron	99.166

2.1. Preparation of specimens (surface)

The mild steel samples used were machined into rectangular pieces of 20 mm breadth, 40 mm length by 10 mm width. The samples surfaces were treated by abrading them through successive grades of silicon carbide paper of grades P60, P120, P320, P400, P6600 grit and finally on the emery cloth to get the surfaces ready for electroplating. They were rinsed in distilled water and then in acetone before drying. The prepared samples were then stored in desiccators until they were needed for the experiments.

2.2. Seawater

The seawater used for the research was collected from Lagos Lagoon, Nigeria and the chemical composition as carried out at the Chemistry Department laboratory of the Covenant University, Canaan land, Ota is presented in Table 2.

Table 2. Chemical composition of seawater

Analysis	Concentration (mg/l)
Chloride (Cl^-)	314
Sulphate (SO_4^{2-})	80
Sodium (Na^+)	60
Potassium (K^+)	48
Magnesium (Mg^{2+})	50
Nitrate (NO_3^-)	70

2.3. Preparation of zinc bath/electroplating operation

Zinc plating solution was prepared in conformity with the Surtec®760K solution in which the chemical reagents used are zinc sulphate, zinc chloride, boric acid, leveler and brightener. The samples were removed from the desiccators in turn and pickled in 0.5M H_2SO_4 for 2 minutes, then rinsed in distilled water before degreasing in an 100 litre electrolytic degreasing tank containing 200 g KOH and 100 g NaOH solution and rinsed in distilled water for 2 minutes. The samples were weighed using a digital weighing balance model Metler Toledo Pb153 of accuracy ± 0.001 g and the weight was recorded as the initial weight.

The laboratory zinc electroplating bath was stirred with the aid of a stirrer for 2 minutes. The sample already attached to the flexible copper wire was then hanged on the cathode arm of the zinc electroplating bath after which the electroplating rectifier was switched on. The samples were electroplated at different plating times ranging from 20 – 60 minutes and at varying voltages from 0.6-1.5V. The electroplated samples were removed and passivized, dried and the weights recorded.

2.4. Corrosion resistance in seawater environment

The zinc electroplated samples were immersed in seawater environment for duration of 30 days, including the un-plated sample as control. The electrode potential (mV) measurements between the sample surface and the chloride environment were done at regular interval of 24 hours using a DT8300D digital multimeter with a lead electrode used as a reference electrode. The reference electrode was not left in the cell for the duration of the experiment but used only at time of measurement of potential and removed afterwards. Values obtained were converted to Saturated Calomel Electrode (SCE) values (George, 1994). The investigation also involved the measurement of pH of the chloride (Medium) with the aid of the pH meter (Digital) each time the samples were withdrawn from media for weighing at regular interval of five days. Weight change determination was

used due to its simplicity. The corrosion samples were removed from the corrosion environment (seawater) with the aid of a tong after which the samples were properly cleaned in distilled water and then dried with a cotton wool. The dried samples were weighed with a digital chemical weighing balance and recorded, and this continued at regular intervals of five days. Corrosion rates in $\text{mg}/\text{cm}^2/\text{yr}$ were obtained from weight loss analysis using the expression

$$R = W/A \times (T/365) \text{ mg}/\text{cm}^2/\text{yr} \tag{1}$$

Where, W is the weight in mg , A is the total surface area of the specimen in cm^2 , $T/365$ is the exposure time in days extrapolated to a year. R is the corrosion penetration rate expressed in milligram per area per year.

3. RESULTS AND DISCUSSION

Table 1 shows the chemical composition of the mild steel sample used while Table 2 shows the average chemical analysis of seawater. The electroplating weight gained and the corresponding coating thickness values, for zinc plated steel sample at different times and voltages is shown in Table 3. It could be seen that the resulting zinc plating thickness varied linearly with plating time. The coating thickness varied from about $0.95 \mu\text{m}$ to $5.72 \mu\text{m}$ for samples plated at 0.6 V , $1.58 \mu\text{m}$ to $4.28 \mu\text{m}$ for samples plated at 0.8 V , $1.97 \mu\text{m}$ to $7.34 \mu\text{m}$ at 1.0 V and $6.4 \mu\text{m}$ to $16.7 \mu\text{m}$ for samples plated at 1.5 V respectively. Figure 1 shows the coating thickness in respect of plating time for zinc-plated mild steel.

