

Determination of Cathodic Protection of Galvanized and Mild Steels in Ibeshe Seawater using Zinc as Sacrificial anode

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ABSTRACT

The impact of corrosion on metallic structures which are in electrolytes can be prevented by means of cathodic protection technique. The research aimed in studying of the cathodic protection of galvanized and mild steels in Ibeshe seawater using zinc as sacrificial anode. Galvanic protection method was adopted and the dimension steels of 30 x 5 x 0.2 cm³ were connected to the sacrificial anodes of zinc independently with cables and each assembly was submerged in Ibeshe seawater. The characterization of all examined samples were done by using scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopic (EDX) machines. The corrosion rates were examined by gravimetric analysis and potentiodynamic polarization technique. Generally, pitting corrosion were observed on zinc anodes used. The SEM showed that there was corrosion attack of pitting and erosion on the whole surface which was less intense than unprotected samples. EDX exhibited that there was significant alteration in the chemical composition after submersion in marine environment, for the unprotected sample the percentage of iron content reduced drastically from 78.70% to 23.50% while the protected reduced to 65.5%. There was great correlation between the results from both weight loss and electrochemical methods. It was showed that galvanized steel had higher resistance to corrosion than mild steels as revealed in both methods used. It can then be concluded that the wide gap of weight loss values between the protected and unprotected samples showed that the zinc anode played a significant role in protecting the steels.

1. Introduction

Steels dominate the industrial landscape as the most widely utilized structural materials. Steels are the predominant constructional materials in seashore structures including desalination plants which are subjected to general or localized corrosion of varying degree. Mild steel is the most versatile general purpose material due to its good mechanical strength, easy fabricability, formability and weldability, abundance and low cost [1].

In general, galvanized steel should have a carbon content of less than 0.25%, phosphorus of less than 0.05%, and manganese of less than 1.3%. Silicon should run between 0% and 0.25%. Fe-99.210%; C-0.210%; Si-0.380%; P-0.090%; S-0.005%; Mn, 0.050%, and Al-0.010% [2]. The main constituents of GS are 0.0633% C, 0.0253% Si, 0.164% Mn, and the balance is Fe % in wt% [3]. Cathodic protection is an electrical method of preventing corrosion on metallic structures which are in electrolyte such as soil or water. [4] stated that the cathodic protection aims to polarize the potential of the metal to be protected to the point of the anode's open circuit potential, making anodic protective currents zero, which is achieved by applying an external protective current to the metal in the cathodic direction.

Galvanized steel is used in aqueous environments in many indoor and outdoor applications where rust resistance is needed. It is used in applications such as underground pipelines, undersea water, frames to build houses, and many household appliances, automotive body parts, telecommunication industry, power transmission lines, thermal power plant

Zinc is commonly employed to protect steel from corrosion because it acts sacrificially: with its redox potential being more negative (less noble) than that of steel under identical conditions, zinc deposits act as sacrificial anodes, providing cathodic protection to the steel substrate. High-potential electrons are produced via the corrosion of an active metal like magnesium or zinc. In such a system, the anodes material is consumed or sacrificially used in the process, necessitating periodic replacement of the anodes in order to obtain continued protection [5, 6].

An oxidation-reduction reaction is any chemical reaction in which the oxidation number of a molecule, atom, or ion changes by gaining or losing an electron. Redox reactions are common and vital to some of the basic functions of life, including photosynthesis, respiration, combustion, and corrosion or rusting, a redox reaction is one of the types of chemical reaction that

involves the alteration in the oxidation states of atoms. In this reaction, there is the actual transfer or shifting of electrons that takes place among different chemical species. In this reaction, one species loses electrons while the other gains the electron [7]. Their importance lies in the fact that we can use the transfer of electrons between species to do useful work. This is accomplished by constructing a voltaic cell.

Galvanic corrosion arises from inherent disparities in energy levels or potentials, emerging when metals are submerged in an electrolyte. Galvanic corrosion is a process where one metal corrodes preferentially in the presence of another metal, resulting in a galvanic cell. When two conducting materials of different compositions are in electrical contact with each other and being immersed into an electrolyte, a protective current, called the galvanic protective current, flows from one to the other. Galvanic corrosion is that part of the corrosion that specifically affects the anodic member of such a couple, directly linked to the galvanic protective current by Faraday's law [8].