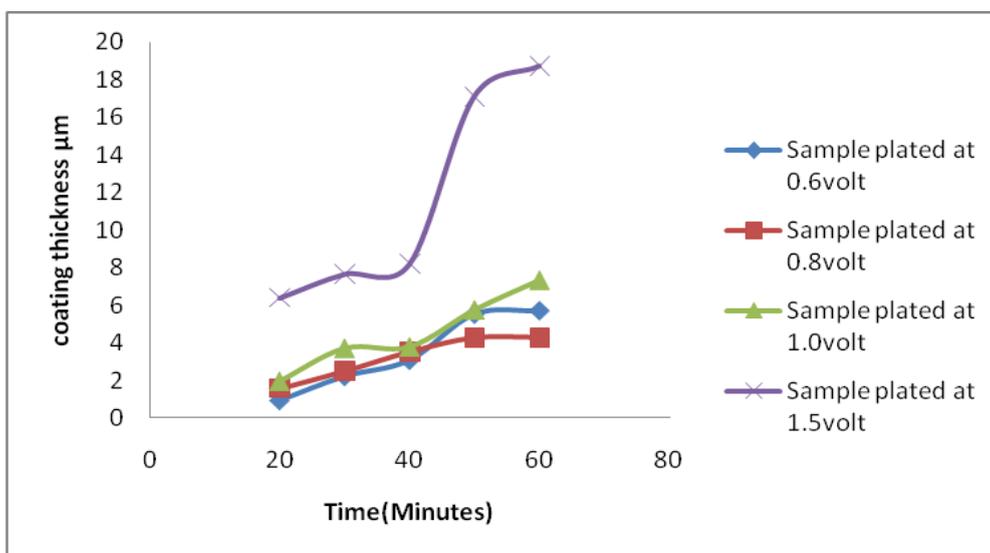


Figure 1. Coating thickness and Plating time relation for zinc plated mild steel

Table 3. Weight Deposit (g) of zinc on mild steel at various voltage 0.6, 0.8, 1.0 and 1.5 V and at various plating time of 20 to 60 mins

Sample Numbers	Time (Min)	Coating Thickness (μm)	Weight Gained (g)	Coating per unit area mg/mm^2	Voltage (volt)
1	20	0.95	0.041	0.017	0.6
2	30	2.23	0.123	0.045	0.6
3	40	3.09	0.142	0.056	0.6
4	50	5.54	0.273	0.104	0.6
5	60	5.72	0.291	0.109	0.6
6	20	1.58	0.069	0.028	0.8
7	30	2.50	0.109	0.044	0.8
8	40	3.51	0.165	0.064	0.8
9	50	4.26	0.189	0.076	0.8
10	60	4.28	0.220	0.082	0.8
11	20	1.97	0.088	0.035	1.0
12	30	3.72	0.164	0.066	1.0
13	40	3.80	0.181	0.070	1.0
14	50	5.76	0.295	0.110	1.0
15	60	7.34	0.374	0.140	1.0
16	20	6.40	0.299	0.117	1.5
17	30	7.67	0.344	0.136	1.5
18	40	8.20	0.359	0.145	1.5
19	50	17.10	0.797	0.302	1.5
20	60	18.70	0.825	0.314	1.5

3.1. Effect of exposure time on electrode potential

All the zinc plated samples showed good potential characteristics to steel. It was observed that un-plated sample displayed low electrode potential, while the zinc sample plated at 0.8 V, 1.0 V and 1.5 V for 20 minutes recorded high electrode potential. On the 23rd day of immersion, sample plated at 0.6 V, 0.8 V, 1.0 V and 1.5 V for 30 minutes displayed high electrode potential which means high corrosion resistance. The high electrode potential recorded in plated samples were attributed to the zinc coating on the mild steel which serves as protective film, while the decrease in electrode potential observed in un-plated sample was due to film breakdown.

3.2. Effect of exposure time on corrosion rate

The extent of susceptibility to corrosion in natural seawater depends on the aggressiveness of chemical composition, transport properties of environment, concentration of corrosion species in the medium (pH), the mechanical properties of the alloy sample and temperature of the corrosion medium (Oluwole et al, 2009). In seawater environment, the corrosion rates of all the zinc plated mild steel samples decreased with time, tending toward relatively lower rate throughout the 30 days of immersion

as shown in Figures 2a-2e. It was generally observed that the un-plated sample displayed higher corrosion rate on the 15th day of immersion compared to that of plated samples. However there the corrosion attack on the 20th and 25th days of immersion for the samples plated for 20 minutes, 30 minutes and 40 minutes was very small, while samples plated for 50 minutes and 60 minutes also displayed very little corrosion attack on the 15th and 25th days of immersion.

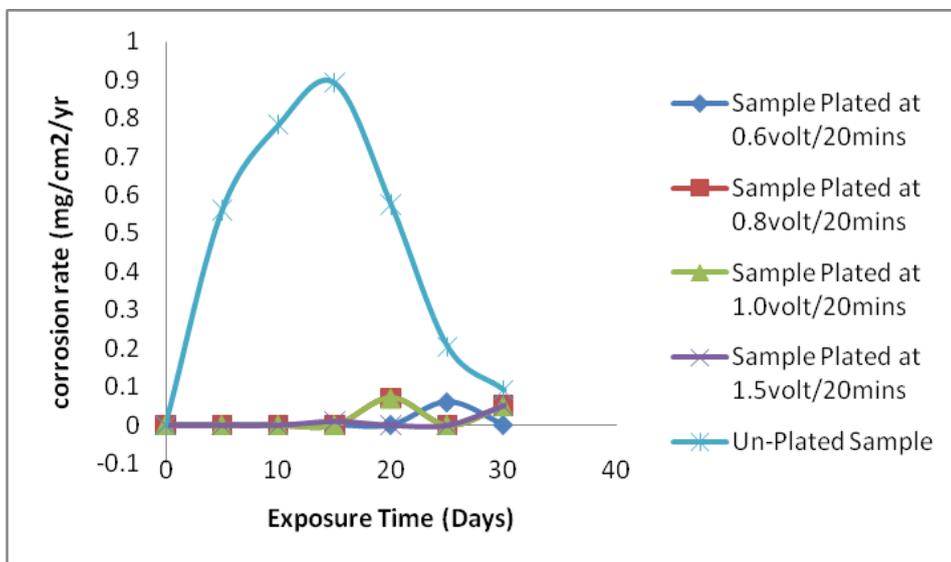


Figure 2a. Corrosion rate (mg/cm/yr) versus exposure time (day) for zinc plated mild steel at varying voltage for 20 mins and the un-plated sample immersed in seawater

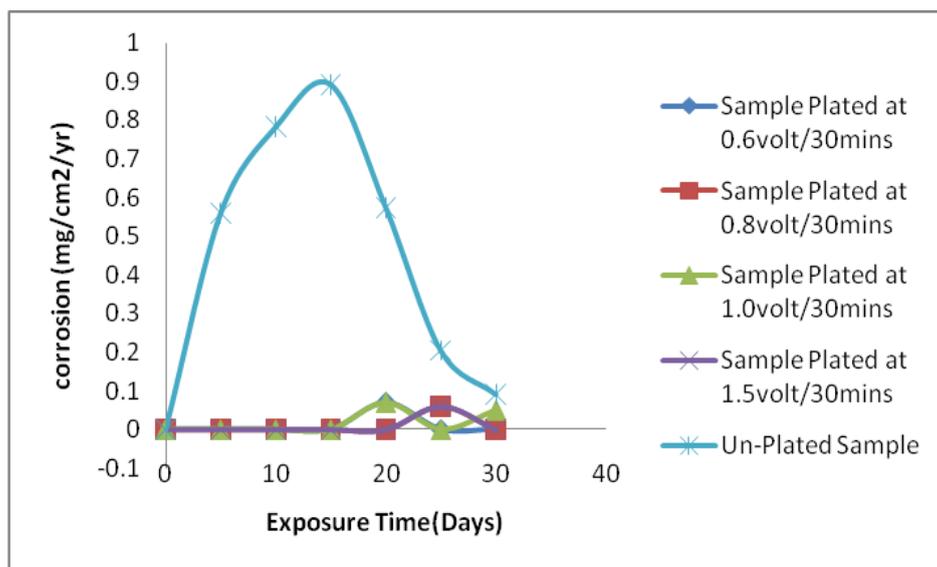


Figure 2b. Corrosion rate (mg/cm/yr) versus exposure time (day) for zinc plated mild steel at varying voltage for 30 mins and un-plated sample immersed in seawater

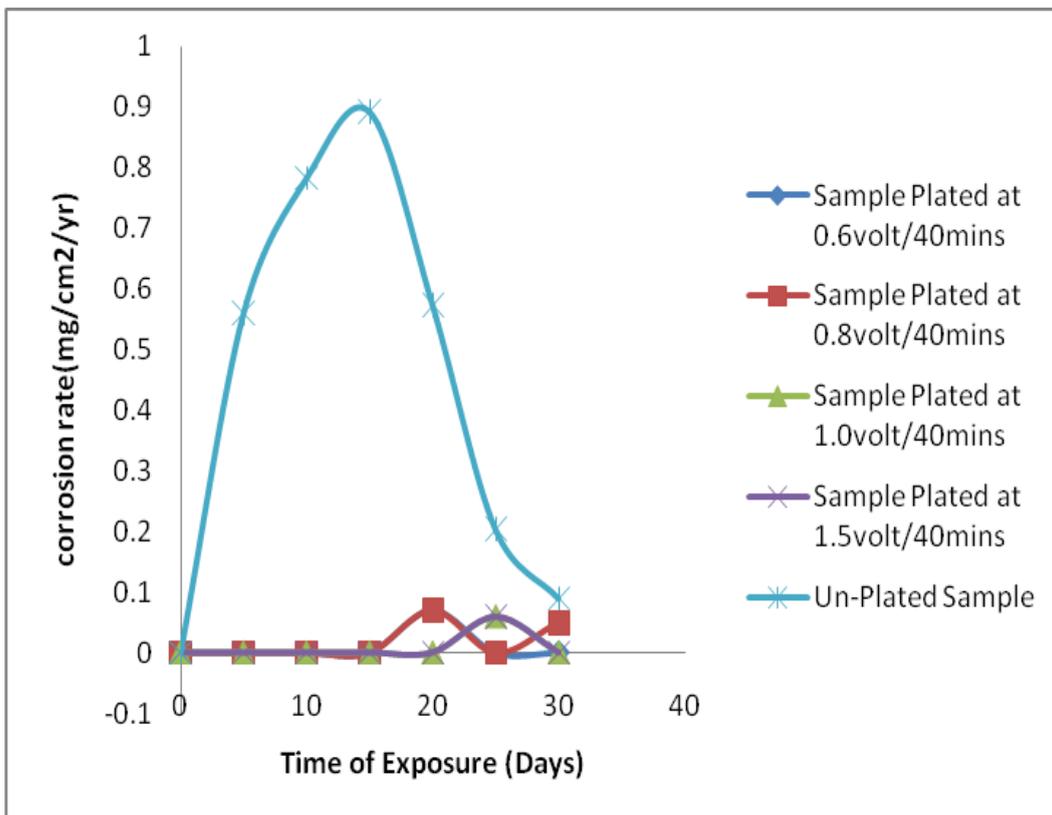


Figure 2c. Corrosion rate (mg/cm/yr) versus exposure time (day) for zinc plated mild steel at varying voltage for 40 mins and un-plated sample immersed in seawater