2. Methodology

This research studied the cathodic protection of galvanized steel and mild steels in Ibeshe seawater using zinc as sacrificial anode. The metallic samples (coupons) were dimensioned by 300 x 50 x 20 mm³ followed by progressive polishing with SiC paper. This was also followed by mild polishing with abrasive paper, ultrasonic cleaning in a dilute acetone solution, and air drying. After attaching to the sample holders (cables), the specimens were rinsed with deionized water and dried in air. Two cathodic materials were connected independently to the zinc with two sets of control samples all assembled in plastic container and then submerged in Ibeshe seawater for 16 weeks with average temperature of 24.8°C. The sacrificial anode used that its more electronegative than the two cathodic metals to be protected were connected with the cathodic metals. As electrons flow from the anode to the metal, the metal ions did not leave the metal, and corrosion is prevented.

The corrosion rates of the materials were determined by gravimetric analysis and potentiodynamic polarization technique. Gravimetric Analysis: The initial weights of all the steels that were cathodically protected were measured and recorded and thereafter the weights of all the steels at specified times of immersion were measured against each of the steel by digital weighing balance model number AG-TT (weighing capacity 0-30Kg) and weight loss was determined. From the weight loss, the corrosion rate (CR) was calculated as shown in equation 1 [8]:

$$CR(mm/yr) = \frac{87.6 \times weight\ loss\ (mg)}{Density(g/cm^3) \times Area\ (cm^2) \times Time\ (hr)} \dots\dots\dots 1$$

Potentiodynamic polarization technique: This was used to evaluate parameters related to localized corrosion. The tests that are run using the potentiostat are potentiodynamic and will generate polarization curves for each of the alloys. The potentiodynamic test involves a "sweep" in which the potential is increased at a linear rate until an upper limit is reached. During the sweep, the resultant current is monitored and plotted in real time as shown in Figure 1.

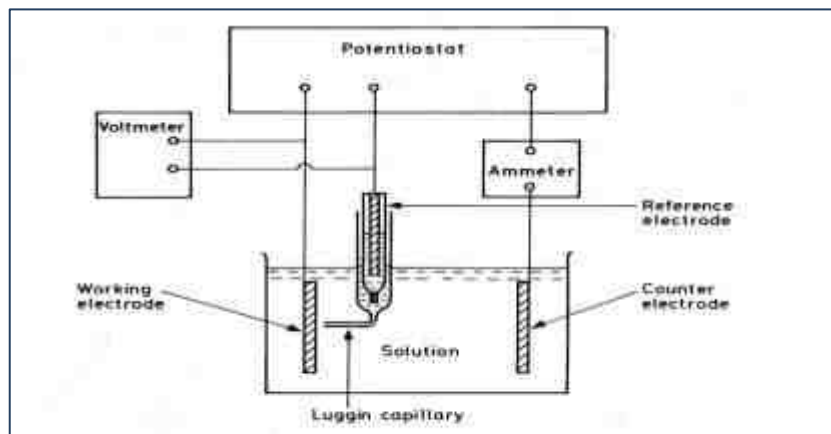


Figure 1: Experimental set up for Polarization

2.1 Characterization of Samples

The characterization of all examined samples were done by using scanning electron microscopy machine (SEM) to examine surfaces cross sectional analyses. X-Ray Fluorescence Spectroscopy was used to determine the chemical compositions of the samples while Energy Dispersive X-ray spectroscopic (EDX) was used to determine the chemical analysis of corrosion products and the seawater analysis was carried out by digital refractometer.

3 Results and Discussions

3.1 Chemical Composition of Sacrificial Anode and the Steels

Table 1 shows the percentage of chemical composition for the sacrificial anode of zinc that was used for the research while Table 2 displays the chemical composition of the steels. The sacrificial anode of zinc used had certain degree of purity since the percentages of all trace elements were less than 5% while the percentage of composition of purity for sacrificial anode of zinc was 96.52%. The major constituents for the two steels of mild steel had 99.34% of iron while galvanized steel had 78.7 and 11.2% for iron and zinc respectively.