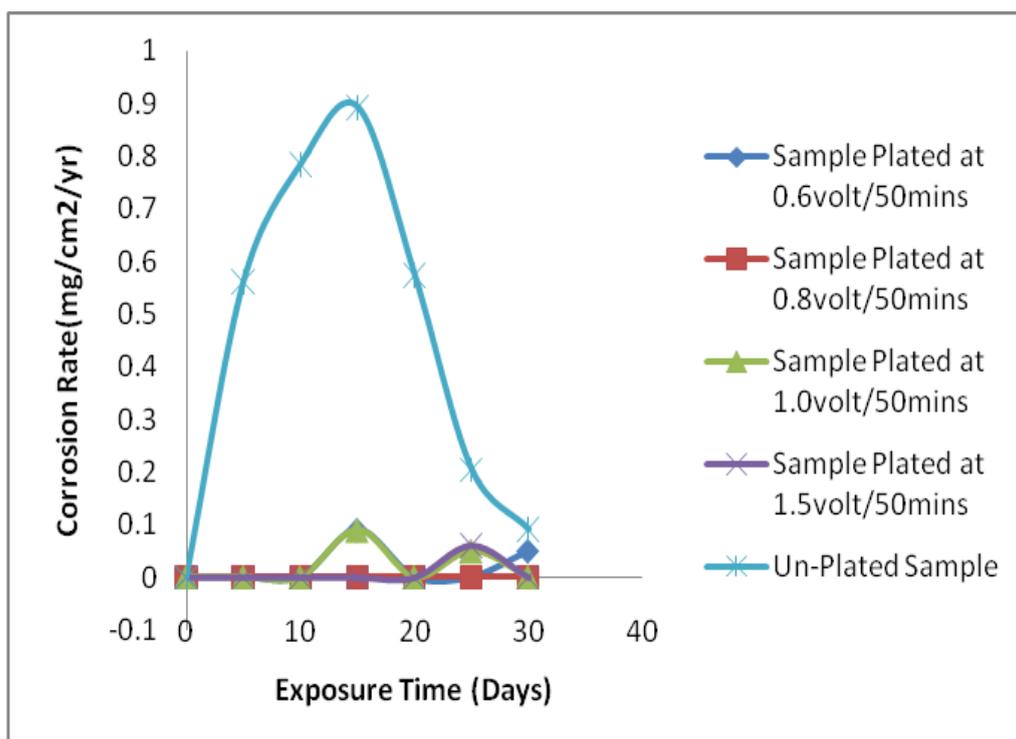


Figure 2d. Corrosion rate (mg/cm/yr) versus exposure time (day) for zinc plated mild steel at varying voltage for 50 mins and un-plated sample immersed in seawater