3.2 Analysis of Seawater Used

Table 3 shows Ibeshe seawater analysis used as the electrolyte for this research as determined by digital refractometer, it was revealed that the conductivity and salinity of the seawater were 5156.00 $\mu\text{s}/\text{cm}$ and 2.06 mg/l respectively. It was also shown th at the higher the salinity the higher the conductivity [9-10].

Table 1: Percentage of Chemical Compositions of Sacrificial Anode

Elements (%)	Fe	Si	Cu	Al	Cd	Pb	Zn
Zn Anode	0.007	0.123	0.004	3.220	0.120	0.006	96.520

Table 2: Percentage of Chemical Compositions of the steels

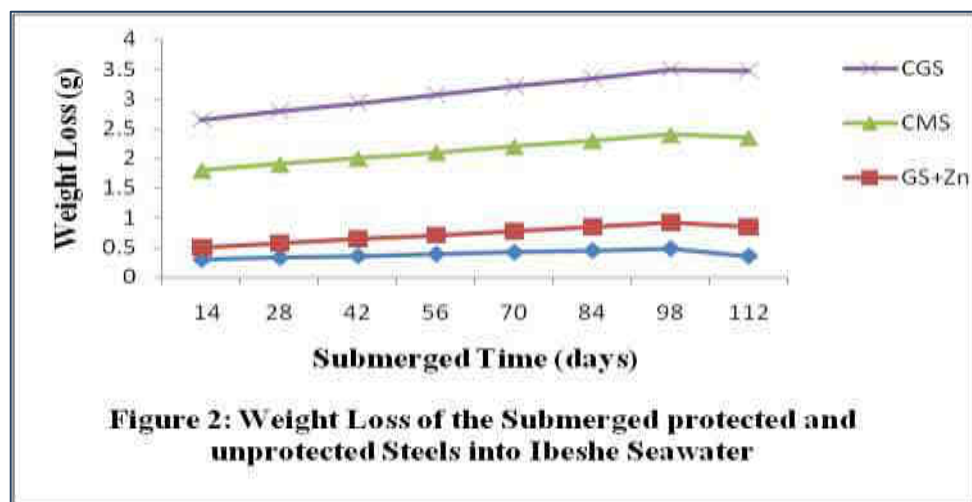
Elements (%)	Mn	Fe	S	C	P	Zn
Mild Steel	0.46	99.34	0.03	0.10	0.07	-
Galvanized Steel	0.800	87.776	0.040	0.140	0.044	11.200

Table 3: The Analysis of Ibeshe Seawater

Parameters	Values
pH	6.70
Conductivity ($\mu\text{s}/\text{cm}$)	5156.00
Salinity (mg/l)	2.06
Temperature ($^{\circ}\text{C}$)	24.10
TDS (mg/l)	2089.80
Acidity	83.58
Alkalinity	241.00
Chloride	1406.20
Sodium	15.08
Calcium	120.28
Magnesium	3.92

3.3 The Weight Loss of the Submerged Steels into Ibeshe Seawater

Figure 2 shows the comparison of weight loss of cathodic materials connected with and without (unprotected samples) sacrificial anodes that were submerged in Ibeshe seawater for 112 days (2688 hours). It was observed generally that the weight loss of the two protected steels increased progressively with an increase in submersion times while the values of unprotected materials (not connected with the sacrificial anodes) doubled the values of protected samples. It was shown that the galvanized steel had higher resistance to corrosion than mild steel. The effect of Ibeshe seawater on unprotected metallic samples as recorded by weight loss values was too conspicuous and such materials cannot last longer when being submerged in the seawater but when such materials were cathodically protected, the rate of dissipation drastically reduced.



Key: CGS = control galvanized steel , CMS = control mild steel; GS+Zn = protected galvanized steel by zinc; MS+Zn = protected mild steel by zinc

3.4 Corrosion Rates of Protected and Unprotected Steels by Zinc Anode

The corrosion rate of steels been connected with and without sacrificial anodes against the submersion time in Ibeshe seawater is exhibited in Figure 3. The highest values of corrosion rate were observed at first submersion time of 336 hours and declined to the

least at final submersion time of 2688 hours. It was observed that the sacrificial anode reduced the rate of deterioration of the two steels while galvanized steel had higher resistance to corrosion than mild steel. There was significant different between the protected samples by zinc anode and unprotected steels in the value of corrosion rate while unprotected mild steel had the highest value of corrosion rate [11].