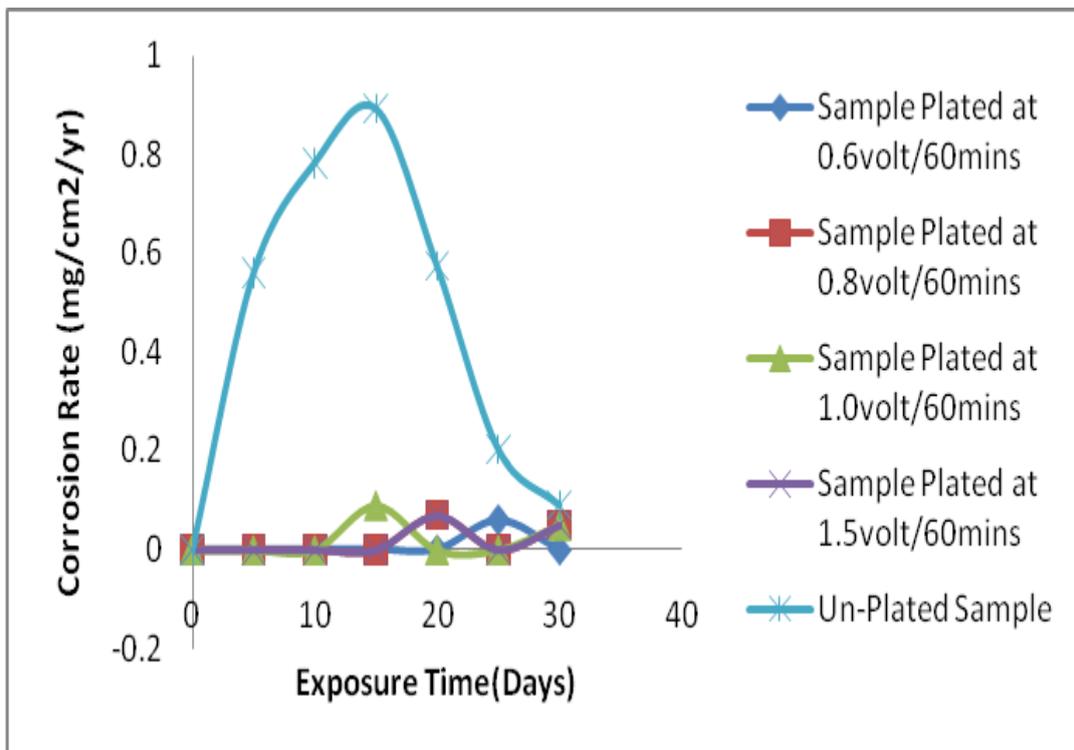


Figure 2e. Corrosion rate (mg/cm²/yr) against exposure time (day) for zinc plated mild steel at varying voltage for 60 mins and un-plated sample immersed in seawater

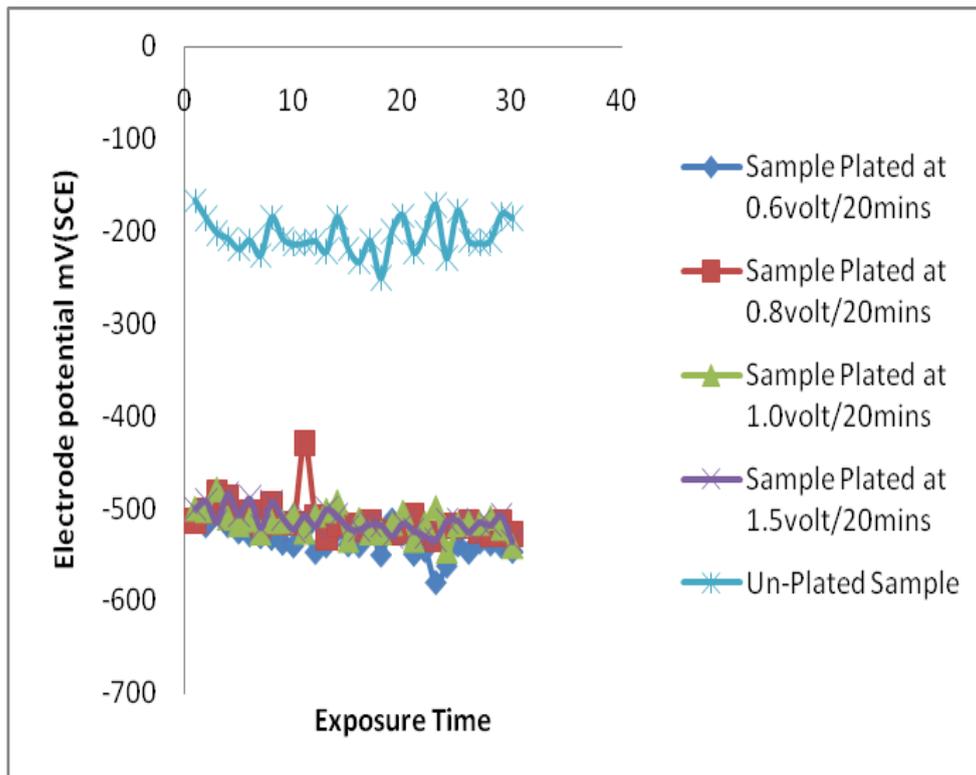


Figure 3a. Plot of electrode potential mv (sec) against exposure time (day) for zinc plated mild steel at varying voltage for 20 mins and un-plated sample immersed in seawater