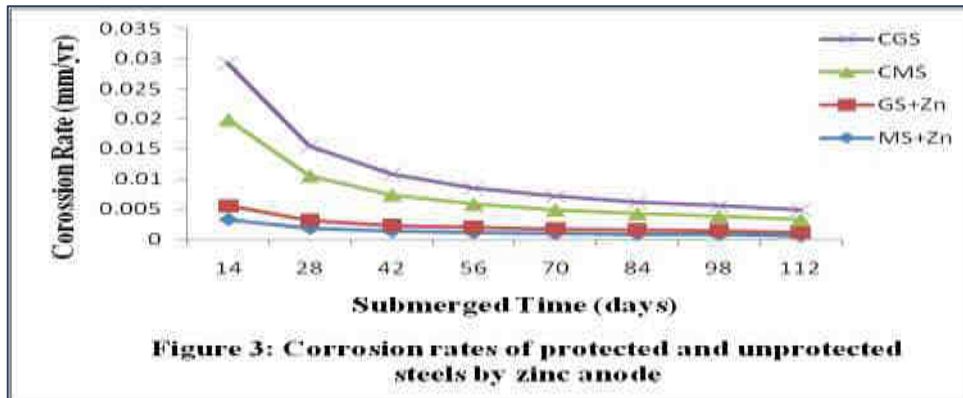


Figure 3: Corrosion rates of protected and unprotected steels by zinc anode

Key: CGS = control galvanized steel; CMS = control mild steel, GS+Zn = protected galvanized steel by zinc; MS+Zn = protected mild steel by zinc

3.5 Potentiodynamic Polarization Curves

Figure 4 exhibited the graph of corrosion potential of steels been protected by zinc anodes against the current density, it was observed that the polarization curves were not superimposed. The samples' resistance to corrosion reduced in order of galvanized and mild steels as the corrosion potential values shift from negative to positive of -0.5943 and -0.5156V respectively. The current densities for the galvanized and mild steels were 0.0270 and 0.0359A/cm² respectively in which the corrosion rates increased automatically in that order [12]. The values of protective potential generated by the connection of zinc anodes with galvanized and mild steels (cathodic materials) decreased negatively steadily with an increase in the submersion time. The potentiodynamic polarization (PDP) was used to assess the mechanistic and kinetic information on corrosion of galvanized and mild steels that measured the variation in current for the potential sweep in both the cathode and anode sides of the potential of corrosion. The polarization curves of steels were examined by their immersion in seawater for various exposure periods. The use of polarization curve is very limited due to its destructive nature. However, it has to be stressed because from the shape of the experimental curve it may be possible to obtain important information on the kinetics of the corrosion reactions. With increasing of immersion time, the corrosion potential (E_{corr}) shifted to toward positive value and almost unchanged [13]. It was observed that as the corrosion potentials tend towards positive values, there was an increase in the current density, which also led to an increase in the corrosion rates of the samples. It could be deduced from the chart that galvanized steel had the highest resistance to corrosion with the most negative value of corrosion potential (E_{corr}) and the least corrosion density. Also from the Tafel representation of potentiodynamic polarization diagrams, it can be observed that the decrease of current density is associated to the decrease of corrosion rate for the steels. The sacrificial anodes increase the lifetime for submarine equipment (steels) and this is materialized in lowering maintenance costs [14]. It can be inferred that in the potentiodynamic polarization test, the curve which shifts toward the negative value of corrosion potential (E_{corr}) with reduction in current density (i_{corr}) had the highest resistance to corrosion [15]. It was also observed that the size of zinc anodes used for this research can cathodically protect conveniently the submersion materials for a long period of time since the least protective potential generated at last submersion time was not less than -800 mV. There was a great distinct in the values of corrosion rate between the samples that were protected by sacrificial anodes of zinc and the unprotected sample. The rate of dissipation of unprotected steels shows that there shall be frequent replacement of engineering materials being submerged in seawater. Cathodic protection produced evolution of hydrogen at the metal surface. Within the potential range for cathodic protection by zinc production of hydrogen increases exponentially towards the negative potential limit. The of zinc anode scarified itself by releasing electrons to protect the steels and therefore reduced in weight after been submerged for period of time.

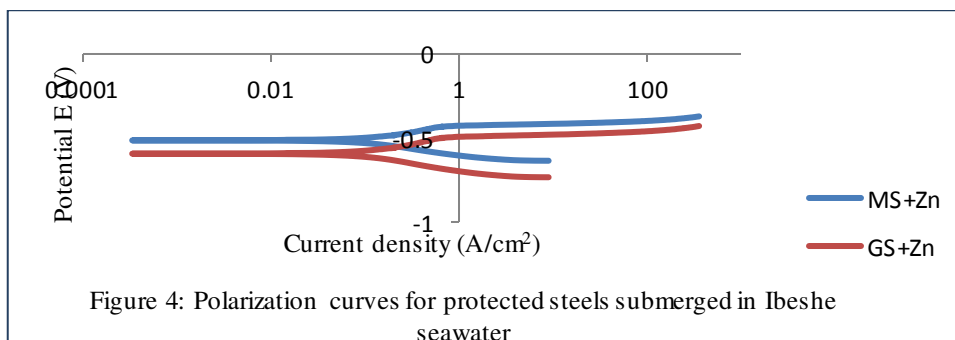
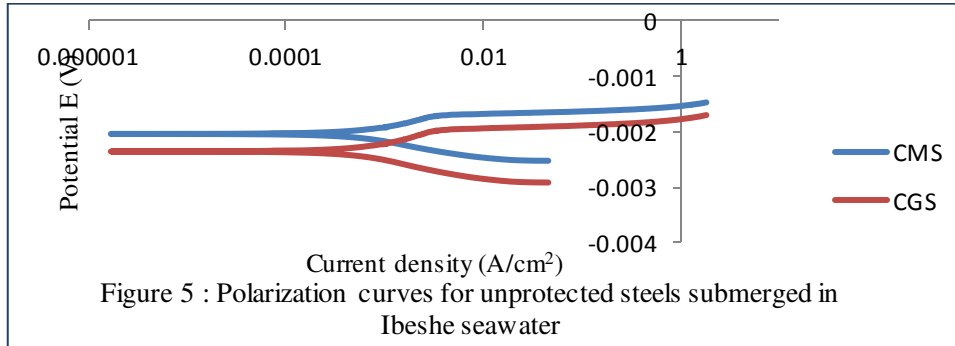


Figure 4: Polarization curves for protected steels submerged in Ibeshe seawater

Figure 5 revealed the graph of corrosion potential of unprotected steels against the current density, the polarization curves were not also superimposed against each other. The samples produced small values of protective voltages due to absent of sacrificial

anodes and this led to much attack by corrosion. The corrosion potential of unprotected samples of galvanized and mild steels were -0.00238 and -0.00207V respectively while the values of current densities increased as 0.000173 and 0.000227 A/cm² in the same order. In Table 5 which shows the Tafel fit results for Table 6 exhibited the Tafel fit results for steels with zinc as the sacrificial anode. The steel that was least susceptible to corrosion was also noticed to be the protected galvanized steel with corrosion rate of 0.089655 mm/yr while the protected mild steel had 0.148770 mm/yr. The highest susceptible to corrosion was noticed on unprotected mild steels of 0.859890 mm/yr and unprotected galvanized steel had 0.518205 mm/yr [9].