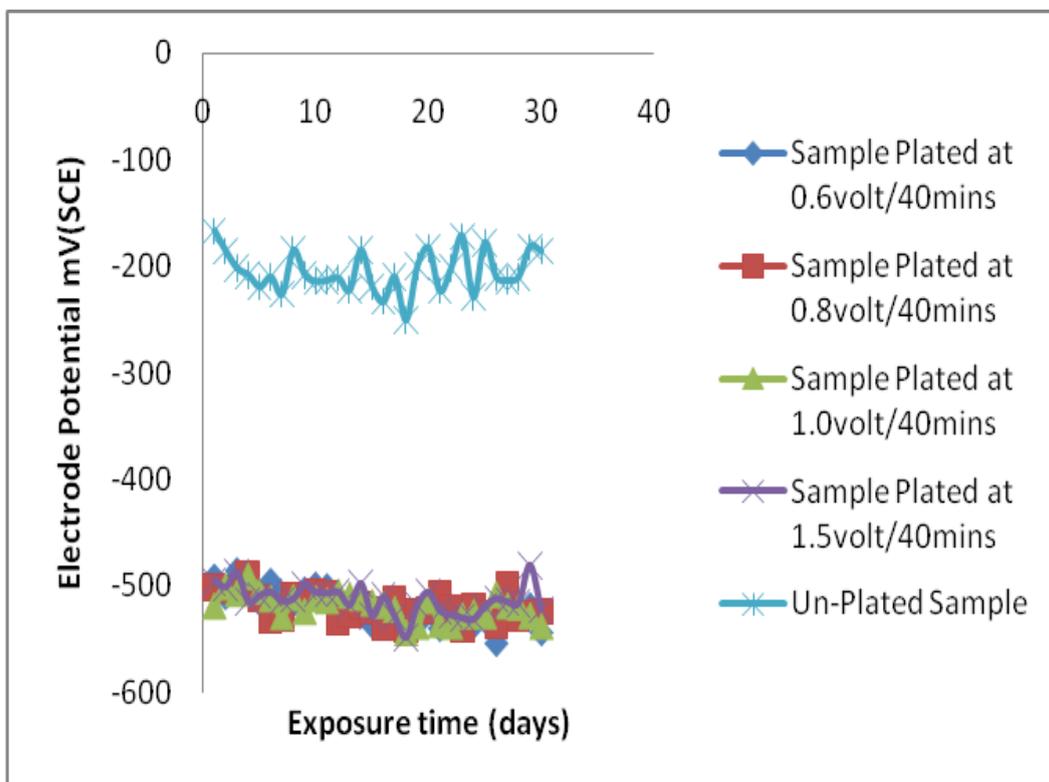


Figure 3c. Electrode potential mv (sec) against exposure time (day) for zinc plated mild steel at varying voltage for 40 mins and un-plated sample immersed in seawater

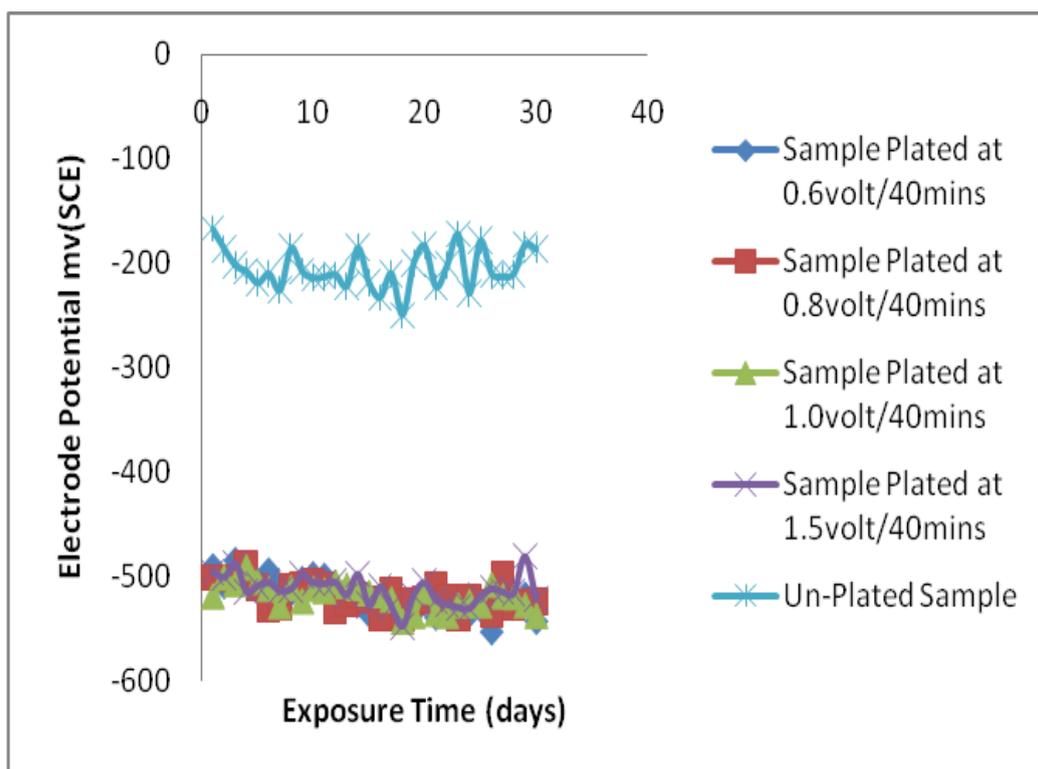


Figure 3d. Plot of electrode potential mv (sce) against exposure time (day) for zinc plated mild steel at varying voltage for 50 mins and un-plated sample immersed in seawater