Key: CMS = control mild steel; CGS = control galvanized steel

Table 5: Tafel Fit Results for Steels with Zinc Anode

Samples	E _{corr} (V)	I _{corr} (A/cm ²)	C.R (mm/yr)	Remark on susceptibility to corrosion
GS+ Zn	-0.5943	0.0270	0.089655	least affected
MS+ Zn	-0.5156	0.0359	0.148770	more affected
CGS	-0.00238	0.000173	0.518205	Much affected
CMS	-0.00207	0.000227	0.859890	Most affected

3.6 Characterization of Steels

3.6.1 Scanning Electron Microscope

The scanning electron microscopes (SEM) of the four cathodic materials were examined before and after certain period of submersion times and were carried out with the following major parameters: working distance (WD) of 10.5mm, high voltage of 15kV, horizontal field with (HFW) of 124µm, pressure of 70Pa at magnification of 10,000x as shown in Plates 1 and 2. In Plate 1 that exhibits the SEM of Mild steels where a-image before submersion, b-image was unprotected while c-image was protected steels that were submerged in Ibeshe seawater. a-image showed crystalline grains throughout the surface, in b-image the degree of corrosion of mild steel was depicted on the SEM image with deep eroded portions and some white patches were depicted at magnification of 10,000x since the samples were not cathodically protected. The SEM image of protected displayed some dapples due to surface erosion [9,13].

Plate 2 displayed the SEM of Galvanized steels in which a-image was before submersion, b-image unprotected steel and c-image was protected samples been submerged in Ibeshe seawater. SEM image of galvanized steel before submersion showed a repeated pattern of crystals in the whole surface. The unprotected samples showed that the SEM images exhibited some combination of gray patches and little white crystals on the sample surfaces due to deep corrosion attack, while the protected SEM image showed conspicuous crystalline grains [16-17].

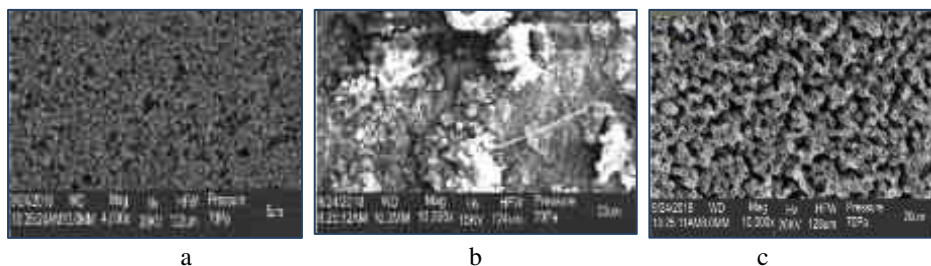


Plate 1: SEM of Mild steels: a-before submersion b-unprotected and c-protected samples submerged into Ibeshe seawater

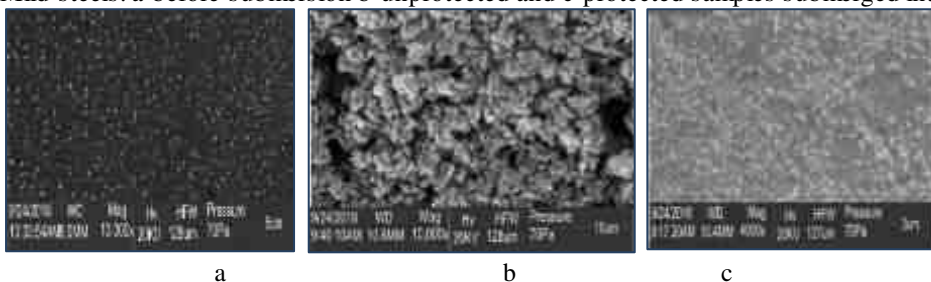


Plate 2: SEM of Galvanized steels: a-before submersion, b-unprotected and c-protected samples submerged into Ibeshe seawater

3.6.2 Energy Dispersive X-ray spectroscopy (EDX) Analysis

Energy dispersive X-ray spectroscopy (EDX) analysis was used to obtain details information about the composition of the corrosion of cathodic materials used in this research as exhibited from Plates 3 to 4.

Plate 3 showed the EDX of Mild steels in which image a was sample before submersion n into the marine environment, image b was unprotected sample while image c was the cathodically protected sample. Image a had the following elements of Cr, O, Si, S, Cu and Fe with percentage of compositions of 3.00, 18.00, 10.50, 4.00, 2.50 and 63.00% respectively. Image b had elements C, O, Mn, Cu, S and Fe with percentage compositions of 14.47, 22.68, 3.67, 30.93, 25.06 and 3.40% respectively and the percentage of Fe showed the degree effect of corrosion. The elements found in image c were P, C, O, Mn, S, Cr and Fe with percentage composition of 14.50, 10.00, 24.50, 3.70, 20.50, 3.40 and 24.20% respectively.