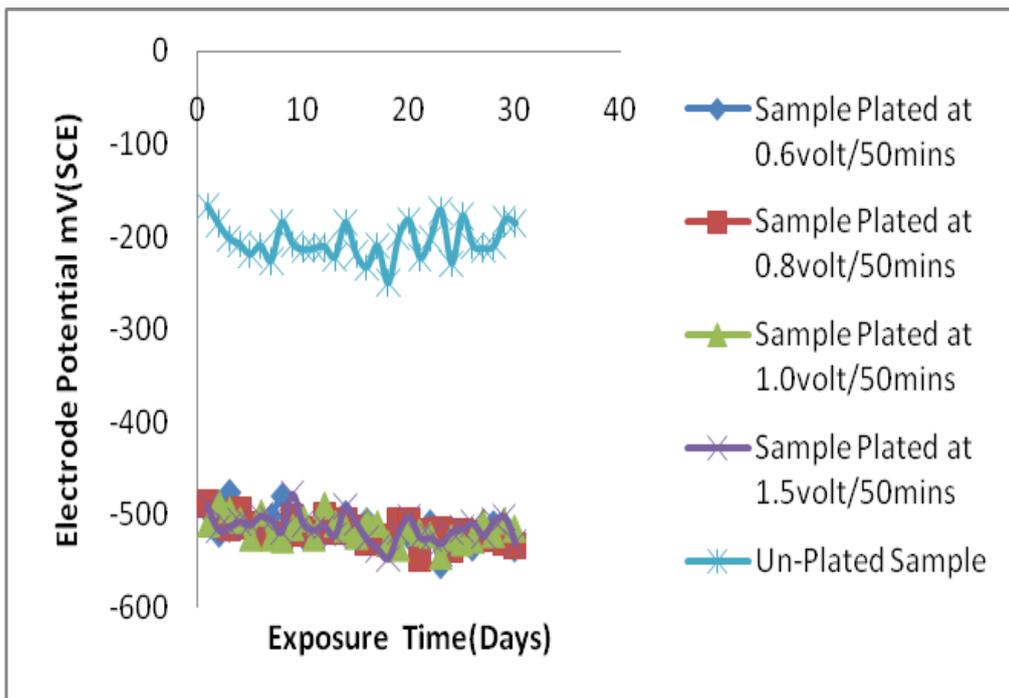


Figure 3e. Graphical plot of electrode potential mv (sce) versus exposure time (day) for zinc plated mild steel at varying voltage for 60 mins and un-plated sample immersed in seawater

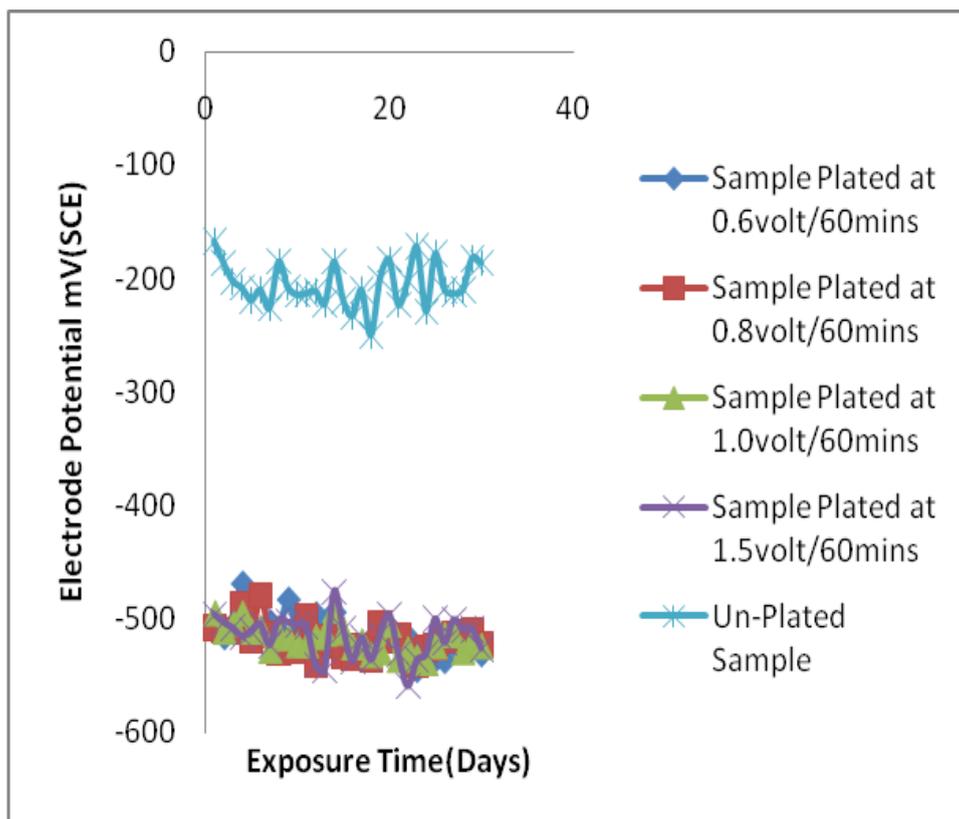


Figure 3f. Plot of electrode potential mv (sce) against exposure time (day) for zinc plated mild steel at varying voltage for 70 mins and un-plated sample immersed in seawater

3.3. Suitability of zinc coating in seawater environment

It is evident that uncoated mild steel is unsuitable for material for application in marine automobile and construction. In this work, the use of zinc coatings as a potential protective coating was tested. Thick zinc coating appears to offer protection in this environment. Low coating thicknesses certainly have marginal protection.

3.4. SEM studies

Fig. 4(a-d) shows a scanning electron microscope (SEM) photomicrograph of zinc coated surface before and after immersion in sea water medium at two different voltages of 0.8 and 1.5V which were considered for surface morphology and effect of chloride on plated substrate.