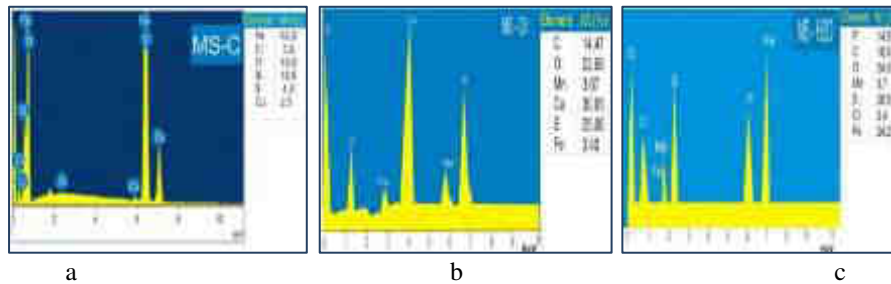


Plate 3: EDX of Mild steels: a-before submersion b-unprotected c-cathodically protected sample submerged in Ibeshe seawater

Plate 4 displayed the EDX analysis of Galvanized steels in which image a was sample before submersion, image b was unprotected sample and image c was cathodically protected sample. The EDX analysis of the sample at natural state had the following elements of Mn, C, O, P, S and Fe with percentage compositions of 0.80, 0.35, 20.00, 0.040, 0.044 and 78.70% respectively. There was significant alteration in the chemical composition after the samples were submerged in marine environments, for the unprotected sample the percentage of Fe content reduced drastically from 78.70% to 23.50% while the protected sample only reduced to 65.5% as a result of cathodic protection by sacrificial anodes which reduced the rate of dissipation [9].

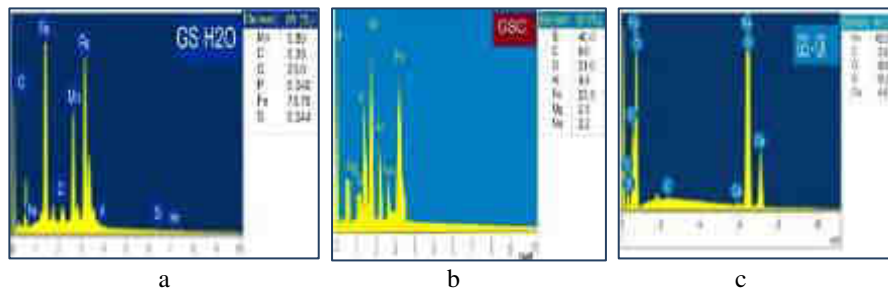


Plate 4: EDX of Galvanized steel: a-before submersion b-unprotected and c-cathodically protected sample submerged in Ibeshe seawater

4. Conclusion

It was noticed that galvanized steel had the higher resistance to corrosion than mild steel as displayed by both gravimetric and potentiodynamic polarization methods. Cathodic protection produced evolution of hydrogen at the metal surface. Within the potential range for cathodic protection by zinc production of hydrogen increases exponentially towards the negative potential limit. The of zinc anode scarified itself by releasing electrons to protect the steels and therefore reduced in weight after been submerged for period of time. Anode sacrifices itself for protecting the cathodic material, as it is used for protecting underground structures as well as ships. It can then be concluded that the wide gap of weight loss values between the protected and unprotected samples showed that the zinc anode played a significant role in protecting the steels been submerged in Ibeshe seawater.

Competing Interests

There is no competing interest among the authors

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Authors' contributions

Femi T. Owoeye contributed to the conceptualization, investigation, methodology, writing of the original draft, funding acquisition and editing.

Olayide R. Adetunji contributed to the conceptualization, methodology, supervision

Adinife P. Azodo contributed to the conceptualization, investigation, and methodology.

Emoekpere, Michael contributed to the conceptualization, methodology and supervision.

Adekoya A, Olayinka contributed to the conceptualization, methodology and analysis

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