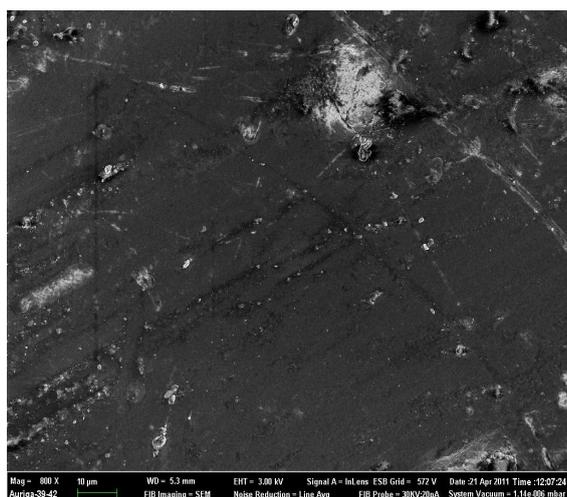


Figure 4a

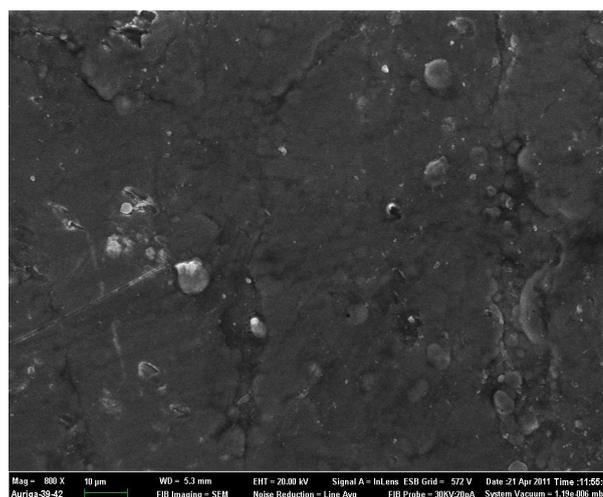


Figure 4b

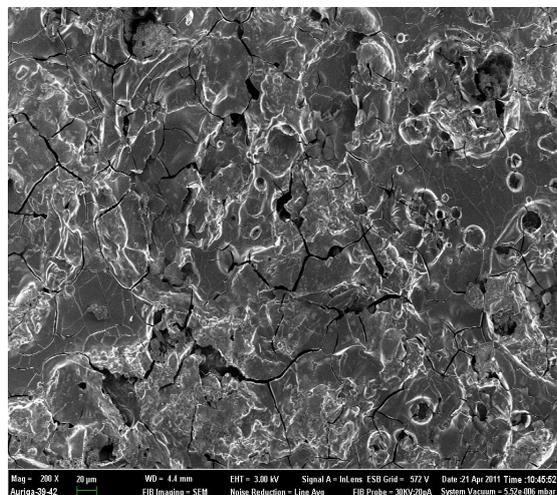


Figure 4c

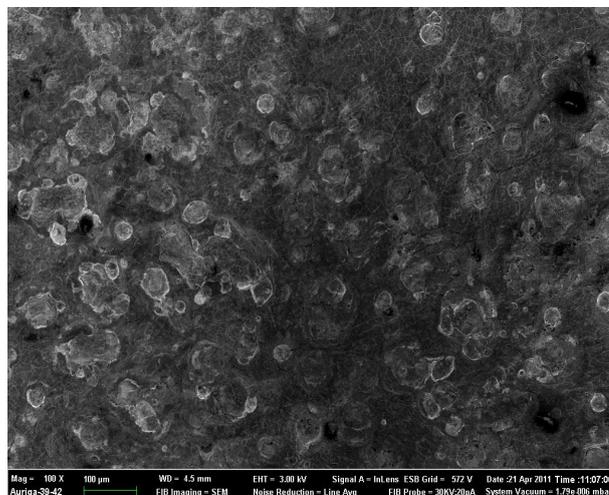


Figure 4d

Figure 4: SEM morphology of zinc plated steel. (4a) 1.5 V before immersion (4b) 0.8 V before immersion (4c) 1.5 V after immersion in sea water medium (4d) 0.8 V after immersion in sea water.

Careful examination of Figure 4b shows good homogeneous and surface adhesion of zinc on the substrate, which is better than Figure 4a with dendrite morphology. This indicates that plating voltage determines bright surface finish that could be obtained as a result of plating bath. In Fig. 4c, the surface appears to be roughened by the influence of salty environment due to poor plating fusion obtained from Figure 4a. Figure 4d maintained its morphology to certain extent, by retarding the corrosion product influence that may occur.

4. CONCLUSIONS

Improved mechanical and physical properties were obtained from zinc coated mild steel in the presence of aggressive chloride containing seawater element from sea water. Uncoated mild steel has been found to be unsuitable for use in seawater environment due to its relatively high corrosion rate. However, electroplated zinc sample was able to protect mild steel in seawater or chloride environment with the use of zinc as protection material to retard corrosion attack. Thick zinc coating was also observed to offer protection in seawater environment at a moderate plating voltage.

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